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Short Communication

Decarbonizing the cement industry is crucial for reducing CO_2 emissions: Myth or reality?

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ABSTRACT

The cement production contributes to about ~8% (≈2.5 gigaton by the year) of total anthropogenic CO_2 emissions in the world. About 2/3 of these emissions are related to limestone calcination during cement clinker fabrication using mainly limestone, clay and silica sand. In this way, decarbonation of this industry is therefore a key challenge for a reduction of CO_2 emissions. In this communication letter, an innovative chemical process is reported in order to avoid the CO_2 emissions related to limestone calcination process. In effect, limestone ($CaCO_3$) calcium source can be previously transformed into portlandite mineral ($Ca(OH)_2$). In this manner, if the limestone is replaced by engineered portlandite, the cement clinker production will only reject vapor water during calcium silicates formation at high temperature as simplified for tri-calcium silicate:

$$3Ca(OH)_2 + SiO_2 \rightarrow 3CaO.SiO_2 + 3H_2O_{(vapor)} \quad \text{(Innovative Reaction)}$$

In this experimental-technological study (TRL close to 2), portlandite production from limestone concerns well-known chemical reactions and the use of conventional reactants (e.g., HCl and NaOH). Acid reactant in order to extract calcium in solution ($CaCO_3 + 2HCl \rightarrow Ca^{2+} + 2Cl^- + H_2O + CO_{2(gas)}$) (unit or reactor 1) and soda reactant to sequester simultaneously the produced carbon dioxide by chemisorption process ($CO_{2(gas)} + 2NaOH \rightarrow CO_3^{-2} + 2Na^+ + H_2O$) leading to a carbonated solution (unit or reactor 2). Soda solutions are also utilized to produce portlandite from calcium solution ($Ca^{2+} + 2Cl^- + 2NaOH \rightarrow Ca(OH)_2 + 2NaCl$). Portlandite mineral is then recovered from slurry by simple settling and water washing to remove residual sodium chloride. Moreover, alkaline-carbonate solution obtained in reactor 2 by CO_2 chemisorption process can be utilized to produce magnesite ($MgCO_3$) "the most stable carbonate under Earth surface conditions" via indirect carbonation of Mg-silicates minerals or other stable carbonates. In this study, all main chemical reactions at the lab scale were optimized/characterized by Raman spectroscopy in real-time, X-ray diffraction and FESEM.

In summary, this basic technology research (≈TRL 2) offers a realistic possibility/process to produce low-carbon cement and concrete by using the current existing technologies at the industrial scale.

1. Introduction

Concrete is the world's most manufactured product, with an amount of around 20 Gt/year. The related production of Portland cement accounts for 36% of the 7.7 Gt of CO_2 released (in 2010) by construction activities [1] and ~8% of total anthropogenic CO_2 emissions [2]. Decarbonation of this industry is therefore a key challenge for a reduction of Greenhouse gas (GHG) emissions. CO_2 emissions of the cement industry come mainly from energy consumption (~1/3) and calcination of limestone (~2/3) during cement clinker fabrication [1–5]. If the first source can be significantly reduced through efficiency and the use of low-carbon energies, direct emissions of CO_2 from calcination raise deeper problems. In this way, the CO_2 capture from industrial sources (e.g., cement fabrication, metallurgy and power plants) and its transformation into re-usable products (e.g., ethanol, syngas, etc.) and/or non-energetic materials (e.g., magnesite, dolomite, siderite and other stable carbonates) appears now as a realistic strategy to reduce significantly the CO_2 industrial emissions into the atmosphere [6–10]. In the practice, CO_2 capture from industrial sources (hot gas stream containing N_2 and other minor gas NOx, SOx, etc.) does not represent a technological or scientific obstacle, but the existing methods and technologies (including recovery of high-purity of CO_2 and its

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liquefaction) remain highly expensive [11–14]. For the cement production and particularly concerning the limestone calcination during cement clinker fabrication, an innovative process is proposed in the present study. In effect, the CO_2 emissions related to limestone calcination process can be avoided. Because, limestone ($CaCO_3$) calcium source can be previously transformed into portlandite mineral ($Ca(OH)_2$). Engineered portlandite can then substitutes the limestone in the clinker formulation. Technically, this means that during cement clinker fabrication at high temperature from 800 to 1400 °C in the furnaces only water from clays and portlandite will be rejected, i.e., CO_2-free cement clinker production. A simplified material flow diagram and the main concerned reactions are reported in this letter communication.

