Adsorption of multivalent ions in cementitious materials: importance of electrostatics

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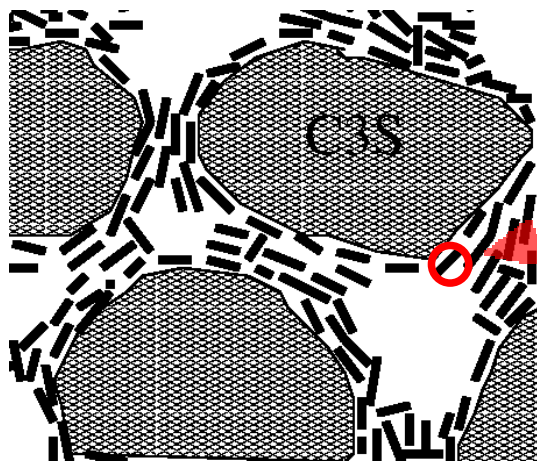
Mechanisms and modelling of waste/cement interactions- Le Croisic 2008

Generalities on ion adsorption

- Ion adsorption is important in many context:
  - water treatment
  - electrolyte transport
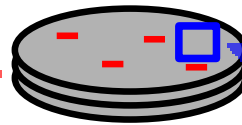 - protein association
  - colloidal stability...

- The driving forces of ion adsorption may be:
  - Coulomb interactions
  - Dispersion interactions
  - Hydrophobic interactions
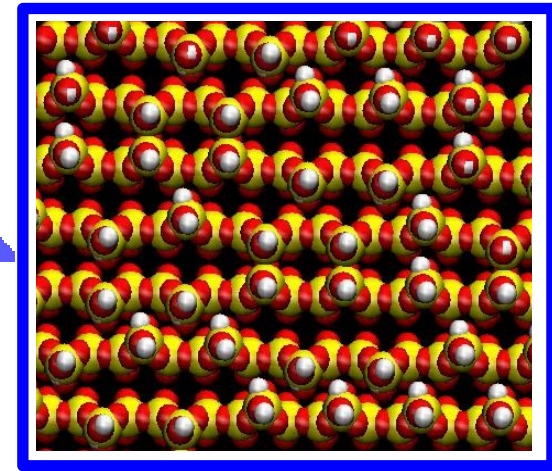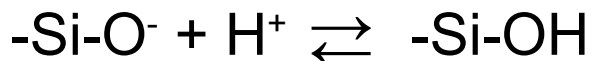 - Ion pairing

Calcium silicate hydrate (C–S–H)

— **C-S-H**

C-S-H Crystallite
60x40x5 nm

hydrated cement paste cartoon

○ Si
● O
○ H

Surface detail of **C-S-H**

• C–S–H : nanoparticles, lamellar structure;

• Negative surface charge due to the titration of silanol groups:

$-Si-O^- + H^+ \rightleftarrows -Si-OH$

Questions

• What role is played by electrostatic in the retention of ions in cement systems?

• Can electrostatic explain the adsorption of anions on the negatively charged C-S-H particles?

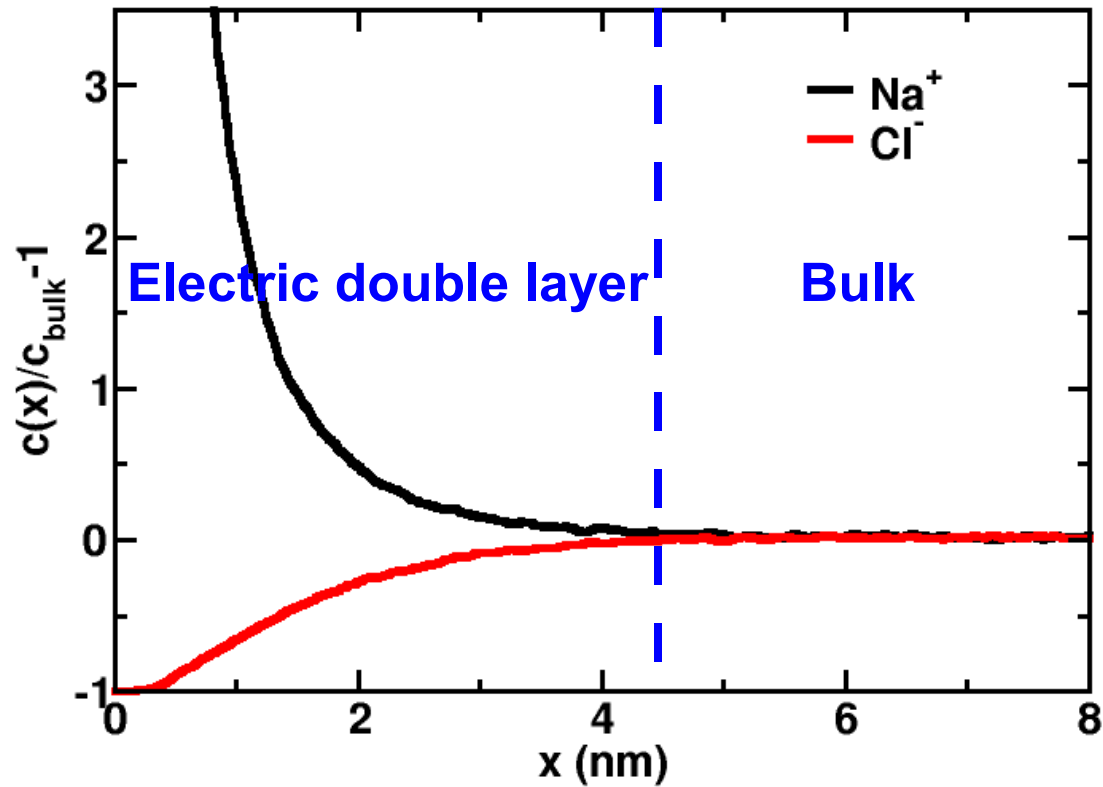• How strong is the adsorption of traces of multivalent cations on the C-S-H particles?

