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(54) **Title:** PRODUCTION OF MAGNESIUM CARBONATE

(57) **Abstract:** A process for producing magnesium carbonate by carbonating a magnesium silicate ore containing iron is disclosed. It is characterised by the step of contacting a slurry of the ore in water with a gaseous mixture comprising carbon dioxide and oxygen. The process is suitably carried out at elevated temperature and pressure wherein the gaseous mixture is in supercritical fluid form. It is particularly suitable for the processing of olivine and serpentine ores wherein iron is present in the +2 oxidation state. The process also optionally comprises the separation of silica and/or discrete iron oxide or hydroxide phases(s) co-produced with the magnesium carbonate. Also disclosed are downstream processes for converting the magnesium carbonate into magnesium oxide and compositions derived therefrom having cementitious properties. Cement products and concrete building materials produced from these compositions have useful structural properties and have a low carbon footprint relative to traditional Portland cement.



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PRODUCTION OF MAGNESIUM CARBONATE

The present invention relates to an improved process for manufacturing magnesium carbonate from magnesium silicate ores by carbonation (i.e. treatment with carbon dioxide and/or carbonic acid H_2CO_3). In particular, it relates to a process in which magnesium silicate ores containing a significant amount of iron are carbonated so that the magnesium carbonate produced is free or substantially free from iron in its lattice. Such magnesium carbonates are especially useful as precursors for the manufacture of cement-based products for the construction industry.

The production of magnesium carbonate from magnesium silicate ores by mineral carbonation is known in the art. For example, O'Connor *et al*, in a paper presented at the 5th International Conference on Greenhouse Gas Technologies, in Cairns, Australia on August 14-18, 2000 and entitled 'CO₂ Storage in Solid Form: A Study of Direct Mineral Carbonation', have disclosed that aqueous slurries of magnesium silicate ores such as olivine and hydrated magnesium silicate ores such as serpentine can be readily converted into magnesite ($MgCO_3$) by treatment with carbon dioxide at elevated temperature and pressure and in an aqueous medium containing carbonate and hydrogen carbonate anions. Such a process has attracted considerable interest because the magnesite so formed can be buried underground thereby opening up the possibility that it can be used to capture and sequester deleterious greenhouse gases. A more complete report of this work by O'Connor *et al* can be found in DOE Final Report DOE/ARC-TR-04-002 dated 15th May 2005 and in Environmental Progress, 25(2), pp.161-66 (2006).

Numerous other disclosures about this process may also be found in the art. For example, Béarat *et al*, Environmental Science and Technology, 40(15), pp.4802-08 (2006) have reported mechanistic studies carried out using olivine, whilst in WO 02/085788 Shell have reported the mineral carbonation of ortho-, di-, ring and chain silicates in the presence of an aqueous electrolyte such as sodium nitrate. Shell and others have also reported mineral carbonation processes involving the use of serpentine where the serpentine is thermally activated before undergoing carbonation; see for example WO 2008/142017, WO 2008/142025, WO 2009/092718 and WO 2008/061305.

More recently, in WO 2009/156740, we have taught that compositions comprised of magnesium carbonate, magnesium oxide and optionally magnesium hydroxide exhibit desirable cementitious properties making them viable alternatives to traditional Portland cement. We have furthermore reported in GB 1014991.2 (dated 9th September 2010) that the mineral carbonation

process of O'Connor can be modified to produce an integrated process for making these cement formulations from mineral silicate ores with reduced carbon dioxide emissions relative to the traditional methods of making Portland Cement: in many instances to the extent that these formulations can be characterised as being carbon neutral or even 'carbon negative'. It is our
5 belief that our integrated process is also less energy intensive and environmentally problematic than the alternative two step mineral carbonation processes described in for example WO 2010/006242.

We have now found that the integrated process described in our earlier application can produce cement formulations with improved performance properties if the mineral carbonation
10 step is operated under conditions which prevent the iron impurities present in the magnesium silicate ore becoming chemically incorporated into the magnesium carbonate product. For example, naturally occurring olivines, which have the empirical chemical formula $Mg_xFe_ySiO_4$, (wherein $x+y=2$) can be regarded as a family of solid solutions of the two end members fosterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4) in which the oxidation state of both metals is +2 and whose
15 structures are derived by isomorphous replacement of one cation for the other in one or other end member's crystal lattice. For these reasons, the iron content of this ore can vary widely depending on its source and it is hard to remove the iron impurity from it by physical means. As a consequence, the products of the carbonation reaction tend to be mixed magnesium-iron carbonates having the general formula $Mg_aFe_bCO_3$ wherein $a+b=1$. These mixed metal carbonates
20 when calcined tend to produce magnesium oxides of low reactivity thereby adversely affecting the performance of the final cement formulation.

