MAGNESIUM CARBONATE PRODUCTS

FIELD OF THE INVENTION

The present invention relates to carbon dioxide (CO_2) capture, sequestration and utilisation through the production of magnesium carbonate products.

BACKGROUND OF THE INVENTION

The rapid increase in atmospheric carbon dioxide concentrations is of concern due to its properties as a greenhouse gas and its contribution to the phenomena of global warming and climate change.

The sequestration of carbon dioxide gas in repositories that are isolated from the atmosphere is a developing field of technology that is widely recognised as an essential element in global attempts to reduce carbon dioxide emissions to the atmosphere.

Prototype demonstration facilities for carbon dioxide capture and sequestration (CCS) exist in several countries and commercial scale operations have recently also emerged. While various technologies exist for the capture and concentration of carbon dioxide from combustion flue gases, such as in coal combustion for electrical power generation, most current or proposed facilities utilise underground sequestration by injection of pressurised carbon dioxide into suitable underground repositories. That is commonly known as geosequestration and may be performed in depleted oil or gas reservoirs or other underground porous formations that are suitably isolated from the atmosphere. Those reservoirs or formations may be situated under land or sea. Another possible subterranean repository for carbon dioxide gas is so-called saline aquifers. Direct storage of carbon dioxide on the floor of the deep ocean has also been investigated but has yet to be successfully demonstrated on any significant scale.

Another field of study for carbon dioxide sequestration is that known as mineral carbonation, whereby carbon dioxide is chemically reacted with alkali or alkaline-earth metal oxide or silicate minerals to form stable solid carbonates. That approach is known as *ex-situ* mineral carbonation, as opposed to *in-situ* carbonation whereby carbon dioxide is deposited into underground mineral formations and reacts over longer timeframes with suitable minerals in existing underground formations.

The present invention is concerned with the *ex-situ* approach to carbon dioxide sequestration via mineral carbonation of silicate minerals to form carbonates.

Mineral carbonation has many potential advantages over other methods of carbon dioxide sequestration. Those include permanence and stability of the formed carbonates and the elimination of any risks of leakage of carbon dioxide gas. Furthermore, suitable subterranean sites for geosequestration do not exist at all locations where they are required near to carbon dioxide emission sources.

The chemical reactions of mineral carbonation are also thermodynamically favoured, with an exothermic release of energy due to the formation of the carbonates. The raw silicate minerals required for mineral carbonation are abundant and widely distributed globally. Those minerals may be readily mined and subjected to comminution and other mineral and chemical processing technologies. They are generally benign and the environmental and safety risks are readily manageable. In particular, the magnesium silicate mineral broadly known as serpentinite has been estimated to be available in quantities sufficient to sequester all global emissions of carbon dioxide from known fossil fuel reserves.

So-called single stage carbonation processes comprise the dissolution of magnesium ions from the activated mineral and precipitation of magnesium carbonate within a single stage, thereby producing a mixture of unreacted mineral, magnesium carbonate and silica. That mixture is difficult to separate into viable products, rendering the magnesium carbonate to have little or no economic value. The extent of conversion of magnesium ions to magnesium carbonate is also limited.

So-called two stage or multi-stage carbonation processes comprise separate magnesium dissolution and magnesium carbonate precipitation stages. The magnesium ion dissolution stage uses a carbon dioxide (CO_2) containing gas stream.

Such two- or multi-stage processes for carbonation of mineral ores are at relatively low pressures and temperatures, at least relative to single-stage processes. Those processes produce hydrated or hydroxy magnesium carbonates, as opposed to anhydrous magnesium carbonate (magnesite).

The production of anhydrous magnesium carbonate through carbonation of magnesium silicates typically requires high pressure and temperature thereby reducing its economic viability. In some cases, a mixed product, such as anhydrous magnesium carbonate plus unreacted magnesium silicate plus silica is produced. Such mixtures are of little utility or economic value.

An opportunity therefore remains to develop a process that not only sequesters carbon dioxide, but is also capable of producing various magnesium carbonate products, including anhydrous magnesium carbonate, in a scalable, efficient and cost effective manner.

SUMMARY OF THE INVENTION

The present invention provides a process for carbon dioxide (CO_2) capture, sequestration and utilisation through the production of magnesium carbonate product, the process comprising:

a) contacting an aqueous slurry of magnesium silicate with CO_2 to produce an aqueous slurry comprising hydrated magnesium (hydroxy) carbonate;

b) subjecting the aqueous slurry comprising hydrated magnesium (hydroxy) carbonate to a separation process at a first temperature to produce a concentrate having an increased concentration of the hydrated magnesium (hydroxy) carbonate relative to that of the aqueous slurry comprising hydrated magnesium (hydroxy) carbonate produced in step (a); and

c) subjecting the concentrate to a second temperature above the first temperature to produce a magnesium carbonate product having (i) a reduced molar ratio of hydroxyl group (OH) or water of crystallisation to magnesium, and (ii) a different crystal structure to the hydrated magnesium (hydroxy) carbonate in the concentrate.

A versatile integrated CO_2 sequestration process has now been developed that can produce various magnesium carbonate products, including anhydrous magnesium carbonate, in an efficient manner using substantially lower pressures and/or temperatures than conventional techniques. The process is economic to run, produces high purity magnesium carbonate products and can be industrially scaled.

