Nano-structure, decalcification and kineteics. Based on literature.

13.3.2024 Anna Kronlöf

Kinetics of carbonation

Thermodynamically all binders (both OPC and blended) are going to be de-calcified to $CaCO_3$ and silica gel with time.

It is a question of time only.

- Moisture.
- The effect of SCMs on pore size.
- The effects of pore size on carbonation kinetics.

Kinetics: Understanding the rates of chemical reactions

Understanding the carbonation of concrete with supplementary cementitious materials: a critical review by RILEM TC 281-CC. Materials and Structures (2020) 53:13

The effect of pore size

The dense initial pore structure due to pozzolanic reaction limits carbonation rate.

- Low water to binder ratio.
- Long curing time. SMC reactions are slow.
- "… a factor of 4 improvement is gained by increasing from 1 to 7 days of wet curing."

Misunderstandings in testing

- Accelerated carbonation is more aggressive for concrete with SCM.
- CO_2 concentration above 10% leads to incomplete reaction of portlandite due to fast overgrowth of portlandite with calcite, which permanently prevents further portlandite carbonation.

RH, H_2O

High degree of pore saturation due to dense initial pore structure.
Capillary condensation limits carbonation rate.

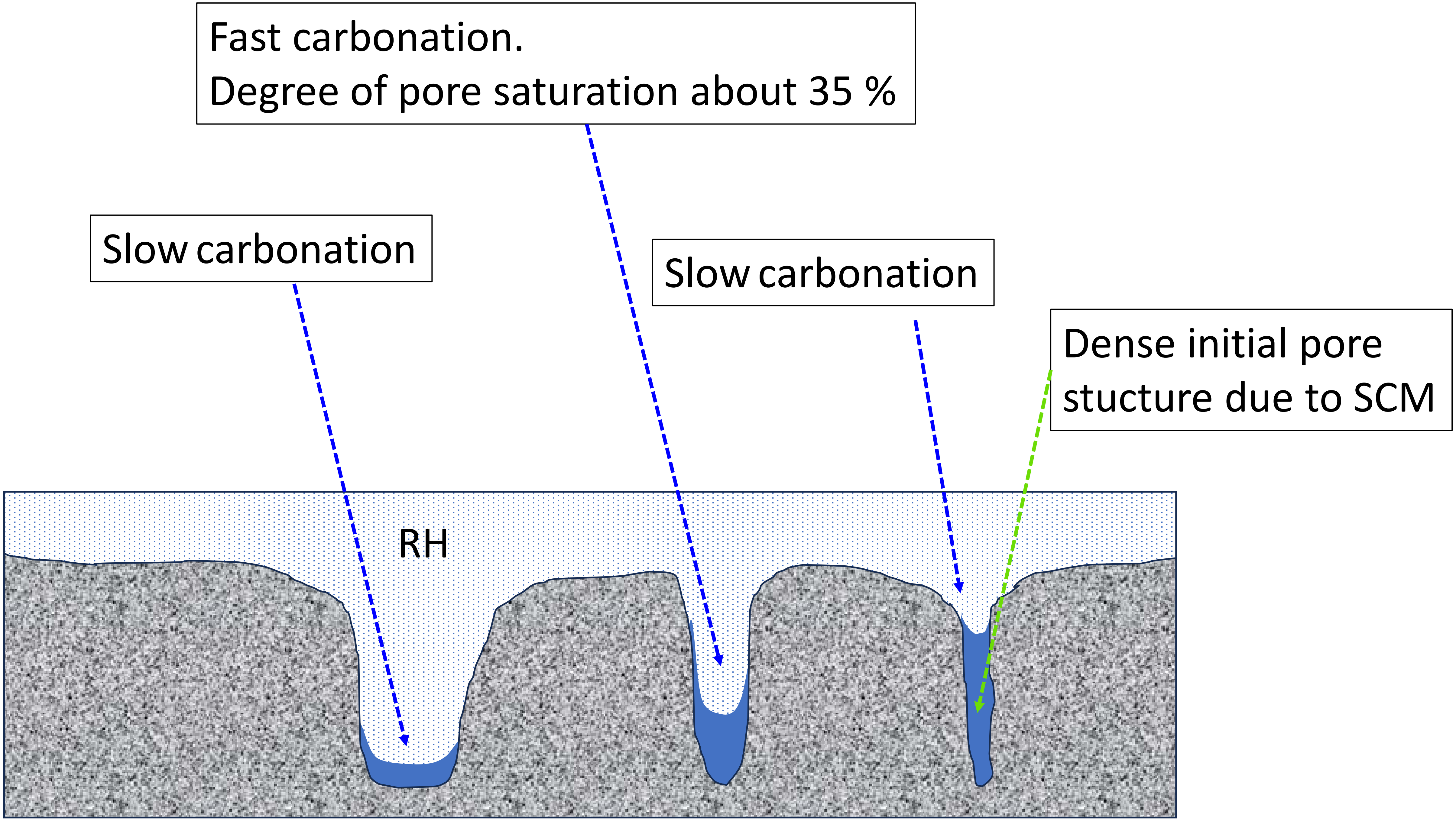
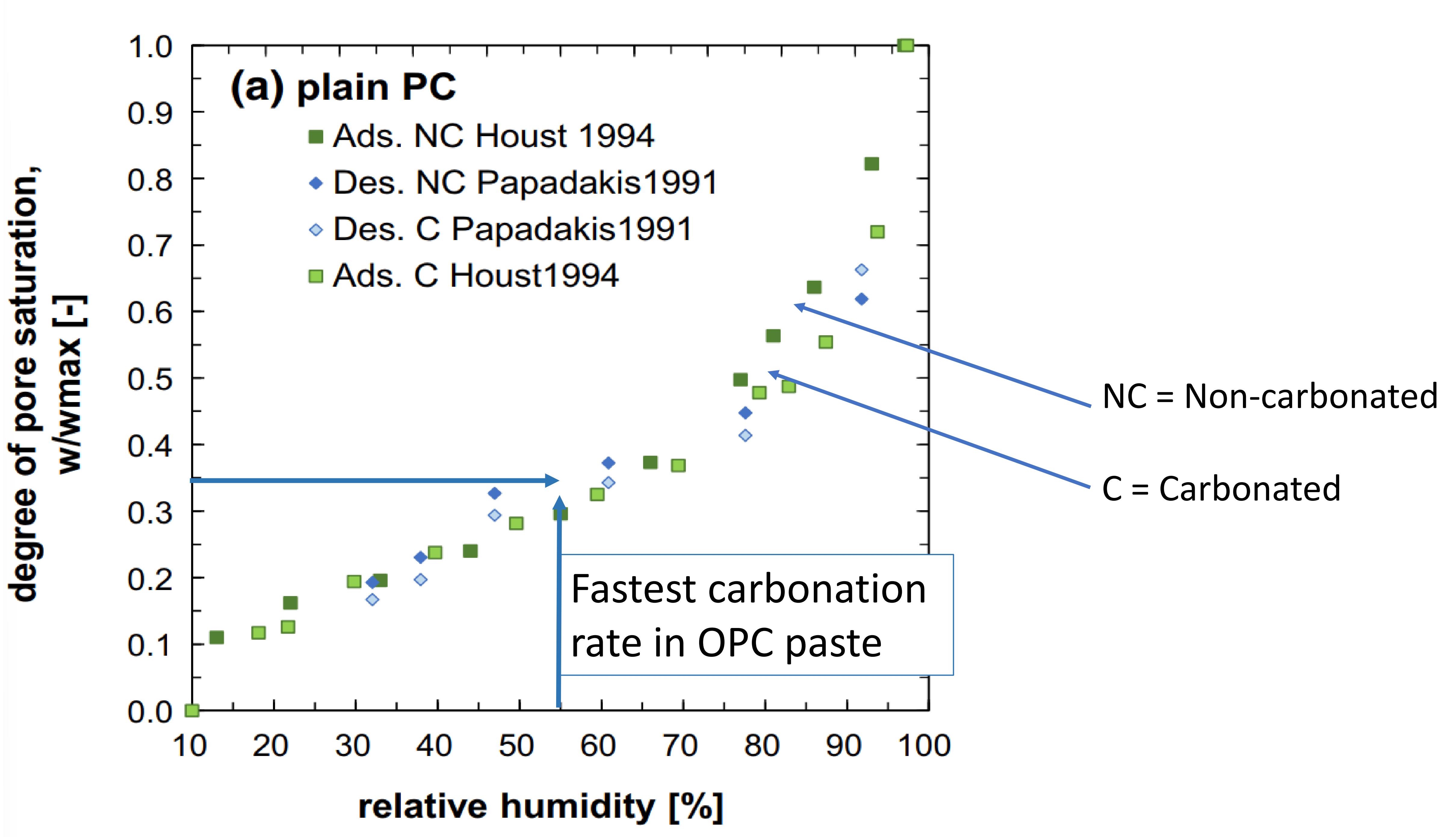


Fig. Capillary condensation and carbonation rate in different pore sizes. (AK)

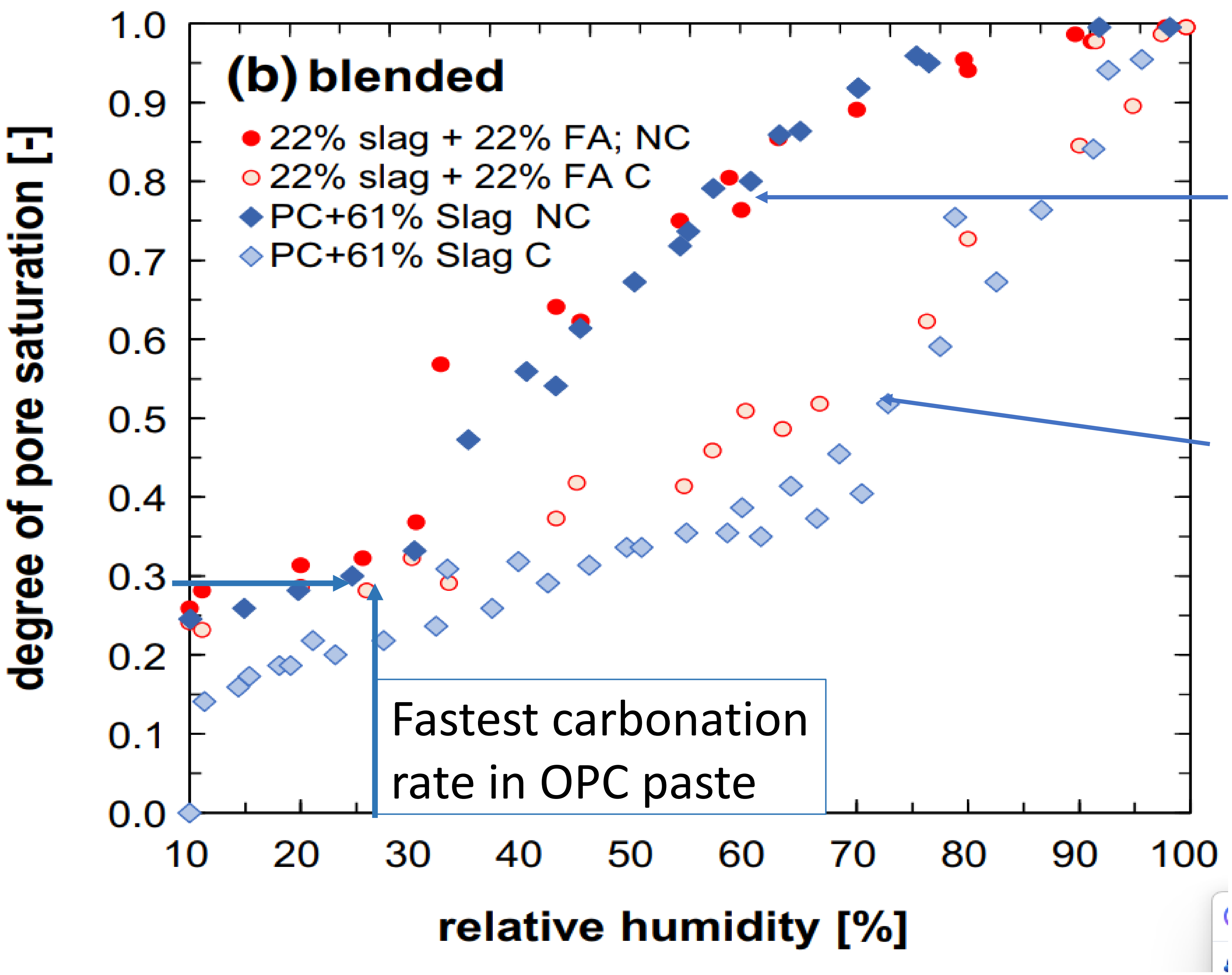
Kinetics - Carbonation rate depends on the degree of pore saturation

Plain OPC-paste



Kinetics - Carbonation rate depends on the degree of pore saturation (3/n)

Blended-paste



NC = Non-carbonated
Dense pore structure.
High RH ”stops” carbonation.

