



Low CO₂ Cement Hydration Inspired From Nature

1. Abstract

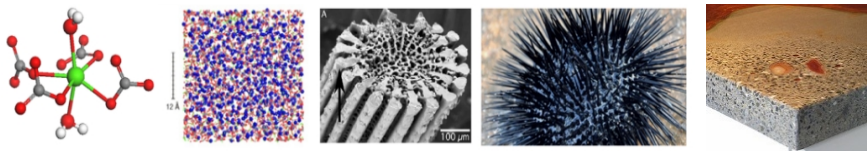
Carbonate biominerals form the shells of many marine organisms. These natural cements are formed through a multi-step nucleation pathway, involving the precipitation of metastable phases such as aqueous clusters or amorphous intermediates. These precursor phases interact with small fractions of organic and inorganic ions and molecules, which regulate the biomineralization process. Recent advances in the last few years have greatly contributed to the understanding of these natural crystallization processes. In the case of engineered cements, a quest for new organic molecules controlling the hydration (hydrate particles crystallization) of alternative low-CO₂ cement formulations is ongoing. Here, we propose a cross-disciplinary project to bring concepts learned during biomineralization to inform the development of new polymers to control the setting of low-CO₂ cement formulations.

2. Keywords

Nucleation ; cement ; hydration ; low CO₂ ; polymer ; biomineral ; decarbonization

3. Scientific project

3.1. State of the art



Hydrated –engineered– cement is made of a dense and cohesive percolated network of nanosized inorganic hydrates formed during the cement hydration, which involves the dissolution of the cement clinker phases and concomitant formation (nucleation/growth) of the cement hydrates [1]. This cohesive network glues together the stone aggregates of concrete and shapes the physical skeleton of our modern cities and infrastructure. An analogy with living organisms and the biominerals they form can be made: indeed, engineered cement, as bio-minerals, are also composed of the major elements of the earth's crust (Ca, Si, O, Al), hardens in water at room temperature and pressure and, once fully hydrated, are composed of mineral nanoparticles (cement hydrates) [2]. This confers cement many advantages such as its wide availability, ease of implementation and high strength performance and explains why concrete is the man-made material most massively produced and consumed in the world.

Still, cement remains a pale copy of biominerals. These exhibit extraordinary toughness, strength,

hardness and sustainability that out-weights that of hydrated cement and of human-made materials in general. In particular, much lower amount of raw material is employed to perform the appropriate function. As an example, it suffices to compare a bunker with the shell of a winkle -*Littorina littorea*- built to resist the shock of pebbles at each tides. Their secret: the chemical, spatial and structural control of the mineralization by (bio)polymers which results in highly-organized and mechanically optimized hybrid materials [3].

What is more: cement production, unlike polymer-assisted biomineralization, requires a lot of thermal energy, which makes it responsible for about 10% of anthropogenic CO₂ emissions¹. In the long term, biomimeticism is a promising route to solve this problem. In the short term, the most pragmatic solution is to develop low-CO₂ cement formulation by substituting part of the cement clinker by supplementary cementitious materials, among which calcined clays and limestones (due to their wide availability) are the best candidates. Above 15 wt% of cement-clinker substitution, however, these blended cements suffer from a low reactivity (long setting time) and very high water demand (poor workability) [4]. These issues are partially solved by the use of water reducer organic admixtures commonly employed in the concrete industry -PolyCarboxylate Ester (PCE) based superplasticizers- but at the cost of a much longer setting time (delayed cement hydration), and very high PCE dosage. It is clear that, whether for short- or long-term solutions to the carbon footprint of cement, there is a growing need for a new generation of polymer-based admixtures to improve low-CO₂ cement reactivity and thus control the formation of cement hydrates.

This project aims to unravel the nanoscale mechanisms by which polymers interact with the inorganic nanoparticles formed during the nucleation and growth of cement hydrates in low-CO₂ cement formulations. The main caveat is that very little is known about how polymers control the formation, i.e. nucleation/growth, of cement hydrates, and much can be learned from the control exerted by marine organisms during the biomineralization process of their shells and skeletons.

