Anhydrous stable divalent-cation Carbonates as strategic mineraLs to storE and recycling the industriAl CO_2. From fuNdamental aspEcts to concRete fabrication

Executive Summary of Research Outlook and strategy for next five years

The proposal **CLEANER** presents a compelling plan conducting both basic and applied research in order to produce anhydrous divalent-cation (Ca, Mg, Fe, Cd, Cu, Pb….) carbonates through indirect carbonation of raw silicate rocks (including mining and carriers wastes) or in general all mineral-silicates containing divalent cations (including solid and brine wastes from industries). Additionally, we will investigate the potential of produced carbonates to serve as a partial substitute (up to 30%) of traditional cement in concrete production with a particular focus on its mechanical and textural impact on concrete. This multi-disciplinary project will integrate two main research topics by (1) pinpointing the optimal mild conditions for production of cation-divalent carbonates through indirect carbonation of mineral silicates, and (2) meticulously assessing the incorporation of fabricated carbonates as a partial cement replacement in concrete manufacturing, as depicted in the simplified circular material flow process below. To implement this project, researchers from various disciplines such as geochemistry, mineralogy, material sciences and civil engineering will be involved.

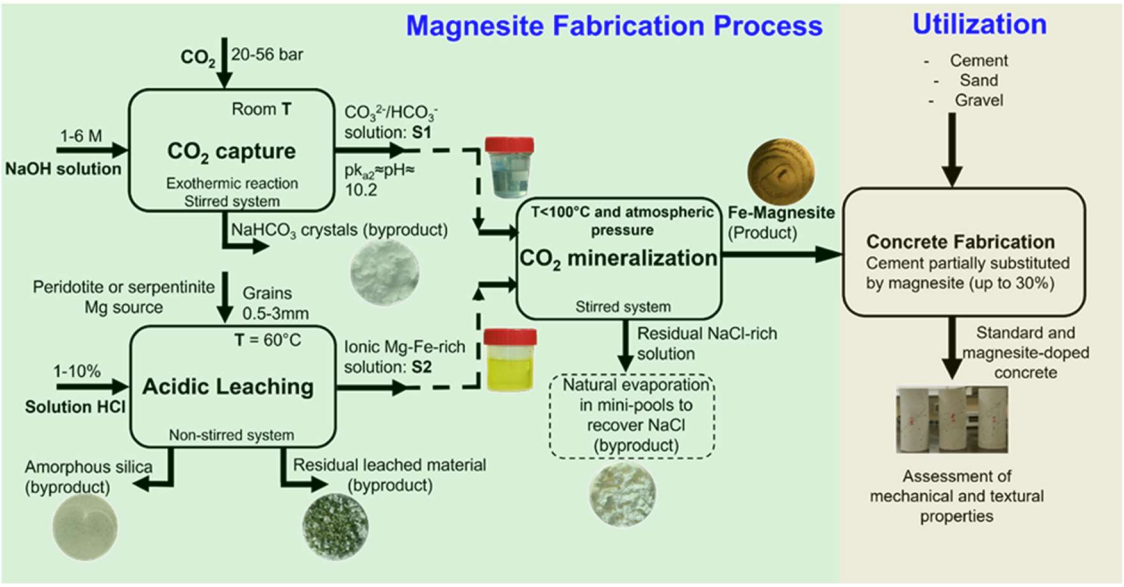

Figure 1. Schematic diagram flow of materials used in three fundamental interdependent steps for production of anhydrous stable divalent-cation carbonates and its utilization as partial substitute for concrete fabrication.

CLEANER will seek a new optimized circular material flow process as illustrated in Figure 1. Herein, several experimental and analytical techniques will be used in order to first analyze and then optimize the solid-fluid interactions, including a deep characterization of solids and interacting solutions as described in specific below tasks. The main novelty of **CLEANER** lies in its combination of experimental techniques and its synergy of different expertise in geochemistry, geomechanics, material science, and civil engineering, that will allow us to develop novel concepts and optimized technologies to progress on Carbon Capture, Utilization, and Storage (**CCUS**), beyond existing knowledge. Currently, the technology readiness level

(TRL) for **CLEANER** is close to TRL 2; in addition to novel insights and/or fundamental research, the present project aims to reach a TRL 4 for the next five years by optimizing the key parameters/indicators. In this way, a life cycle assessment (LCA) of processes will be implemented during the project via a subcontracting or collaborating action with specialized experts in this field.

The **CLEANER** program and strategy for the next five years is in line with my research topics in the last ten years. Moreover, this research agrees with various topics existing at the ISTerre that concerns mainly the geochemistry, mineralogy and faults teams and the cross-disciplinary axis on the energy transition. In this way, my leadership in various management and scientific tasks in geochemistry team (as scientific supervisor from 2017 to 2019), in ANR coro (2012-2015), three PhD French thesis (2011-2019), FUNMIN (European collaborative project from 2019 to 2023), CEMENTO project (PEPS-CNRS 2023), SOLUTION project (MITI-CNRS 2024-2025) and various graduated/ungraduated students (M2, M1, DUT, BUT, L2) have strongly contributed to my current perspective on the nucleation, growth and transformation of minerals. In this way, I aim to build a cross-disciplinary research group at ISTerre, with strong national and international collaborations as implemented from my arrival to Grenoble in 2006, working on the nucleation and growth processes of minerals and crystalline particles under mild and hydrothermal conditions; and processes preferentially monitored in real time by Raman spectroscopy and/or imagery (optical and atomic force microscopy). Obviously, the mass balance simulation by a classical nucleation approach and the molecular dynamics (MD) simulations are not excluded in the present program.

I. Positioning with respect to the state od the art

About 38±3 Gt of CO_2 from fossil fuel and industry (CO_2FFI) are annually emitted into the Earth atmosphere; i.e., an increase of about 67% with respect to the 90's. The CO_2 emitted is naturally transformed by photosynthesis and chemisorbed and/or physically adsorbed in soils and oceans contributing to the life and development in the ecosystems. Unfortunately, a significant surplus is annually cumulated and directly related to so-called global warming, a significant acidification in oceans and in general significant perturbation of ecosystems and climate as claimed by scientists and institutions in the last three decades (1). In this context, 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 (2) and ~8% of total anthropogenic CO_2 emissions (3). 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 clinker fabrication (2). 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 stabilize the CO_2 concentration in the atmosphere (1, 4-7). This will be supported and intensified in the coming years by the energy transition, i.e., the use of carbon-free energy sources such as hydrogen, solar, wind, marine, hydraulic, geothermal than has been already initiated in the last decades (8). In this context, the process of indirectly carbonating raw or waste silicates containing divalent cations (Mg, Ca, Fe…) to produce readily usable anhydrous stable-

carbonates (e.g., calcite, aragonite, magnesite, dolomite and solid-carbonate solutions), is a potent strategy for significantly reducing industrial CO_2 emissions. This approach aligns with international program focused on carbon capture, utilization and storage (CCUS) (1, 4-12). Of notice, the input raw materials and solid waste containing high concentrations of Mg and other divalent cations such as Fe and Ca, necessary to produce stable carbonates, are widely available over the planet. However, optimized process conditions to produce ready-use anhydrous stable divalent-cation carbonates (e.g., magnesite, dolomite, aragonite, nanosized calcite, carbonate mesocrystals, etc.) under mild conditions and the validation of specific carbonate uses remain outstanding challenges.

