Modelling chloride transport in cementitious materials at the nanoscale

PhD candidate

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Content

Chloride ingress: A durability issue for reinforced concrete

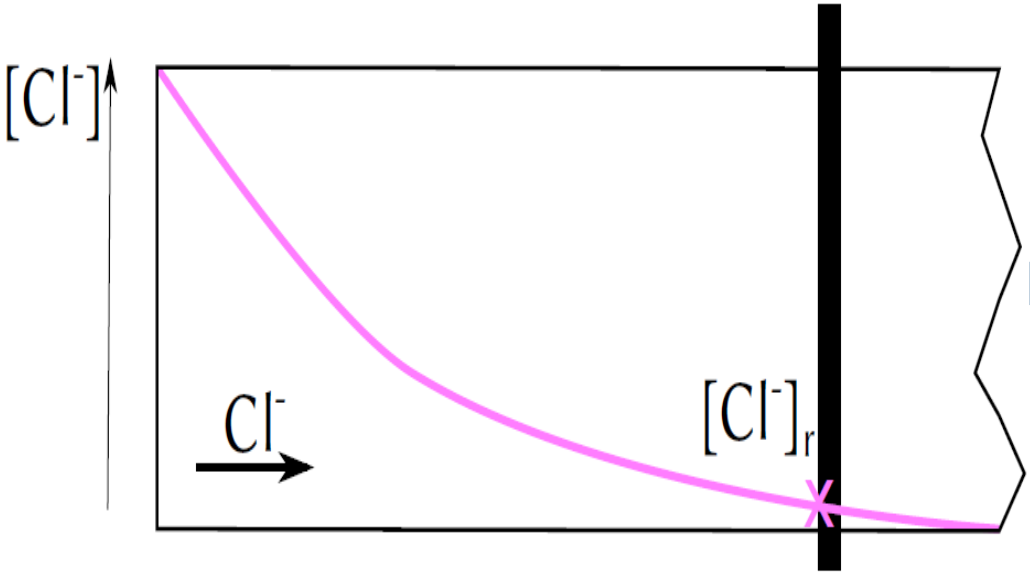

Fig.1. Chloride ingress (F. Georget)

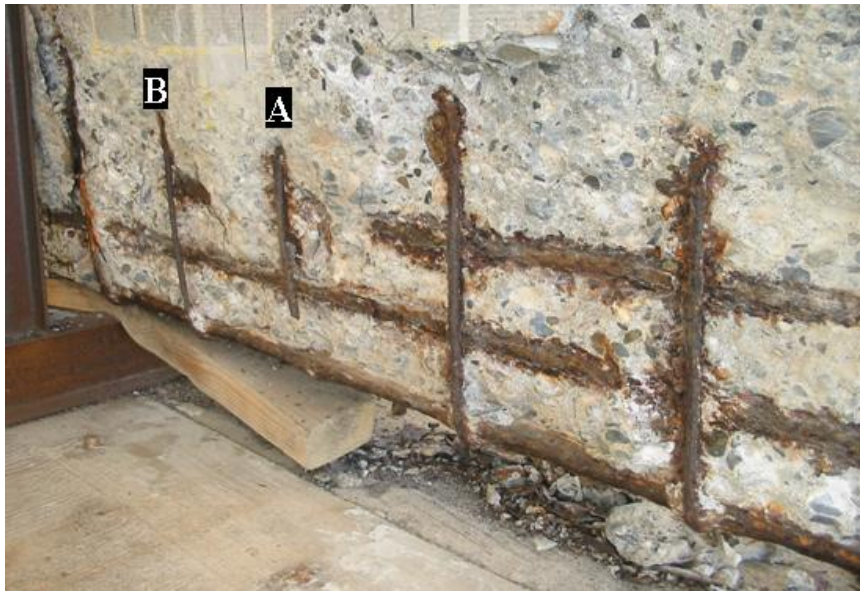

Fig.2. Corroded steel bars in reinforced concrete

Chloride ingress is the most common reason for steel to corrode especially when exposed to moisture atmosphere or exterior chlorides (seawater or deicer salts)

Content

Standardized characterization of the diffusion properties

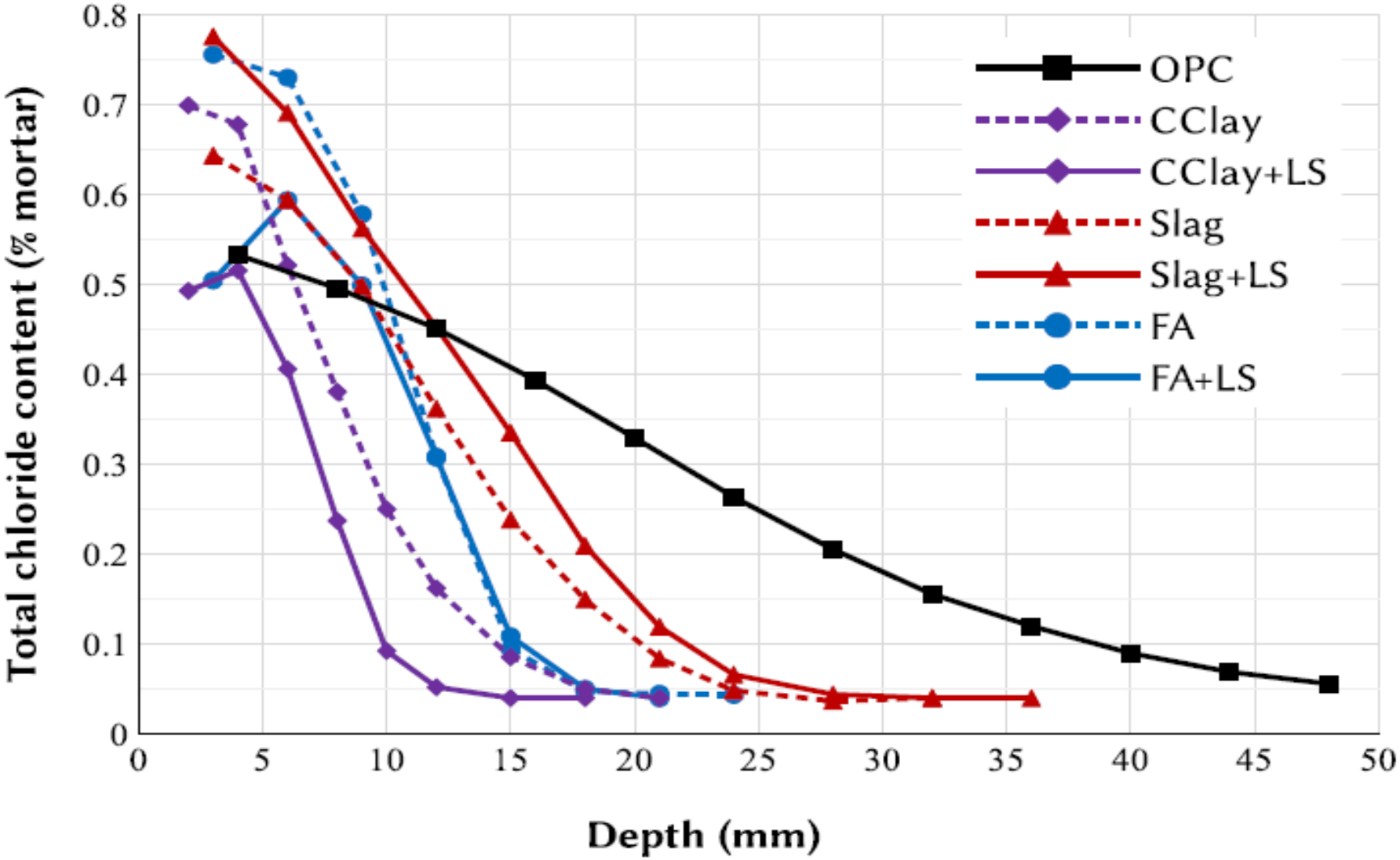

Fig.5. Total chloride content with respect to the depth for different blended systems (S. Sui et al. [CCR 2019])