C = Carbonated

Capillary suction

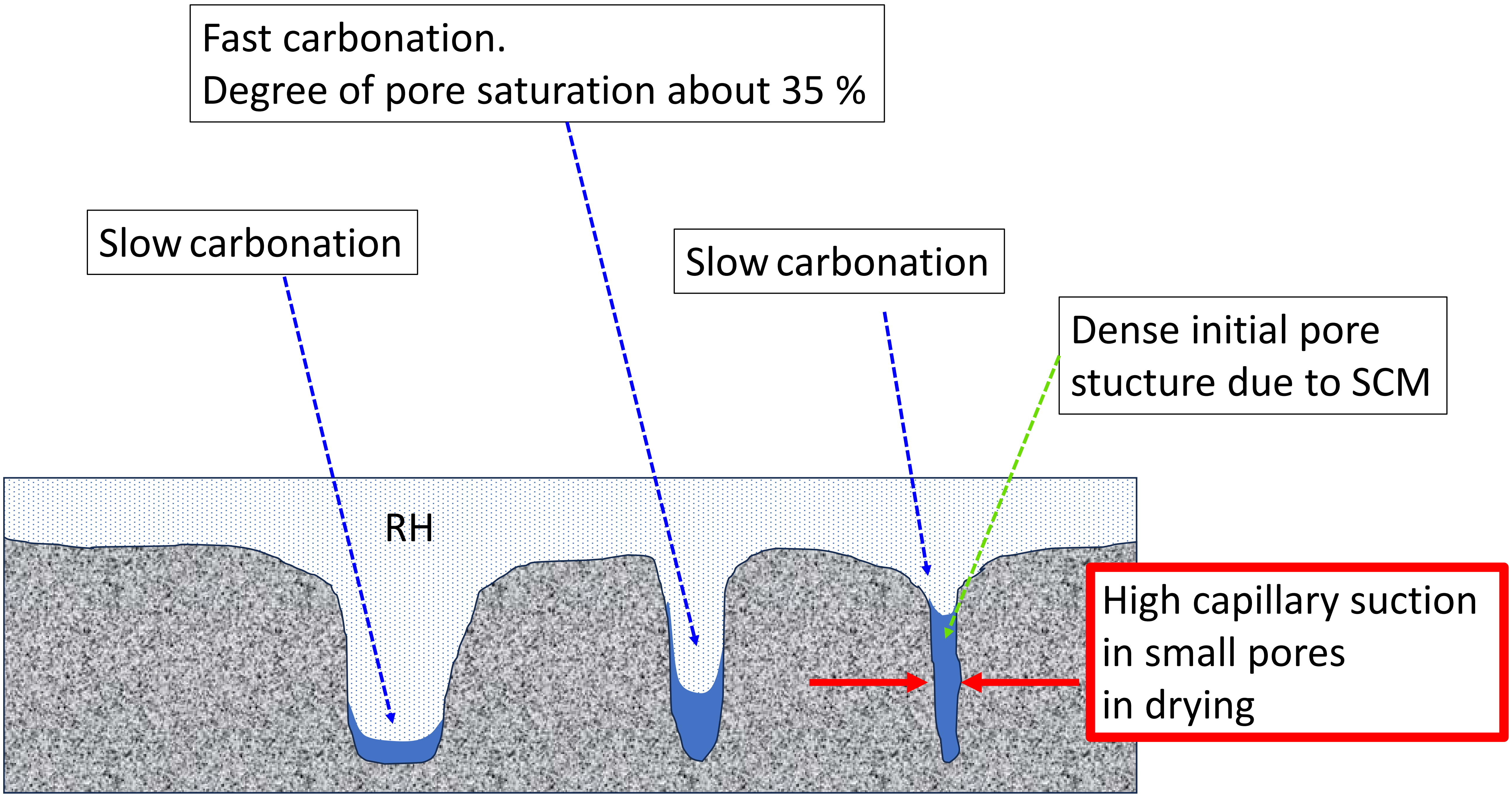


Fig. Capillary condensation and carbonation rate in different pore sizes. (AK)

Evolution of microstructural changes in cement paste during environmental drying.

Wioletta Soja, Fabien Georget, Hamed Maraghechi 1, Karen Scrivener. Cement and Concrete Research. Volume 134, August 2020

CO_2-free RH 70% drying after 3 d and 28 d curing.

What happens to the pore structure during a 12 month CO_2 free drying **?**

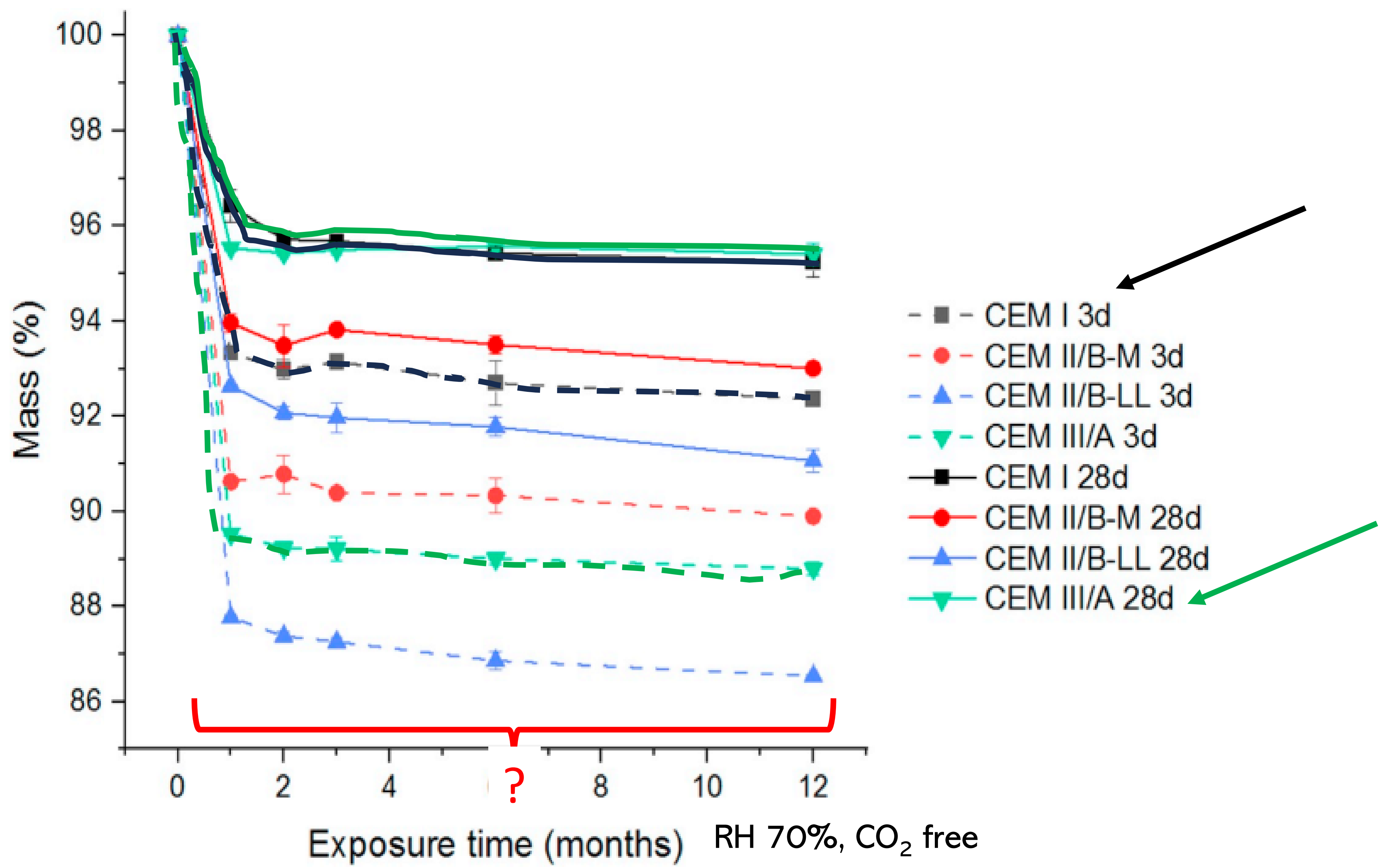


Fig. 2. Mass evolution during 12 months exposure at 70% RH in CO_2-free atmosphere for all studied cements.

Evolution of microstructural changes in cement paste during environmental drying.

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Cements characterizations.

European terminology – EN 197	CEM I	CEM II/B-M	CEM II/B-LL	CEM III/A	MixSL
Components (wt%)					
Clinker	93.8	69.6	61.9	43.8	46.9
Limestone	–	12.5	28.7	–	20
Burnt oil shale	–	13.8	–	–	20
Slag	–	–	–	48.7	10
MAC[a]	–	1.2	4.9	3.3	–
Gypsum	6.2	2.9	4.5	4.2	3.1

a Minor Additional Constituent - (According to EN 197-1 it is allowed to add up to 5% of MAC.

Evolution of microstructural changes in cement paste during environmental drying.

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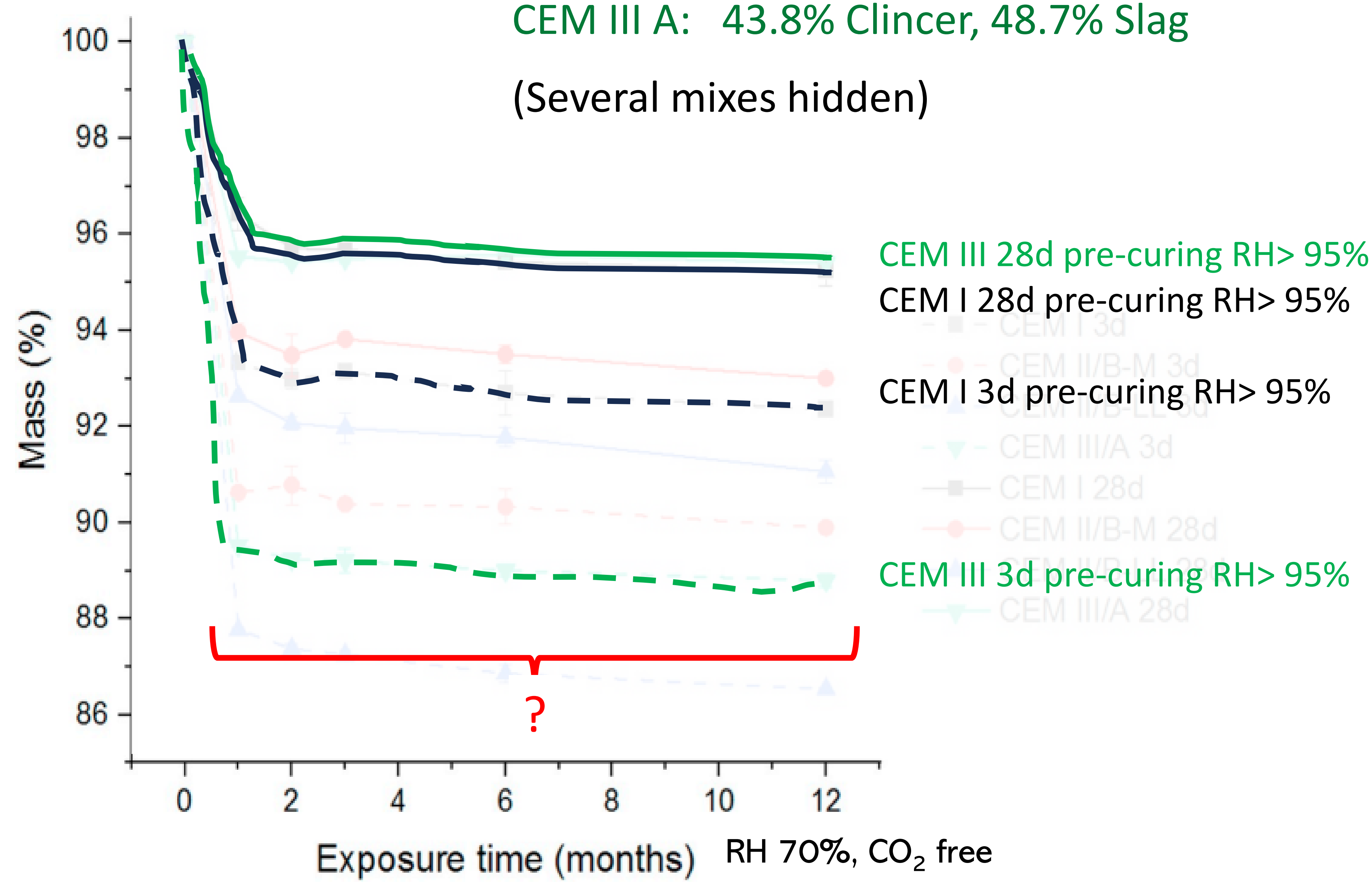
CO_2-free RH 70% drying after 3 d and 28 d curing.
What happens to the pore structure during a 12 month CO_2 free drying **?**

CEM I: 93.8% Clincer

CEM III A: 43.8% Clincer, 48.7% Slag

(Several mixes hidden)



RH 70%, CO_2 free

Fig. 2. Mass evolution during 12 months exposure at 70% RH in CO_2-free atmosphere for all studied cements.