2. Materials and methods

2.1. Limestone decarbonation coupled to CO_2 capture

Two connected/coupled reactors were used here, both operating at room temperature (22–23 °C) in order to minimize the energetic requirements. In the first reactor (1 L of capacity) centimetric limestone pieces (50 g) are placed in contact with 500 mL of an acidic solution (e.g., 5% of HCl solution) under static regime. The limestone decarbonation initiates rapidly producing carbon dioxide gas (CO_2). Herein, produced CO_2 gas is directly conducted to a second reactor (600 mL of capacity) containing 400 mL de soda solution (from 1 to 2.5 M). In this way, the CO_2 is rapidly sequestered as carbonate ions as determined by the Raman spectroscopy. In effect, the CO_2 capture was monitored in real-time by Raman spectroscopy. This allows a precise monitoring of progression CO_2 capture/chemisorption process [e.g., 15]. In summary, in each reactor a key ionic solution is obtained at the equilibrium. Ca-rich solution from the first reactor was used to produce portlandite ($Ca(OH)_2$) material and alkaline carbonate solution from second reactor was used to produce magnesite ($MgCO_3$) and vaterite ($CaCO_3$) as commented below.

2.2. Portlandite production

1 L of Ca-rich solution is placed in a conventional baker (2 L in total). Soda solution (2 M) is then added at a controlled flowrate of 12 mL/min until complete pH stabilization at 12.2. Herein, the pH was monitored in real-time (imacimus sensors) in order to obtain a respective titration curve (time vs pH). Similar experiments using only 200 mL de Ca-rich solution were also performed by using time-resolved Raman spectroscopy measurements in order to determine kinetics and reaction mechanism of portlandite. This spectroscopy method has been already used for other several minerals [16–19].

2.3. Magnesite ($MgCO_3$) and vaterite ($CaCO_3$) production

The alkaline-carbonate solution (CO_3^{-2} or CO_3^{-2}/HCO_3^- mixture) obtained from CO_2 capture during limestone decarbonation was used to produce anhydrous carbonates with particular applications and stabilities. Below two significant examples are suggested.

Magnesite ($MgCO_3$) from indirect carbonation of peridotite or serpentinite (ultrabasic rocks). A specific method was developed and a first study was submitted for publication (unpublished data). Briefly, this method is based in three steps: (1) acidic leaching of ultrabasic rocks (including mining waste) in order to obtain a Mg-rich ionic solution, (2) CO_2 capture by chemisorption in soda solution in order to obtain an alkaline-carbonate ionic solution as described in sub-section 2.1 and (3) controlled mixture of Mg-rich ionic solution with alkaline solution and heating at 150 °C for 1 h or at 90 °C for 24 h.

Vaterite ($CaCO_3$) from direct carbonation of natural gypsum ($CaSO_4{\cdot}2H_2O$). Herein, the alkaline-carbonate ionic solution is placed in contact with gypsum particles at room temperature. Vaterite is then rapidly formed from slurry and it remain stabilized for various days in its mother solution or for weeks in Mg solutions. Then its transformation into calcite or aragonite can be easily controlled (unpublished confidential data).