For example, magnesite ($MgCO_3$) and dolomite ($MgCa(CO_3)_2$) are the most stable carbonate minerals under typical Earth surface conditions, with the highest resistance to leaching and weathering. Their dissolution rates are for example 100-1000 times lower than that of calcite ($CaCO_3$) in a wide range of conditions, from ambient temperature to 150°C and pH from 1 to 14. For this reason, engineered magnesite and dolomite have been considered as relevant minerals to store permanently anthropogenic carbon dioxide. Moreover, both minerals are ready-to-use as profitable construction materials (5). Magnesite and dolomite precipitation kinetics have been widely studied because their abiotic precipitation at ambient temperature (~25°C) is virtually impossible within feasible experimental time scales, which has led to a long-lasting scientific debate about the origin of these minerals in the last two centuries. The strong solvation shell of magnesium ions in aqueous media plays an important role in this limitation. However, the sole effect of Mg hydration might not be the only factor of inhibition of magnesite and/or dolomite formation. Recent studies claim that a more intrinsic crystallization barrier and the influence of fluid chemistry (e.g., relative size of the constituting cations) prevent the formation of long-range ordered crystallographic structures at ambient conditions (e.g., 13-15). In this context, our recent results have revealed that the carbonate speciation close to pK_{a2} (pH~10.3), high ionic concentration (<1M) and the presence of other competitive divalent cations and counterions accelerates the magnesite and proto-dolomite formation at room and moderate temperature (≤90°C) (15-16). Various other studies have also reported magnesite precipitation under mild conditions, but in general catalytic agents (biotic and abiotic) are claimed and several days or weeks are also required (17-19). In order to overcome these limitations and in continuity with our research progress on this primordial topic, the **CLEANER** proposal suggests a novel circular-material-flow lab method at the liter scale for the fabrication of Fe-magnesite and dolomitic materials under mild conditions (T≤90°C and atmospheric pressure) via indirect carbonation of peridotites, serpentinites, basalts and/or mining waste. First results recently published by our team (20). However, as claimed above **CLEANER** project is not only limited to magnesite and dolomite investigation. In fact, all anhydrous stable and low-soluble carbonates containing divalent-cations will be investigated. Moreover, the use of produced carbonates will be systematically assessed as partial substitute of cement in the fabrication of concrete, as illustrated in the simplified diagram of material flow (Figure 1). Claiming that produced carbonates could have other industrial applications, as mineral additive for example in paper, paints, plastics, etc. as clearly revealed in the modern world.

In summary (Figure 1), **CLEANER** method/process includes three separate but dependent steps: (1) capture of CO_2 in concentrated NaOH solutions, (2) leaching of millimetric grains of raw or waste silicate minerals containing divalent cations in HCl solution (up to 10%), and (3) carbonate formation/precipitation by mixing abruptly or with controlled rate the alkaline (from

step 1) and acidic (from step 2) solutions. In addition to amorphous silica, sodium bicarbonate crystals and NaCl-rich materials (byproducts), several hydrated and anhydrous carbonate products of industrial interest can be also obtained depending on the nature and origin of silicate sources. However, anhydrous stable carbonates containing divalent-cation will be mainly targeted. All these powdered carbonate products will be assessed as partial substitute of cement in the concrete fabrication. We note that the presence of iron oxides and stable LDHs (possible byproducts in our process) could improve the concrete performance in specific engineered storage systems such as repository systems of radioactive waste as claimed in the literature (21-23). Here, iron oxides can act as physicochemical barriers for the ionic radioactive and/or pollutants migration to biosphere.

This original concept claims then two benefits in terms of CO_2 reduction for the cement industry: (i) as for another supplementary cementitious material (SCM), a reduction of clinker production, but (ii) more importantly, a permanent storage of carbon dioxide as stable anhydrous divalent-cation carbonate, without risks of later re-emission during the lifetime of the concrete structure and/or during reuse as aggregate for new concrete. Our preliminary results have revealed for example that if a substitution of 15% (in weight) of cement by magnesite-rich material would represent a global reduction of the CO_2 footprint of about 200 kg per ton of cement-magnesite mixture, the impact of this substitution on the mechanical properties of concrete (Young's modulus and strength) is small. These preliminary results recently obtained from our group (exploratory PEPS-INSIS and MITI CNRS projects) are very encouraging for magnesite-concrete (20). However, various critical points should be investigated with more care in a near future.

(i) We prepared our samples from a simple partial substitution of cement, without modifying the content of other elements (water, sand, aggregates) in the concrete mix, or the preparation and casting procedure. This means that we followed the French Standard NF EN 206-1 (24) for the three materials (except cement substitution), but we did not explore a possible optimization of the mix or of the preparation to improve the mechanical properties of the Magnesite ($MgCO_3$) or other MCO_3 (M=divalent cation) concretes.

(ii) The rheology and viscosity of the fresh concrete pastes (e.g., 25) were not analyzed, as we only compared the mechanical properties of hardened concrete samples.

(iii) It would be essential in future work to explore, from micro/nano-indentation techniques (26), the mechanical properties of the obtained cements at scales ranging from the nanometer-sized particles of calcium-silicate-hydrate (C-S-H) to the size of the carbonate particles (few µm).

(iv) Finally, owing to the necessarily limited amount of magnesite synthetized at the liter scale of the lab, we only prepared and tested a limited number of samples (14 of each material), a statistical set smaller than generally recommended for a proper estimation of the characteristic strength of concrete in regulation codes (e.g., 27).

All of this calls for further, more detailed studies that we propose to perform within the **CLEANER** project, with the final aim of a significant reduction of CO_2 industrial emissions and its utilization and storage in concrete materials.