Solid/solution Interface

Contact of a charged solid to a solution:
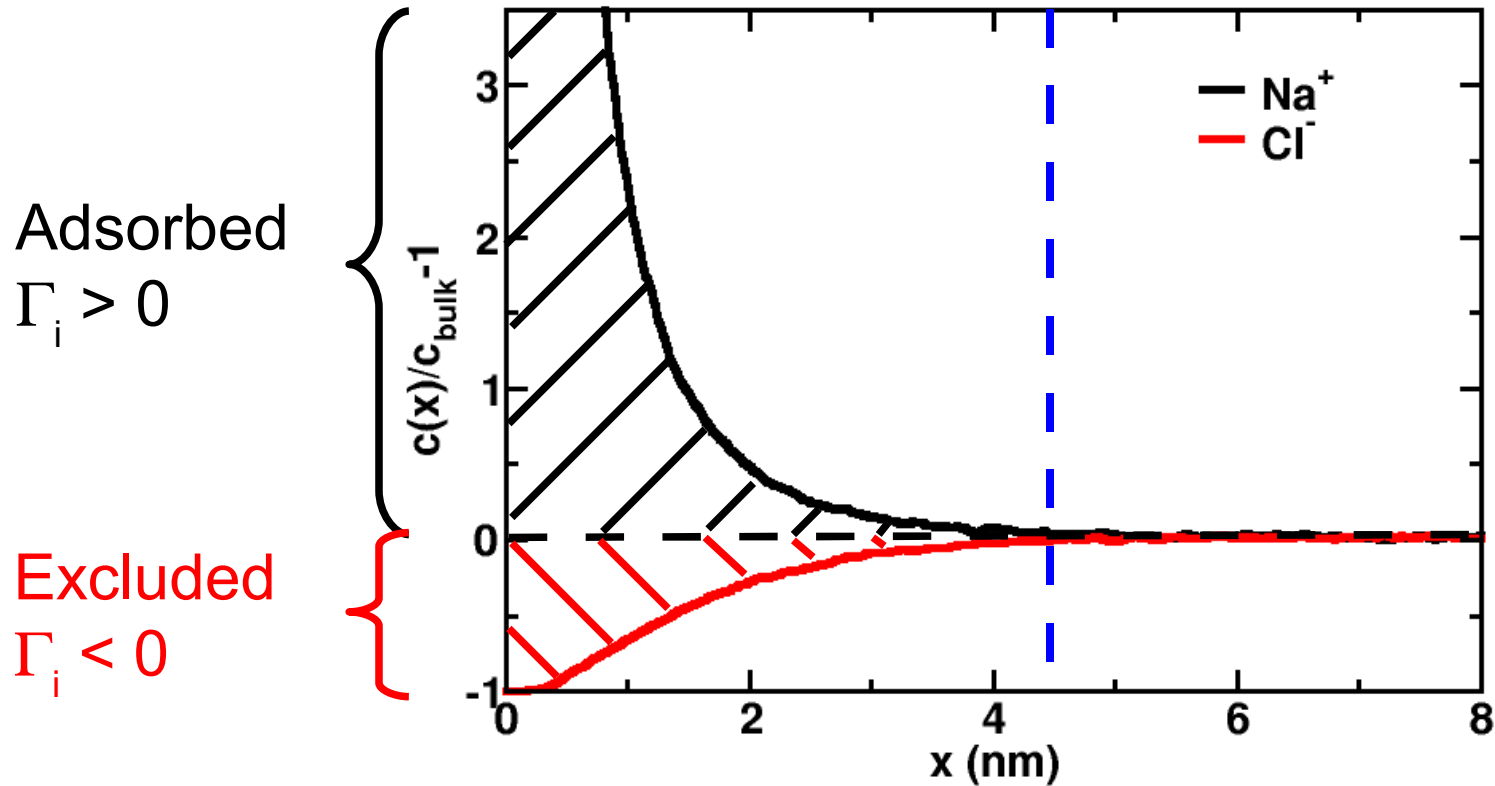=> formation of the electric double layer (DL).
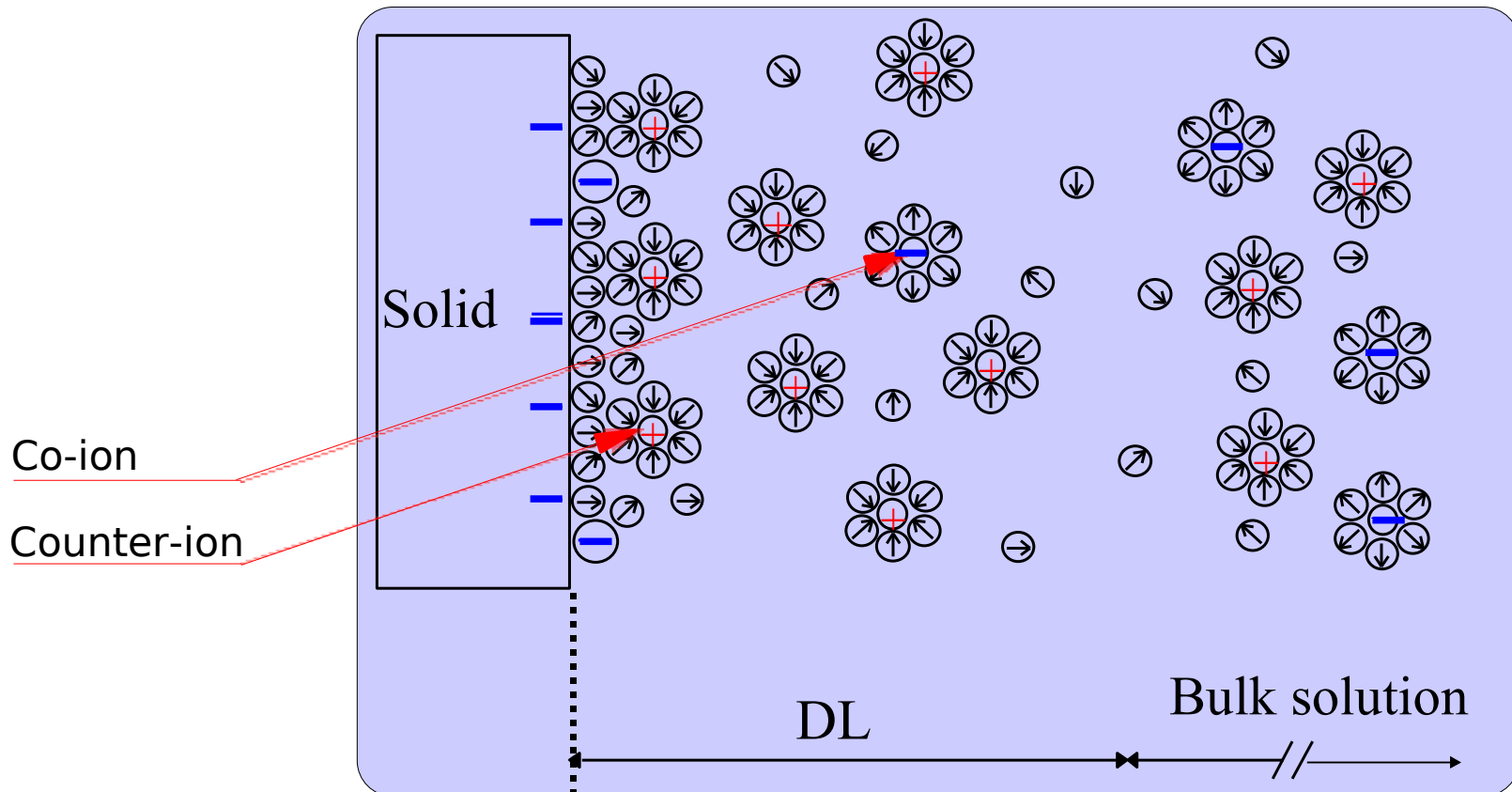
Solid/solution Interface
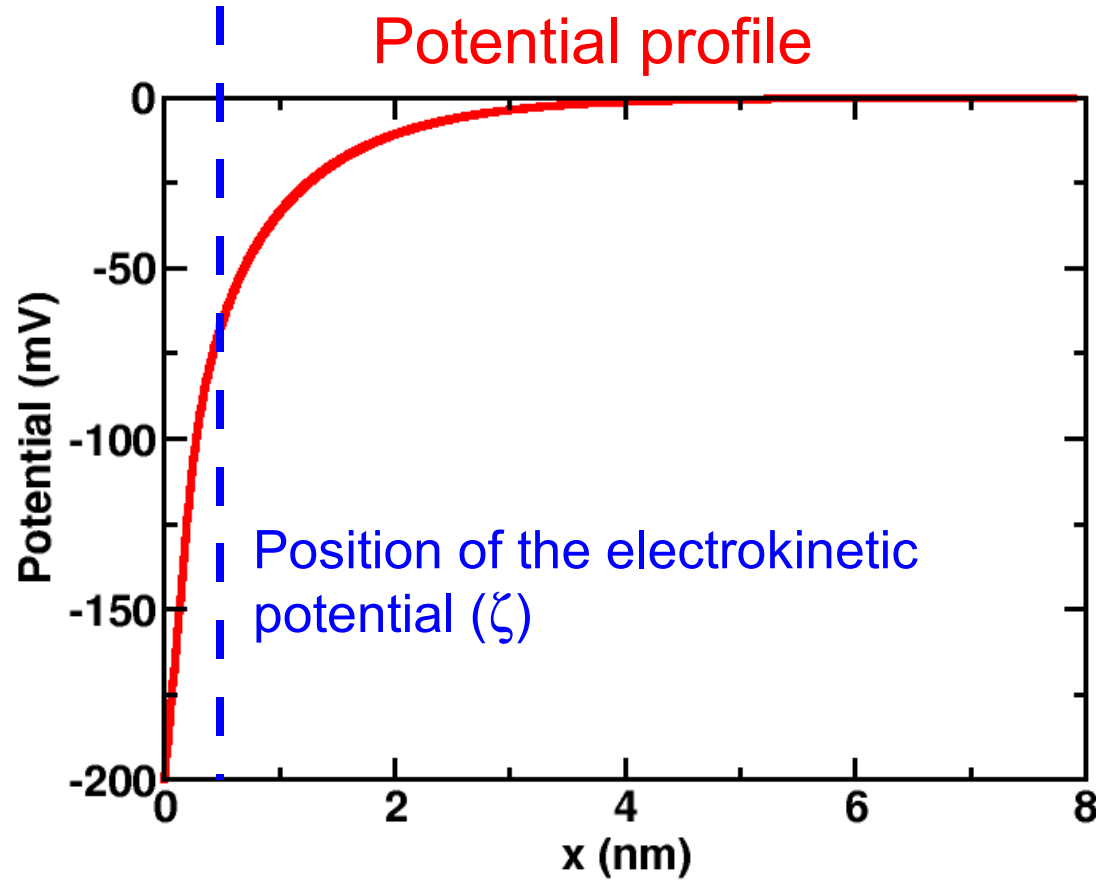
Concentration profiles

Ion adsorption at the solid/solution interface

Adsorbed
$\Gamma_i > 0$

Excluded
$\Gamma_i < 0$

$$\Gamma_i^{ads} = \int\limits_{x=0}^{x=\infty} \rho_i(x) - \rho_i(bulk)\,dx$$

with ρ: ion density at the position x

Solid/solution Interface

Potential profile

Position of the electrokinetic potential (ζ)

Model and simulation

- ## Model:

- Surface:
  discrete titratable sites
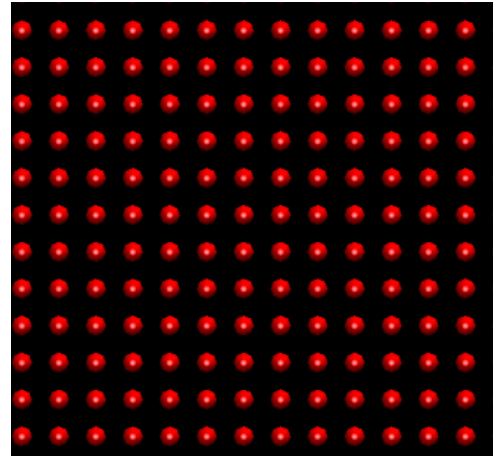
  $-Si-O^- + H^+ \rightleftharpoons -Si-OH$
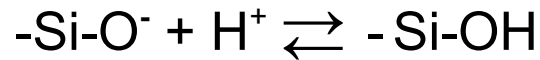
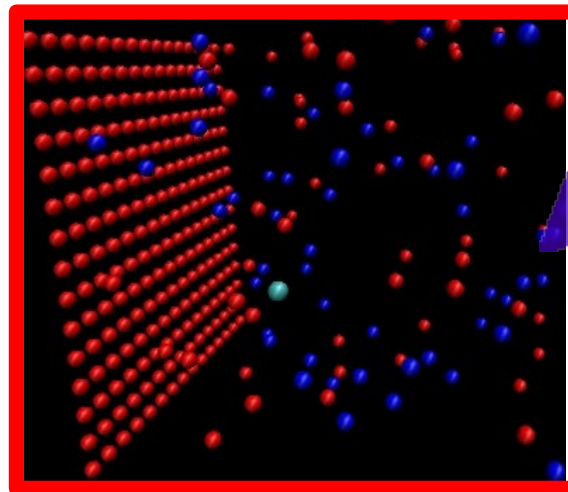 $pK_a = 9.8$

- Electrolyte solution:
  primitive model

- ## Simulation:

- Grand Canonical
  Monte Carlo
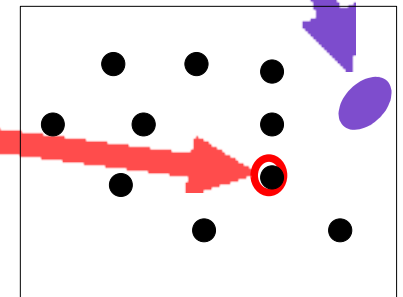

model surface details;
Site density (Si-OH) 4.8 / nm^2

Simulation box detail

Bulk solution
$\mu_i, ..., \mu_N$

Equilibrium

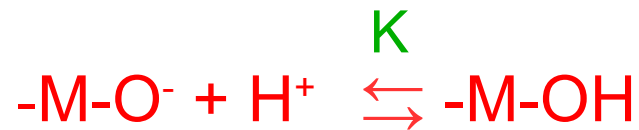Particle dispersion

Primitive model

➢ Coulomb interaction :

$$u(r_i, r_j) = \frac{z_i z_j e^2}{4\Pi \epsilon_0 \epsilon_r (r_i - r_j)} \quad \text{when } (r_i - r_j) > (\sigma_i + \sigma_j)/2$$

➢ Hard sphere interaction :

$$u(r_i, r_j) = \infty \quad \text{when } (r_i - r_j) < (\sigma_i + \sigma_j)/2$$

Model for surface ionisation

- Protonation and deprotonation of metal oxide (M-O):

$$-M\text{-}O^- + H^+ \underset{\longrightarrow}{\overset{K}{\longleftarrow}} -M\text{-}OH$$

- Equilibrium constant is the activity product of the chemical species:

$$K = \frac{a_{MOH}}{a_H\, a_{MO}} = \frac{c_{MOH}}{a_H\, c_{MO}} \cdot \underbrace{\frac{\gamma_{MOH}}{\gamma_{MO}}}_{}$$

Non ideal term
\# site-site interactions
site-ion interactions

Grand Canonical Titration

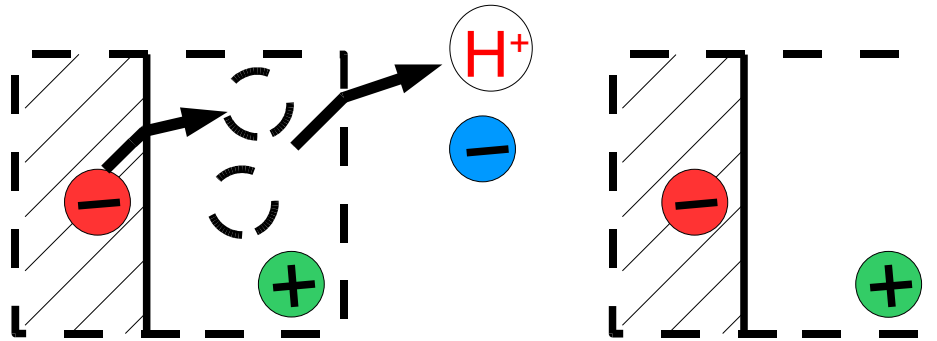

Illustration of the 2 step process for the deprotonation:
release of a proton and removal of an ion pair

One can show that the Boltzmann factor of the trial energy can be expressed as

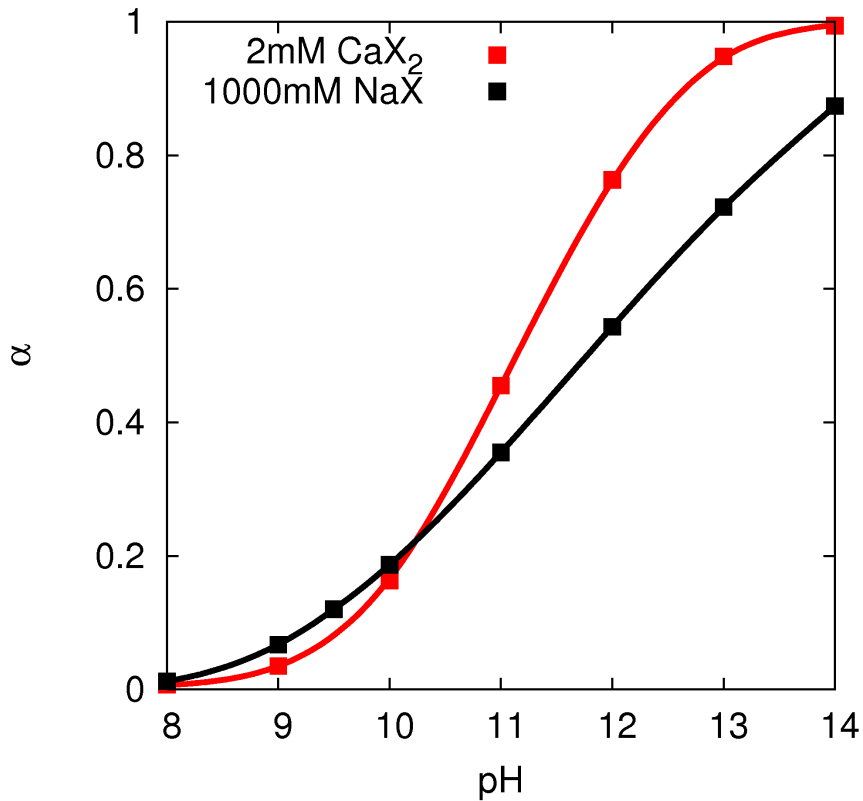$$\exp(-\beta\Delta U)=\frac{V}{N_{an}+1}\exp(+\beta\mu_{an})\exp(-\beta\Delta U^{el})\exp(-\ln 10.(pH-pK_a)) \text{ for protonation}$$

$$\exp(-\beta\Delta U)=\frac{N_{an}}{V}\exp(-\beta\mu_{an})\exp(-\beta\Delta U^{el})\exp(+\ln 10.(pH-pK_a)) \text{ for deprotonation}$$

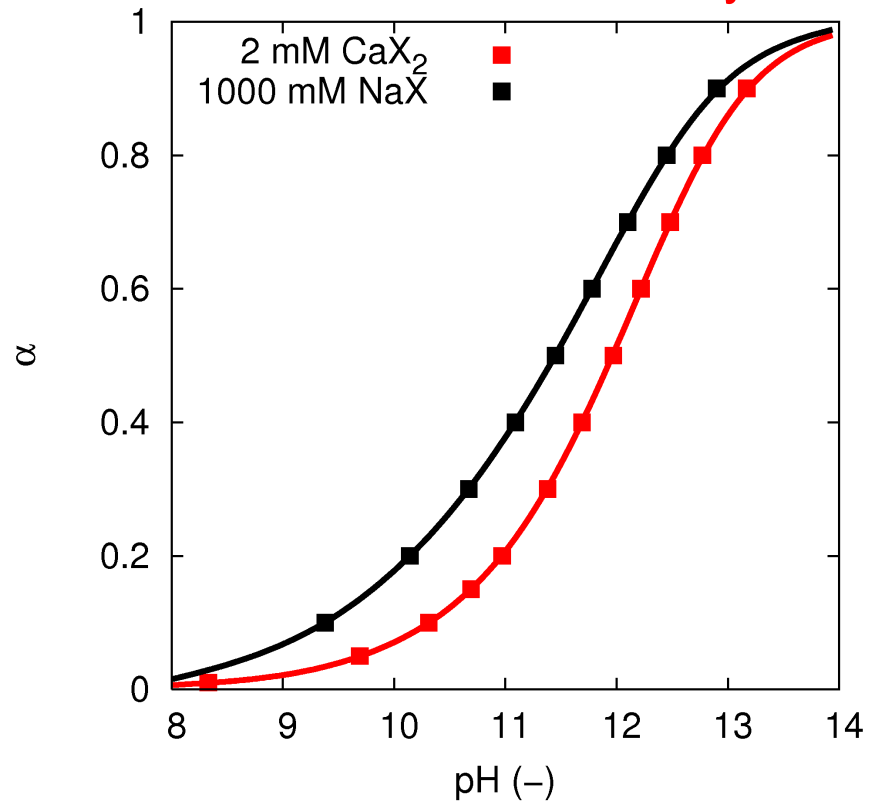where V is the volume of the box, N_{an} and μ_{an} the number and the chemical potential of the anion.

Labbez, C., Jönsson, B. Lect. Note in Comp. Sci. (2007)

Surface charge density
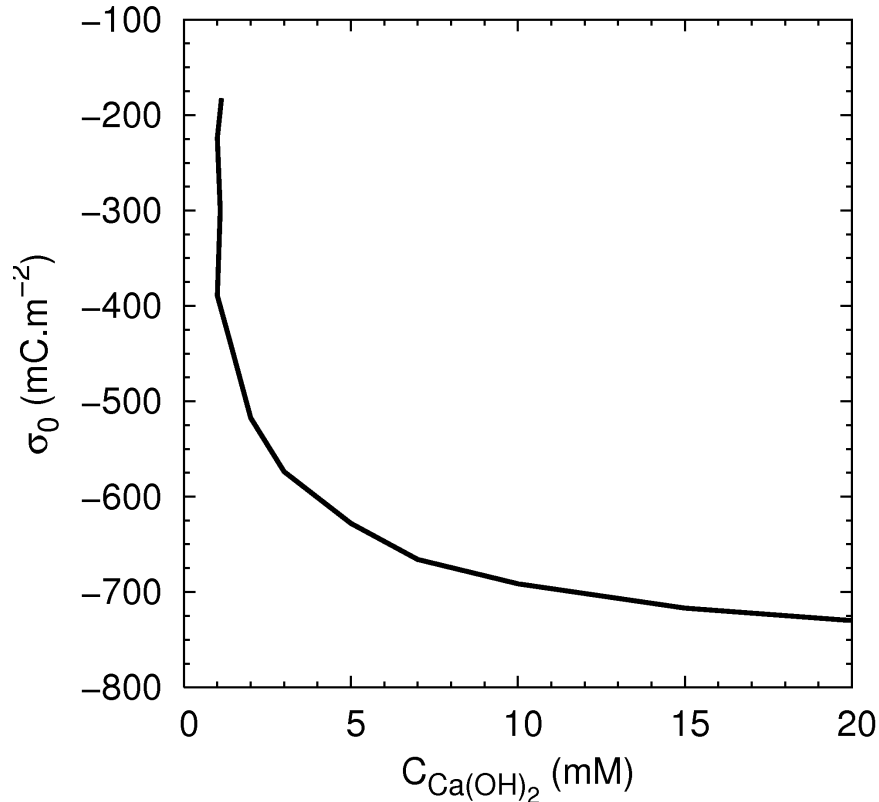
Grand Canonical Titration

