> JOURNEE DES DOCTORANTS

> CSTB - PARIS

Reactive transport in cement paste: coupling between hydration, drying and carbonation

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CONTEXT AND OBJECTIFS

Context

- **5% to 7% of global CO_2 emissions come from the cement industry.**
  - To reduce this number despite increasing demand, cement manufacturers " dilute " Ordinary Portland Cement (OPC) with **Supplementary Cementitious Materials** (SCM) (pozzolana, fly ash, blast furnace slag…)
- **What is the impact of SCMs on the durability of concrete ?**
  - Although most SCMs are hydraulic binders, their chemistry, and in particular, their hydration kinetics is different from OPC.
  - Carbonation is the reaction of concrete with atmospherical CO_2
  - It may lead to huge damage inside the concrete.
  - In a first approximation, the lifespan of concrete is determined by the time needed for CO_2 to diffuse from the surface to the rebar.
  - The impact of SCM need to be quantified and modelled to guarantee the durability of these cements.

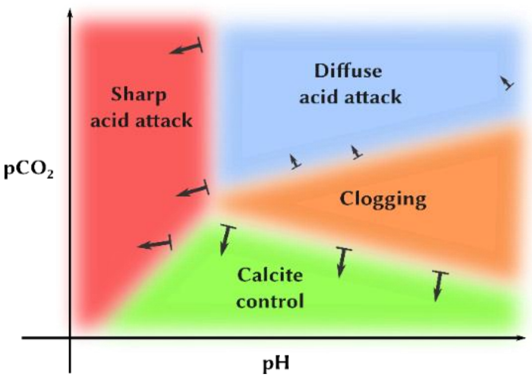
Objectif

The objectives of this Ph.D. is to study the physical and numerical coupling of hydration, drying and carbonation of cement paste.

- The physical coupling is obtained by building a consistent model of the porous media and its evolution
- The numerical coupling is obtained by building a robust and efficient reactive transport solver

The steps to achieve these objectives are :

1. Development of a speciation solver for cement paste
2. Development of a saturated reactive transport solver for cement paste
3. Validation of the solver : leaching of cement paste in CO2-rich brines
4. Development of a multiphase reactive transport solver for cement paste
5. Validation of the multiphase reactive transport solver
6. Simulation of hydration, drying and carbonation



> Fig. 1: The four main mechanisms of leaching of cement paste in brines. Arrows represent the gradient of reactivity

MAIN RESULTS

1. **A robust and flexible reactive transport framework was implemented using a new algorithm to include custom-made microstructure models.**
2. **Due to its numerical features, it is well adapted for the modelling of cement pastes.**
3. **In particular, its speciation solver implements a new algorithm to find the equilibrium phase assemblage efficiently**
4. **The reactive transport framework was validated by investigating the influence of the boundary conditions on the leaching of cement pastes in brines.**
5. **A two-phase system is implemented to study the coupling between drying and hydration.**
6. **The preliminary results reveals that our approach captures the coupling between carbonation and drying. The limiting phenomena is the release of water to the environment**

CURRENT PROGRESS

SpecMiCP [1] and ReactMiCP [2]

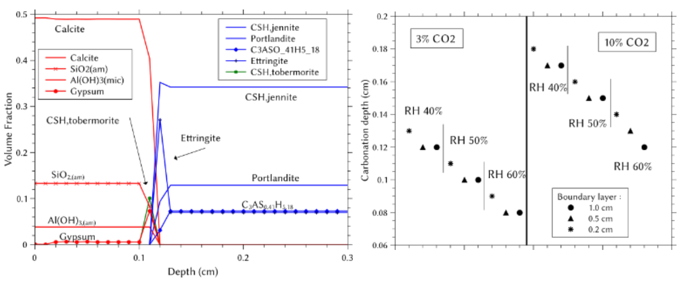
- A new speciation solver, SpecMiCP, was developed especially for cement and concrete problems. It uses a complementarity condition to express the solid phase assemblage equilibrium. The system is solved using a custom semismooth newton solver. These features ensure the robustness and efficiency of the solver. For cement related problems, SpecMiCP is 10 to 15 times faster than PHREEQC.
- A new reactive transport solver, ReactMiCP, was implemented on top of SpecMiCP. It uses a sequential iterative algorithm (SIA)
- SIA was shown to be critical to obtain a correct solution efficiently, especially in variable porosity problems.
- The solver was validated using the MoMas reactive transport benchmark and by studying the leaching of cement paste in CO2-rich brines
- It is available at http://bitbucket.org/specmicp/specmicp (with documentation)

Leaching of cement paste in brines [3]

- Carbon capture and sequestration relies on the assurance that the carbon dioxide can be trapped safely and will not leak through the wells. A necessary step to assess the long-term safety of the operation is to predict the cement durability. We investigated the impact of the boundary conditions and the modelling choices on the simulation results.
- The efficiency of ReactMiCP allowed us to test many conditions and set of parameters. We were able to reproduce experimental results and propose different mechanism as function of the boundary conditions. (see Fig. 1)

Coupled simulation : carbonation and drying

- An unsaturated system of equations was implemented into ReactMiCP
- The numerical features of ReactMiCP allows to implement a custom-made microstructure modelling
- We hope to use this feature to fully capture the feedbacks between carbonation and drying
- Preliminary results shows that we can solve the problem. The water transport properties are the limiting kinetics factors for the advancement of the reaction.



> Fig. 2: Coupled simulation of drying and carbonation of cement paste. Results after 30 days of simulation. Left: solid phase profiles. Right: influence of the boundary conditions. Experiments are reproduced only qualitatively.

CONCLUSION ET PERSPECTIVES

1. **A robust reactive transport solver was implemented and applied to the leaching of cement paste in brines**
2. **Our proof-of-concept simulations demonstrate our abilities to capture complex feedbacks due to the microstructure**
3. **Future works include the improvement of the coupled carbonation and drying simulation to include a more physical microstructure model**

[1] F. Georget, J. H. Prévost, and R. J. Vanderbei. A speciation solver for cement paste modeling and the semismooth Newton method . Cement and Concrete Research, 68(0):139--147, 2015.
[2] F. Georget, J. H. Prévost, and B. Huet. A reactive transport framework for variable porosity problems
[3] F. Georget, J. H. Prévost, and B. Huet. Reactive transport modelling of cement paste leaching in brines (in preparation)

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