II. Objectives and strategy

The project **CLEANER** focuses on two main specific goals. First, it proposes to optimize the fabrication of anhydrous divalent-cation (Mg, Ca, Fe, Cd, Cu, Pb…) carbonates under mild conditions (T≤100°C and atmospheric pressure) via indirect carbonation of divalent-cation-silicates (raw or waste), abundant on the Earth. Here, particular attention is dedicated to magnesium chemistry because the precipitation/formation of anhydrous magnesium carbonate is most challenging with respect to other divalent-cation carbonates. Second, the produced carbonates will be used as a partial substitute of fresh cement and admixture for concrete. This second step requires a deep analysis of the physical, mechanical and textural properties of the resulting carbonate-doped concrete. We briefly present below these fundamental independent but complementary tasks.

To implement **CLEANER** project, researchers from various disciplines such as geochemistry, mineralogy, material sciences and civil engineering will be involved, as illustrated in the following diagram (Figure 2) that summarizes the tasks, sub-tasks, the research consortium, the required disciplines and involved researchers.

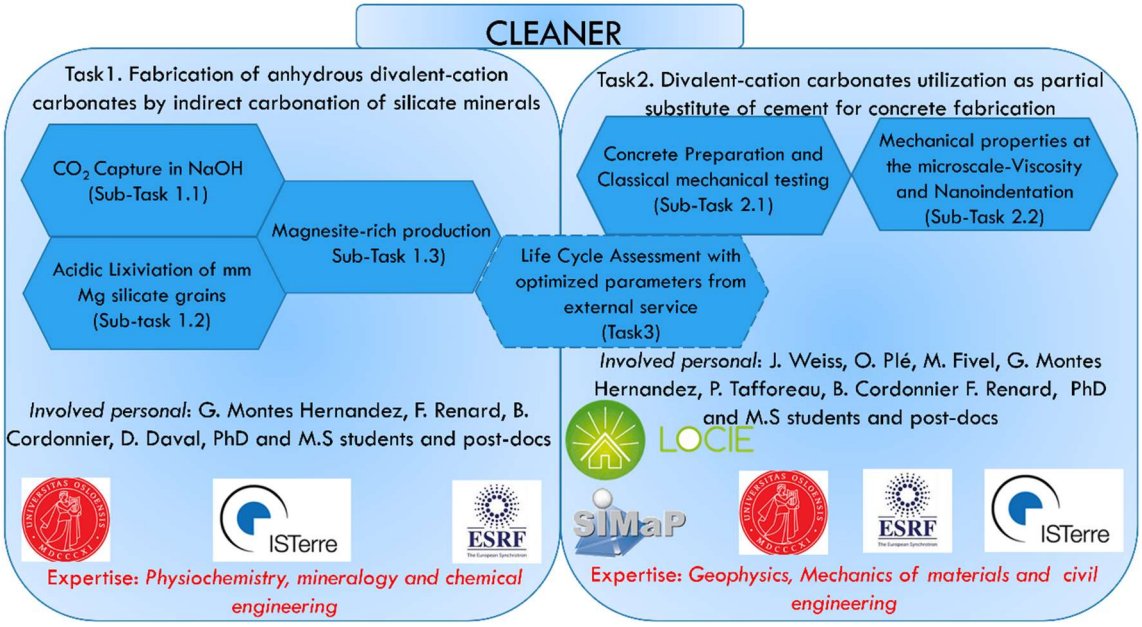

*Figure 2. **CLEANER** project indicating main tasks and sub-tasks, the research consortium (logo of labs) and involved people. Training of students is strongly expected.*

We present below these all fundamental independent but complementary tasks.

Task (1). Production of anhydrous divalent-cation carbonates. This fundamental task seeks how the production of anhydrous magnesium carbonates can be accelerated from indirect carbonation of peridotite, serpentinite, basalt or mining waste materials. The alteration of peridotite, serpentinite, basalt and other basic and/or ultrabasic rocks providing Mg carbonates occurs in natural environments over geological time scales. Here, we will implement a geo-inspired process in order to produce magnesite-rich material in reasonable time (<24h) and ready to be used in construction materials. Anhydrous calcium (e.g., calcite, aragonite and vaterite) and iron carbonates (e.g., siderite) are also targeted, but these carbonates are more

easily produced with respect to magnesite and dolomite (two enigmatic minerals). For this reason, the following paragraphs describe mainly the production of magnesium carbonates.

The fabrication process of magnesite-rich material involves three dependent steps to be separately optimized in the project. For simplicity each process step corresponds here to an independent sub-task as described below.

Sub-Task 1.1 *CO_2 capture step*. CO_2 capture from industrial sources does not represent a technological or scientific obstacle, but the existing methods and technologies (including recovery of high-purity of CO_2 and its liquefaction) remain highly expensive (28-29). Consequently, the improvement and optimization on the CO_2 capture units still represent important challenges. In this way, the **CLEANER** project suggests the capture of CO_2 by chemisorption in concentrated NaOH solutions. This chemical method concerns well understood reactions, but NaOH solution has not been proposed to capture carbon dioxide from industrial sources to the best of our knowledge; probably, because the CO_2 is mainly captured in ionic form (rich-carbonate CO_3^{2-}/HCO_3^- solution) and also in crystalline form as $NaHCO_3$ at specific precipitating conditions as already demonstrated in preliminary experiments at ISTerre lab (20). Conversely, NaOH micro-drops solutions have been particularly suggested to remove/capture the CO_2 from atmospheric air (30-32).

The advantage using NaOH solutions to capture industrial CO_2 is that obtained ionic carbonate solutions can be easily manipulated and used to form stable carbonates such as calcite, aragonite, magnesite, dolomite, etc. as claimed in the present proposal. Moreover, the NaOH solutions are selective for CO_2, i.e., that the annex gases (NOx, SOx, N_2…) have no significant and/or only slight influence on the sequestration reactions. The critical point here is that the flue gases from industrial chimneys is hot. In this way, the gas cooling seems necessary (recovery energy) to a better control of CO_2 chemisorption process.

In the present proposal, concentrated NaOH solutions (from 1 to 6M) will be used to simulate the capture of CO_2 as ionic species (CO_3^{2-} and HCO_3^-) at moderate pressure capture ($P_{CO2}\leq$55bar) and at room temperature. Here, a given amount of NaOH and 1L of water will be placed in a reactor cell of 2L of total capacity. Then up to 55 bars of CO_2 will be injected into the reactor. Pressure drop related to CO_2 chemisorption process and exothermicity (temperature increase during CO_2 chemisorption) will be directly monitored in this anisobaric system. Isobaric conditions (20 bar) and sequential CO_2 injections (20+10+10…up to 100 cumulated bars for higher NaOH concentration), the presence of annexes gases (N_2, NOx, SOx, etc.) and hot gas mixture injection will be also tested. In all cases, the maximum of reaction duration will be imposed to 24h. The optimization, the reaction mechanisms and kinetics will be determined by using time-resolved Raman spectroscopy measurements as already demonstrated for several precipitation reactions by our research team (5, 14-16, 20, 33-34). In this way, real-time monitoring by Raman spectroscopy will allow a better control of carbonate speciation of obtained alkaline solutions (CO_3^{2-}-rich solution, CO_3^{2-}/ HCO_3^--mixed solution or HCO_3^--rich solution). Moreover, $NaHCO_3$ crystalline-powdered byproduct with several industrial applications can be also directly obtained during carbonation process of NaOH solutions as illustrated in the simplified flow material diagram (Figure 1) and directly monitored by Raman spectroscopy (see below the Figure 3).