XRD analysis. Almost nothing happens.

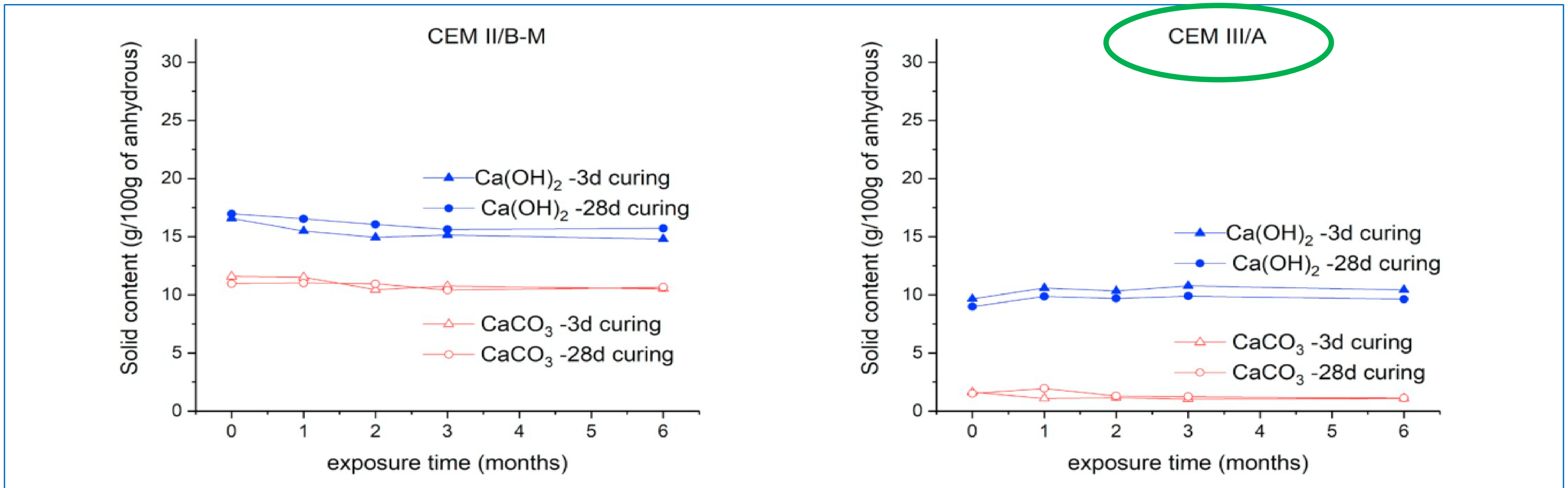


Fig. 3. Portlandite ($Ca(OH)_2$) and calcium carbonate ($CaCO_3$) content as a function of exposure time in CO_2-free atmosphere and 70% RH, for mixes cured 3 and 28 days before exposure (w/c = 0.40).

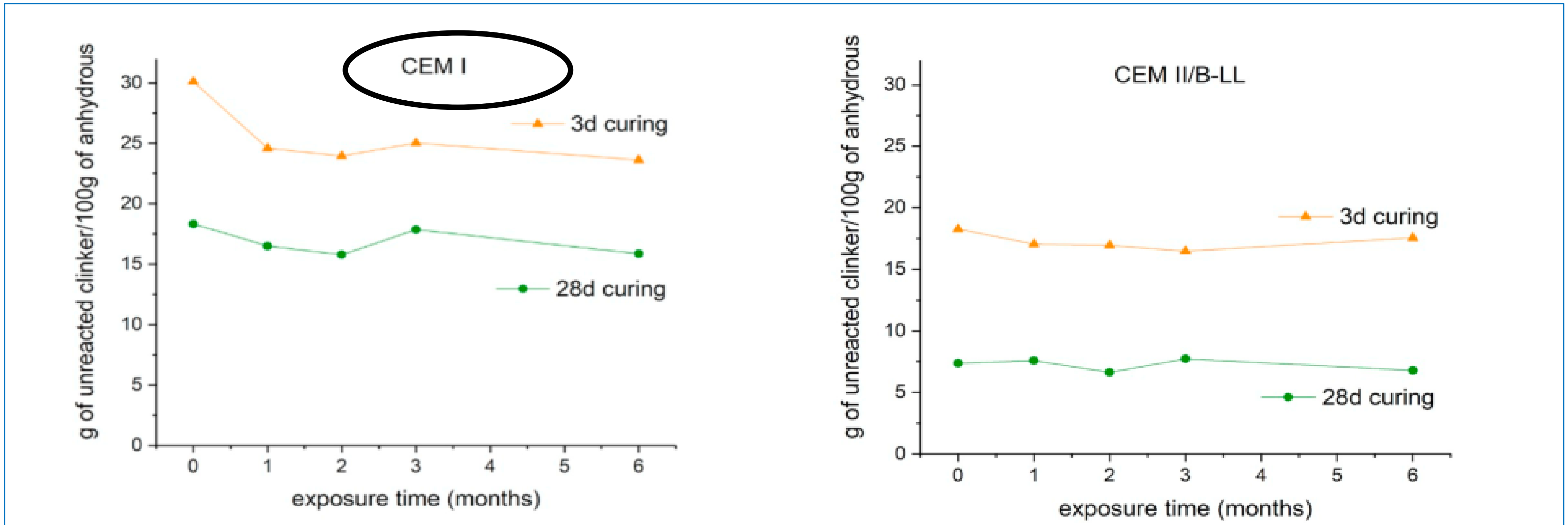
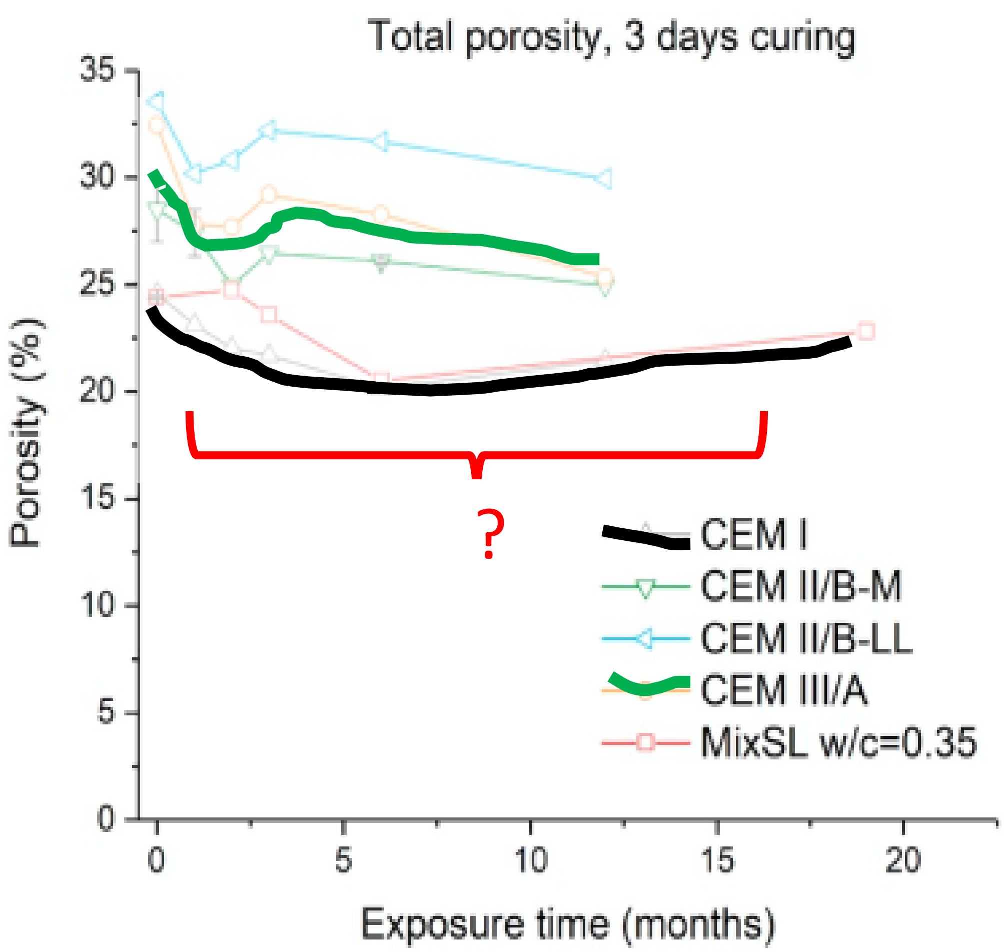


Fig. 4. Changes in unreacted clinker content as a function of exposure time in CO_2-free atmosphere and 70% RH, for 3 and 28 days of curing.

Total Porosity. Not much happens.

MIP



MIP

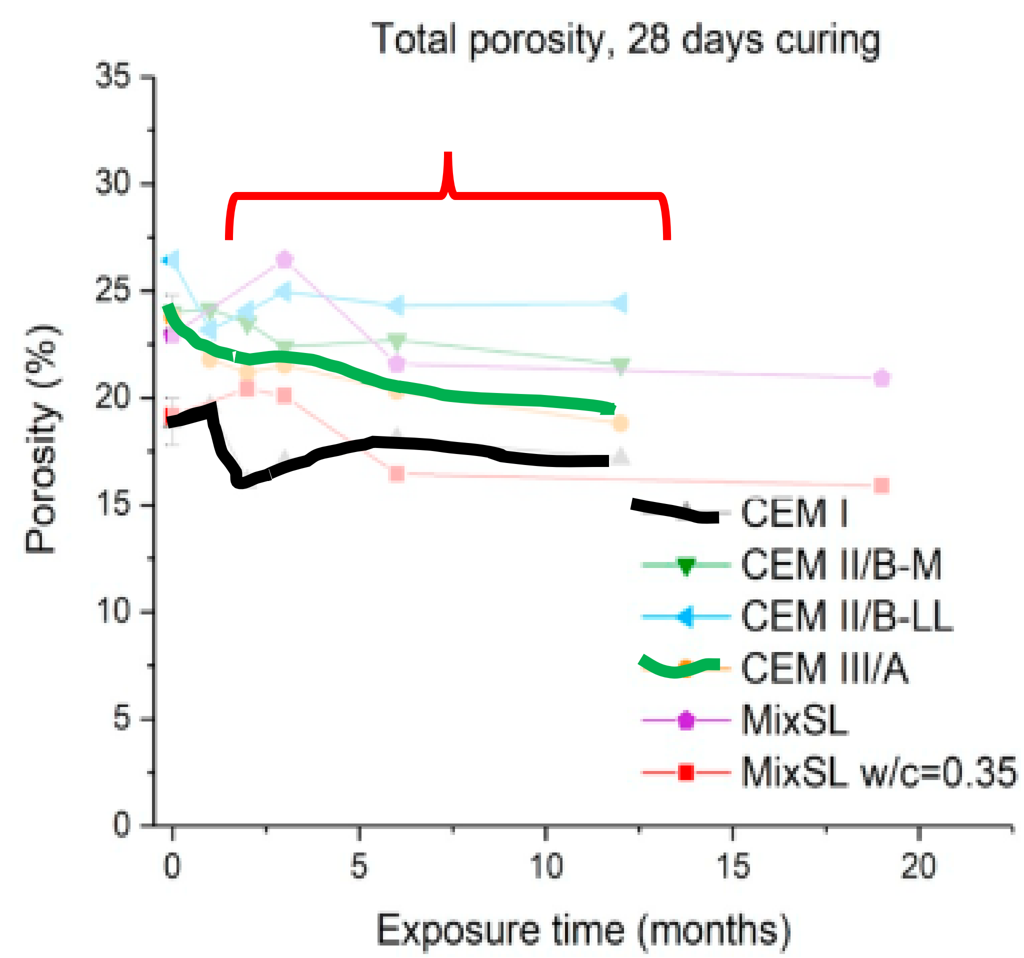


Fig. 8. Total porosity quantification of OPC and blended cement pastes after curing for 3 and 28 days, followed by exposure at 70% RH in CO_2-free atmosphere.

Pore structure coarsening in CO_2-free RH 70% drying after 3 d and 28 d curing.

Dramatic !

This has nothing to do with carbonation!

