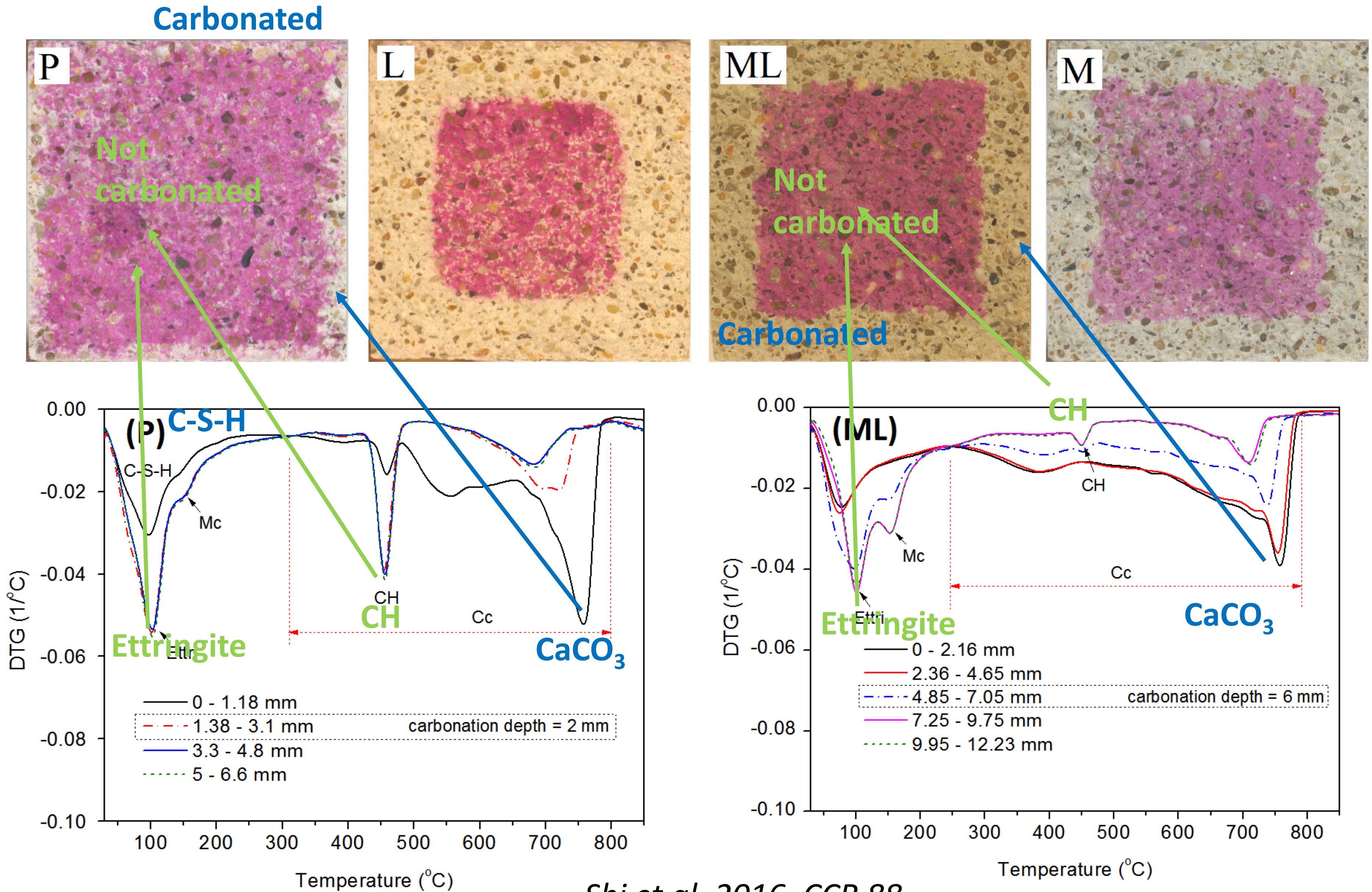
Empa
Materials Science and Technology

Effect of carbonation on hydrate assemblage and pore solution

Barbara Lothenbach*,, Klaartje De Weerdt**, Gilles Plusquellec**, Andres Belda Revert** , Mette Geiker**, Zhenguo Shi*, Frank Winnefeld*, Maciej Zajac***, Mohsen Ben Haha***, Blandine Albert******

*Empa, Laboratory for Concrete & Construction Chemistry;
NTNU Trondheim; * Heidelberg Cement; ****LafargeHolcim

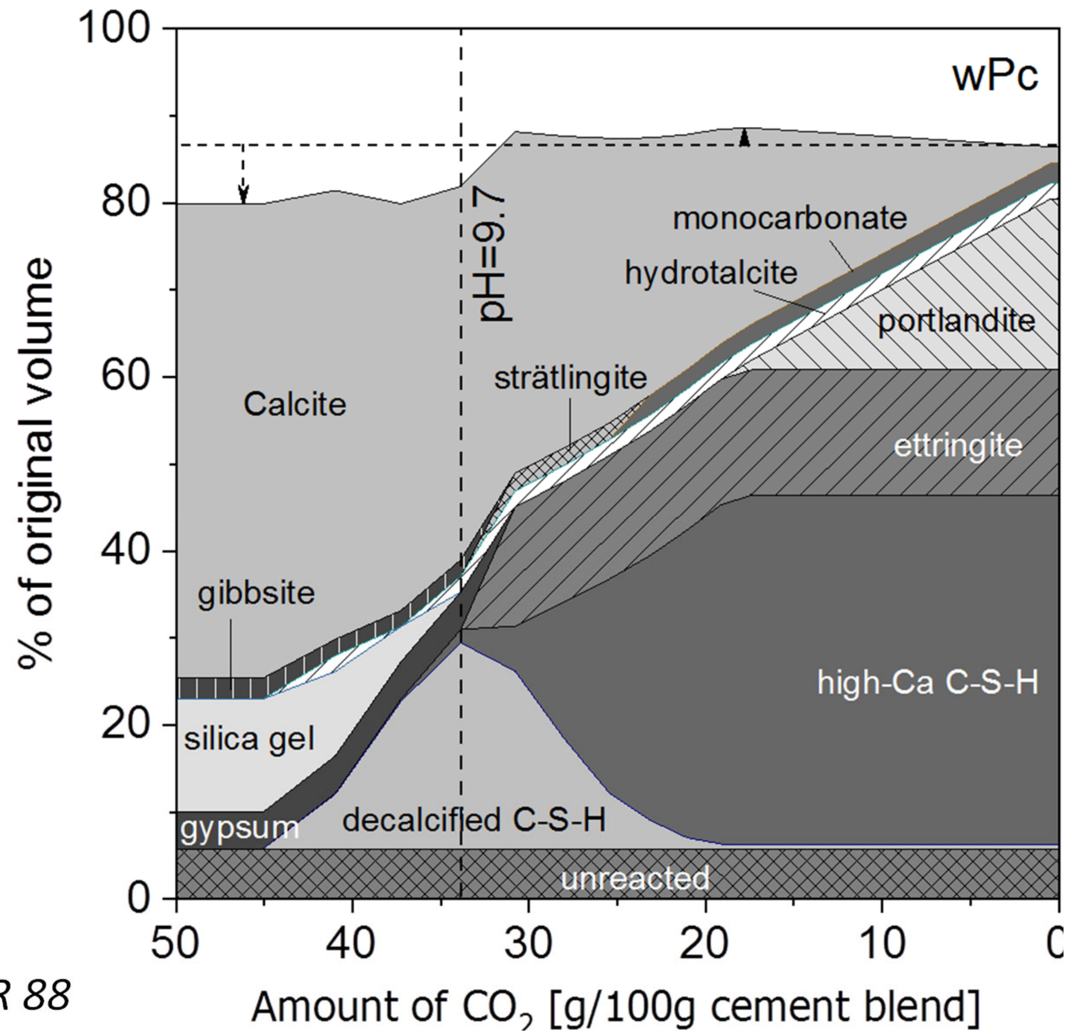
Mechanisms of carbonation



Shi et al. 2016, CCR 88

Mechanisms of carbonation

- Carbonation in presence of **CO_2 and water**
- Sequence based on thermodynamics:
  - Monosulfate, Friedel's salt => monocarbonate
  - Portlandite => $CaCO_3 + H_2O$
  - High Ca/Si C-S-H
    => low Ca/Si C-S-H, $CaCO_3 + H_2O$
  - Monocarbonate
    => Strätlingite, $CaCO_3 + H_2O$
  - Ettringite =>
    $CaSO_4$, AH_3, $CaCO_3 + H_2O$
  - low Ca/Si C-S-H =>
    $SiO_2 + CaCO_3 + H_2O$

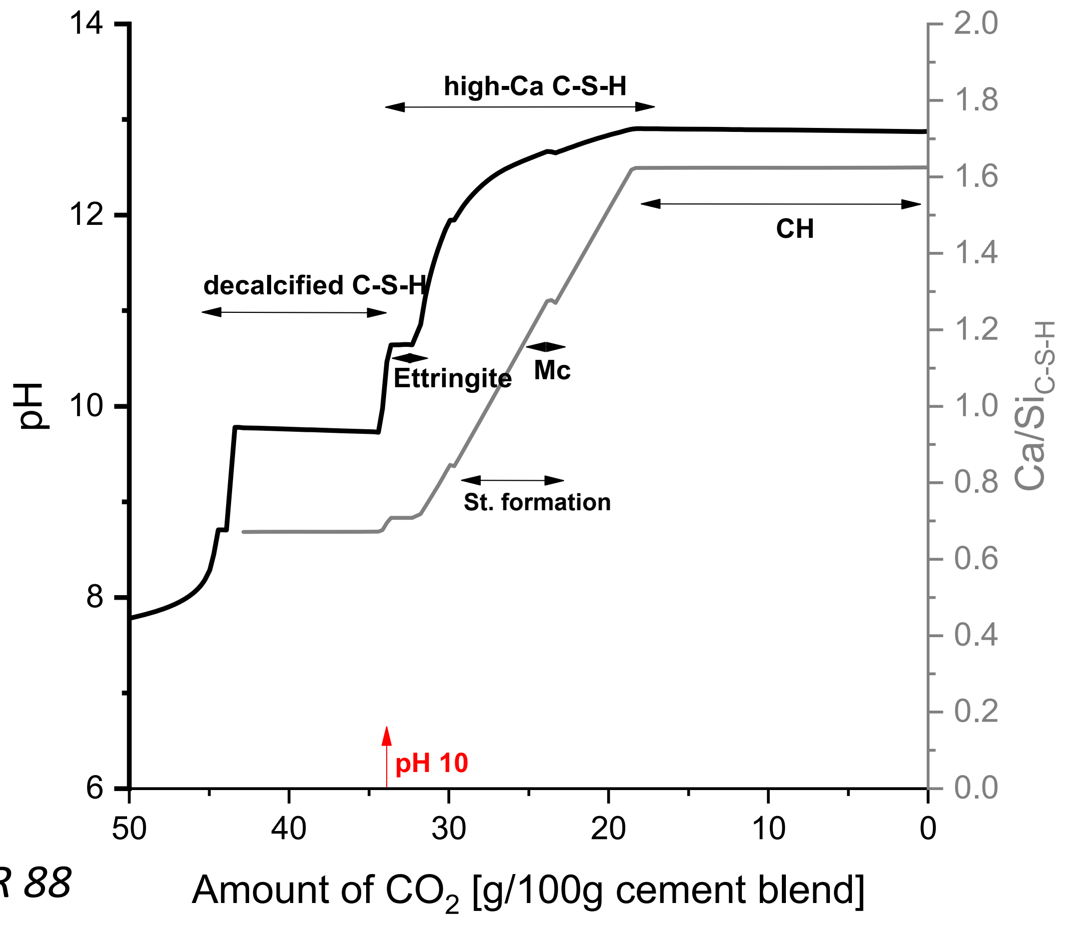


- Final reaction products:
  $CaCO_3 + H_2O$, SiO_2, AH_3, $CaSO_4$
  possibly zeolites
- Decalcification and pH decrease

Shi et al. 2016, CCR 88

Mechanisms of carbonation

- Carbonation in presence of **CO_2 and water**
- Sequence based on thermodynamics:
  - Monosulfate, Friedel's salt => monocarbonate
  - Portlandite => $CaCO_3$ + H_2O
  - High Ca/Si C-S-H
    => low Ca/Si C-S-H, $CaCO_3$ + H_2O
  - Monocarbonate
    => Strätlingite, $CaCO_3$ + H_2O
  - Ettringite =>
    $CaSO_4$, AH_3, $CaCO_3$ + H_2O
  - low Ca/Si C-S-H =>
    SiO_2 + $CaCO_3$ + H_2O