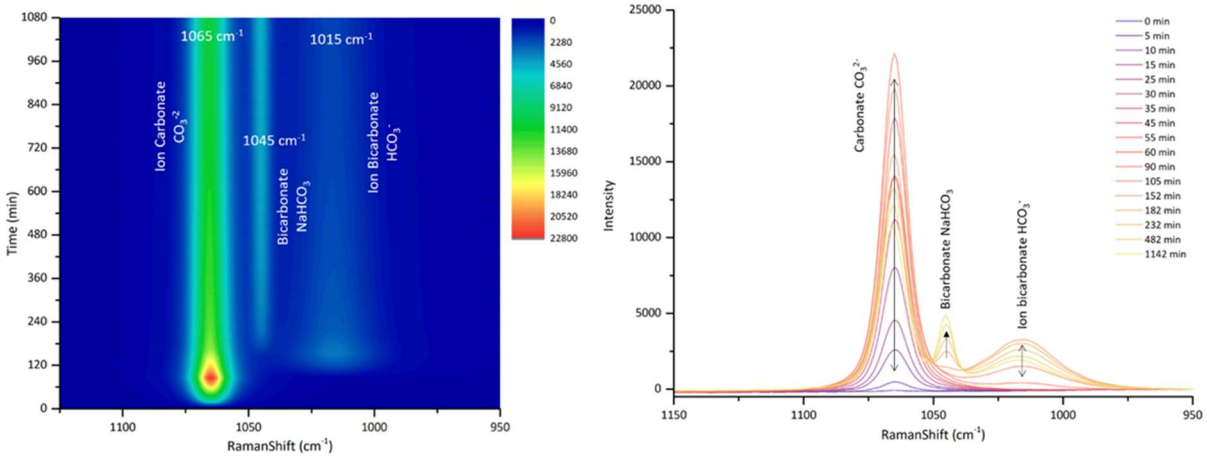

Figure 3. Chemisorption of CO_2 in concentrated NaOH solution monitored in real-time by Raman spectroscopy. See also ref. (20)

Sub-Task 1.2. *Acidic leaching step of mm Mg silicate grains*. High-soluble Mg hygroscopic salts such as chloride, sulfate, nitrate and acetate of magnesium may be produced from serpentinite, peridotite and other Mg-rich silicates by corresponding acidic leaching (35). All these obtained soluble Mg salts have numerous industrial applications as solids salts, and have been also proposed as sinks to store anthropogenic carbon dioxide by transforming the carbon dioxide into magnesium carbonate minerals via a so-called indirect carbonation process (36). In our process, the production of solid soluble salts is not concerned. In fact, our process suggests the acidic leaching of basic and ultrabasic rocks, but only to obtain acidic Mg-rich solutions as illustrated in Figure 1. Herein, Mg, Fe, and Ca divalent cations will be leached from rocks (peridotite, serpentinite or basalt) and/or industrial or mining wastes containing Mg-rich silicates. The grinded samples (millimetric grains) will be treated with concentrated acidic HCl solutions (concentration up to 10%) at moderate temperature (T up to 60°C) for varying durations (up to days) in reactors without stirring in order to minimize energy requirements and then obtain Mg-Fe-Ca-rich solutions. Reaction-time duration, HCl concentration, solution/solid weigh ratio, cycles number and temperature parameters need to be optimized. Preliminary results have revealed that peridotite from French Massif Central can be efficiently leached at 60°C using 10% of concentrated HCl solution for 5 days because significant amount of magnesite-rich material (about 40g) can be obtained using 400ml of leached solution. Herein, ion concentration by ICP-AES and solution ionic concentration (density) by conventional measurements will be fundamental to control the leaching efficacity as recently demonstrated in a preliminary study by our team (20). Moreover, the optimized conditions should be adapted as a function of mineral composition of rocks and/or cation-divalent-rich silicate waste. We note that this leaching process produces also amorphous silica that can be recovered as a byproduct with several industrial well-known applications, including for example the use of silica fume (amorphous silica) as partial replacement of cement in concrete (37). This expected replacement does not store carbon dioxide, but it can improve the mechanical properties of concrete (high-performance concretes). Moreover, the residual leached material could be re-used for additional leaching cycles or as fill material in concretes, replacing partially the sand material that have in general similar grain dimensions (≈2-3mm). These latter possibilities will be also investigated in the **CLEANER** project.

Sub-Task 1.3. *Fe-magnesite production*. Our previous studies in the last 12 years have revealed that high amounts of magnesite can be produced in reduced time using commercial Mg sources such as fine-powdered brucite ($Mg(OH)_2$ or also using various soluble Mg salts of chloride ($MgCl_2.6H_2O$), sulphate ($MgSO_4.7H_2O$), nitrate ($Mg(NO_3)_2.6H_2O$) and acetate ($Mg(CH_3COO)_2.4H_2O$) (5, 14-16). In all studies, a temperature of at least 90°C was required to produce magnesite in reasonable time (1-5 days). Herein, high carbonate alkalinity close to pk_{a2} concerning the ionic carbonate speciation was also a fundamental parameter on the magnesite production (15-16). In the continuity of this scientific effort, **CLEANER** project suggests a novel circular material flow process by indirect carbonation of basic and ultrabasic rocks and/or divalent-cation-rich silicate wastes as illustrated in Figure 1.

