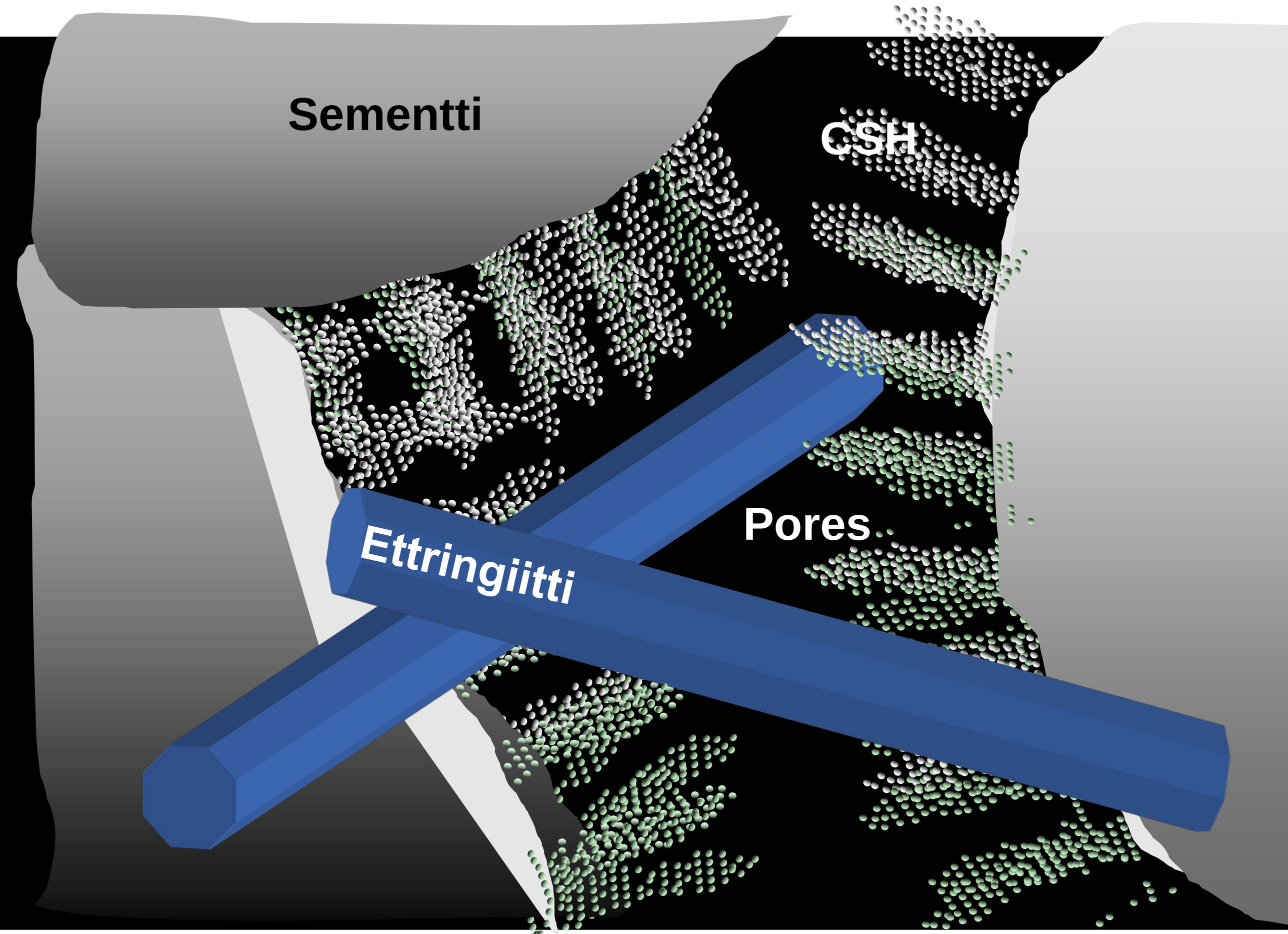
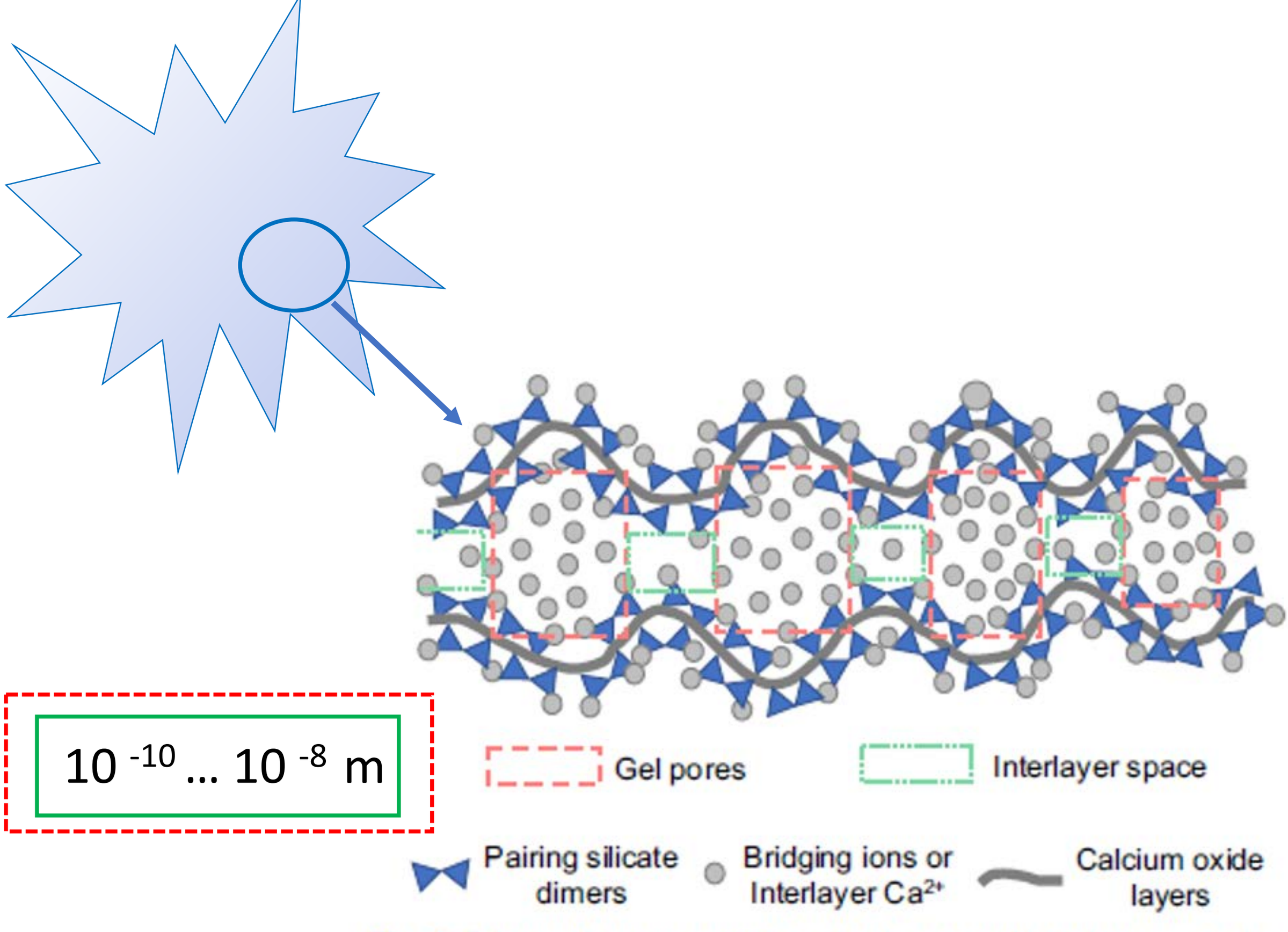
SCM composition, carbonation and the freeze–thaw resistance.
Based on literature.