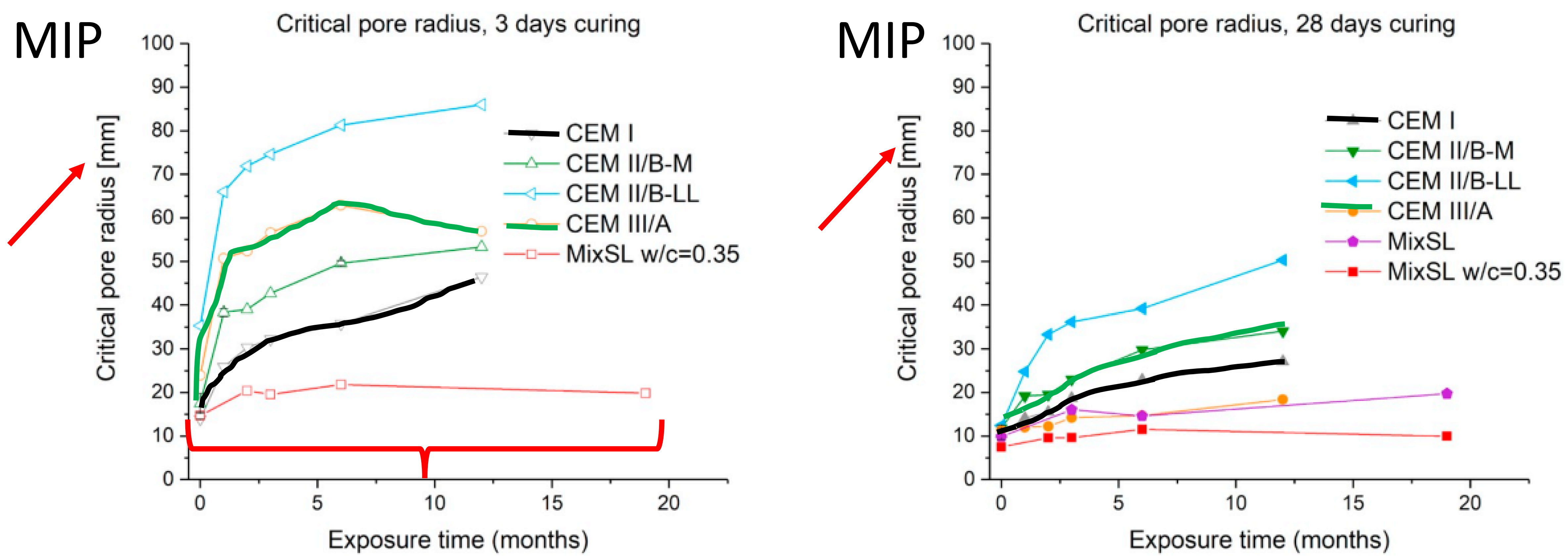


Fig. 7. Critical entry pore size for OPC and blended cement pastes after curing for 3 and 28 days, followed by exposure at 70% RH in CO_2-free atmosphere.

Pore structure coarsening in CO_2-free RH 70% drying after 3 d and 28 d curing.

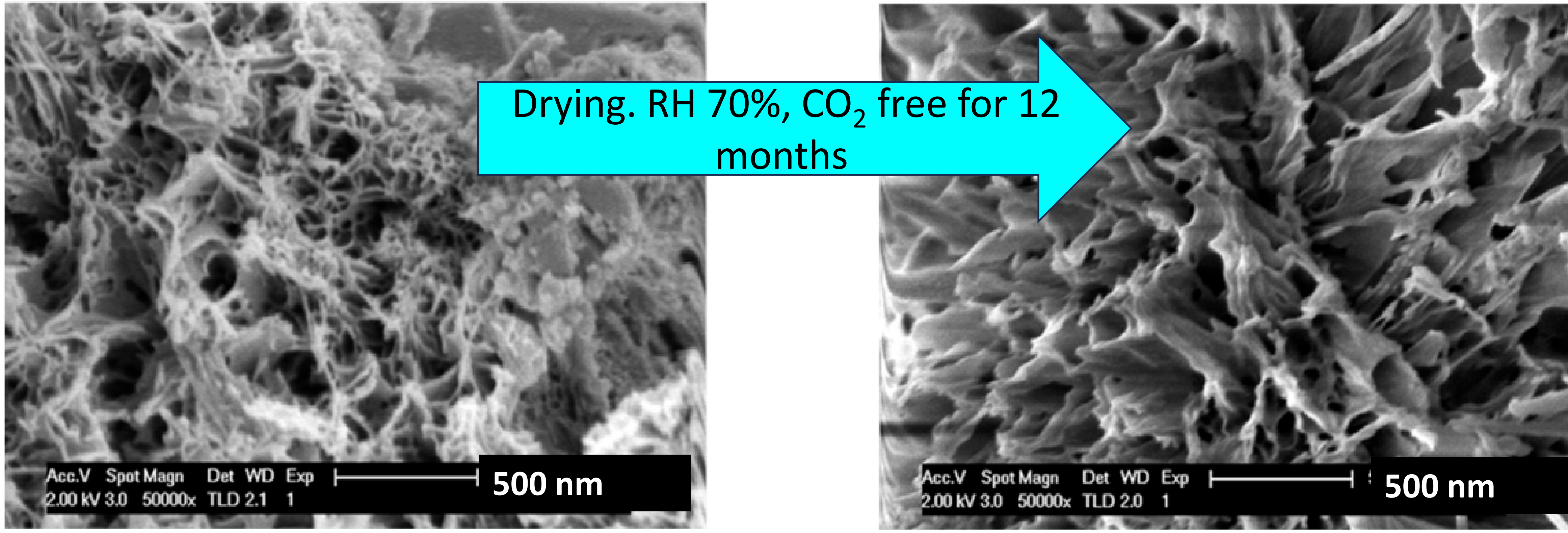
Dramatic !
This has nothing to do with carbonation!

- "Most past research studies into the effect of carbonation on porosity neglected the effect of relative humidity alone on the porosity changes, and they attribute the findings only to carbonation.
- This has resulted in some contradictory conclusions.

- "This study shows the importance of subtracting the effect of the drying during carbonation to describe the effect of carbonation on microstructure."

The explanation – Capillary suction

- Evolution of microstructural changes …Wioletta Soja, Fabien Georget, Hamed Maraghechi 1, Karen Scrivener



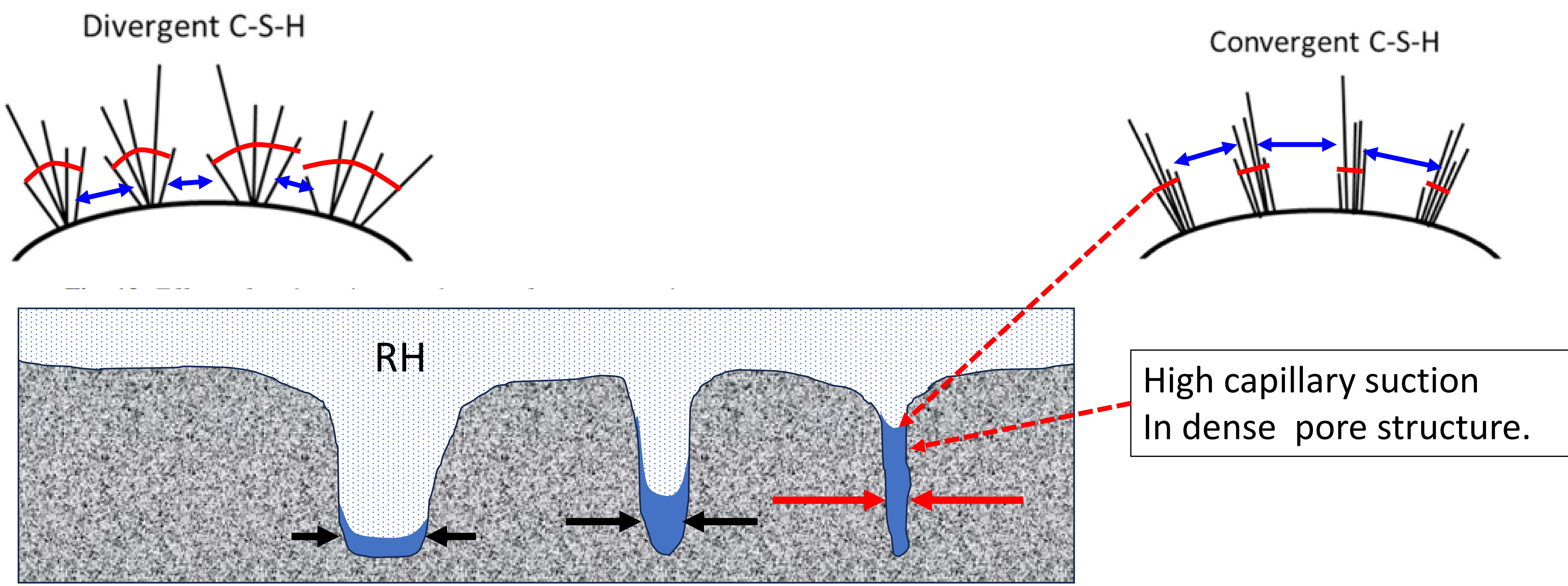
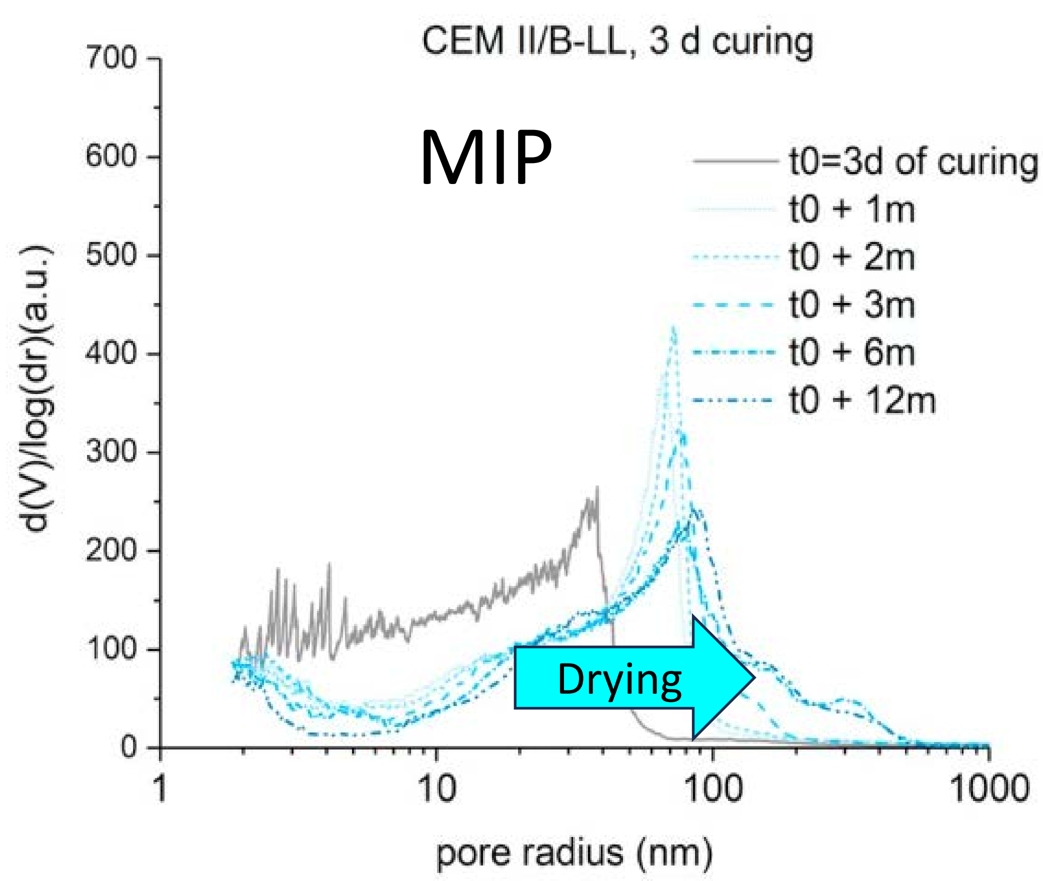
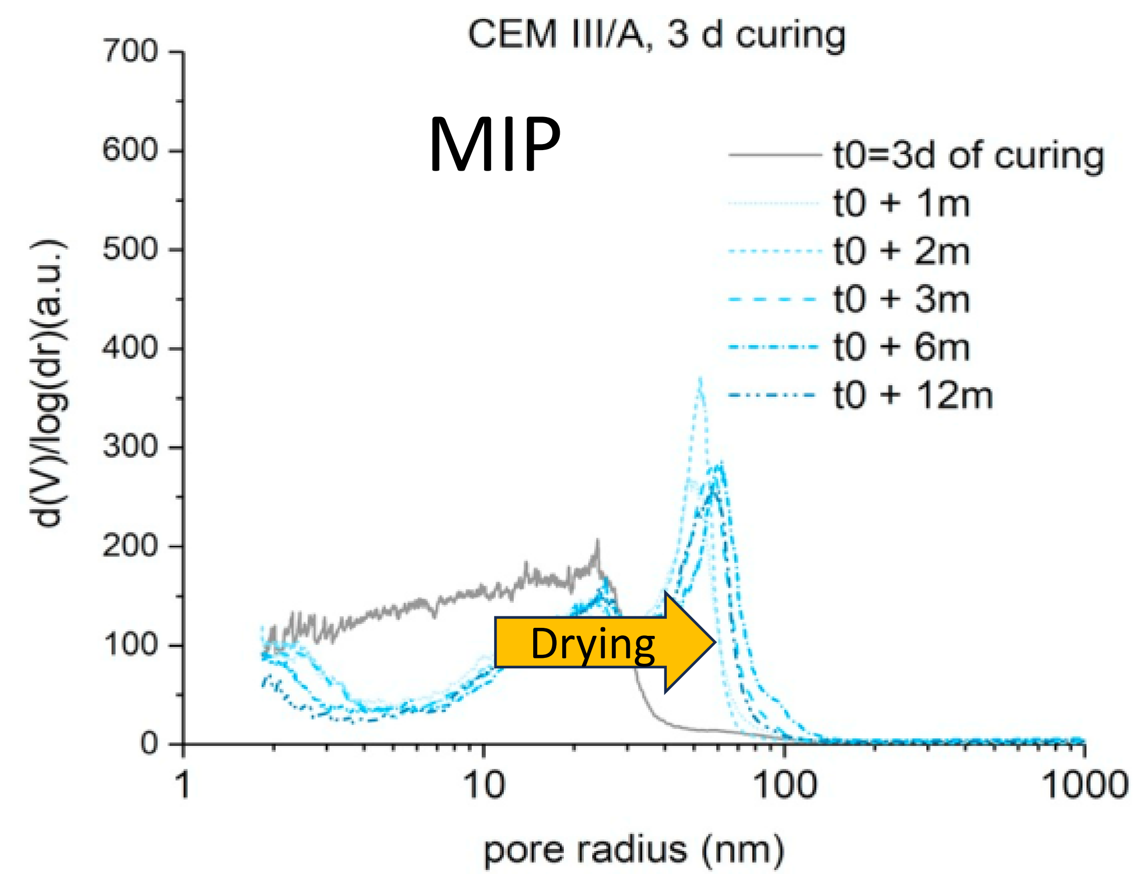


