Low CO_2 Cement Hydration Inspired From Nature

1. Abstract

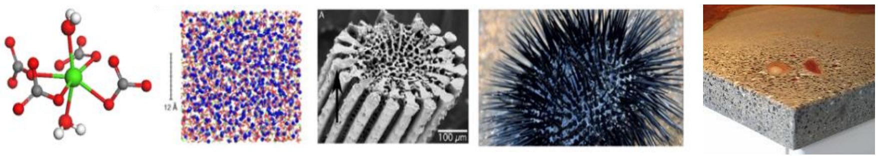
Carbonate biominerals form the shells of many marine organisms. These natural cements are formed through a multi-step nucleation pathway, involving the precipitation of metastable phases such as aqueous clusters or amorphous intermediates. These precursor phases interact with small fractions of organic 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-CO_2 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-CO_2 cement formulations.

2. Keywords

Nucleation ; cement ; hydration ; low CO_2 ; 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-weight 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 CO_2 emissions[1]. In the long term, biomimetism is a promising route to solve this problem. In the short term, the most pragmatic solution is to develop low-CO_2 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

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[1] Cement clinker is produed from a mixture of clay (~20%) and $CaCO_3$ (~80%) burned at high temperature (~1500°C); ~60% of CO_2 emissions comes from the decarbonation of $CaCO_3$

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-CO_2 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-CO_2 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 learn from the control exerted by marine organism during the biomineralization process of their shells and skeletons.

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 $CaCO_3$ system, which has been shown to form in some cases via an amorphous calcium carbonate (ACC) precursor, formed itself via the aggregation of $CaCO_3$ prenucleation 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 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.

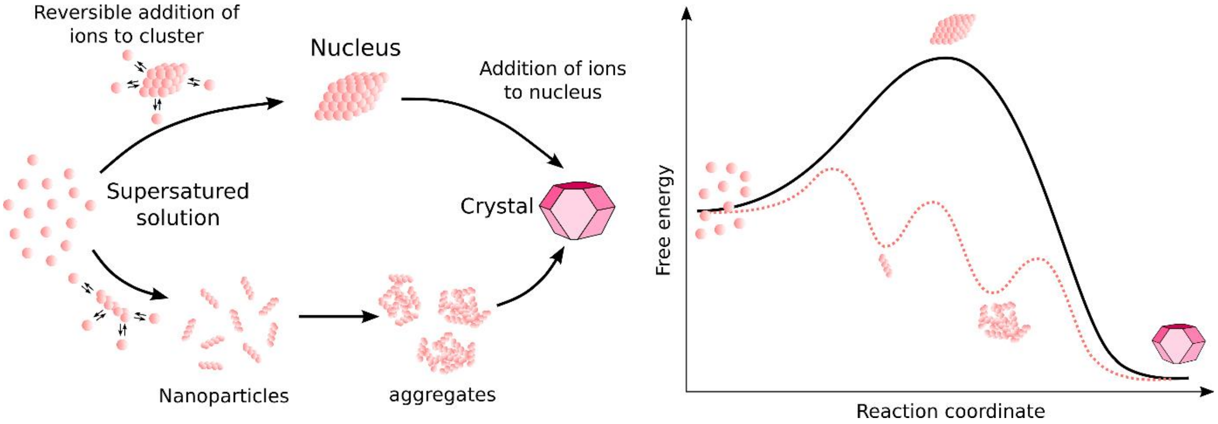

Figure 1. Classical (top arrow) and so-called ‘non-classical’ (bottom arrow) nucleation pathways through the formation of nanoparticles, aggregates (amorphous intermediates), and a schematic energetic landscape.

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 $CaCO_3$-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-CO_2 cement formulations. Specific research questions are:

- Is an amorphous precursor formed during the hydration of low-CO_2 cement formulations?
- How do the polymers interact / modify the nucleation pathways of low-CO_2 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-CO_2 cement formulations such as Mg^{2+} and Al^{3+}. 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-CO_2 cements. These processes will be studied at the ICB and ISTerre laboratory using methods developed for the study of biomineral formation. These include:
    - Potentiometric titrations of calcium and silicate solutions, in the presence of inorganic (Mg^{2+}, Al^{3+}) 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, Raman, AFM, DSC (sensor to be ordered via this project) and SEM.
    - 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.
    - In situ synchrotron-based X-ray techniques (PDF and SAXS) will be used to characterize the early stages of formation of low-CO_2 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 FAUNUS[2] 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-CO_2 cements. A nanoscale structural description of

