(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
2 September 2010 (02.09.2010)

PCT

(10) International Publication Number
WO 2010/097449 A1

(51) International Patent Classification:
B01D 53/62 (2006.01) *C01F 11/18* (2006.01)
C01F 5/24 (2006.01) *C04B 2/00* (2006.01)

(21) International Application Number:
PCT/EP2010/052439

(22) International Filing Date:
25 February 2010 (25.02.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09153965.0 27 February 2009 (27.02.2009) EP

(71) Applicant *(for all designated States except US)*: **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: **BOERRIGTER, Harold** [NL/NL]; Grasweg 31, NL-1031 HW Amsterdam (NL).

(74) Agent: **MATTHEZING, Robert Maarten**; Shell International B.V., Intellectual Property Services, PO Box 384, NL-2501 CJ The Hague (NL).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

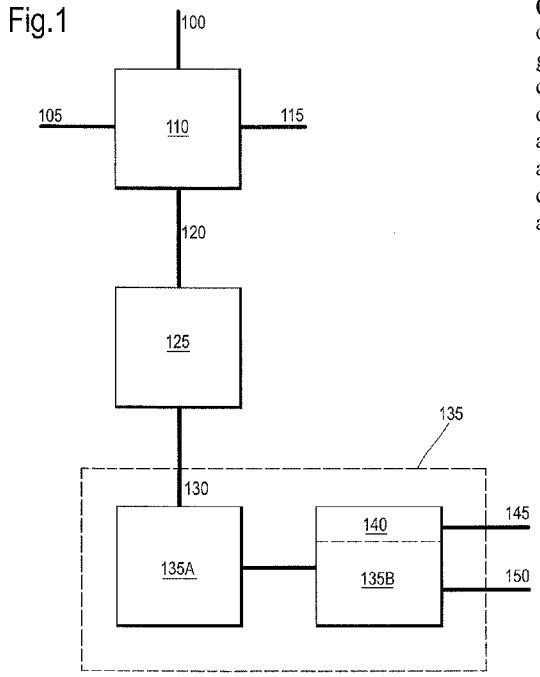
(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) Title: A PROCESS FOR CARBON DIOXIDE SEQUESTRATION

Fig.1



(57) Abstract: The present invention provides a process for sequestration of carbon dioxide comprising: a. contacting a carbon dioxide-comprising gas stream with an aqueous slurry comprising magnesium or calcium-comprising silicate particles under low temperature and low pressure conditions to obtain an aqueous bicarbonate solution; b. pressurising the aqueous bicarbonate solution to a pressure above atmospheric pressure; and c. heating the pressurised aqueous solution to induce bicarbonate decomposition, the formation of solid magnesium and/or calcium carbonate and the formation of high pressure carbon dioxide.

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A PROCESS FOR CARBON DIOXIDE SEQUESTRATION

Field of the invention

The present invention provides a process for carbon dioxide sequestration.

Background of the invention

The rising carbon dioxide concentration in the atmosphere due to the increased use of energy derived from fossil fuels potentially may have a large impact on the global climate. Thus there is an increasing interest in measures to reduce the carbon dioxide concentration emissions to the atmosphere.

In order to reduce the carbon dioxide emission a number of carbon dioxide capture and carbon dioxide sequestration processes have been studied. One such process involves the sequestration of carbon dioxide by mineral carbonation (or mineralisation) to form a mineral carbonate.

In nature, stable mineral carbonate and silica are formed by a reaction of carbon dioxide with natural silicate minerals. This process of reacting carbon dioxide with mineral substances is also referred to as mineralisation and follows for instance in the case of olivine (Forsterite) mineral the overall reaction:

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2\ MgCO_3 + SiO_2 \quad (1)$$

Two intermediate reactions can be identified. The first intermediate reaction, also referred to as leaching, frees the magnesium ions from the mineral, following:

$$Mg_2SiO_4 + 4\ CO_2 + 2H_2O \rightarrow 2Mg^{2+} + 4\ HCO_3^- + SiO_2 \quad (1a)$$

In the second intermediate reaction, also referred to as precipitation, relates to the formation of solid magnesium carbonate.

Recent feasibility studies of the application of mineralisation for industrial application concentrate on the overall reaction. In WO02/085788, for example, is disclosed a process for mineral carbonation of carbon dioxide wherein particles of silicates selected from the group of ortho-, di-, ring, and chain silicates, are dispersed in an aqueous electrolyte solution and reacted with carbon dioxide.

A disadvantage of this process is that only one mole of carbon dioxide is captured from the carbon dioxide-comprising gas per mole of magnesium and/or calcium ions, see reaction 1. Therefore, large amounts of mineral are required and in practice the carbon dioxide-comprising gas is provided at high pressure and with high carbon dioxide partial pressure, ideally even pure carbon dioxide.

In EP 1836127 a process for preparing pure magnesium or calcium carbonate is disclosed. In EP 1836127, the overall mineralisation reaction is separated into the two intermediate steps, however this is only done to allow removal of the solids from the aqueous bicarbonate solution after leaching. Although the intermediate leaching step and precipitation step separated, they are performed under generally the same conditions.