Mathematical justification of the empirical model

Total chloride diffusion profile looks like a diffusion profile

➢ So why not fit a diffusion equation on it such as Fick's law:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

Assuming that

- ❖ D is homogeneous
- ❖ Boundary conditions are fixed for e.g. Semi-infinite domain

Analytical solution:

$$C(x,t) = C_s \,\mathrm{erfc}\left(\frac{x}{2\sqrt{D_a t}}\right)$$

No clear correlation between D_{app} and porosity

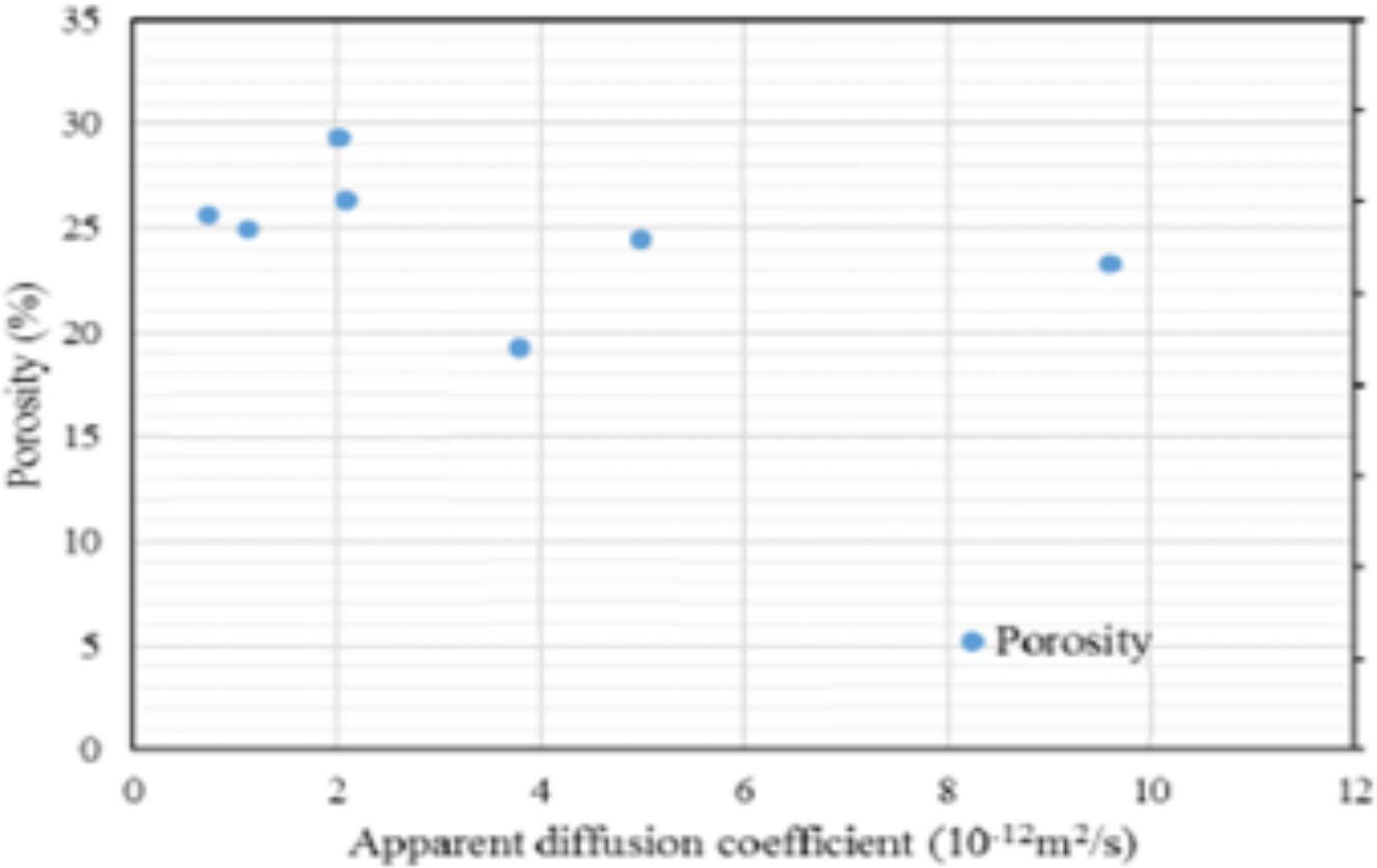

Fig.6. Relationship between apparent diffusion coefficient and porosity (S. Sui et al. [CCR 2019])

Binding Mechanisms in chloride transport

Chloride ions can be trapped within the cement pore network through **two mechanisms**

Chemical binding:

Formation of **Friedl's salt**

$$X-Afm + zCl^- \rightleftharpoons Cl_z-AFm + X^{z-}$$

Physical binding

Adsorption of Cl^- on C-S-H surface

?

$$-SiO-Ca^+ + Cl^- \rightleftharpoons -SiO-Ca(-)Cl$$

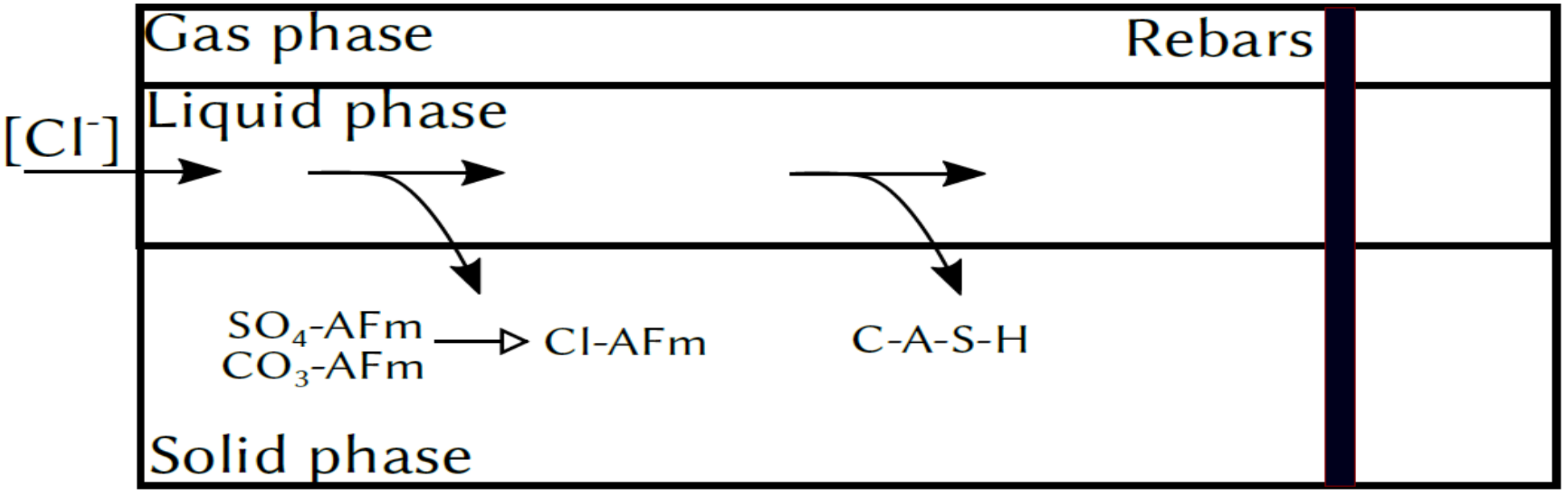

Fig.3. Binding mechanisms of chloride in a cementitious material (F. Georget)