Conventional techniques for carbon dioxide (CO_2) capture, sequestration and utilisation through the production of magnesium carbonate product typically produce the magnesium carbonate product in one or more precipitation stages, with the specific form of magnesium carbonate produced being dependant on the temperature at which the precipitation takes place. In contrast,

the process according to the present invention comprises a first step of producing an aqueous slurry of hydrated magnesium (hydroxy) carbonate, which may involve conventional precipitation techniques. The process then subjects the so formed slurry to a separation step that is conducted at a first temperature to produce a concentrate having an increased concentration of the hydrated magnesium (hydroxy) carbonate relative to that of the aqueous slurry comprising hydrated magnesium (hydroxy) carbonate produced in previous step. The resulting concentrate is then subjected to a second temperature above the first temperature to promote production of the magnesium carbonate product that has (i) a reduced molar ratio of hydroxyl group (OH) or water of crystallisation to magnesium, and (ii) a different crystal structure to the hydrated magnesium (hydroxy) carbonate in the concentrate

Through use of at least the combination of concentration and heating features, the process according to the invention can not only advantageously readily tailor the form of magnesium carbonate product produced, but that product can be produced more efficiently and effectively than conventional techniques. For example, to produce the magnesium carbonate product conventional techniques typically control the temperature and/or pressure of the bulk aqueous liquid that is used in producing/precipitating at the magnesium carbonate product, the process of which is very energy intensive. In contrast, the process in accordance with the present invention subjects a concentrate of hydrated magnesium (hydroxy) carbonate to a second temperature (above the first temperature used in preparing the concentrate) as a means of controlling the form of magnesium carbonate product produced. The energy input required for processing the concentrate in that matter is substantially lower than that required using conventional techniques. Furthermore, the process in accordance with the invention affords a high degree of versatility in the ability to produce an array of different magnesium carbonate products.

In one embodiment, step (a) comprises contacting the aqueous slurry of magnesium silicate with CO_2 to provide a slurry comprising a magnesium ion enriched carbonated aqueous liquid and thereafter, in a precipitation stage, a pH shift is induced in the magnesium ion enriched carbonated aqueous liquid by removing CO_2 therefrom to promote precipitation of the hydrated magnesium (hydroxy) carbonate.

In another embodiment, the magnesium carbonate product produced comprises anhydrous magnesium carbonate.

In a further embodiment, prior to subjecting the concentrate to the second temperature, magnesium (hydroxy) carbonate seed particles having a volumetric median diameter (D_{50}) of 100 microns or less are combined with the hydrated magnesium (hydroxy) carbonate.

In another embodiment, the process comprises: (d) recovering the so formed magnesium carbonate product.

Further aspects and/or embodiments of the invention are discussed in more detail below.

BRIEF DESCRIPTION OF DRAWINGS

The present invention will herein be described with reference to the following non-limiting drawings in which:

Figure 1 illustrates a schematic of the process according to the invention;

Figure 2 illustrates magnesite transformation rate at 165 °C and 14 barg total pressure (8 barg CO_2 partial pressure). The two curves represent the direct transformation from nesquehonite alone (10% NQ) and the transformation in the presence of equal concentration seed (10% NQ & 10% MAG). Time zero references the official onset of the reaction, whereby the reaction temperature and pressure conditions are met; and

Figure 3 illustrates seed and resultant product particle size distribution for experiments one and two associates with Example 2. Reaction conditions as per example one, albeit at a total solids content of 10% w/w (5% NQ & 5% MAG).

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process for carbon dioxide (CO_2) capture, sequestration and utilisation (CCSU). The process advantageously provides for the permanent and safe capture and sequestration of CO_2 while producing magnesium carbonate product of economic value. The process of the present invention comprises the chemical reaction of CO_2 (that would typically be discharged into the atmosphere) and magnesium silicate feedstock to produce magnesium carbonate product, thereby promoting a reduction in atmospheric CO_2 while simultaneously producing magnesium carbonate product of economic utility and value.

The process of the invention involves the production of magnesium carbonate product. By "magnesium carbonate product" is meant one or more magnesium carbonates species, including hydrated magnesium (hydroxy) carbonate(s) and anhydrous magnesium carbonate. As those skilled in the art will appreciate, so-called "hydrated" magnesium carbonate product comprises one or more water of crystallisation (·H_2O).

As used herein the expression "magnesium (hydroxy) carbonate(s)" is intended to mean one or both of magnesium carbonate(s) and magnesium hydroxy carbonate(s).

Accordingly, reference herein to "magnesium carbonate product" is intended to include anhydrous magnesium carbonate, hydrated magnesium carbonate and hydrated magnesium hydroxy carbonate.

The magnesium carbonate product may conveniently be represented by the formula: $(Mg(CO_3))a.(Mg(OH)_2)b.xH_2O$, where $a > 0$, $b \geq 0$, and $x \geq 0$.

In one embodiment, the magnesium carbonate product may be represented by the formula: $(Mg(CO_3))a.(Mg(OH)_2)b.xH_2O$, where a = 1-4 (1, 2, 3, 4), b = 0 or 1, x = 0-5 (0, 1, 2, 3, 4, 5), or where a = 1-4 (1, 2, 3, 4), b = 0 or 1, x = 0-4 (0, 1, 2, 3, 4).

In another embodiment, the magnesium carbonate product may comprise one or more of lansfordite ($MgCO_3.5H_2O$), nesquehonite ($MgCO_3.3H_2O$), dypingite ($(MgCO_3)_4.Mg(OH)_2.5H_2O$), hydromagnesite ($(MgCO_3)_4.Mg(OH)_2.4H_2O$) and magnesite ($MgCO_3$).

In a further embodiment, the magnesium carbonate product may comprise one or more of lansfordite ($MgCO_3.5H_2O$), nesquehonite ($MgCO_3.3H_2O$), hydromagnesite ($(MgCO_3)_4.Mg(OH)_2.4H_2O$) and magnesite ($MgCO_3$).

The process according to the invention makes use of an aqueous slurry of magnesium silicate. The aqueous slurry is a dispersion and/or suspension of magnesium silicate particles within an aqueous medium.

Magnesium silicate is a well-known and readily available material.

The magnesium silicate may be provided in the form of a mineral such as olivine, serpentine, dunite and mixtures thereof, or in rock formation such as seperntinite, ultramafics and mixtures thereof.

The magnesium silicate used (i.e. that used to form of the aqueous slurry) may present a particle size whereby the volumetric median diameter (D_{50}) is in the range 5-250 microns, or 20-150 microns, or less than 100 microns.

The aqueous medium that forms part of the aqueous slurry will generally comprise water in an amount of at least 50% by mass.

The magnesium silicate that forms part of the aqueous slurry will generally be present in the slurry in an amount ranging from about 1% to about 50% w/w.