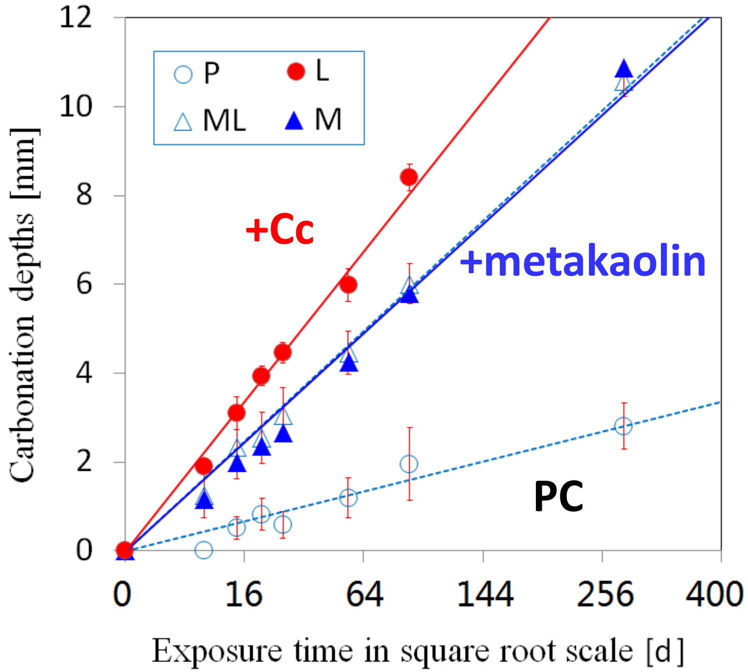


- Final reaction products:
  $CaCO_3$ + H_2O, SiO_2, AH_3, $CaSO_4$
  possibly zeolites
- Decalcification and pH decrease

Shi et al. 2016, CCR 88

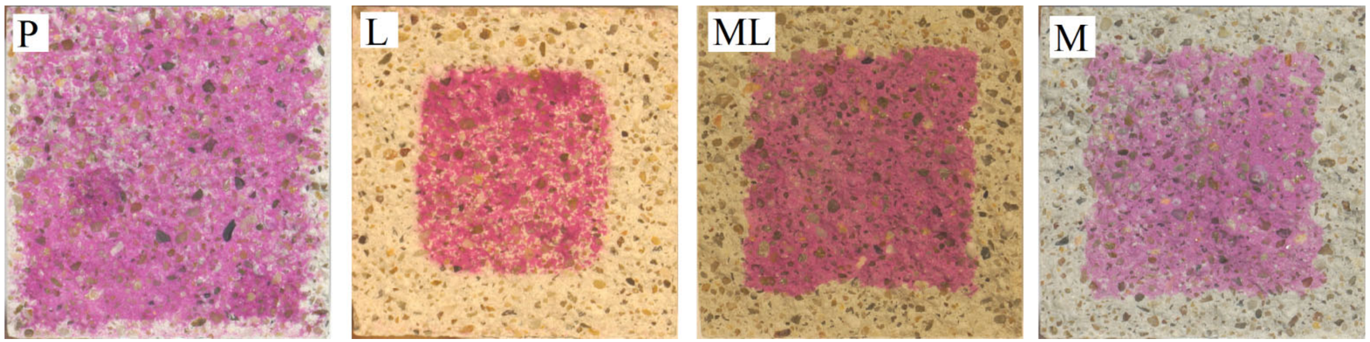
Effect of SCMs (32% limestone, metakaolin):

1% (v/v) CO2,
57% RH, 20 oC



Carbonation depths indicated by phenolphthalein

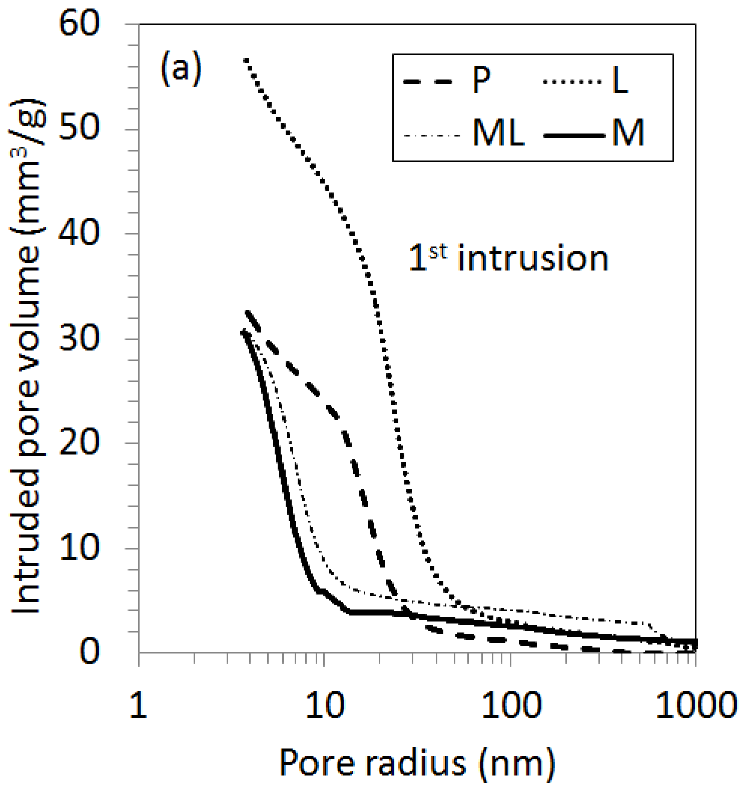
What causes differences in carbonation depths ?



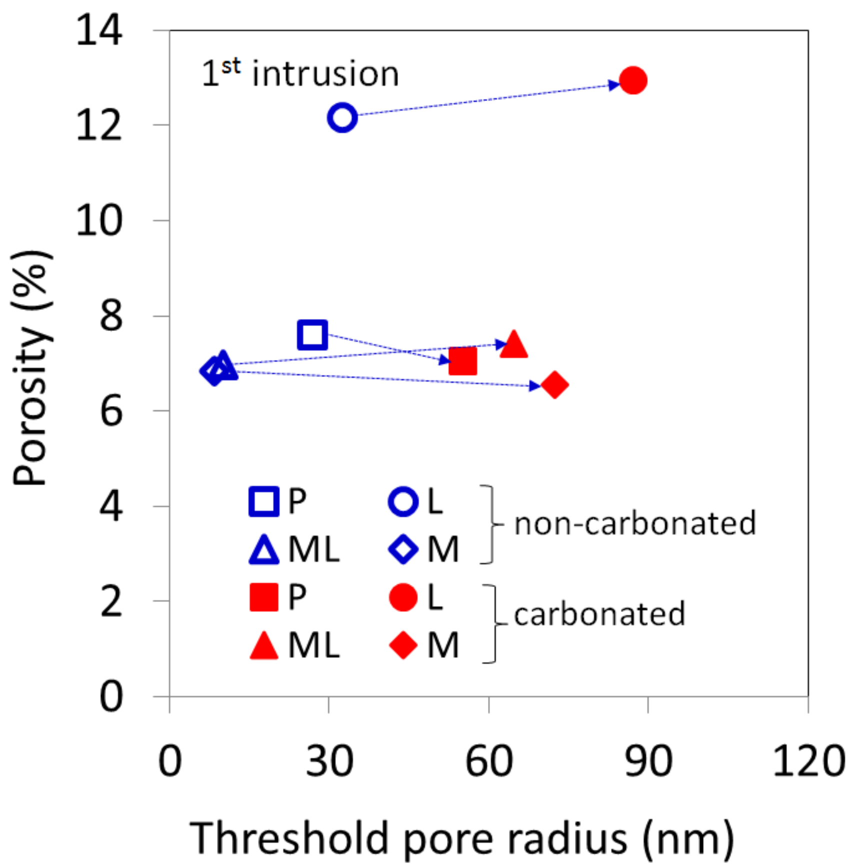
Shi et al. 2016, CCR 88.

1) + MK => refined porosity for ML/M

Non-carbonated samples



M: Coarsening during carbonation

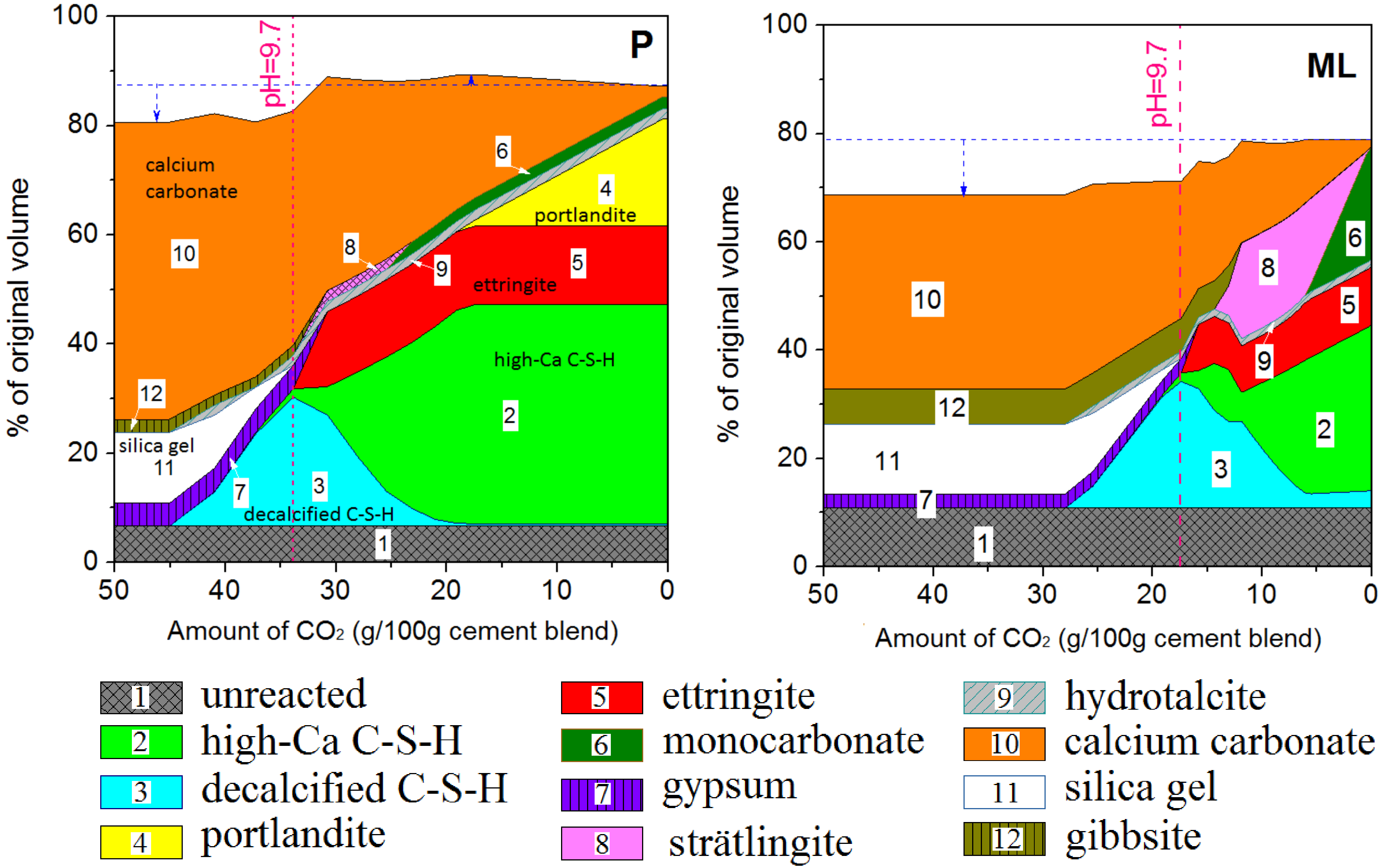


little difference P, M, ML after carbonation

L: larger pororsity

Shi et al. 2016, CCR 88.

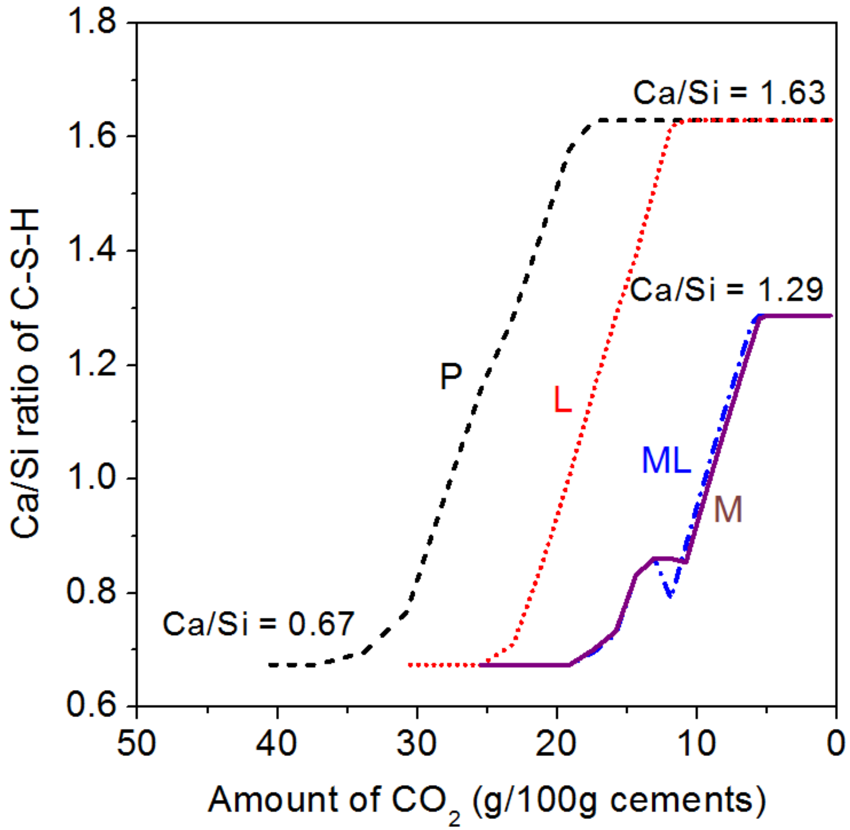
Impact of chemistry – phase assemblages (GEMs)