Physical binding VS Chemical binding

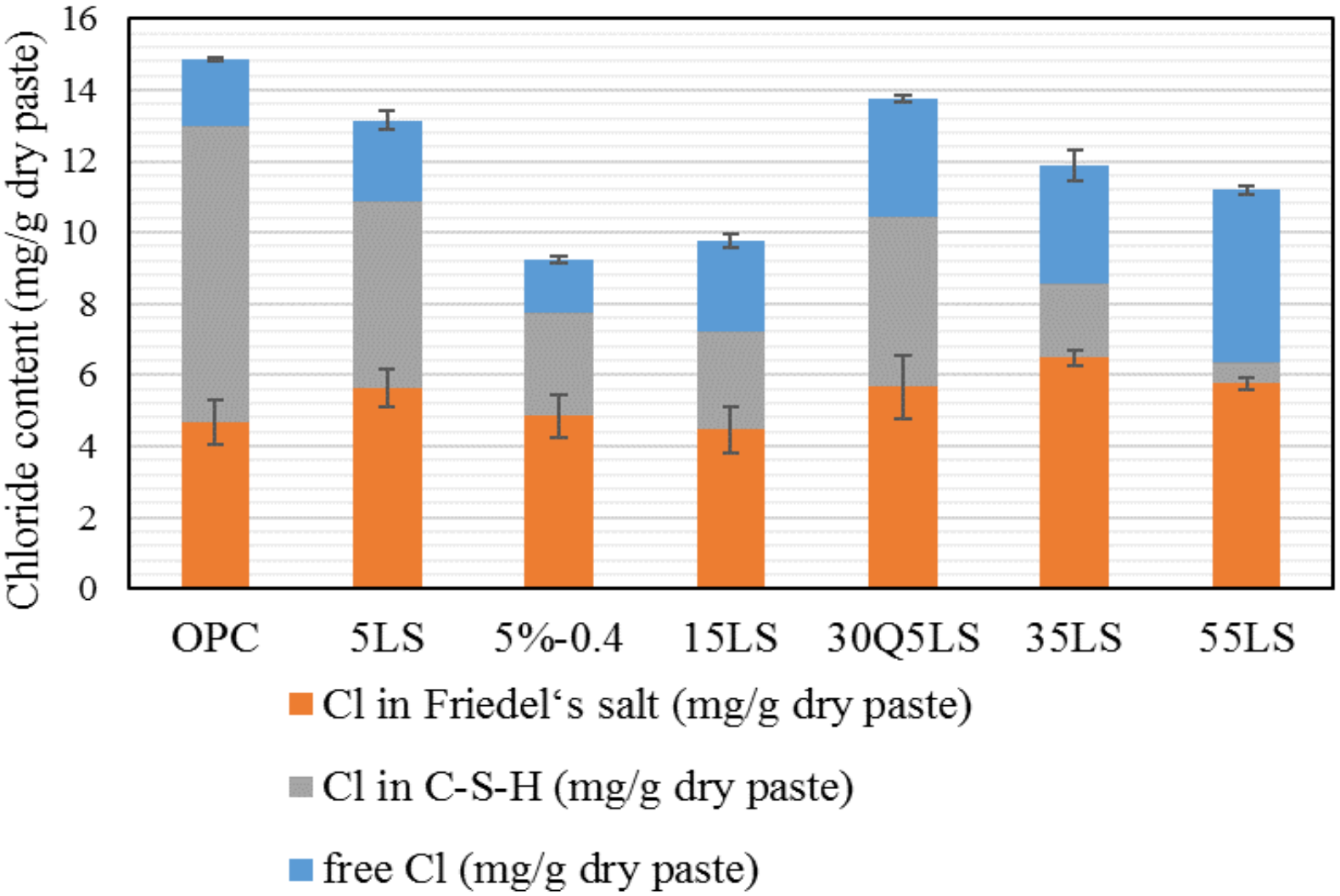

Fig.4. Total chloride proportions in various systems (S. Sui et al. [CCR 2019])