3. Results and discussion

The tricalcium ($3CaO.SiO_2$) and dicalcium ($2CaO.SiO_2$) silicates are the main components in the cement clinker. Their formation at high temperature (800–1400 °C) produces high amount of CO_2 because calcium is systematically provided by limestone ($CaCO_3$) as illustrated for tri-calcium silicate:

$$3CaCO_3 + SiO_2 \rightarrow 3CaO.SiO_2 + 3CO_{2(gas)} \quad \text{(Conventional Reaction)}$$

In the present letter communication, an innovative process is suggested in order to avoid the CO_2 emissions during cement clinker fabrication. In effect, engineered/synthetic portlandite ($Ca(OH)_2$) can be utilized by replacing the raw limestone. In this case, only water vapor is emitted during cement clinker fabrication as illustrated below:

$$3Ca(OH)_2 + SiO_2 \rightarrow 3CaO.SiO_2 + 3H_2O_{(vapor)} \quad \text{(Innovative Reaction)}$$

In practice, the same technology for production of cement clinker can be used, but, a supplementary chemical process must be involved in order to produce portlandite from limestone decarbonation at ambient temperature and by using common reactants (acid and soda) as illustrated in the simplified material flow diagram (Fig. 1).

The main innovative idea of this process concerns the instantaneous and/or simultaneous sequestration of produced CO_2 during limestone decarbonation at room/ambient temperature (23–25 °C). For this, two connected reactors are involved. In the first reactor, the limestone is decarbonated in an acidic aqueous medium leading to a Ca-rich solution, for example:

$$CaCO_3 + 2HCl \rightarrow Ca^{2+} + 2Cl^- + H_2O_{(liquid)} + CO_{2(gas)} \quad (1)$$

The produced CO_2 gas is simultaneously captured by chemisorption in soda solution in the second connected reactor leading to an alkaline-carbonate solution as monitored in real-time by Raman spectroscopy (Fig. 2).

$$CO_{2(gas)} + 2NaOH \rightarrow CO_3^{2-} + 2Na^+ + H_2O_{(liquid)} \quad (2)$$

In this way, portlandite mineral can be easily produced by controlled mixture of Ca-rich solution (from reaction 1) with a soda solution as illustrated by the following reaction:

$$Ca^{2+} + 2Cl^- + 2NaOH \rightarrow Ca(OH)_2 + 2NaCl \quad (3)$$

pH and Raman spectroscopy in real time confirm a fast formation of portlandite at room temperature (Fig. 3). Portlandite mineral/material can be separated from salt solution by simple settling and recovered portlandite washed in order to remove residual NaCl salt.

On the other hand, the alkaline carbonate solution can be utilized to produce calcium or magnesium carbonates with ready-use as mineral additives in drugs, plastics, paper and/or construction materials [15–17]. In this letter communication two original examples concerning vaterite (recycling CO_2 perspective) and magnesite (permanent CO_2 storage) are provided in the following reactions.

Vaterite mesocrystals can be easily produced at ambient temperature (23–25 °C) by using gypsum ($CaSO_4.H_2O$) mineral as calcium source:

$$CaSO_4.2H_2O + CO_3^{2-} + 2Na^+ \rightarrow CaCO_3 + SO_4^{2-} + 2Na^+ + 2H_2O \quad (4)$$

The nucleation of vaterite for this reaction was monitored in real-time by Raman spectroscopy as illustrated in Fig. 4.

Magnesite crystals (the most stable carbonate under Earth surface conditions) can be also produced, but in this case a Mg-rich ionic solution is need (e.g. from acidic leaching of Mg-silicates).

$$Mg^{2+} + 2Cl^- + CO_3^{2-} + 2Na^+ \rightarrow MgCO_3 + 2Cl^- + 2Na^+ \quad (5)$$