Mean Field Theory

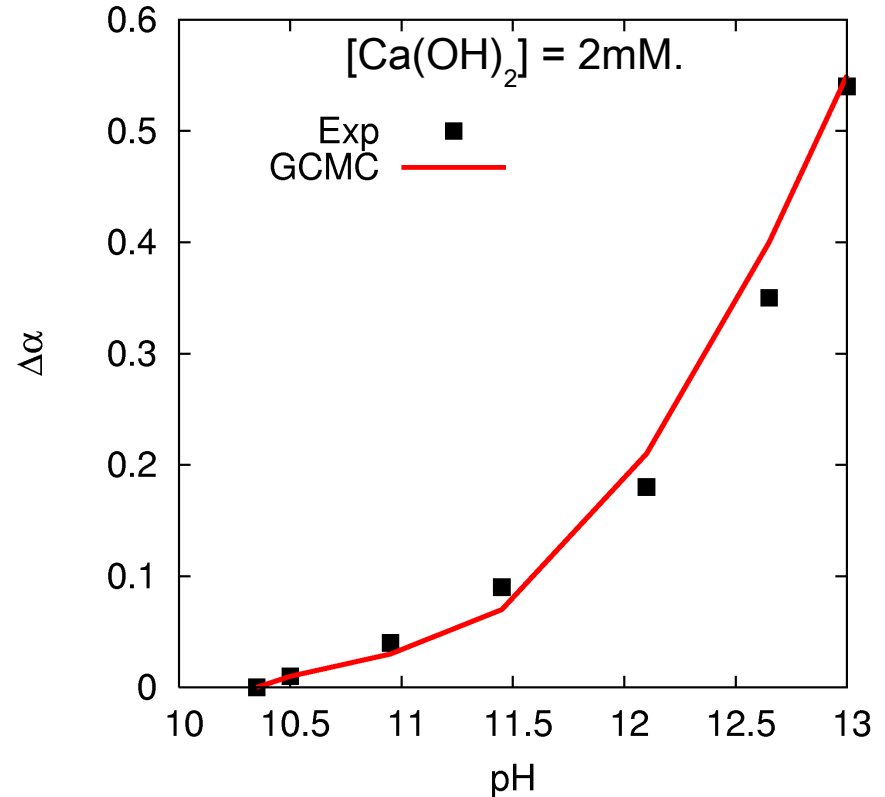Ionisation fraction (α) as a function of pH

Ion-ion correlations strongly promote surface charge density

Surface charge density
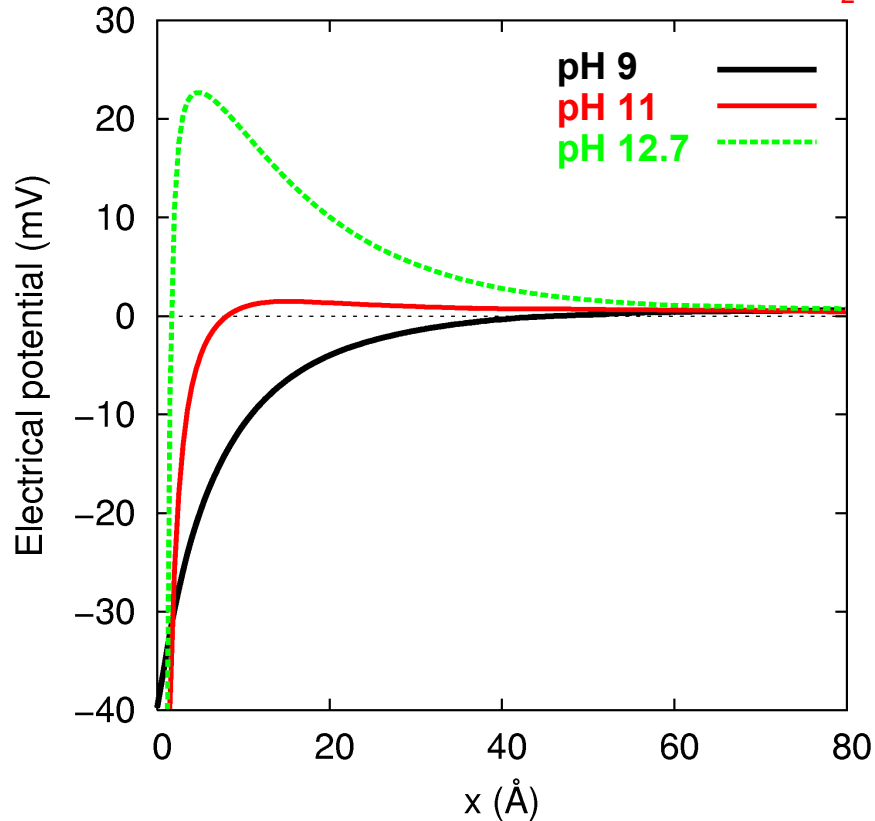
Surface charge prediction

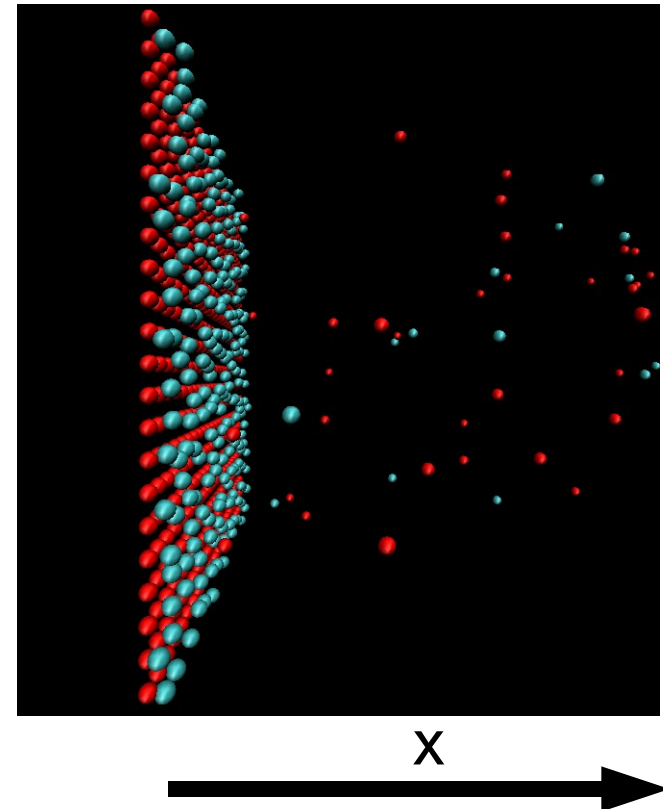## Simulated vs experimental net increase of the surface ionization fraction of C-S-H

⇒ The charge formation on C-S-H is well described by the electrostatic interactions.

Labbez, C.; Jönsson, B.; Pochard, I.; Nonat, A.; Cabane B., J. Phys. Chem. B 2006, 110, 9219