13.3.2024 Anna Kronlöf

Nano-structure

x10000 2μm 2.00kV 6mm
#55 DSM 982


Sementti
CSH
Pores
Ettringiitti



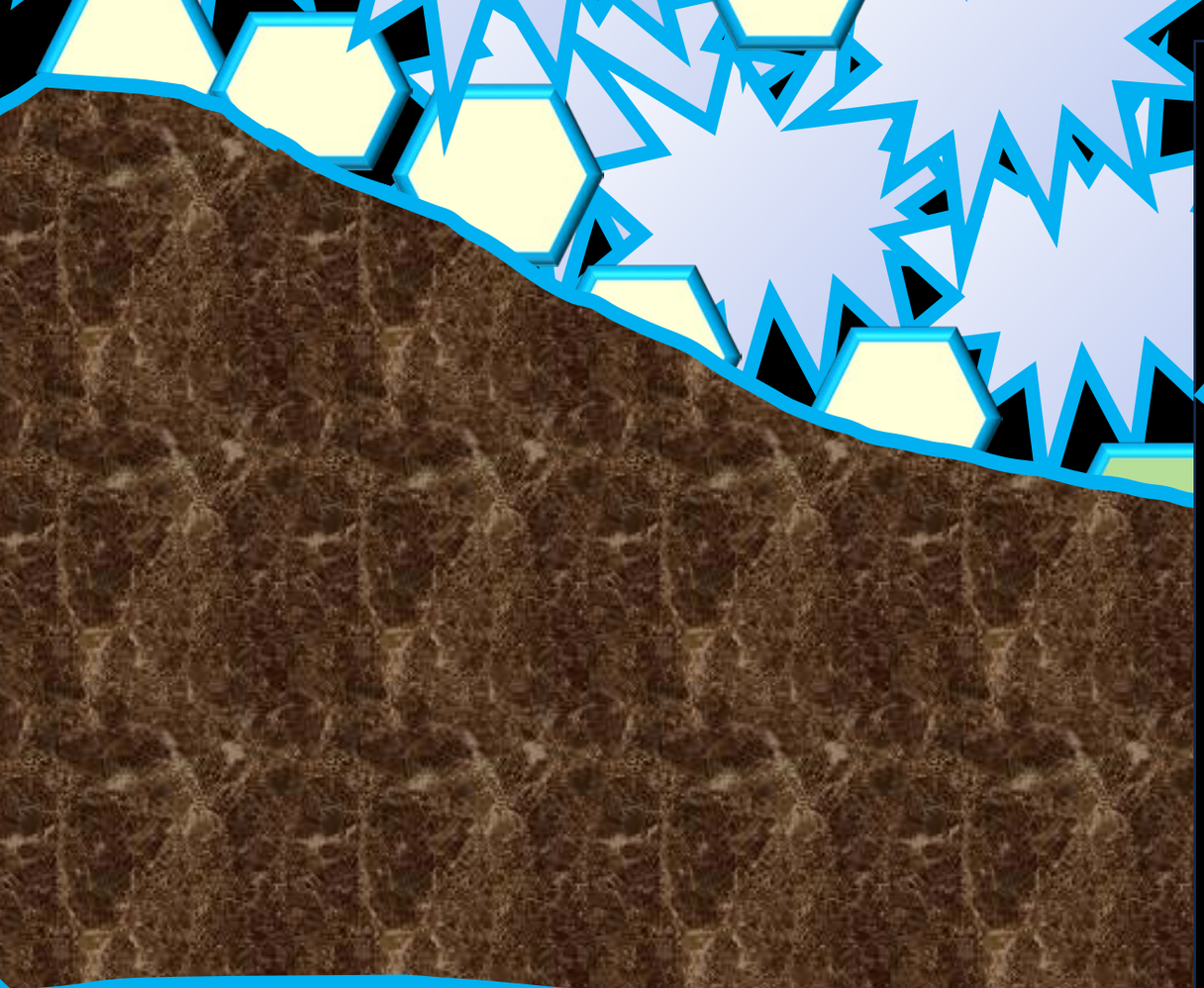