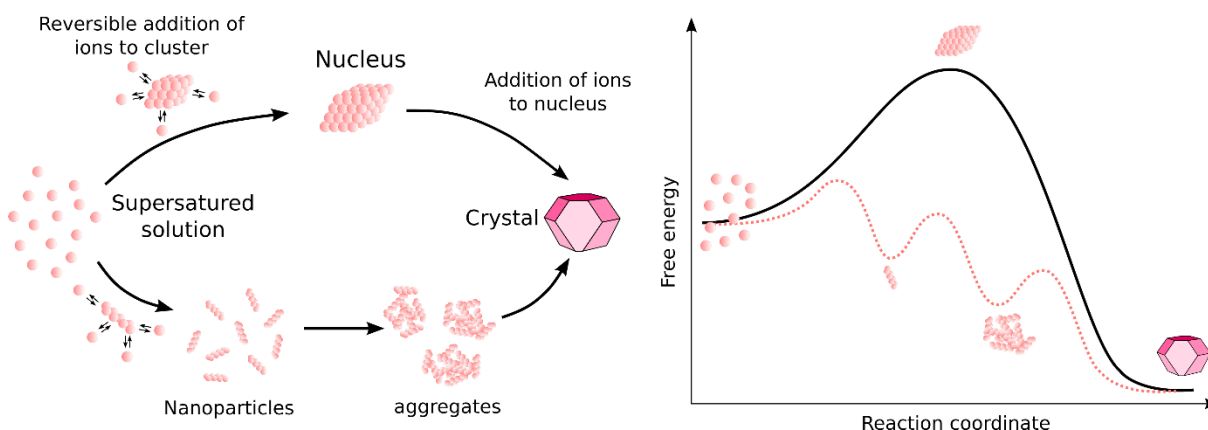


Figure 1. Classical (top arrow) and so-called ‘non-classical’ (bottom arrow) nucleation pathways through the formation of nanoparticles, aggregates (amorphous intermediates), and a schematic energetic landscape.

3.1. Specific research questions

In recent years, multi-step nucleation pathways involving the formation of pre-nucleation clusters, nanocrystalline and amorphous precursors, have been reported for a wide variety of inorganic and organic phases, including both biominerals and engineered cements (see Fig. 1 and the review in [5]). A paradigmatic example is that of the CaCO₃ system, which has been shown to form in some cases via an amorphous calcium carbonate (ACC) precursor, formed itself via the aggregation of CaCO₃ pre-nucleation clusters [6]. In a very recent study we have shown that C-S-H, the main component of hydrated cement, is also formed in solution via amorphous precursor clusters [7]. This amorphous precursor pathway offers a ‘cheaper’ alternative route through the free energy landscape, due to the lower interfacial energies of the intermediate phases, which considerably reduce the nucleation barrier. In addition, these pathways probably present evolutionary advantages for biominerals, due to the easiness by which the organisms can

¹Cement clinker is produced from a mixture of clay (~20%) and CaCO₃ (~80%) burned at high temperature (~1500°C); ~60% of CO₂ emissions comes from the decarbonation of CaCO₃

mold these precursor phases into intricate shapes [8]. However, and in spite of the large number of studies aimed at understanding the amorphous precursor pathway and its thermodynamics and kinetics characteristics, many open questions remain unanswered, blocking the development of effective additives to control the crystallization process in engineered cements.

The key question that still need to be resolved is:

What are the nanoscale mechanisms by which organic polymers control the nucleation and growth of natural and engineered cement hydrates?

Previous research in our groups has shown that, in CaCO₃-based biominerals, an amorphous precursor to calcite is stabilized via the addition of highly and strongly hydrated ions and organic polymers, which retard the crystallization via steric hindrance [9], [10]. Calcifying organisms take advantage of this delayed crystallization to mold the shapes of their shells and skeletons, due to the hydrated, malleable character of the amorphous precursor. A recent study by our groups has shown that the same process is also at play in Portland cements [7].

