French Polytech network form for PhD Research Grants from the China Scholarship Council

This document describes one of the PhD subjects proposed by the French Polytech network. The network is composed of engineering schools/universities. The document also provides information about the supervisor.

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PhD information	
Title	Multiscale study of ions diffusion in concrete: application for Durability of low-impact materials
Main topics regards to CSC list (3 topics at maximum)	IV-2. Nanomaterials IV-6. Calculation of materials and simulation for design IV-7 Materials for environment and ecology IV-12. Environmental behavior and failure of materials

Required skills in science and engineering	Cliquez ou appuyez ici pour entrer du texte.

Subject description (two pages maximum including biblio)

Corrosion of steels in reinforced concrete structures is the leading cause of degradation, with significant repair costs mainly due to the diffusion of CO_2 and chlorides. Predicting the service life is therefore of paramount importance in order to optimize the maintenance operations of the structures. In the case of chlorides, many models for predicting the diffusion coefficient have been developed at different microscopic and macroscopic scales. Most of them attribute the low ratio between the diffusion coefficient of an ionic specie in concrete to its value in a bulk solution to a tortuosity factor defined by topological approaches where the geometry of the porous medium is taken into account. Other approaches have shown the limits of the geometric approach because ionic exchanges between the porous solution and the cementitious matrix can induce electric fields which can thus strongly affect the diffusion process: these exchanges are known under the name of electrical double layer (EDL). They are taken into account through the Stern model (1924) and the influence of EDL appears through the zeta potential, the diameter of the pores and therefore the pore network.

In cement paste, the porous network is influenced by the chemical composition of the binder and by the water/cement (w/c) ratio. Three classes of pores coexist in the absence of micro-cracks: capillary pores, gel pores and calcium silicate hydrates (C-S-H) nanopores [1, 2]. During the curing of concrete, in particular for mixtures with a low w/c ratio, the size of the porous network decreases and thus causes the depercolation or disconnection of the network of capillary pores. As a consequence, ionic species diffuse mainly in the nanopores [2-4,15]. Moreover, the specific surface of the porous network is greater, resulting in a stronger interaction between the ionic species and C-S-H. Under such conditions, the influence of the electrical double layer (EDL) formed between the surface of C-S-H (negatively charged) and the pore solution (rich in cations) is important [5-7]. The behavior of ions in the diffuse layer is complex and mainly influenced by the size of the pore and the composition of the solution.

The quantification of the effect of the EDL on the diffusion of ionic species remains an open problem because it occurs at the nanometric scale for which experimental methods are still limited. Understanding this phenomenon therefore requires the use of atomistic simulation methods. Molecular dynamics (MD) has improved the understanding of phenomena occurring at the nanoscopic scale and is particularly suitable for simulating solid/liquid interfaces [8, 9]. This method employs force fields describing atomic interactions and allows simulating systems of several thousand atoms for several nanoseconds using Newton's equation of motion. Force fields can be derived from experimental measurements and from so-called ab initio calculations such as density functional theory (DFT). In the last decades, the development of force fields have allowed to simulate and compute accurately the bulk and interfacial properties of anhydrous and hydrated cement phases [10]. Many works have notably improved the understanding of clays from molecular simulations and paved the way for the study of C-S-H based on the crystal structure of tobermorite [11, 12]. The decrease in the Ca/Si ratio and the increase in the water content and the degree of amorphism have made it possible to generate models of C-S-H in better agreement with experimental measurements [13, 14].

The EDL and the diffusion of water and ionic species in nanopores can be calculated from MD simulations. However, MD is limited by its low temporal and spatial resolution. To upscale the information available at the nanoscale from MD to the scale of a representative volume element of concrete (several centimeters), various homogenization methods (analytical and/or numerical) can be used [15]. Such multiscale methods can be fed by the local parameters obtained by MD at the nanoscale, but also account for the change in percolation and the tortuosity of the capillary pores (10nm-10µm), the effect of aggregates (few mm to few cm) and interfacial transition zone at the cement paste/aggregate interface. MD and multiscale modeling methods are thus complementary as the latter suffer from a lack of information at the molecular scale [2, 3]. The major goal of MD is to preserve the physical meaning of the system under study and to provide a more accurate description of its properties at the nanoscale.

This project aims to contribute to a better understanding of the effect of EDL on transfer mechanisms of chlorides from the nanoscale to the microscale. In a first time, the PhD student will create atomistic models and perform MD simulations to assess the diffusion coefficient of chloride ions at the interface with C-S-H under different conditions. In a second time, an Eshelby-based multiscale model will be developed to upscale the diffusion properties up to the macroscale. The multi-scale model will include the contribution of the aforementioned three types of pores and their change in percolation with w/c ratio and hydration degree. The results of this numerical assessment will be compared to experimental measurementswhich will be made using low environmental impact concretes such as geoplymers or calcined clay-based concretes, which are new materials and very little studied, in terms of zeta potential, porous network distribution and diffusive properties.
Finally, the results of this thesi will help to assess with more precision the service life of concrete structures located at coastal environment such as harbor and floating offshore.

Globally, the obtained results could open the path to a better design of concrete and to the development of more efficient binders for the durability of concrete structure, and help to find a performance – environmental cost optimum.

Supervisor Team

- Prof Ouali AMIRI: Physical and chemical macroscopic modelling and experimental aspects of durability
- Assistant prof: Jerome CLAVERIE : Molecular Dynamic and atomistic studies
- Assistant Prof: François BIGNONNET : Scaling modelling

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