$10^{-10} \ldots 10^{-8}$ m

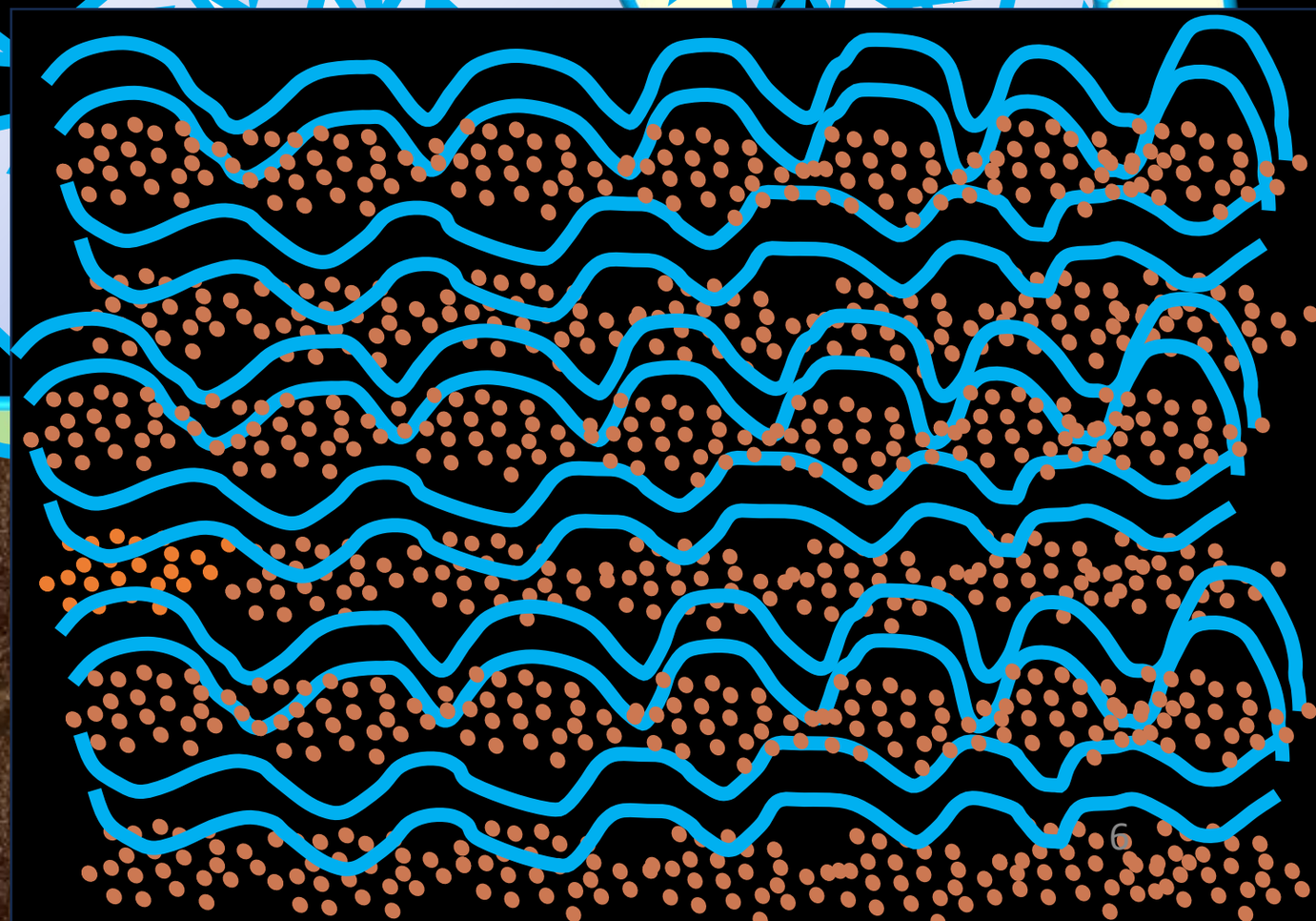
Fig. 1 Schematic representation of gel pore and interlayer space in C–S–H by winding calcium oxide layers.