In practice, the solutions obtained in CO_2 capture (**sub-task 1.1**) and acidic leaching (**sub-task 1.2**) steps will then be used to produce magnesite-rich materials by simple abrupt or controlled mixture of both solutions. The main target is to produce magnesite and magnesite solid solutions at moderate temperature (<100°C) or at high temperature (>100°C) but in very reduced time (<2h). As above invoked 400ml of leached peridotite mixed to 800ml of alkaline solution produces about 40g of magnesite-rich material. This amount is interesting but it could be optimized in order to dimension the volume of the reactor. Similar to CO_2 capture, the monitoring in real-time by Raman spectroscopy will be a crucial tool to optimize kinetics and reaction mechanism as recently demonstrated for various minerals precipitation (5, 14-16, 33-34) and preliminary also demonstrated for magnesite-rich material production by indirect carbonation of peridotite at different temperature (see Figure 4 below and ref. (20)). Herein the in-situ monitoring by time-resolved Raman spectroscopy has revealed for the first time the magnesite formation at 60°C in only two days via an amorphous-to-nesquehonite-to-magnesite transformation route. As expected, the synthesis time of magnesite is significantly reduced when the temperature is increased, only 90 minutes at 150°C, 5-6 hours at 90°C and only 60 minutes at 200°C. In all cases (except to 60°C) hydromagnesite is also a transient phase and its lifetime in the system decreases significantly with temperature. Magnetite-magnesite or hematite-magnesite mineral composites can be also produced in only 60 minutes at 200°C. In summary, this circular flow material method at the liter scale to produce magnesite-rich materials under mild and hydrothermal conditions in reasonable times, with high-use applications and storing permanently industrial captured CO_2, is a fundamental task in **CLEANER** project and it will be extended to a diversified series of divalent-cation-rich silicate available materials (raw or waste materials). Moreover, the utilization of produced anhydrous stable carbonate materials as partial substitute of cement in concrete fabrication will be carefully investigated as described in the **task 2**.

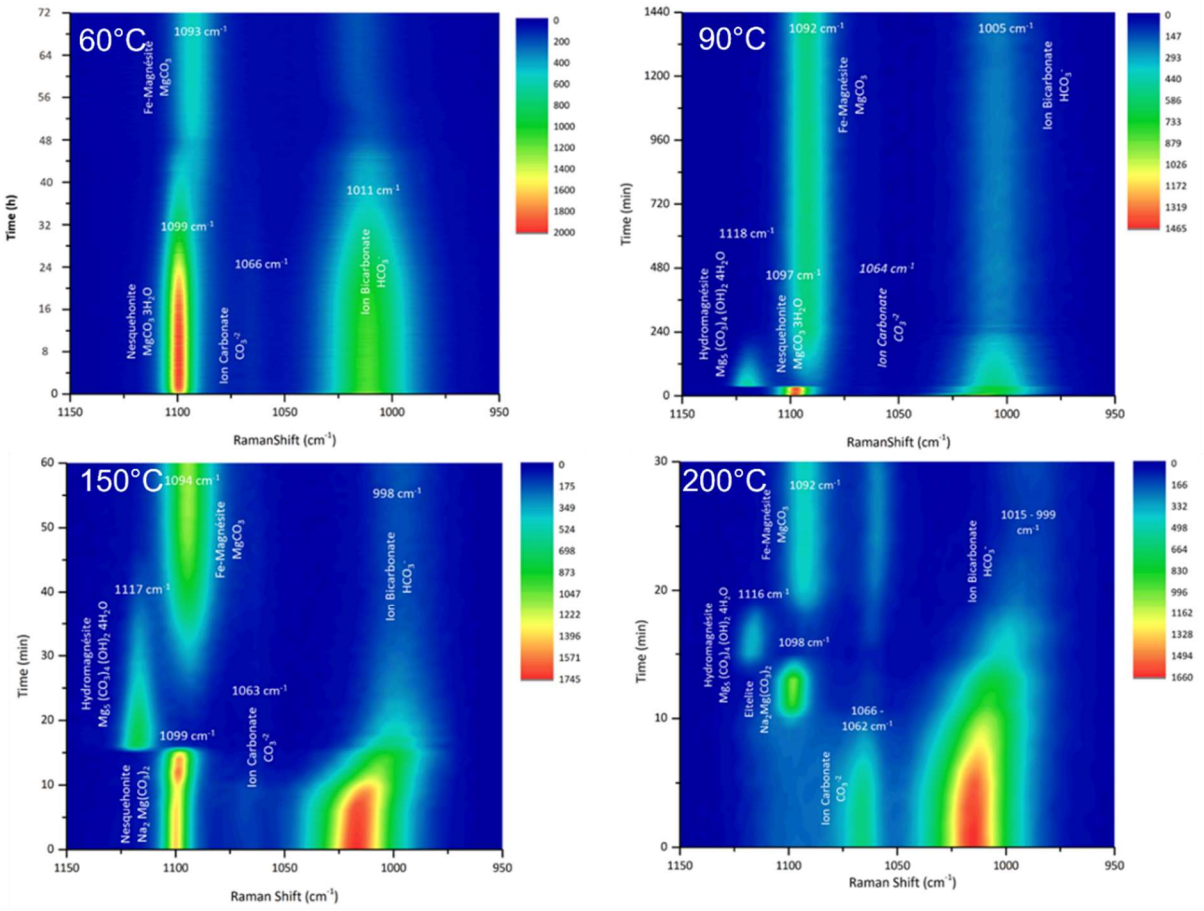

Figure 4. Magnesite-rich material production by indirect carbonation of peridotite. Kinetics and reaction mechanism monitored in real-time by Raman spectroscopy (20).

Task (2). Utilization of anhydrous stable carbonates. The utilization of produced carbonate material as partial substitute of cement and admixture for concrete. This fundamental second task seeks to assess the effect of carbonate material on the physical, mechanical and textural properties of concrete, using both classical mechanical tests following standards (e.g., EN 1992 Eurocode 2 or ASTM) as well as a state-of-art characterization of the matrix (pure cement or cement/magnesite) from micro and nano-indentation testing (26), as well as X-ray microtomography at the European Synchrotron Radiation Facility (ESRF).

See for example the recent preliminary measurements obtained by our team (Figure 5 and ref. (20)).

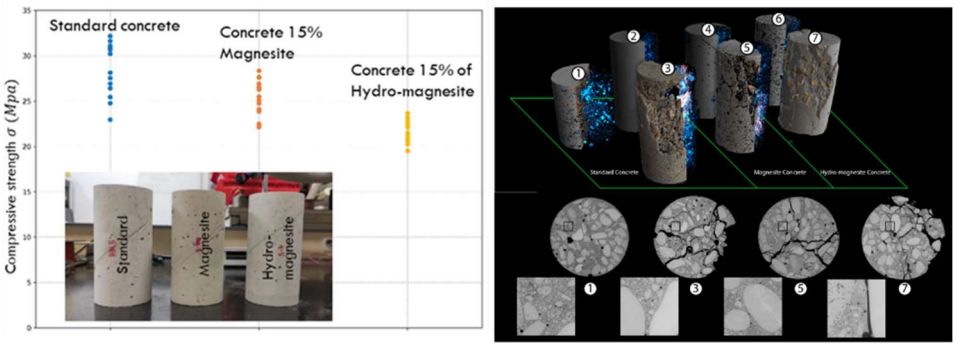

Figure 5. Preliminary measurements on the compressive strength for standard and cement-substituted concrete samples (on the left). Tomographic analysis of standard, magnesite, and

hydro-magnesite concretes. The images labeled 1, 2, 4, and 6 show the samples before testing deformation, while those labeled 3, 5, and 7 display the samples after failure. The top section presents 3D volume rendering with transparency to highlight pores (blue) and cracks (red). The bottom section shows the middle slice of samples 1, 3, 5, and 7, including a zoomed-in view. Porosity is indicated by black regions, and the cement phase in shown in gray.