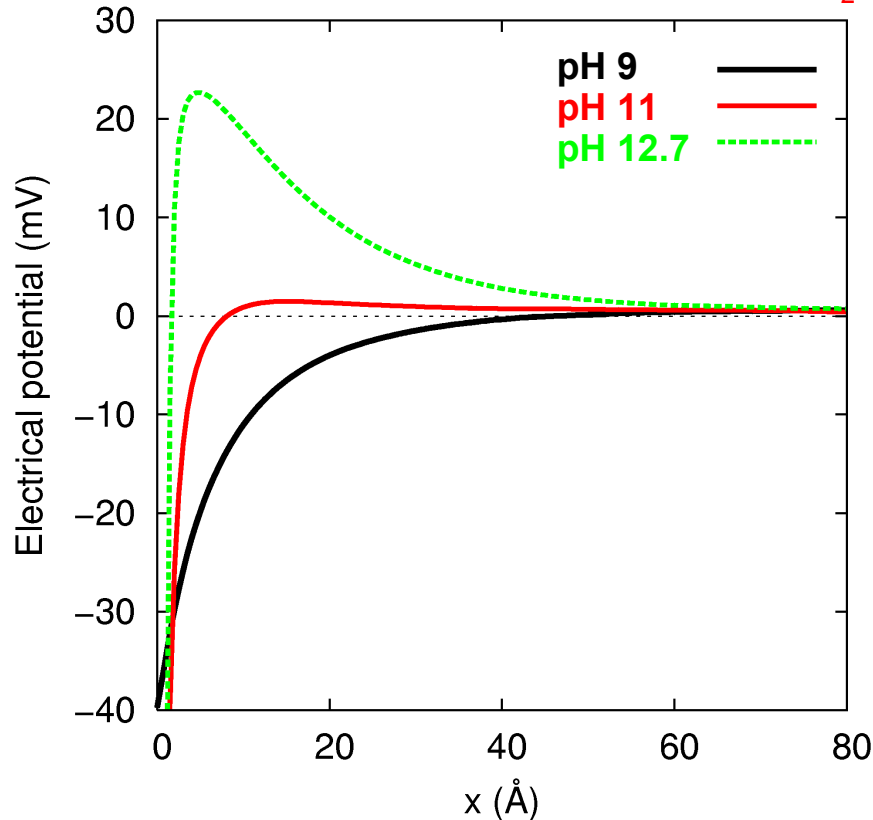# Charge reversal

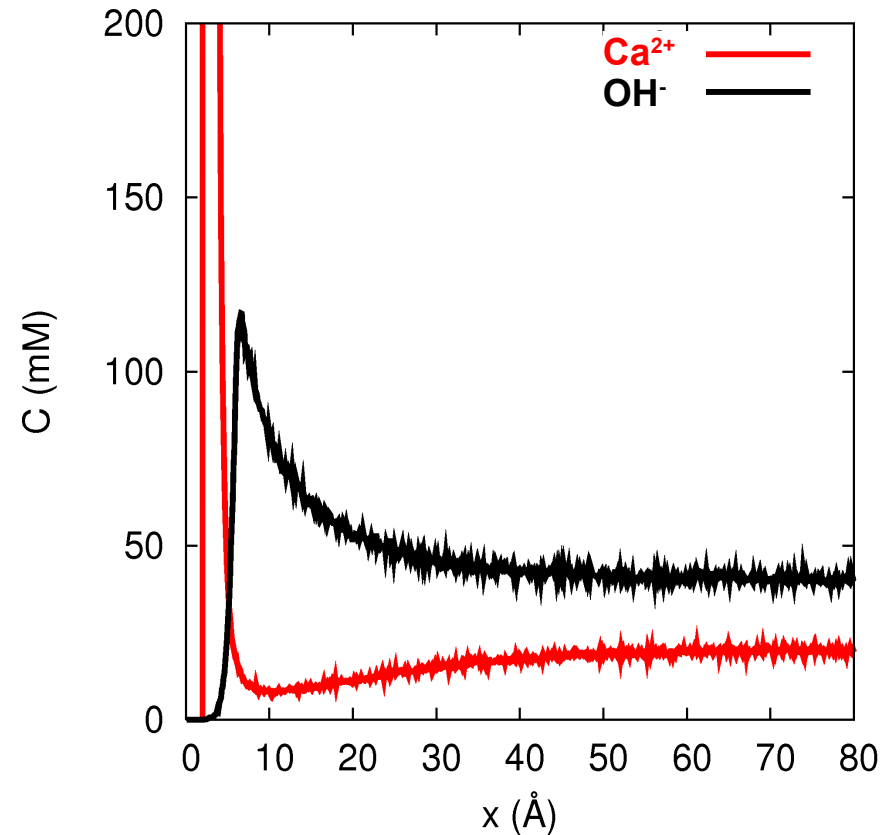Potential profile varying $c_{Ca(OH)_2}$

Model C-S-H/solution interface

Charge reversal

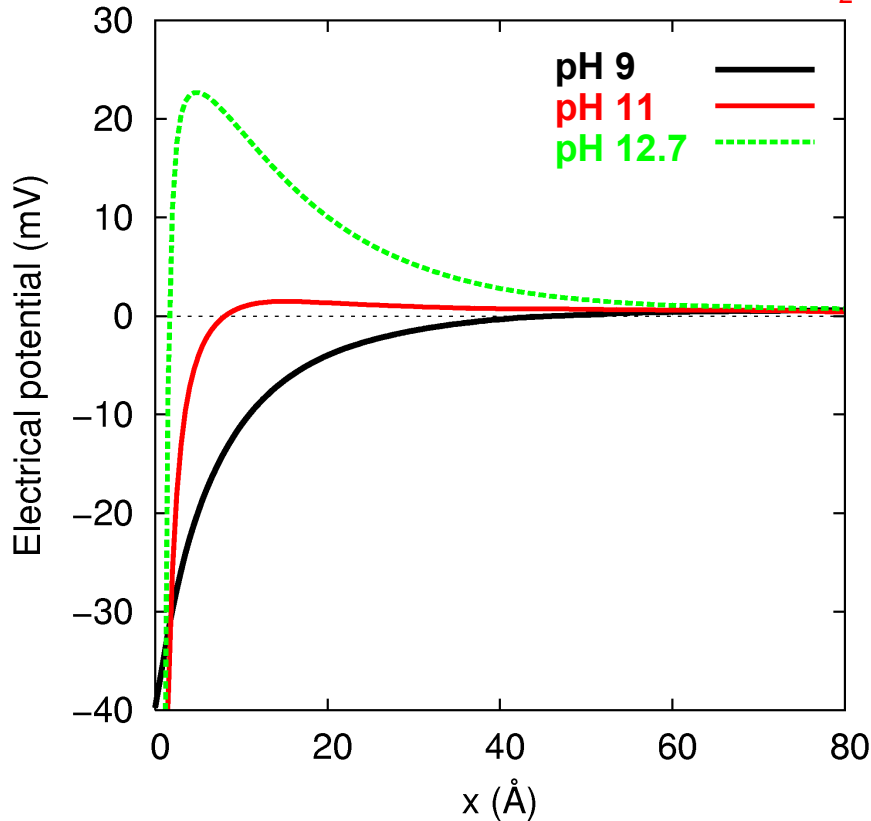Potential profile varying $c_{Ca(OH)_2}$

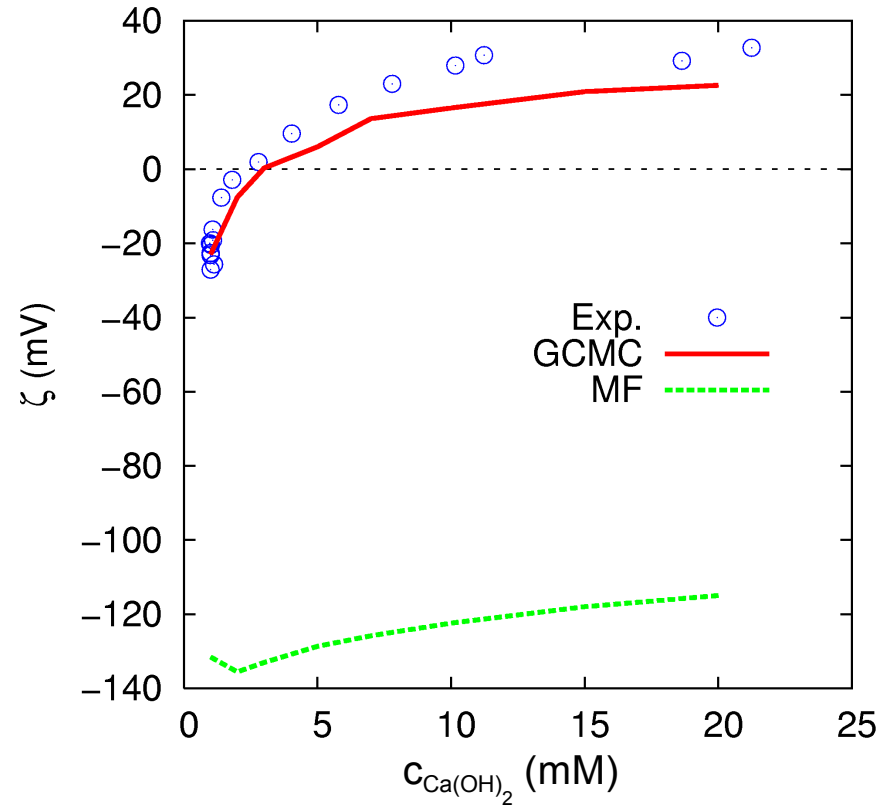Concentration profile at pH 12.7

Ion-ion correlations induce Ca^{2+} condensation at the C-S-H surface that eventually overcompensate its surface charge

Charge reversal
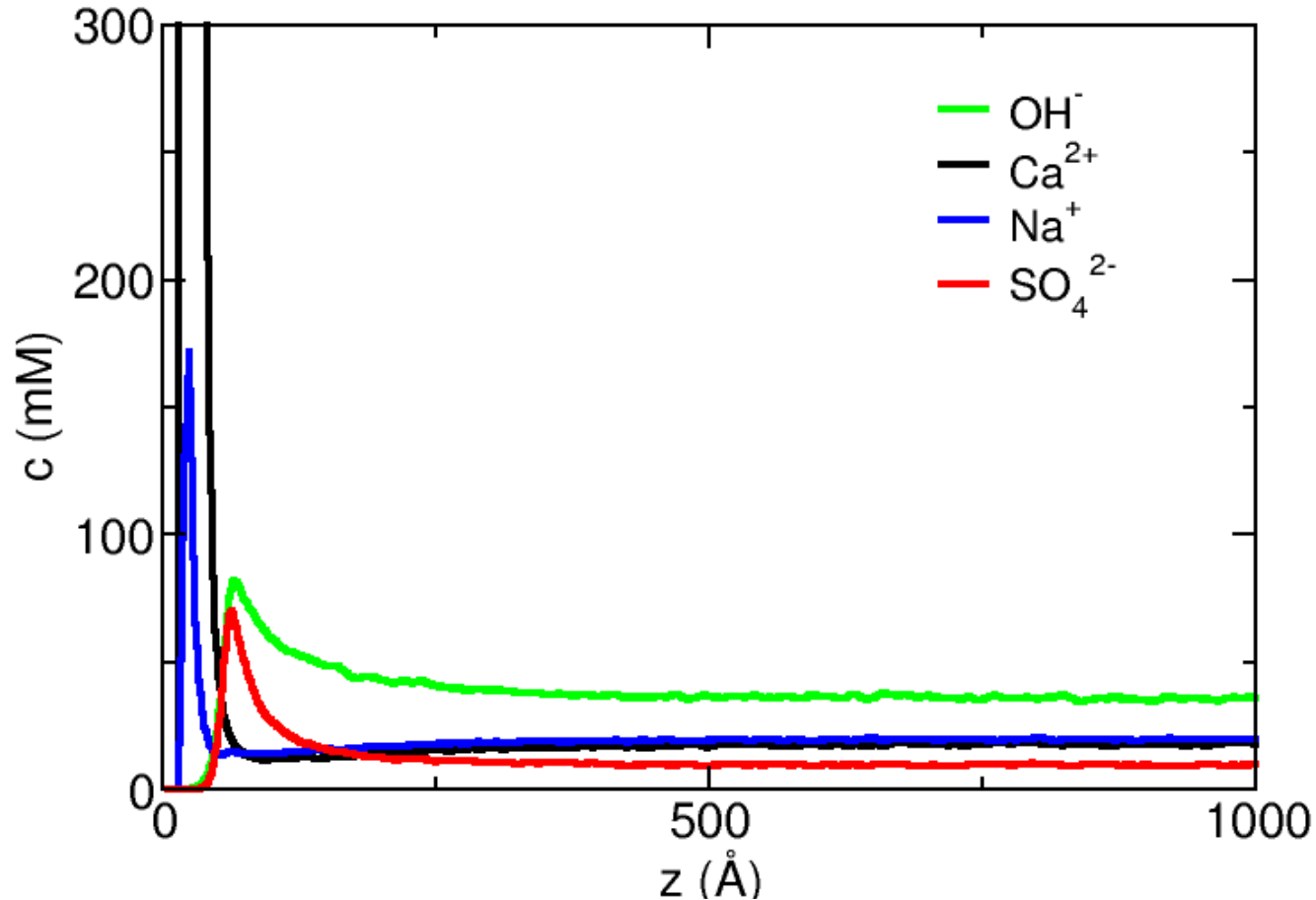
Potential profile varying $c_{Ca(OH)_2}$

