Changes of microstructure and diffusivity in blended cement pastes exposed to natural carbonation

Wioletta Soja, Hamed Maraghechi, Fabien Georget and **Karen Scrivener**

EPFL

LABORATORY OF CONSTRUCTION MATERIALS

Supplementary Cementitious Materials → an efficient way to reduce CO_2 emission during cement production

Current typical level of SCM replacement in Europe is up to 35% for CEM II/B

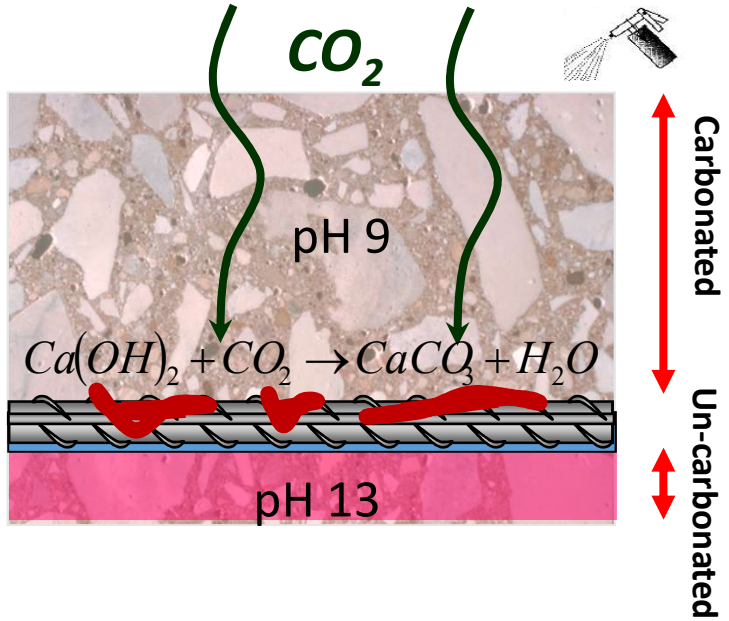
Factors inhibiting increase of SCMs:

- Decreased early-age mechanical properties (slower reaction of SCMs)

- Uncertainties about long-term performance: CARBONATION (lower buffer capacity)

B. Metz, O. Davidson, H. de Coninck, M. Loos, and L. Meyer, "IPCC Special Report on Carbon Dioxide Capture and Storage," 2005.

Carbonation reaction → rebar corrosion



- Lowering pH of concrete pore solution
- Dissolution of protective surface oxide layer of steel bars
- Steel rebar corrosion

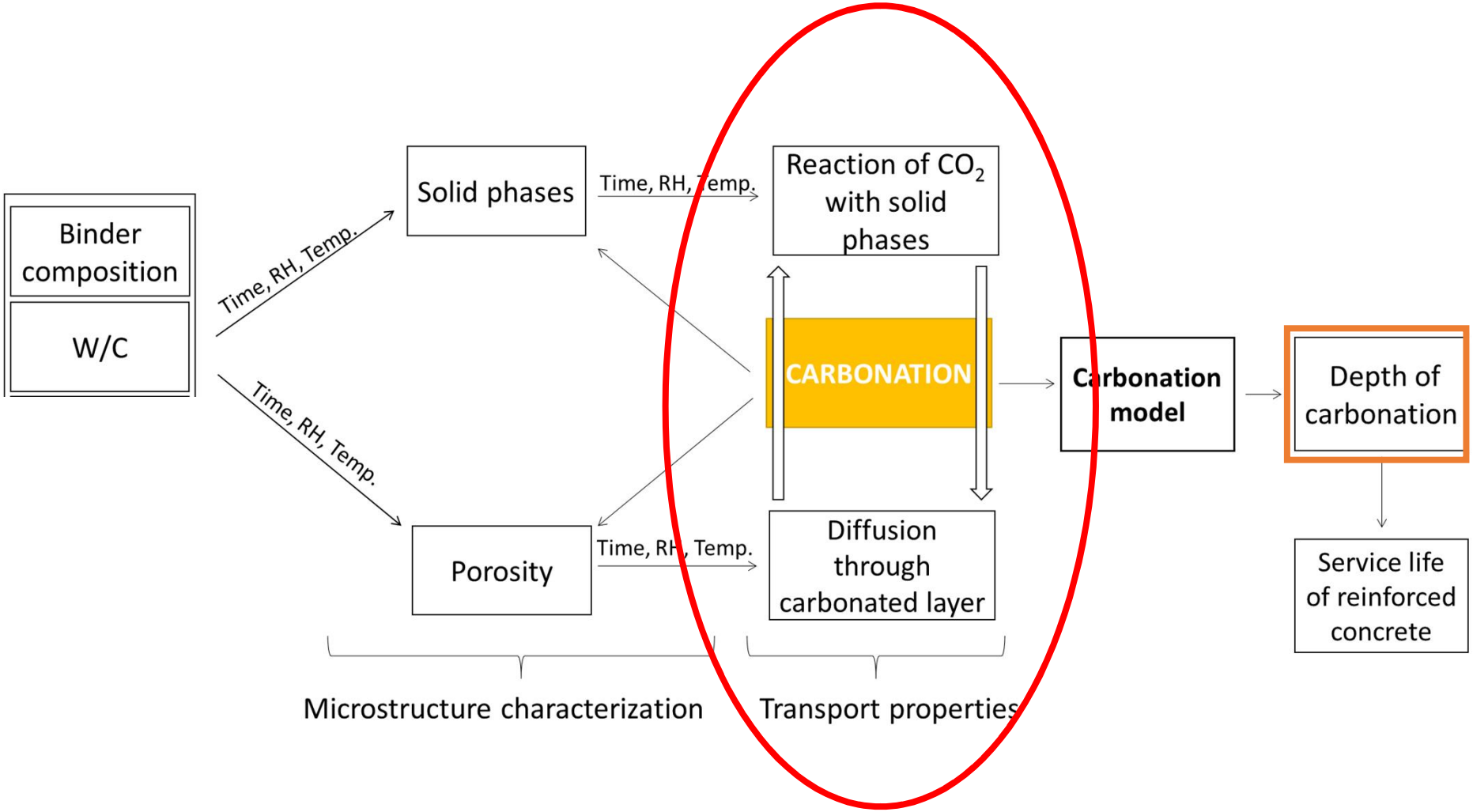
$CH + CO_2 \rightarrow CaCO_3 + H_2O$

C-S-H + CO_2 → various intermediates → $CaCO_3 + SiO_2nH_2O + H_2O$

Aluminate hydrates + CO_2 → $CaCO_3$ + hydrated alumina

Ferrite hydrates + CO_2 → $CaCO_3$ + hydrated alumina + iron oxides

Factors involved in prediction of carbonation rate – Research Matrix

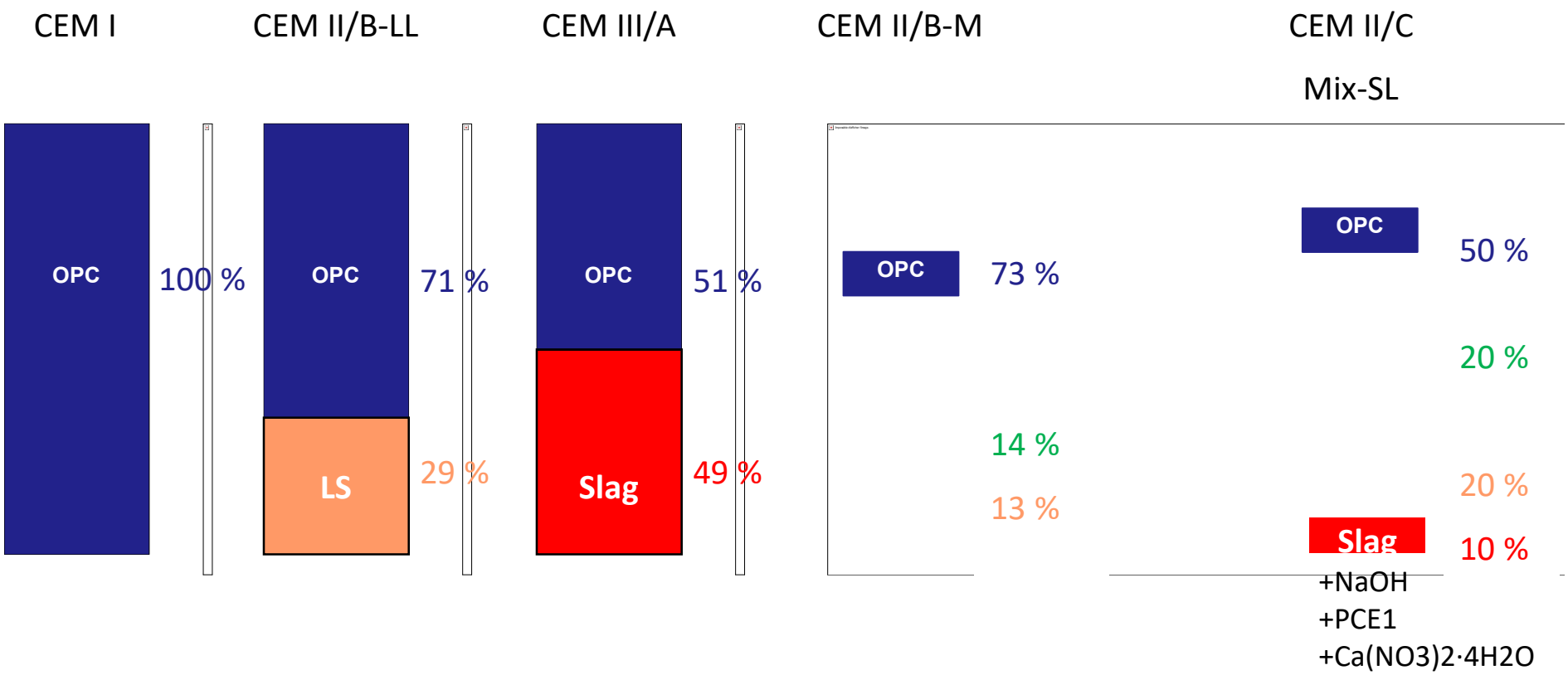


SMALL INTERLUDE ON MODELLING:
FABIEN GEORGET

Materials

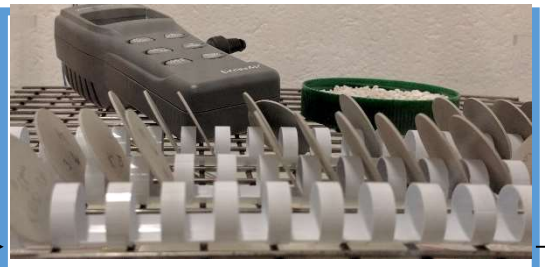
Cements available on the market provided by Lafarge-Holcim:

New mix developed at ETHZ:



Techniques - cement paste study

Samples preparation and exposure conditions:



Conditioning:
RH= 70 %
CO_2: Ambient (400ppm) and 0 ppm

70% RH pores > 3-4 nm contain gas

Mixing with vacuumed mixer (w/c=0.40)

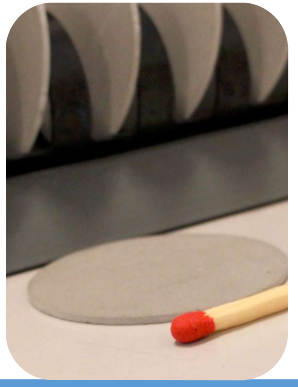
24h

Demolding

Curing up to 28 days in RH>95%

Cutting 1 mm thin slices, diameter of 32 mm

Testing at different ages:
1, 2, 3 and 6 mounths



Influence of ITZ in concrete

Data from: "The Role of Paste Volume on Performance of Concrete" by G. Hermida, M. Moranville, and R.J. Flatt:

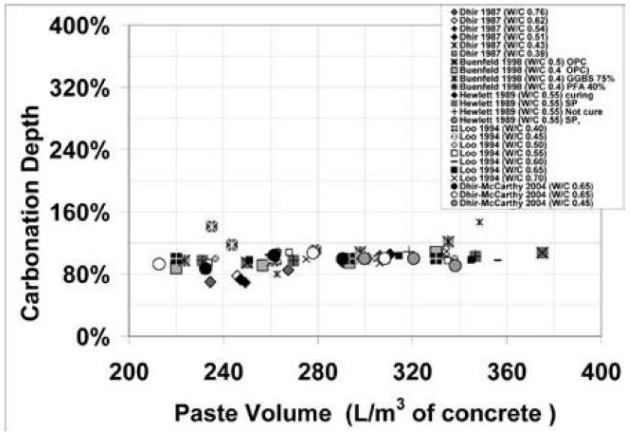
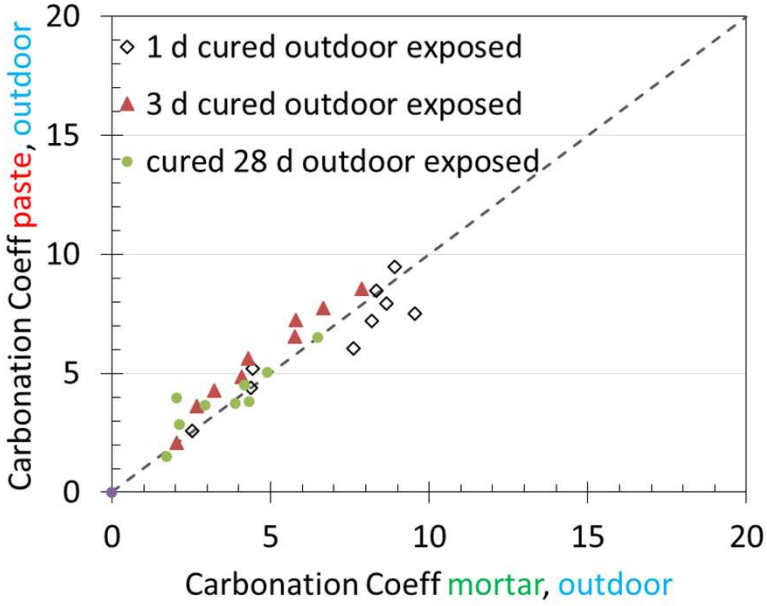
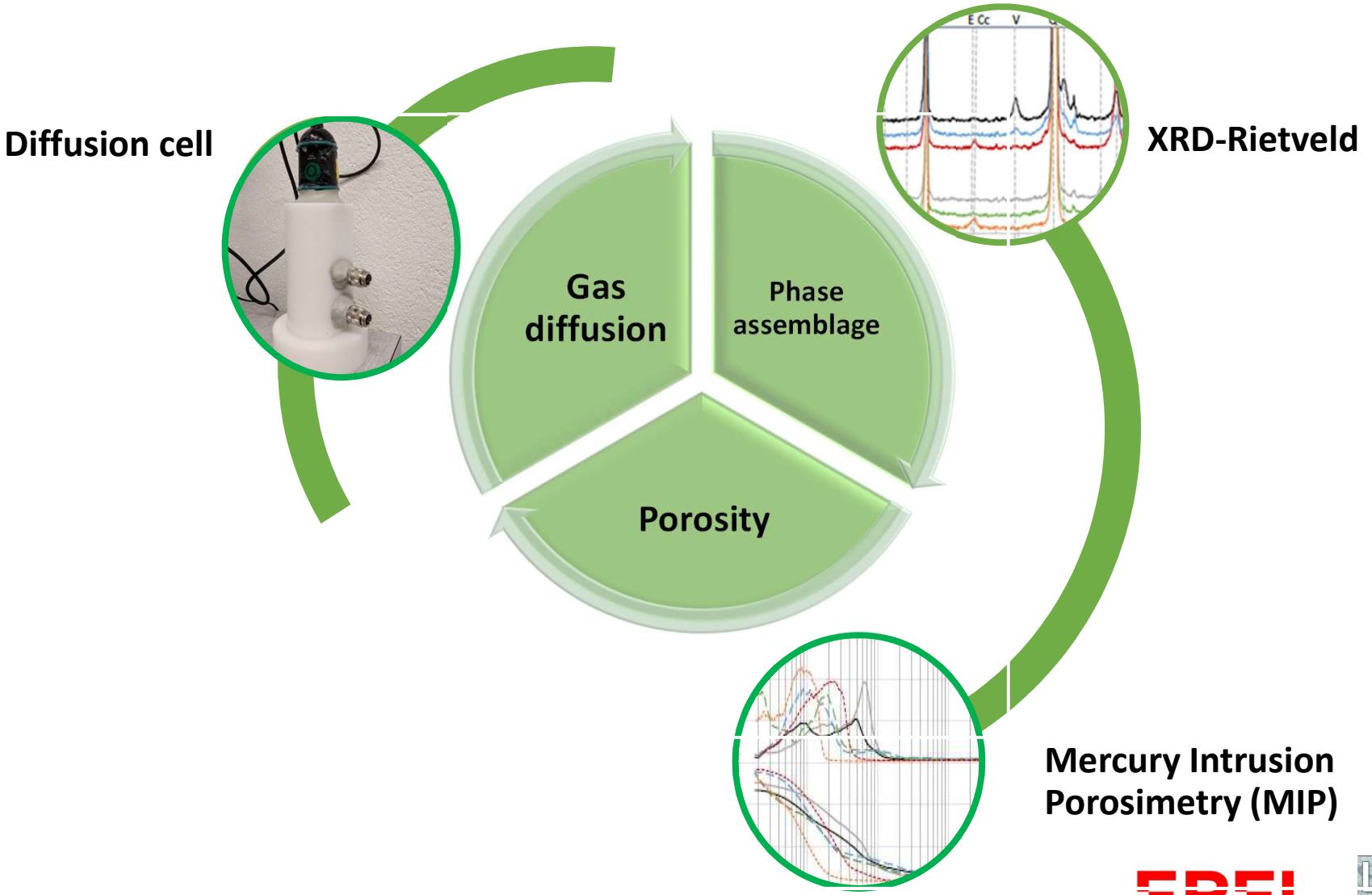