To assist with the conversion of the magnesium silicate into the hydrated magnesium (hydroxy) carbonate, the magnesium silicate used may be activated magnesium silicate. By the magnesium silicate being activated is meant it has been processed to make it more reactive with the CO_2. For example, the magnesium silicate may be activated through grinding (increasing surface area) and/or being heated (thermal activation).

For thermal activation the magnesium silicate may be heated to a temperature in excess of 500 °C. Such activated magnesium silicate will generally comprise dehydroxylated magnesium silicate and be cooled to below about 200°C prior to mixing with aqueous liquid (e.g. water) to provide the aqueous slurry. Heat from the heated activated magnesium silicate may be recovered for beneficial use, such as heating another process stream or producing steam for electrical power generation. Heat recovery may be conducted in a suitable heat exchanger system with heat from the activated magnesium silicate either directly or indirectly heating another process stream.

In one embodiment, the magnesium silicate is activated magnesium silicate.

According to the process of the invention, the aqueous slurry of magnesium silicate is contacted with CO_2. In this contacting step the CO_2 reacts with the magnesium silicate to ultimately produce the hydrated magnesium (hydroxy) carbonate, for example through precipitation (see below). The CO_2 may be provided in any suitable form, for example as CO_2 gas, a CO_2

containing gas and/or carbonic acid (i.e. CO_2 gas dissolved in water). Reference to CO_2 in accordance with the invention is therefore intended to include CO_2 gas, a CO_2 containing gas and/or carbonic acid.

Accordingly, the aqueous slurry of magnesium silicate can also be described as being contacted with CO_2 gas, a CO_2 containing gas and/or carbonic acid.

There is no particular limitation on the source of CO_2 that may be used in accordance with the invention. The CO_2 used may be from the same or different sources.

For example, the CO_2 used may be derived from a flue gas of a hydrocarbon combustion process or it may be a purified stream of CO_2 captured from a hydrocarbon combustion, oxidation or reforming process or from natural gas processing.

The CO_2 used may range in CO_2 concentration, for example, from 0.1-100% by volume.

CO_2 capture processes are well known in the art and may involve the use of amines or other CO_2 absorbents or adsorbents or selective membranes to separate CO_2 from flue gas, or pre-combustion capture such as by so-called oxy-fuel combustion.

As will be discussed in more detail below, at least some of the CO_2 used may be sourced (recycled) from one or more stages of the process according to the invention.

The CO_2 used may be partially or completely derived through capturing and concentrating CO_2 from the atmosphere.

Contact of the CO_2 with the aqueous slurry of magnesium silicate might be achieved by any suitable means. For example, by passing CO_2 gas, including a gas comprising CO_2, into the aqueous slurry.

The aim of the contacting step is to promote reaction of the CO_2 with the magnesium silicate and produce hydrated magnesium (hydroxy) carbonate. Silica will also be produced as part of the reaction.

The hydrated magnesium (hydroxy) carbonate produced in accordance with the invention may conveniently be represented by the formula: $(Mg(CO_3))a.(Mg(OH)_2)b.xH_2O$, where $a > 0$, $b \geq 0$, and $x > 0$.

In one embodiment, the hydrated magnesium (hydroxy) carbonate may be represented by the formula: $(Mg(CO_3))a.(Mg(OH)_2)b.xH_2O$, where a = 1-4 (1, 2, 3, 4), b = 0 or 1, x = 1-5 (1, 2, 3, 4, 5).

In another embodiment, the hydrated magnesium (hydroxy) carbonate may comprise one or more of lansfordite ($MgCO_3.5H_2O$), nesquehonite ($MgCO_3.3H_2O$), dypingite ($(MgCO_3)_4.Mg(OH)_2.5H_2O$), and hydromagnesite ($(MgCO_3)_4.Mg(OH)_2.4H_2O$).

As a result of the reaction, the aqueous slurry of magnesium silicate is converted into an aqueous slurry comprising the hydrated magnesium (hydroxy) carbonate.

Contacting the aqueous slurry of magnesium silicate with CO_2 may be assisted with agitation and/or stirring of the aqueous slurry.

Contacting the aqueous slurry of magnesium silicate with CO_2 may be performed at ambient temperature and pressure. Alternatively, the aqueous slurry of magnesium silicate may be contacted with CO_2 at greater than ambient temperature and pressure, for example at temperatures ranging from about 40ºC to about 150ºC and/or pressures ranging from greater than 1 bar to about 100 bar.

Accordingly, production of the hydrated magnesium (hydroxy) carbonate in the contacting step may be undertaken at ambient temperature and pressure. Alternatively, production of the hydrated magnesium (hydroxy) carbonate in the contacting step may be undertaken at greater than ambient temperature and pressure, for example at temperatures ranging from about 20ºC to about 150ºC, or from about 40ºC to about 150ºC and/or pressures ranging from greater than 1 bar to about 100 bar.

In some embodiments, the contacting step during which the hydrated magnesium (hydroxy) carbonate is produced may be performed at temperatures ranging from about 20 ºC to less than 100 ºC, or about 20 ºC to about 65 ºC, or about 25 ºC to about 50 ºC.

The contacting step (a) according to the process can be performed using equipment and conditions known in the art, with the aim being to convert/sequester the CO_2 into hydrated magnesium (hydroxy) carbonate. For example, the contacting step may be undertaken in a stirred tank reactor or bubble column reactor that allows for efficient contacting of the CO_2 with the magnesium silicate aqueous slurry.

The contacting step (a) provides for the aqueous slurry comprising hydrated magnesium (hydroxy) carbonate. That aqueous slurry is a dispersion and/or suspension of hydrated magnesium (hydroxy) carbonate particles within an aqueous medium.

The contacting step (a) gives rise to the chemical reaction that results in formation of the hydrated magnesium (hydroxy) carbonate via precipitation. Those skilled in the art will appreciate that such precipitation may occur at the time when the CO_2 makes contact with the aqueous slurry of magnesium silicate or that precipitation may occur at a later stage in the contacting step (a).