Fig. Capillary condensation, carbonation rate and capillary suction in different pore sizes. (AK)

Evolution of microstructural changes …Wioletta Soja, Fabien Georget, Hamed Maraghechi 1, Karen Scrivener





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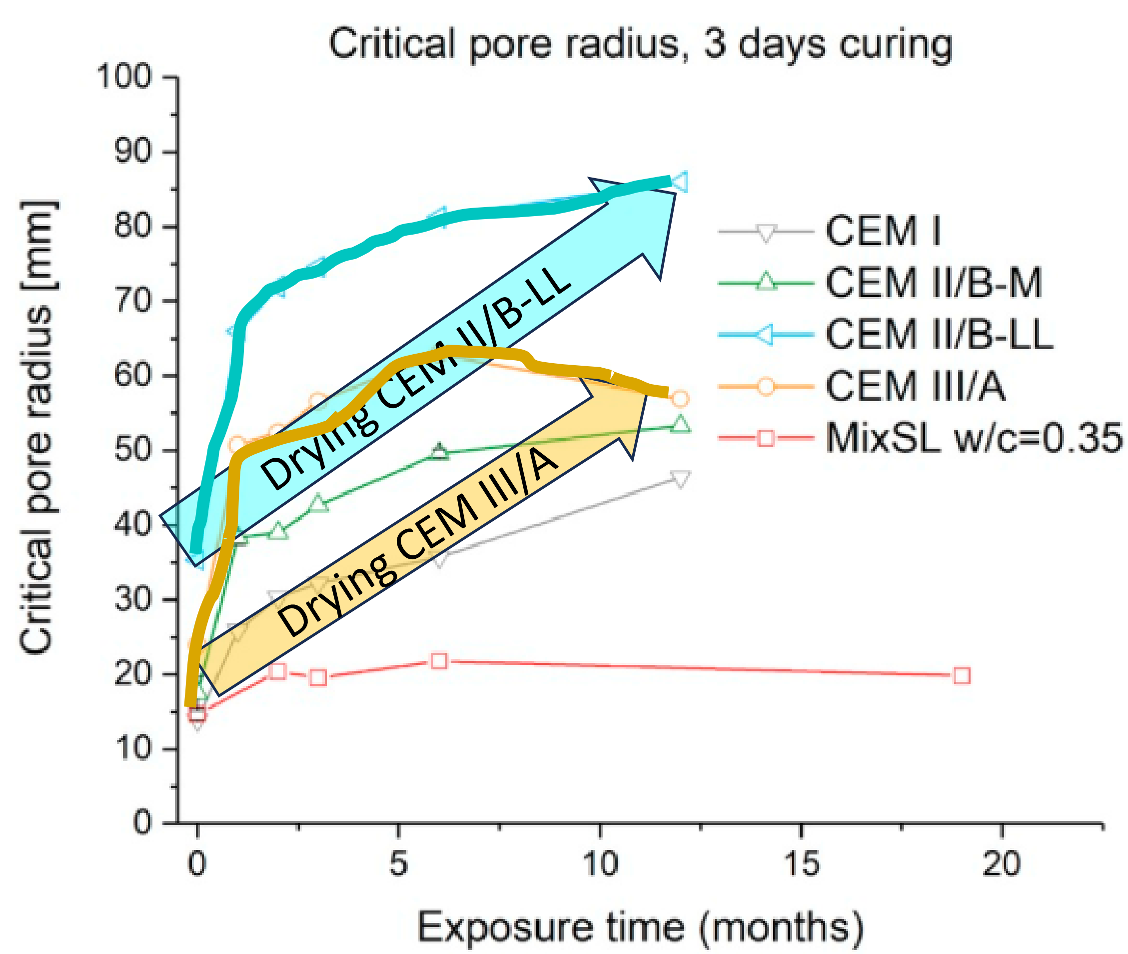


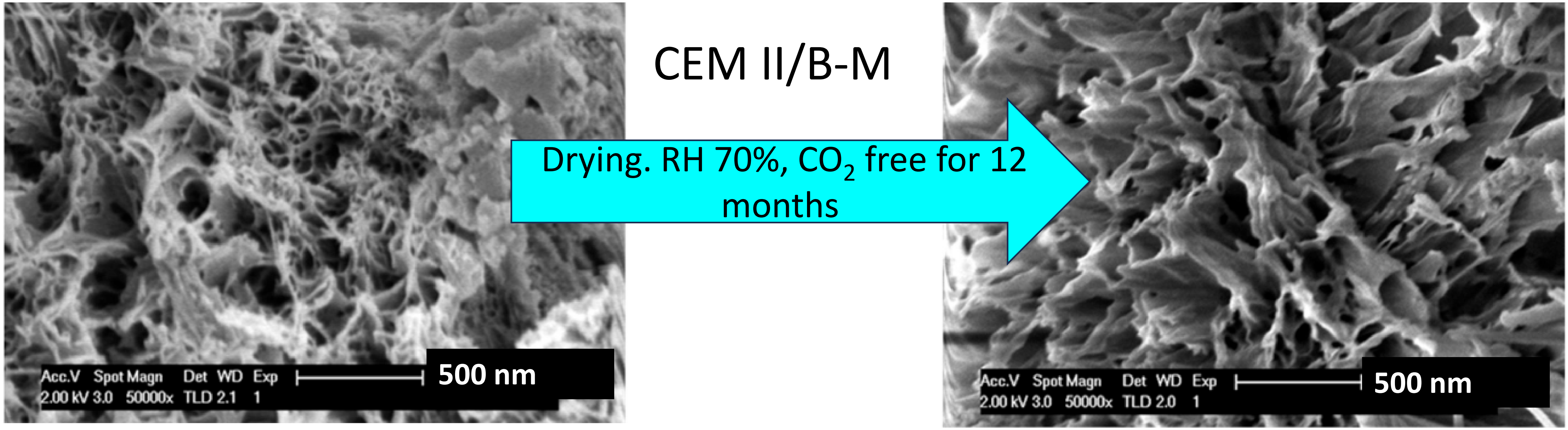


Fig. 11. Micrographs of CEM II/B-LL at 3 days of curing (on the left) vs. additional 12 months of drying at 70% RH (on the right).

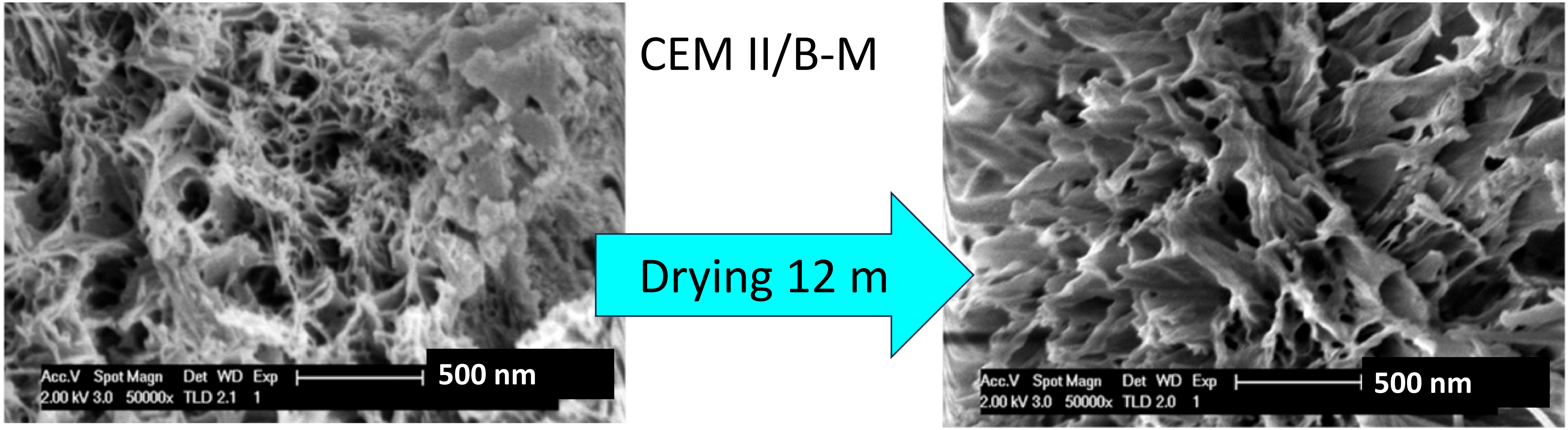
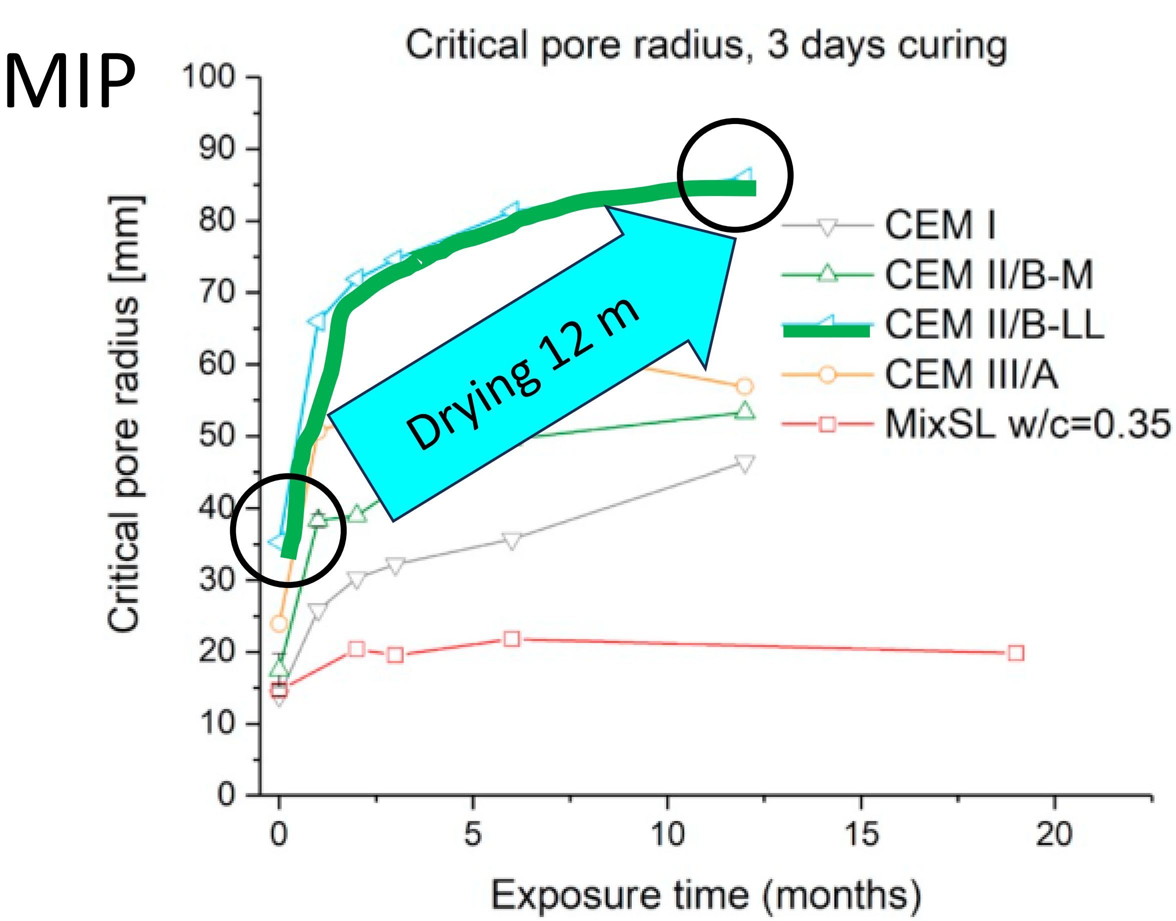
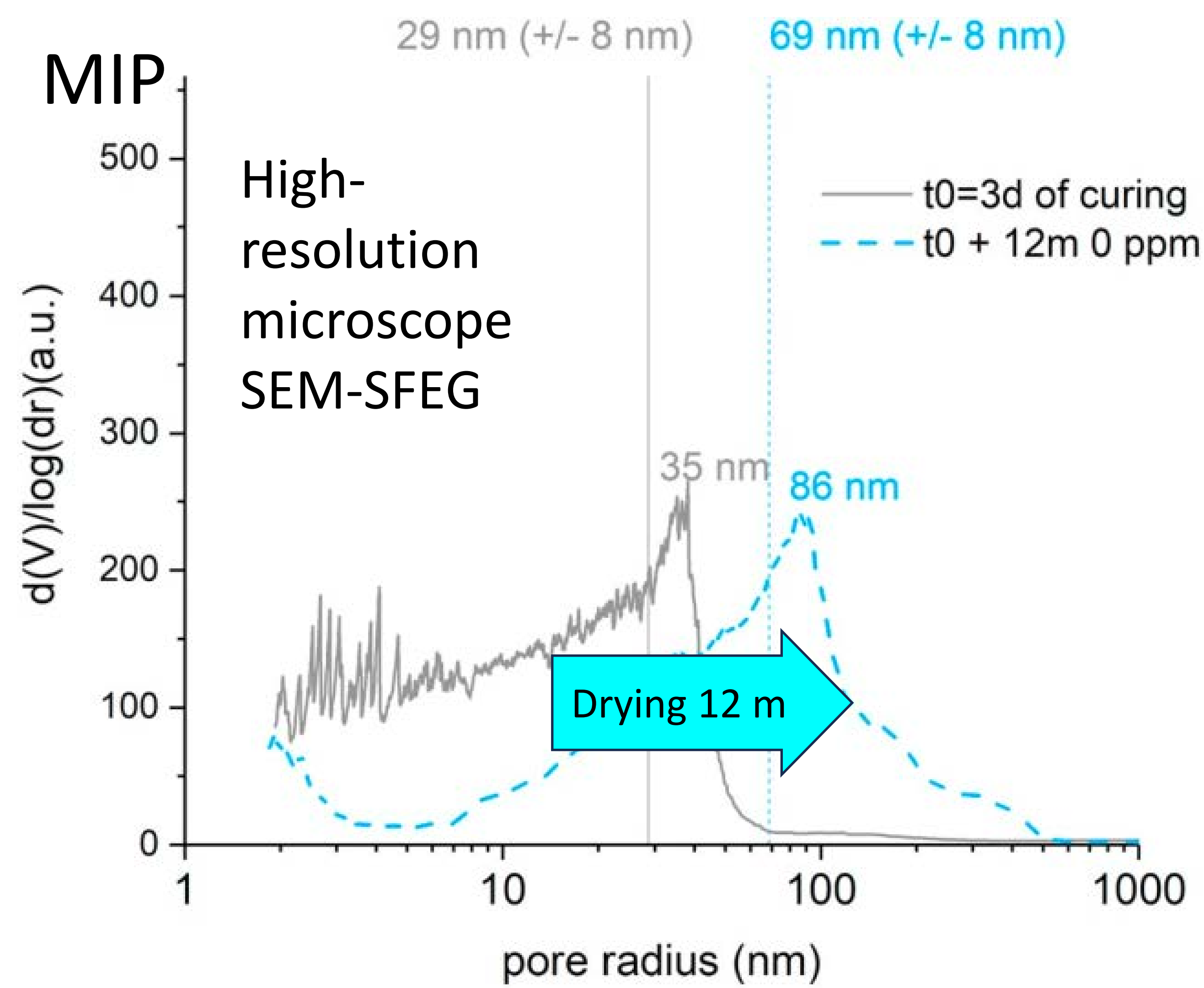


