# Investigation of the role of alkali cation in early stage of oligomerization in silicate fluids: a molecular dynamics study

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EuCheMS European Chemical Sciences

7th EuCheMS Chemistry Congress | LIVERPOOL UK 26–30 August 2018

# Investigation of the role of alkali cation in early stage of oligomerization in silicate fluids: a molecular dynamics study

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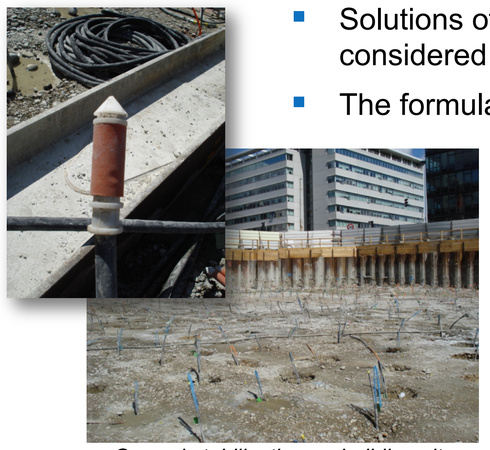
PROJET FINANCÉ PAR L'ANR – PROJECT FUNDED BY THE ANR

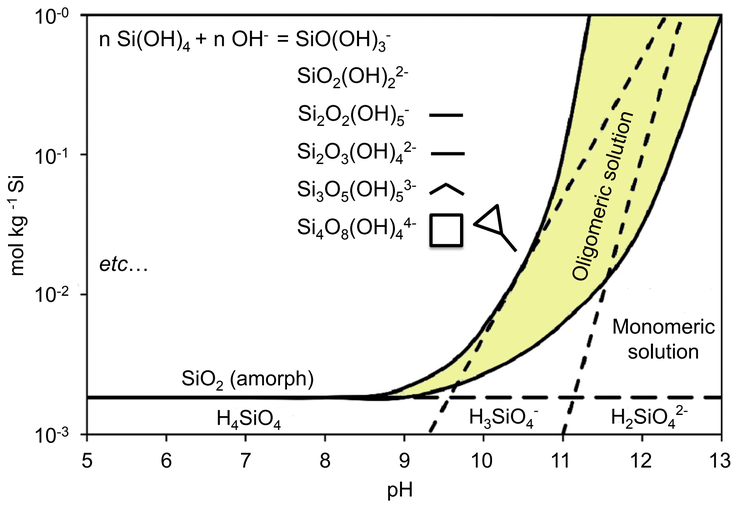
## Context



*Ground stabilization on building site (Wöllner GmbH&Co.KG)*

- Solutions of activation (= alkali media) of alumino-silicate are environmentally friendly and considered as green chemistry (used for ground stabilization, painting….)
- The formulation is complex since the parameters are various and numerous

- Understanding the ion-ion interactions for the oligomerization process where the nature and concentration of alkali drives the final properties of the gel [1]
- Molecular dynamics is a useful tool to fill the gap between theoretical and experimental studies
- Molecular dynamics allows the calculation of the structural and dynamical properties of the solutes in solution
- Effect of water, alkali and hydroxide are explicitly taking into account

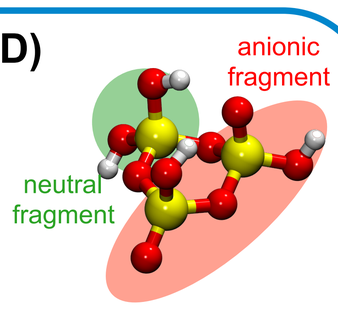


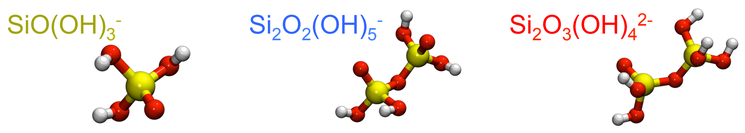

*Stability diagram for soluble silicates at 298 K [2]*

## Method

### Classical Molecular Dynamics (MD)

- Molecular dynamics simulations using explicit polarization with AMBER14 [3]
- Development of a polarizable silicate force field for describing all the silicate oligomers by assembling neutral and anionic fragment (10 types of atom)
- MD simulations focused on 3 species:



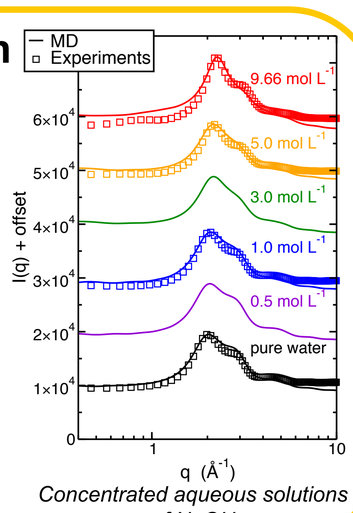

### X ray scattering intensity from MD simulation

- Calculation of I(q) from radial distribution functions

$$I(q) = \sum_{\alpha}\sum_{\beta} f_{\alpha}(q) f_{\beta}(q) \sqrt{N_{\alpha} N_{\beta}} S_{\alpha\beta}(q)$$

$$S_{\alpha\beta}(q) = \delta_{\alpha\beta} + \sqrt{\rho_{\alpha}\rho_{\beta}}\ \mathrm{FT}_{3\mathrm{D}}(g_{\alpha\beta}(r) - 1)$$

- Theoretical I(q) directly comparable to experimental one
- Efficient method for describing alkali media [4] ➔ study of silicate oligomers in such media




*Concentrated aqueous solutions of NaOH*

## Silicate in NaOH concentrated media

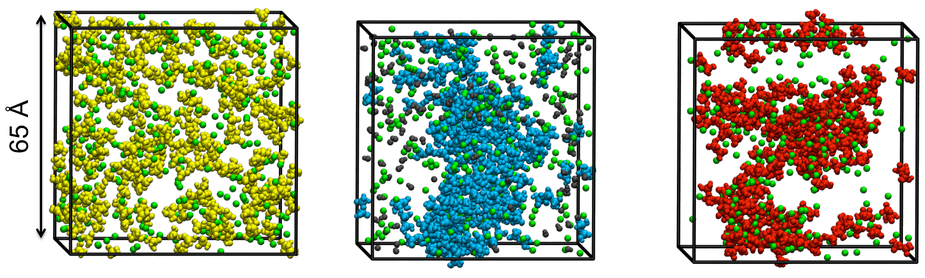
### Pure oligomer solutions

[Si]/[Na+] = 1

300 $Na^+$
300 $SiO(OH)_3^-$

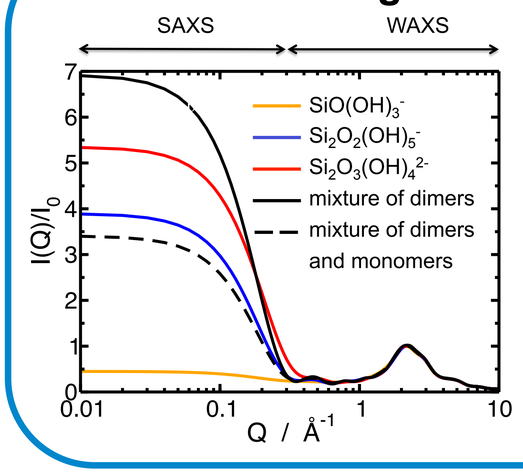
300 $Na^+$
150 $Si_2O_2(OH)_5^-$
150 $OH^-$

300 $Na^+$
150 $Si_2O_3(OH)_4^{2-}$



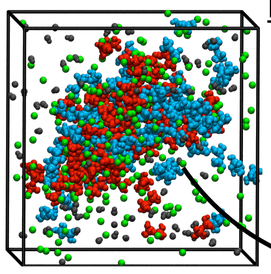

- Monomers: “homogeneous” media
- Dimers: spontaneous aggregation

### Scattering intensities from MD



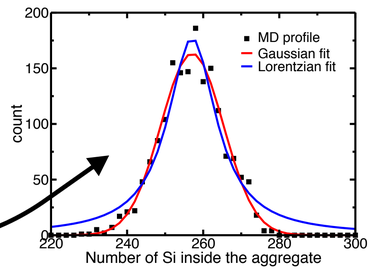

- Same structure for Q > 1 Å$^{-1}$
- Rise for Q < 0.4 Å$^{-1}$ (aggregation)
- Presence of monomers decreases the I(Q) at small angles