Fig. 6—Relation between volume of paste (cement volume + free water volume) and depth of accelerated carbonation for different test series (300 L/m³ of paste corresponds to a depth of 100%). Each series had a constant *w/cm*.[8,23,24,32,36]

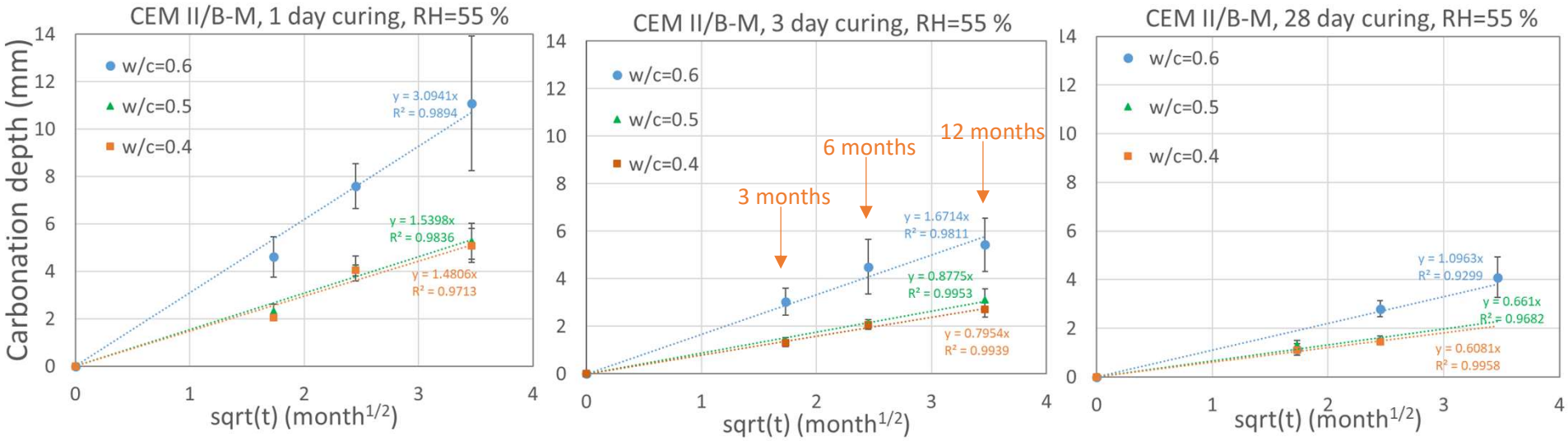
Data from H. Maraghechi, LC3 systems:



Techniques - cement paste study



Carbonation depth (influence of curing time and w/c)

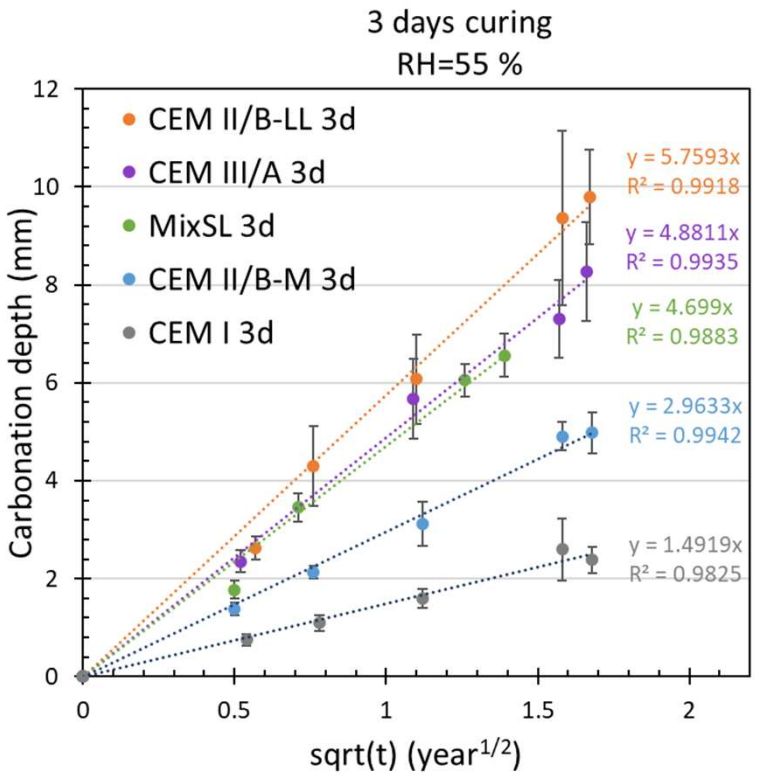


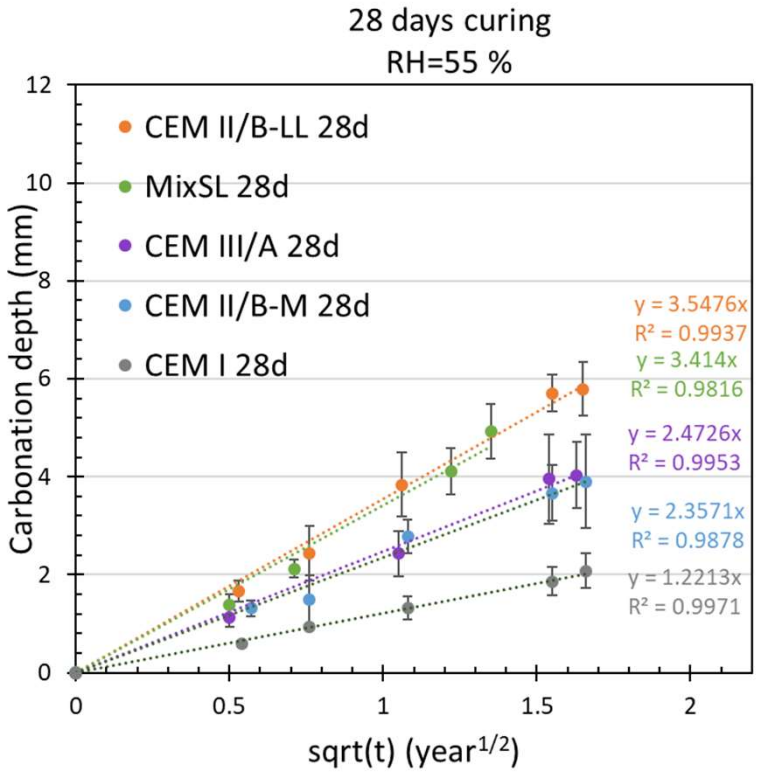
Increase of carbonation depth in concrete with:

- decrease of curing time (more significant difference between 1 and 3 days than 3 and 28 days of curing)
- increase of w/c (decrease of w/c from 0.6 to 0.5 lowers the carbonation depth by factor of 2, further decrease to 0.4 does not have significant influence)

Straight line along carbonation depth at different times gives carbonation coefficient

Carbonation of microconcrete





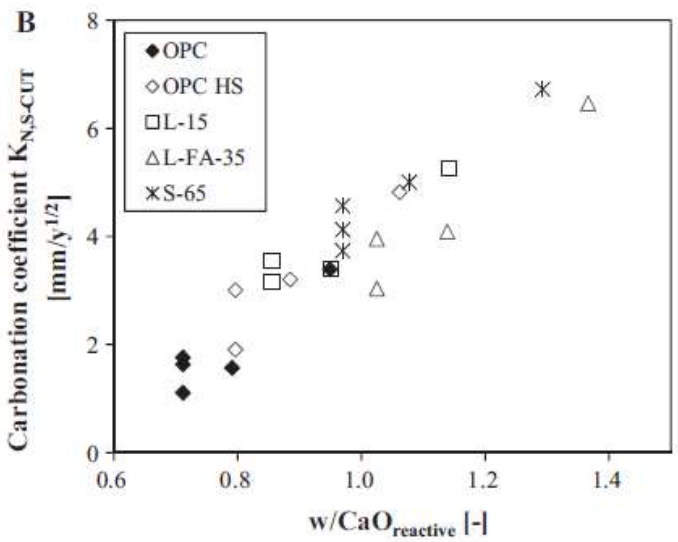
K_{3d} vs K_{28d}
-38 %
-27 %
-49 %
-20 %
-18 %

- All pastes showed carbonation depth = sq rt time

- Carbonation resistance of MixSL with 50 % of clinker replacement is as good as for CEM II/B-LL with 30 % of clinker replacement.

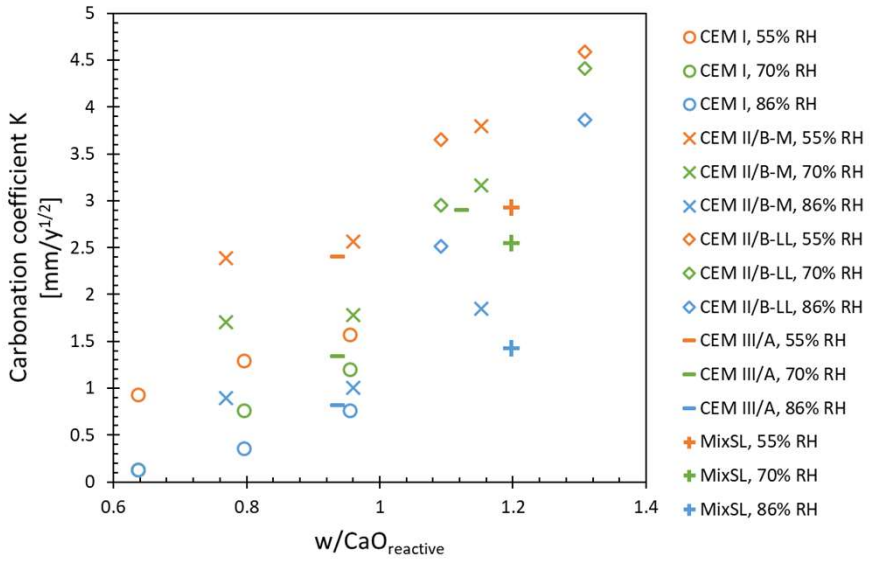
Carbonation coefficient K as a function of $CaO_{reactive}$

Paper of A. Leemann, P. Nygaard, J. Kaufmann, R. Loser (2015) (EMPA):



Carbonation coefficient KN,S in the sheltered outdoor exposure as a function of the w/$CaO_{reactive}$ of the mortar (A: R2 = 0.79) and of the concrete mixtures (B: R2 = 0.87).

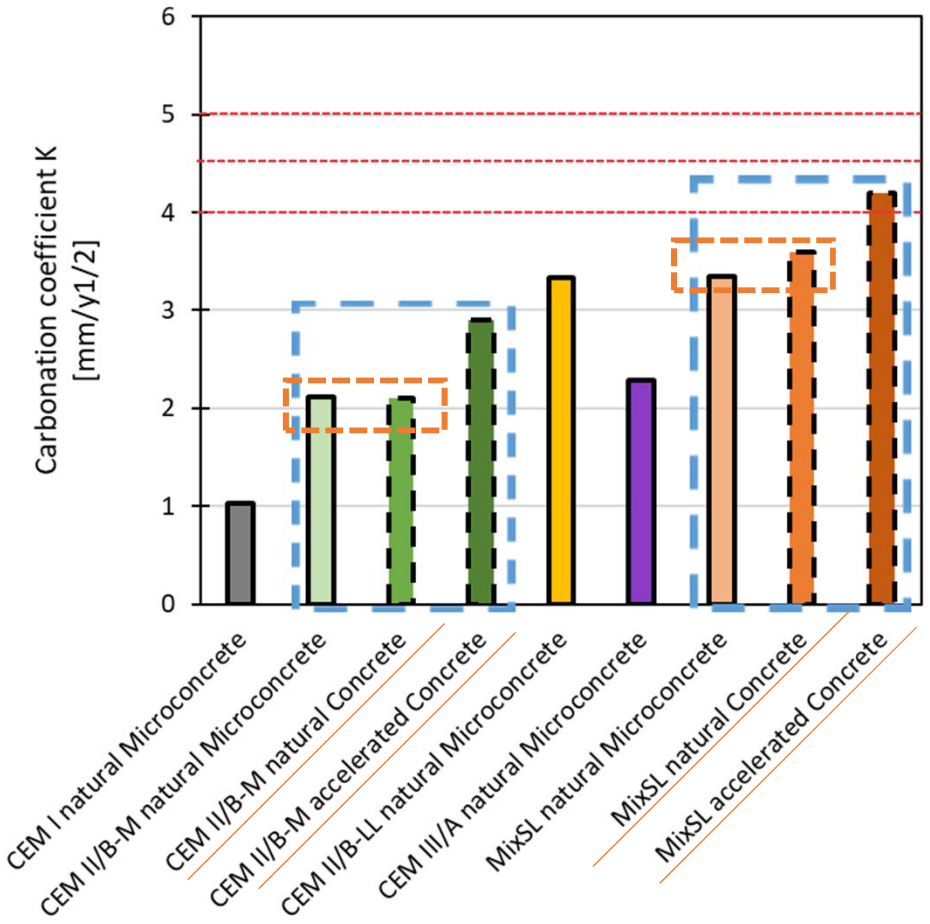
Experiments at EPFL:



Carbonation coefficient as a function of the w/$CaO_{reactive}$ of the microconcrete cured for 28 days and exposed to natural carbonation at three different RH conditions.