Here, we aim to study how this amorphous precursor strategy varies in the case of low-CO₂ cement formulations. Specific research questions are:

- Is an amorphous precursor formed during the hydration of low-CO₂ cement formulations?
- How do the polymers interact / modify the nucleation pathways of low-CO₂ cement hydrates?

3.2 Methodology and working plan

We plan to provide answers to these questions by using a combination of state-of-the-art scattering, imaging and spectroscopy techniques combined with computer modeling techniques.

The object of study will be the silicate-calcium system in the presence of foreign ions susceptible of be present in low-CO₂ cement formulations such as Mg²⁺ and Al³⁺. The Ca-Si-Al system can lead to the formation of the so called C-A-S-H, a binding phase similar to C-S-H but rich in Al. A selection of organic polymers will be made from the families of polycations, anionic block copolymers, and amphoteric polymers.

- **Task 1** of this project will deal with the study of the structure of aqueous (pre-nucleation) clusters in low-CO₂ cements. These processes will be studied at the ICB laboratory using methods developed for the study of biomineral formation. These include:
 - o Potentiometric titrations of calcium and silicate solutions, in the presence of inorganic (Mg²⁺, Al³⁺) and of selected polymers. These experiments will serve to study the chemical evolution of the system and the formation of the first organo-mineral clusters and their aggregation stages. The formed solids will be characterized by lab-based techniques including ICP-OES, TGA, FTIR, AFM, DSC and SEM.
 - o TEM experiments will be performed to characterize the shape and chemical composition of the precursor phases. Electron tomography, specifically, will be used to restore the 3D structure of a specimen from a series of 2D micrographs. Detailed information will be obtained on the structure, morphology or 3-dimensional spatial organization of macromolecules and (macro)molecular assemblies. Moreover, in-situ TEM experiments will be carried out using a specific sample holder allowing to image samples in a self-contained and fully hydrated flowing and mixing chamber.
 - o In collaboration with ISTERre Laboratory, in situ synchrotron-based X-ray techniques (PDF and SAXS) will be used to characterize the early stages of formation of low-CO₂ cement hydrates. These experiments will be performed under controlled chemical conditions, using an in-situ titration setup developed for the study of the formation of amorphous precursors.
- **Task 2** of the project will involve the modeling of the nucleation processes characterized during the Task 1. Experimental information obtained during the characterization of the early stage formation of the cement hydrates will be used to inform simulations, with the aim of predicting the behavior and of understanding the relative importance of the different physico-chemical parameters at play (e.g., pH, surface charge, chemical composition, presence of organics). These

simulations will be developed at the ICB laboratory using FAUNUS² an open source code for Monte Carlo simulations. These include:

- Speciation of supersaturated solutions in presence and in absence of the selected polymers. These simulations will serve (i) to study the formation and distribution of the silicate prenucleation clusters (ii) to calculate the supersaturation index and thus the driving force for the hydrate nucleation (iii) to feed the mesoscale simulations of hydrate nucleation. The simulation will be performed in the recently developed reactive ensemble for chemical speciation.
- Gibbs free energy barrier of the homogeneous nucleation of the main cement hydrate (calcium silicate hydrate) in presence and in absence of the selected polymers. To do this the Umbrella sampling will be used. The simulations will be performed in the isochore isobaric isothermal ensemble (NPT) using the supersaturated solution model described above.

3.3 Expected results

The results of this research will have a large impact on our understanding of the physico-chemical processes leading to the nucleation and growth of hydrates in low-CO₂ cements. A nanoscale structural description of the different stages leading from the supersaturated solution to the formation of the cement hydrates will be provided. The main stage at which the organics interact with the mineral particles will be identified. This fundamental question is nowadays one of the more important unresolved points that blocks the development of additives to improve the workability of low-CO₂ cement pastes.

The work will also have an impact on our fundamental understanding of organo-mineral interactions, which have been shown to regulate not only biomineralization processes, but also the permanent storage of carbon in organic matter fractions of soils.