Fig. 11. Micrographs of CEM II/B-LL at 3 days of curing (on the left) vs. additional 12 months of drying at 70% RH (on the right).





Drying in different CO_2-free humidities, RH = 70% and 55%

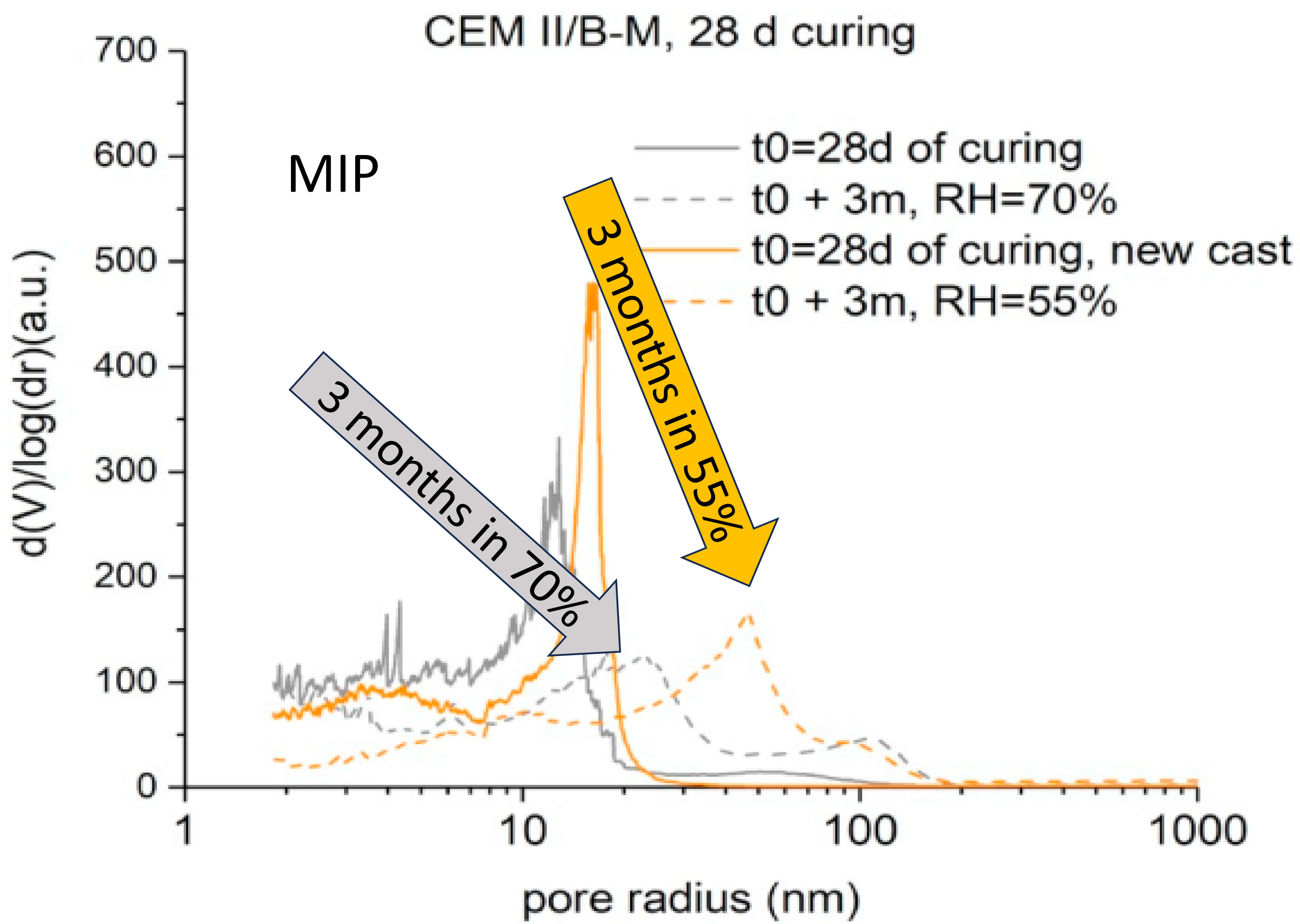


Fig. 9. Consequence of the exposure at different relative humidities on the coarsening effect.
(For interpretation of the references to color in this figure, the reader is
referred to the web version of this article.)

Re-immersion in solution.

- Re-immersion in pore solution for 3 months was done to 2 CEM I samples.
- Exposed for 1 month and for 6 months at 70% RH in CO_2-free environment.

Both radii decreased dramatically.
All measurable porosity is now below 10 nm.
The range of the critical entry-pore size is on the border of the MIP detection limit, which is 2 nm.

- Total porosity decreased by 10%. The reasons are not clear.
- The test was not done to blended cements.
- So, we do not know, how the blended cements would have behaved.

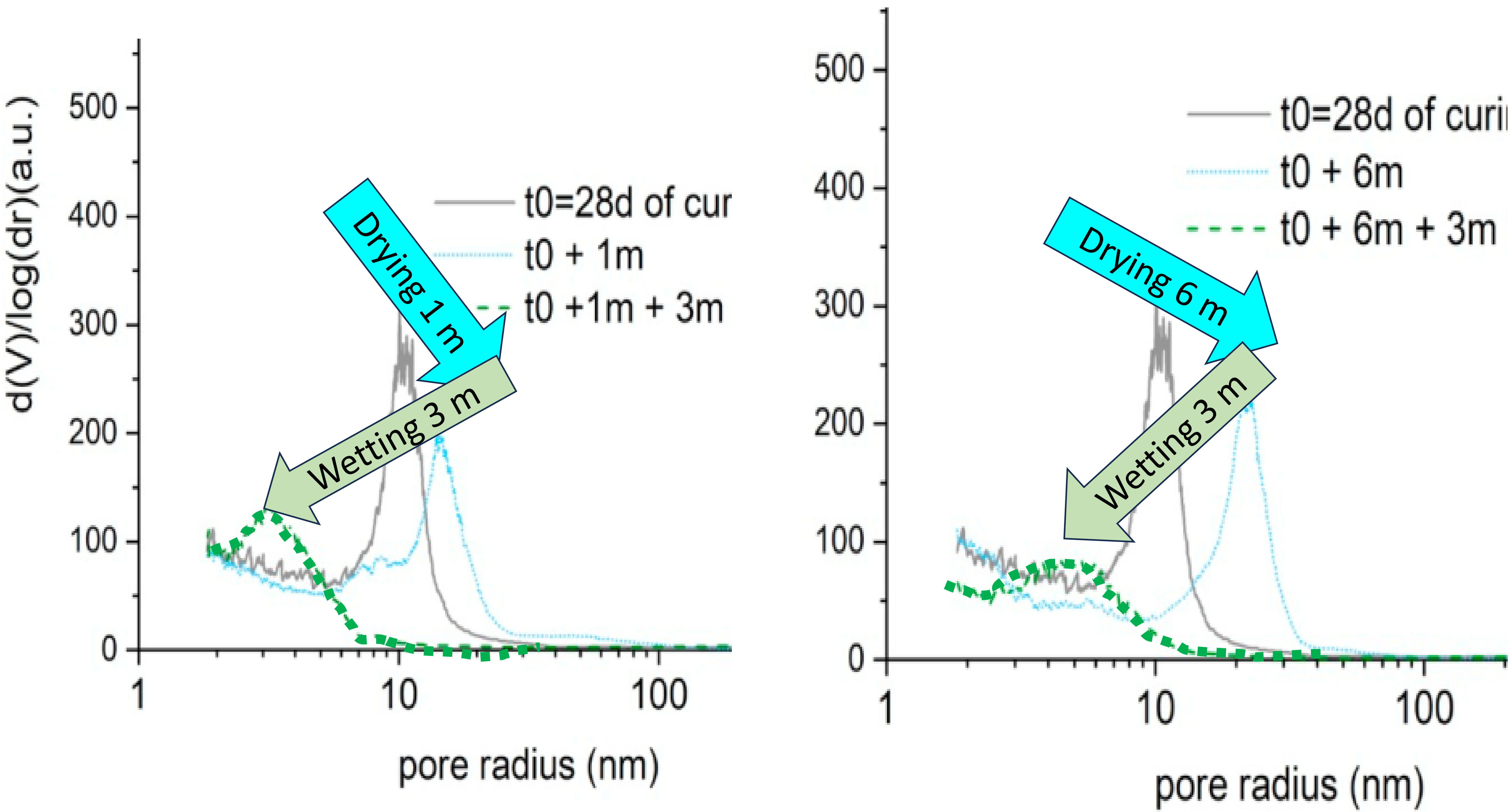
Drying is reversible. Carbonation is not.

What kind of porestructure developes in natutural varying humidity conditions?
How would the pore structure effect the carconation ?

Re-immersion in solution.

(Drying is reversible. Carbonation is not.)