Specific surface area (SSA) - methods

Surface area Gas adsorbtion and desorbtion isoterms on surfaces

- The formation of mono- and multilayers etc. are explained by **BET-theory**
- Gases N_2 Ar, CO_2
- Drying may change the sample.





Pore structure - methods

MIP Pore size distribution by Mercury intrusion porosimetry

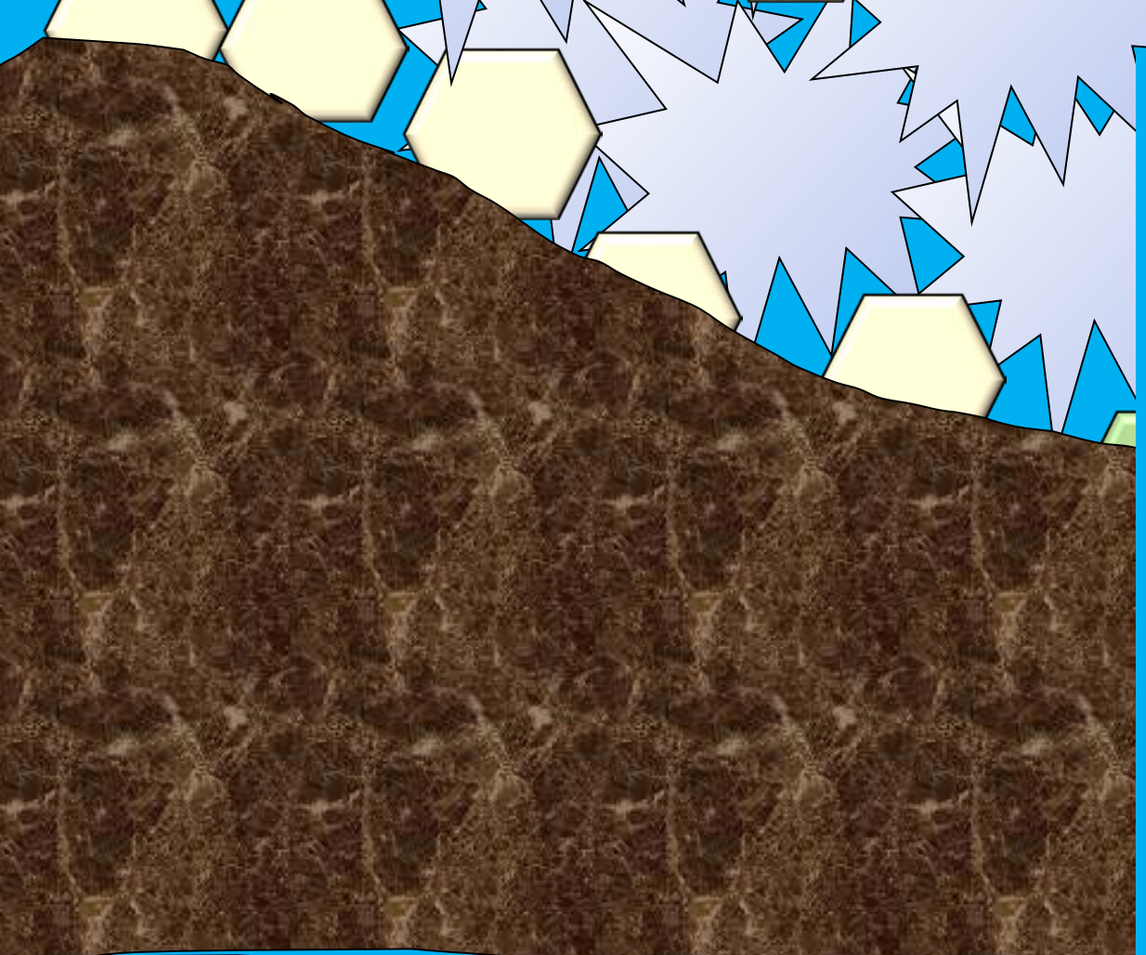
- Different pore sizes are filled in different pressures.
- Pressures are high and could damage the sample.