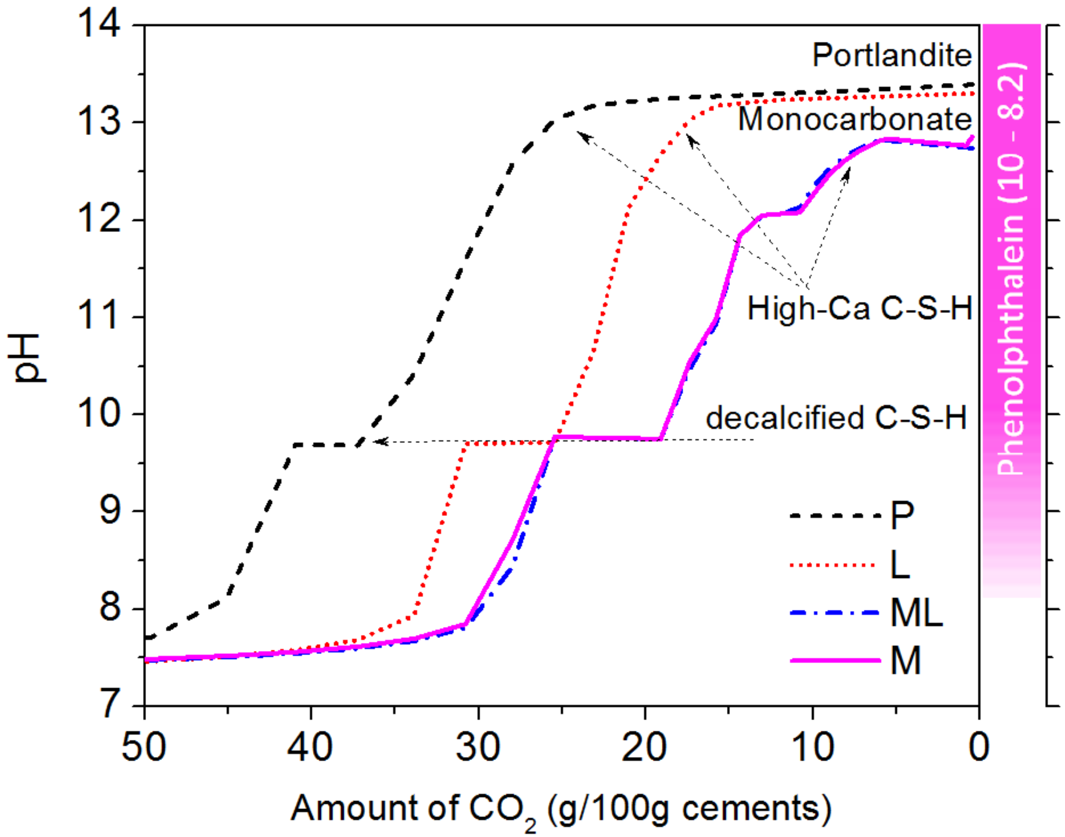


Shi et al. 2016, CCR 88.

Impact of chemistry – Ca/Si and pH (calculated)

Change of Ca/Si ratio for the C-S-H phase



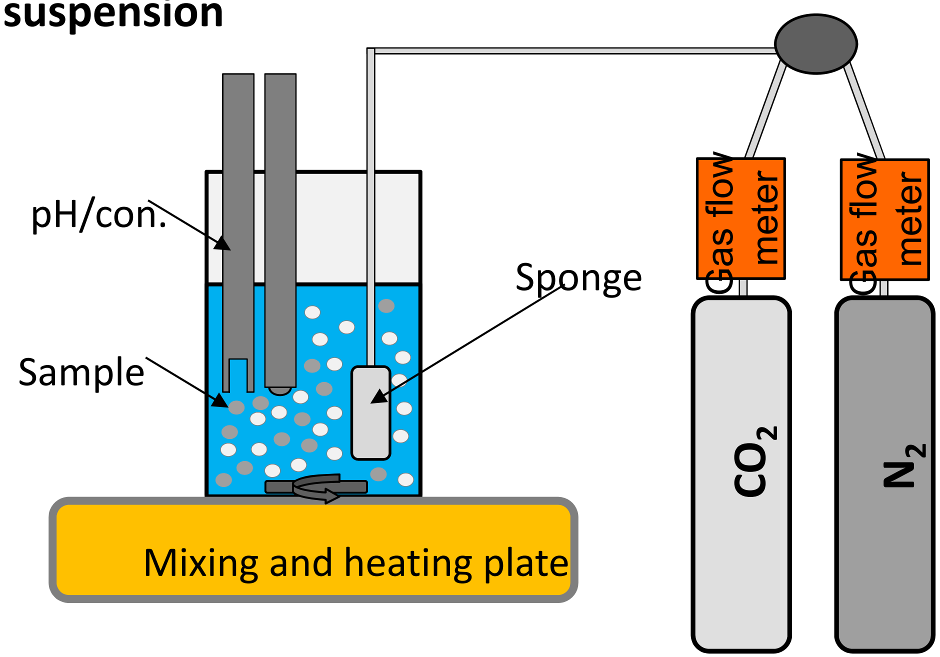


Predicted pH changes upon phase changes
=> complete degradation of C-S-H

Shi et al. 2016, CCR 88.

Effect of carbonation on pore solution

- Carbonated concrete usually has low moisture content
- Challenging to obtain pore solution by extraction under pressure
- Possibilities:
  1. **Carbonation in diluted suspension**

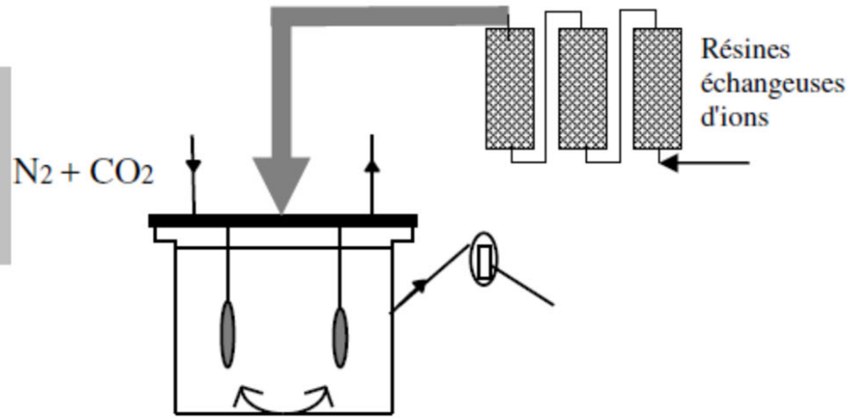


  2. **Cold water extraction (CWE + ICP), a leaching method**

Carbonation of cements in solution: PhD Albert

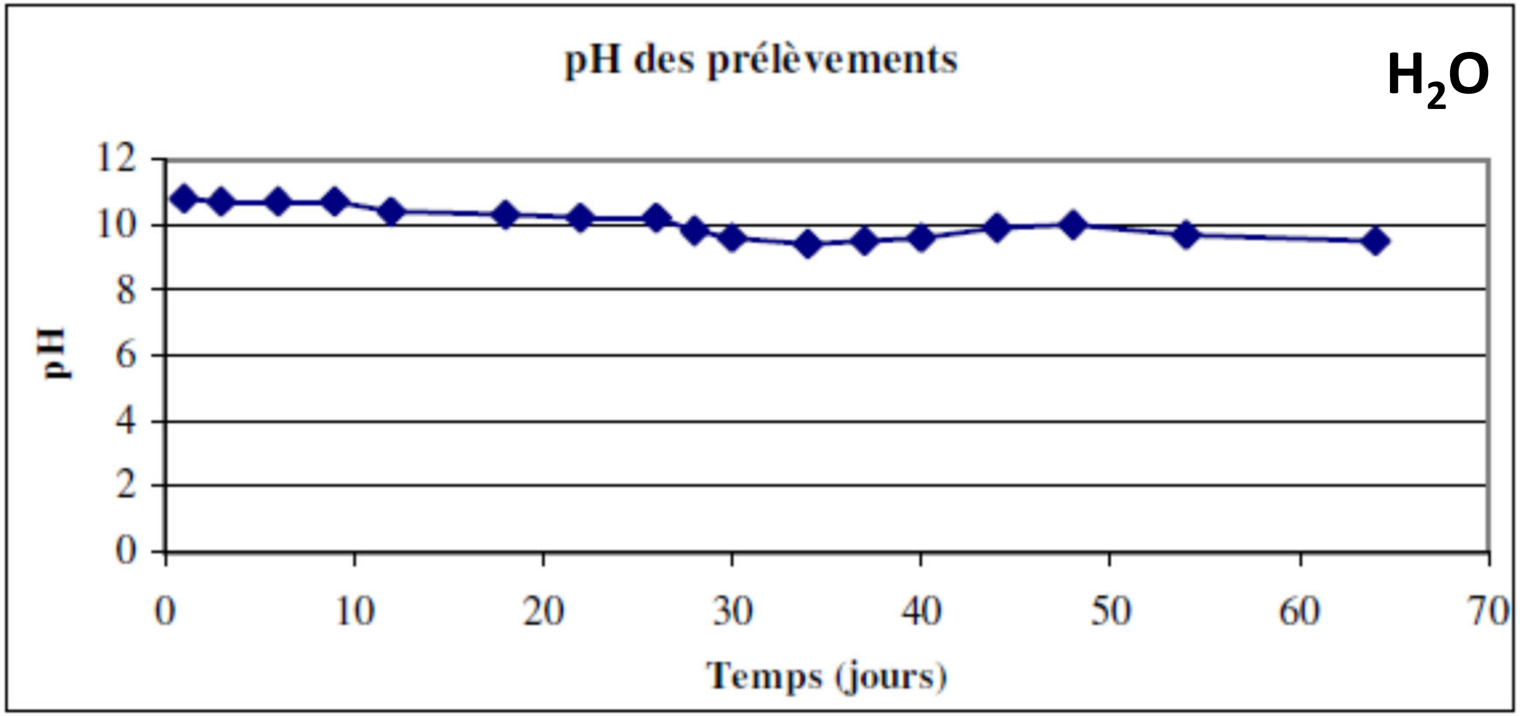
Débit d'alimentation du réacteur :
5,7 ml/minute