A number of approaches to extracting iron from such ores have been published. For example WO 2010/132784 discloses a method whereby the olivine is completely dissolved and a chelating agent (e.g. an organic acid such as citric acid) is used to capture and precipitate the iron
25 as iron oxide. WO 2008/300142 and WO 2008/403490, on the other hand, describe processes for separating iron impurities from crude magnesite by calcination, slurrying the crude magnesium oxide so produced and treating it with carbon dioxide to produce either pure magnesium carbonate or bicarbonate. CA 1093280 discloses a process in which crude magnesite is mixed with magnesium chloride and heated in oxygen to produce volatile iron chloride which can then be
30 removed by distillation or sublimation. JP 2010/132504 discloses a process for making pure magnesium carbonate from low-grade magnesium hydroxide by treating a slurry of this feedstock with a mixture of carbon dioxide and an oxygen containing gas. WO 2010/022468 discloses an integrated process in which thermally activated serpentines are subject to a separation stage

before carbonation occurs in order to remove metal oxide impurities. A similar process is described in the above-mentioned O'Connor 2000 paper at pp. 5-6 where the serpentine is heat treated at 600-650°C. Finally, WO 2007/069902 discloses a process for preparing pure magnesium carbonate from olivine but this involves the use of separate magnesium silicate dissolution and carbonate precipitation steps.

We have now found that by modifying the carbonation disclosed by O'Connor so that it is carried out in the presence of oxygen a magnesium carbonate can be produced which can be used advantageously in the manufacture of the cement formulations which are the subject of our earlier patent application. Whilst not wishing to be bound by theory, we believe that under such conditions the iron impurities are oxidised either wholly or in part from the +2 to the +3 oxidation state thereby reducing their tendency to be incorporated into the lattice of the magnesium carbonate. Rather discrete iron oxide and hydroxide phases such as Fe_2O_3 , Fe_3O_4 or $\text{Fe}(\text{OH})_3$ are formed which if so desired can be separated more easily. According to the present invention there is therefore provided a process for producing magnesium carbonate by carbonating a magnesium silicate ore containing iron characterised in that the process comprises contacting a slurry of the ore in water with a gaseous mixture comprising carbon dioxide and oxygen.

Whilst the process of the present invention is particularly applicable to the processing of olivine it can in principle be applied to any ortho-, di-, chain or ring magnesium silicate, including hydrated magnesium silicates such as serpentines and talcs, which contain iron in the +2 oxidation state. In the case of serpentine, the process can be employed after an optional thermal pre-treatment of the ore in the temperature range 500-700°C along the lines taught in the O'Connor paper and Shell applications referred to above as it is likely that such heat treated materials will still contain residual Fe^{2+} cations within the silicate lattice even after most of the iron has been removed by magnetic separation. The process described is especially suitable for the processing of magnesium silicate ore in which the molar ratio of magnesium to iron is in the ratio 1000:1 to 1:10, preferably 500:1 to 1:1 and most preferably 250:1 to 2:1. Typically, the magnesium silicate ore will be supplied from a mine in particulate form and can therefore often be used without further mechanical treatment. However if the average particle size of the materials so obtained is relatively large it is preferred to grind or mill them further so that their average particle size is less than 1000 microns preferably in the range 100 to 500 microns.

The process of the present invention is suitably carried out at a temperature in the range from 25 to 250°C depending on which form of magnesium carbonate is desired. For example, if the object is to produce magnesite the temperature should be suitably from 120 to 250°C; if it is

to produce hydromagnesite it should be from 65 to 120°C and if it is to produce nesquehonite it should be from 25 to 65°C. However in order to obtain optimum reaction rates it is usually preferred to work at a temperature in the range 100 to 225°C. In other words the magnesium carbonate product will typically be magnesite or mixtures of magnesite and hydromagnesite. At the same time the pressure should be maintained in the range from 7.1 to 25MPa, preferably from 7.1 to 20MPa most preferably from 7.1 to 9.7MPa.