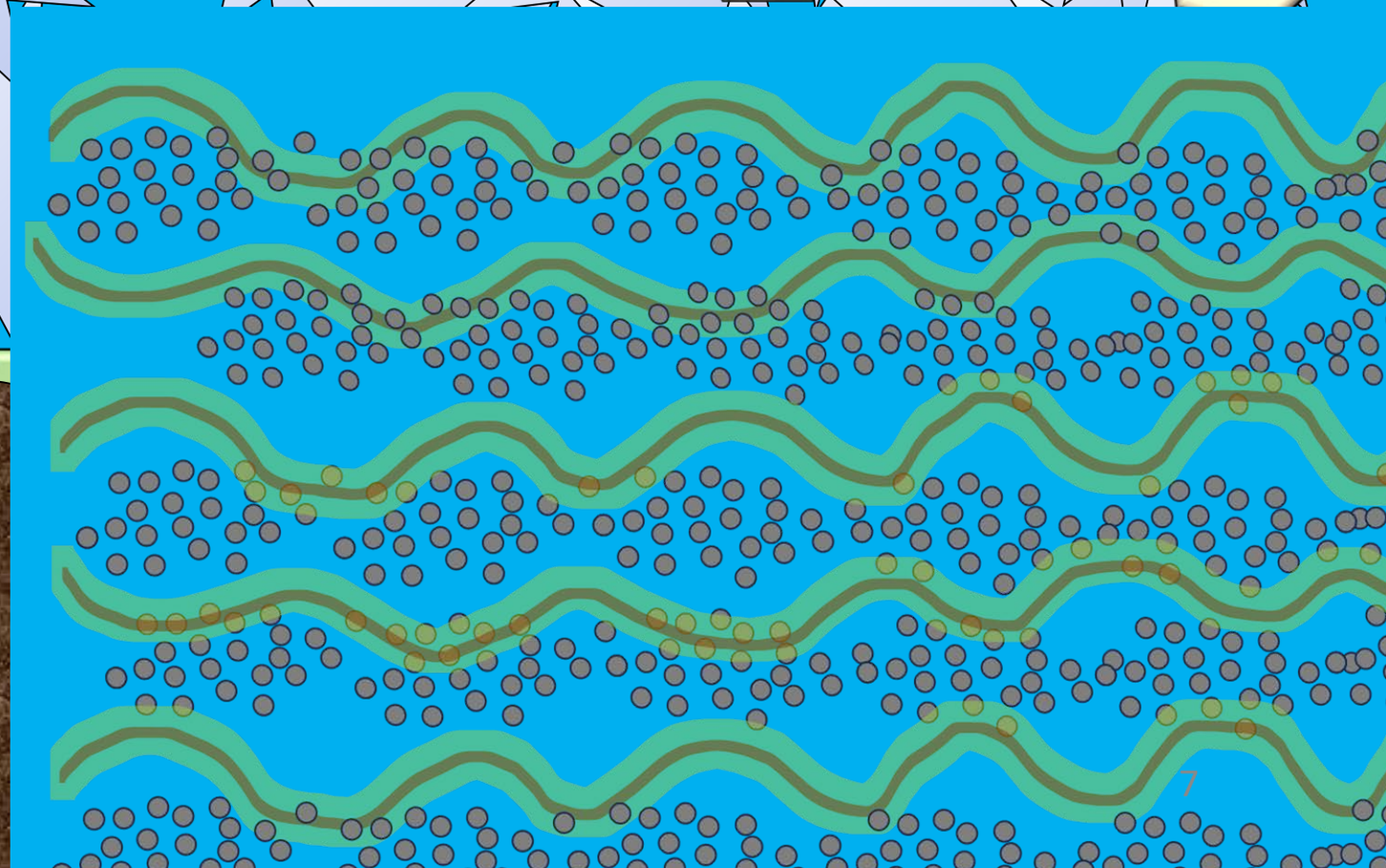
Pore size distribution by adsorption and desorption isotherms.

- Different pore sizes are filled in different relative pressures. Gases N_2 Ar, CO_2, H_2O

Total pore volume Helium pyctonometer

- All pores are filled with Helium. The total volume is measured.
- Also other gases can be used.