- Carbonation resistance can be expressed by the ratio between water and $CaO_{reactive}$
- Increase of K with increase of w/$CaO_{reactive}$ factor
- High scatter due to differect exposure conditions (different RH for experiments at EPFL)

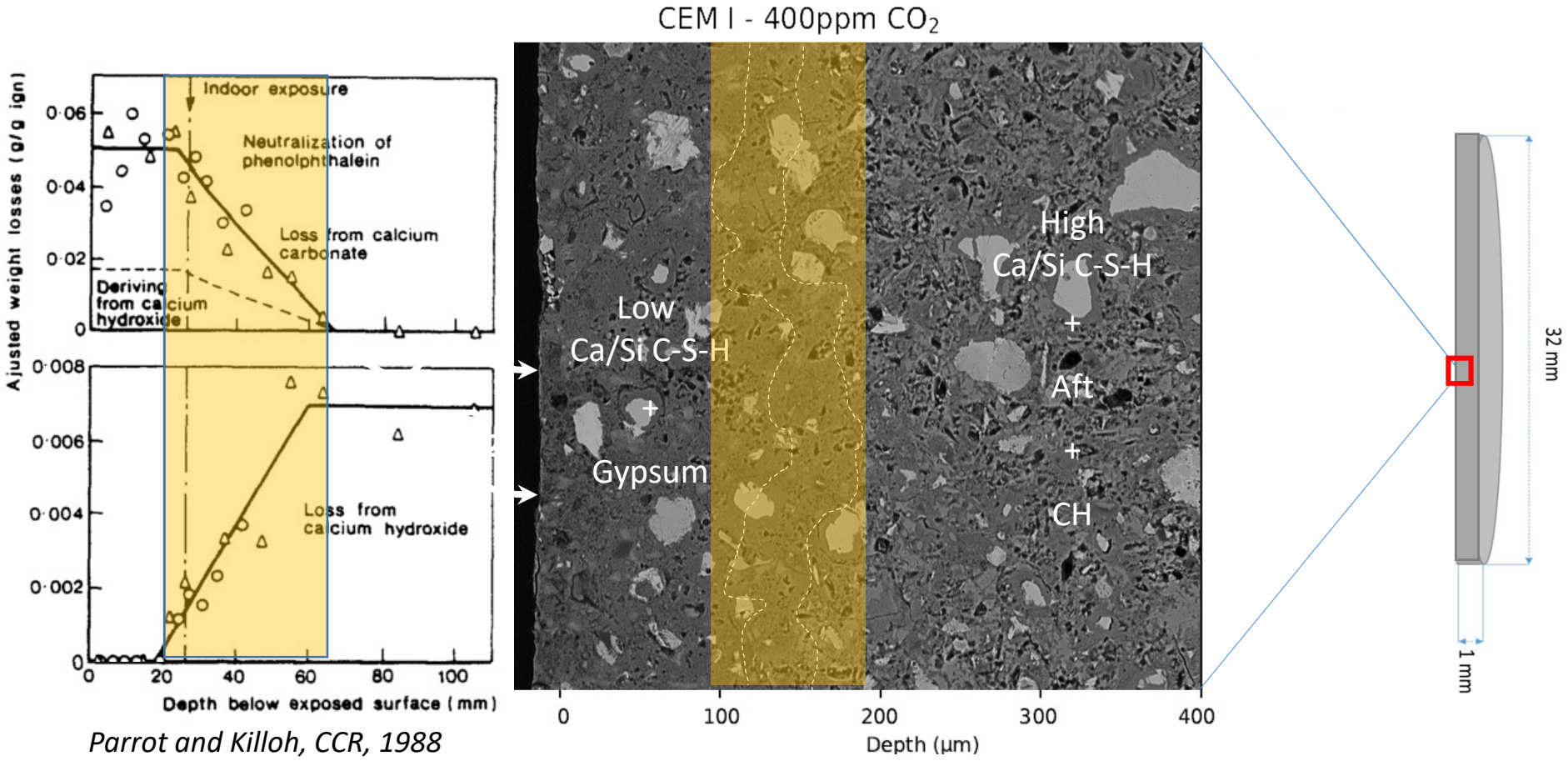
Are accelerated test reliable?



Swiss requirements:
←life span of 50 years
←life span of 100 years for XC4 exposure class
←life span of 100 years for XC3 exposure class

	Accelerated carbonation on concrete (LafargeHolcim)	Natural carbonation on microconcrete (EPFL)	Natural carbonation on concrete cast at Lafarge-Holcim exposed at EPFL
Curing:	28 days, underwater	28 days, moist room at 95% RH	28 days, underwater
CO_2: RH: T:	4% 57% ± 3% 20°C	0.04% 55% ± 5% 22°C ± 3°C	0.04% 55% ± 5% 22°C ± 3°C
Sample size: Max. aggregate size:	12 x 12 x 36 cm 32 mm (wet)	4 x 4 x 4 cm 8 mm (dry)	12 x 12 x 36 cm 32 mm (wet)

Is carbonation front sharp?



Parrot and Killoh, CCR, 1988

- Larger apparent reaction front due to the inhomogeneity of the transition front
- Actual transition front is sharp but tortuous

Carbonation Front

- Microscopically pretty sharp ~50 µm
- Macroscopic heterogeneity caused by aggregate particles

CHANGES IN SOLID PHASES

Volume changes

portlandite

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

vol 33.0 36.9 ΔV = + 11.8%

C-S-H

$$Ca_{1.7}SiH_8O_{7.7} + CO_2 \rightarrow 1.7CaCO_3 + SiO_2nH2O + 4H_2O$$

vol 113.7 62.8 22-85

ΔV = - 25.4% +30%

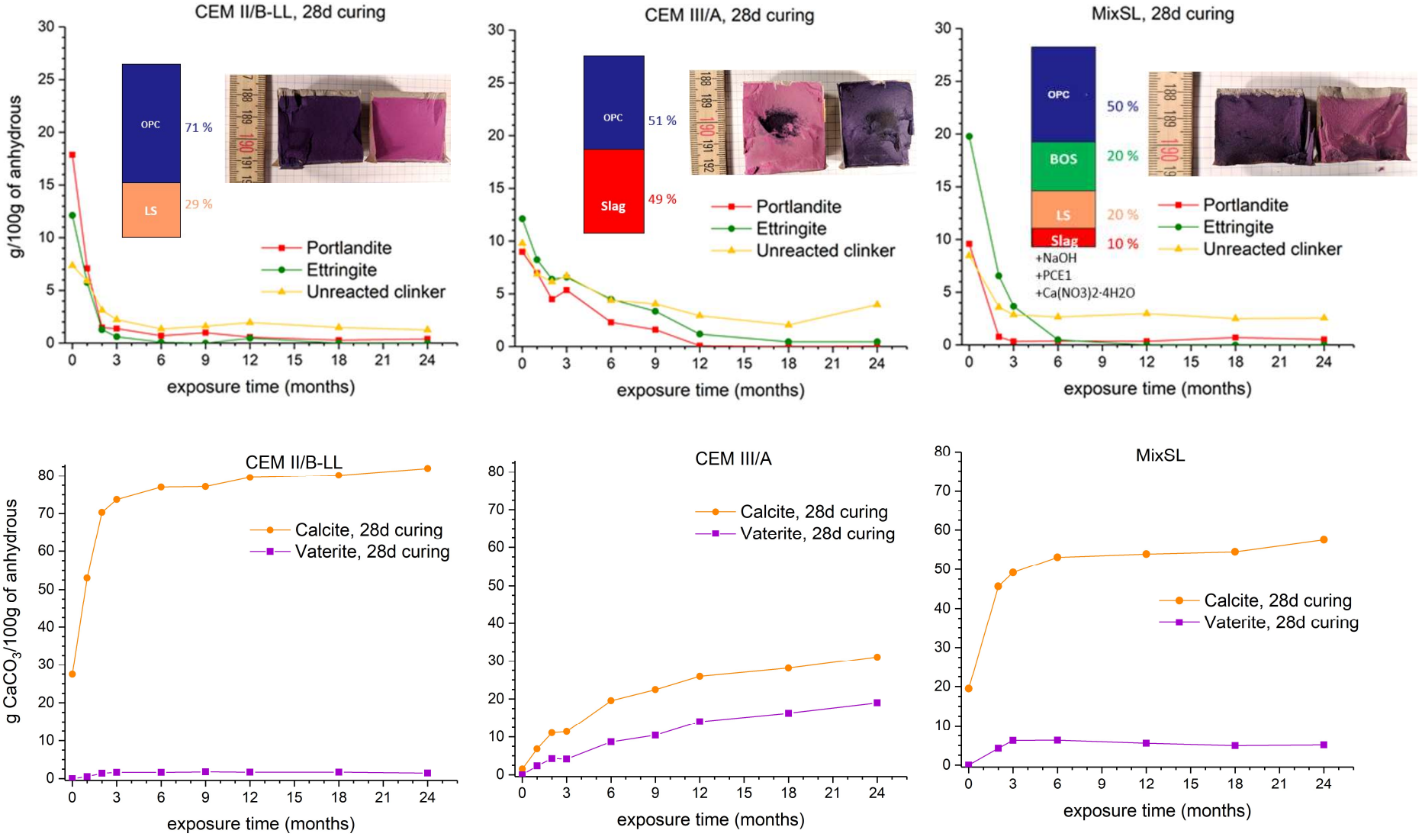
ettringite

$$C_3A(C\$)_3.32H + CO_2 > 3CaCO_3 + 3C\$H_2 + AH_3 + 23H_2O$$

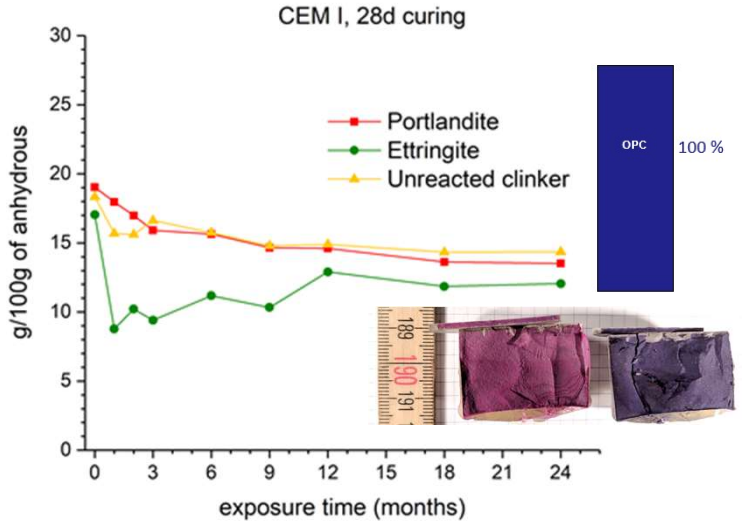
706.7 110.8 223.6 66.4

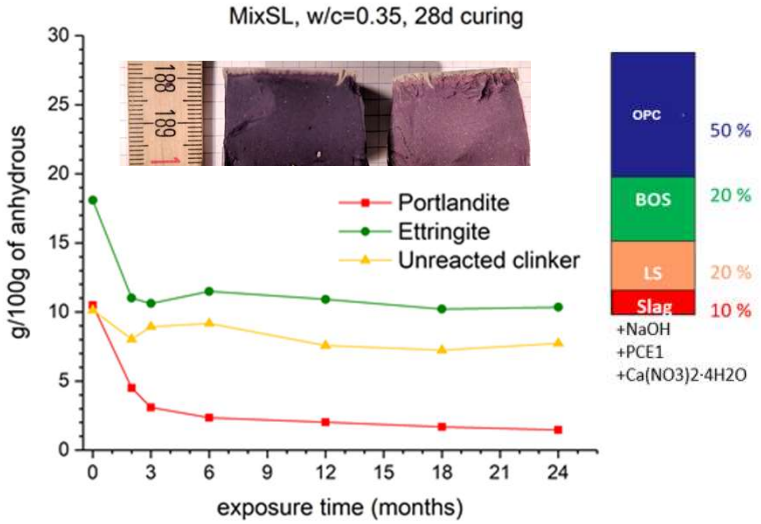
total = 511.6 $\Delta V = -27.6$

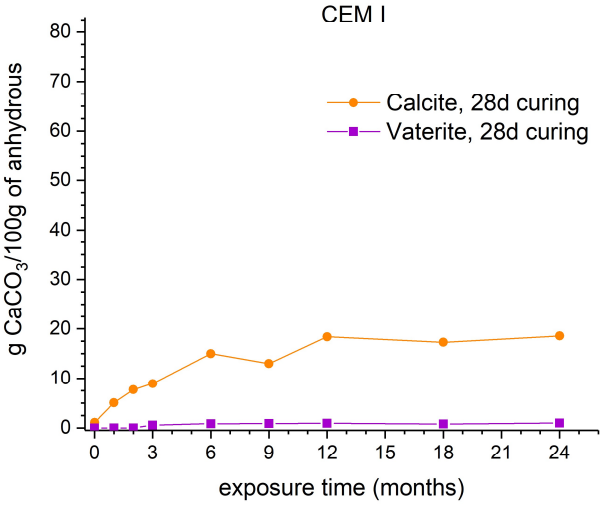
XRD-Rietveld analysis – quantification of the phases

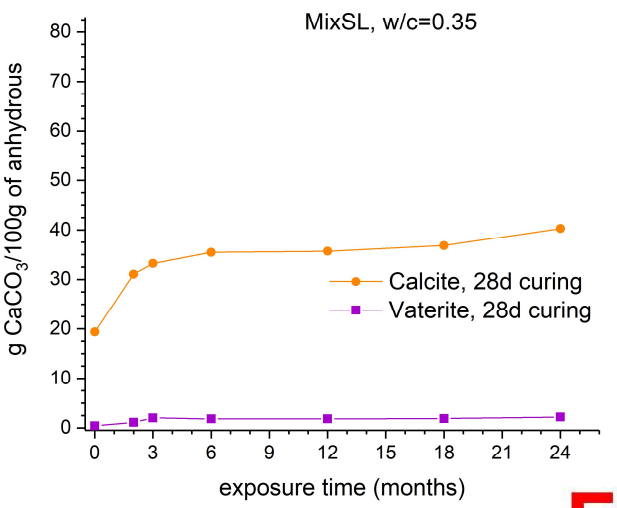


Can carbonation stop? Why?