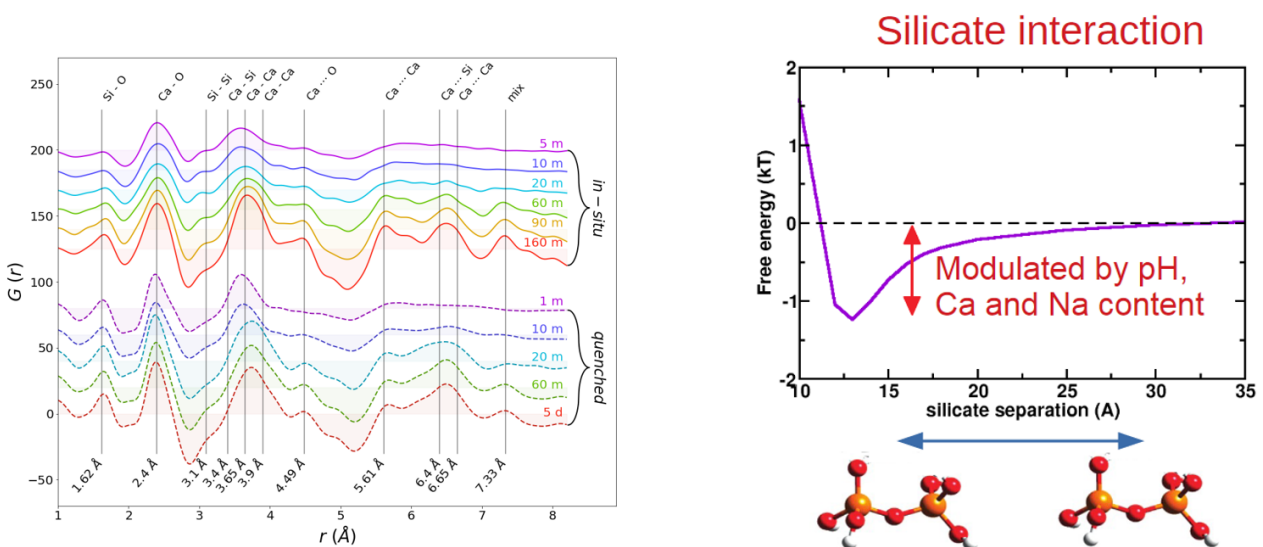


Figure 2. Left: Experimental synchrotron-PDF characterization of the amorphous precursors during the hydration of Portland cement, performed by the ISTERre team. The use of in-situ synchrotron techniques allows observing the early stages of mineral formation (Besselink, et al., in preparation). Right: Example of the kind of interactions leading to the formation of the amorphous precursors, as studied by computer modeling. The relative weight of different physico-chemical parameters on the aggregation barriers can be determined. The synergistic approach will be used in the present project to study the early stages of low-CO₂ hydrate formation.

3.4 Synergy between the research teams

The teams of ICB (INP) and ISTERre (INSU) have already collaborated in the past through ‘NanoCem’, an academic-industrial network to develop pre-competitive research in the field of cement chemistry. The

ISTerre team performs in-situ synchrotron characterization studies of nucleation and growth processes in biominerals and engineered cements [9–12]. The ICB team is a world recognized group in cement chemistry and performs experimental characterization and advanced computer modeling of chemical reactivity, aggregation and self-assembly processes [13-14]. This combination of expertise has been used in the frame of a collaborative PhD thesis and resulted in a joint publication series which highlights the added-value of the approach [15-17].