Review of Several Experimental Methods for Characterization of Micro- and Nano-Scale Pores in Cement-Based Material (1/2)

Aili and Maruyama *Int J Concr Struct Mater (2020) 14:55*

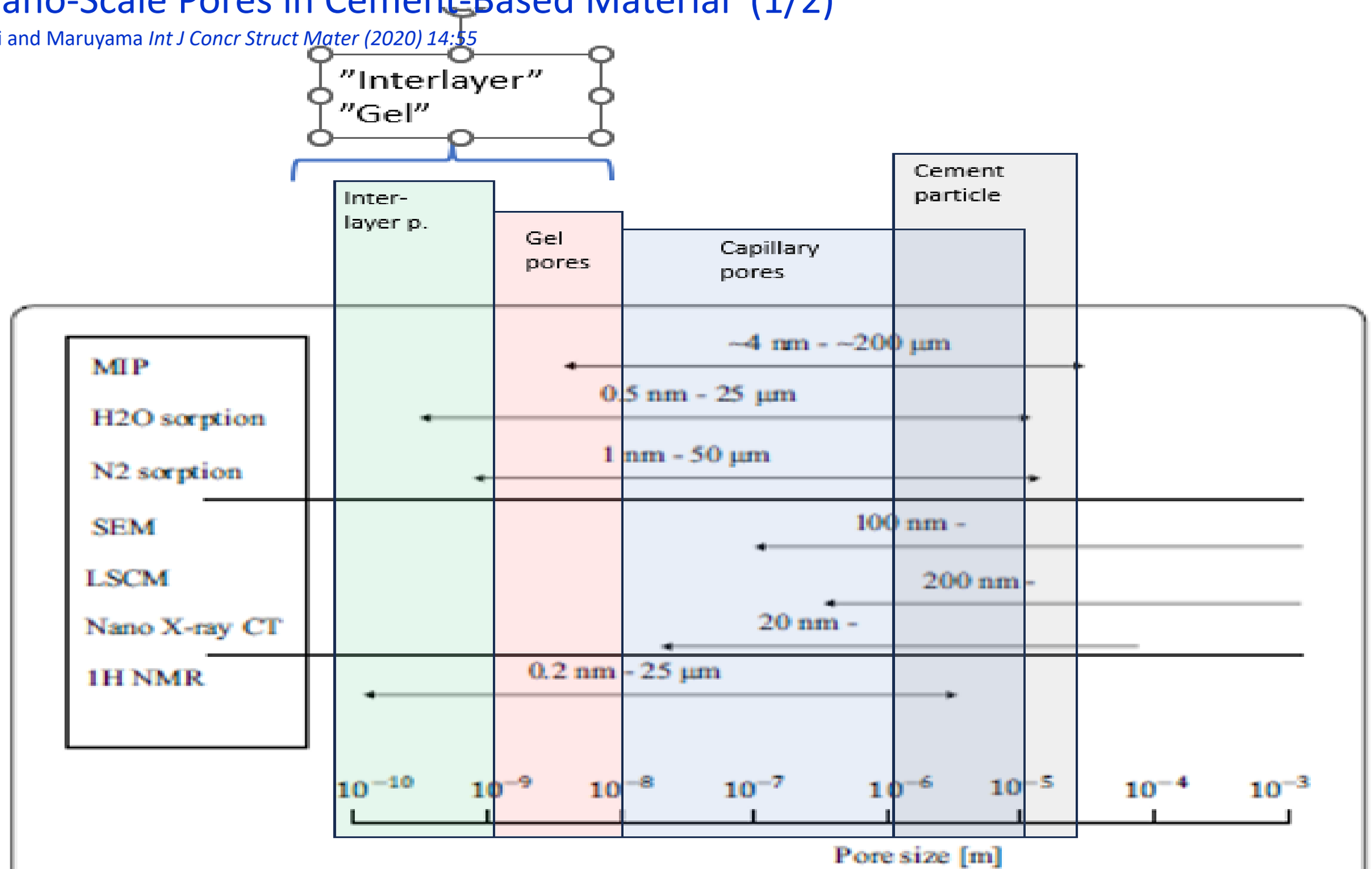


Fig. 2 Range of pore sizes seen in different measurement techniques, adapted from Muller (2014).

Review of Several Experimental Methods for Characterization of Micro- and Nano-Scale Pores in Cement-Based Material (1/2)

Aili and Maruyama *Int J Concr Struct Mater (2020) 14:55*

The reviewed experimental techniques are nitrogen and water vapor sorption isotherm, proton nuclear magnetic resonance (1 H-NMR) and small-angle scattering (SAS). Different pretreatment methods are compared for sorption measurements