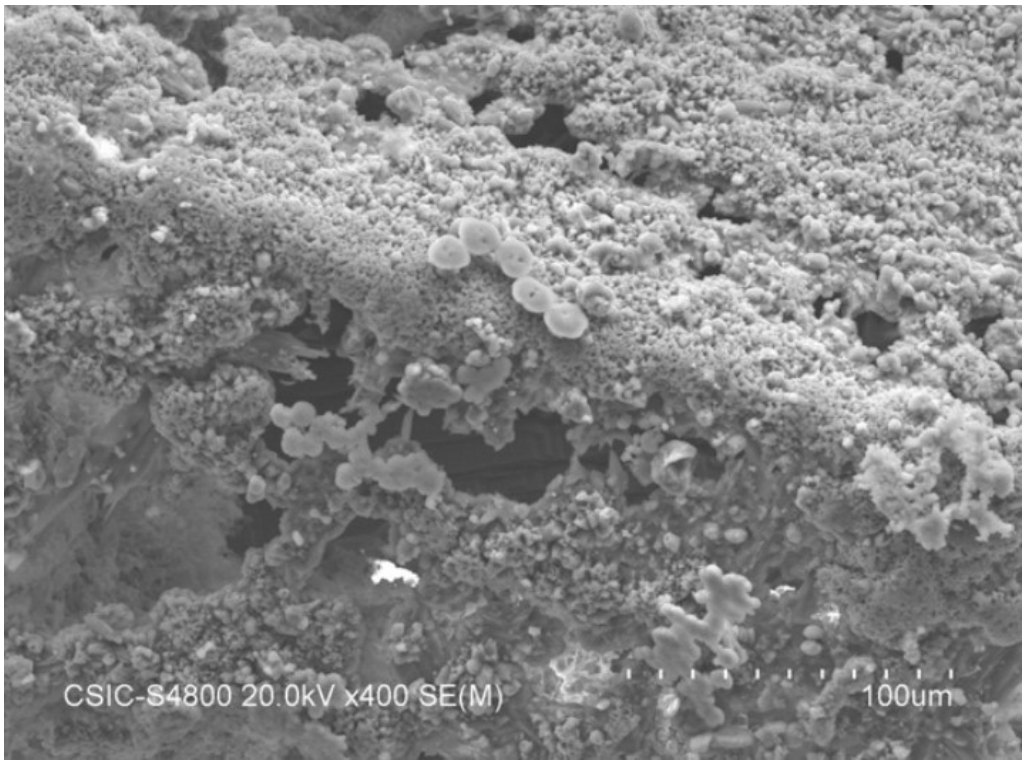


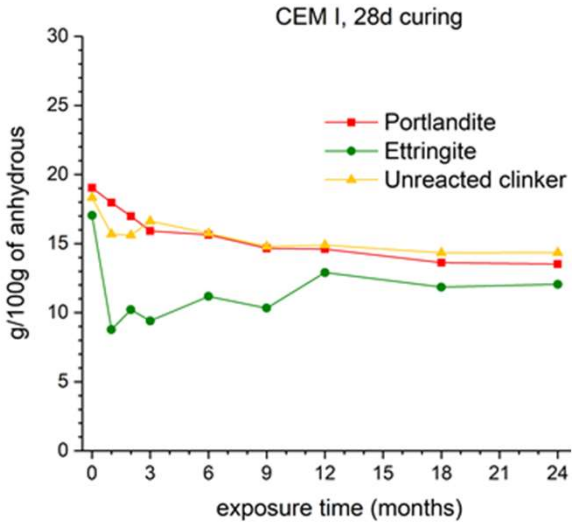






Can carbonation stop? Why?
Theory about existence of diffusion barrier





I. Galan et al., CCR, 2015

- Portlandite crystals develop a layer of calcium carbonate that inhibit further portlandite dissolution

Can carbonation stop? Why?
Thermodynamic limitations for calcite precipitation

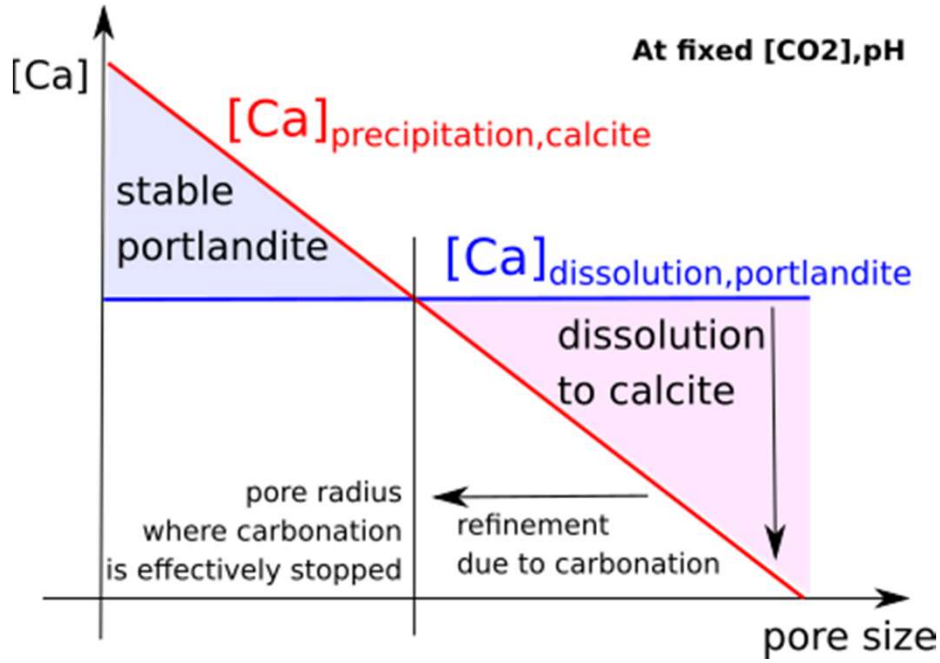
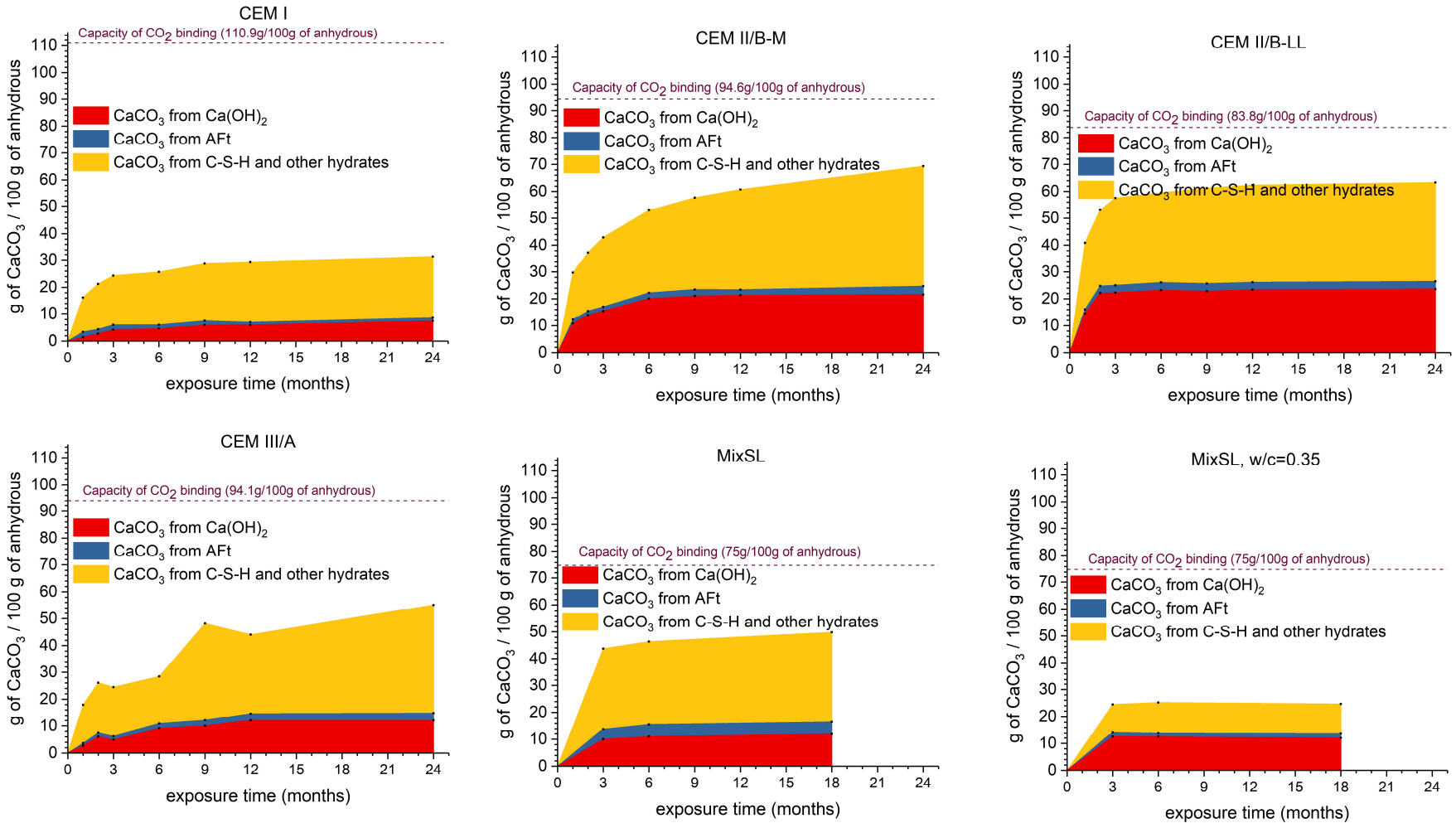


Figure used with permission of F. Georget

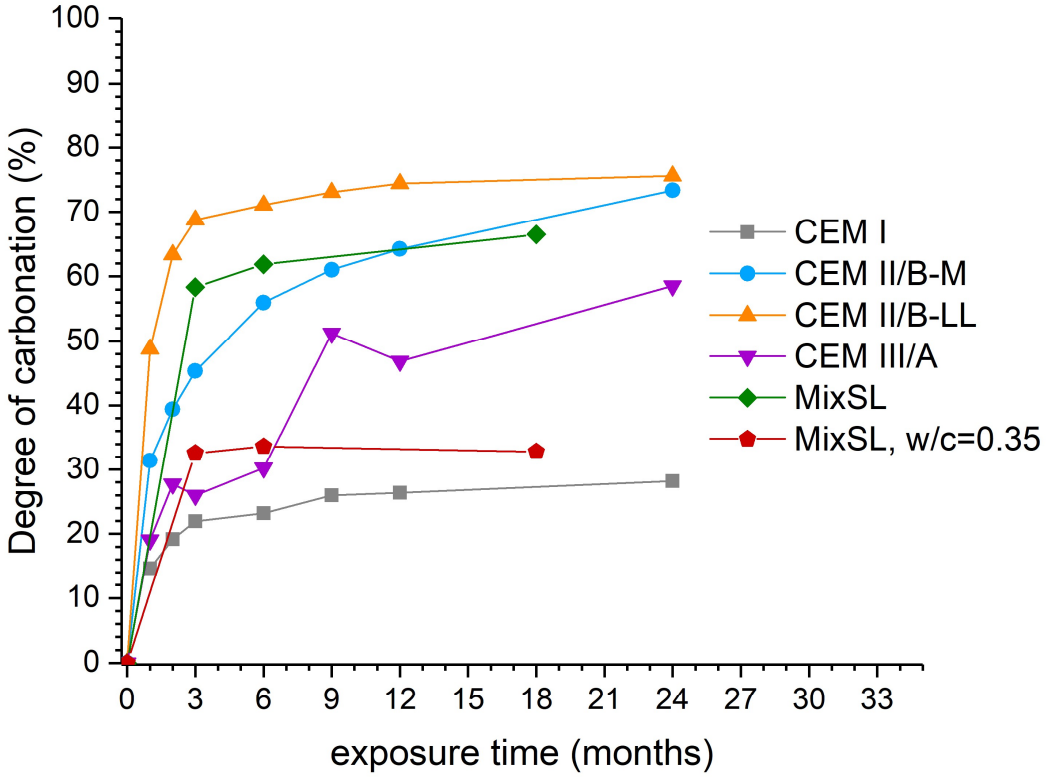
Pore structure gets finer → calcium concentration required for calcite precipitation becomes higher and higher → Portlandite becomes more stable than calcite → carbonation is effectively stopped

Average of $CaCO_3$ origin during carbonation



- In all cement types C-S-H is contributing into forming $CaCO_3$, but the values are count from the average of the different zones (carbonated, non-carbonated and transition zone)

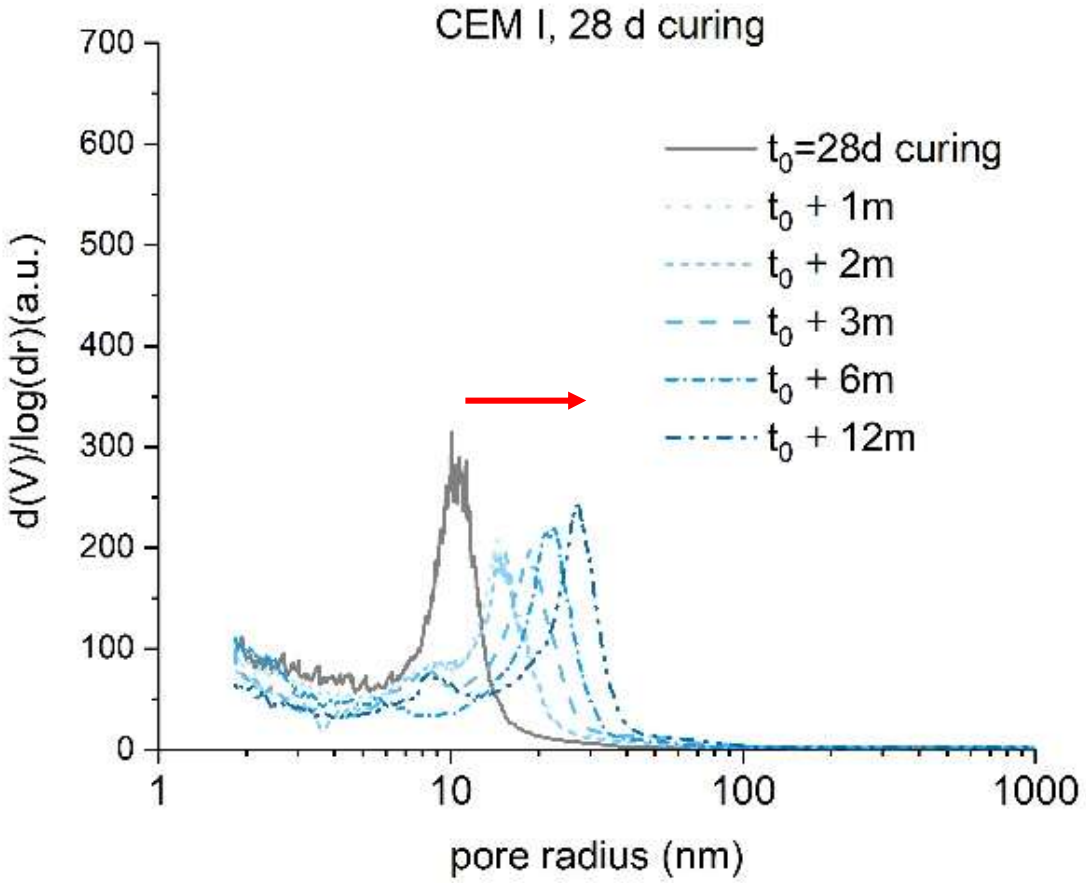
Degree of carbonation (DoC)



- Degree of carbonation advances in time
- Some mixes reached a plateau after few months of exposure
  - CEM I and MixSL with w/c 0.35: to lack-of-space theory
  - CEM II/B-LL and MixSL: reaching full carbonation capacity (assumed $CaO_{reactive}$ did not react completely)

POROSITY

How to define non-carbonated sample?