Electrokinetic potential

Ion-ion correlations quantitatively explain charge reversal of C-S-H

Labbez, C.; Jönsson, B.; Pochard, I.; Nonat, A.; Cabane B., J. Phys. Chem. B 2006, 110, 9219
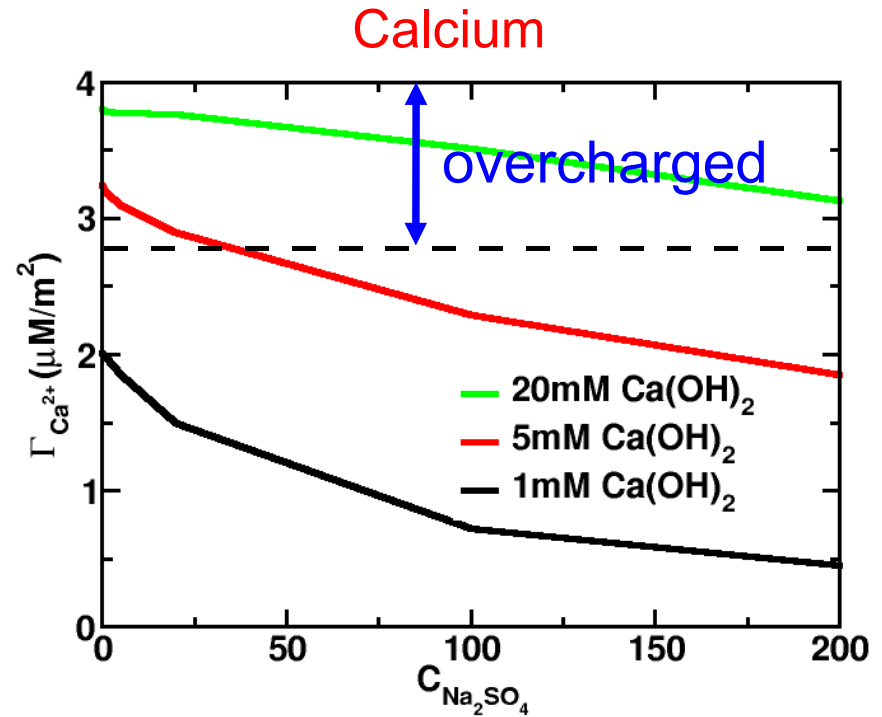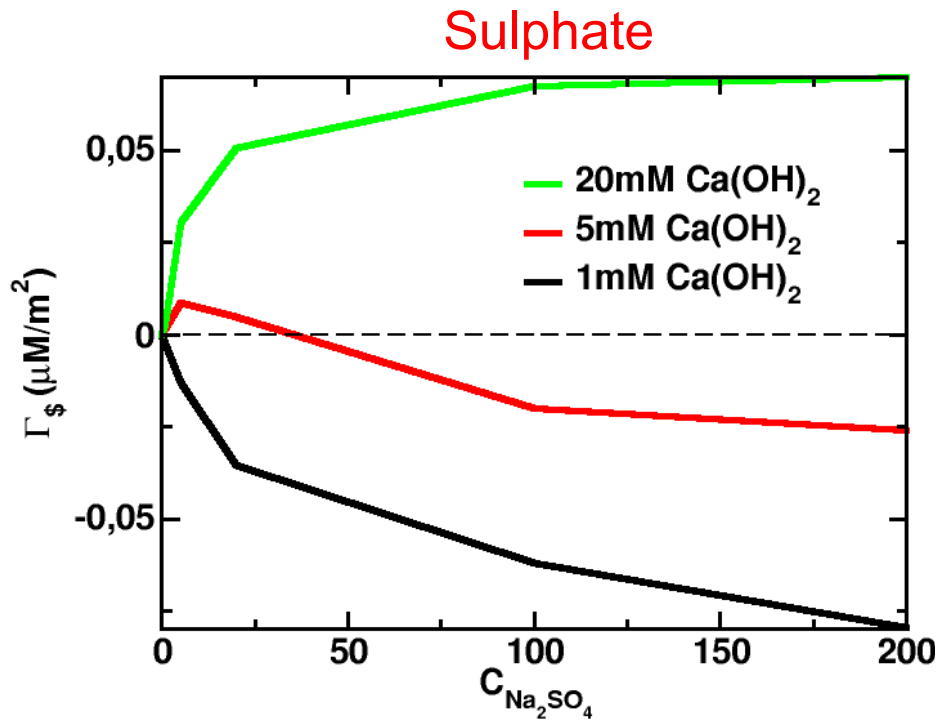
Concentration profile

Bulk solution: 18 mM $CaOH_2$ + 10 mM Na_2SO_4, pH 12.7

Charge reversal explains adsorption of anions

SO_4^{2-} versus Ca^{2+} adsorption on C-S-H
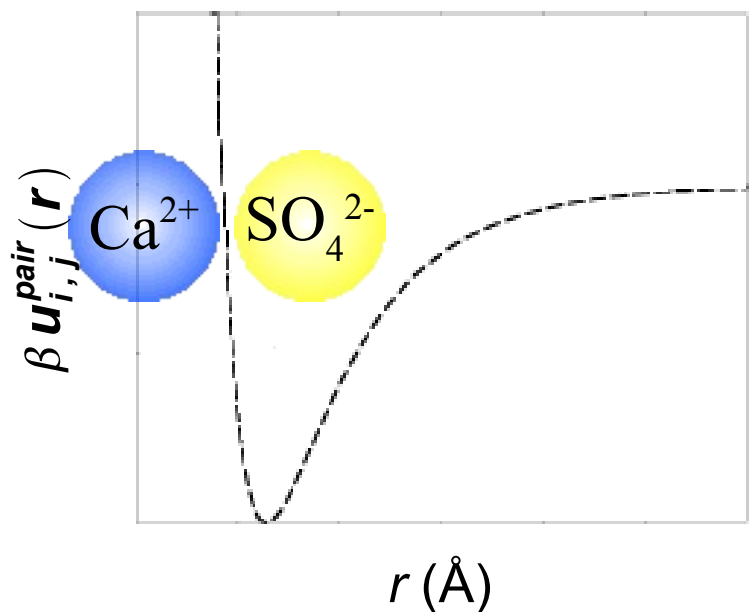

Sulphate

Calcium

Increasing the Na_2SO_4 concentration results in the desorption in calcium and the subsequent lost of the overcharging of C-S-H which, in turn, causes the desorption of sulphate.
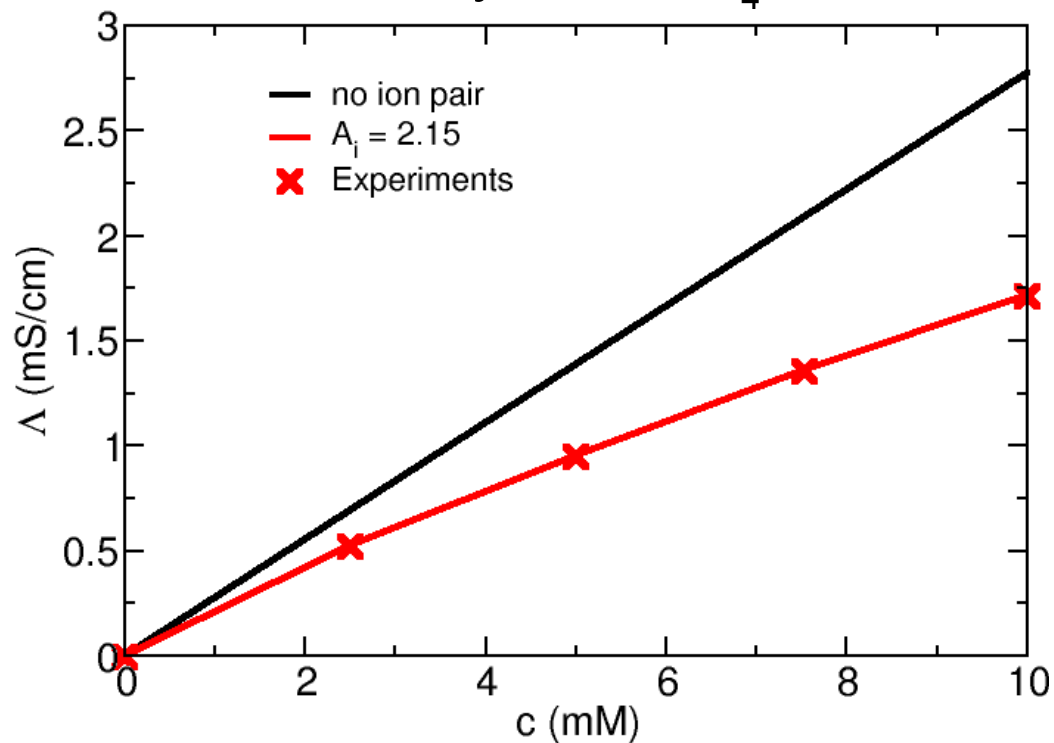
Ca^{2+}--SO$_4^{2-}$ ion pairs