For example, in one embodiment, the aqueous slurry of magnesium silicate is contacted with the CO_2 to provide a slurry comprising a magnesium ion enriched carbonated aqueous liquid and a magnesium depleted silicate solid, collectively defined as a magnesium ion enriched carbonated aqueous slurry. The so formed magnesium depleted silicate solid is “magnesium depleted” in the sense that a fraction of the magnesium component of the magnesium silicate material has been removed by the reaction of CO_2 in the contacting step (a). That magnesium depleted silicate residual solid can be removed from the magnesium ion enriched carbonated aqueous slurry to give a magnesium ion enriched aqueous liquid. That separation step can be achieved through an appropriate solid-separation technology such as filtration, centrifugation etc. In a subsequent precipitation stage of the contacting step (a), a pH shift can induced in the magnesium ion enriched carbonated aqueous liquid by removing CO_2 therefrom to promote precipitation of the hydrated magnesium (hydroxy) carbonate. That precipitation gives rise to the aqueous slurry comprising the hydrated magnesium (hydroxy) carbonate. It will be appreciated removing CO_2 from the magnesium ion enriched carbonated aqueous liquid will

increase the pH of that liquid. In other words, a pH increase is induced in the magnesium ion enriched carbonated aqueous liquid by removing CO_2 therefrom.

In such an embodiment, the magnesium ion enriched carbonated aqueous liquid is formed as a result of the CO_2 reacting in the aqueous liquid with the magnesium silicate to provide dissolved magnesium ions within a carbonated aqueous liquid. The so formed magnesium ions are "enriched" in the sense that the magnesium ion enriched carbonated aqueous liquid contains a higher concentration of dissolved magnesium ions compared to the initial aqueous slurry of magnesium silicate. That is a consequence of an increase (i.e. enrichment) in the aqueous liquid magnesium ion concentration as the CO_2 begins to react with the magnesium silicate. Those skilled in the art will appreciate the magnesium ions will be present in solution together with bicarbonate and carbonate counterions.

Irrespective of whether the hydrated magnesium (hydroxy) carbonate formed in the contacting step (a) (i) precipitates immediately upon the CO_2 coming into contact with the aqueous slurry of magnesium silicate, or (ii) precipitation is promoted at a later stage in the contacting step (a) through, for example, inducing a pH shift in a magnesium ion enriched carbonated aqueous liquid formed as part of the contacting step (a), those skilled in the art will appreciate that the temperature at which precipitation of the hydrated magnesium (hydroxy) carbonate occurs will primarily dictate the specific chemical/physical composition of the so formed hydrated magnesium (hydroxy) carbonate in that step.

Accordingly, reference herein to a temperature at which the contacting step (a) is performed to produce the hydrated magnesium (hydroxy) carbonate is intended to mean the temperature in the contacting step (a) at which precipitation of the hydrated magnesium (hydroxy) carbonate occurs.

The hydrated magnesium (hydroxy) carbonate that forms part of the resulting aqueous slurry will generally have a volumetric median diameter (D_{50}) particle size ranging from about 1 μm to about 100 μm.

The hydrated magnesium (hydroxy) carbonate that forms part of the resulting aqueous slurry will generally be present in the slurry in an amount ranging from about 1% w/w to about 50% w/w.

In another embodiment, removal of the CO_2 (from the magnesium ion enriched carbonated aqueous liquid) is performed by application of reduced pressure to the magnesium ion enriched carbonated aqueous liquid. By application of reduced pressure is meant reducing the pressure to below atmospheric pressure surrounding the magnesium ion enriched carbonated aqueous liquid in order to withdraw/remove CO_2 from the liquid. Provided the CO_2 is withdrawn/removed from the liquid there is no particular limitation on the degree of reduced pressure that can be applied. For example, a reduced pressure at an absolute pressure of about 1 kPa to about 95 kPa may be applied. That reduced pressure may be applied by any suitable means using any suitable equipment. For example, vacuum pumps or condensing heat exchangers may be used.

The temperature of the aqueous slurry on forming (i.e. precipitating) the hydrated magnesium (hydroxy) carbonate in step (a) will generally range from about 20 ºC to less than 150 ºC, from about 40 ºC to less than 150 ºC, or from about 20 ºC to less than 100 ºC, or from about 20 ºC to about 65 ºC, or about 25 ºC to about 50 ºC.

As will be discussed in more detail below, to produce the magnesium carbonate product having (i) a reduced molar ratio of hydroxyl group (OH) or water of crystallisation to magnesium, and (ii) a different crystal structure to the hydrated magnesium (hydroxy) carbonate in the concentrate, the process according to the invention includes step (c) that comprises subjecting the concentrate produced according to step (b) to a second temperature above the first temperature adopted in step (b). For that dehydroxylation/dehydration and crystal structure transformation to occur in step (c), those skilled in the art will appreciate that the temperature at which the hydrated magnesium (hydroxy) carbonate is produced in contacting step (a) must inherently be lower than the second temperature adopted in step (c). If that was not the case at the dehydroxylation/dehydration and crystal structure transformation required for step (c) would not occur.

The temperature at which the hydrated magnesium (hydroxy) carbonate is produced in the contacting step (a) may be similar to or the same as the first temperature used in step (b).

The temperature at which the hydrated magnesium (hydroxy) carbonate is produced in step (a) may range from ambient temperature to a less than 100 ºC. For example, the temperature at which the hydrated magnesium (hydroxy) carbonate is produced in step (a) may range from about 20 ºC to less than 100 ºC, or about 20 ºC to about 65 ºC, or about 25 ºC to about 50 ºC.

In one embodiment, the temperature at which the hydrated magnesium (hydroxy) carbonate is produced in step (a) ranges from about 20 °C to less than 100 °C, or about 20 °C to about 65 °C, or about 25 °C to about 50 °C.

As mentioned, those skilled in the art will appreciate that to achieve the required dehydroxylation/dehydration and crystal structure transformation, the second temperature of step (c) must be higher than the temperature at which the hydrated magnesium (hydroxy) carbonate is produced in step (a). Generally, the second temperature will be at least about 10°C, or at least about 20°C, or at least about 30°C, or at least about 40°C higher than the temperature at which the hydrated magnesium (hydroxy) carbonate is produced in step (a).