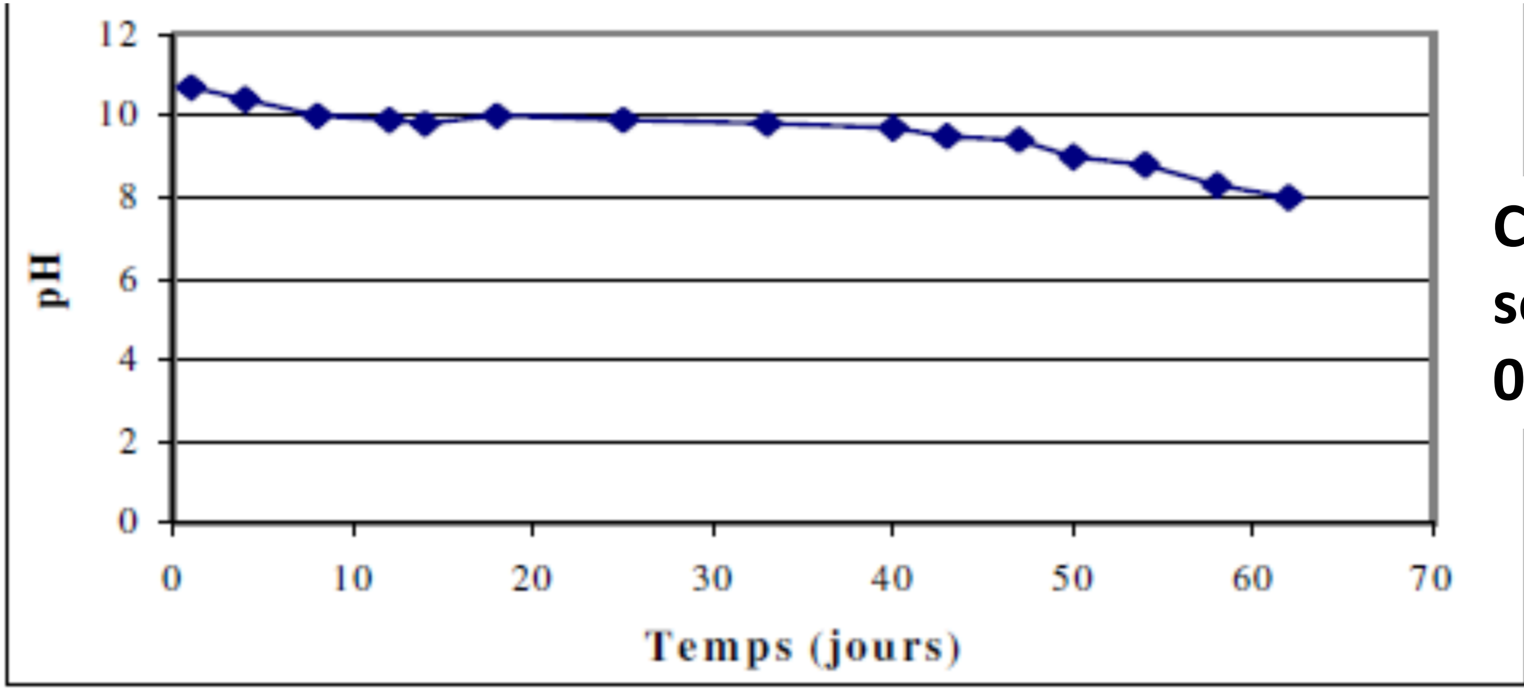
Durée de l'expérience :
2 mois



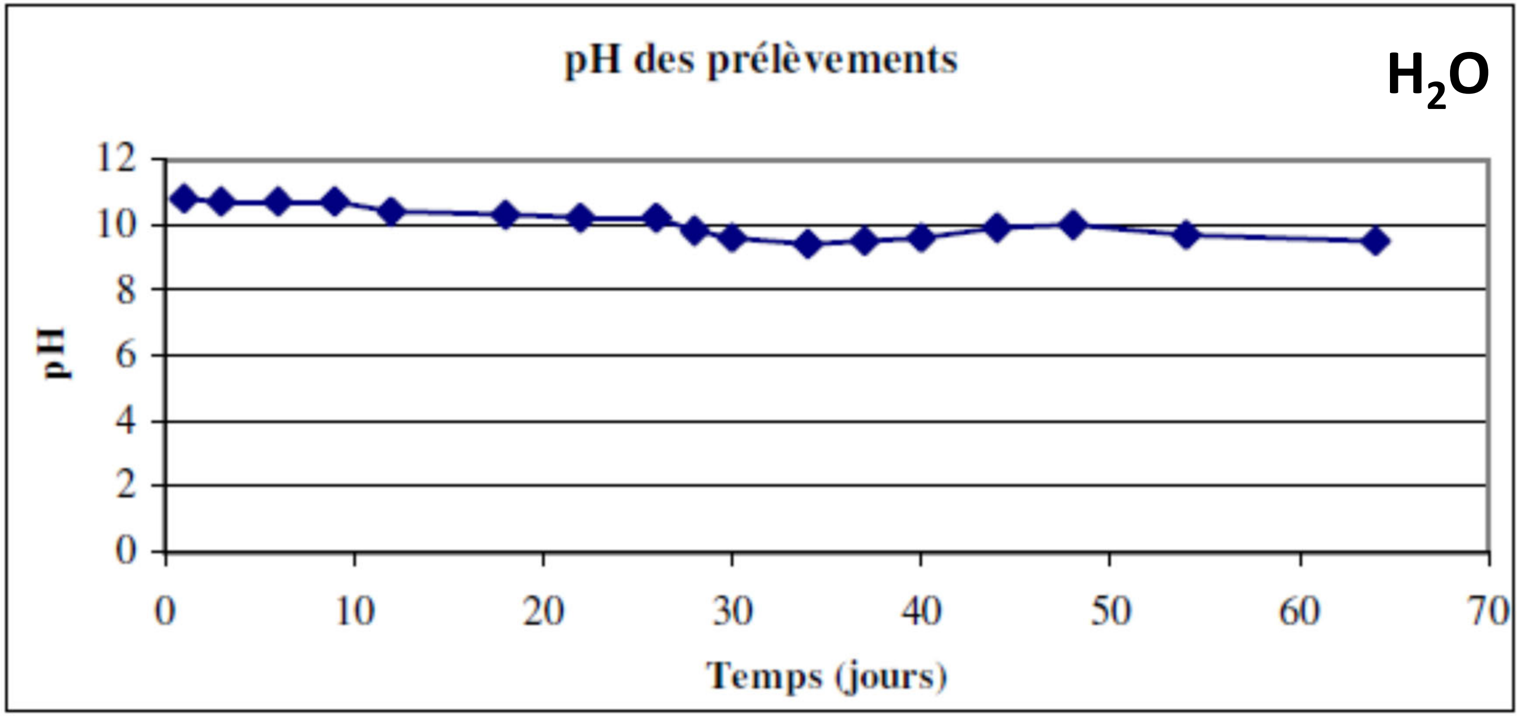
Flow through reactor

Fig. V-31 : Cellule d'altération par de l'eau en atmosphère carbonatée

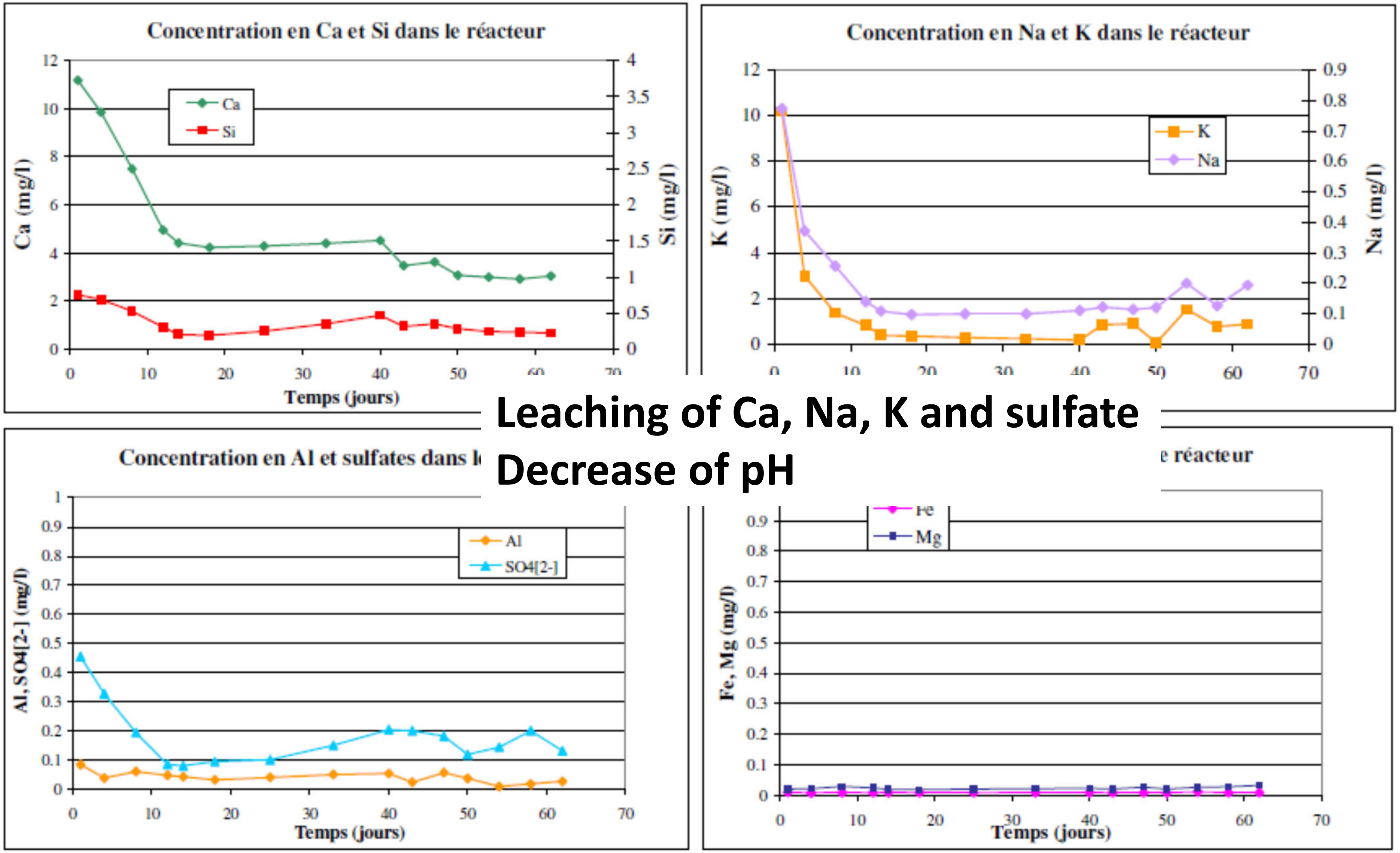




CO_2 solution 0.035%



Carbonation of cements in solution: B) PhD Albert



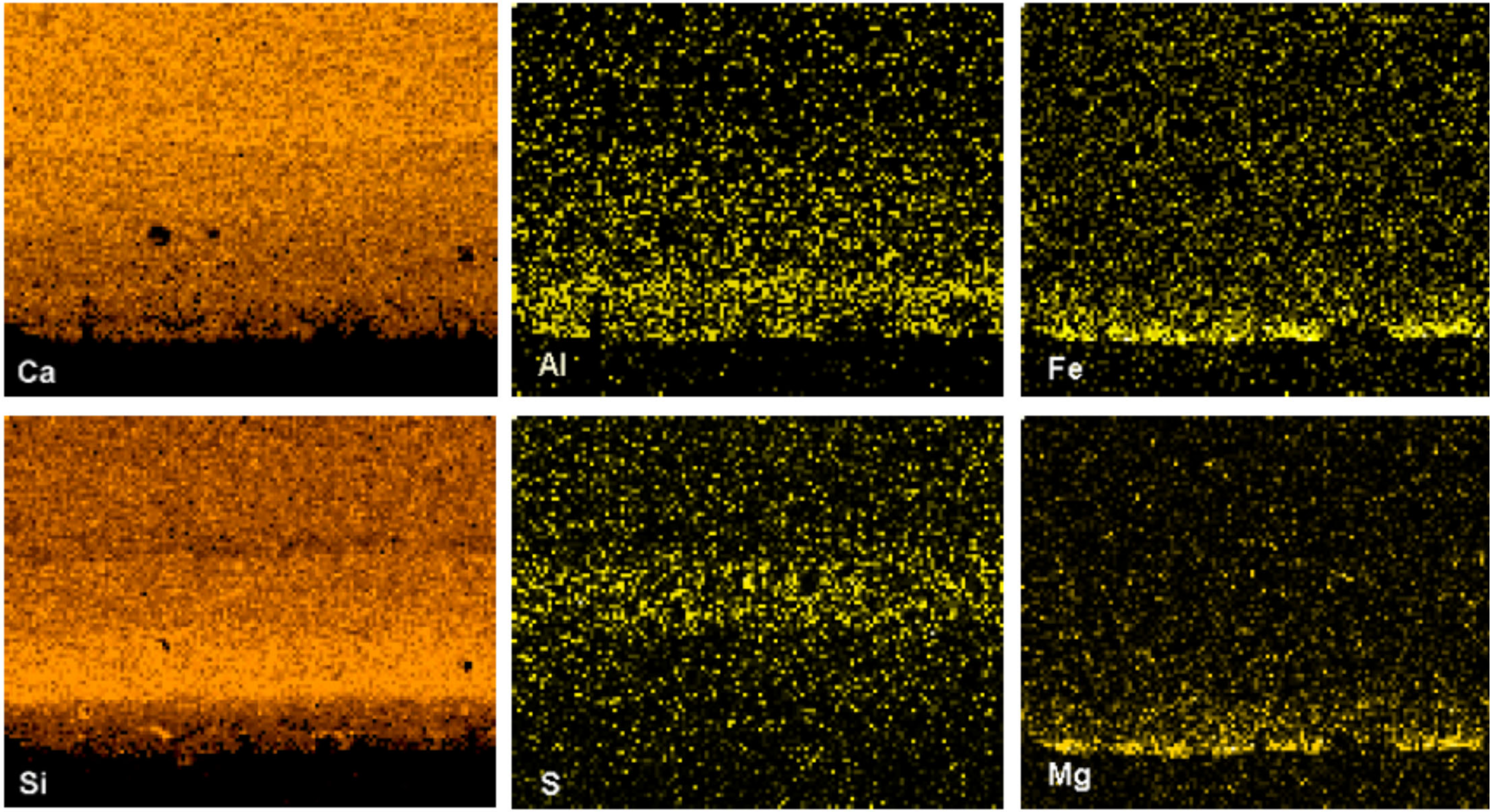
Leaching of Ca, Na, K and sulfate

Decrease of pH

Fig. V-34 : Concentrations en Ca, Si, Na, K, Fe, Mg, Al et SO_4^{2-} dans la solution du réacteur (altération par de l'eau sous atmosphère carbonatée)

Carbonation of cements in solution: B) PhD Albert

Layers at surface enriched in Al, Fe, Mg => Hydrotalcite, Fe(OH)3
Sulfate accumulation, Leaching of Ca



Carbonation of cements in solution: B) PhD Albert

Layers at surface enriched in Al, Fe, Mg => Hydrotalcite, Fe(OH)3
Sulfate accumulation, Leaching of Ca and calcite formation

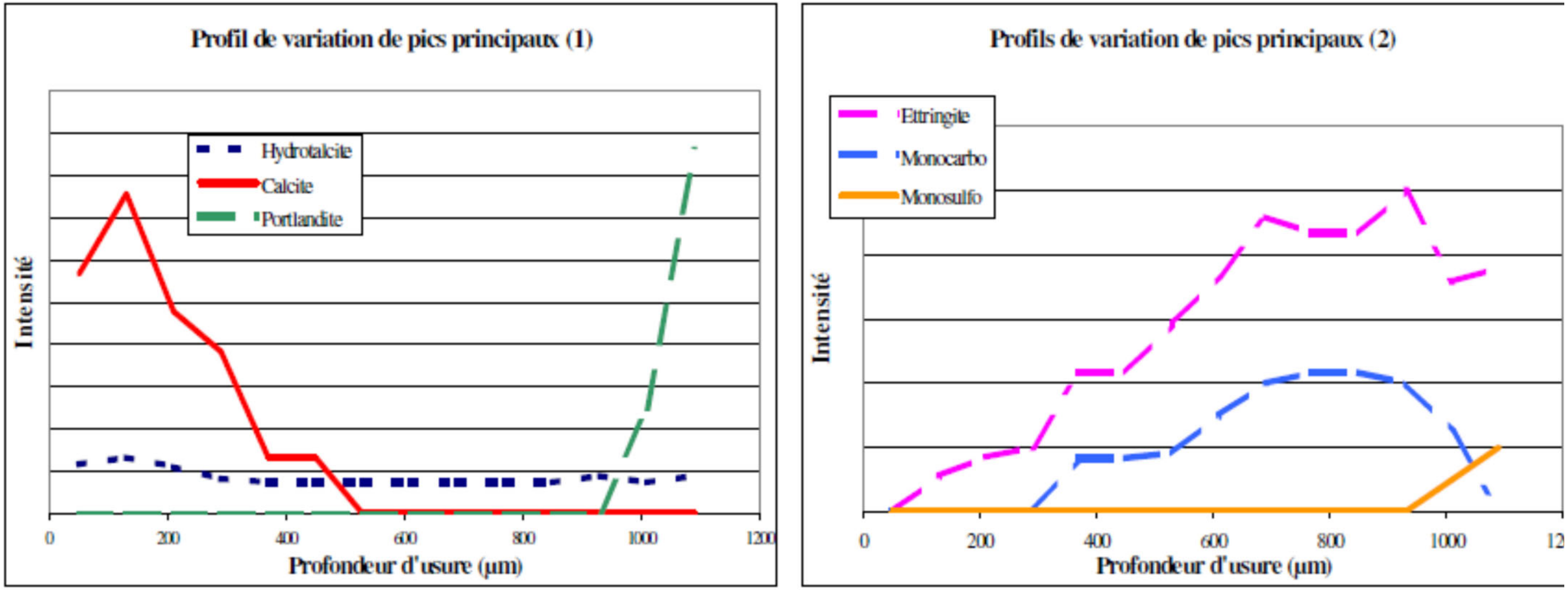


Fig. V-45 : Profils d'intensités de pics principaux des phases détectées dans l'échantillon altéré par de l'eau sous atmosphère carbonatée.