By removing the remaining solids prior to precipitation further leaching of magnesium ions during precipitation is no longer possible, as a result only part of the mineralisation capacity of the mineral is utilized.

During the precipitation step of EP 1836127, low-pressure carbon dioxide is obtained. Further processing of this carbon dioxide typically requires the carbon dioxide to be provided at high pressure. Pressurising the low-pressure carbon dioxide will require a significant energy input, which in turn may result in more carbon dioxide being produced.

There is a need in the art for a process that allows for the sequestration of carbon dioxide by means of mineralisation, which makes efficient use of the carbon dioxide capture capacity of the mineral, while allowing high-pressure carbon dioxide to be obtained without the need to pressurise the carbon dioxide.

Summary of the invention

It has now been found that an improved process for sequestration of carbon dioxide can be obtained by operating the intermediate leaching and precipitation steps of the overall mineralisation under different conditions.

Accordingly, the present invention provides a process for sequestration of carbon dioxide comprising:

a. an aqueous slurry comprising magnesium or calcium-comprising silicate particles under low temperature and low pressure conditions to obtain an aqueous bicarbonate solution;
b. pressurising the aqueous bicarbonate solution to a pressure above atmospheric pressure; and
c. heating the pressurised aqueous solution to induce bicarbonate decomposition, the formation of solid magnesium and/or calcium carbonate and the formation of high pressure carbon dioxide.

An advantage of the process according to the invention is that up to twice the amount of carbon

dioxide may captured from the carbon dioxide-comprising gas compared to the amount of carbon dioxide, which is mineralised. In addition, a high-pressure concentrated carbon dioxide-comprising gas may be obtained.

A further advantage is that there is no need to provide the carbon dioxide-comprising gas to the process at high pressure nor is there a need to provide a carbon dioxide-comprising gas comprising high carbon dioxide partial pressures. Therefore, there is no need to pre-treat, e.g. by upstream amine absorption processes the carbon dioxide-comprising gas prior to applying the process according to the invention.

Brief description of the drawings.

In Figure 1 a schematic representation is given an embodiment of a carbon dioxide sequestration process according to the invention.

Detailed description of the invention

The present invention provides a process for the sequestration of carbon dioxide by reacting the carbon dioxide with a mineral, typically a silicate mineral, to form a carbonate.

Suitable silicate minerals may have different structures. For instance, silicates may be composed of orthosilicate monomers, i.e. the orthosilicate ion SiO_4^{4-} which has a tetrahedral structure. Orthosilicate monomers form oligomers by means of O-Si-O bonds at the polygon corners. The Q^s notation refers to the connectivity of the silicon atoms. The value of superscript s defines the number of nearest neighbour silicon atoms to a given Si. Orthosilicates, also referred to as nesosilicates, are silicates which are composed of distinct orthosilicate tetrathedra that are not bonded to each other by means of O-Si-O bonds (Q^0 structure). Other structures include

chain silicates, also referred to as inosilicates, which might be single chain (SiO_3^{2-} as unit structure, i.e. a $(Q^2)_n$ structure) or double chain silicates ($(Q^3Q^2)_n$ structure). Also known are sheet silicate hydroxides, also referred to as phyllosilicates, which have a sheet structure $(Q^3)_n$.

It is known that orthosilicates or chain silicates can be relatively easy reacted with carbon dioxide to form carbonates and can thus suitably be used for carbon dioxide sequestration. Examples of magnesium or calcium orthosilicates suitable for mineral carbonation are olivine, in particular forsterite, and monticellite. Examples of suitable chain silicates are minerals of the pyroxene group, in particular wollastonite.

The more abundantly available magnesium or calcium silicate hydroxide minerals, for example serpentine, are sheet silicates and are more difficult to convert into carbonates, i.e. the reaction times for carbonation are much longer. Such sheet silicate hydroxides need to undergo a heat treatment or activation at elevated temperatures prior to the reaction with carbon dioxide.

Above a certain temperature, the serpentine mineral is at least partly converted into its corresponding ortho- or chain silicate mineral, silica and water. Additionally, the activation of silicate hydroxide minerals may include a conversion of part of the silicate hydroxide minerals into an amorphous sheet silicate hydroxide mineral derived compound.

In the process according to the invention a carbon dioxide-comprising stream is contacted with an aqueous slurry comprising magnesium or calcium-comprising silicate particles.

Preferably, the carbon dioxide partial pressure in the carbon dioxide-comprising gas that is contacted with the aqueous slurry is at least 0.01 bar, more preferably the carbon dioxide partial pressure is in the range of from 0.01 bar to 0.5, even more preferably 0.1 bar to 0.2 bar at Standard Temperature and Pressure conditions of 0 °C and 1 bar. Such carbon dioxide partial pressures allow for the direct capture of carbon dioxide from dilute carbon dioxide-comprising gases, without the need for a pre-treatment of the dilute gas in order to increase the carbon dioxide partial pressure.