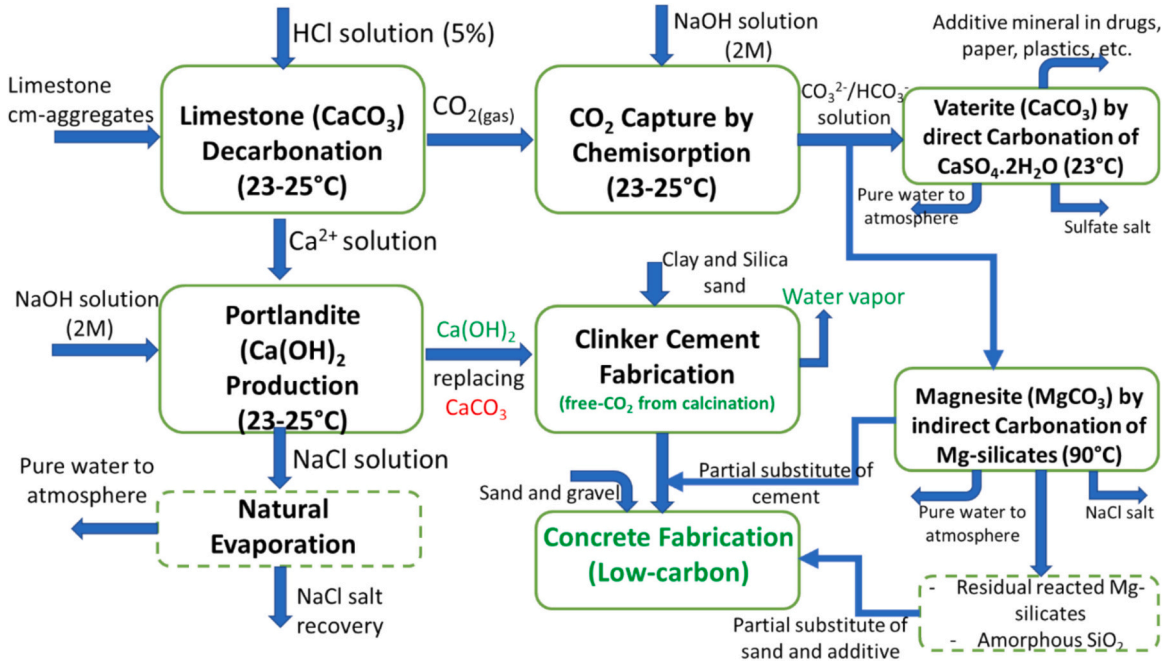

Fig. 1. Material flow diagram for an innovative process on the portlandite ($Ca(OH_2)$) fabrication coupled to CO_2 sequestration by chemisorption. In order to produce "low-carbon" cement clinker and concrete. Main overall reactions are described in the results and discussion section and also illustrated in the Figs. 2 to 5.

