Ph.D.: Study of crystallization pressure by molecular simulation and microfluidics experiments

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Context

Salt crystallization in porous media is a major cause of damage of materials involved in the degradation of heritage (Fig. 1), in geotechnical disorders[1], in geomorphological processes[2], or in the durability of cementitious materials[3,4,5]. Yet, salt crystallization damage within a porous medium remains one the most poorly understood phenomenon in mechanics of porous media[6]. The degradations strongly depend on the nature of the salt, on the type of porous medium, on the dissolution-precipitation cycles, on the kinetics of diffusion of the solutes, or on the scale of the porosity involved. The fact that a crystal in contact with a super-saturated solution can grow while being compressed was identified long ago during the 19^{e} century[7]. Correns law[8] (1949) provides a first theoretical prediction of the phenomenon based on the equality of the chemical potentials between the super-saturated solution and the crystal. It predicts a 'crystallization pressure', which can exceed a hundred MPa for highly super-saturated solutions, more than enough to damage construction materials and rocks. Correns law was further refined since then[9], but it does not explain why, from one salt to another, there are such large differences in induced damage, under identical experimental conditions[10]. In particular, recent studies have shown the key role of the nanometric interface crystal-aqueous film-solid where is generated the disjoining pressure at the origin of the stress transfer[11,12,13,14,15,16,17,18].

Fig. 1: Examples of salt weathering of heritage and monuments, from Flatt et al.[6]

Objective

In this project, we propose to use molecular simulation approaches (Navier, LMPS) in complement of microfluidics experiments (ISTO) in order to unravel the origin and quantify the crystallization pressure phenomena in model systems. Microfluidics consists in the use of micromodels that offer a precise control and a quantitative monitoring of the crystallization at the scale of a model pore. The molecular

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simulation will complement the experiments with a nanometric description of the solute-crystal coexistence at the scale of the crystal-solid interface. This work is expected to provide quantitative measurements and theoretical estimations of the crystallization pressure, in order to evaluate the role of the key factors (super-saturation, disjoining pressure, film thickness, nature of the salt and of the surface) and to converge to a consistent thermodynamic. This work can be transposed to cases of applicative interest, which are also studied by the members of the consortium (crystallization of thenardite/mirabilite, concrete, limestone, built heritage).

Practical information and applications

This Ph.D. project will be located alternatively between the Paris region (Navier laboratory and LMPS) for the simulation part in 1st year, and Orléans (ISTO) for the experimental part in 2nd year (3rd year to see, depending on the progress of the work). The Ph.D. candidate will be enrolled in the doctoral school 'Science, Ingénierie, Environnement' of the Ecole des Ponts ParisTech. The project is funded by CNRS within the scope of the mission for transverse initiatives and interdisciplinarity (project ESOPE). The Ph.D. funding is granted for a total of three years starting on 1st October 2022, with a gross stipend of 2135€/month for full time work.

The applicants must hold a Master of Science or equivalent in the field of physics and/or (geo)-mechanics of materials (or close subject), with a taste for both numerical and experimental work. They must be able to communicate fluently in French and/or English, both written and spoken. The interested applicants are invited to apply on the CNRS career portal (https://emploi.cnrs.fr/Offres/Doctorant/UMR8205-LAUBRO-001/Default.aspx?lang=EN) or by email by sending a CV, a motivation letter and their transcripts to L. Brochard (laurent.brochard@enpc.fr) before 6th May 2022.

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