Carbonation of cements in solution:

Layers at surface enriched in Al, Fe, Mg => Hydrotalcite, Fe(OH)3
Sulfate accumulation, Leaching of Ca and calcite formation

$\Rightarrow$ **Complex behavior in solid phases**
$\Rightarrow$ **Changes in liquid with time**
$\Rightarrow$ **Decrease of pH, Ca, Na, K and sulfate**
$\Rightarrow$ **Solution experiments: leaching and carbonation**

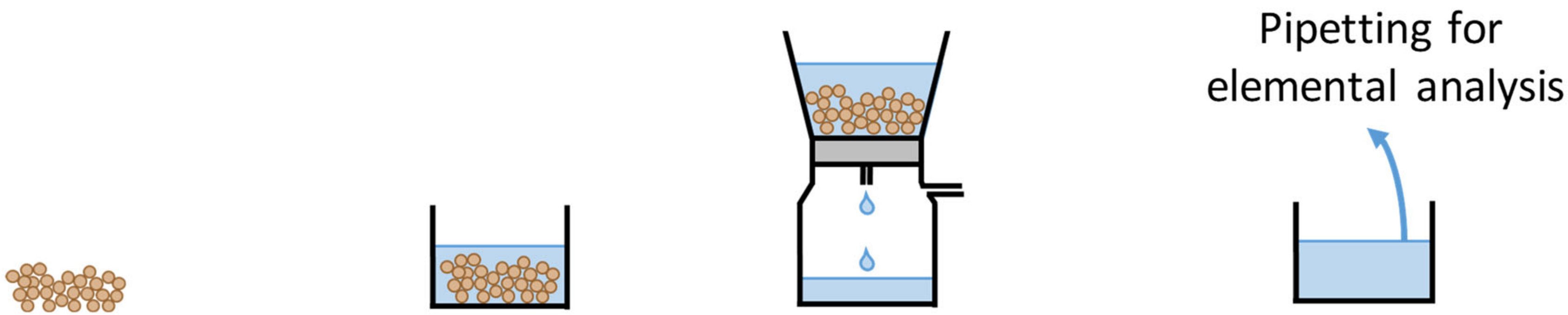
⇕

Pore solution in mortars?

Effect of carbonation on pore solution

- Carbonated concrete usually has low moisture content
- Challenging to obtain pore solution by extraction under pressure

2. cold water extraction (CWE + ICP), a leaching method



1) Preparation (grinding)

2) Extraction (leaching + filtering)

3) Analysis of the pore solution

De Weerdt K., Plusquellec G., Belda Revert A., Geiker M.R., Lothenbach B. (2019), Effect of carbonation on the pore solution of mortar, CCR 118, 38-56

Effect of carbonation on pore solution

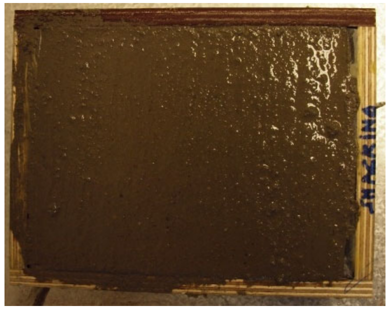
CEM I
CEM II/B-V
(30% fly ash)

w/b = 0.55
s/b = 3

Sealed reference
20 °C, 100% RH, 9 weeks

Casting → Wrapping in plastic
20 °C, 13 days

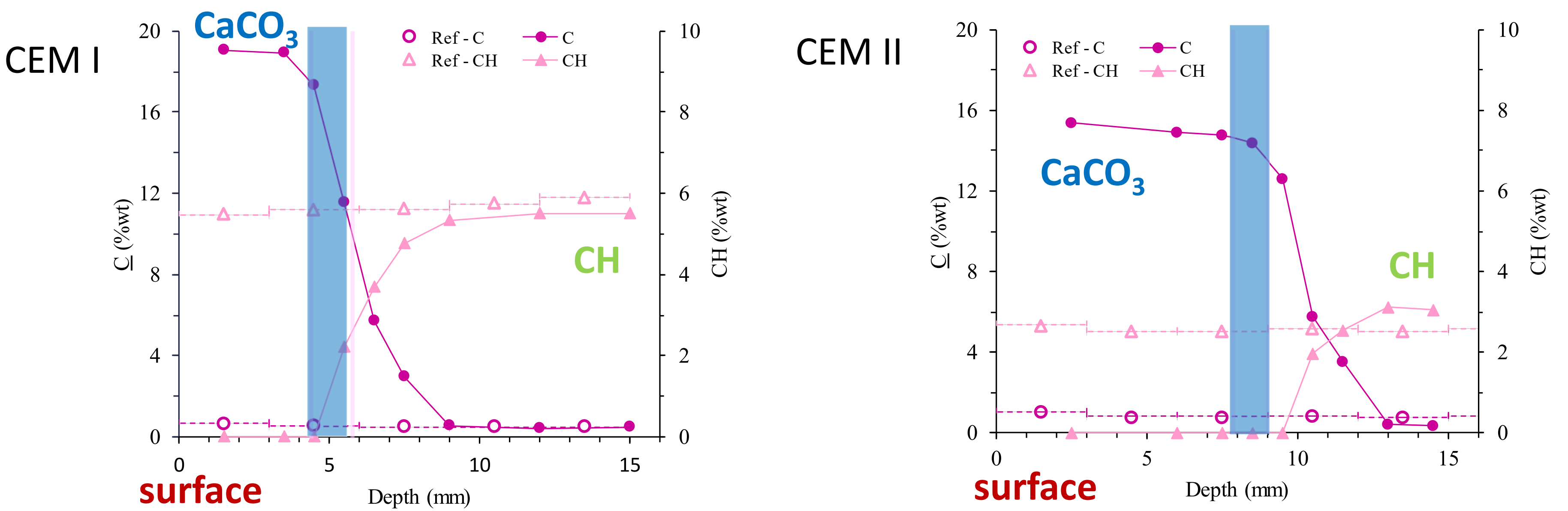
Carbonation
20°C, **60% RH, 1% CO_2**, 9 weeks



Effect of carbonation on pore solution

- pH indicators and TGA

First plateau detected using TGA corresponds to carbonation depth distribution determined using pH indicator thymolphthalein



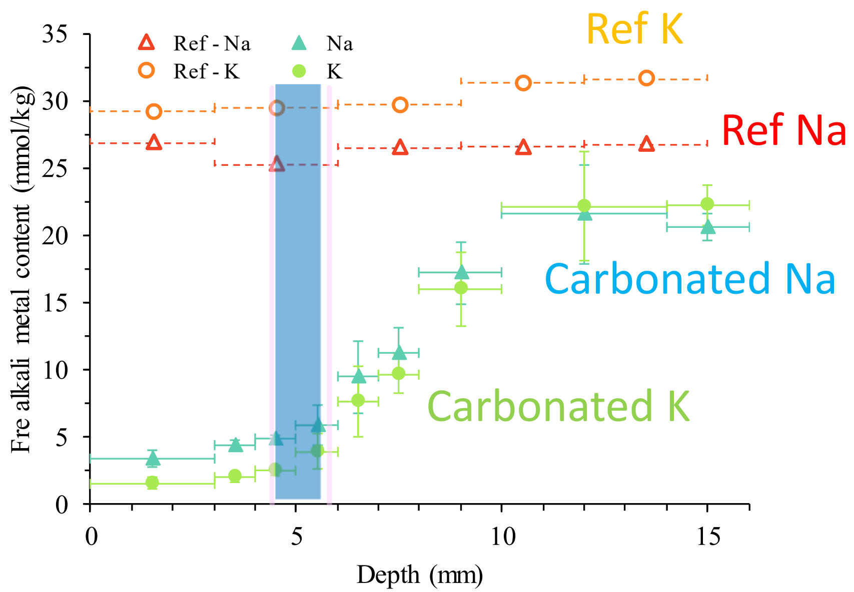
- CEM II/B-V lower carbonation resistance than CEM I
- Decrease of portlandite content with carbonation
  Increase of carbonate content

Effect of carbonation on pore solution

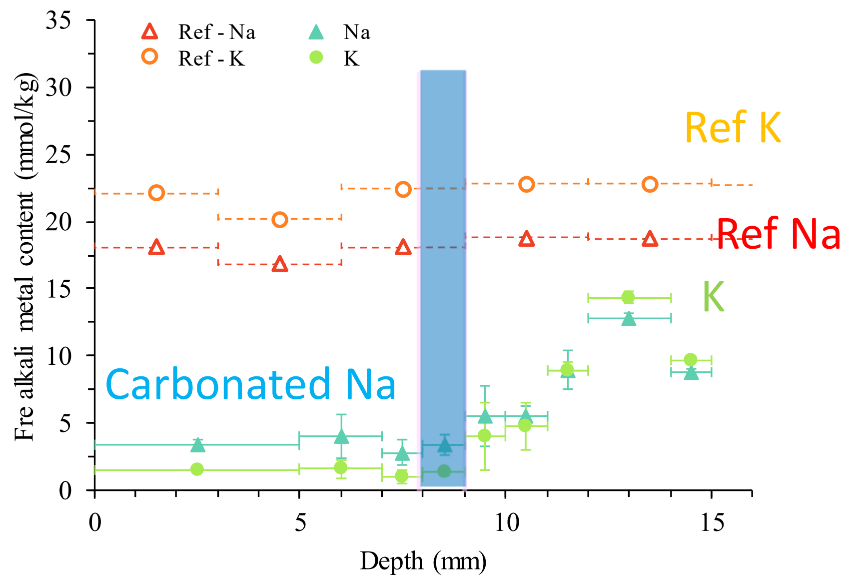
CWE corresponds to carbonation depth
No release of sorbed ions during CWE