Having produced the aqueous slurry comprising hydrated magnesium (hydroxy) carbonate in step (a), the process according to the invention comprises subjecting it to a separation process at a first temperature to produce a concentrate having an increased concentration of the hydrated magnesium (hydroxy) carbonate relative to that of the starting aqueous slurry.

Provided the concentration of the hydrated magnesium (hydroxy) carbonate is increased (relative to the starting aqueous slurry), there is no particular limitation on the type of separation process that may be used. Conventional separation processes/techniques/equipment can advantageously be used. For example, one or more of filtration, decantation, settling and centrifugation techniques can be employed. Other means of separation may include evaporation of the aqueous component.

It will generally be desirable for the concentrate produced to have a concentration of hydrated magnesium (hydroxy) carbonate of at least about 5% w/w, or about 10% w/w, or about 15% w/w, or about 20% w/w, or about 25% w/w, or about 30% w/w.

The separation process according to the present invention is conducted at a first temperature. As will be discussed further below, the first temperature will be lower than the second temperature used in step (c). Generally, the first temperature will range from ambient temperature to a less than 100 °C. For example, the first temperature may range from about 20 °C to less than 100 °C, or about 20 °C to about 65 °C, or about 25 °C to about 50 °C.

In one embodiment, the first temperature at which the separation process is undertaken ranges from about 20 ºC to less than 100 ºC, or about 20 ºC to about 65 ºC, or about 25 ºC to about 50 ºC.

In another embodiment, the first temperature at which the separation process is undertaken is about the same temperature as the temperature at which the hydrated magnesium (hydroxy) carbonate is produced in step (a).

Where heat input is required to achieve the first temperature, it may be provided by any suitable means. For example, recovering low grade heat from any process including the linked process that produces the CO_2.

Having produced the concentrate according to step (b), the process in accordance with the invention include subjecting that concentrate to a second temperature, that is above the first temperature, to produce a magnesium carbonate product having (i) a reduced molar ratio of hydroxyl group (OH) or water of crystallisation to magnesium, and (ii) a different crystal structure to the hydrated magnesium (hydroxy) carbonate in the concentrate.

Accordingly, step (c) of the process converts the hydrated magnesium (hydroxy) carbonate from step (b) into a magnesium carbonate product through loss of one or both of hydroxyl group (OH) or water of crystallisation. The resulting magnesium carbonate product also has a different crystal structure to the hydrated magnesium (hydroxy) carbonate in the concentrate from which it is derived.

Conventional production of magnesium carbonate products from magnesium rich brines derived from either sea water or natural magnesium carbonates is an energy intensive process. Through the adjustment of pH at temperatures exceeding 100 °C, it is possible to precipitate hydroxy magnesium carbonates directly from the brine. To produce anhydrous magnesium carbonate, temperatures exceeding 100 °C, in addition to elevated CO_2 pressures, typically greater than 100 bar (absolute), are required. That is typically performed with long residence times, exceeding several hours. Heat recovery from such a system is critical to ensure energy efficiency. However, the relative dilute nature of magnesium in such brines, e.g. typically 1-10 g/L of Mg, makes that difficult. The large volumes of water resulting from the dilute nature of such brines requires the need for high efficiency heat exchanges to promote sufficient heat recovery.

Furthermore, the dilute nature of such brines introduces additional engineering challenges due to their high susceptibility in inducing heat exchanger fouling. The combined effect of those two problems results in higher capital and operating costs.

The process according to the present invention provides a pathway for the controlled production of a magnesium carbonate product at a reduced energy input and CO_2 footprint. In the process, the volume of the intermediate hydrated magnesium (hydroxy) carbonate is reduced using conventional separation techniques (e.g. filtration, settling and the like) to create a concentrate slurry (e.g. 10-20% w/w solids, equivalent to 20 to > 40 g/L of Mg). That step can advantageously be performed relatively quickly at ambient temperatures and pressures. The resulting concentrate comprising the hydrated magnesium (hydroxy) carbonate produced according to the invention is then heated, and in some embodiments, pressurized with CO_2, to the desired operating temperature to produce the required magnesium carbonate product. By utilizing the concentrate in that step, a significant reduction in the sensible heat load of the aqueous component results, thereby yielding energy savings (and thus CO_2 footprint) and maximizing the sequestered CO_2 achieved by the invention. Such efficiencies are achieved by ensuring at least the first temperature adopted in step (b) is lower than the second temperature adopted in step (c). If the first temperature was higher than the second temperature, then any dehydroxylation/dehydration and crystal structure transformation that is intended to occur in step (c) according to the invention would prematurely occur in step (b) on the basis of the higher volume non-concentred aqueous slurry from step (a). That in turn would result in unfavourable energy efficiency. As previously noted, the temperature at which the hydrated magnesium (hydroxy) carbonate is produced in step (a) must of course also be lower than at least the second temperature adopted in step (c) to achieve the required dehydroxylation/dehydration and crystal structure transformation.

The collective use of steps (a)-(c) in accordance with the invention therefore provides a unique means to produce magnesium carbonate products in a cost-effective and environmentally friendly manner.

Furthermore, the magnesium carbonate product produced in accordance with the invention has the potential to displace CO_2 intensive precipitated carbonates and fillers such as precipitate calcium carbonate (PCC) and precipitated silica, with the added benefit of improved thermal stability, higher density, and superior blending properties owing to its tailorable morphology.

Generally, the second temperature will be at least about 10 °C, or at least about 20 °C, or at least about 30 °C, or at least about 40 °C higher than the first temperature.

The second temperature may be at least about 80 °C, or at least 100 °C, or at least about 105 °C, or at least about 110 °C, or at least about 115 °C, or at least about 120 °C.

The second temperature may range from about 40 °C to about 250 °C, or about 40 °C to about 190 °C, or about 60 °C to about 150 °C, or about 70 °C to about 140 °C, or about 80 °C to about 140 °C, or about 90 °C to about 140 °C, or at least 100 °C to about 140 °C.

In one embodiment, the first temperature is below 100 °C and the second temperature is equal to or greater than 100 °C.