Sub-Task 2.1. *Elaboration, rheology and classical mechanical testing*. Concrete materials with the carbonates partially substituting the cement content (from 0% up to 30%) will be prepared, at first using classical concrete formulations. The impact of this substitution on the rheology of the fresh paste will be explored (38). For that a shear rheometer will be used whose principle is based on the measurement of the torque developed by rotation of a propeller in the mixture (39). Comparisons with classic mixtures and mixtures including commercial cements with mineral additions will be made.

Then cylindrical standard concrete samples will be prepared. The preparation and casting procedure will follow the French standard NF EN 206-1 (2004) (40). Recent preliminary tests showed that so-prepared 15%-magnesite concrete samples have a texture and a (macro) porosity very similar to that of classical concrete. Mechanical properties used in standards will be determined as follows, and compared between classical and magnesite-concretes: The Young's elastic modulus will be evaluated following our acoustic measurements' method (41), while the characteristic strength will be obtained from classical monotonic compression tests (42) by following a statistical analysis of the experimental tests. Our preliminary tests have revealed that the magnesite-rich material substituting 15% of cement has only a slight impact on the compressive strength (see for ex. Figure 5) and Young's modulus: ~9.5% decrease of the Young's modulus and 1.3 MPa (~5.5%) decrease for the compressive strength. Conversely, the introduction of hydro-magnesite seems to have a more significant impact on these mechanical properties. A deeper investigation is proposed within the **CLEANER** project in order (i) to understand the origin of these small changes at the micro- to nano-scales within the hardened cement paste (see Sub-Task 2.2) and (ii) to optimize the concrete mix (e.g., W/C ratio) and/or the preparation procedure for the magnesite-concretes (e.g., magnesite/cement ratio).

While the elastic modulus and compressive strength are the main mechanical characteristics used in standards, the mechanical resistance of concretes under static loads, i.e., creep, is of upmost importance for long-term design in civil engineering, as structures deform under their own weight. We will therefore explore the time-dependent deformation and lifetimes of classical and magnesite-concretes from uniaxial compression creep tests, under constant loads representing a variable fraction of the characteristic strength. 70×140 mm samples will be used in this case, due to the limited device capacity of our high-precision creep machine.

Sub-Task 2.2. *Mechanical properties at the micro/nanoscales*.

While sub-task 2.1 will allow a validation of magnesite-concretes for civil engineering applications, a detailed physical analysis of the impact of the introduction of $MgCO_3$ particles within the cement matrix is obviously critical. Indeed, if these $MgCO_3$ particles, of typical size of ~2-5µm, are expected to not chemically interact with the hydration products of the cement paste (C-S-H nanoparticles), their potential role on the cement pastes and on the mechanical properties of the matrix at the microscopic scale is unknown, and should be explored for a proper interpretation of the macroscopic mechanical tests. We recall here that the hardened cement is structured at the nanoscale (C-S-H particles and nanopores (43)), while carbonates

particles are of a wide scale from nanometric to micrometric size. This calls for an exploration of the mechanical properties of our classical or carbonate-rich hardened cements at those scales. For this purpose, we will perform nanoindentation measurements (26) using two instruments: A fast, displacement-driven platform will allow a precise mapping of elastic and yield strength properties of the cement from numerous indents (~1s/indent, i.e. ~10^5 indents/24h). In addition, a high-precision, force-controlled indentation platform will be used to test the creep properties at those scales.

Finally, the evolution of damage and microstructure within our hardened cements during in-situ compression tests will be monitored up to failure using synchrotron X-ray-computed micro-tomography at the European Synchrotron Radiation Facility (ESRF). We will employ cutting-edge multiresolution approaches, including low-resolution scans of the full sample at 8um and local tomography around the $MgCO_3$ particles at 0.7um. These features will be tracked throughout the entire experimental study. This methodology, previously validated for various rocks (e.g., 44), enables the exploration of the potential role of $MgCO_3$ particles in damage nucleation at the micro-scale.

Task (3). Task (3). Life Cycle Assessment (LCA) of the processes. At the present time, the technology readiness level (TRL) concerning the **CLEANER** project is close to TRL 2. As mentioned above, this project focuses simultaneously on the basic and applied research. Applied research seeks to the optimization of the production of anhydrous stable divalent-cation carbonates and its use as partial substitute of cement in concrete as illustrated in Figure 1. In fact, the present project aims to reach a TRL 4 at the end of project. In such case, a life cycle assessment on the carbonates production including inputs and outputs seems necessary. For this reason, a LCA will be performed and/or planned in parallel to project experimental progress via a subcontracting external service or via an academic collaboration from specialized consulting offices or research academic teams. Herein, for example, a partial LCA on the magnesite production will be firstly conceptualized and then an LCA extent to the entire cycle of life, i.e., production and use of the magnesite in concrete will be assessed as illustrated in the Figure 6.

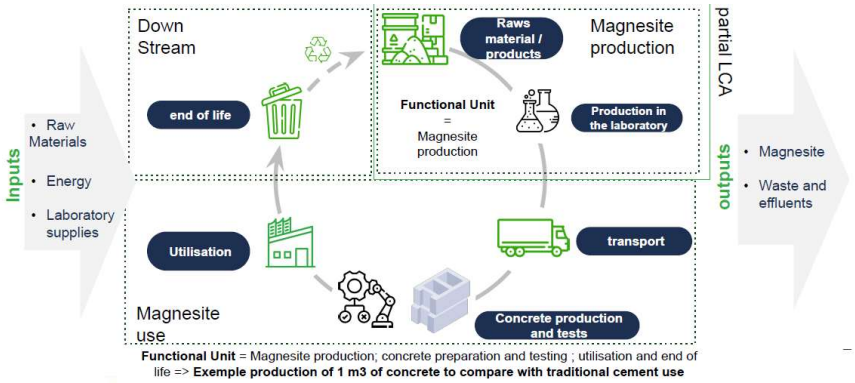

Figure 6. Illustration of LCA for magnesite fabrication and its use as partial substitute of cement in the concrete

The Simapro 8 software and Ecoinvent data base will be used to perform the conceptualized scenarios. This could be an additional benefit for **CLEANER**, which will further strengthen the reliability and relevance of the materials optimized process.