When in step (a) of the process according to the invention, the carbon dioxide-comprising gas stream is contacted with the aqueous slurry comprising magnesium or calcium-comprising silicate particles, magnesium and or calcium ions are leached from the mineral and an aqueous bicarbonate solution is formed following reaction (1a).

Reference herein to leaching is to a conversion of the silicate mineral wherein at least part of the magnesium of calcium is removed from the mineral and dissolved in the aqueous medium as magnesium or calcium cations. Reference herein to the extent of leaching is to the mole% of magnesium and/or calcium leached from the mineral, based on the total number of moles of magnesium and/or calcium present in the original mineral. Reference herein to an aqueous bicarbonate solution is to a solution comprising dissolved bicarbonate anions and dissolved cations of metals, which were originally part of the mineral provided to the process by the aqueous slurry comprising magnesium or calcium-comprising silicate particles, wherein the moles of dissolved bicarbonate anions in the aqueous bicarbonate solution is

equal to or more than twice the moles of the mentioned metal cations in the aqueous bicarbonate solution.

In step (a), the carbon dioxide-comprising gas stream is contacted with the aqueous slurry comprising magnesium or calcium-comprising silicate particles under low temperature and low carbon dioxide partial pressure conditions. Preferably, the carbon dioxide-comprising gas stream is contacted with the aqueous slurry comprising magnesium or calcium-comprising silicate particles at a temperature in the range of from 1 to 100°C, more preferably 10 to 60°C, even more preferably 15 to 50°C and at a carbon dioxide partial pressure in the range of from 0.01 to 35 bara, more preferably 0.05 to 25 bara, even more preferably 0.1 to 10 bara. By maintaining low temperature and carbon dioxide partial pressure conditions during the leaching step, i.e. step (a), the solubility of the bicarbonate is maximised, and thus as a consequence so is the extent of leaching which may be achieved. Due to the low carbon dioxide partial pressure requirements there is no need to pressurise the carbon dioxide-comprising gas prior to contacting it with the aqueous slurry. It will be appreciated that in case the temperature of the carbon dioxide-comprising gas is to high it can advantageously be cooled by heat-exchange with another process stream.

Preferably, an electrolyte is added to the aqueous slurry in order to improve the formation of the bicarbonate and the leaching of metal ions from the mineral and improve precipitation in the later stages of the process. Preferably, sodium or potassium bicarbonate is provided to the aqueous slurry and/or optionally to the aqueous bicarbonate solution, preferably in an amount as to obtain a sodium or potassium bicarbonate

concentration of 1 mol or less per litre of the aqueous medium, i.e. not including solids.

The magnesium or calcium-comprising silicate particles may have any suitable size, preferably the particles have an average particle size in the range of from 0.1 μm to 5 cm, more preferably 0.5 to 500 μm. Reference herein to average diameter is to the volume medium diameter D(v,0.5), meaning that 50 volume% of the particles have an equivalent spherical diameter that is smaller than the average diameter and 50 volume% of the particles have an equivalent spherical diameter that is greater than the average diameter. The equivalent spherical diameter is the diameter calculated from volume determinations, e.g. by laser diffraction measurements.

In order to reach optimal leaching of the magnesium and/or calcium cations from the mineral particles it is preferred that the mineral particles have an average particle size of 50 μm or less, more preferably 15 μm or less.

The preferred particle size may be obtained by any suitable process for reducing the size of particles. Preferably, the process for reducing the particle size is a mechanical process, further referred to as grinding. Examples of grinding processes are for instance dry or wet grinding. Reference herein to wet grinding is to grinding in the presence of a suitable grinding fluid. Dry grinding of mineral to obtain particles of such small dimensions, however, is difficult, requires significantly more power and may require additional safety measure due to the formation of dust particles. Therefore, preferably, at least part of the mineral grinding is performed by wet grinding, preferably using an aqueous medium as grinding fluid.

For instance, the mineral may by dry grinded to an average particle size of approximately 500 μm and subsequently, after addition of the aqueous medium, wet grinded to the desired final average particle diameter. However, it is also possible to perform the complete grinding in the presence of the aqueous medium.

It is particularly advantageous and therefore preferred to combine the treatment to reduce the average particle size of the mineral particles with step (a) of the process according to the invention. More preferably, during step (a) the magnesium or calcium-comprising silicate particles are treated to reduce the average particle size to an average particle size in the range of from 0.1 to 50 μm, even more preferably of from 0.5 to 15 μm. Typically, the treatment for reducing the average particle size will be grinding, or wet grinding as the mineral is provided to step (a) in the form of an aqueous slurry. When carbon dioxide is contacted with the aqueous medium and the mineral during grinding, the extent of magnesium and/or calcium cation leaching from the mineral is increased and consequently the amount of carbon dioxide that can be captured per unit of raw mineral is increased.

During step (a), the aqueous slurry of magnesium or calcium-comprising silicate particles is contacted with carbon dioxide-comprising gas for in the range of from 1 to 60 minutes, preferably 10 to 30 minutes. Preferably, at least 35 mol%, more preferably at least 40 mol% of magnesium and calcium cations present in the mineral is leached and dissolved in the aqueous medium to form an aqueous bicarbonate solution, based on the total amount of magnesium and calcium cations present in the mineral prior to step (a).