CEM I



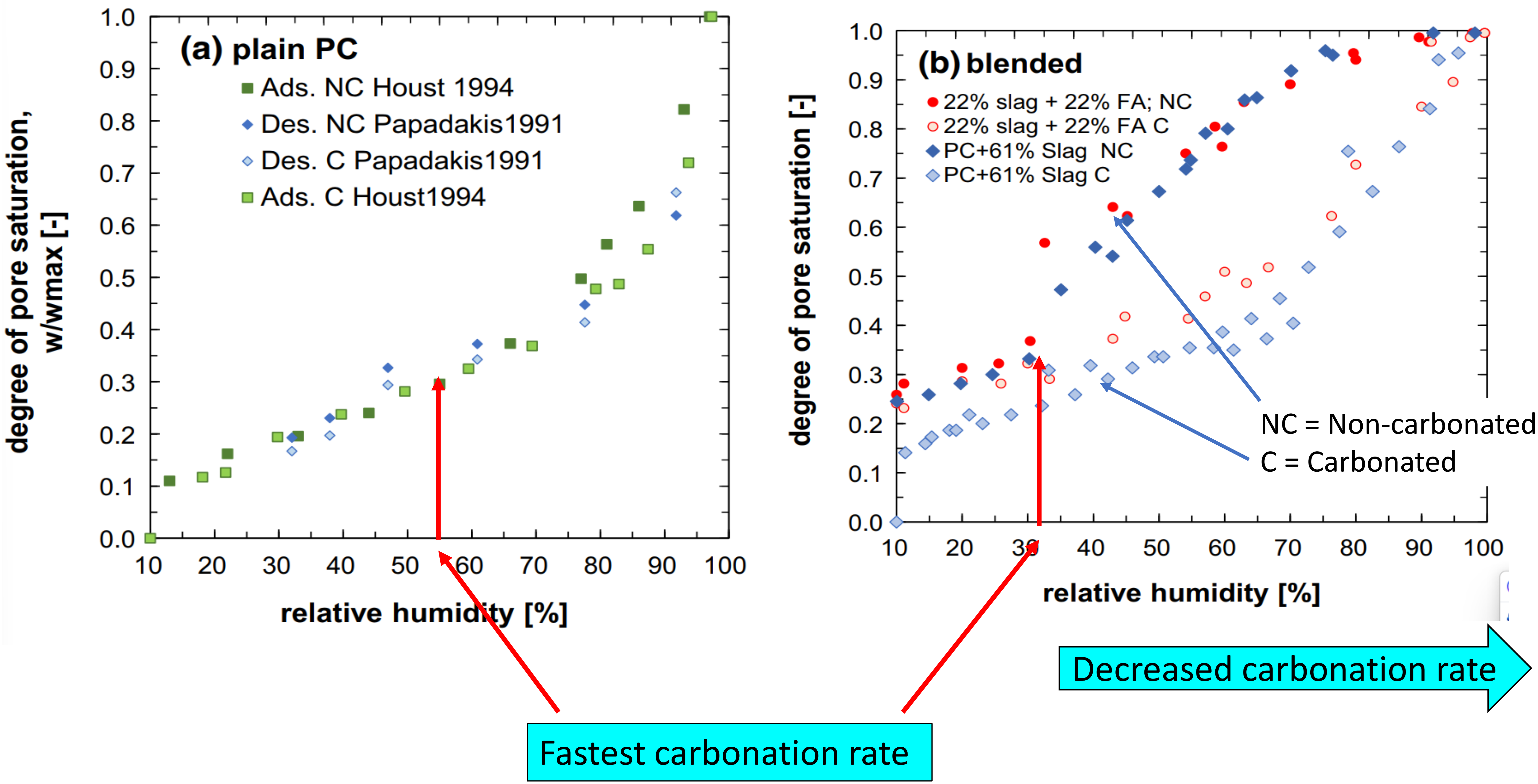
Effect of curing on carbonation resistance

With blended cements (CEM II A-M and CEM IV A-M) based on natural carbonation tests for 1 year ….

- an extension of the wet curing period from 1 to 3 days increased the predicted service life by a factor of more than 2
- a factor of 4 improvement is gained by increasing from 1 to 7 days of wet curing
- It was found that 3 days of curing should be enough for replacement levels of less than 30 wt% for FA or 50 wt% for BFS.
- For higher replacement levels, longer curing periods are desirable.
- Higher temperature, better carbonation resistance.

Effect of curing on carbonation resistance

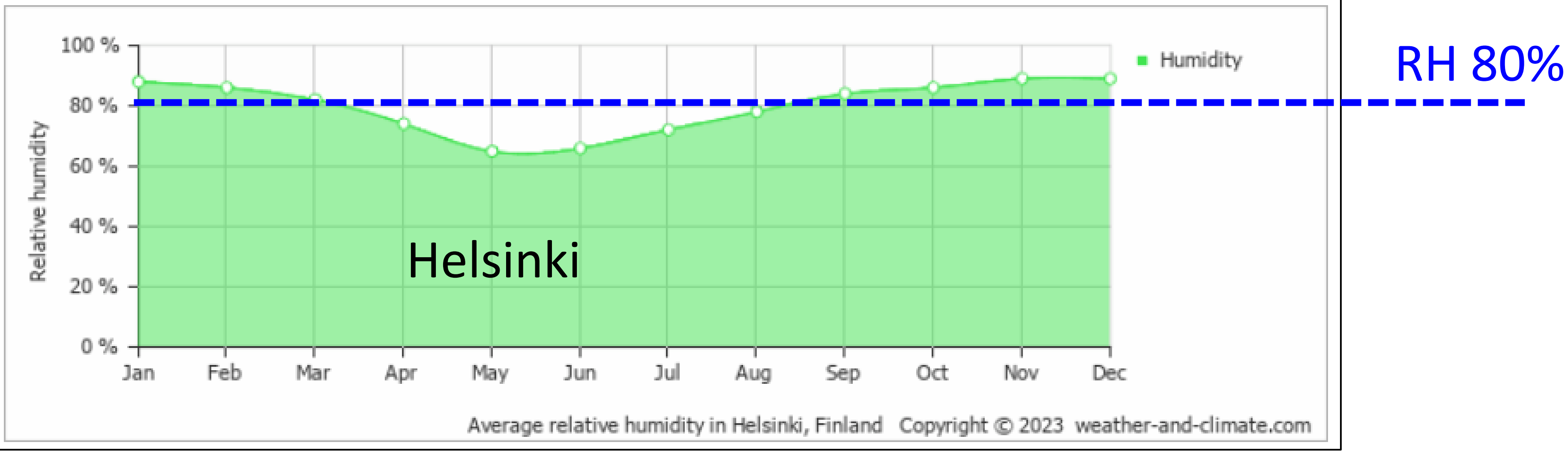
- Curing has an important effect on the carbonation resistance of concrete…
- The effect is less pronounced for plain PC concrete than for concrete with SCMs…
- If adequate precautions are taken, e.g. sufficiently long curing and reduced w/c ratio, the depth of carbonation of concrete with binders containing SCMs may be the same as for concrete with PC.
- Thus, the type of curing, its duration and temperature as well as other environmental and geometrical conditions like wind speed, size of structural element, and type of formwork need to be considered when estimating the impact on the carbonation resistance.
- (Curing compounds may become useful. Anna’s opinion)
- Carbonation rate of water-cured samples was only 17% of the carbonation rate of aircured samples (28 days)…..

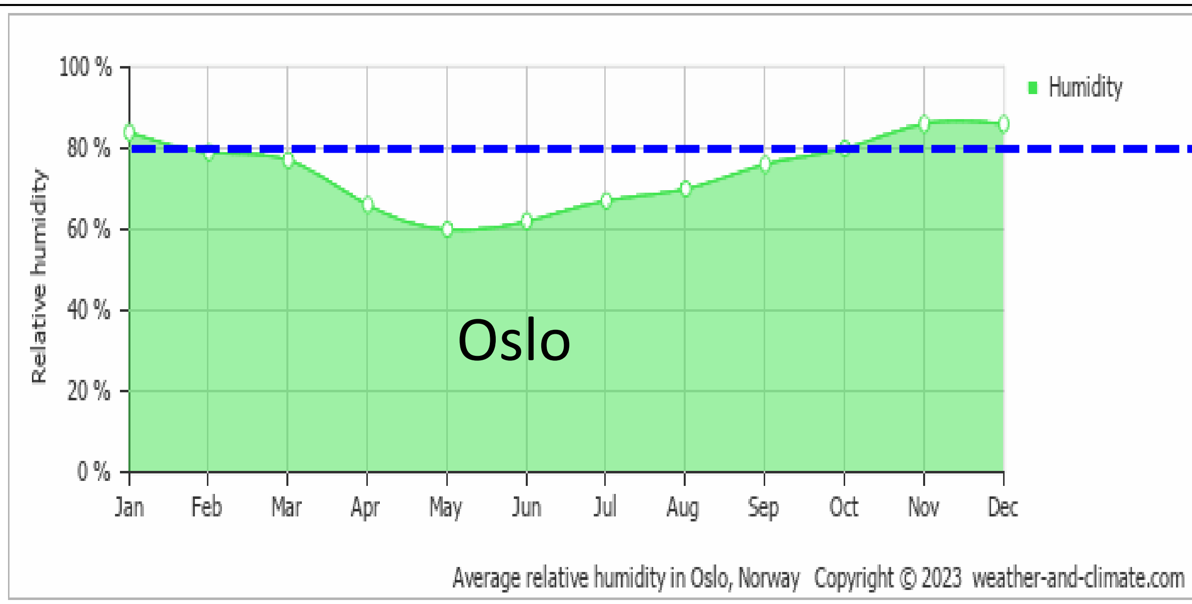


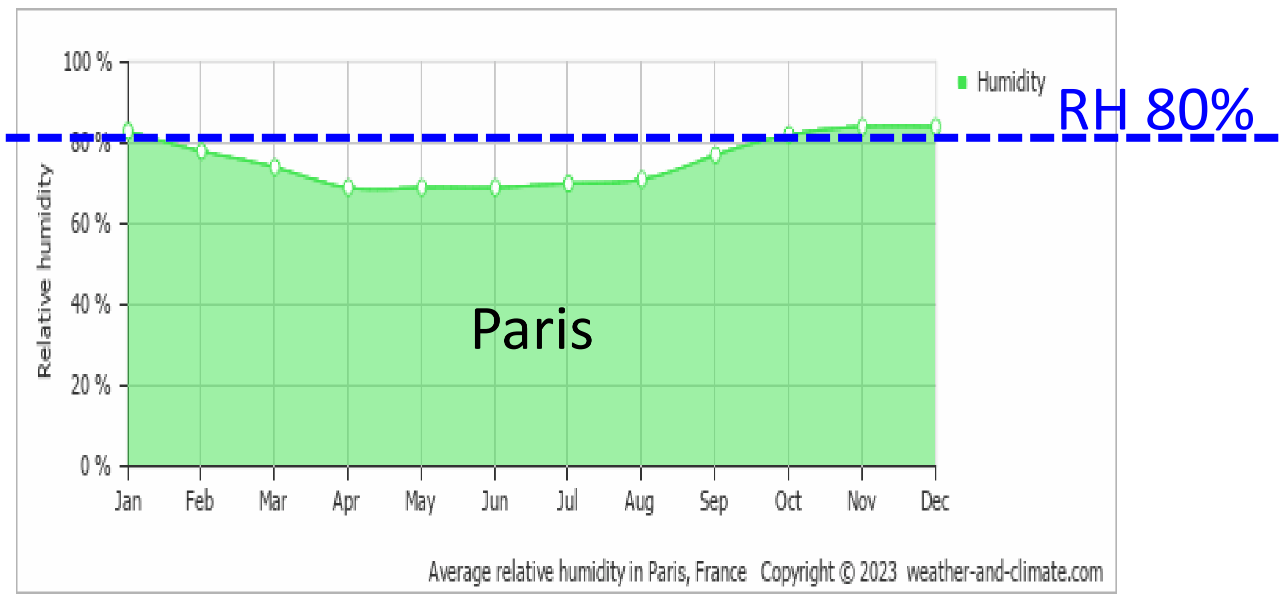
- The higher the RH,
- the denser the pore structure and
- slower the carbonation