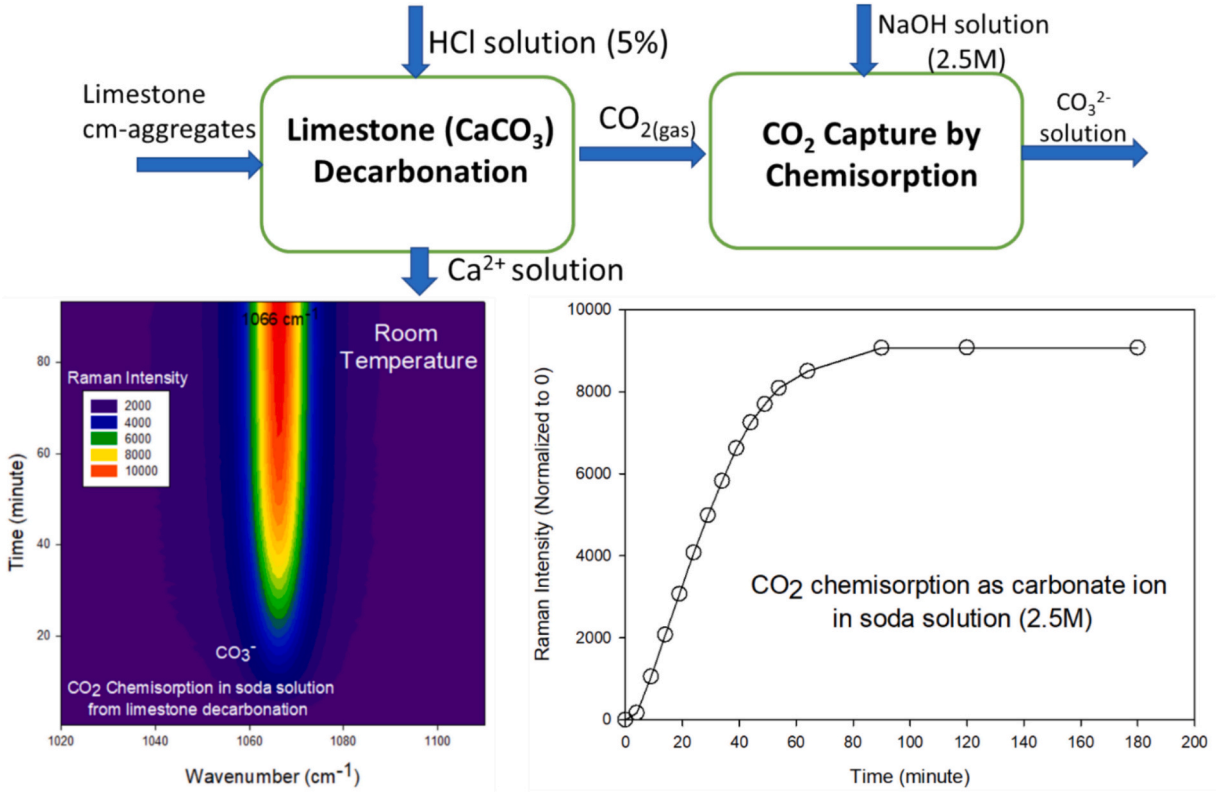

Fig. 2. Limestone decarbonation in HCl solution (reactor/unit 1) coupled to simultaneous chemisorption of produced CO_2 in soda solution (2.5 M) (reactor/unit 2). Here, the chemisorption kinetics of CO_2 was monitored in real-time by Raman spectroscopy.

Here, magnesite production requires also a heat-ageing step of at least 90 °C (see Fig. 5 and also ref. [17]). Magnesite crystals can be separated from salt solution by simple settling and recovered magnesite washed in order to remove residual NaCl salt. Magnesite has well-known industrial applications as mineral additive in plastics and as retardant fire for example. In a perspective of permanent storage of CO_2; magnesite "the most stable" carbonate can be also utilized as partial substitute of cement clinker in the concrete manufacturing as proposed in a recent study (unpublished data).

All these chemical reactions (1 to 5) are then involved in this

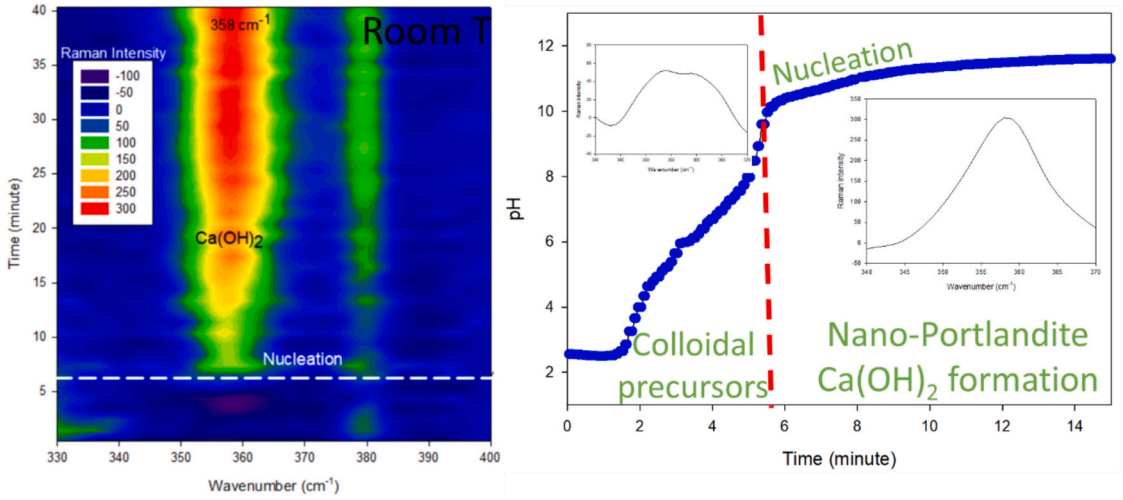

Fig. 3. Portlandite nucleation using Ca-rich solution from limestone decarbonation neutralized with soda solution at room T (≈23 °C) (see also Fig. 1). Portlandite nucleation was monitored in real-time by Raman spectroscopy and pH probe.