The carbonation reaction is suitably carried out at a pH in the range 2 to 8.5 preferably in the range 6 to 8.5 most preferably in the range 7 to 8. In order to buffer the reaction medium and to improve the concentration of reactive carbonate and hydrogen carbonate anions therein it is preferred to include an alkali metal (Group 1A) salt of carbonic acid preferably a water-soluble sodium or potassium salt more preferably one selected from the group consisting of sodium carbonate, sodium hydrogen carbonate, potassium carbonate and potassium hydrogen carbonate. Most preferred of all is the use of sodium carbonate and/or sodium hydrogen carbonate. The alkali metal salt may for example be added either as a separate aqueous solution to any carbonation reactor employed or performed or pre-mixed with the aqueous slurry of magnesium silicate ore fed thereto. The amount of alkali metal salt utilised is preferably up to its saturation limit in the aqueous slurry under the carbonation conditions.

Additionally, an alkali metal nitrate or halide salt (preferably selected from sodium nitrate, potassium nitrate, sodium chloride, and potassium chloride) can be added in like manner. The amount of such salt should likewise be in the range up to its saturation level in the slurry under the carbonation conditions. When this embodiment is employed, the alkali metal salt is most preferably selected from sodium nitrate, potassium nitrate or mixtures thereof to minimise corrosion problems.

As regards the gaseous mixture, this is comprised of carbon dioxide and oxygen. It can be generated by mixing carbon dioxide with pure oxygen or an oxygen-containing gas or industrially available mixtures of oxygen with one or more other gases which are inert under the reaction conditions such as nitrogen, the noble gases and the like. In order to ensure that the carbonation progresses at a reasonable rate and to avoid the use of unnecessarily high pressures it is preferred that the gaseous mixture comprises a major amount of carbon dioxide and a minor amount of other gaseous components (including the oxygen). In other words the partial pressure of the carbon dioxide present should be greater than 50% more preferably greater than 75% of the total pressure employed. Preferably the partial pressure of the oxygen in the total of those gaseous

components other than carbon dioxide should be greater than 10% of the total partial pressure of said components.

In a preferred embodiment of the present invention the temperature and pressure employed are such that the components of the gaseous mixture (or at least the carbon dioxide and oxygen components thereof) are provided and/or maintained in a supercritical fluid state. More preferably using a supercritical gaseous mixture at a pressure in the range 7.5 to 9.7MPa has the additional advantage that the design pressure of the carbonation reactor and its associated piping systems is such that these items can be sourced preferentially from standard off-the-shelf components which meet the ASTM International Standards for a 900# rated system or equivalent standards e.g. DIN, COST and the like. Alternative embodiments employing higher pressures up to 25 MPa (which would require ASTM 1500 or 2500# rated systems) can also be used albeit with a loss of economic advantage.

The carbonation reaction can be carried out batch-wise, semi batch-wise or continuously under steady state conditions. In chemical engineering terms, a variety of process configurations can be employed and examples which utilise moving or fluidised bed technologies are specifically contemplated. One suitable way of carrying out the carbonation reaction is by using one or more heated and insulated 'closed-loop' reactors in which a slurry of the magnesium silicate ore, the supercritical gaseous mixture and the products of the reaction are during operation continuously contacted and recycled around a tubular closed-loop maintained at the desired reaction conditions. The closed-loop itself is generally provided with one or more inlets and outlets, for respectively the periodic introduction of the various reactants and the periodic withdrawal of the reactor contents, and a one or more pumps which drive circulation of the reactor contents around the loop and ensure that the re-circulating slurry remains well-mixed and above its settling velocity. Preferably the re-circulating slurry is maintained at a Reynolds number such that it undergoes turbulent as opposed to laminar flow.

It is also preferred that the amount of magnesium silicate ore in the slurry is up to 60% of the latter's total weight, preferably from 15 to 20% by weight. Typically the residence time in the carbonation reactor is between 0.5 and 6 hours preferably between 0.5 and 1.5 hours although the exact figure will depend to a certain extent on whether one or a multiplicity of reactors arranged in series are utilised. In the latter case, the residence time in any one reactor may be below the lower limit of 0.5 hours specified above provided that cumulative residence time across the whole reactor train is within the broadest range quoted above.