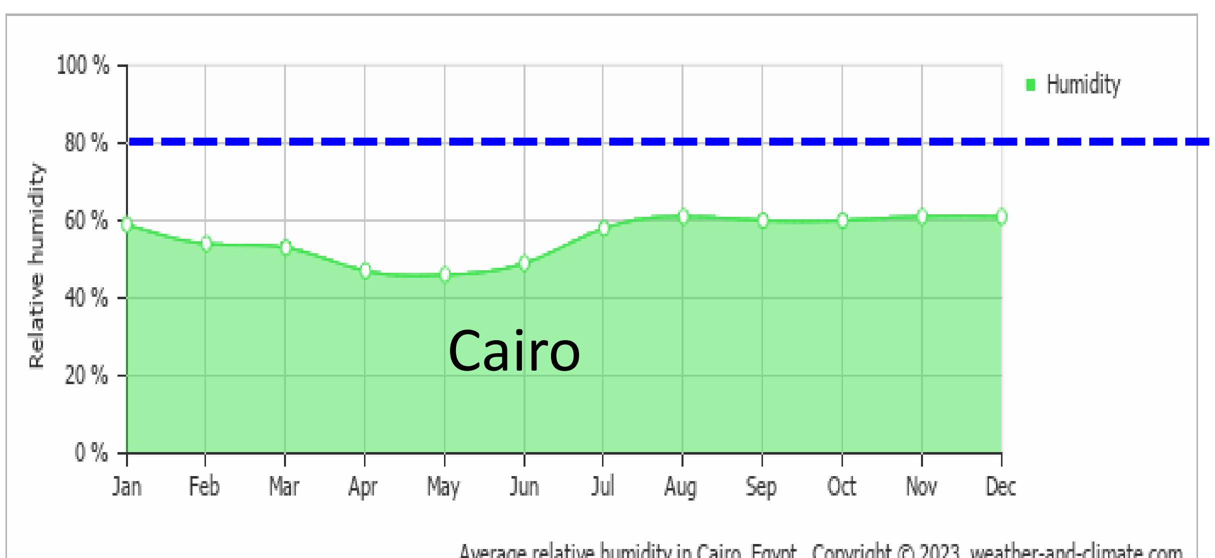
Average humidity in Helsinki

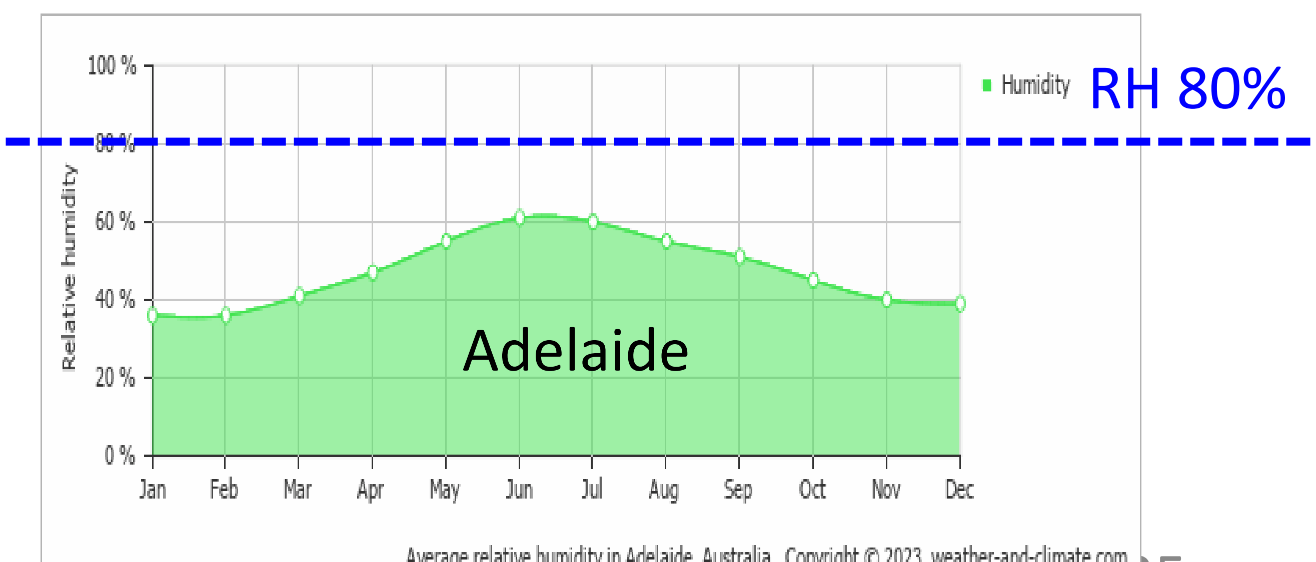
The mean monthly relative humidity over the year in Helsinki (Southern Finland), Finland.











Effects of carbonation on the pore structure of granulated blastfurnace slag concrete

Seppo Matala

- In curing procedure "Curing 1", also termed "non-aged" or "28 days", the specimens were stored for 21 days at 45% RH before testing.

- "Curing 2" or "cycled" involved precuring for 21 days at 45% RH, followed by six drying and wetting cycles, each with
  - wetting in water for 1 week and
  - drying at 45% RH for 6 weeks (atmospheric CO_2), and
  - thereafter storage at 45% RH until the start of tests at an age of 1 year.

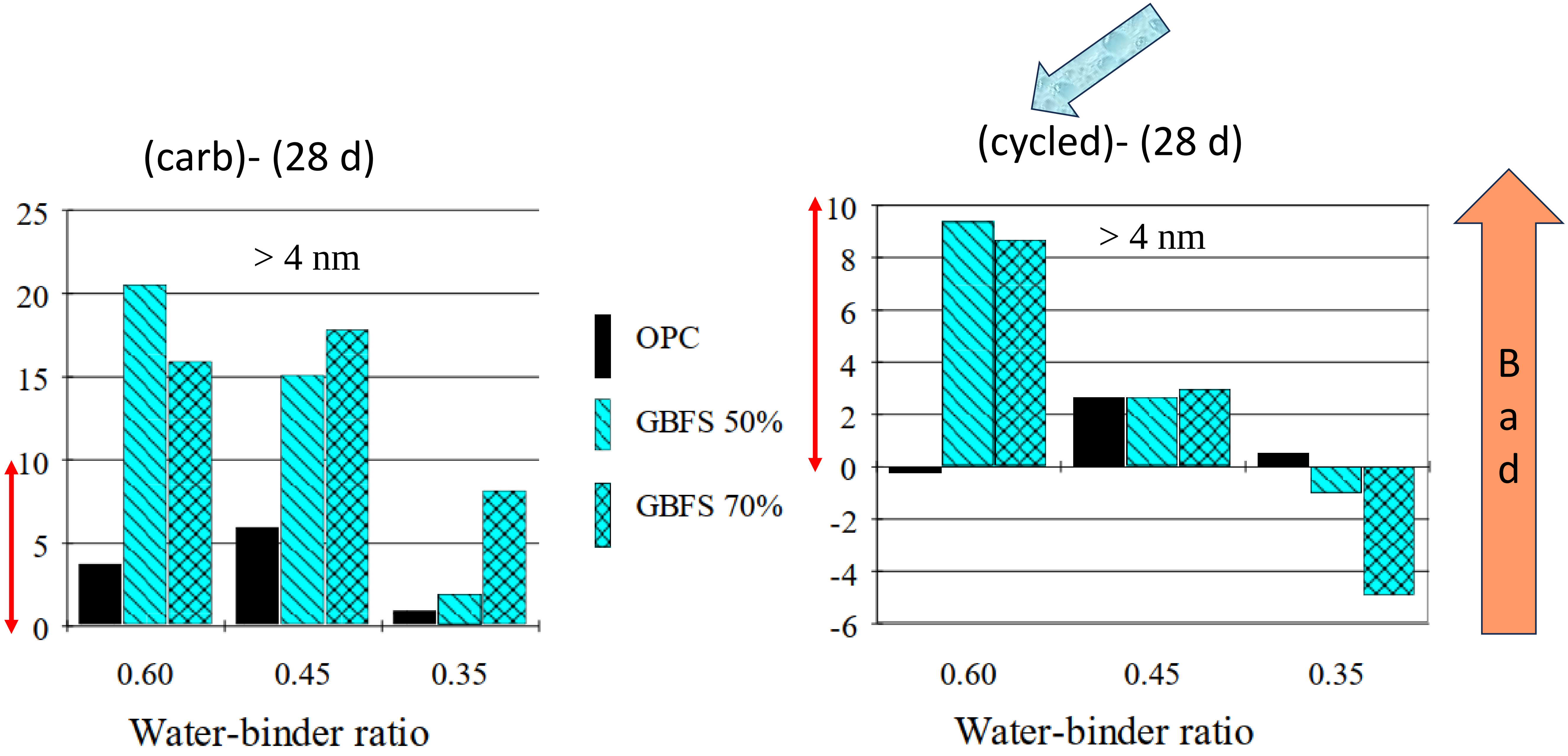
- The third curing procedure, "Curing 3" or "carbonated" involved storage at 45% RH and atmospheric CO_2 concentration until age 13 months for concretes and 15 months for pastes and mortars.

- The temperature in all curing procedures was 20° C.

Effects of carbonation on the pore structure of granulated blastfurnace slag concrete

Seppo Matala

- Difference in macroporosity (> 4 nm) values after carbonation and cycled treatments.
- Effect of W/B and cycled curing

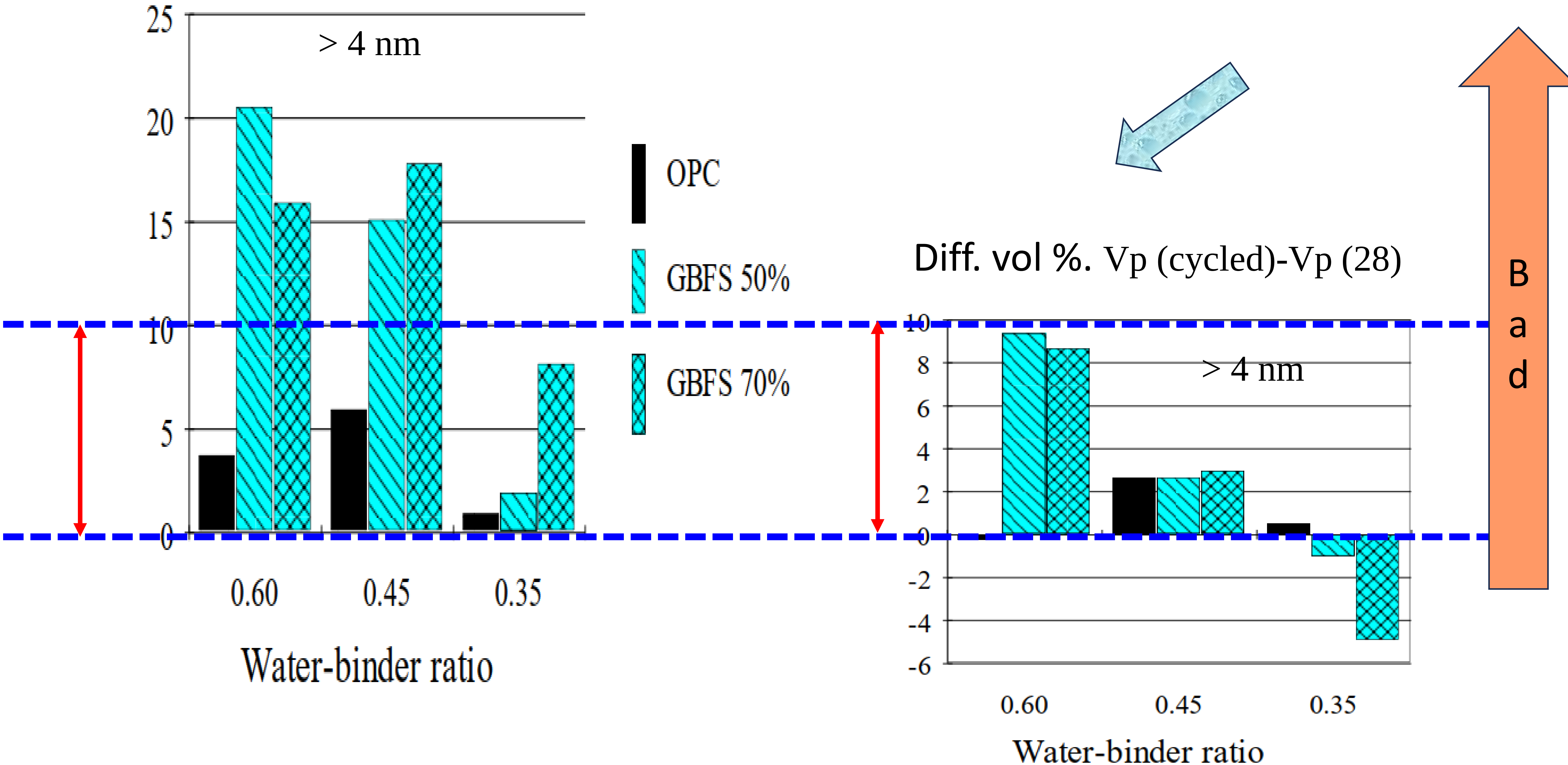


Effects of carbonation on the pore structure of granulated blastfurnace slag concrete

Seppo Matala

Effect of W/B and cycled curing

Diff. vol %. Vp (carb)-Vp (28)



Difference in macroporosity (> 4 nm) values after carbonation and cycled treatments.

Conclusions on kinetics

1. Curing increases carbonation resistance on in blended-systems much more than in PC-systems.

2. High RH slows down the carbonation rate in blended-systems more that in PC-systems. The relative humidity in Finland is high.

3. Carbonation reaction produces water. The increased RH slows down the reaction.

4. Coarse pore size due to drying will recover in high RH. (Anna´s opinion.)

5. When testing
   - Make the distinction between carbonation and drying. Both make pore size larger.
   - Drying is reversible. Carbonation is not. Re-wetting decreases pore size dramatically.
   - High CO_2-concentration accelerates the carbonation rate more in blended systems that in PC-systems.

Thank you !