- pH indicator and CWE

CEM I

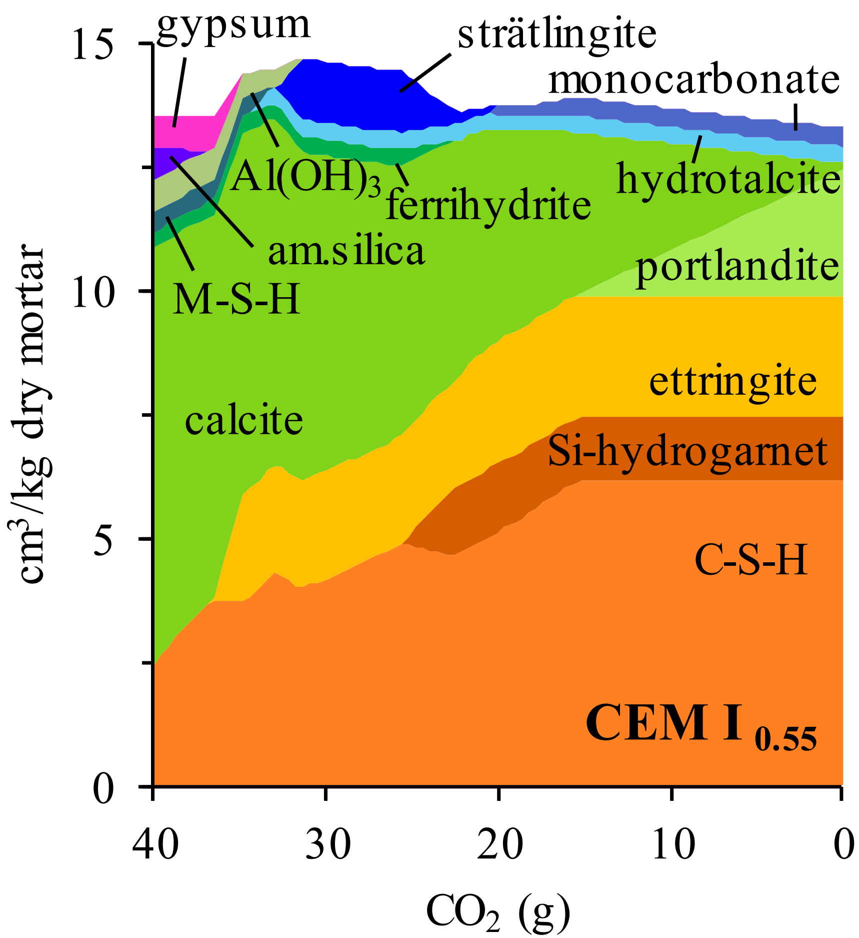


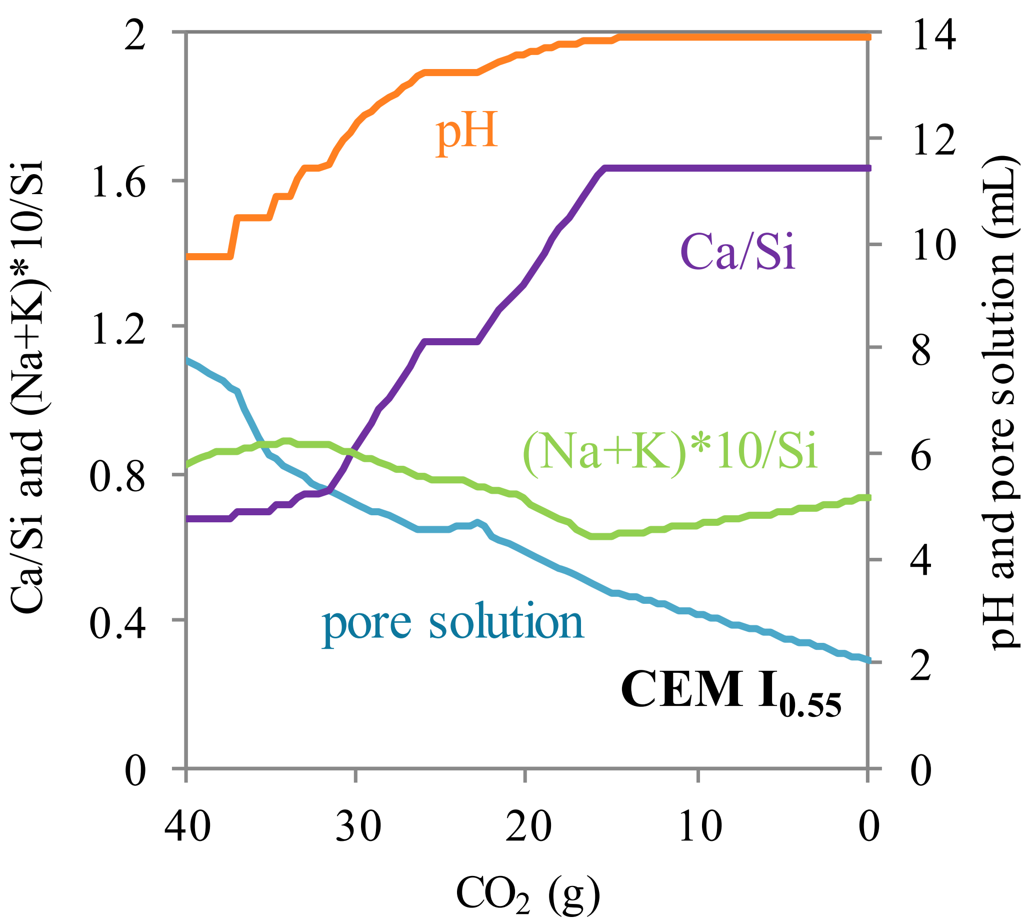
CEM II



- Ref samples. Na & K constant with depth: homogeneous
  K > Na : reflects the raw materials composition
- Decrease of Na & K content upon carbonation → binding. Where?
- Decrease occurs deeper for CEM II (less CaO)

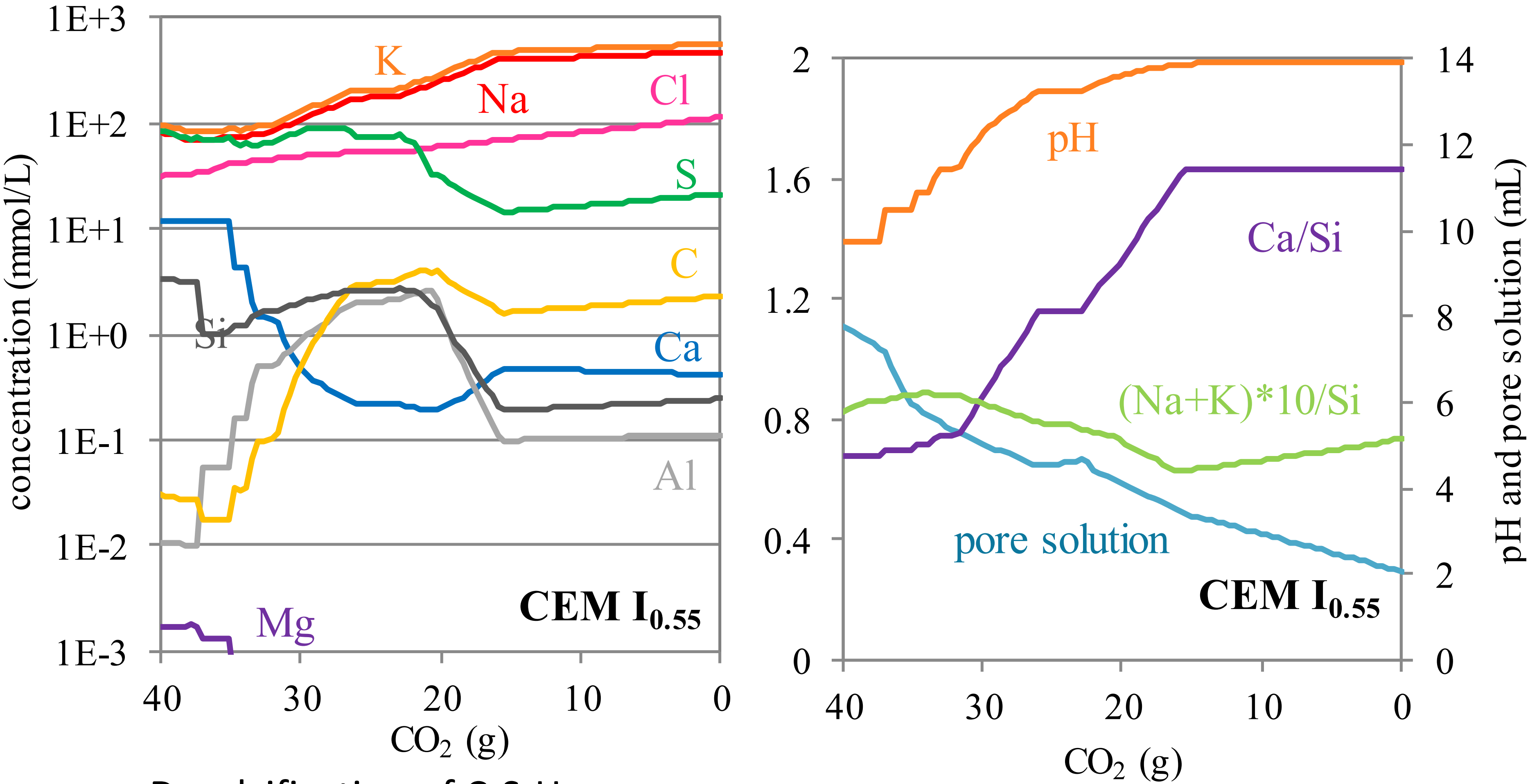
Effect of carbonation on pore solution: modelling





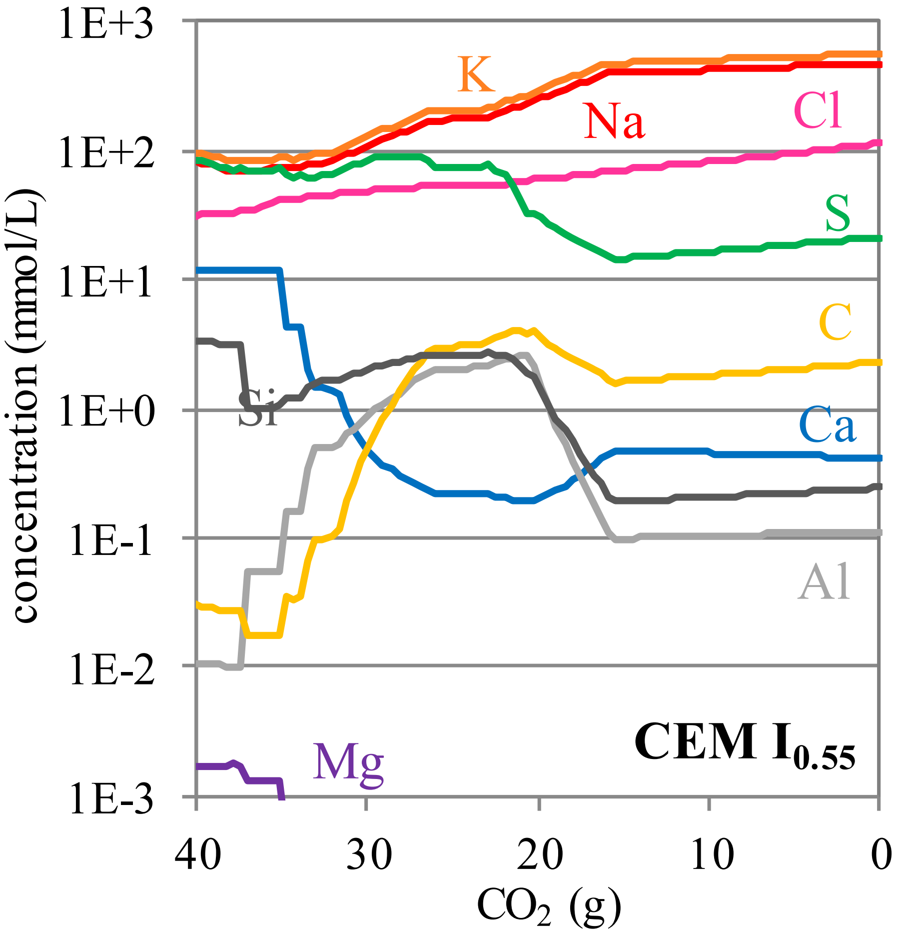
- Decrease of CH
- Decrease of pH
- Decalcification of C-S-H
- Increase of alkali binding by C-S-H

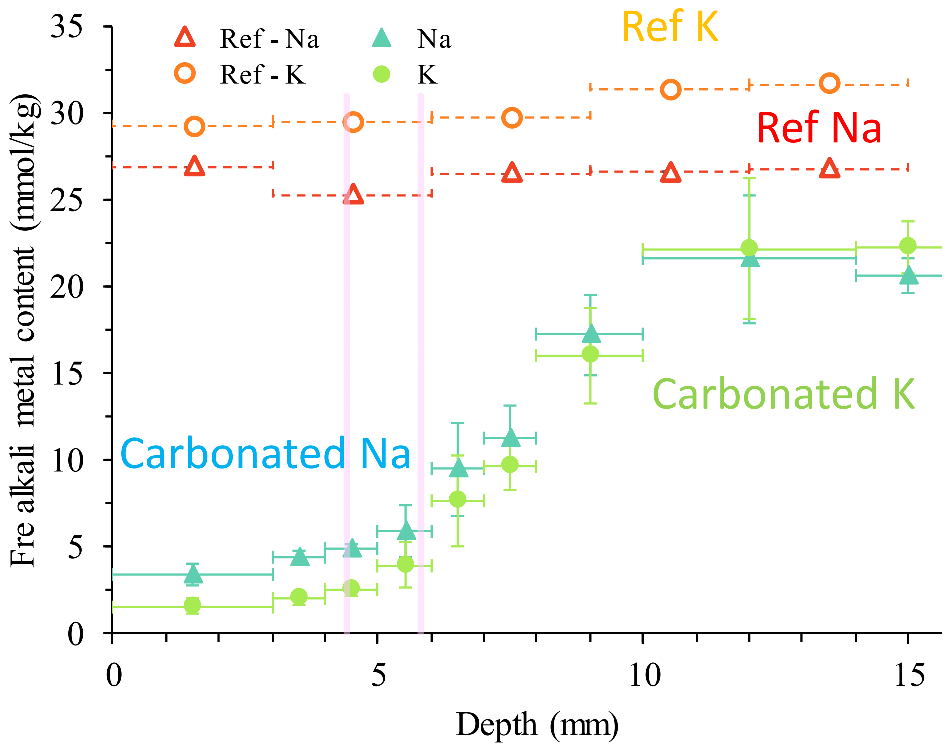
Effect of carbonation on pore solution: modelling



- Decalcification of C-S-H
- Increase of alkali binding by C-S-H
- Drop of Na and K in the pore solution
- **Increase of S in pore solution**