- [1] J. W. Bullard *et al.*, “Mechanisms of cement hydration,” *Cem. Concr. Res.*, vol. 41, no. 12, pp. 1208–1223, Dec. 2011.
- [2] S. Mann, *Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry*. New York: Oxford University Press, 2001.
- [3] J. Aizenberg, “New Nanofabrication Strategies : Inspired by Biomineralization,” *MRS Bull.*, vol. 35, no. April, pp. 323–330, 2010.
- [4] J. S. J. van Deventer, C. E. White, and R. J. Myers, “A Roadmap for Production of Cement and Concrete with Low-CO₂ Emissions,” *Waste and Biomass Valorization*, pp. 1–31, Aug. 2020.
- [5] J. J. De Yoreo *et al.*, “Crystallization by particle attachment in synthetic, biogenic, and geologic environments.,” *Science (80-.)*, vol. 349, no. 6247, p. 6760, 2015.
- [6] L. Addadi, S. Raz, and S. Weiner, “Taking advantage of disorder: Amorphous calcium carbonate and its roles in biomineralization,” *Adv. Mater.*, vol. 15, no. 12, pp. 959–970, 2003.
- [7] N. Krautwurst *et al.*, “Two-Step Nucleation Process of Calcium Silicate Hydrate, the Nano-Brick of Cement,” *Chem. Mater.*, vol. 30, no. 9, pp. 2895–2904, 2018.
- [8] L. Yang, C. E. Killian, M. Kunz, N. Tamura, and P. U. P. A. Gilbert, “Biomineral nanoparticles are space-filling.,” *Nanoscale*, vol. 3, no. 2, pp. 603–9, 2011.
- [9] M. P. Asta *et al.*, “Nanoscale ion dynamics control on amorphous calcium carbonate crystallization: Precise control of calcite crystal sizes,” *J. Phys. Chem. C*, vol. 124, no. 46, pp. 25645–25656, 2020.
- [10] A. Koishi *et al.*, “Role of Impurities in the Kinetic Persistence of Amorphous Calcium Carbonate: A Nanoscopic Dynamics View,” *J. Phys. Chem. C*, vol. 122, no. 29, pp. 16983–16991, 2018.
- [11] A. F. Wallace *et al.*, “Microscopic evidence for liquid-liquid separation in supersaturated CaCO₃ solutions,” *Science (80-.)*, vol. 341, no. 6148, pp. 885–9, 2013.
- [12] A. Fernandez-Martinez, B. Kalkan, S. M. Clark, and G. A. Waychunas, “Pressure-induced polyamorphism and formation of ‘aragonitic’ amorphous calcium carbonate,” *Angew. Chemie Int. Ed.*, vol. 52, pp. 8354–8357, 2013.
- [13] Picker, A.; Nicoleau, L.; Burghard, Z.; Bill, J.; Zlotnikov, I.; Labbez, C.; Nonat, A.; Cölfen, H. Mesocrystalline Calcium Silicate Hydrate: A Bioinspired Route toward Elastic Concrete Materials. *Science Advances*, vol. 3, no. 11, p. e1701216, 2017.
- [14] Picker, A.; Nicoleau, L.; Nonat, A.; Labbez, C.; Cölfen, H. Influence of Polymers on the Nucleation of Calcium Silicate Hydrates. *arXiv:2111.04445 [cond-mat, physics:physics]* 2021.
- [15] Bouzouaid, L.; Lothenbach, B.; Fernandez-Martinez, A.; Labbez, C. Gluconate and Hexitols Effects on C-S-H Solubility. *Cement and Concrete Research*, vol. 160, p. 106894, 2022.
- [16] Bouzouaid, L.; Van Driessche, A. E. S.; Martinez, J. C.; Malfois, M.; Lothenbach, B.; Labbez, C.; Fernandez-Martinez, A. Impact of Gluconate and Hexitol Additives on the Precipitation Mechanism and Kinetics of C-S-H. *ArXiv:2111.02743*, 2021.
- [17] Bouzouaid, L.; Lothenbach, B.; Fernandez-Martinez, A.; Labbez, C. Portlandite Solubility and Ca²⁺ Activity in Presence of Gluconate and Hexitols. *Cement and Concrete Research*, vol. 149, p. 106563, 2021.