During contact with the aqueous slurry at least part of the carbon dioxide comprised in the carbon dioxide-comprising gas is transferred to the aqueous phase, either in the form of bicarbonate or as dissolved carbon dioxide and a carbon dioxide-depleted gas is obtained. Preferably, the carbon dioxide content in the carbon dioxide-depleted gas is at most 50%, more preferably at most 30% of the carbon dioxide content in the carbon dioxide-comprising gas, based on the carbon dioxide content in the carbon dioxide-comprising gas.

In step (a) an aqueous bicarbonate solution is formed comprising dissolved magnesium and/or calcium bicarbonate, as part of the aqueous slurry. In addition, the aqueous bicarbonate solution may also comprise dissolved carbon dioxide. As the leaching reaction proceeds an increasing part of the silicate mineral is converted into dissolved (magnesium and/or calcium) bicarbonate, silica and optionally water. As a result, the composition of the aqueous slurry changes and will typically comprise an aqueous bicarbonate solution, residual magnesium or calcium-comprising silicate mineral particles and silica. It will be appreciated that at least part of the silica may be deposited in or on the residual mineral particles. The aqueous slurry obtained from step (a), i.e. the aqueous slurry comprising the aqueous bicarbonate solution, residual magnesium or calcium-comprising silicate mineral particles and silica is further referred to as the treated slurry.

Optionally, in case the mineral comprises of iron cations it may be advantageous to subject the treated slurry to an iron separation process. One effect of grinding the mineral comprising iron to a particle size below approximately 20 μm is that the iron is released

form the mineral may suitably be removed from the treated slurry using any suitable separation process, preferably a magnetic separation. An advantage of such a separation of iron clusters is that the iron can be used for other purposes and additionally the quantity of the solid effluent, which needs to be disposed of, is reduced.

In step (b) of the process according to the invention, the aqueous bicarbonate solution is pressurised to a pressure above atmospheric pressure. Preferably, the aqueous bicarbonate solution is pressurised to a pressure in the range of from 20 to 200 bara, preferably of from 50 to 150 bara.

Although, the aqueous bicarbonate solution may first be separated from the treated slurry this is not necessary. Preferably, the aqueous bicarbonate solution is provided to step (b) in the form of the treated slurry obtained from step (a).

Pressurising the aqueous bicarbonate solution provides significant advantages compared to pressurising any gaseous stream, such as a carbon dioxide-comprising stream. Pressurizing liquid or liquid slurry streams requires significantly less energy and can be accomplished using compact devices such a for instance a liquid or liquid slurry pump.

The pressurised aqueous bicarbonate solution is subsequently heated to induce bicarbonate decomposition. The dissociation products are solid magnesium or calcium carbonate, carbon dioxide and water. Preferably, the pressurised aqueous bicarbonate solution is heated to a temperature in the range of from 120°C or higher, preferably 140°C or higher. At temperatures above 120°C, the predominantly formed carbonates are magnesite (in case of magnesium) and calcite and aragonite (in case of

calcium). Below 120 °C, also hydromagnesite or nesquehonite (in case of magnesium) and hydrocalcite (in case of calcium) may be formed. The latter carbonates have significant amounts of water incorporated in their crystal structure, which leads to a higher weight of the precipitated carbonate material, and thus may lead to increased transportation and storage or disposal cost. It should be noted that some hydrocalcite, hydromagnesite and/or nesquehonite may be formed during the heating of the pressurised aqueous bicarbonate solution when the temperature is still low. However, at least part of these carbonates will be converted to respectively calcite/aragonite and/or magnesite at temperatures above 120°C.

The pressurised aqueous bicarbonate solution may be heated by any suitable means for heating liquids or liquid slurries. Preferably, the pressurised aqueous bicarbonate solution is heated or at least pre-heated by heat exchange with other stream in the process, such as the carbon dioxide-comprising gas or carbon dioxide-depleted gas of step (a). Alternatively, the heat of an optional mineral activation process as described herein below, for e.g. serpentine mineral, may be used to heat the pressurised aqueous bicarbonate solution.

During the dissociation of the bicarbonate, carbon dioxide is formed. Due to the elevated pressure, the concentration of dissolved carbon dioxide in the pressurised aqueous bicarbonate solution remains high allowing additional leaching of magnesium or calcium from the mineral during the dissociation of the bicarbonate and precipitation of the carbonate, thus a further increase the extent of leaching may be achieved.

In order to allow the dissociation reaction to proceed to completion of at least close to completion, the heated, pressurised aqueous bicarbonate solution is preferably maintained at elevated pressure and elevated temperature for an extended time period. Preferably, the heated, pressurised aqueous bicarbonate solution is maintained at elevated pressure and temperature for a time period of at least 1 minute, more preferably at least 20 minutes.