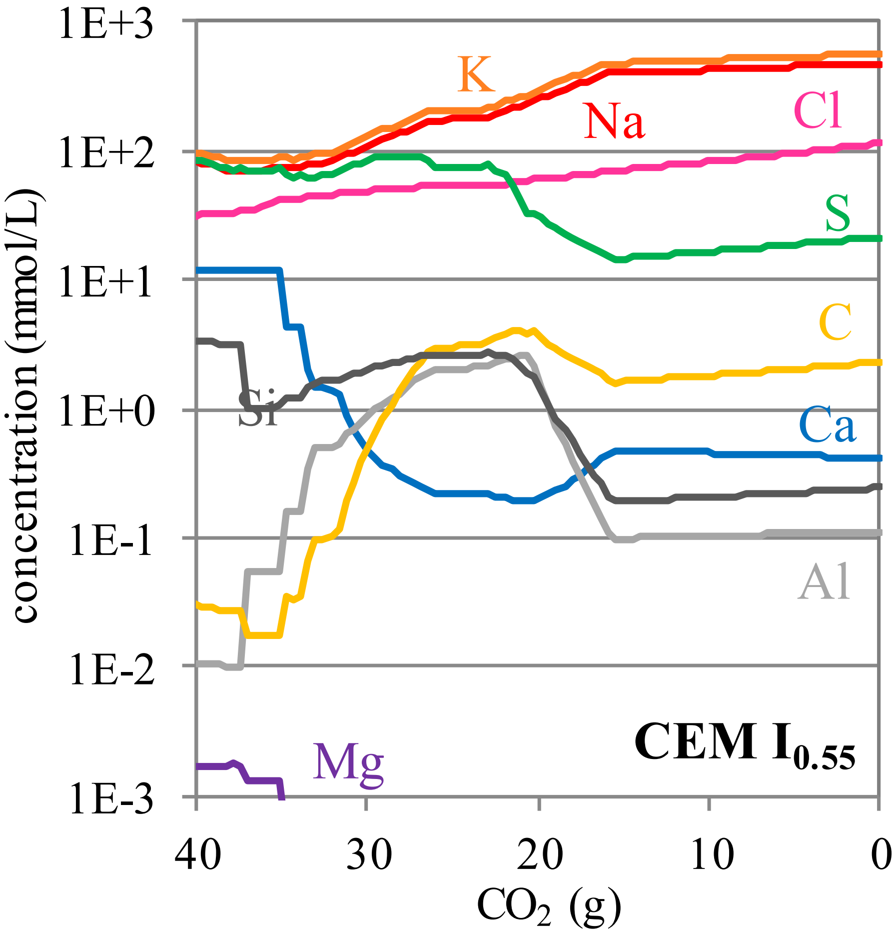
Effect of carbonation on pore solution: modelling

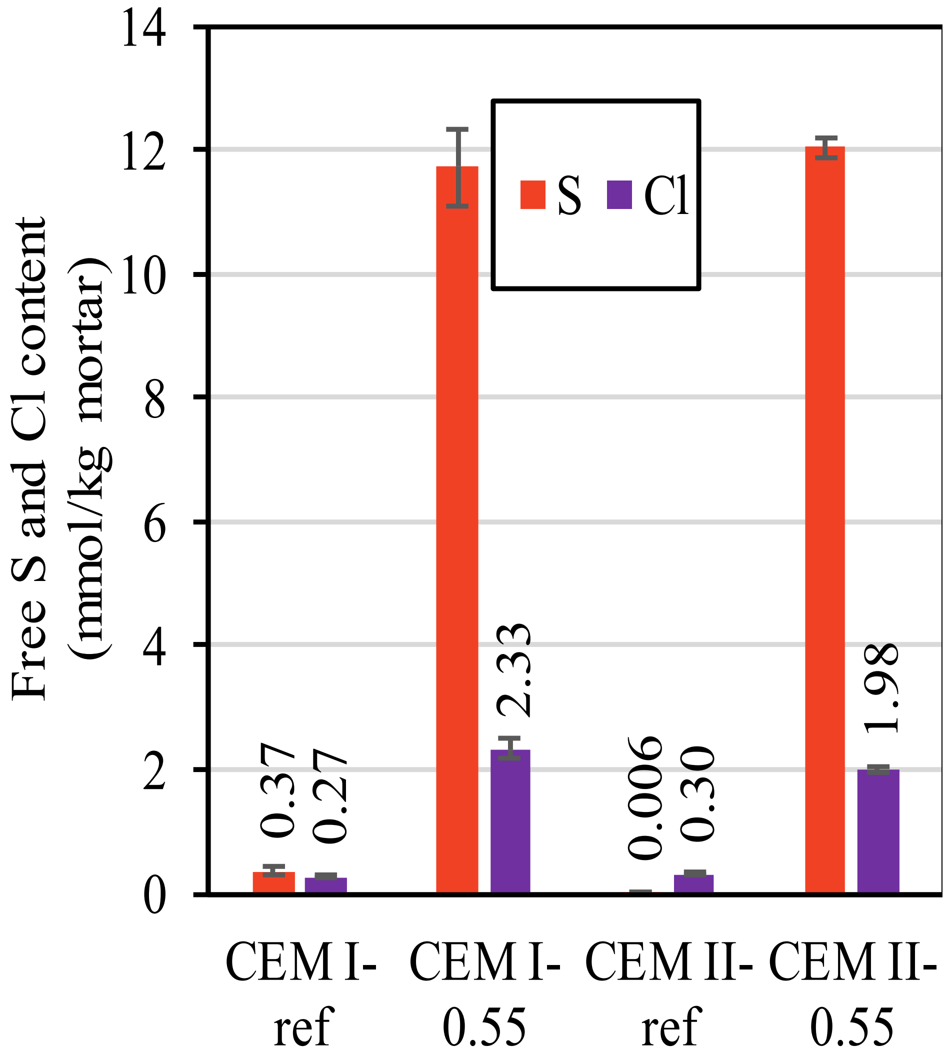




- Decalcification of C-S-H
- Increase of alkali binding by C-S-H
- Drop of Na and K in the pore solution
- **Increase of S in pore solution**

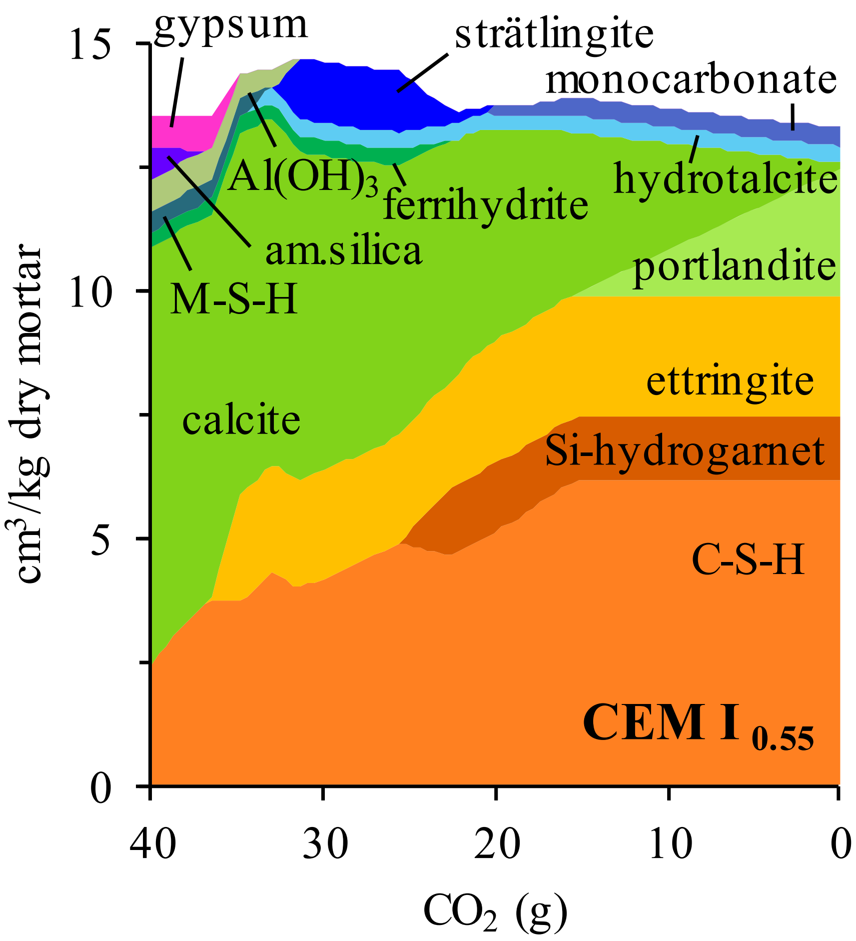
Effect of carbonation on pore solution: modelling

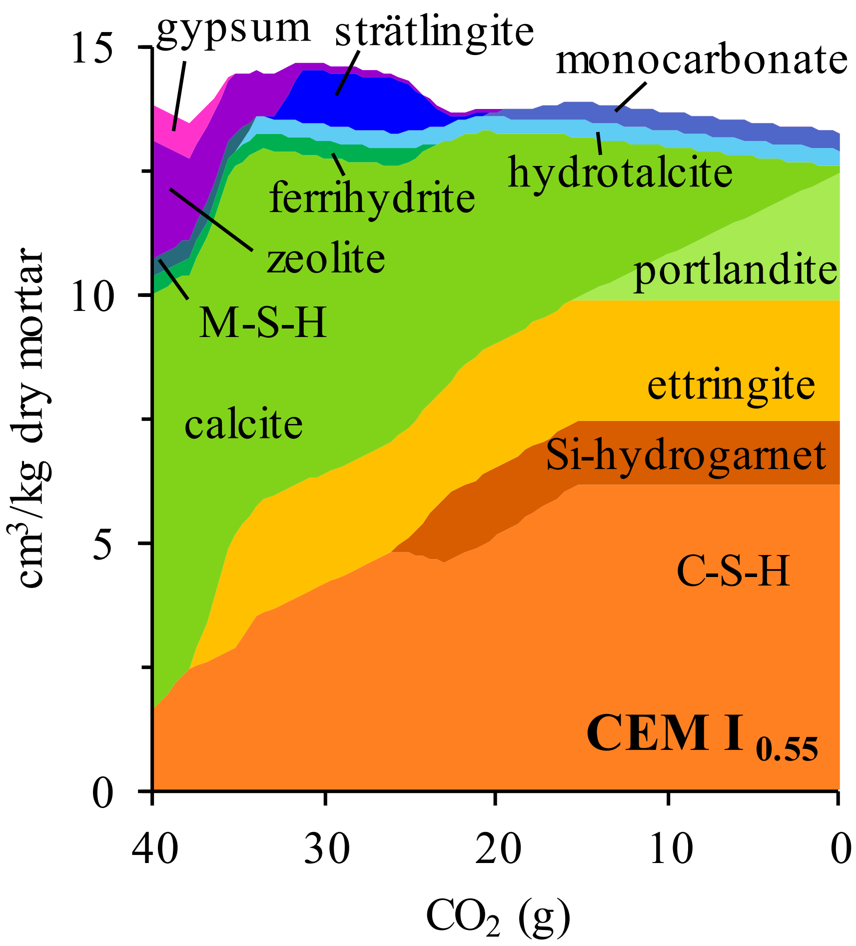




- Decalcification of C-S-H
- Increase of alkali binding by C-S-H
- Drop of Na and K in the pore solu
- **Increase of S in pore solution**

Effect of carbonation on pore solution: zeolites?