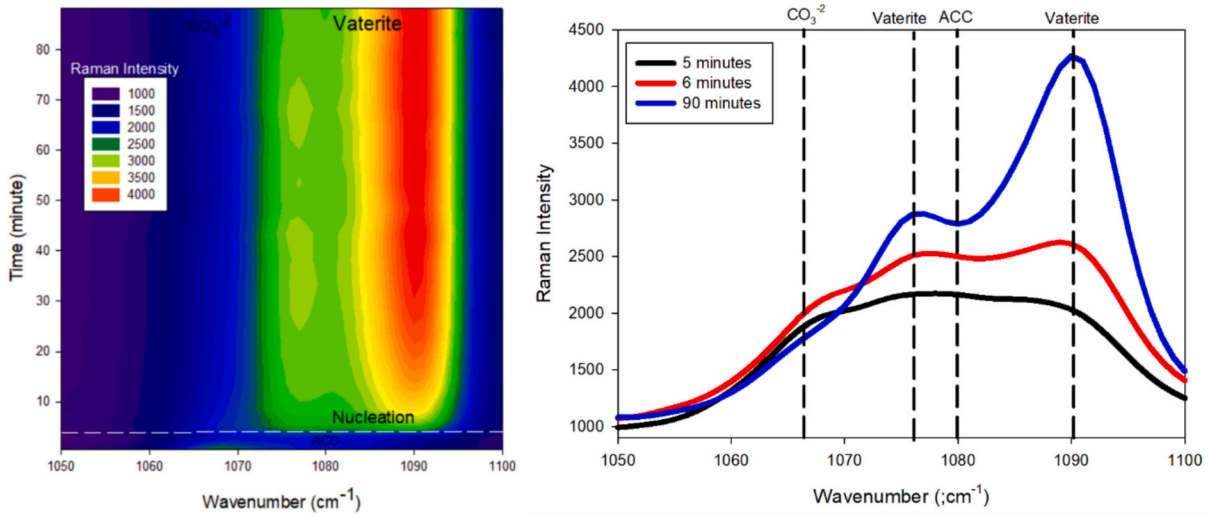

Fig. 4. Vaterite nucleation using carbonate solution obtained by CO_2 chemisorption during limestone decarbonation at room T (≈23 °C) (see also Fig. 1). Vaterite nucleation was monitored in real-time by Raman spectroscopy. Here, synthetic gypsum ($CaSO_4.H_2O$) was used as calcium source.

innovative chemical process to produce engineered portlandite and useful carbonates in order to avoid the CO_2 emissions during cement clinker fabrication as summarized by a material flow diagram (Fig. 1) indicating mainly input and output materials. This demonstrates that the cement industry can be decarbonized by using the existing technology and the complementary suggested process (illustrated in Fig. 1) at the lab scale can be easily-technically extrapolated to the industrial scale.

4. Conclusion

The reduction and/or elimination of CO_2 emissions related to limestone decarbonation in cement (clinker fabrication) and metallurgy (attenuation of heat propagation around high-temperature furnaces) industries is crucial to reduce significantly the global CO_2 industrial emissions in the world. In this context, the present communication letter reports a basic technology research (≈TRL 2) study in order to avoid the CO_2 emissions during cement clinker fabrication. In effect, an innovative process is suggested in order to produce portlandite ($Ca(OH)_2$) coupled to simultaneous CO_2 chemisorption (CO_3^{2-}) from limestone decarbonation. In this manner, the limestone ($CaCO_3$) utilized classically to produce cement clinker at high temperature (≈1400 °C) can be replaced by engineered "low-carbon" portlandite. This means that during calcium silicates formation (or cement clinker) only water will be rejected during calcination processes as simplified by the following reaction concerning tri-calcium silicate:

$$3Ca(OH)_2 + SiO_2 \rightarrow 3CaO.SiO_2 + 3H_2O_{(vapor)} \quad \text{(Innovative Reaction)}$$

The cement clinker production without CO_2 emissions is technically possible and realistic, but, significant amounts of acid and soda are required. For example, to produce 1ton of portlandite ($Ca(OH)_2$) about 1ton of HCl and 1ton of NaOH are required. Fortunately, all required chemical elements (Ca, Na, Cl, H and O) are widely available in the biosphere.