Alkalinity: A misunderstood pore solution effect on diffusion

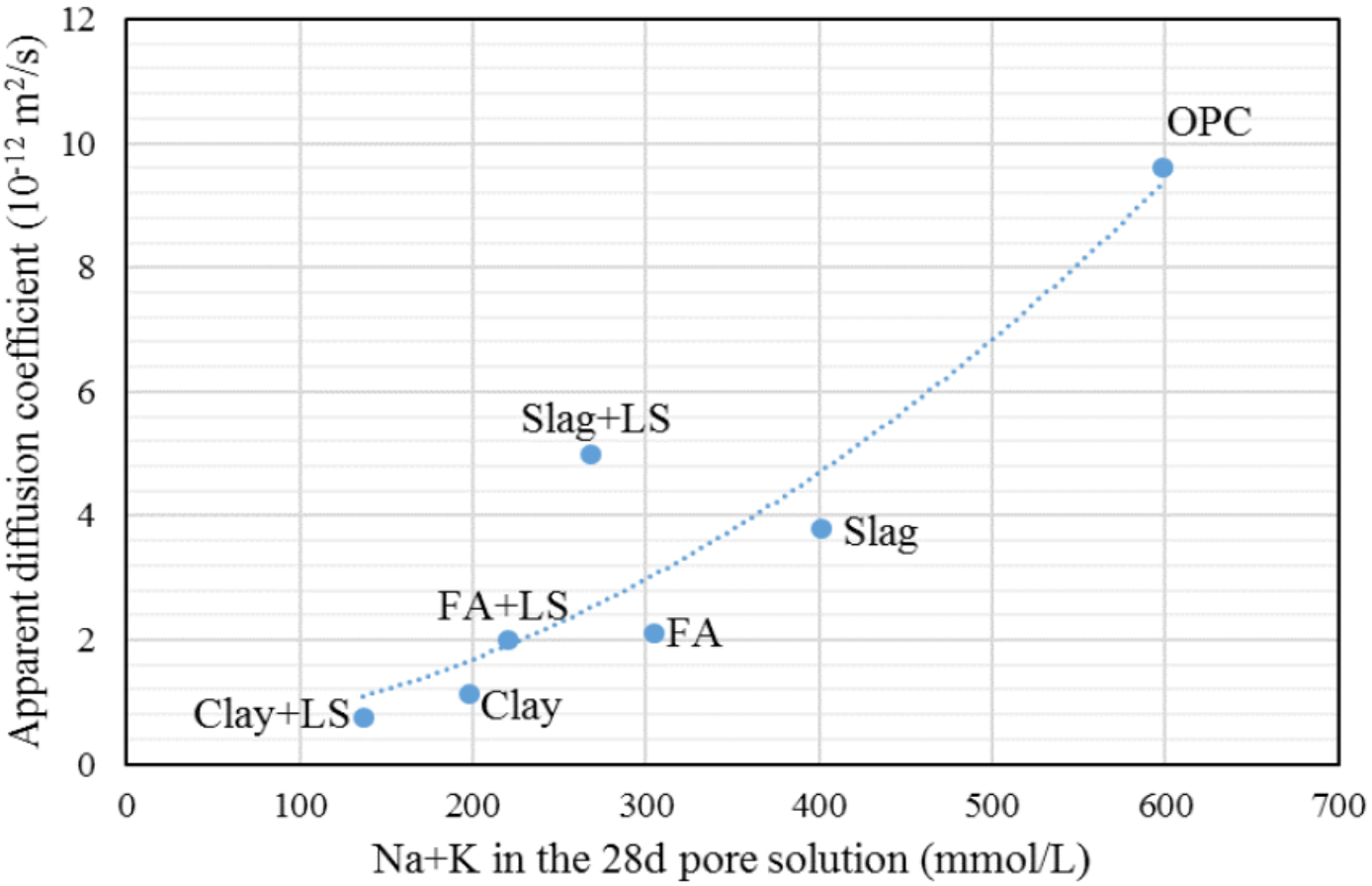

Fig.7. Relationship between apparent diffusion coefficient and alkali ions content in pore solution (S. Sui et al. [CCR 2019])

- **This correlation is neither obvious nor systematic.**
- **Need for a better understanding of microstructure's parameters such as pore solution or porosity on diffusion processes.**

Deconvoluting transport and chemistry

Reactive transport governing equations

Change in concentration = transport + chemistry

Separation between matter transport and chemical processes

Simple reactive transport:

$$\frac{\partial [Cl^-]}{\partial t} = -\frac{\partial}{\partial x}\left(D_{e,0} \frac{\partial [Cl^-]}{\partial x} \right) - \frac{\partial s_{Cl^-}([Cl^-])}{\partial t}$$

Effective Diffusion coefficient D_e

! USUALLY FITTED

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I. Introduction and context

II. Modelling of chloride ingress mechanisms

III. My project

IV. Preliminary results and future work

Bottom-Up approach

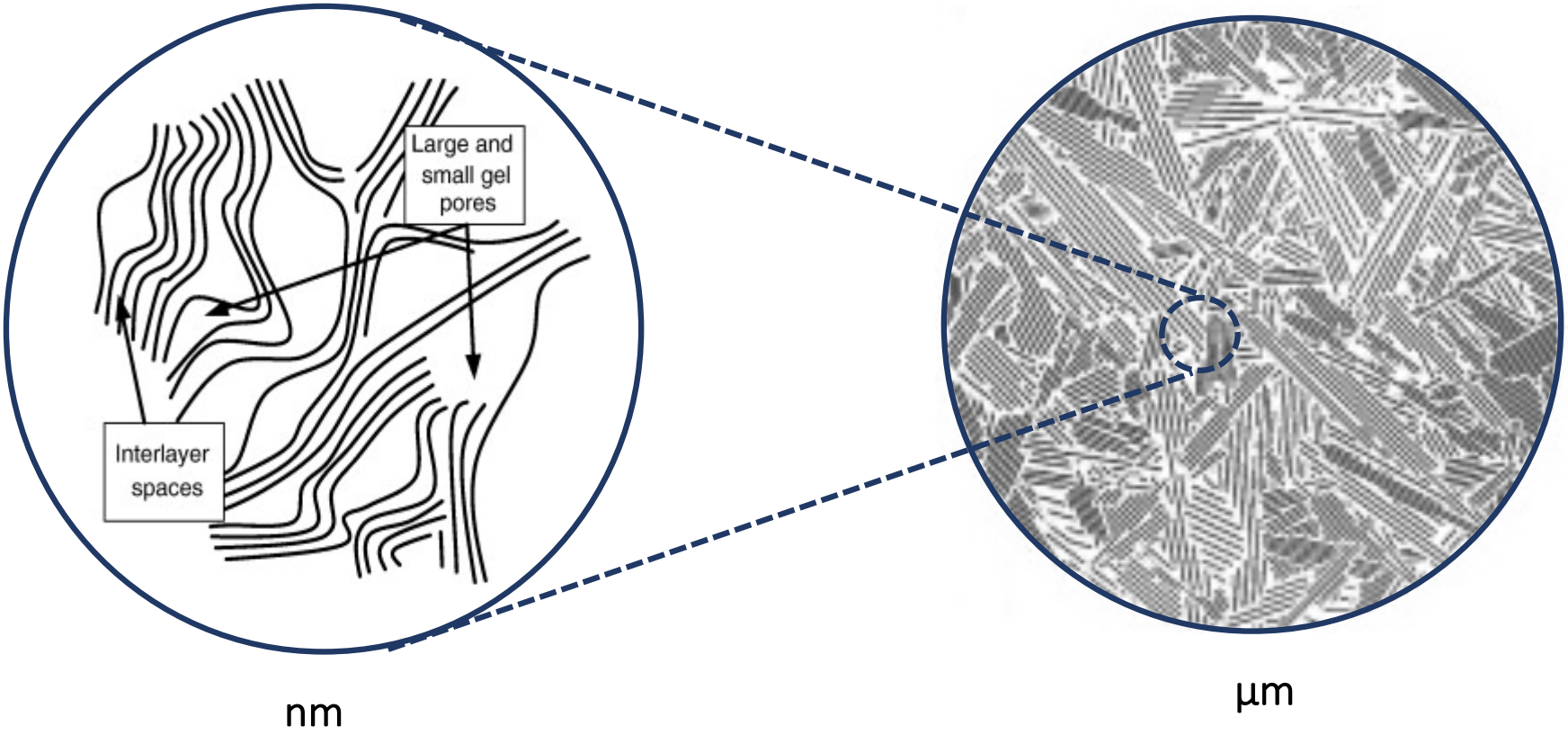

Fig.8. Chloride transport through different scales (inspired from Etzold [CCR 2014] et al. and Y. Yang et al. [CCR 2019]