Preferably, the elevated pressure is above atmospheric pressure, more preferably is the range of from 20 to 200 bara, preferably of from 50 to 150 bara. Additionally, it is preferred that the elevated pressure is approximately equal to the pressure of the heated, pressurised aqueous bicarbonate solution, i.e. with in a range of from 10 bar below to 10 bar above the pressure of the heated, pressurised aqueous bicarbonate solution. Preferably, the elevated temperature is a temperature above at which the aqueous slurry is contacted with the carbon dioxide-comprising gas in step (a). More preferably the elevated temperature is a temperature in the range of from 120°C or higher, preferably 140°C or higher. Additionally, it is preferred that the elevated temperature is approximately equal to the temperature of the heated, pressurised aqueous bicarbonate solution, i.e. with in a range of from 20°C below to 20°C above the temperature of the heated, pressurised aqueous bicarbonate solution.

Preferably, the pressurised aqueous bicarbonate solution is heated and/or the heated, pressurised aqueous bicarbonate solution is maintained at elevated pressure and elevated pressure under a carbon dioxide-comprising

atmosphere. The partial pressure of the carbon dioxide in the atmosphere influences the formation of carbonates.

Therefore, preferably, the pressurised aqueous bicarbonate solution is heated and/or the heated, pressurised aqueous bicarbonate solution is maintained at elevated pressure and elevated pressure under a carbon dioxide-comprising atmosphere with the partial pressure of carbon dioxide of at least 1 bara, more preferably the partial pressure of carbon dioxide is in the range of from 1 to 200 bara, even more preferably of from 20 to 150 bara. Most preferred is an essentially pure carbon dioxide atmosphere, not taking steam into account.

An advantage of maintaining a carbon dioxide atmospheres that the concentration of dissolved carbon dioxide remains sufficiently high to allow further leaching of magnesium or calcium from the residual mineral, thereby increasing the extent of leaching that may be achieved. It should be noted that not only the temperature influences the preferred formation of the preferred carbonates, i.e. including magnesite, calcite, and aragonite.

It will be appreciated that the carbon-dioxide atmosphere will automatically be formed during the dissociation of the bicarbonate. The thus formed carbon dioxide atmosphere is essentially pure and will have a pressure equal to the pressure of the heated, pressurized aqueous bicarbonate solution. At least part of the pressurised carbon dioxide can be withdrawn from the process in the form of a high-pressure carbon dioxide stream. Preferably, the carbon dioxide partial pressure in the high pressure carbon dioxide stream is, while again excluding the presence of steam, in the range of from 0.5 bar to 1, even more preferably 0.9 bar to 1 bar,

still more preferably 0.95 to 1 bar at Standard Temperature and Pressure conditions of 0 °C and 1 bar.

When determining the carbon dioxide partial pressure in the high pressure carbon dioxide stream the presence of steam is not included. Most preferably, the high-pressure carbon dioxide stream consists of essentially pure carbon dioxide, not taking steam into account. This high-pressure carbon dioxide steam can be further used. For example, the high-pressure carbon dioxide stream may be used in enhanced oil recovery applications or in chemical synthesis processes using carbon dioxide. Additionally, the high-pressure carbon dioxide stream is particularly suitable for sub-surface carbon dioxide storage.

If desired additional carbon dioxide can be added to the atmosphere initially, preferably this additional carbon dioxide is carbon dioxide withdrawn form the process via the high-pressure carbon dioxide stream.

Maintenance of the heated, pressurized aqueous bicarbonate solution at elevated temperatures and pressures may be done separately from the heating of the pressurized solution in step (c). For instance, by first heating the pressurised aqueous bicarbonate solution in a heat exchanger and subsequently providing the heated, pressurised to a separate unit. However, as precipitation of carbonate is already initiated at low temperatures it is preferred that the maintenance of the heated, pressurized aqueous bicarbonate solution at elevated temperatures and pressures is combined with the heating of the pressurized solution in step (c).

Maintenance of the heated, pressurized aqueous bicarbonate solution at elevated temperatures and pressures and the heating of the pressurized solution in

step (c) may be performed continuously, semi-continuously or batch-wise. Suitable reactors units include for instance tubular flow reactor units or high-pressure reactor vessel units. Preferably, a batch-wise or semi-continuously operated autoclave is used.

A bicarbonate-depleted aqueous effluent is obtained from step (c). This effluent typically comprises solid magnesium carbonate and/or calcium carbonate, silica and residual mineral, e.g. in the form of an aqueous slurry. This aqueous slurry may still be at elevated temperature. Therefore, the effluent can be used for instance to heat or preheat the pressurised aqueous bicarbonate solution. This may be done using any suitable means for heat exchange, including a heat exchanger. The effluent of step (c) can suitably be further treated by filtration, preferably at high pressure. The solid residue obtained after filtration, preferably comprising significant amounts of magnesium or calcium carbonate next to residual mineral and silica, may be disposed of in any suitable way. Preferably, the solid residue is fist dried, e.g. by contacting it with the carbon dioxide-comprising gas or carbon dioxide-depleted gas of step (a). Alternatively, the heat of an optional mineral activation process as described herein below, for e.g. serpentine mineral, may be used to dry the solid residue.