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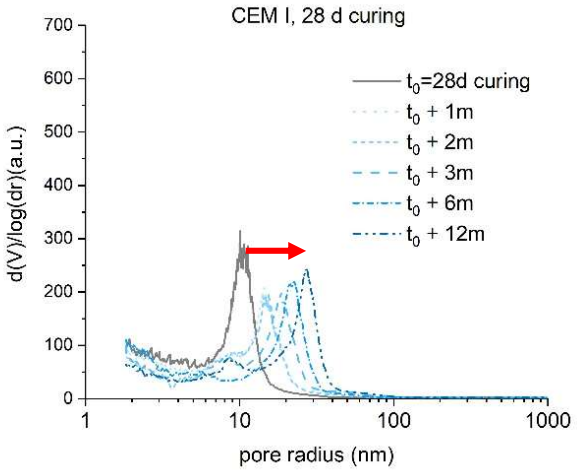
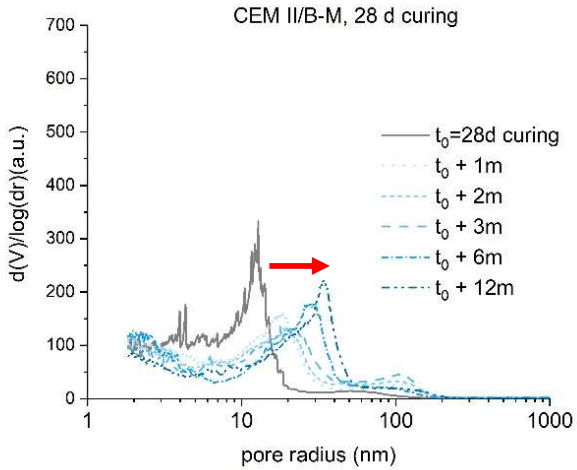
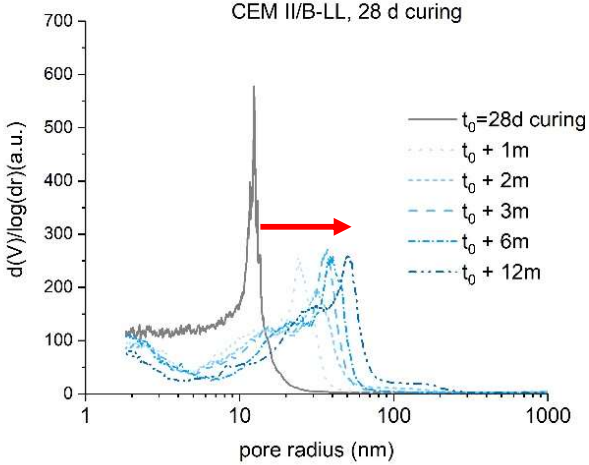
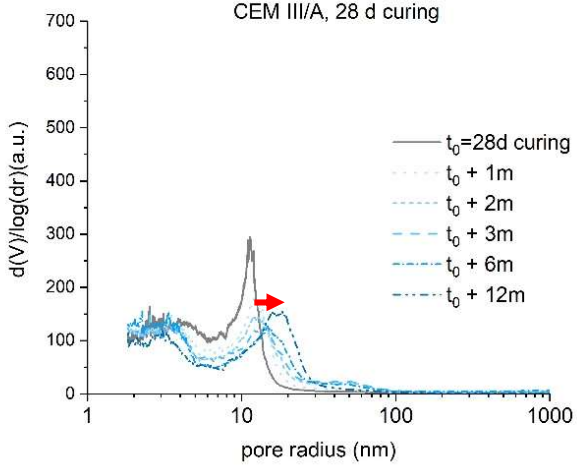
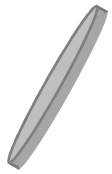
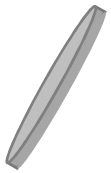


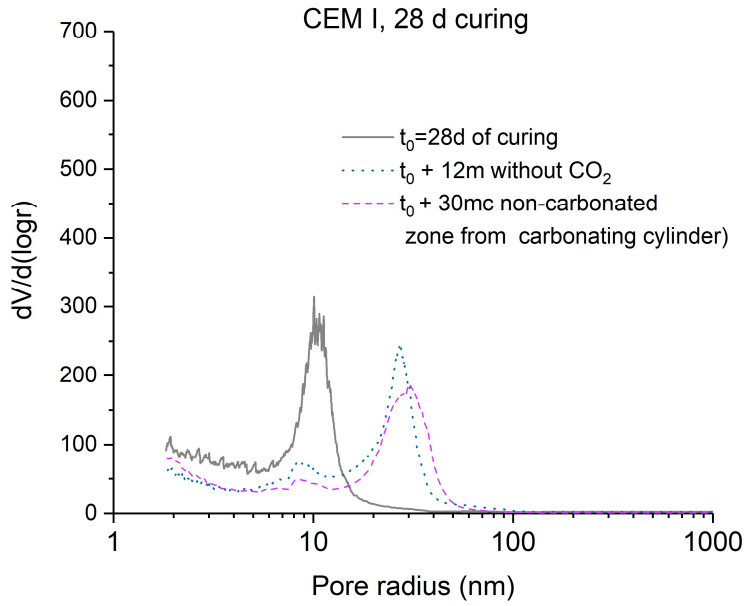






How to define non-carbonated sample?

t_0=28 d curing (sample before exposure)	**t_0+ 12 m without CO_2** (sample exposure without CO_2)	**t_0+ 30 m with CO_2** (sample exposure to natural carbonation)
RH > 95 % for 28 days 	0 ppm of CO_2 70 % RH 	

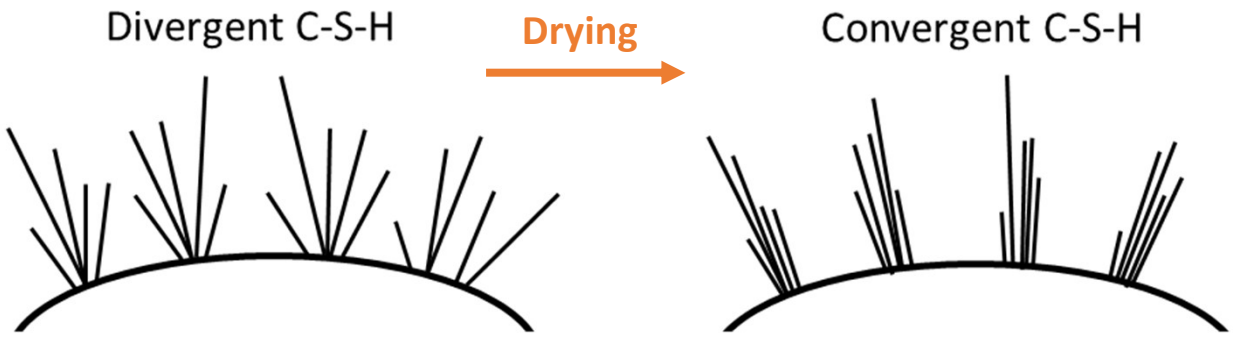


Coarsening porosity due to drying –possible explanation

Samples at 95% RH

Samples at 70% RH

?



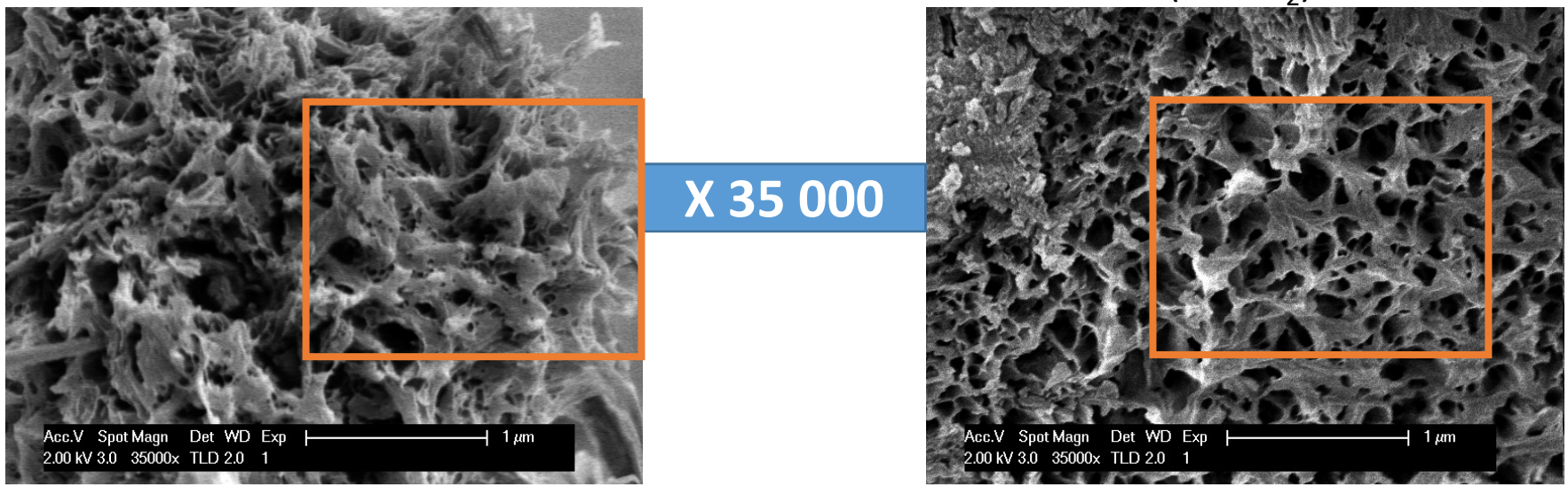
Possible changes of C-S-H morphology: drying might cause convergent C-S-H what would result in coarser porosity

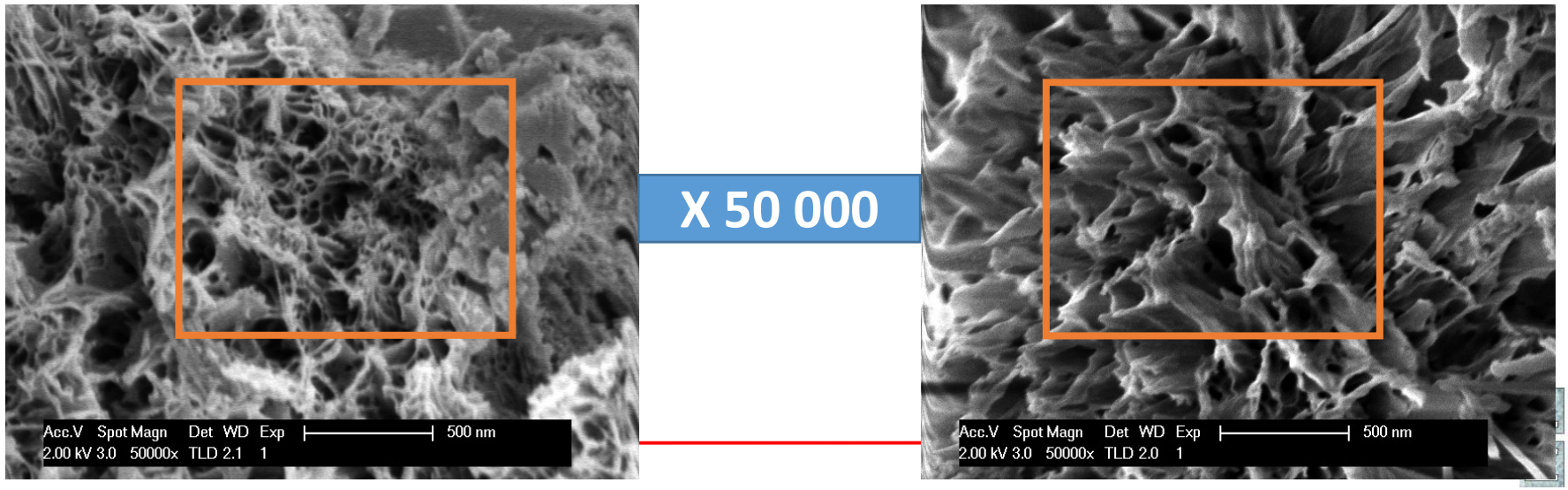
Adapted from: B. Mota Gassó, K. Scrivener and T. Matschei (Dirs.). Impact of alkali salts on the kinetics and microstructural development of cementitious systems. EPFL, Lausanne, 2015.

Change of C-S-H morphology

3 days of hydration

3 days of hydration + 12 months exposure (no CO_2)