The Electrical Double Layer

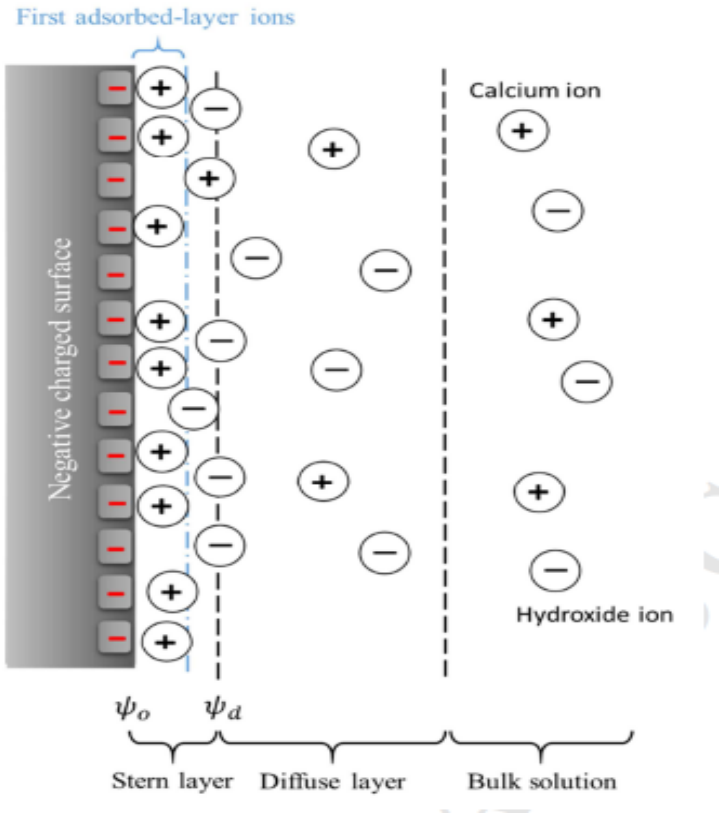

Fig.9. Schematic of the Stern EDL model (Y. Yang et al. 2018)

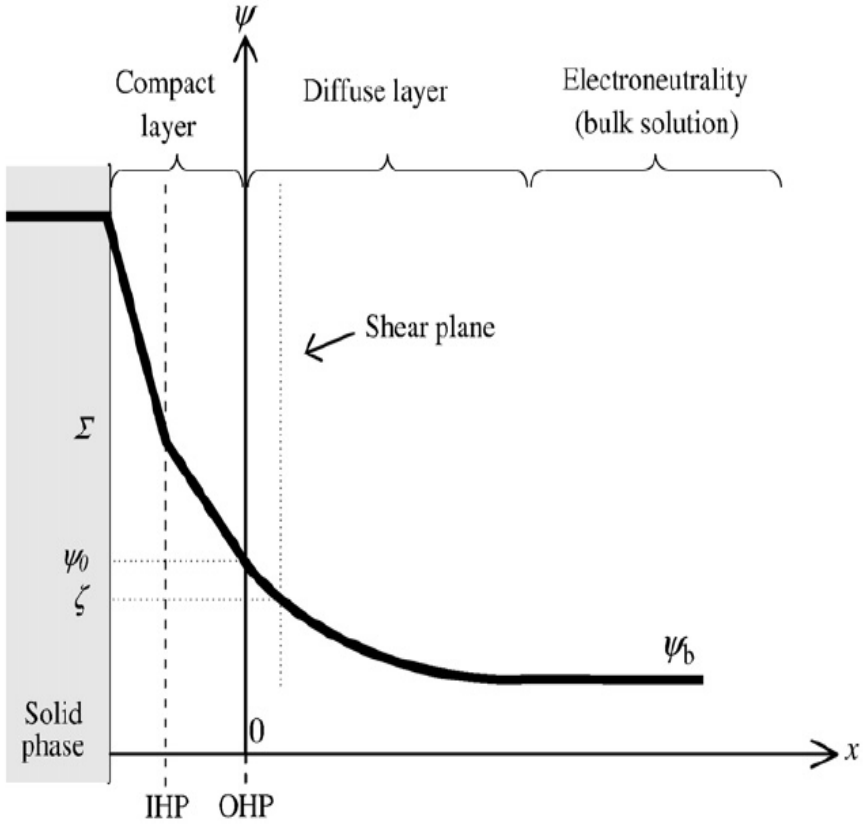

Fig.10. Schematic of the solid phase electrostatic potential (H. Friedmann et al. 2008)

The Classical Theory: Poisson-Boltzmann equation

- **Gauss' law (Poisson equation):**

$$\Delta\Psi = -\frac{\rho}{\epsilon_0\epsilon}$$

- **The Boltzmann distribution**

$$\rho = eN_A \sum_i z_i C_{b,i} \exp\left(\frac{-z_i e\Psi}{k_B T}\right)$$

- **The Debye length L_D=1/K** (for low $C_{b,i}$ values)

$$\kappa^2 = \frac{e^2 N_A}{\epsilon_0 \epsilon k_B T} \sum_i C_{b,i} z_i^2$$

- **Order of magnitude:**

L_D = 0,96 nm for C_b = 0.1 M

Classical Theory VS Molecular Modelling

	Gouy-Chapman Theory (Poisson-Boltzmann)	Molecular Modelling	
		Monte Carlo	Molecular Dynamics
Complexity / Validity	**Limited** • Low concentration electrolytes (up to 0.1 M for 1:1 electrolytes)** • Symmetric (1:1) electrolytes • Low surface charge (< 30 µC cm^{-2}) **	**More detailed** • A better depiction of the solvent (water) molecules • Accounts for steric forces • Valid for highly concentrated asymmetric electrolytes	
Extensibility	**Modified PB** • Better fitting with the molecular modelling * • Fails to depict 2:1 electrolytes**	• Gets better with more accurate input data.	

*Y. Yuankai, et al., 2019, "Multiscale modeling of ion diffusion in cement paste: electrical double layer effects." Cement and Concrete Composites