Effective ion pair potential

$$\beta u_{i,j}^{pair}(r) = A_i e^{-(r-\sigma)} \Phi_{L-J}(r)$$

$\beta u_{i,j}^{pair}(r)$

Ca^{2+} SO$_4^{2-}$

r (Å)

Conductivity of CaSO$_4$ solutions

- —— no ion pair
- —— A$_i$ = 2.15
- ✖ Experiments

Λ (mS/cm)

c (mM)
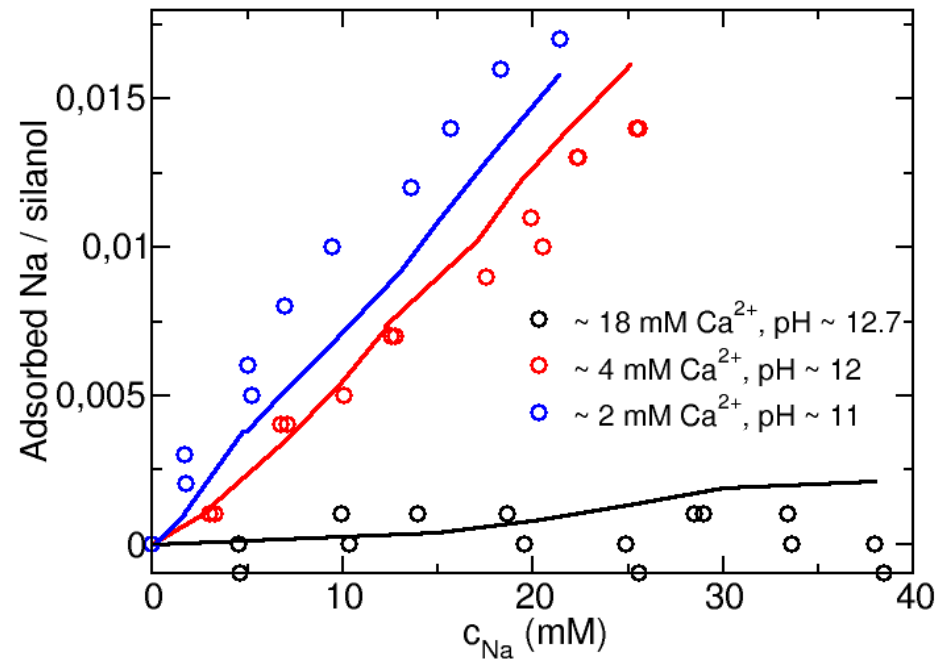
Sulfate and sodium adsorption

Simulations (▬) versus experiments (o)
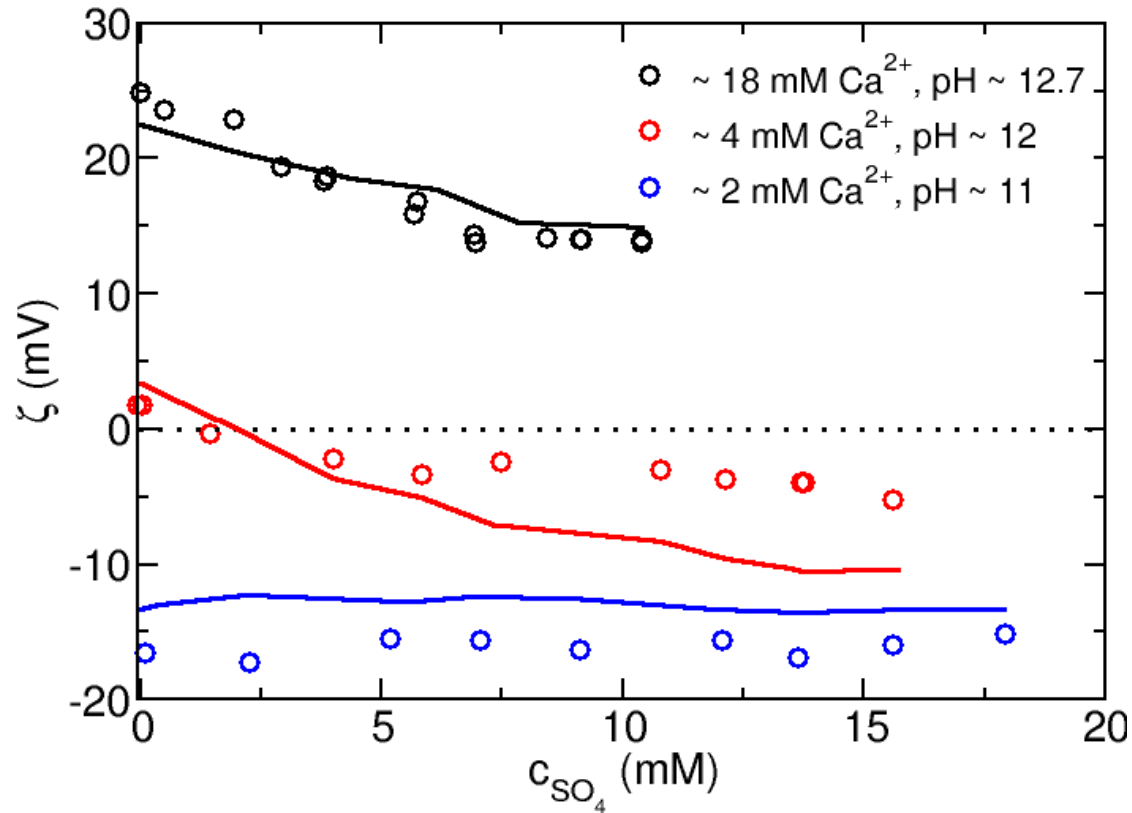

Sulfate adsorption
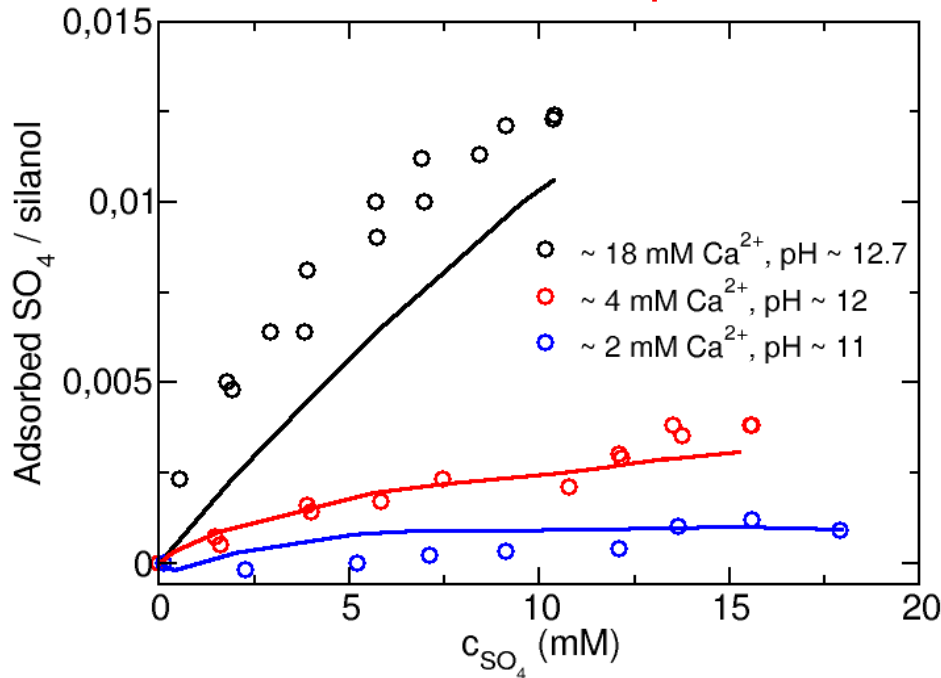
Sodium adsorption

A very good agreement between the experiments and simulations is obtained when both the electrostatic interactions and the specific ion pairing between Ca and SO_4 ions are accounting for.
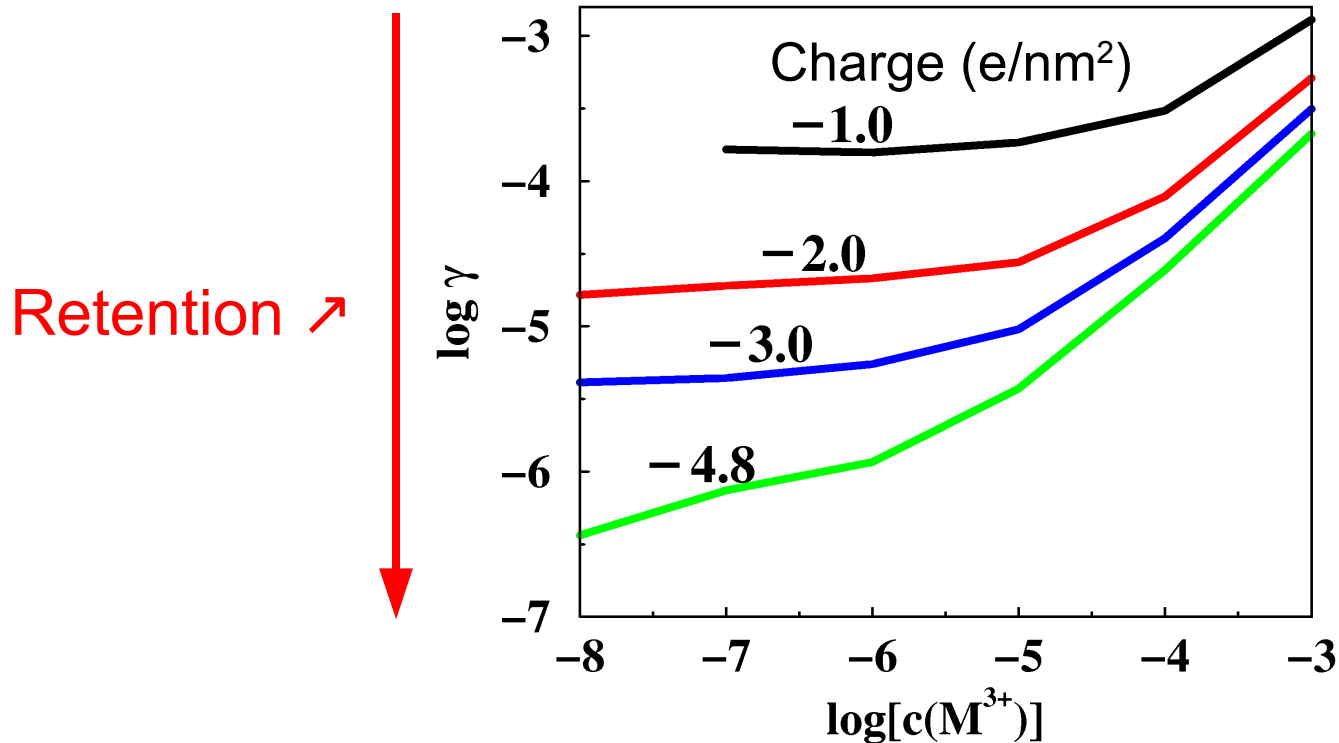
Electrokinetic potential