The liquid filtrate obtained after filtration may be further treated to remove, if any, electrolyte and can be disposed of or recycled to step (a) of the process.

Any magnesium and/or calcium-comprising silicate mineral may be used. The magnesium and/or calcium-comprising silicate mineral may for example be a mixed silicate-oxide compound and/or a mixed silicate-oxide-

hydroxide compound. The magnesium and/or calcium-comprising silicate mineral may be in its hydrated form. Reference herein to magnesium or calcium-comprising silicate is to silicates comprising magnesium, calcium or both. Silicates comprising magnesium are preferred due to their abundances in nature. Part of the magnesium or calcium may be replaced by other metals, for example iron, aluminium or manganese.

Examples of suitable magnesium and/or calcium silicate minerals are natural occurring calcium or magnesium silicate minerals, e.g. wollastonite, olivine, sepiolite or serpentine, and industrial waste streams such as steel slag, paper bottom ash, or coal fly ash. Preferably, the magnesium and/or calcium-comprising silicate mineral is a magnesium-comprising silicate mineral, more preferably olivine or serpentine.

Serpentine is most preferred due to its natural abundance. Serpentine is a general name applied to several members of a polymorphic group of minerals having comparable molecular formulae, i.e. $(Mg,Fe)_3Si_2O_5(OH)_4$ or $Mg_3Si_2O_5(OH)_4$, but different morphologic structures. Serpentine with a high magnesium content, i.e. serpentine that has no Fe or deviates little from the composition $Mg_3Si_2O_5(OH)_4$, is preferred since a possible resulting mineral after activation is has a chemical composition resembling an olivine, which has the composition Mg_2SiO_4 and can sequester more carbon dioxide than olivine with a substantial amount of magnesium replaced by iron.

Olivine is a general name applied to several members of a polymorphic group of minerals having comparable molecular formulae, i.e. Mg_2SiO_4 or $(Mg,Fe)_2SiO_4$, depending on the iron content.

As mentioned herein above sheet silicate minerals such as serpentine require a heat treatment or activation prior to being contacted with the carbon dioxide-comprising gas. Activation of serpentine minerals for mineralisation purposes has been described in for instance EP1951424. In EP1951424, the activation is performed by contacting the mineral with hot synthesis gas. However, it will be appreciated that also other hot gasses may be used such as for instance hot flue gas.

Preferably, such an activation is performed in a fluidized bed reactor, in particular in a fluidized bed reactor, wherein a combustible fuel is provided together with a molecular oxygen-comprising gas, for instance natural gas and air, and the combustible gas is combusted inside the fluidized bed. This allows for a better control of the temperature in the fluidized bed and may result in an improved activated mineral quality, i.e. a high possible extent of leaching.

Preferably, the sheet silicate mineral, e.g. serpentine, is provided to the activation process in the form of particles having an average particle size in the range of from 100 to 750 μm, more preferably 200 to 500 μm. Such particles are especially suitable when the activation is performed in a fluidized bed reactor. Such particles sizes may be conveniently obtained by crushing the raw mineral. Crushing is a relatively simple method that does not require a high energy input. Additionally, there is no direct need to add significant amounts if any of liquids, in that sense crushing is comparable to a dry grinding process. The presence of additional components such as liquids during the activation of the mineral is disadvantageous, as these components require additional energy to be heated.

Subsequent to the activation, the activated mineral particle size can be further reduced by dry of wet grinding, preferably wet grinding, more preferably wet grinding during step (a) of the process according to the invention, as described herein above.

The aqueous slurry, which is contacted with the carbon dioxide-comprising gas in step (a) of the process according to the invention, may be any suitable aqueous slurry comprising an aqueous medium, preferably water, and solid material particles.

The solid material is a material at least comprising a magnesium and/or calcium silicate. Preferably the solid material comprises at least 50 wt%, more preferably 75 wt% more preferably more than 90 wt% of magnesium and/or calcium silicate, based on the total weight of the solid material. Other components comprised in the solid material may include for instance sand, clay, metal oxides, metal hydroxides or one or more metal carbonates, such as magnesium carbonate or calcium carbonate.

The aqueous slurry suitably contains up to 60 wt% of solid material, based on the total weight of the aqueous slurry, preferably 10 to 50 wt%. The aqueous slurry may, for example, be formed by mixing magnesium or calcium-comprising silicate particles with the aqueous medium.

The carbon dioxide-comprising gas may be pure carbon dioxide or a mixture of carbon dioxide with one or more other gases. Preferably, the carbon dioxide is a dilute carbon dioxide-comprising gas. It is an advantage of the present invention that such dilute carbon dioxide-comprising gases may be used without the need to for pre-treatment, i.e. pre-concentrating (for instance by an amine absorption process), pre-pressurising or pre-heating. Examples of suitable dilute carbon dioxide-

comprising gases include flue gas, synthesis gas or the effluent of a water-gas-shift process. Reference herein to synthesis gas is to a gas comprising at least hydrogen, carbon monoxide and optionally carbon dioxide. The carbon monoxide content of synthesis gas may be reduced by a water-gas-shift process wherein carbon monoxide is converted with water to hydrogen and carbon dioxide.