** Torrie, G. M., and Valleau, J. P., 1982, "Electrical Double-Layers .4. Limitations of the Gouy-Chapman Theory,"

Characterizing the Stern layer: A Monte Carlo algorithm

Grand Canonical Monte Carlo

$$C_i^{GCMC}$$

$$\rho = \sum_i z_i C_i^{GCMC}$$

$$\psi^{GCMC}(x) = -\frac{1}{\epsilon_0 \epsilon} \int_x^{\infty} \rho(t) dt$$

The actual physical binding

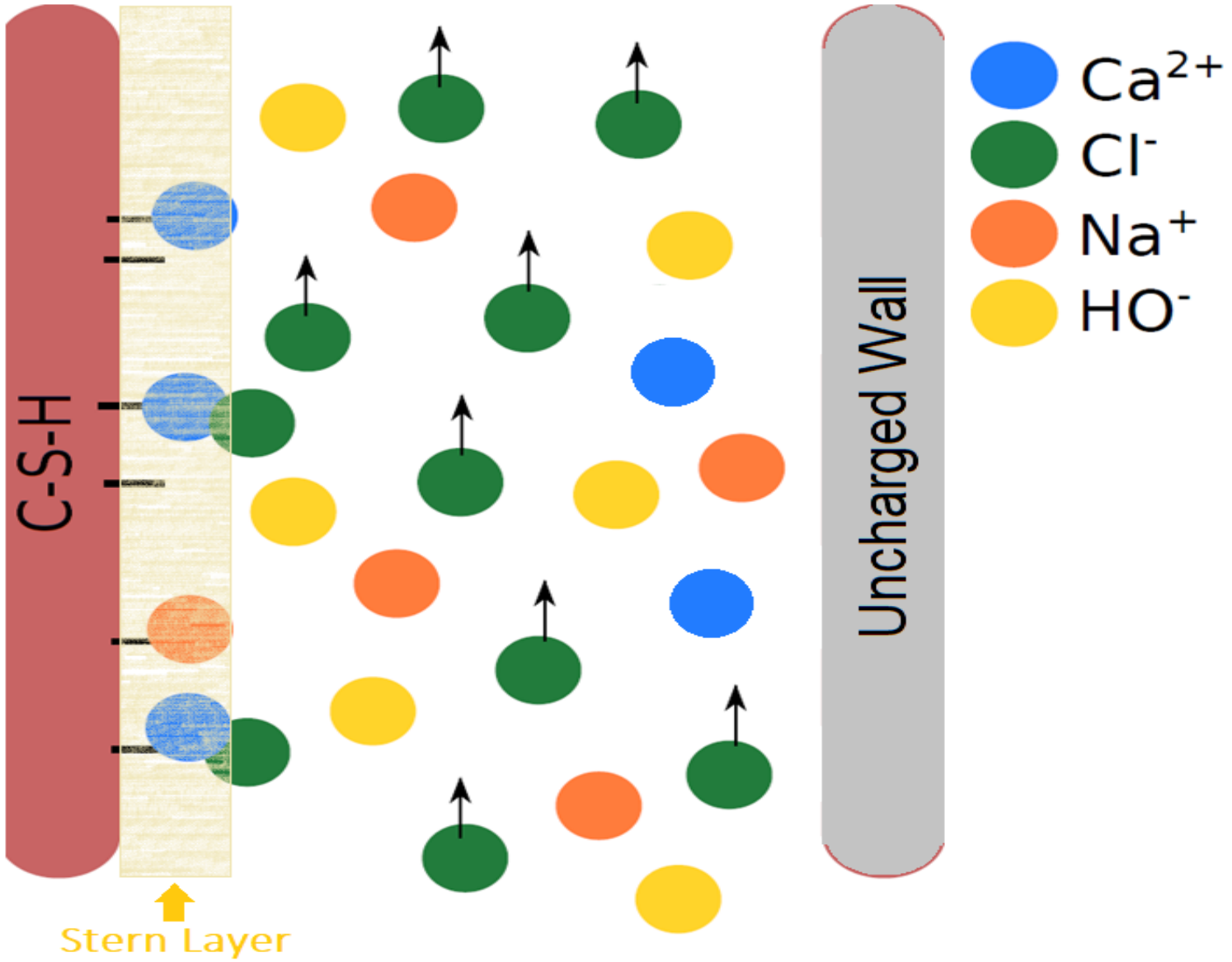

Fig.11. Chloride ions transporting in a pore (F. Georget)

Expected results

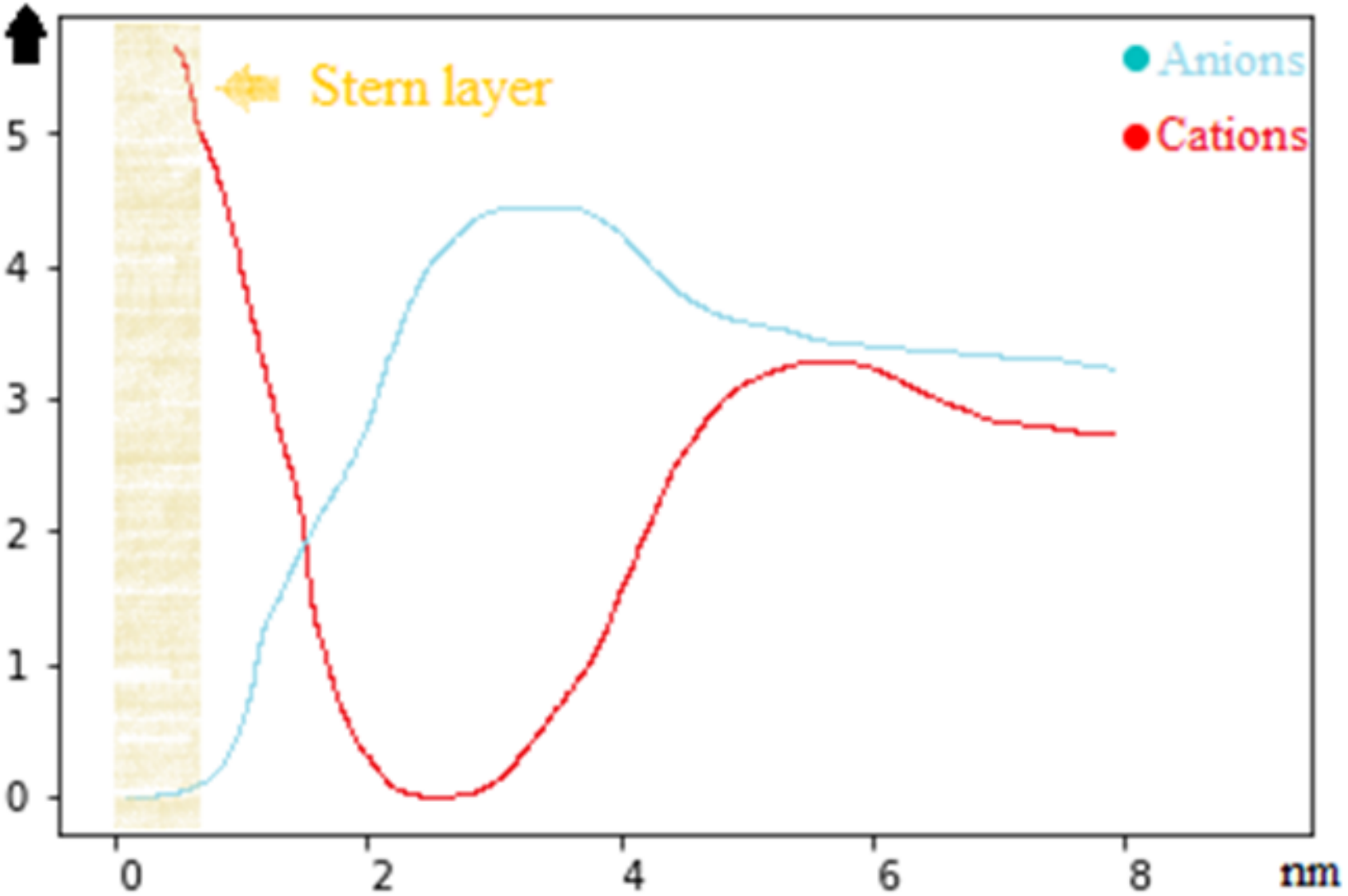

Fig.13. Expected ionic distribution of species in a solution in contact with a negatively charged surface of C-S-H.

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Preliminary results

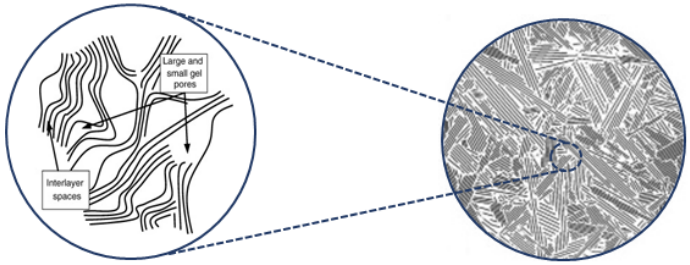
- An implemented GCMC code in Python for the better understanding of Monte Carlo modelling techniques accounting for:

  ✓ Simplified geometry and morphology of the pores.

  ✓ Thermodynamic equilibrium of pore solution

  ✓ Monte Carlo moves for convergence toward equilibrium.