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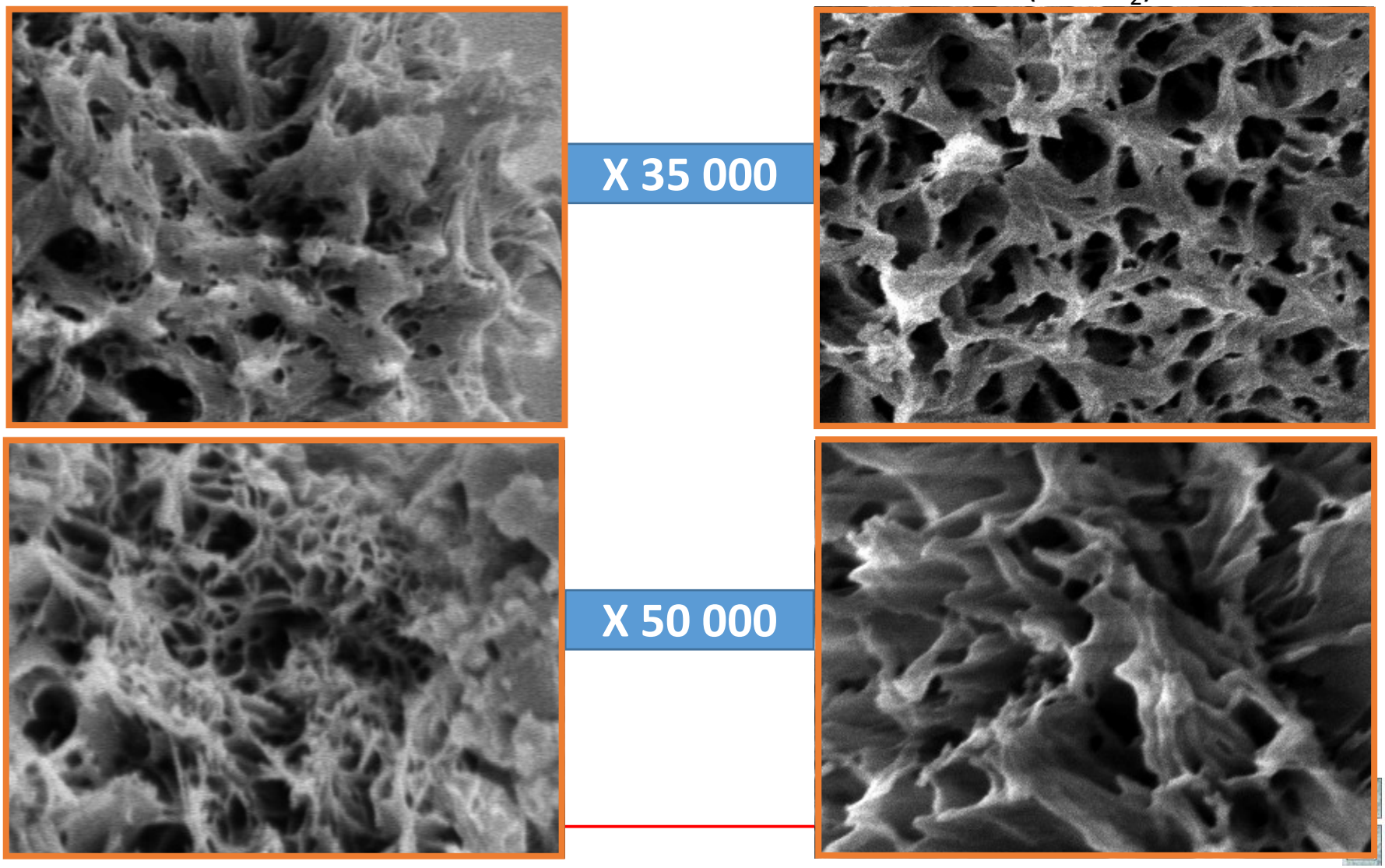
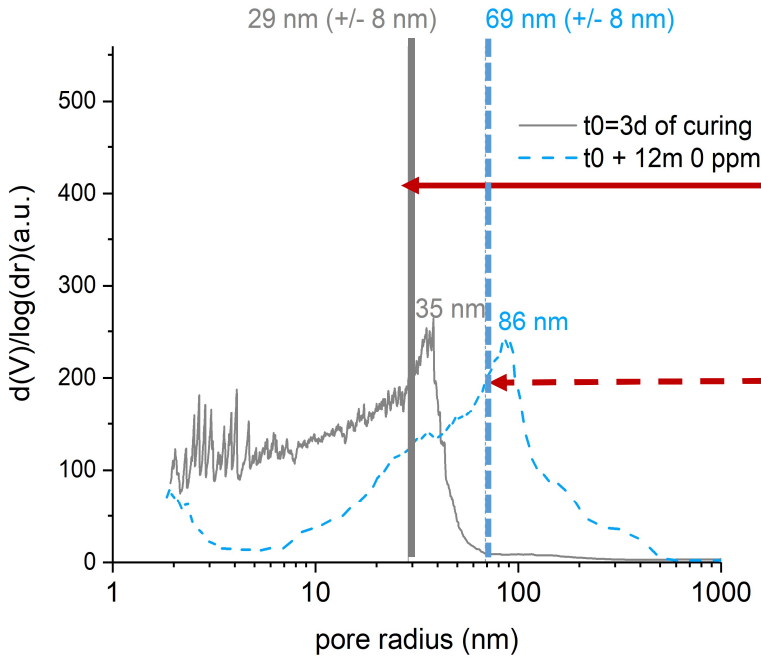
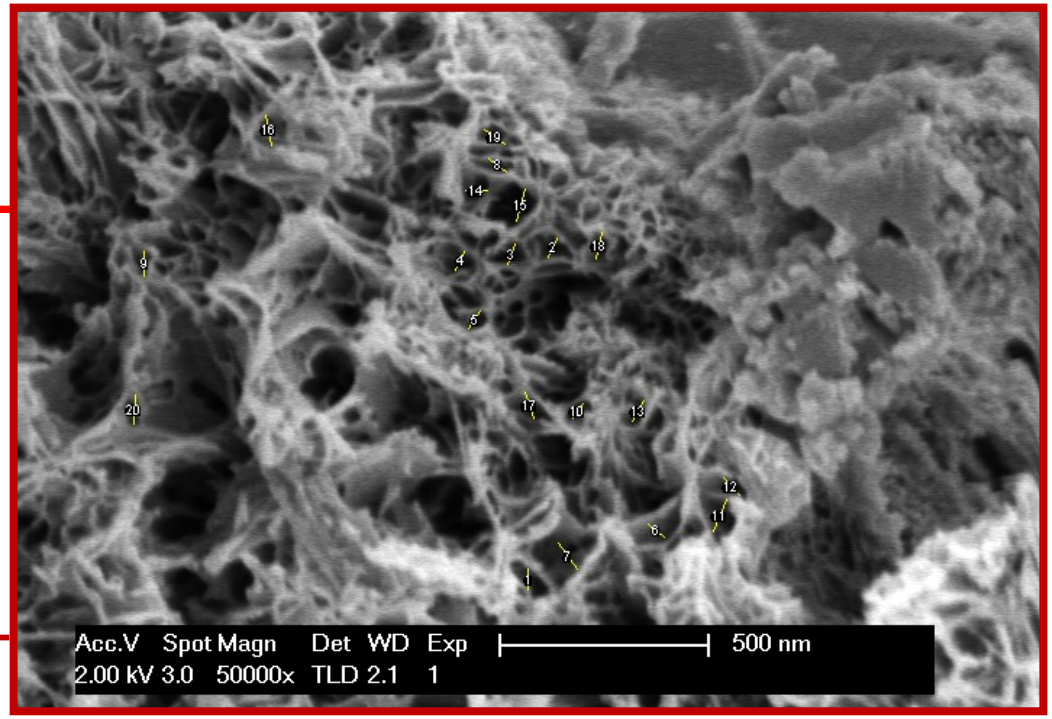
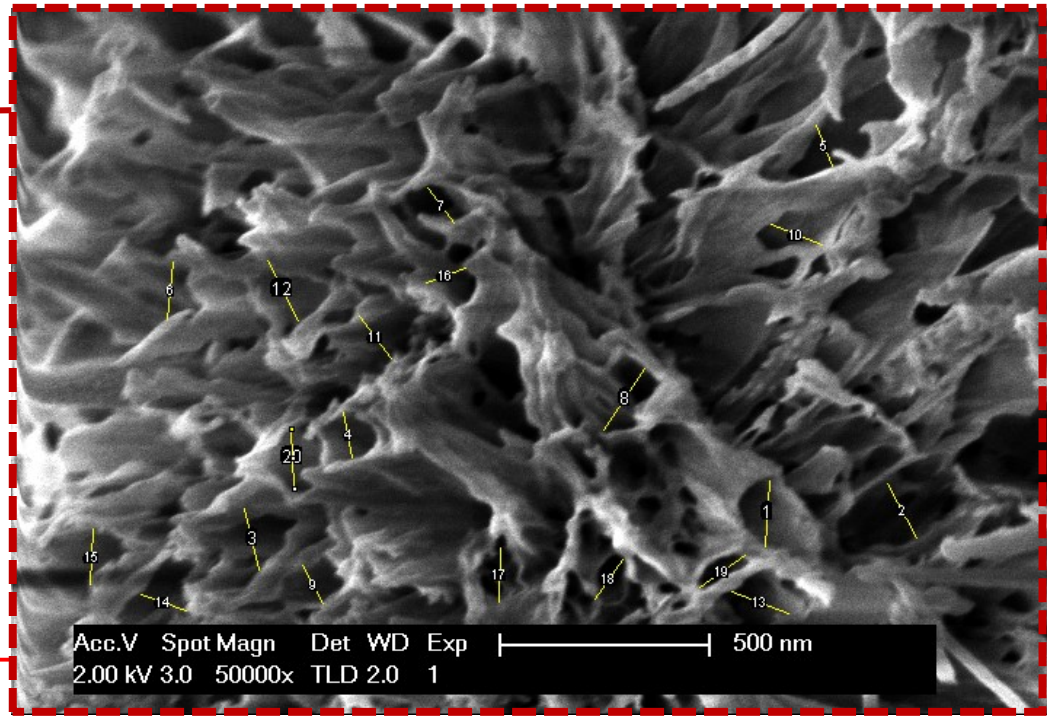


Semi-quantitative analysis with high-resolution microscopy







GAS DIFFUSION

New non-steady state diffusion set-up based on LCR design

LCR set-up

Volume: 113 cm³

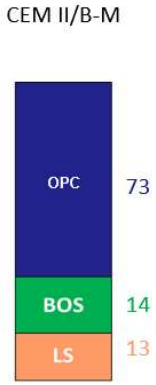
EPFL set-up

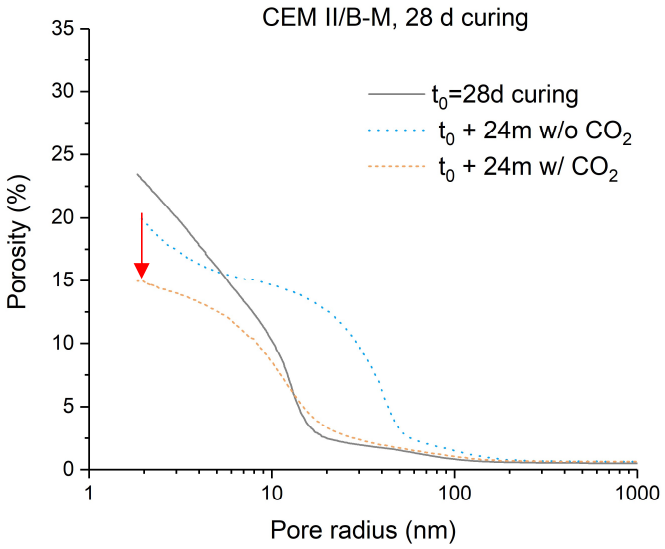
Volume: 55 cm³

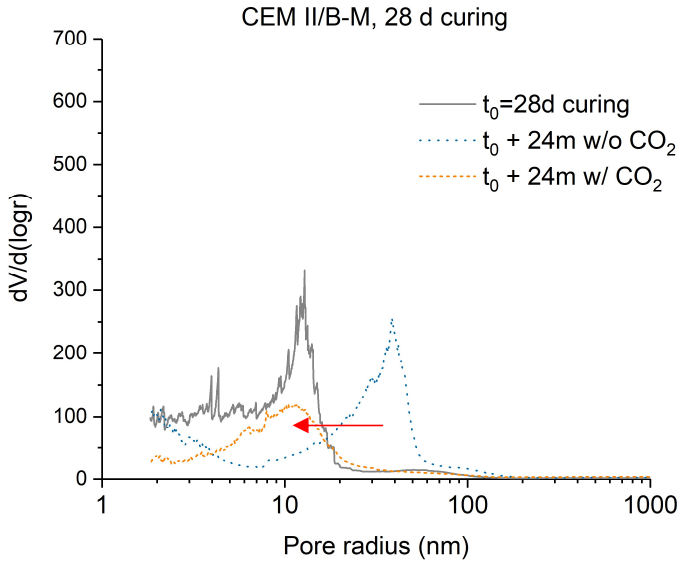
- Adapted to enable measurement of 1 mm thin samples

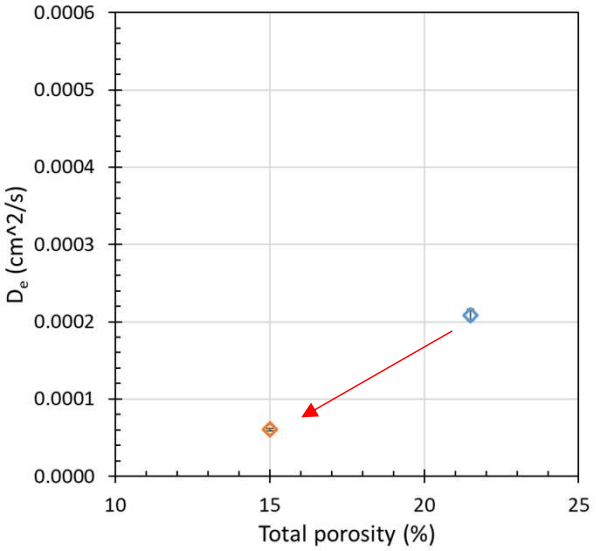
	LCR Diffusion (cm^2/s)	EPFL Diffusion (cm^2/s)
#24 (CEM II/B-M)	6.1×10^{-5}	6.1×10^{-5}
#35 (CEM II/B-LL)	3.65×10^{-4}	3.70×10^{-4}
#30 (CEM III/A)	4.6×10^{-5}	4.7×10^{-5}
#60 (CEM I)	5.6×10^{-5}	5.3×10^{-5}

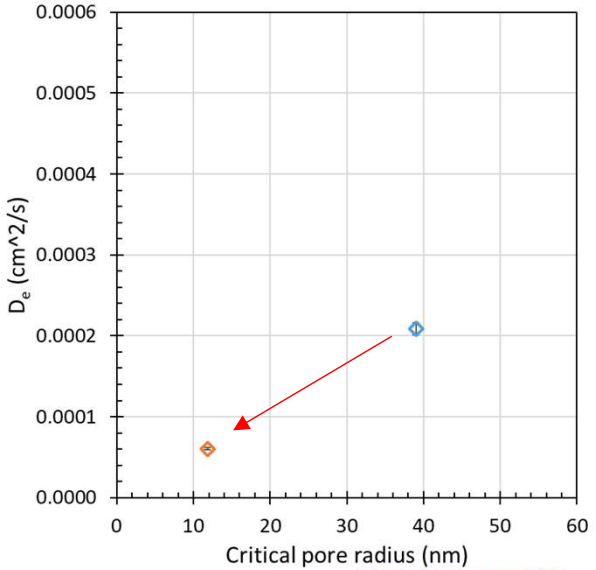
Can we relate diffusion with pore structure?





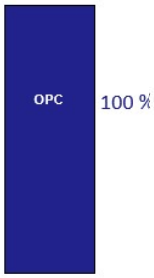


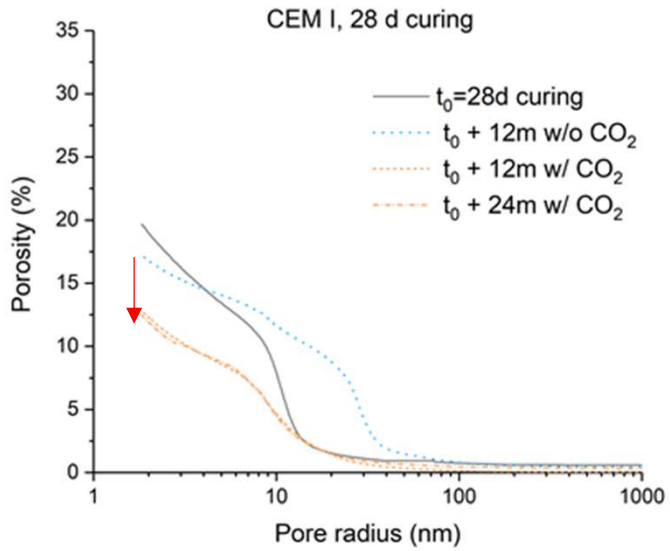


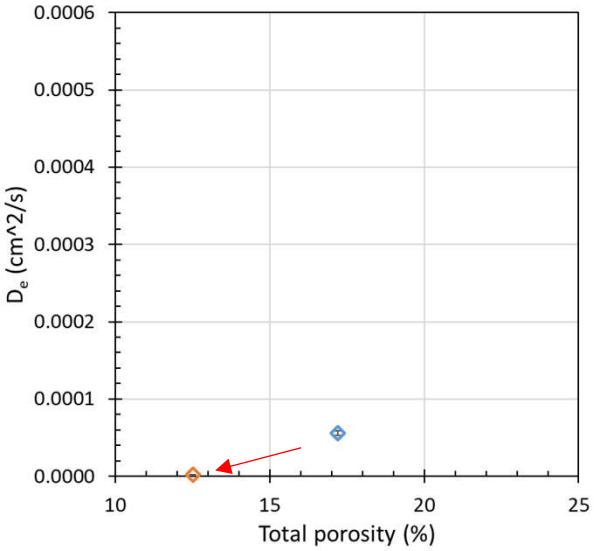


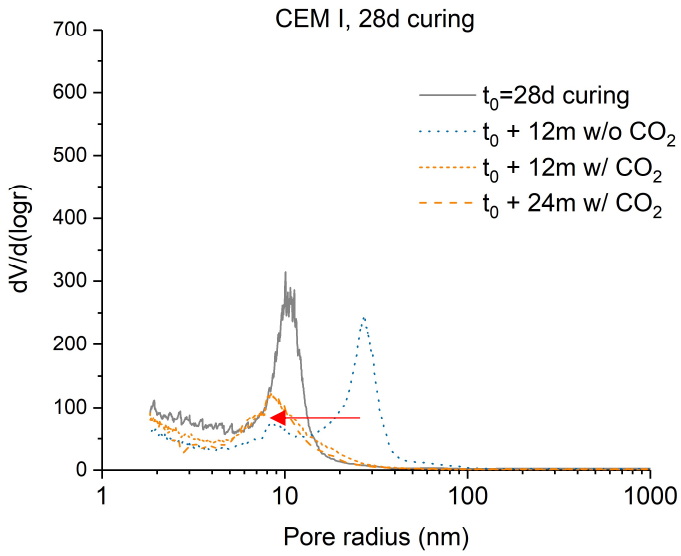
Can we relate diffusion with pore structure?