In an alternative operation it is possible to direct at least part of the aqueous bicarbonate solution obtained in step (a) to an alternative sequestration process. Suitable sequestration alternative include landfill, sub-surface storage onshore or offshore, i.e. deep ocean sequestration. In case of the later, it is preferred that the mineral is a magnesium based mineral as, contrary to calcium bicarbonate, the ocean water are typically not saturated with magnesium carbonate.

Detailed description of the drawings.

In Figure 1 a schematic representation is given an embodiment of a carbon dioxide sequestration process according to the invention. It will be appreciated that features described in the embodiment of Figure 1 may also be used alone or in combination with any other feature in the process according to the invention. In figure 1, aqueous slurry comprising magnesium and/or calcium silicate particles 100 and carbon dioxide-comprising gas 105 are provided to contactor 110. In contactor 110 aqueous slurry comprising magnesium and/or calcium silicate particles 100 and carbon dioxide-comprising gas 105 are contacted and optionally the magnesium and/or calcium silicate particles are in-situ grinded to a smaller particle size. Carbon dioxide-depleted gas 115 exits contactor 110 and may be released in to the

atmosphere or may be further processed, e.g. in the case of synthesis gas. An aqueous bicarbonate solution is withdrawn from contactor 110 in the form of treated slurry 120. Treated slurry 120 may optionally be provided to a separator (not show) to remove iron particles. When the magnesium and/or calcium comprising silicate mineral comprises iron and the mineral is grinding below 20 μm iron clusters present in the mineral may be liberated and these may be recovered by magnetic separation. Treated slurry 120 is pressurised in slurry pump 125 and pressurised treated slurry 130 exists slurry pump 125. Pressurised treated slurry 130 is subsequently provided to reactor 135, wherein pressurised treated slurry 130 is heated under pressure in the presence of carbon dioxide atmosphere 140. Optionally, reactor 135 may consist of a slurry heater 135a connected in series to vessel 135b. If desired, carbon dioxide can be retrieved from reactor 135 or vessel 135b via line 145. Bicarbonate depleted aqueous effluent 150 of reactor 135 can be disposed of or further treated.

C L A I M S

1. A process for sequestration of carbon dioxide comprising:

a. contacting a carbon dioxide-comprising gas stream with an aqueous slurry comprising magnesium or calcium-comprising silicate particles under low temperature and low carbon dioxide partial pressure conditions to obtain an aqueous bicarbonate solution;

b. pressurising the aqueous bicarbonate solution to a pressure above atmospheric pressure; and

c. heating the pressurised aqueous solution to induce bicarbonate decomposition, the formation of solid magnesium and/or calcium carbonate and the formation of high pressure carbon dioxide.

2. A process according to claim 1, wherein in step (a) the carbon dioxide-comprising gas stream is contacted with the aqueous slurry comprising magnesium or calcium-comprising silicate particles at a temperature in the range of from 1 to 100°C, preferably 10 to 60°C, more preferably of from 15 to 50°C and a carbon dioxide partial pressure in the range of from 0.01 to 35 bara, preferably 0.05 to 25 bara, more preferably of from 0.5 to 10 bara.

3. A process according to claim 1 or 2, wherein in step (b) the aqueous bicarbonate solution is pressurised to a pressure in the range of from 20 to 200 bara, preferably of from 50 to 150 bara.

4. A process according to any one of the preceding claims, wherein in step (c) the aqueous solution is

heated to a temperature in the range of from 120°C or higher, preferably 140°C or higher.

5. A process according to any one of the preceding claims, wherein the carbon dioxide-comprising gas comprises a carbon dioxide partial pressure of at least 0.01 bar to 0.5, preferably 0.1 bar to 0.2 bar at Standard Temperature and Pressure conditions of 0 °C and 1 bar.

6. A process according to any one of the preceding claims, wherein during step (a) additionally the magnesium or calcium-comprising silicate particles are treated to reduce particle size, preferably to a particles having a particle size in the range of from 0.1 to 50 μm, more preferably of from 0.5 to 15 μm.

7. A process according to any one of the preceding claims, wherein in step (a) the aqueous slurry of magnesium or calcium-comprising silicate particles is contacted with carbon dioxide comprising gas for in the range of from 1 to 60 minutes, preferably 10 to 30 minutes.

8. A process according to any one of the preceding claims, wherein following step (c) the heated, pressurised aqueous solution maintained at elevated pressure and elevated temperature for an extended period of time, preferably at least 1 minute, more preferably at least 20 minutes.