Future work



- Resolve transport equation at the nanoscale and compute Chloride nanoscopic diffusion coefficient.
- Validate model with more robust simulation tool.
- Investigating a consistent C-S-H microstructure which account for porosity at both nanoscopic (nm) and microscopic (µm) scales.

Secondments

- **April 2020:** Design of a validation experiment for the nanoscale model ⟹ **NTNU**

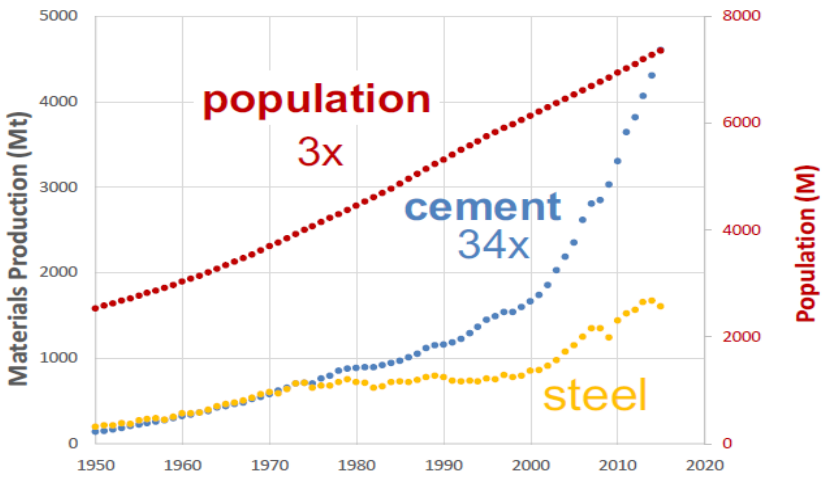
- **April 2021:** Investigation of the thermodynamic background for the proper averaging of nanoscale transport information up to the microstructure scale ⟹ **NTNU**

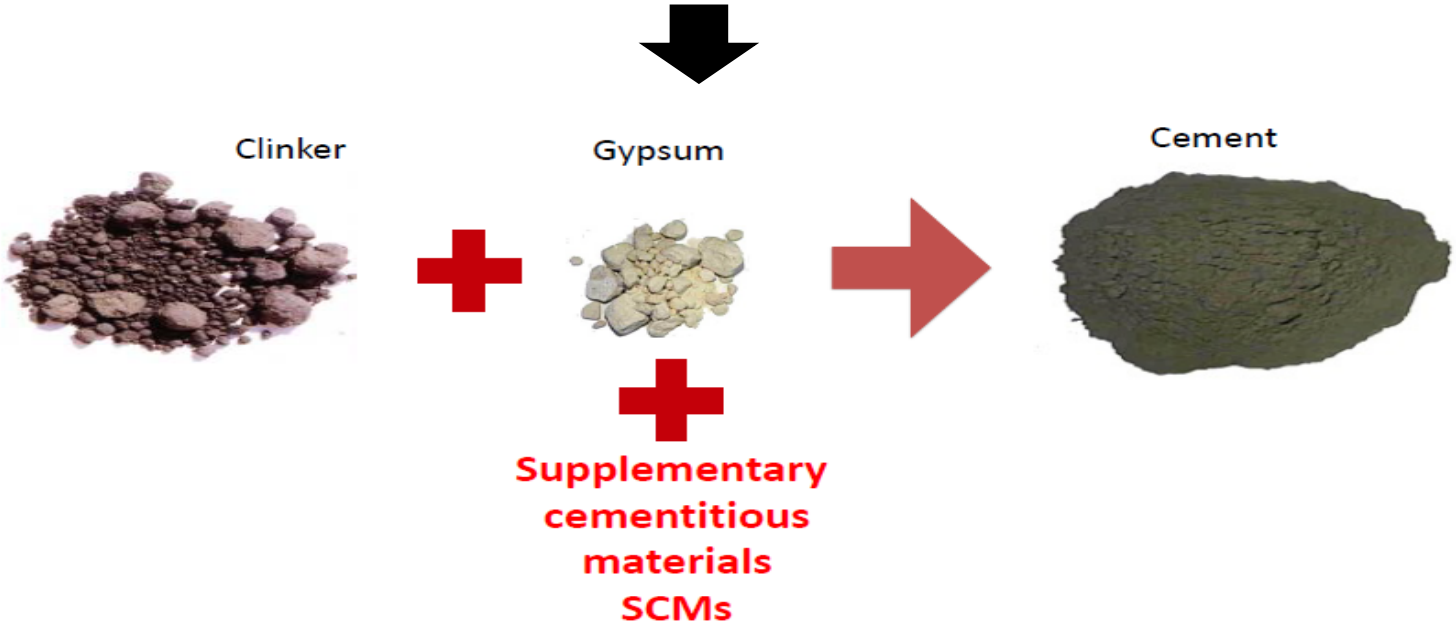
- **June to August 2021:** Validation of the multiscale model ⟹ **Heidelberg Cement**

Outreach: Kids class day at EPFL

Appendix

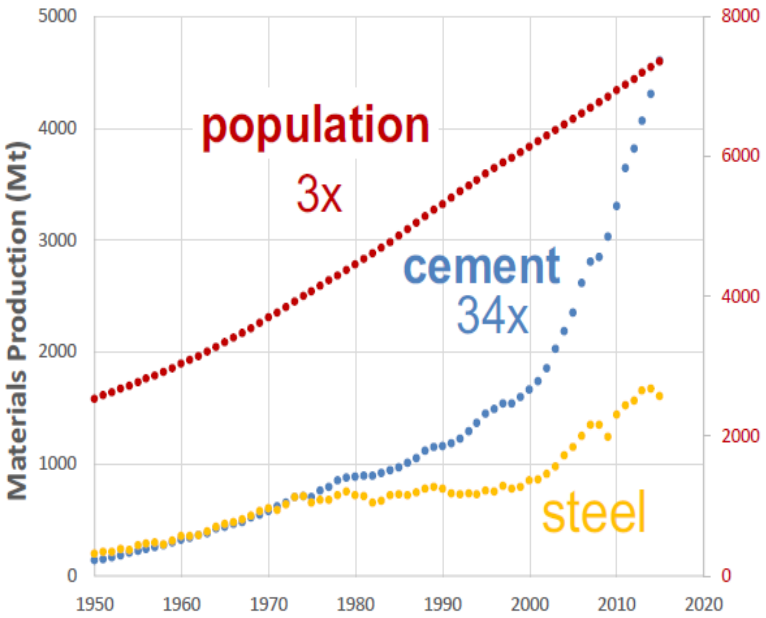
Sustainable and durable cement is an urgent need