In another embodiment, the temperature at which the hydrated magnesium (hydroxy) carbonate is produced in step (a) and the first temperature used in step (b) is below 100 °C and the second temperature used in step (c) is equal to or greater than 100 °C.

In a further embodiment, the temperature at which the hydrated magnesium (hydroxy) carbonate is produced in step (a) and the first temperature used in step (b) independently range from about 20 °C to less than 100 °C, or about 20 °C to about 65 °C, or about 25 °C to about 50 °C and the second temperature used in step (c) is at least about 10 °C, or at least about 20 °C, or at least about 30 °C, or at least about 40 °C higher than the temperature at which the hydrated magnesium (hydroxy) carbonate is produced in step (a) and the first temperature used in step (b).

The concentrate produced in step (b) will generally need to be heated to achieve the second temperature. Conventional heating processes/techniques/equipment can advantageously be used. For example, heating may be achieved through the direct injection of steam as generated from electricity or combustion process, or alternatively by the indirect contacting of the concentrate with a heat transfer medium through an appropriately sized heat exchanger.

The process may be performed in a continuous or batch mode.

In a continuous mode it may be advantageous to recover at least a portion of the heat required for step (c) from the magnesium carbonate containing slurry produced in step (a) to reduce the net energy input required.

The concentrate produced in step (b) may comprise one, two or more hydrated magnesium (hydroxy) carbonate species that are converted into one, two or more magnesium carbonate products in step (c).

The process in accordance with the invention advantageously provides an efficient, cost-effective and industrially scalable means for producing a diverse range of magnesium carbonate products through the sequestration of CO_2. According to the process, the hydrated magnesium (hydroxy) carbonate is converted into a magnesium product through loss of one or both of a hydroxyl group or water of crystallisation. In other words, the magnesium carbonate product produced has a reduced molar ratio of hydroxyl group or water of crystallisation to magnesium.

Those skilled in the art can readily evaluate the conversion that occurs in step (c). For example, magnesium carbonate products in accordance with the present invention are shown in the table directly below, together with their molar ratio of water of crystallisation to magnesium:

Common name	Formula	# mols Mg	# mols H_2O	ratio H_2O:Mg
lansfordite	$MgCO_3.5H_2O$	1	5	5
nesquehonite	$MgCO_3.3H_2O$	1	3	3
dypingite	$(MgCO_3)_4.Mg(OH)_2.5H_2O$	5	6	1.2
hydromagnesite	$(MgCO_3)_4.Mg(OH)_2.4H_2O$	5	5	1
magnesite	$MgCO_3$	1	0	0

Conversion that might occur in step (c) with the required reduction in molar ratio of water of crystallisation to magnesium can include, but is not limited to, one or more of:

$MgCO_3.5H_2O$ to $MgCO_3.3H_2O$;

$MgCO_3.3H_2O$ to $(MgCO_3)_4.Mg(OH)_2.5H_2O$;

$MgCO_3.3H_2O$ to $(MgCO_3)_4.Mg(OH)_2.4H_2O$;

$MgCO_3.3H_2O$ to $MgCO_3$;

$(MgCO_3)_4.Mg(OH)_2.5H_2O$ to $(MgCO_3)_4.Mg(OH)_2.4H_2O$;

$(MgCO_3)_4.Mg(OH)_2.5H_2O$ to $MgCO_3$; and

$(MgCO_3)_4.Mg(OH)_2.4H_2O$ to $MgCO_3$.

In one embodiment, the process comprises the production of $MgCO_3.3H_2O$ in step (c) from the concentrate produced in step (b) that comprises $MgCO_3.5H_2O$.

In one embodiment, the process comprises the production of $(MgCO_3)_4.Mg(OH)_2.5H_2O$ in step (c) from the concentrate produced in step (b) that comprises $MgCO_3.3H_2O$.

In one embodiment, the process comprises the production of $(MgCO_3)_4.Mg(OH)_2.4H_2O$ in step (c) from the concentrate produced in step (b) that comprises $MgCO_3.3H_2O$.

In one embodiment, the process comprises the production of $MgCO_3$ in step (c) from the concentrate produced in step (b) that comprises $MgCO_3.3H_2O$.

In one embodiment, the process comprises the production of $(MgCO_3)_4.Mg(OH)_2.4H_2O$ in step (c) from the concentrate produced in step (b) that comprises $(MgCO_3)_4.Mg(OH)_2.5H_2O$.

In one embodiment, the process comprises the production of $MgCO_3$ in step (c) from the concentrate produced in step (b) that comprises $(MgCO_3)_4.Mg(OH)_2.5H_2O$.

In one embodiment, the process comprises the production of $MgCO_3$ in step (c) from the concentrate produced in step (b) that comprises $(MgCO_3)_4.Mg(OH)_2.4H_2O$.

In addition to undergoing a reduction in the molar ratio hydroxyl group or water of crystallisation to magnesium, the magnesium carbonate product produced in step (c) also presents a different crystal structure to the hydrated magnesium (hydroxy) carbonate in step (b) from which it is derived.

For example, where the process comprises the production of $(MgCO_3)_4.Mg(OH)_2.4H_2O$ in step (c) from the concentrate produced in step (b) that comprises $(MgCO_3)_4.Mg(OH)_2.5H_2O$, the $(MgCO_3)_4.Mg(OH)_2.4H_2O$ will have a different crystal structure from the $(MgCO_3)_4.Mg(OH)_2.5H_2O$. Similarly, where the process comprises the production of $MgCO_3$ in step (c) from the concentrate produced in step (b) that comprises $(MgCO_3)_4.Mg(OH)_2.4H_2O$, the $MgCO_3$ will have a different crystal structure from the $(MgCO_3)_4.Mg(OH)_2.4H_2O$.

Those skilled in the art can readily determine the crystal structure of both the hydrated magnesium (hydroxy) carbonate species and the magnesium carbonate products using standard

techniques and equipment. For example, the crystal structures may be determined by crystallography using techniques such as powdered X-ray diffraction.

When subjecting the concentrate to the second temperature in accordance with the invention, the concentrate may be agitated or stirred.