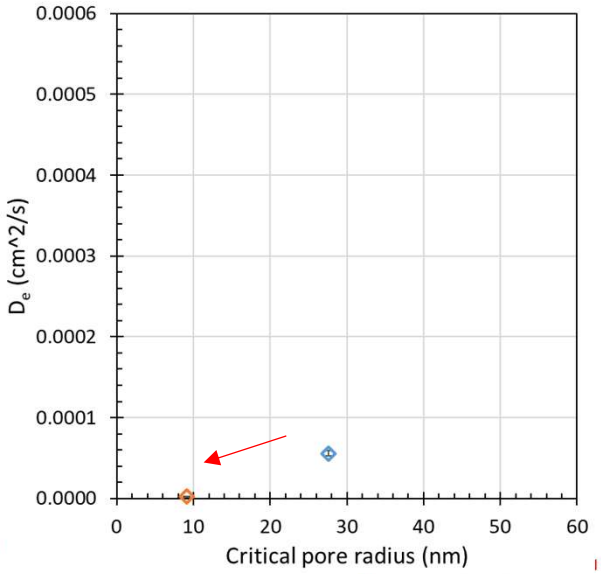
CEM I











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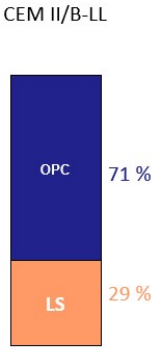
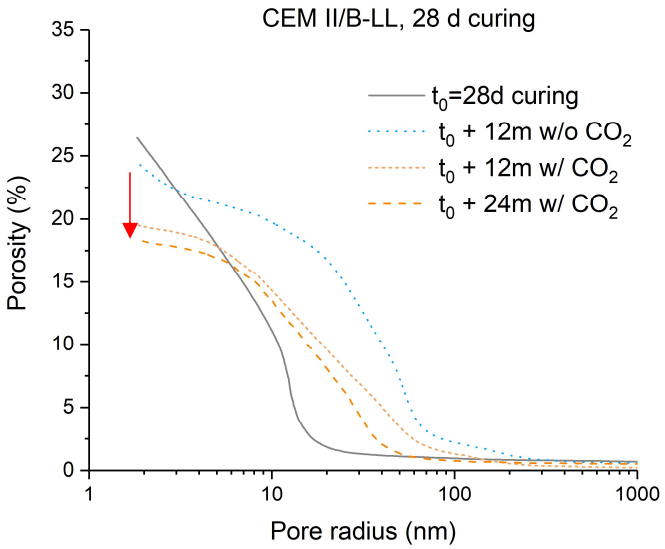
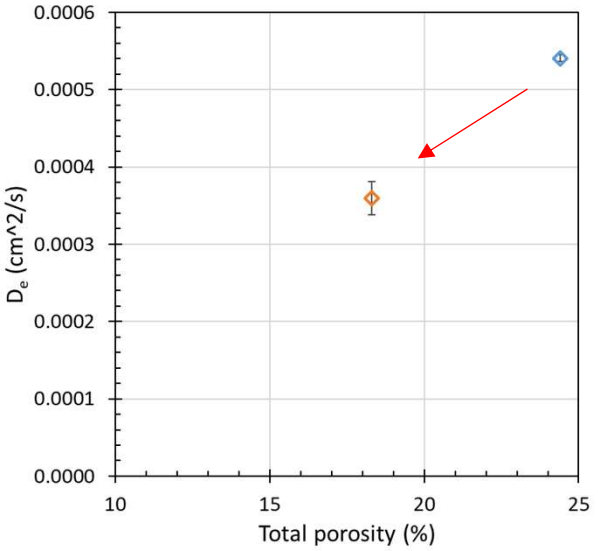
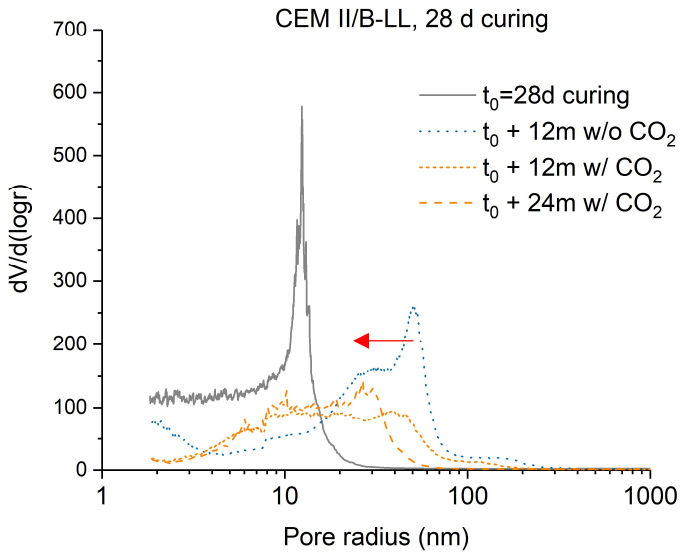
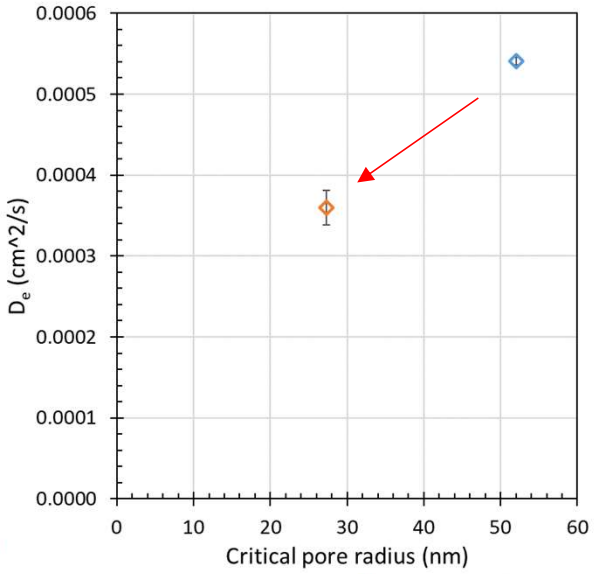


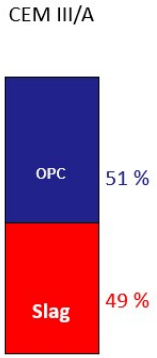


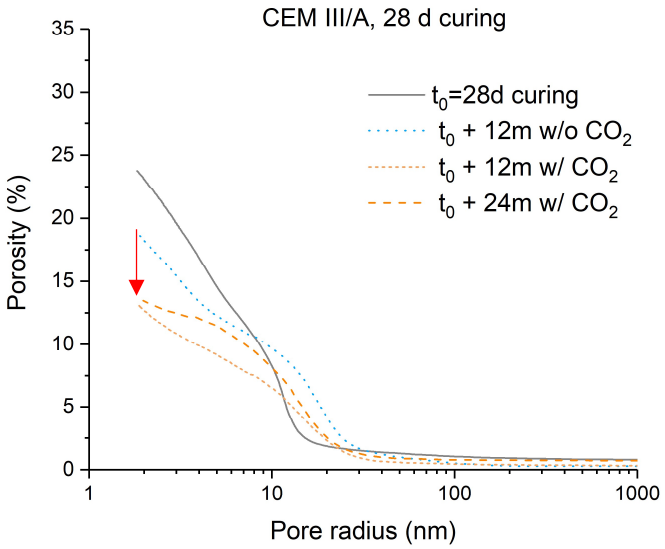


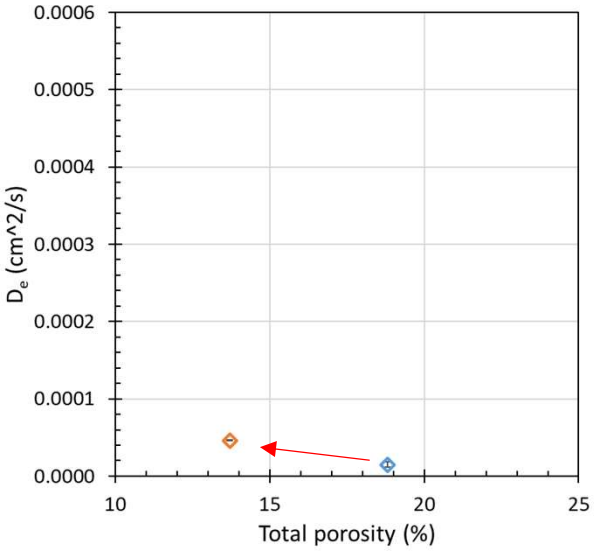


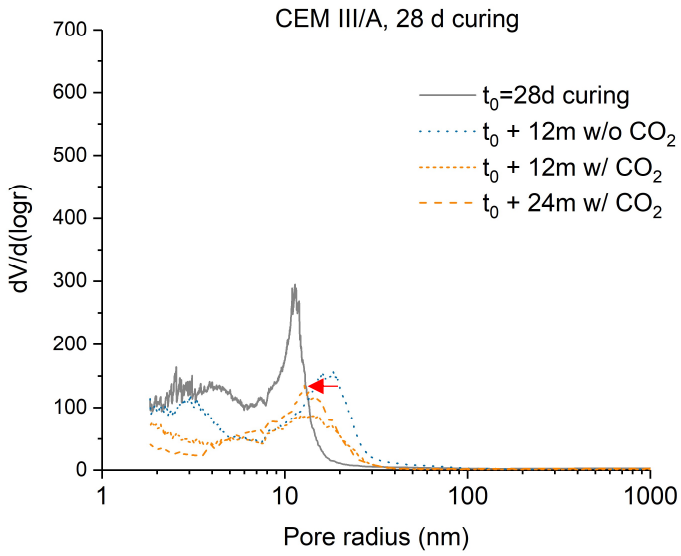


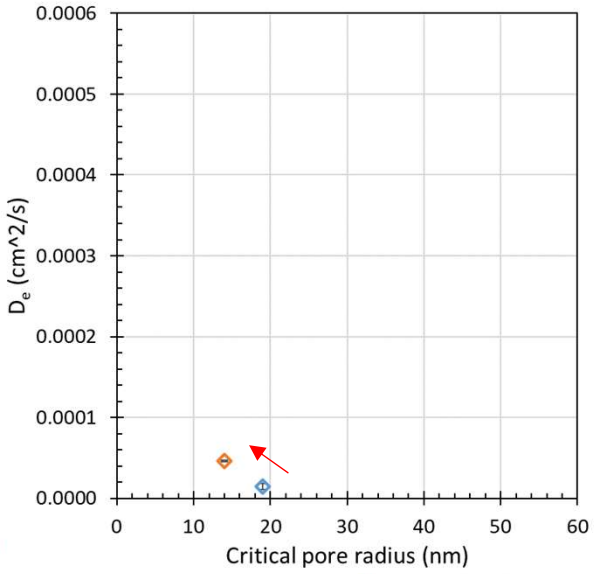
Can we relate diffusion with pore structure?











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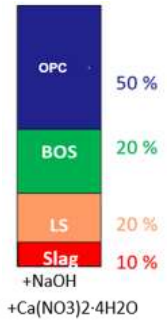

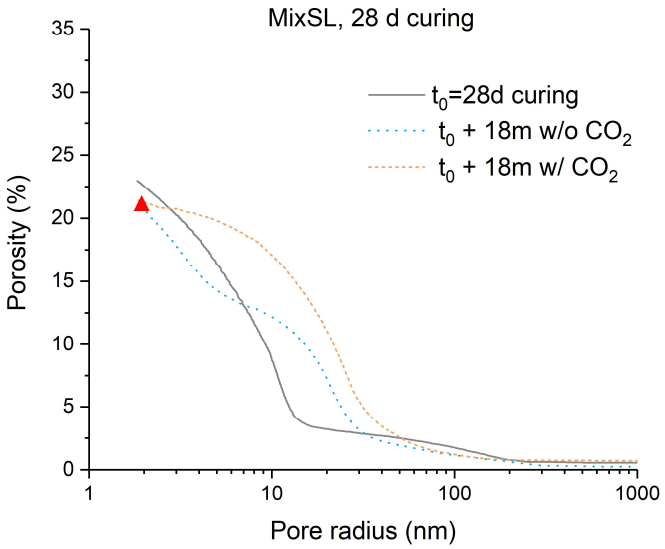

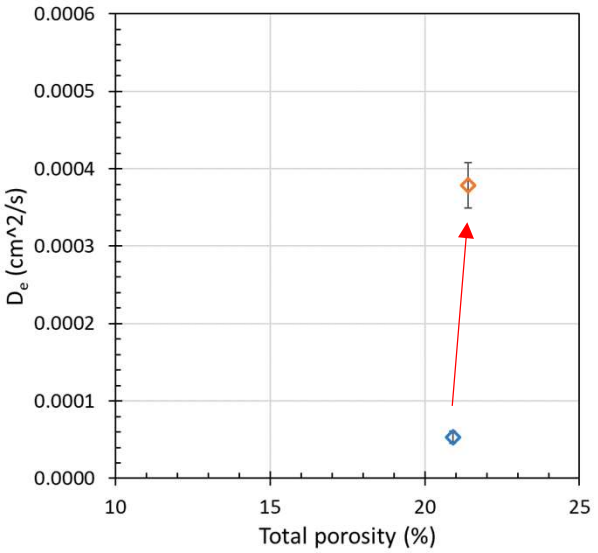

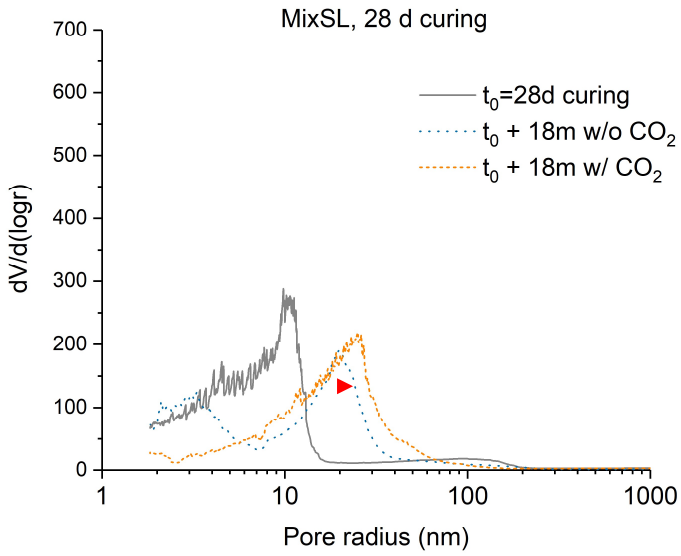

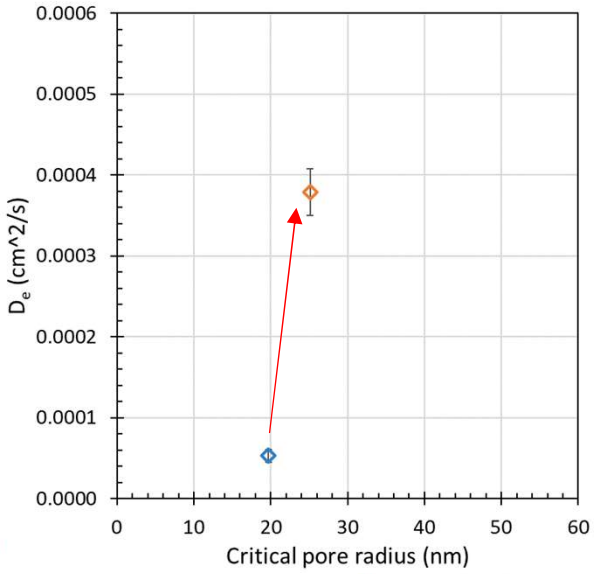

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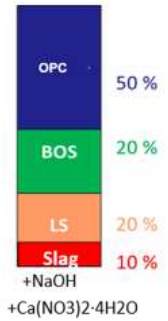