CRediT authorship contribution statement

German Montes-Hernandez: Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization, Writing – review & editing, Writing – original draft.

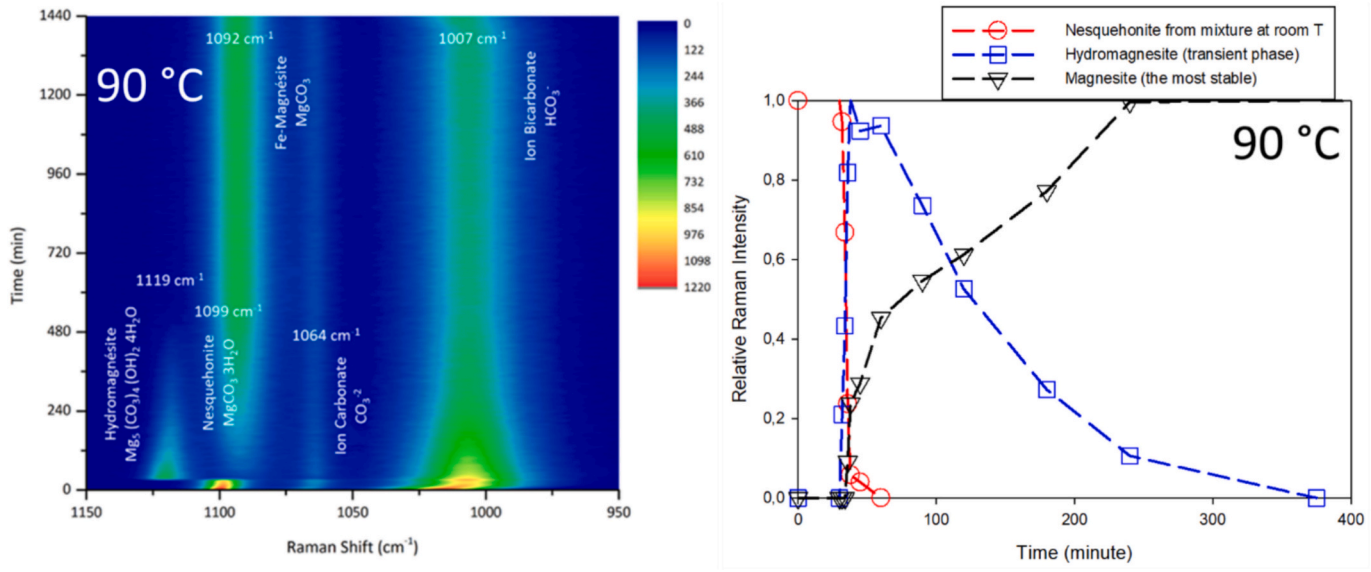

Fig. 5. Fe-Magnesite nucleation at 90 °C using carbonate solution obtained by CO_2 chemisorption during limestone decarbonation at room T (see also Fig. 1). Mg-rich solution was obtained by leaching of peridotite mm-grains at 60 °C (unpublished data). Reaction mechanism and kinetics for magnesite formation at 90 °C were monitored in real-time by Raman spectroscopy.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

German Montes-Hernandez reports financial support was provided by German Montes-Hernandez, CNRS scientist. German Montes-Hernandez reports a relationship with National Centre for Scientific Research that includes: employment. The creation of a startup is explored If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