To facilitate the production of the magnesium carbonate product, step (c) of the process may comprise subjecting the concentrate to the second temperature while it is under a partial pressure of CO_2.

The partial pressure of CO_2 may be provided by any suitable means. For example, it may be provided by an introduced gas stream comprising CO_2.

The partial pressure of CO_2 may range from about 0.1 bar to about 100 bar, or from 0.1 bar to about 50 bar, or from about 1 bar to about 10 bar.

In one embodiment, the partial pressure of CO_2 is provided by an introduced gas stream comprising CO_2.

In a further embodiment, the introduced gas stream comprising CO_2 is sourced from the CO_2 removed from the magnesium ion enriched carbonated aqueous liquid.

Prior to subjecting the concentrate to the second temperature, magnesium (hydroxy) carbonate seed particles having a volumetric median diameter (D_{50}) of 100 microns or less may be combined with the hydrated magnesium (hydroxy) carbonate.

Incorporating the use of such seed particles in accordance with the process of the invention has been found to greatly assist with controlling of the particle size and crystal morphology of the magnesium carbonate products produced. The incorporation of seed particles in accordance with the process of the invention also provides a significant acceleration in the production of the magnesium carbonate when compared with the absence of seed. That can be important for the industrial production of magnesium carbonate products, reducing the overall capital and operating costs.

The seed concentration is dependent on its available surface area as calculated by techniques such as gas adsorption methods (e.g. BET, Langmuir, etc) or air permeability techniques (e.g. Blaine). The concentration of seed particle will typically range from about 0.1% w/w to about

50% w/w.

The process in accordance with the invention is further described with reference to Figure 1 that shows an aqueous slurry of magnesium silicate (1) being contacted with a CO2-containing stream (2) to form a slurry comprising hydrated magnesium (hydroxy) carbonate (3). This slurry is subjected to a separation process (4) at a first temperature T1 to produce a concentrate (5) having an increased concentration of the hydrated magnesium (hydroxy) carbonate relative to that of the aqueous slurry comprising hydrated magnesium (hydroxy) carbonate and a dilute stream (6). The concentrate is then heated (7) to a temperature T2, where T2>T1, to produce magnesium carbonate product having (i) a reduced molar ratio of hydroxyl group (OH) or water of crystallisation to magnesium, and (ii) a different crystal structure to the hydrated magnesium (hydroxy) carbonate in the concentrate (5). The product stream (8) is recovered and optionally subjected to further purification. The dilute stream (6) may be recycled back into the process.

EXAMPLES

Example 1

This example demonstrates the transformation of nesquehonite, obtained from carbonation of activated magnesium silicate, to magnesite at fixed pressure & temperature, according to the invention.

An aqueous slurry of activated magnesium silicate (serpentinite) was reacted with CO_2, producing a magnesium-ion-enriched carbonated solution and a residual silicate solid. The silicate was removed by filtration, yielding a purified magnesium-rich solution.

A pH shift was induced by removing excess dissolved CO_2 at 45 °C under sub-atmospheric pressure (<1 bar), leading to a reduction in carbonic acid concentration and the subsequent precipitation of the hydrated magnesium carbonate (nesquehonite) and the additional release of CO2. The resulting nesquehonite slurry had a concentration of 2% by weight (w/w). To improve process efficiency, the slurry was further concentrated to 10% w/w by gravity settling at 25 °C and ambient pressure (1 bar).

A subsample of this slurry was heated to 165 °C in a sealed pressure vessel. CO_2 was introduced to achieve a partial pressure of 8 bar, bringing the total system pressure to 14 barg. The

transformation of nesquehonite into a lower hydration state magnesium carbonate (magnesite) was monitored through periodic liquid and solid sampling.

Thermogravimetric analysis quantified the conversion by assessing CO_2 mass loss, while scanning electron microscopy (SEM) revealed a morphological transition from the needle-like acicular structure of nesquehonite to the characteristic cubic habit of magnesite. This confirmed the phase transformation from monoclinic nesquehonite to trigonal magnesite.

Figure 2 illustrates the magnesite content of the reactor as a function of time, with zero being no magnesite present and 100% being only magnesite. Time zero on the graph refers to the point where heat up is complete and signifies the onset of CO_2 addition; here, pressurisation is completed in approximately 1 minute. Two trends are shown for demonstration. Trend 1 represents the nesquehonite conversion in the absence of magnesite seed at 165 °C and 14 barg total pressure. Here, it is seen that magnesite formation does not occur until the time zero point has passed, i.e. once the reaction vessel is at temperature and pressure. The transformation to magnesite here occurs slowly until the 60 minute mark, at which point it accelerates to completion at 150 minutes. The second trend contains both nesquehonite and magnesite at equal concentration, specifically 10% w/w nesquehonite and 10% w/w magnesite in water. The presence of magnesite seed material leads to the rapid transformation of the nesquehonite material, with transformation even noted during the heat up period in the absence of additional CO_2.

Example 2

This example demonstrates particle size control of precipitated magnesite according to the invention.

An aqueous slurry of activated magnesium silicate (serpentinite) was reacted with CO_2, producing a magnesium-ion-enriched carbonated solution and a residual silicate solid. The silicate was removed by filtration, yielding a purified magnesium-rich solution.

A pH shift was induced by removing excess dissolved CO_2 at 45 °C under sub-atmospheric pressure (<1 bar), leading to a reduction in carbonic acid concentration and the subsequent precipitation of the hydrated magnesium carbonate (nesquehonite) and the additional release of CO_2. The resulting nesquehonite slurry had a concentration of 2% by weight (w/w). To improve

process efficiency, the slurry was further concentrated to 10% w/w by gravity settling at 25 °C and ambient pressure (1 bar).