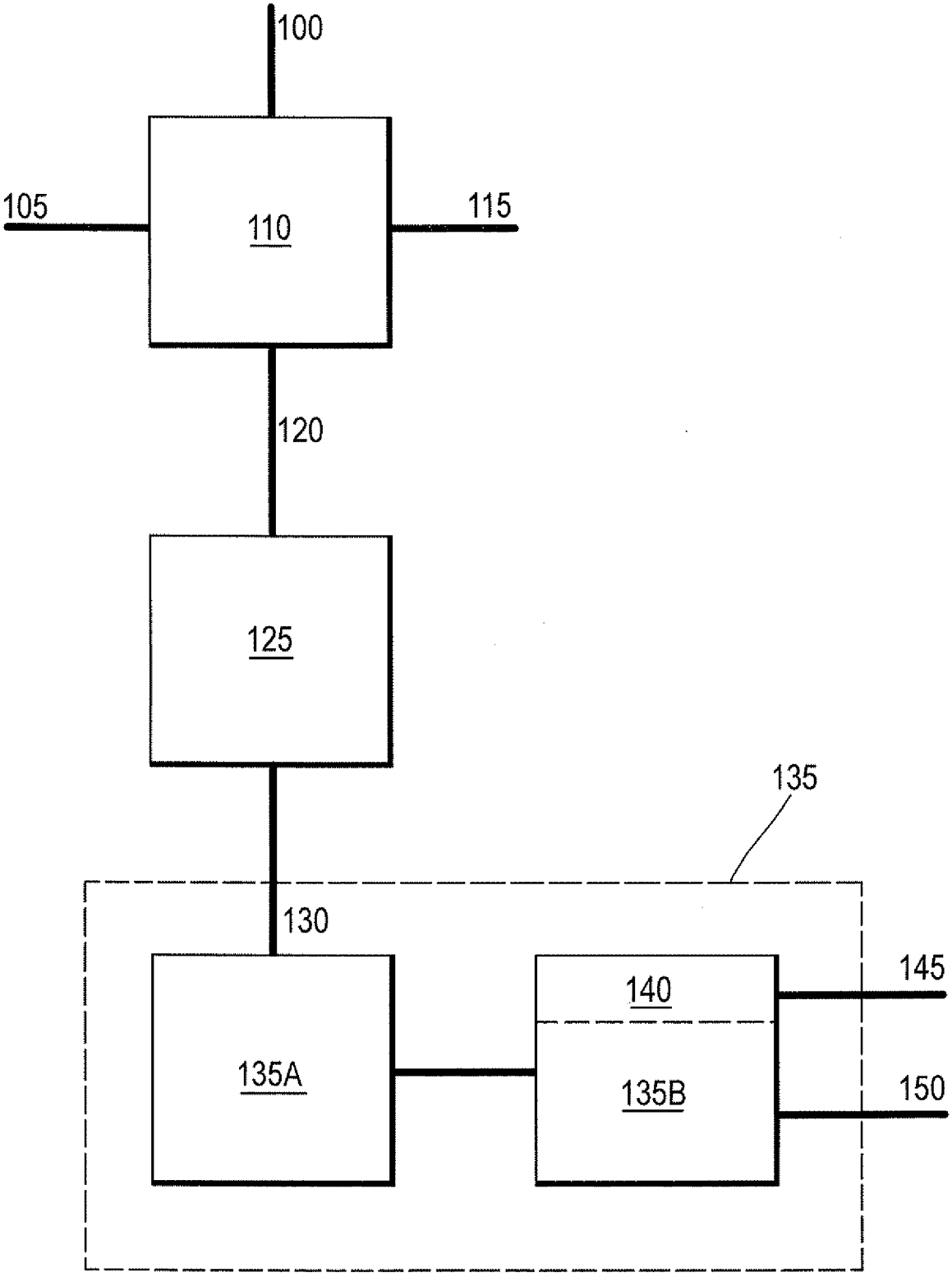
9. A process according to any one of the preceding claims, the pressurised aqueous bicarbonate solution of step (b) is heated and/or the heated, pressurised aqueous bicarbonate solution of step (c) is maintained at elevated temperate and pressure under a carbon dioxide-comprising atmosphere, preferably a carbon dioxide

atmosphere having a pressure of in the range of from 20 to 200 bara, preferably 50 to 150 bara.

10. A process according to any of the preceding claims, wherein the magnesium or calcium-comprising silicate is a magnesium-comprising silicate, preferably olivine, activated serpentine or activated talc, more preferably activated serpentine.

11. A process according to any of the preceding claims, wherein the aqueous slurry of step (a) is provided by addition of water to magnesium or calcium-comprising silicate particles having a particle size in the range of from 0.1 μm to 5 cm, more preferably of from 0.5 to 500 μm, even more preferably of from 0.5 to 15 μm.

Fig.1



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/052439

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/62 C01F5/24 C01F11/18 C04B2/00
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 C01F C04B

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 practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2006/008242 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 26 January 2006 (2006-01-26) cited in the application the whole document	1-11
A	WO 02/085788 A (SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ B.V.) 31 October 2002 (2002-10-31) cited in the application the whole document	1-11
A	US 2008/031801 A1 (K.S. LACKNER ET AL.) 7 February 2008 (2008-02-07) the whole document	1-11

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

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 June 2010	15/06/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Fax: (+31–70) 340–3016	Luethe, Herbert

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2010/052439

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