Overall therefore, in a preferred embodiment of the present invention, there is provided a process for carbonating magnesium silicate ore containing iron characterised by continuously contacting a slurry of the ore in water with a gaseous mixture comprising carbon dioxide and oxygen wherein said contacting is carried out in a closed-loop reactor provided with a recirculation pump, an inlet for introducing the gaseous mixture in a supercritical fluid state into the recirculation pump or at a point in the loop immediately upstream thereof and one or more further inlets for introducing the slurry and removing the products of the carbonation process.

During the carbonation process, the magnesium silicate ore containing iron impurities is progressively converted into a particulate product comprising silica (including optionally insoluble metal silicates), one or magnesium carbonate phase(s) having the general formula:



in which x is a number equal to or greater than 1, and y or z is a number equal to or greater than 0; and x, y and z may be (but need not be) integers and one or more iron oxide or hydroxide phase(s) in which some or all of the iron is in the +3 oxidation state. As mentioned above, the magnesium carbonate phase(s) in this product are preferably selected from nesquehonite, hydromagnesite and magnesite and contain less 8 mole%, preferably less than 5 mole% and most preferably less than 3 mole% iron cations based on the total number of magnesium and iron cations present in the phase. The iron oxide phase(s) which are preferably discrete from the magnesium carbonate phase(s) are suitably selected from the group consisting of hematite, magnetite and ferric hydroxide. Thereafter the product can be separated from the aqueous reaction medium and any soluble salts remaining therein, for example by filtration or use of a hydrocyclone, before being subjected to any washing and drying which is required. In one embodiment of the present invention, the iron oxide phase(s) are separated from the product either before or after washing/drying. Depending on the nature of the iron oxide phase(s) produced this can be achieved by known techniques such as magnetic separation (in the case of ferromagnetic iron oxides such as magnetite) or by a hydrocyclone (where the mass and/or the particle size of the iron oxide phase(s) are either significantly larger or smaller than the other components of the reaction product). The same or further hydrocyclones may also be used to separate the silica phase so that a magnesium carbonate free or substantially free of the other components may be produced if so desired. Thereafter some or all of the magnesium carbonate phase can be calcined at elevated temperature, typically in the range 500 to 850°C, to liberate carbon dioxide (which can be recycled to the carbonation reaction) and generate pure, iron-free, magnesium oxide which can then be blended with magnesium carbonate, and optionally with

silica, silicates, alumina, aluminates, aluminosilicates and pozzolans to produce cement formulations in accordance with our WO 2009/156740 or our GB 1014577.9. Whilst any source of magnesium carbonate can be used in this blending, it is preferred to employ the magnesium carbonate phase produced in the process of the present invention or a magnesium carbonate phase produced by the re-carbonation of part of the magnesium oxide. The latter is advantageous when the magnesium carbonate required for the formulation is nesquehonite as this phase is relatively easy to produce by contacting a slurry of the magnesium oxide in water with carbon dioxide at a low temperature (less than 65°C) and low carbon dioxide pressures.

In an alternative embodiment the separation of the three components of the reaction product can be omitted and the washed and dried product simply calcined as described above to produce a calcined product comprising magnesium oxide and the other two components. This calcined product can then be blended with magnesium carbonate as described above to make the desired cement formulations.

The process of the present invention is now illustrated by the following.

A stainless steel tubular loop reactor having a volume of 5 litres is provided with a first inlet through which an aqueous slurry of magnesium silicate may be fed periodically; a recirculation pump designed to operate at high pressure and at a rate of 3600 litres per hour; a second inlet located at the inlet/seal of the recirculation pump and through which a supercritical carbon dioxide/air mixture is fed and an outlet through which the reactor contents are withdrawn periodically.

Every sixty minutes approximately 4.5 litres of slurry containing 15% by weight olivine particles (e.g. an ore comprising 15% Fayerlite and 85% Fosterite by weight) having an average size of 120 microns, 1M of sodium nitrate and 0.64M sodium hydrogen carbonate is pumped at 80°C into the loop reactor which is maintained at a temperature of 170°C and 8.8MPa. At the same time a supercritical fluid carbon dioxide/air mixture (CO₂ is 90% of total pressure) is added via the second inlet to control the pressure in the reactor. Every sixty minutes 4.5 litres of slurry is removed via the outlet and subsequently filtered, washed at temperature and pressure to recover a solid particulate mixture of magnesite (substantially free of incorporated or lattice iron), separate iron oxide and/or iron hydroxide phase(s) and silica. The mother liquor remaining behind is recycled to a tank where it is mixed with fresh olivine and top-up sodium nitrate and sodium hydrogen carbonate before being fed back into the loop reactor via the first inlet.