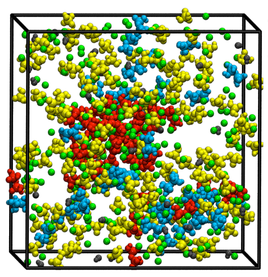
### Mixtures of oligomers



Mixture of dimers

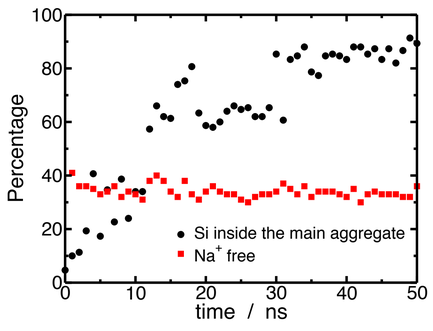
300 $Na^+$
75 $Si_2O_2(OH)_5^-$
75 $Si_2O_3(OH)_4^{2-}$
75 $OH^-$



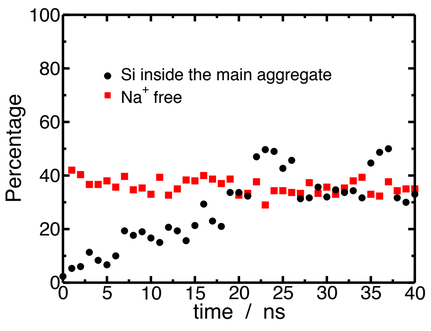



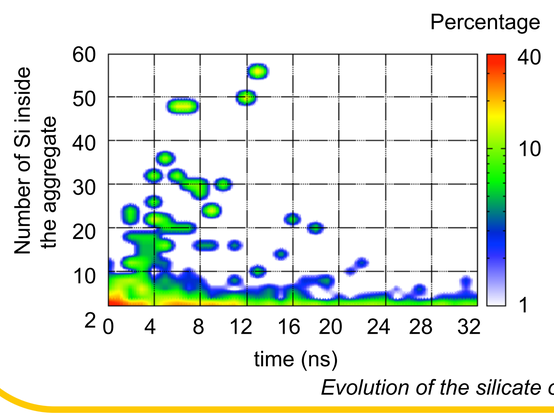
Mixture of dimers and monomers

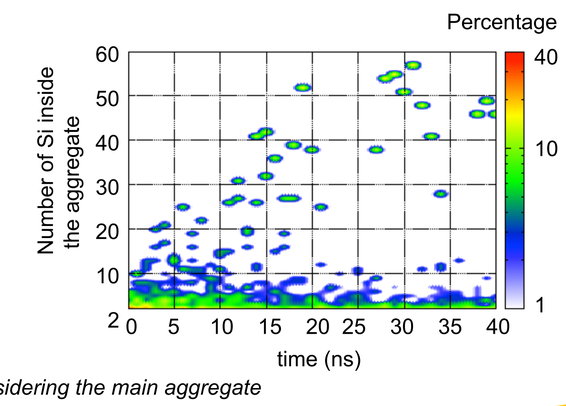
300 $Na^+$
37 $Si_2O_2(OH)_5^-$
37 $Si_2O_3(OH)_4^{2-}$
152 $SiO(OH)_3^-$
37 $OH^-$




- $[Na^+]_{free}$ constant
- Provide a “buffer media”




*Evolution of the silicate oligomers without considering the main aggregate*

## Conclusions and Outlooks

- Structure of the solution depends on the oligomer composition and nature:
  - Spontaneous aggregation of dimers in solution: aggregates composed of silicates and $Na^+$
  - Dimers $Si_2O_3(OH)_4^{2-}$ interact strongly with $Na^+$
  - Monomers $SiO(OH)_3^-$: small aggregates, and destabilize the aggregation (entropic effect)
- Similar behaviours of $Na^+$: “buffer media” with the hydroxide anions
- MD simulations of “real” solutions:
  - Different [Si]/[$Na^+$] ratios with respect to NMR experiments
  - Influence of the alkali nature on the aggregation

## Acknowledgements

This work was made possible thanks to the financial support of the ANR DYNAMISTE (ANR-15-CE07-0013-01) and high performance computing facilities of TGCC/CCRT and the computing center of CEA Marcoule.

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[4] A. Coste *et al.*, J. Chem. Phys., submitted (2018)