RESPONSABLES	Valérie Potin (MCF HDR) valerie.potin@u-bourgogne.fr Christophe Labbez (CR) christophe.labbez@u-bouroggne.fr En collaboration avec Alejandro Fernandez-Martinez Alejandro et Valérie Magnin, ISTerre UMR 5272, Université Grenoble-Alpe
MOYENS/LIEU	ICB (Dijon)

Bref curriculum vitae des porteurs ICB du projet et du responsable de l'équipe partenaire

Christophe LABBEZ

CR-CNRS – ICB (UMR 6303) - <https://icb.u-bourgogne.fr/equipe/christophe-labbez/#carrieres>

Christophe Labbez is performing his research work in the INTERFACES Department of the Laboratoire Interdisciplinaire Carnot de Bourgogne (ICB - UMR 6303 CNRS) of the University of Bourgogne Franche-Comté. His research activities are focused on the physical chemistry of solid/solution interfaces and are recognized in the fields of the reactivity of hydraulic binders and the physical chemistry of concentrated colloidal systems. C. Labbez is a specialist in statistical thermodynamics and molecular and mesoscopic simulations using Monte-Carlo and Molecular Dynamics techniques. His work has focused on understanding and rationalizing the link between the interfacial properties of colloids (charges, electrokinetics, adsorption) and the inter-particle forces and structure of colloidal materials. In recent years his work has focused on hybrid colloidal systems and the chemical speciation of those complex systems. He is co-author of more than 60 publications (H-index 30). C. Labbez is a member of the European consortium NanoCem and the world consortium INNOVANDI as well as of the European Colloid and Interfaces Society (ECIS) and the GDR SLAMM.

Valérie POTIN

MdC- ICB (UMR 6303) - <https://icb.u-bourgogne.fr/equipe/valerie-potin/>

Valérie Potin is performing her research work in the INTERFACES Department of the Laboratoire Interdisciplinaire Carnot de Bourgogne (ICB - UMR 6303 CNRS) of the University of Bourgogne Franche-Comté. V. Potin's main research activity is in the field of nano-structured materials such as ultra-thin films and nano-objects. She is a transmission electron microscopy (TEM) specialist and studies the morphological, chemical, structural properties of such systems at nanometer scale using various TEM techniques, in particular conventional and High Resolution TEM, EDS and STEM. She is responsible of the development of TEM activities in the ARCEN (Applications, Research and Characterization at Nanometer Scale) platform of the University of Burgundy. She is author or co-author of 83 articles in peer-reviewed international journals (H-factor = 26). She has obtained three prizes during her carrier (EMRS 1997, MSM 1999, ANM 2014).

Alejandro FERNANDEZ-MARTINEZ

CR-CNRS – [ISerre](http://isterre.fr) (UMR 5275) - <http://isterre.fr/alex-fernandez-martinez>

- **Since 2015:** Visiting Scientist European Synchrotron Radiation Facility (ESRF), Structure of Materials Group.

- **Since Feb. 2012:** CR-CNRS Researcher at Institut des Sciences de la Terre, Grenoble, France

- **2010-2012:** Postdoc at the Center for Nanoscale Control of Geologic CO₂, LBNL, Berkeley USA

- **2006-2009:** PhD in Environmental Geochemistry, Institut Laue-Langevin & UJF, Grenoble, France

- **2005:** M.Sc. Physics, University of Oviedo, Spain

Research activities

- Nucleation and growth of minerals: 2 ANR projects, 4 industrial projects (BASF, HeidelbergCement, Nanocem, Innovandi network)

- Structure and chemical reactivity of minerals/water interfaces: LABEX, ILL and ESRF PhD projects, industrial collaboration (BioMerieux).

- Development of in situ synchrotron-based methods for the study of mineral formation and reactivity.

Mentoring and teaching

- Co-supervision of 11 PhD thesis students (5 on-going), 6 postdocs (1 on-going) and 9 undergraduate (licence, master, IUT) students.

- Teaching at the Master and doctoral level. Courses on the reactivity of nanoparticles and on physical characterization methods of mineral-water interfaces.

Publications (H-index = 29) https://scholar.google.fr/citations?user=rwx9d_sAAAAJ&hl=en

Others

- Associate Editor American Mineralogist (2012-2019), Frontiers in Earth Materials, PlosONE.
- Member of the Proposal Review Panels PRC6 SOLEIL synchrotron and C11 ESRF.
- Speaker at 40 scientific sessions in international conferences. 20 invited talks.
- Bronze Medal CNRS 2021