The database on which the modelling is based will be Ecoinvent, the most widely recognized in the scientific field (over 4,000 data points).

Production of LCA for the 16 indicators of the PEF (Product Environmental Footprint) + in-depth study on key indicators will be used.

Planning of the CLEANER project

The realization and success of this multidisciplinary project depend on a combination of sophisticated analytical tools and obviously also on the synergy of different expertise as illustrated in above Figure 2. In this context, the planning of tasks and identification of scientific responsible for each task during project realization is primordial. See below a summarized illustration (Figure 7), indicating the project time, tasks and investigator(s) responsible.

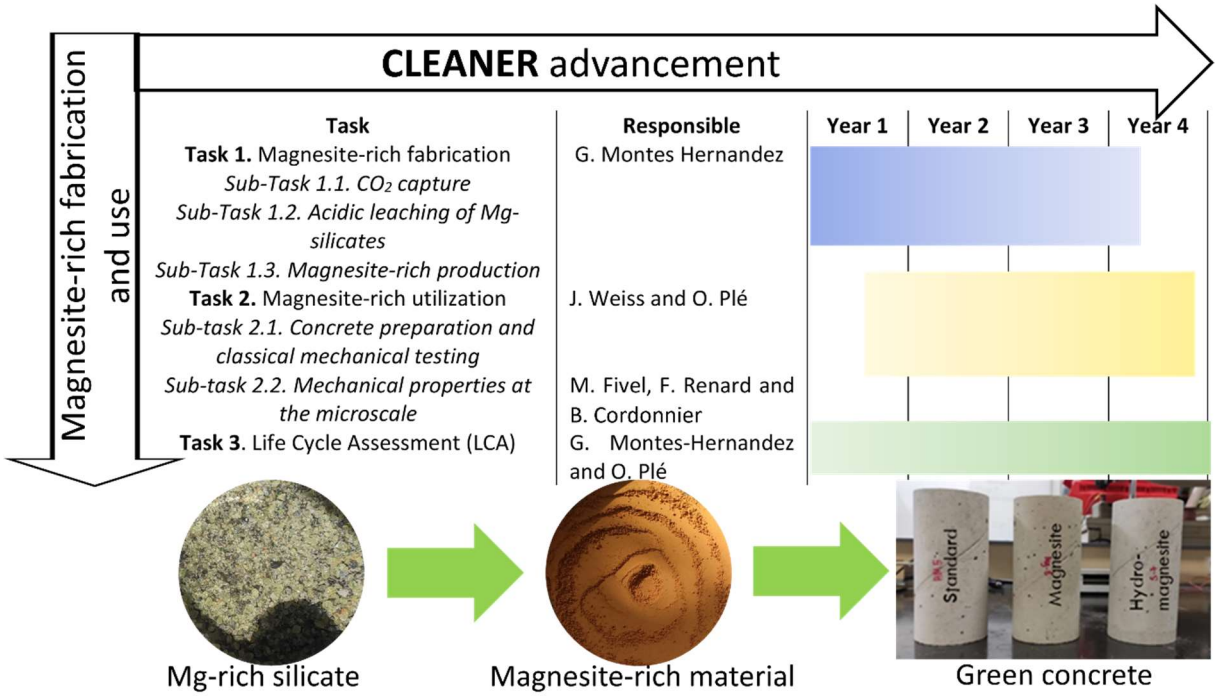

Figure 7. Overall planning indicating the tasks and their advancement with time and scientific responsible

The leaders of the tasks (see Figure 7) ensure the technical advance, thesis progress (if applicable) and results dissemination. Here, the results sharing via publications (open access), conferences in international meetings and science dissemination (including popularization of science) will be strongly encouraged. In addition, the optimized processes could be protected by patents if applicable as the project aims an upscaling from TRL 2 to TRL 4. For example, our technological research progress concerning the Fe-magnesite production by indirect carbonation of peridotite ant its use a partial substitute of cement in concrete was recently published in Industrial & Engineering Chemistry Research (20). Finally, the training of students (PhD, B.S and M.S) will be an important point in the present project. All these comments are simplified and illustrated in Figure 8 that summarizes also the main tasks, their interaction/synergy and the results communication and/or sharing.

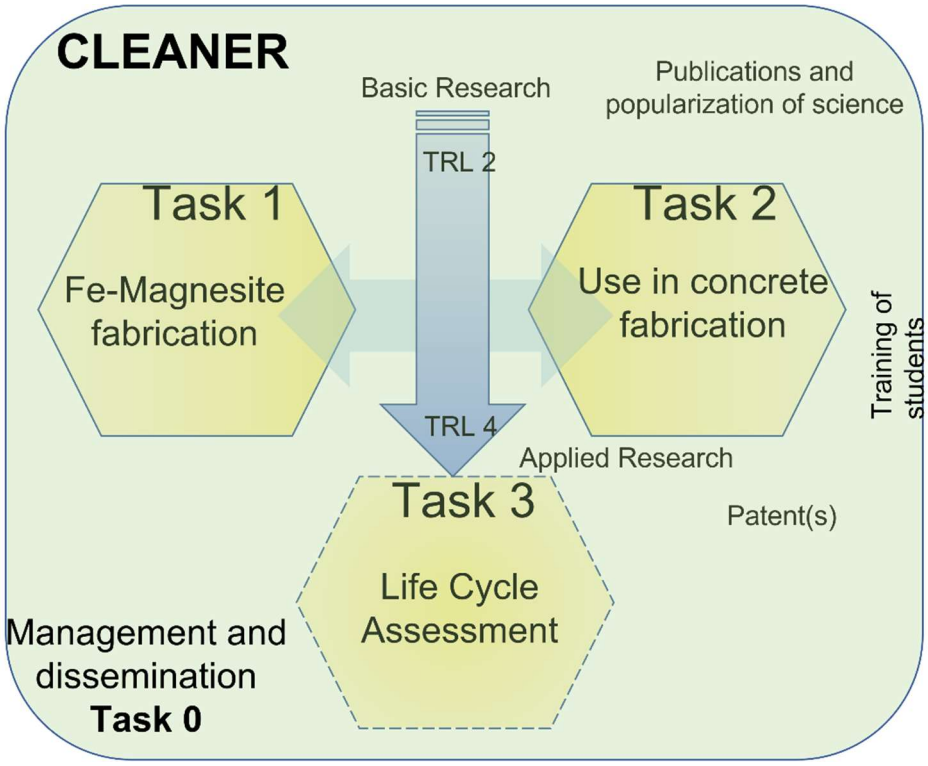

Figure 8. Structuration, task complementarity/synergy and management of CLEANER project.