Magnesite was added to the slurry as a seeding agent (this was added in the form of a slurry, consisting of 10% w/w magnesite in water), resulting in a final solids concentration of 5% w/w nesquehonite and 5% w/w magnesite, with the remaining balance being water.To this slurry, an additional fraction of magnesite was added as a seeding agent, giving a final slurry solid content of 5% w/w nesquehonite and 5% w/w magnesite (water balance). This resultant slurry was heated to 165 °C and pressurised to a total pressure of 14 barg through the addition of CO2, as per example one, leading to the transformation of the nesquehonite to magnesite in alignment to example one. For this example, two individual experiments were conducted that probed the influence of the magnesite seed particle size with respect to the transformation product. In each experiment, the total transformation of nesquehonite to magnesite was achieved over a reaction window of 120 minutes (here, the reaction window refers to that described in example one). Scanning electron microscopy was used to confirm the transformation, displaying a change in the crystal structure from acicular monoclinic nesquehonite to trigonal magnesite.

The particle size distribution of the final reactor contents (i.e. this contains both the initial magnesite seed and the additional magnesite formed through the transformation of the nesquehonite) is presented in Figure 3. Here, four distributions are presented, referred to as S1, P1, S2, and P2, with each S & P series referring to the to the experiment seed and product particle size, respectively. From Figure 3, it is seen that the final product size distribution closely matches that of the initial seed particle. This highlights the capability of product size control based on the seed particle size specification. A summary of the key distribution parameters can be found in Table 1.

Table 1. Key distribution parameters for both seed (S) and product (P) produced through experiments one & two.

Variable	S1	P1	S2	P2
d_{10} (μm)	1.22	1.72	4.70	6.13
d_{50} (μm)	2.75	3.83	11.20	12.19
d_{80} (μm)	4.89	6.22	18.60	19.17
$d_{4,3}$ (μm)	2.31	4.61	12.90	13.74
$d_{3,2}$ (μm)	3.41	3.14	7.99	10.64

Example 3

This example demonstrates the transformation of nesquehonite to hydromagnesite at fixed pressure & temperature.

A dilute nesquehonite slurry (slurry density of approximately 2% w/w nesquehonite) prepared through the carbonation of an aqueous slurry of thermally activated serpentinite was concentrated using gravity-based settling to a slurry density of 10% w/w nesquehonite. A subsample of this slurry was obtained and heated to 125 °C in a closed pressure vessel. The transformation reaction of nesquehonite, a hydrated magnesium silicate, to hydromagnesite, a magnesium silicate having a reduced water of crystallisation, was monitored through the collection of both liquid and solid subsamples through the duration of the reaction. The relative quantities of nesquehonite and hydromagnesite in the solid subsamples were determined through thermogravimetric analysis and quantified through their relative CO2 mass losses. The hydromagnesite content of the reactor, as a function of time, was observed ranging from zero to 100% hydromagnesite. Inspection of the solid sub-samples by scanning electron-microscopy displayed a gradual change from the acicular habit of nesquehonite to the platy habit of hydromagnesite, confirming a change in the crystal structure from monoclinic nesquehonite to monoclinic hydromagnesite.

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

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

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS

1. A process for carbon dioxide (CO_2) capture, sequestration and utilisation through the production of magnesium carbonate products, the process comprising:

a) contacting an aqueous slurry of magnesium silicate with CO_2 to produce an aqueous slurry comprising hydrated magnesium (hydroxy) carbonate;

b) subjecting the aqueous slurry comprising hydrated magnesium (hydroxy) carbonate to a separation process at a first temperature to produce a concentrate having an increased concentration of the hydrated magnesium (hydroxy) carbonate relative to that of the aqueous slurry comprising hydrated magnesium (hydroxy) carbonate produced in step (a); and

c) subjecting the concentrate to a second temperature above the first temperature to produce a magnesium carbonate product having (i) a reduced molar ratio of hydroxyl group (OH) or water of crystallisation to magnesium, and (ii) a different crystal structure to the hydrated magnesium (hydroxy) carbonate in the concentrate.

2. The process according to claim 1, wherein the first temperature is below 100 °C and the second temperature is equal to or greater than 100 °C.

3. The process according to claim 1 or 2, wherein the concentrate is subjected to the second temperature under a partial pressure of CO_2.

4. The process according to claim 3, wherein the partial pressure of CO_2 is provided from an introduced gas stream comprising CO_2.

5. The process according to claim 3 or 4, wherein the partial pressure of CO_2 ranges from 0.1 bar to 100 bar.

6. The process according to any one of claims 1 to 5, wherein step (a) comprises contacting the aqueous slurry of magnesium silicate with CO_2 to provide a slurry comprising a magnesium ion enriched carbonated aqueous liquid and thereafter, in a precipitation stage, a pH shift is induced in the magnesium ion enriched carbonated aqueous liquid by removing CO_2 therefrom to promote precipitation of the hydrated magnesium (hydroxy) carbonate.

7. The process according to claim 6, wherein the removal of the CO_2 is performed by application of reduced pressure to the magnesium ion enriched carbonated aqueous liquid.

8. The process according to claim 6 or 7 when dependent on claim 4, wherein the CO_2 in the introduced gas stream is sourced from the CO_2 removed from the magnesium ion enriched carbonated aqueous liquid.

9. The process according to any one of claims 1 to 8, wherein hydrated magnesium (hydroxy) carbonate produced in step (a) comprises one or more of lansfordite ($MgCO_3.5H_2O$), nesquehonite ($MgCO_3.3H_2O$), dypingite ($(MgCO_3)_4.Mg(OH)_2.5H_2O$), and hydromagnesite ($(MgCO_3)_4.Mg(OH)_2.4H_2O$).

10. The process according to any one of claims 1 to 9, wherein the magnesium carbonate product produced comprises one or both of anhydrous magnesium carbonate and magnesium hydroxy carbonate.

11. The process according to any one of claims 1 to 10, wherein prior to subjecting the concentrate to the second temperature, magnesium (hydroxy) carbonate seed particles having a volumetric median diameter (D_{50}) of 100 microns or less are combined with the hydrated magnesium (hydroxy) carbonate.

12. The process according to any one of claims 1 to 11, wherein the separation process comprises one or more of filtration, decantation, settling and centrifugation.

13. The process according to any one of claims 1 to 10, wherein the second temperature is at least about 30 °C higher than the first temperature.

14. The process according to any one of claims 1 to 10, wherein the second temperature is at least 100 °C to about 140 °C.