N_2 sorbtion

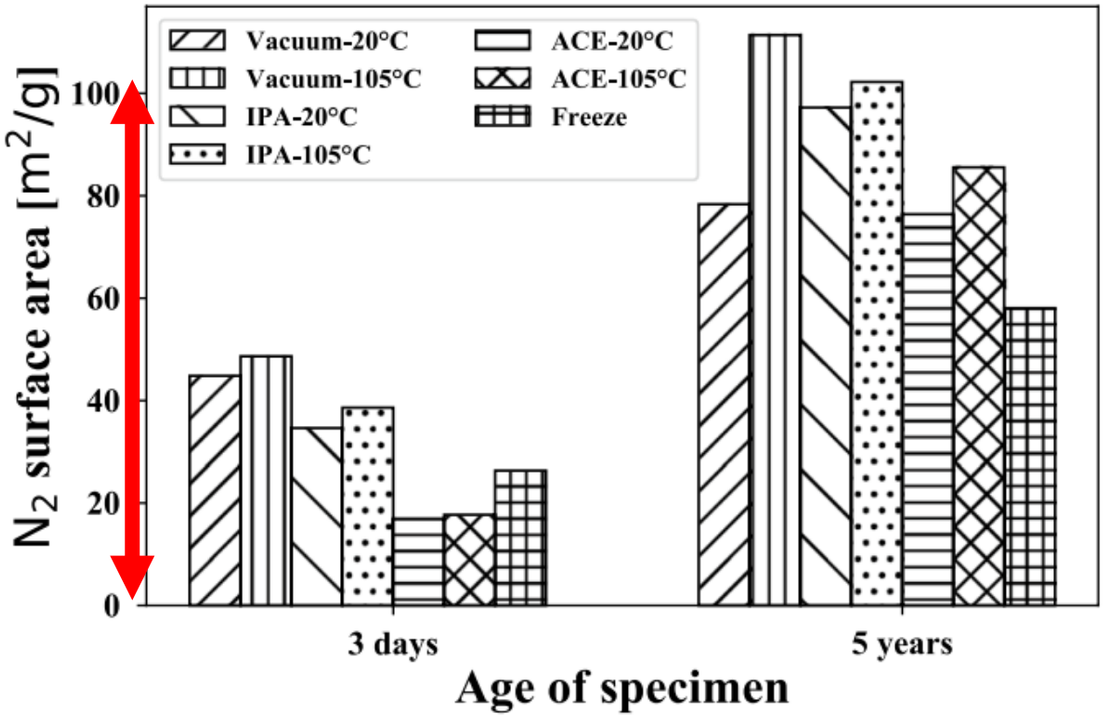


Fig. 9 Influence of pretreatment on nitrogen sorption isotherm, experimental data from Sugimoto et al. (2017).