The **CLEANER** project claims then a back and forth between fundamental and applied research on the physiochemistry at the mineral-solution interfaces with particular focus on the nucleation, growth and transformation of mineral particles and crystals. This fundamental research with direct applications on the carbon capture, utilization and storage in order to decrease/reduce significantly the industrial CO_2 emissions related to global warming.

III. Impact and benefits of the project

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. 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, aragonite, siderite and other anhydrous stable carbonates) appears now as a realistic strategy to reduce significantly the CO_2 industrial emissions into the atmosphere. In this way, **CLEANER** is a multi-disciplinary project that will integrate two main research topics: (1) design of the optimal mild conditions for production of anhydrous stable divalent-cation carbonates through indirect carbonation of mineral silicates (raw or waste materials) containing divalent cations, and (2) assessment of the incorporation of fabricated carbonate materials as a partial cement substitute in concrete manufacturing. In addition to basic technological research, the **CLEANER** project targets a strategic environmental benefit concerning a significant reduction of industrial CO_2 emissions as claimed above. In fact, if 30% of fresh cement is replaced by magnesite-rich material in the concrete fabrication, the CO_2 emissions from the cement industry could be reduced by about 50%. Here, two benefits are mainly claimed in terms of CO_2 reduction for the cement industry. Firstly, a reduction of clinker production and secondly, a permanent storage of carbon dioxide as Fe-magnesite material, without risks of later re-emission during the lifetime of the concrete

structure and/or during reuse as aggregate for new concrete. For this reason, it is fundamental to determine the optimal proportion of fresh cement to be replaced by magnesite-rich material without affecting the concrete performance.
On the other hand, inspired on the **CLEANER** project, recently my team was investigated the option to produce clinker cement without CO_2 emission into the Earth atmosphere. This emergent technology will be also investigated and its feasibility was recently shared as a short scientific communication in Chemical Engineering Journal (45). Herein, an innovative chemical process is proposed 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:

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

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 as described in **CLEANER**.

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 as illustrated in the following simplified material flow diagram. Herein, a maturating experimental study is necessary in order to optimize the operating process units and extend this process to other Ca-sources (e.g., mineral wastes such steel slags, demolition concrete, etc.)

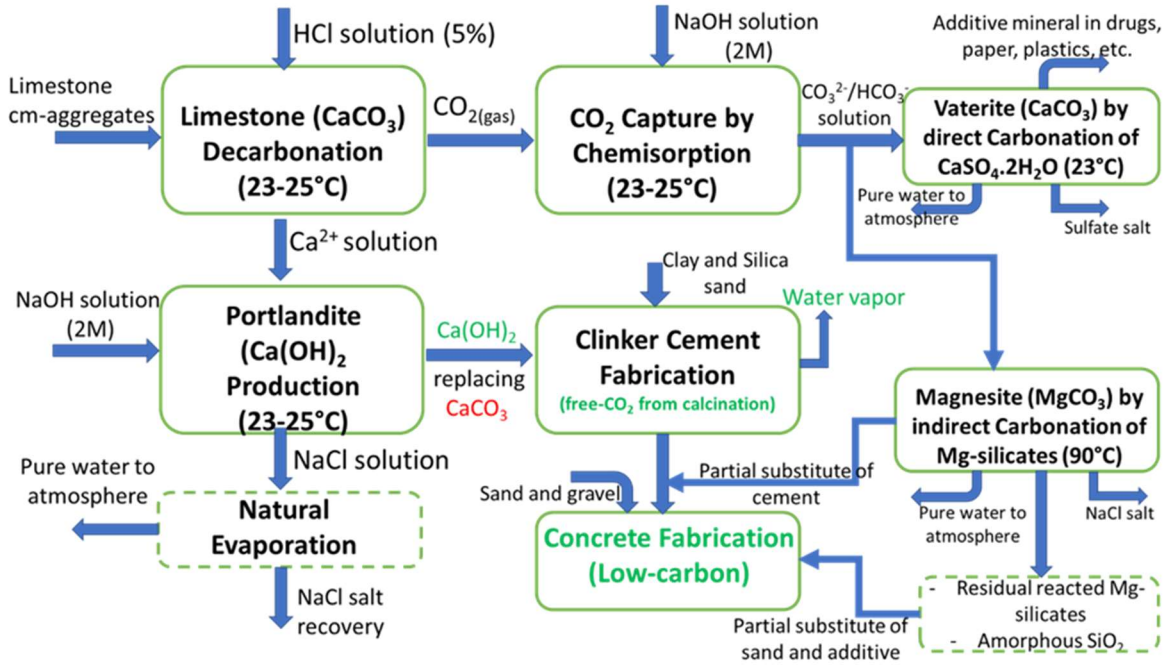

Figure 9. Material flow diagram for an innovative process on the portlandite ($Ca(OH_2)$) fabrication coupled to CO_2 sequestration by chemisorption. In order to produce "low-carbon" cement clinker and concrete. Main overall reactions are described in a short communication recently published in Chemical Engineering Journal (45).

IV. Hosting laboratory and consortium

ISTerre (Institut des Sciences de la Terre/Institute of Earth Sciences) is a joint research unit comprised of 300 people. It operates under the supervision of the CNRS, the University Grenoble Alpes, the University Savoie Mont Blanc, the French National Research Institute for Development (IRD) and University Gustave Eiffel. ISTerre is subsidiary of Observatory of Earth Sciences and Astronomy of Grenoble and of the research center Physics-Astrophysics-Geosciences-Environment (PAGE) of the University Grenoble-Alpes.

Organized in 10 research teams, the primary goal of ISTerre is the physical and chemical study of the planet Earth through a combination of observations of natural objects, experimentation, and the modeling of complex processes. In this way, the **CLEANER** program is in line with the current structuration at ISTerre and it concerns topics developed in geochemistry, mineralogy and faults teams and also agrees with cross-disciplinary topic on the energy transition. This program and strategy for the next five years involves both junior and senior scientists with complementary backgrounds in geochemistry, material sciences, petrology, mineralogy, civil engineering and mechanic of materials. This project will be preferentially supported by Ph.D., B.S and M.S students, and will involve, when possible, post-doctorate fellows and undergraduate students.

I aim to build a cross-disciplinary research group, with strong national and international collaborations, working on the nucleation, growth and transformation processes of minerals and crystalline particles. Obviously, this topic is relevant to geosciences but also to materials sciences, including several societal applications such as Ca looping process, carbon capture, utilization and storage (CCUS), low-carbon fabrication of cement clinkers and concretes, waste

recycling, etc. The current local, national and international collaborations will be reinforced and other will be developed in the coming years.

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