References

[1] G. Habert, S.A. Miller, V.M. John, J.L. Provis, A. Favier, A. Horvath, K. Scrivener, Environmental impacts and decarbonization strategies in the cement and concrete industries, Nat. Rev. Earth Environ. 1 (2020) 559–573.
[2] S.A. Miller, V.M. John, S.A. Pacca, A. Horvath, Carbon dioxide reduction potential in the global cement industry by 2050, Cem. Concr. Res. 114 (2018) 115–124.
[3] S. Barbhuiyaa, F. Kanavaris, B. Bhusan Das, M. Idrees, Decarbonising cement and concrete production: strategies, challenges and pathways for sustainable development, J. Build. Eng. 86 (2024) 108861.
[4] O. Cavalett, M.D.B. Watanabe, M. Voldsund, S. Roussanaly, F. Cherubini, Paving the way for sustainable decarbonization of the European cement industry, Nat. Sustain. 7 (2024) 568–580.
[5] M. Pisciotta, H. Pilorgé, J. Davids, P. Psarras, Opportunities for cement decarbonization, Clean. Eng. Technol. 15 (2023) 100667.
[6] The Intergovernmental Panel on Climate Change (IPCC). https://www.ipcc.ch/report/sixth-assessment-report-cycle/, 2023.
[7] G. Montes-Hernandez, R. Perez-Lopez, F. Renard, J.-M. Nieto, L. Charlet, Mineral sequestration of CO2 by aqueous carbonation of coal combustion fly-ash, J. Hazard. Mater. 161 (2009) 1347–1354.
[8] G. Montes-Hernandez, M. Bah, F. Renard, Mechanism of the formation of engineered magnesite: a useful mineral to mitigate CO2 industrial emissions, J. CO2 Util. 35 (2020) 272–276.
[9] A. Saravanan, P. Kumar, D. Vo, S. Jeevanantham, V. Bhuvaneswari, V. Narayanan, P.R. Yaashikaa, S. Swetha, B. Reshma, A comprehensive review on different approaches for CO2 utilization and conversion pathways, Chem. Eng. Sci. 236 (2021) 116515.
[10] S.Y. Pan, Y.H. Chen, L.S. Fan, H. Kim, X. Gao, T.C. Ling, P.C. Chiang, S.L. Pei, G. Gu, CO2 mineralization and utilization by alkaline solid wastes for potential carbon reduction, Nature Sustain. 3 (2020) 399–405.
[11] T. Kuramochi, A. Ramírez, W. Turkenburg, A. Faaij, Comparative assessment of CO2 capture technologies for carbon-intensive industrial processes, Prog. Energy Combust. Sci. 38 (2012) 87–112.
[12] N.S. Sifat, Y. Haseli, A critical review of CO2 capture technologies and prospects for clean power generation, Energies 12 (2019) 4143.
[13] M. Mahmoudkhani, D.W. Keith, Low-energy sodium hydroxide recovery for CO2 capture from atmospheric air—thermodynamic analysis, Int. J. Greenhouse Gas Control 3 (2009) 376–384.
[14] S. Ghaffari, M.F. Gutierrez, A. Seidel-Morgenstern, H. Lorenz, P. Schulze, Sodium hydroxide-based CO_2 direct air capture for soda ash production—fundamentals for process engineering, Ind. Eng. Chem. Res. 62 (2023) 7566–7579.
[15] G. Montes-Hernandez, F. Renard, Time-resolved in situ Raman spectroscopy of the nucleation and growth of siderite, magnesite and calcite and their precursors, Cryst. Growth Des. 16 (2016) 7218–7230.
[16] G. Montes-Hernandez, F. Renard, A.L. Auzende, N. Findling, Amorphous calcium-magnesium carbonate (ACMC) accelerates dolomitization at room temperature under abiotic conditions, Cryst. Growth Des. 20 (2020) 1434–1441.
[17] G. Montes-Hernandez, Magnesite formation from nesquehonite slurry at 90°C using some soluble mg salts: eitelite as an atypical transient mineral phase, Chem. Eng. Sci. 287 (2024) 119776.
[18] G. Montes-Hernandez, F. Renard, Nucleation of brushite and hydroxyapatite from amorphous calcium phosphate phases revealed by dynamic in situ Raman spectroscopy, J. Phys. Chem. C 124 (2020) 15302–15311.
[19] G. Montes-Hernandez, N. Findling, F. Renard, Direct and indirect nucleation of magnetite nanoparticles from solution revealed by time-resolved Raman spectroscopy, Cryst. Growth Des. 21 (2021) 3500–3510.