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[2] 2 https://github.com/mlund/faunus; Contributors : *Jakub Smutek, Marco Polimeni, Vidar Aspelin, Stefan Hervø-Hansen, Richard Chudoba, Niels Kouwenhoven, Coralie Pasquier, Lukáš Sukeník, Giulio Tesei, Alexei Abrikossov, João Henriques, Björn Stenqvist, Axel Thuresson, Robert Vácha, Magnus Ullner, Chris Evers, Anıl Kurut, Fernando Luís Barroso da Silva, André Teixeira,* ***Christophe Labbez****, Ondrej Marsalek, Martin Trulsson, Björn Persson, Mikael Lund*

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-CO_2 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.

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 combined experimental – modelling approach has been used in the frame of a collaborative PhD thesis and in series of publications which highlights its added-value of the approach [15-17].

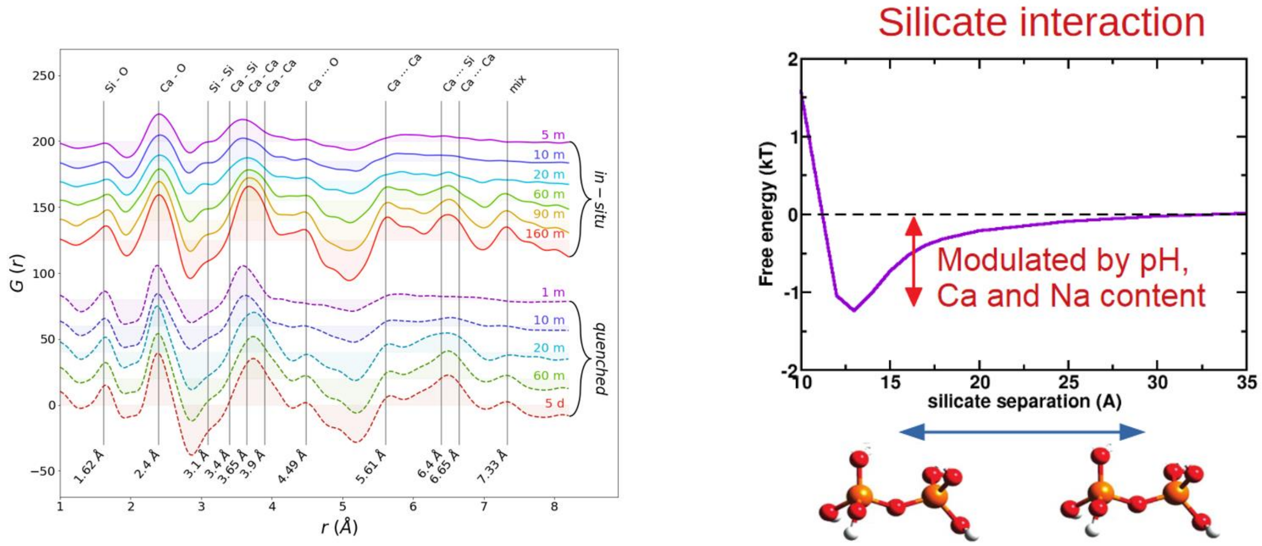

Figure 2. Left: Experimental synchrotron-PDF characterization of the amorphous precursors during the hydration of Portland cement, performed by the ISTerre team. The use of in-situ synchrotron techniques allows observing the early stages of mineral formation (Besselink, et al., in preparation). Right: 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-CO_2 hydrate formation.

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IDENTIFICATION

Civilité/NOM/Prénom du porteur du projet		M. LABBEZ Christophe
Section du comité national de la recherche scientifique		14
Etablissement de rattachement		CNRS
Code Unité		UMR 6303
Nom du laboratoire et/ou de l'équipe		ICB
Rattachement de l'unité	Institut principal	IP
	Délégation régionale	DR06

Identification des équipes travaillant sur le projet

Code Unité (UMR, UPR, etc.)	Nom du laboratoire	Rattachement		Personnes impliquées
		Institut principal	Délégation régionale	
UMR 6303	ICB	INP	DR06	M. LABBEZ Christophe Mme POTIN Valerie
UMR 5275	ISTerre	INSU	DR11	M. FERNANDEZ-MARTINEZ Alejandro Mme. MAGNIN Valerie