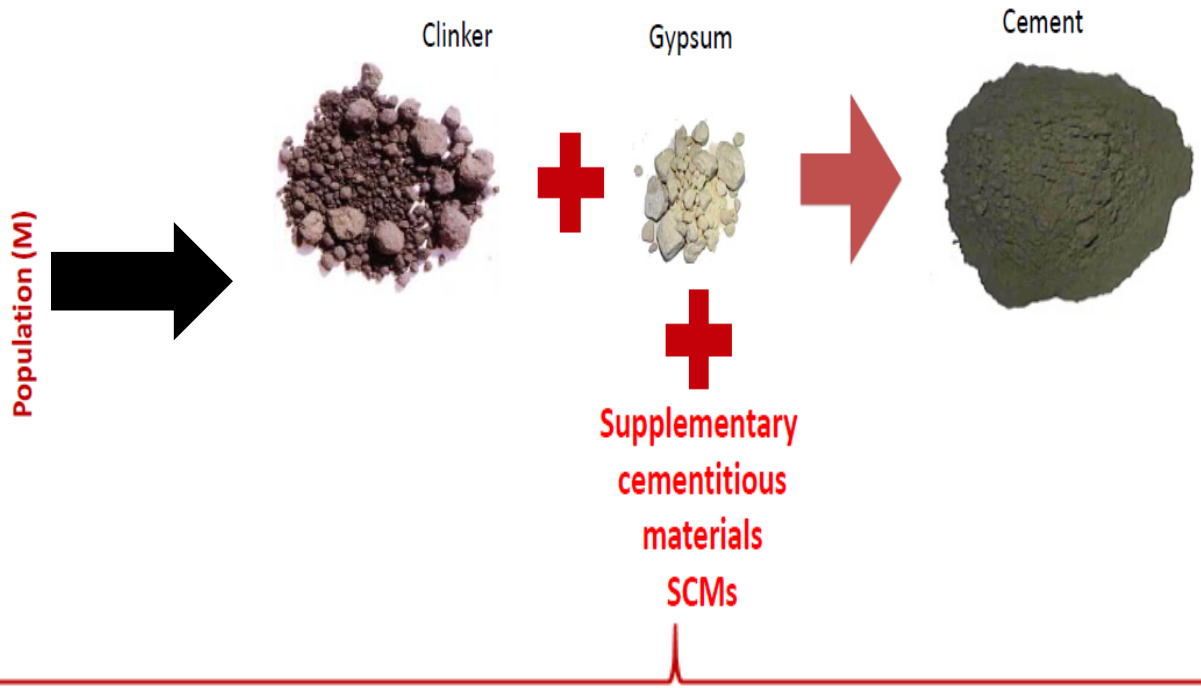




Although eco-friendlier, sustainable cement has to fulfil strength and durability

Sustainable and durable cement is an urgent need





Limestone

Fly ash

Slag

Natural pozzolan

Calcined clay

Although eco-friendlier, sustainable cement has to fulfil strength and durability

Preliminary results

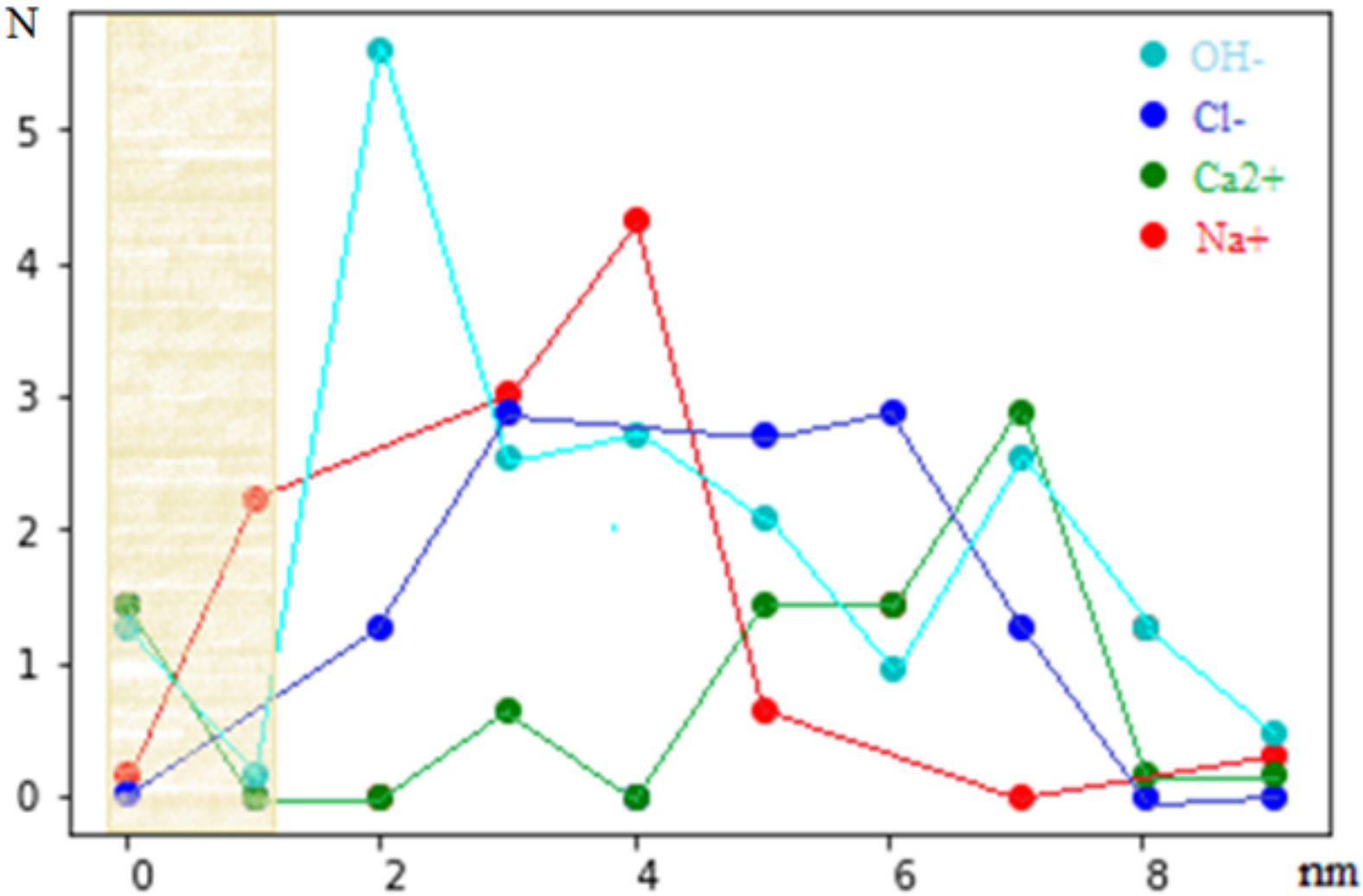


Fig.12. Distribution of ionic species in a 10nm size pore for a 2:1 electrolyte. NaCl concentration is 10 mM and $Ca(OH)_2$ 10 mM. Figures are the average of 10 GCMC simulations with 200 Monte Carlo steps each.

From transport to ionic effective diffusivity

$$\frac{\partial C_i}{\partial t} + \nabla \cdot \boldsymbol{J}_i = 0$$

$$\boldsymbol{J}_i = -D_{i,0}\nabla C_i - D_{i,0}\frac{z_i e C_i}{kT}\nabla\psi - D_{i,0}\frac{C_i}{kT}\nabla\mu_i^{ex}$$

$$\frac{1}{kT}\mu_i^{ex}(x) = -\frac{ez_i}{kT}\psi^{GCMC}(x) - \ln\left(\frac{C_i^{GCMC}(x)}{C_{i,\infty}}\right)$$

$$D_{i,e}^{\text{Micro}} = \frac{\int J_i \, dS}{S} \cdot \frac{L}{\Delta C_i}$$

Effective diffusivity at the nanoscale C-S-H

Species flux per unit cross-section in steady state

Medium length / Mean concentration difference