No zeolites

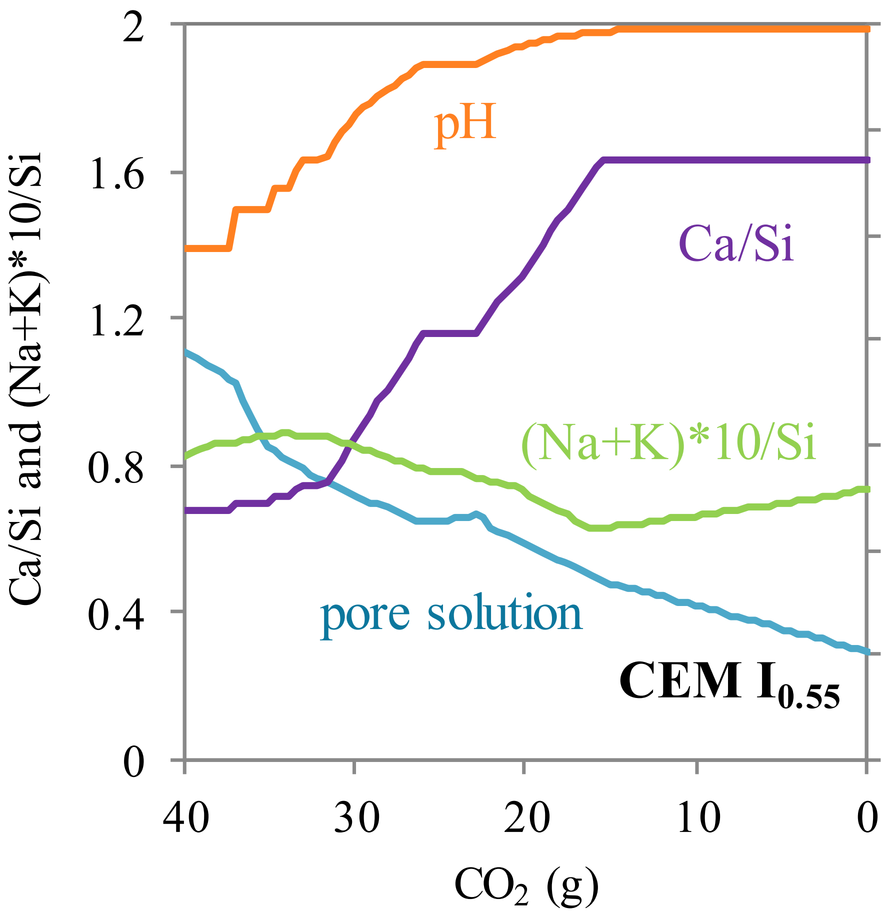
Experimental evidence unclear

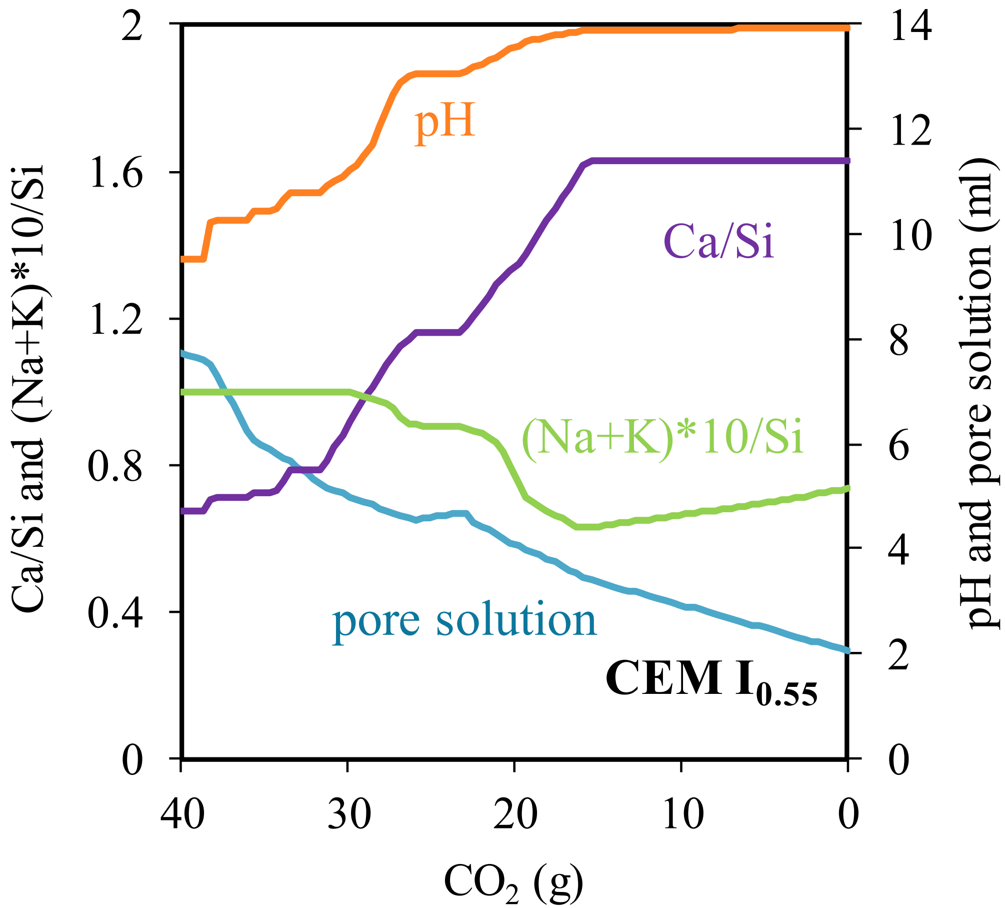
Zeolite formation possible

natrolite: NAS_3H_2,

K-phillipsite: KAS_6H_6

Effect of carbonation on pore solution: zeolites?





No zeolites

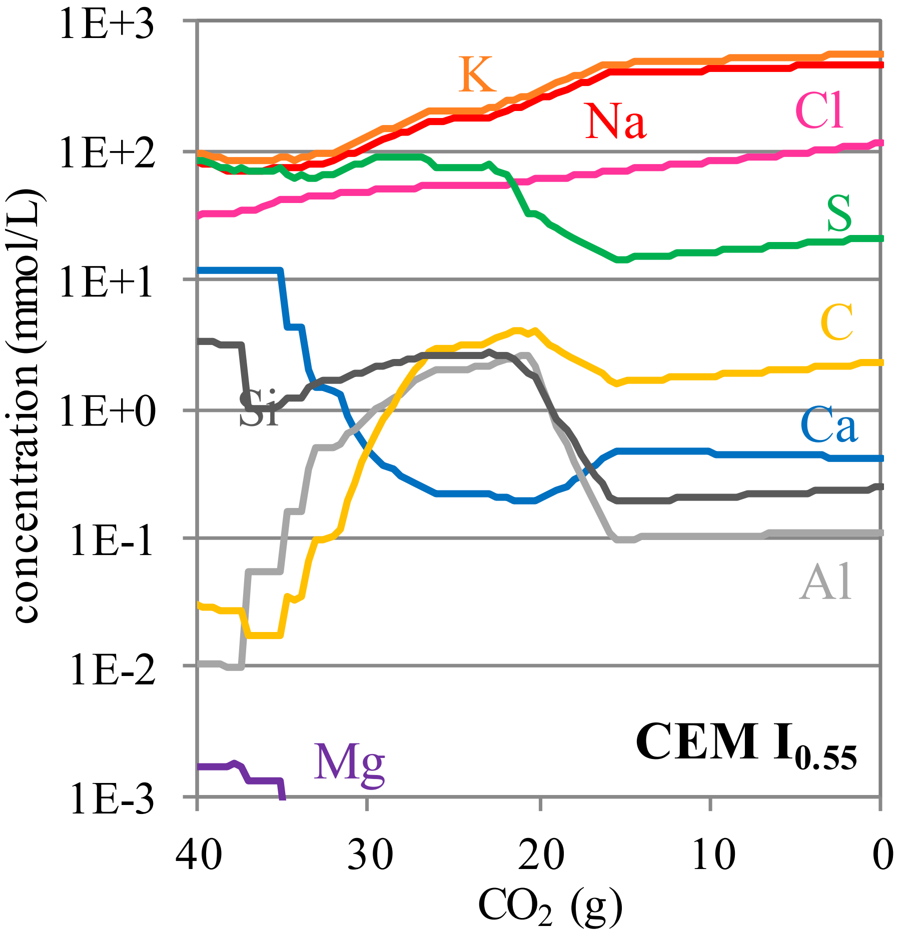
Experimental evidence unclear

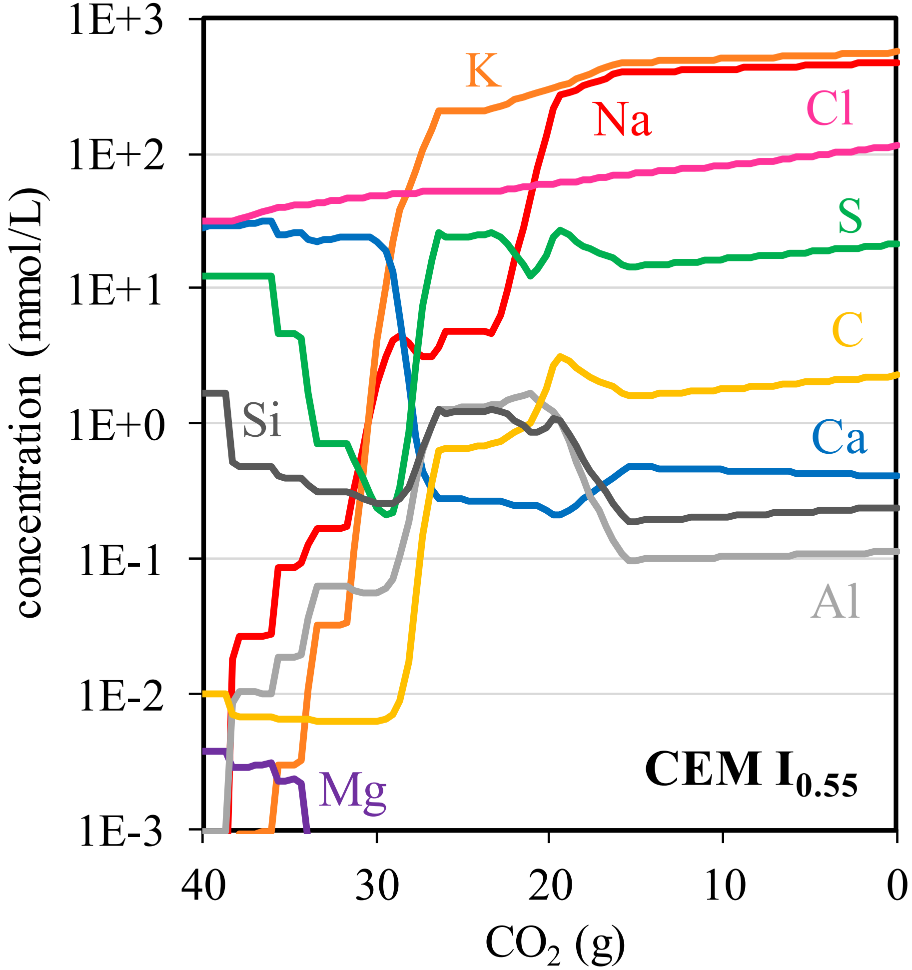
Zeolite formation possible

natrolite: NAS_3H_2,

K-phillipsite: KAS_6H_6

Effect of carbonation on pore solution: zeolites?





No zeolites

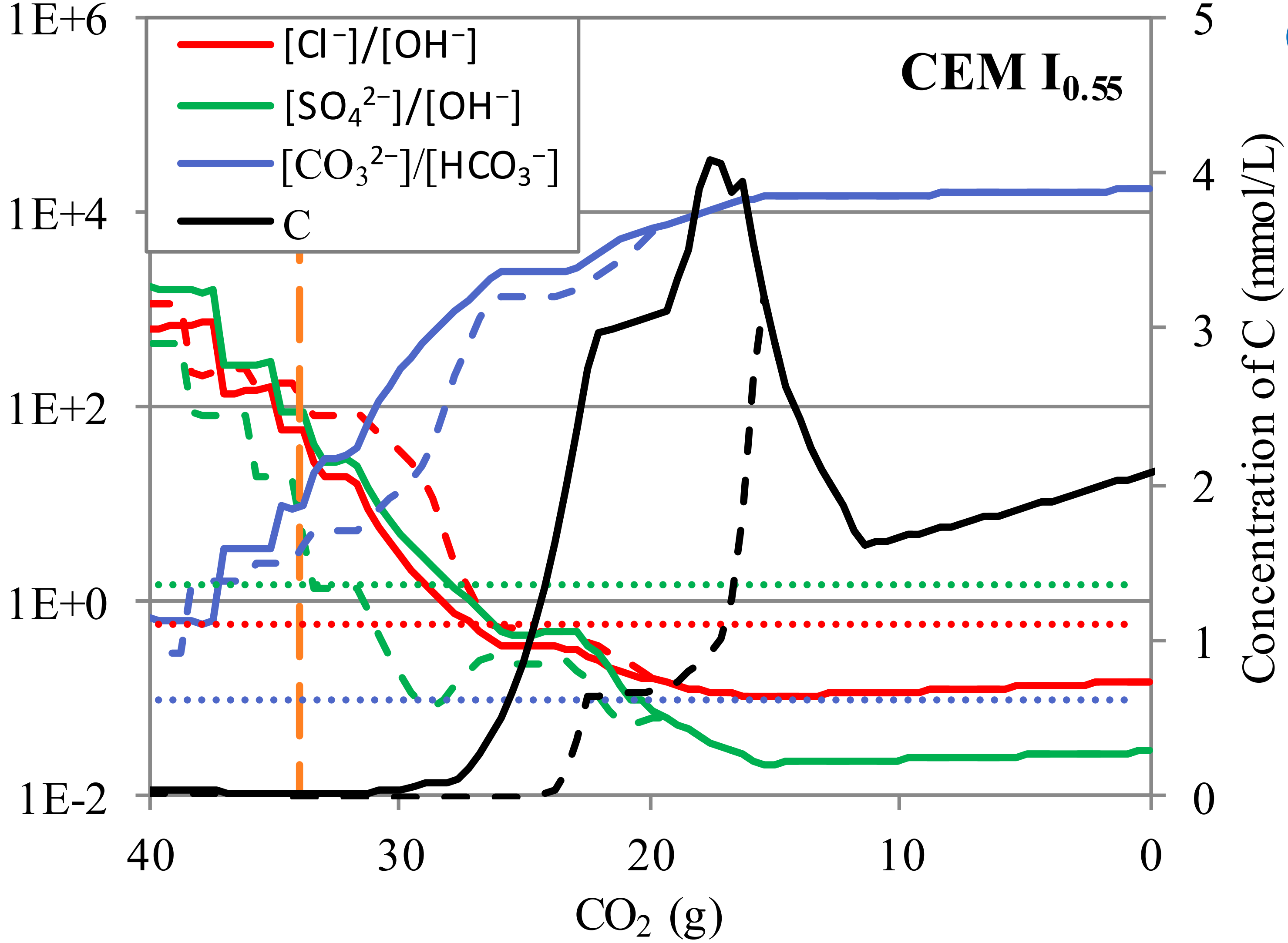
Experimental evidence unclear

Zeolite formation possible

natrolite: NAS_3H_2,

K-phillipsite: KAS_6H_6

Implications on corrosion of embedded steel



Cl^-/OH^- ↑

SO_4^{2-}/OH^- ↑

CO_3^{2-}/HCO_3^- ↓

Increased corrosion risk

Conclusion pore solution

- Different experimental methods give comparable results

- Effect of carbonation on pore solution
  - Decrease of pH
  - Decrease of the free Na and K
  - Increase of sulfate
  - More studies needed
  - Refined experimental methods needed

- Carbonation increases the risk of corrosion as
  Cl^-/OH^- ↑ SO_4^{2-}/OH^- ↑ CO_3^{2-}/HCO_3^- ↓