Simulations (━) versus experiments (o o o)

A very good agreement is obtained
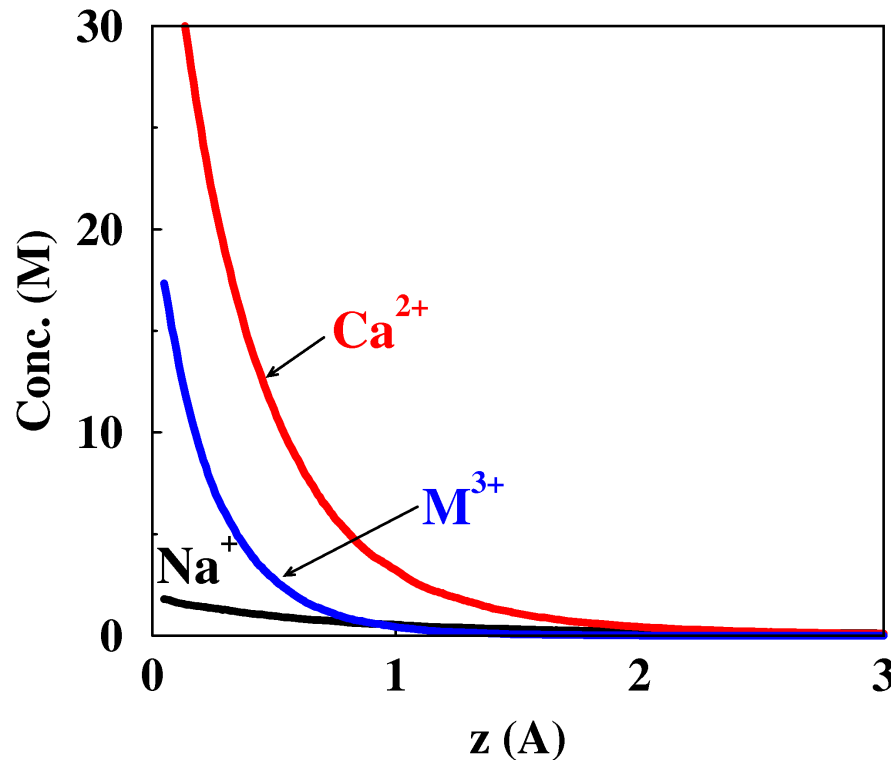
Heavy metal (M^{3+}) retention

$\gamma = C_{bulk}/(C_{bulk}+C_{slit})$

Retention ↗

M^{3+} retention versus their bulk concentration for various charge density. The bulk contains always 100 mM Na^+ and 10 mM Ca^{2+}.
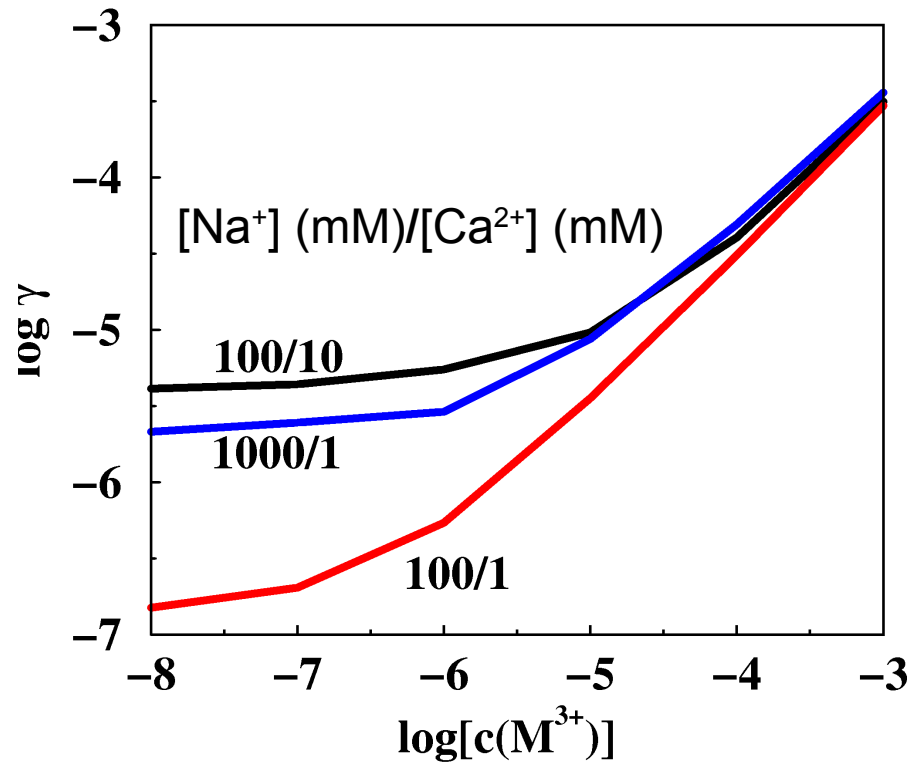
Concentration profile

The bulk contains 100 mM Na^+, 10 mM Ca^{2+} and 0.01 mM M^{3+}.

At the interface $C_{M3+} \gg C_{Na+}$ while in the bulk $C_{Na+} = 10^4\, C_{M3+}$

# Competition Na$^+$-Ca^{2+}/M^{3+}

Retention of heavy metals is all the more important as calcium and sodium bulk concentration is low.

Conclusion

• For systems containing negatively charged calcium silicate hydrate nanoparticles (C-S-H) dispersed in salt solution mixtures $(Ca(OH)_2/Na_2SO)_4$, we presented measurements and Monte Carlo (MC) simulations of sulfate and sodium adsorptions and of electrokinetic potentials (ζ).

• The interplay of coulomb interactions and ion pairing allows us to explain quantitatively the adsorption of sulfate ions.

• For C-S-H particles dispersed in solutions containing traces of multivalent cations in addition to various $(Ca(OH)_2/NaOH)$ salt mixtures a very high multivalent cation retention is found.

Perspective

- Inclusion of heavy metal speciation

- Effect of the C-S-H charge on heavy metal speciation

$$M\text{-}(OH)_4^- \longrightarrow M\text{-}(OH)_3^+ + OH^-$$
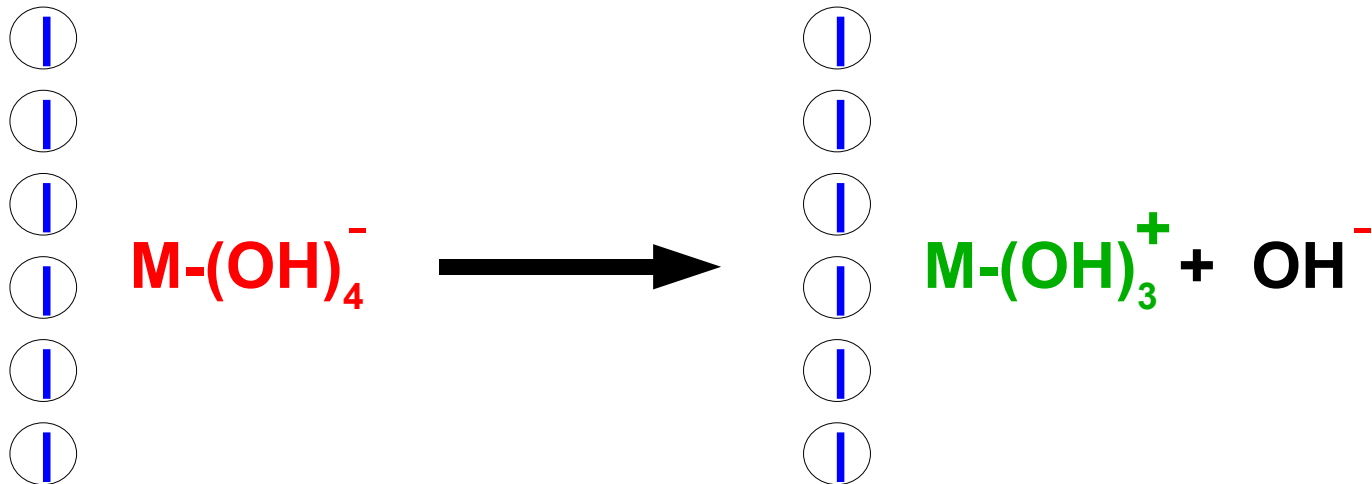
Acknowledgements

- Financial supports:
  - European NANOCEM Consortium
  - Marie Curie Training Network

- Computer Facilities
  - CRI, Université de Bourgogne
  - LUNARC, Lund University

- Colleagues:
  - Bo Jönsson from Lund University
  - Paul Glasser, University of Aberdeen (UK)