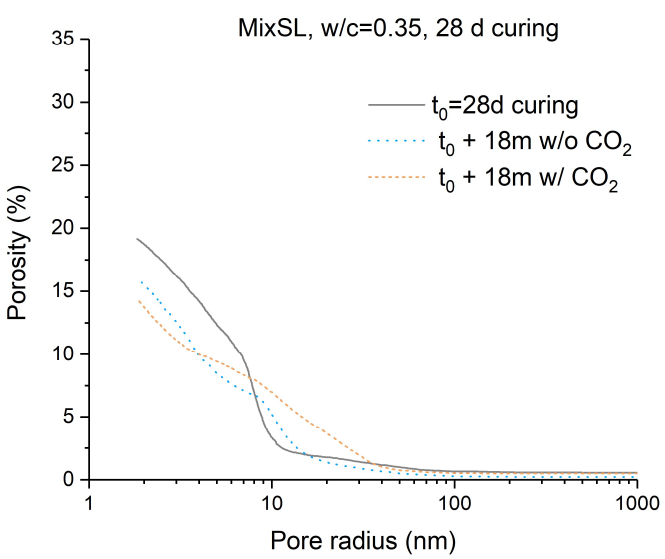

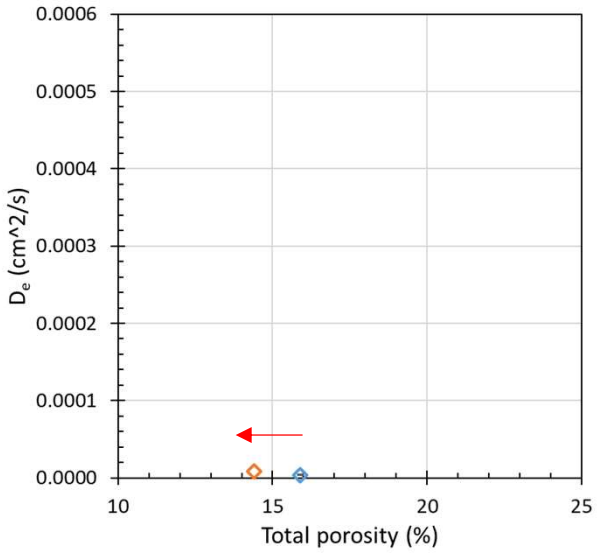

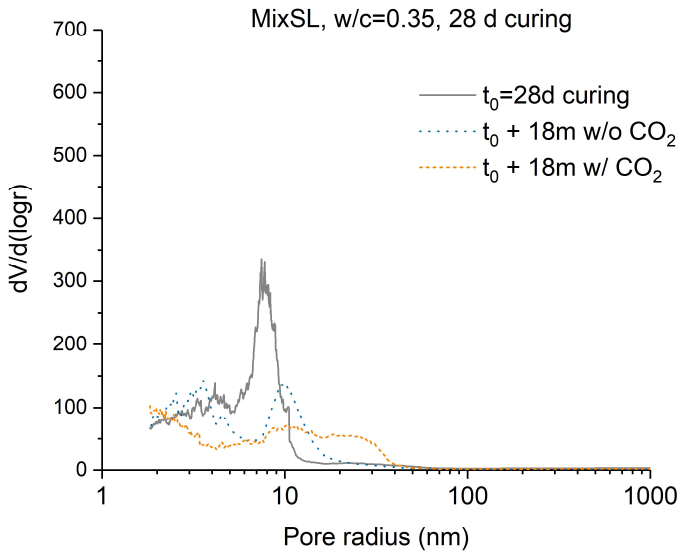

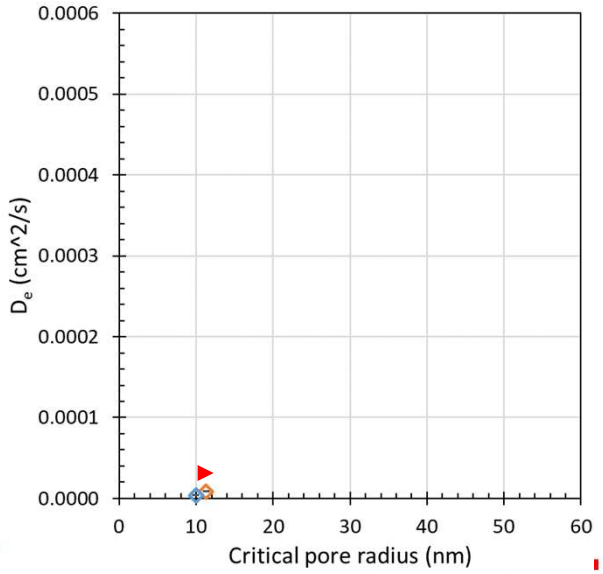

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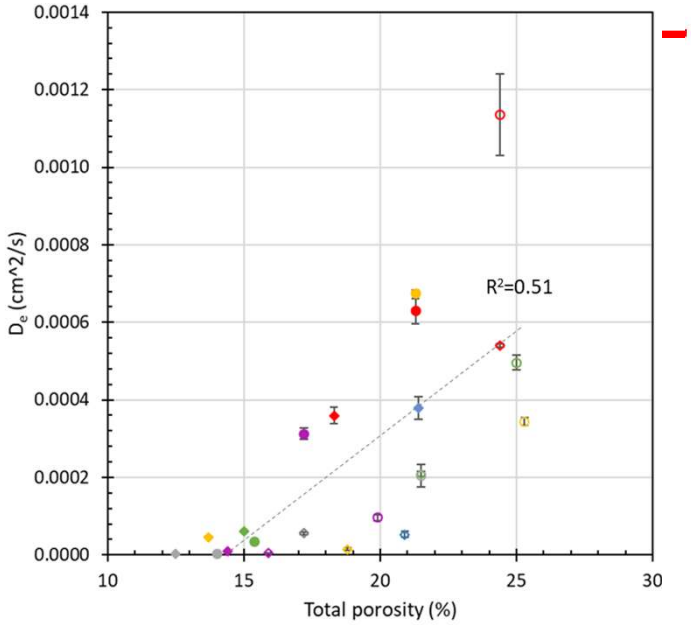
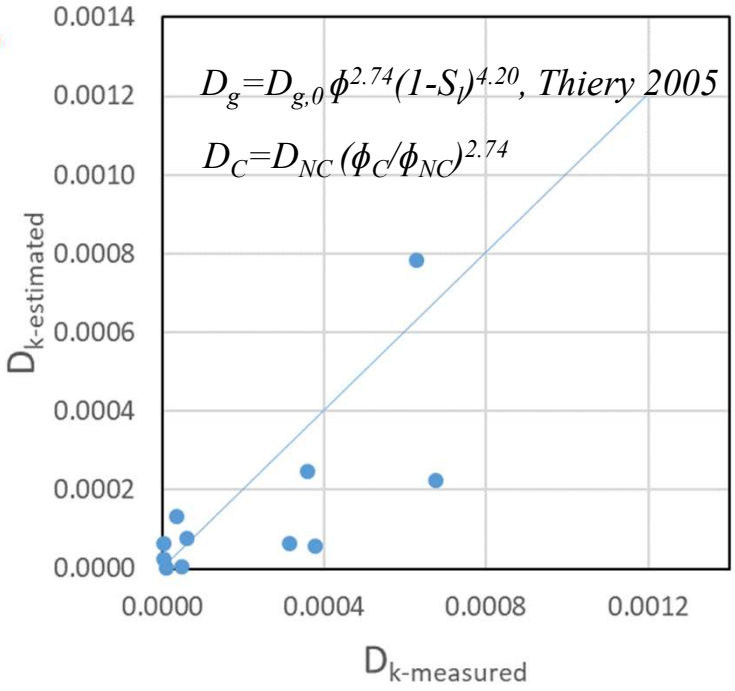
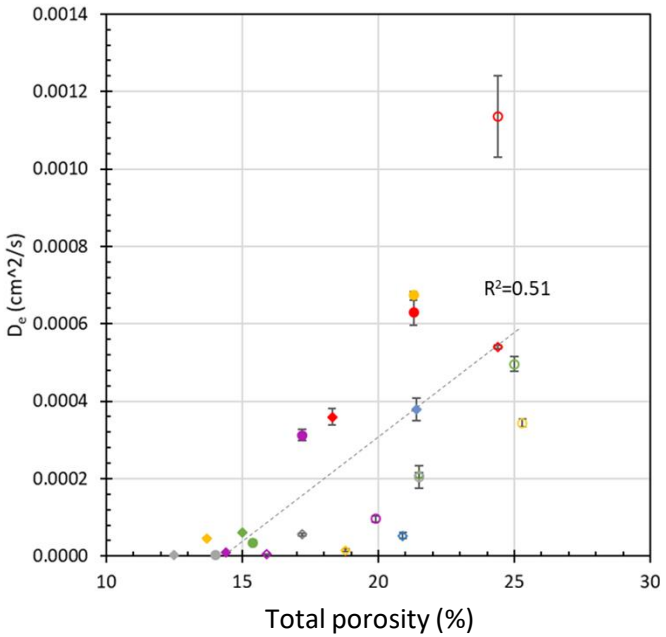
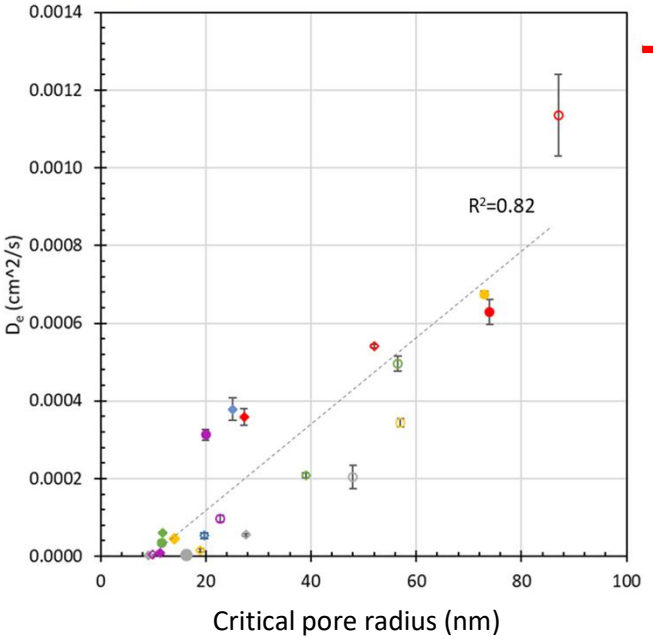


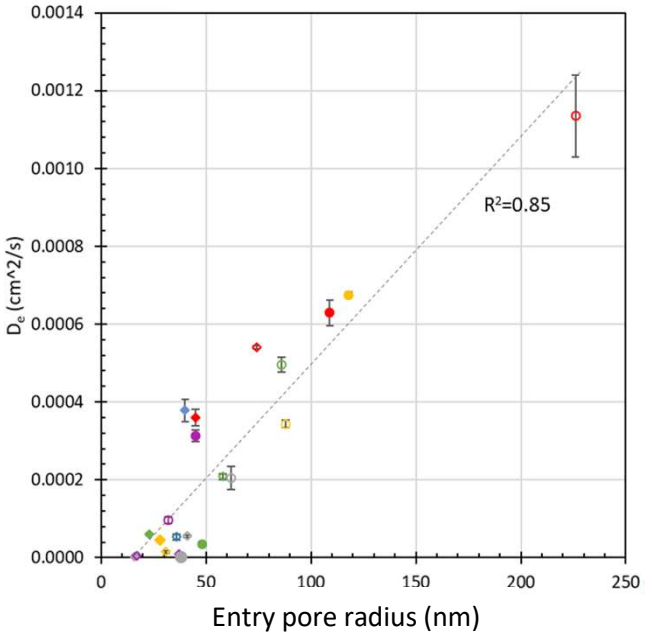


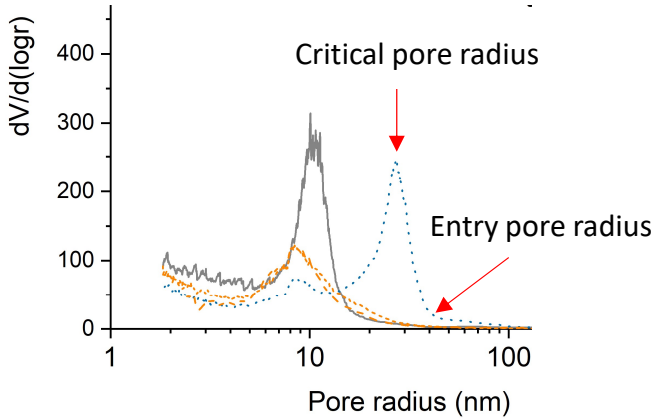
- CEM I_28d_c
- CEM II/B-M_28d_c
- CEM II/B-LL_28d_c
- CEM III/A_28d_c
- MixSL_28d_c
- MixSL, w/c=035_28d_c
- CEM I_28d_nc
- CEM II/B-M_28d_nc
- CEM II/B-LL_28d_nc
- CEM III/A_28d_nc
- MixSL_28d_nc
- MixSL, w/c=035_28d_nc
- CEM I_3d_c
- CEM II/B-M_3d_c
- CEM II/B-LL_3d_c
- CEM III/A_3d_c
- MixSL, w/c=035_3d_c
- CEM I_3d_nc
- CEM II/B-M_3d_nc
- CEM II/B-LL_3d_nc
- CEM III/A_3d_nc
- MixSL, w/c=035_3d_nc

Can we relate diffusion with pore structure?









- CEM I_28d_c
- CEM II/B-M_28d_c
- CEM II/B-LL_28d_c
- CEM III/A_28d_c
- MixSL_28d_c
- MixSL, w/c=035_28d_c
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- CEM II/B-M_28d_nc
- CEM II/B-LL_28d_nc
- CEM III/A_28d_nc
- MixSL_28d_nc
- MixSL, w/c=035_28d_nc
- CEM I_3d_c
- CEM II/B-M_3d_c
- CEM II/B-LL_3d_c
- CEM III/A_3d_c
- MixSL, w/c=035_3d_c
- CEM I_3d_nc
- CEM II/B-M_3d_nc
- CEM II/B-LL_3d_nc
- CEM III/A_3d_nc
- MixSL, w/c=035_3d_nc

Conclusions and perspectives

- Increase of carbonation depth in concrete with decrease of curing time and increase of w/c ratio
- Initial portlandite content does not establish carbonation rate – importance of diffusion properties
- Changing of the diffusion coefficient due to carbonation
- No consistent relationship between total porosity or critical pore radius and diffusion coefficient:

THANK YOU

$$C_3A(C\$)_3.32H + CO_2 > 3CaCO_3 + 3C\$H_2 + AH_3 + 23H_2O$$

706.7 110.8 223.6 66.4

total = 511.6 $\Delta V = 27.6$