The particulate mixture comprising magnesite (substantially free of incorporated or lattice iron), separate iron oxide and/or iron hydroxide phase(s) and silica is next fed to a kiln where it is

heated to 700°C until all the carbon dioxide is evolved and a mixture of magnesium oxide (substantially free of incorporated or lattice iron), separate iron oxide phase(s) and silica remains. After cooling by heat exchange, part of the mixture of magnesium oxide and silica is fed to a stirred tank where it is mixed with water to generate a slurry with a 5% solids content. This slurry
5 is then maintained at less than 45°C for two hours and mixed with fresh or recycled carbon dioxide gas at a pressure of 0.5MPa after which it is cooled and separated to produce a final product comprising nesquehonite (substantially free of incorporated or lattice iron), separate iron oxide phase(s) and silica. This final product is blended with the material obtained directly from the kiln and, if necessary, either pure magnesium oxide or aluminosilicate, and optionally
10 pozzolans to produce compositions which exhibit desirable cementitious properties.

Claims

1. A process for producing magnesium carbonate by carbonating a magnesium silicate ore containing iron characterised in that the process comprises contacting a slurry of the ore in water with a gaseous mixture comprising carbon dioxide and oxygen.
2. A process as claimed in claim 1 characterised in that it is carried out at a temperature in the range 100 to 225°C.
3. A process claimed in either claim 1 or claim 2 characterised in that it is carried out at a pressure in the range 7.1 to 9.7 MPa.
4. A process as claimed in any one of the preceding claims characterised in that the partial pressure of carbon dioxide in the gaseous mixture is greater than 75% of the total pressure of the gaseous mixture.
5. A process as claimed in any one of the preceding claims characterised in that the gaseous mixture comprises carbon dioxide and air.
6. A process as claimed in any one of the preceding claims characterised in that the gaseous mixture is used in supercritical fluid form.
7. A process as claimed in any one of the preceding claims characterised in that the reaction product comprises silica, one or more magnesium carbonate phase(s) having the general formula: $x \text{MgCO}_3 \cdot y \text{Mg(OH)}_2 \cdot z \text{H}_2\text{O}$ in which x is a number equal to or greater than 1, and y or z is a number equal to or greater than 0; and x, y and z may be (but need not be) integers and one or more discrete iron oxide or hydroxide phase(s) in which some or all of the iron is in the +3 oxidation state.
8. A process as claimed in claim 7 characterised in that the magnesium carbonate phase(s) are separated from the silica, the one or more iron oxide or hydroxide phase(s) or both components.
9. A process as claimed in claim 8 characterised in that the magnesium carbonate phase(s) are calcined after separation to produce magnesium oxide.
10. A process as claimed in claim 9 characterised in that the magnesium oxide so produced is blended with magnesium carbonate and optionally silicas, silicates, alumina, aluminates and pozzolans to produce a formulation having cementitious properties.
11. A process as claimed in claim 7 characterised in that the product is calcined to convert the magnesium carbonate phase(s) into magnesium oxide.

12. A process as claimed in claim 11 characterised in that the magnesium oxide so produced is blended with magnesium carbonate and optionally silicas, silicates, alumina, aluminates and pozzolans to produce a formulation having cementitious properties
- 5 13. A process as claimed in either claim 10 or 12 characterised in that the magnesium carbonate used for blending purposes is respectively either the reaction product of claim 7 or the separated magnesium carbonate phases(s) of claim 8.
- 10 14. A process for carbonating magnesium silicate ore containing iron characterised by continuously contacting a slurry of the ore in water with a gaseous mixture comprising carbon dioxide and oxygen wherein said contacting is carried out in a closed-loop reactor provided with a recirculation pump, an inlet for introducing the gaseous mixture in a supercritical fluid state into the recirculation pump or at a point in the loop immediately upstream thereof and one or more further inlets for introducing the slurry and removing the products of the carbonation process.
- 15 15. A process as claimed in claim 14 characterised in that the gaseous mixture is introduced and maintained in supercritical fluid form and the flow of the slurry around the loop is turbulent.