H_2O sorbtion

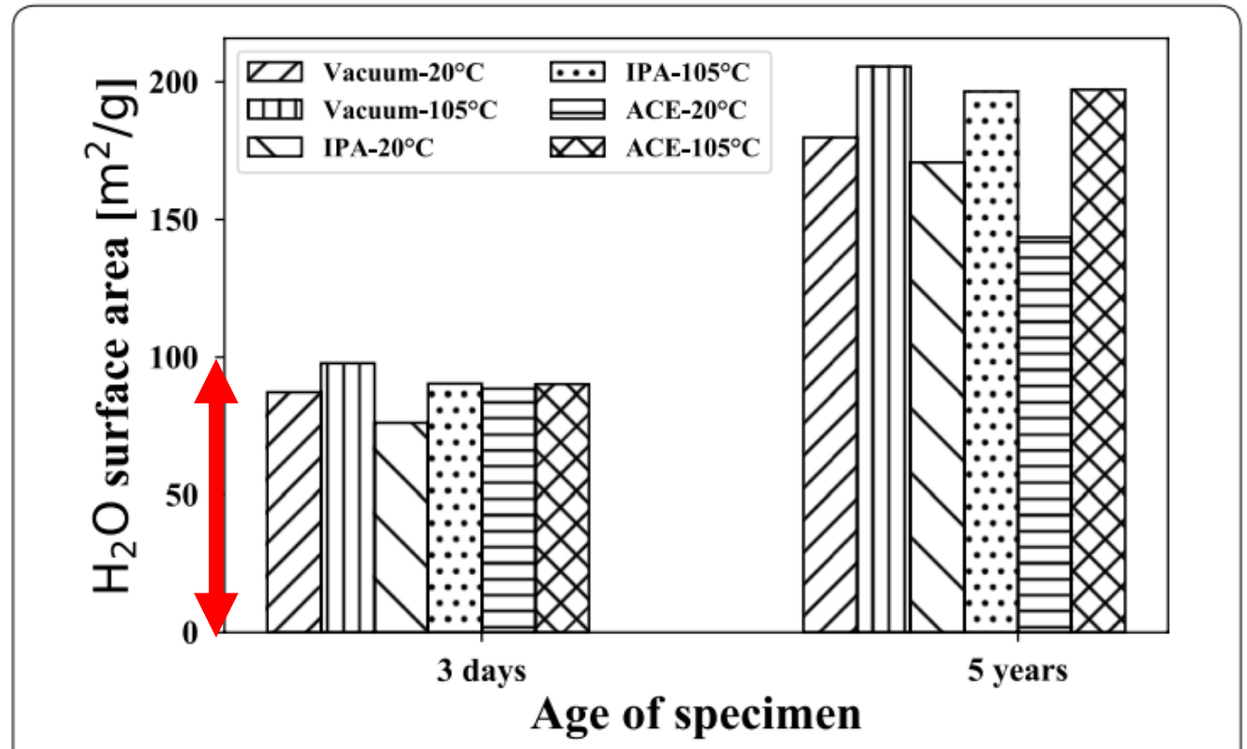


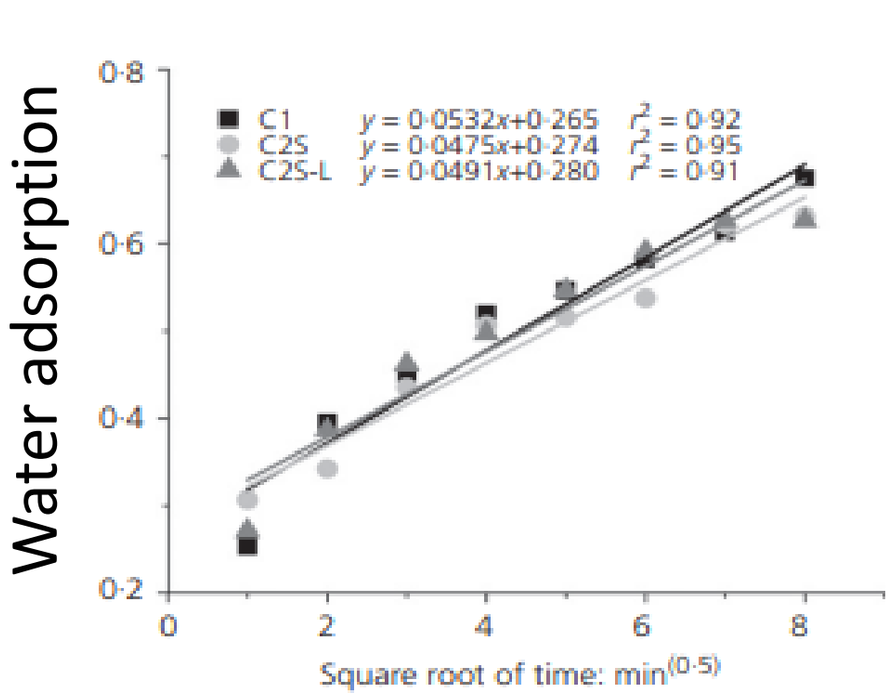
Fig. 10 Influence of pretreatment on water vapor sorption isotherm, experimental data from Sugimoto et al. (2017).

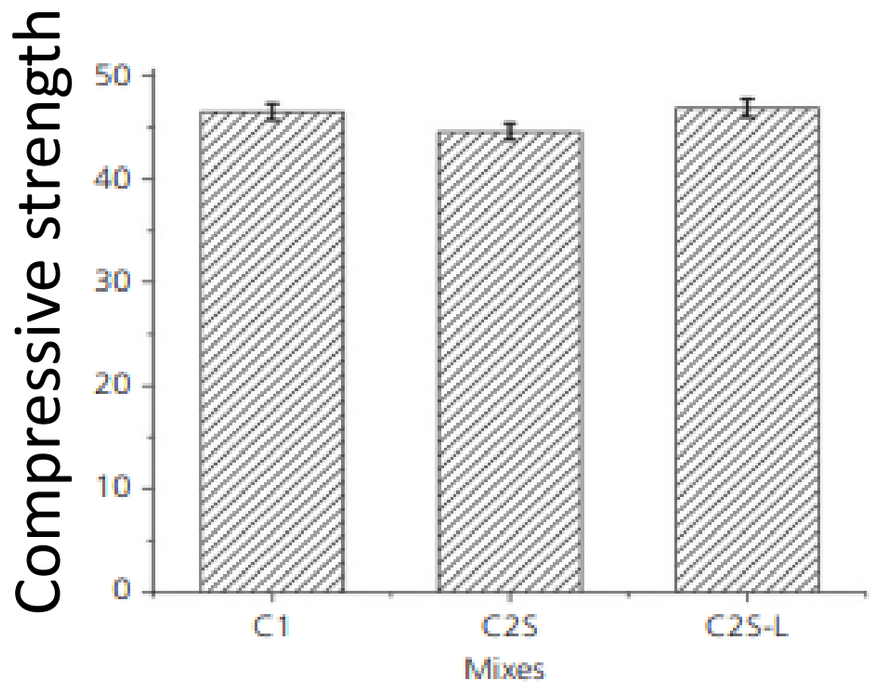
SMC Blends, freeze-thaw resistance, carbonation.

Relationship between cement composition and the freeze–thaw resistance of concretes (1/3)

Adu-Amankwah, Zajac, Skocek, Ben Haha and Black. Advances in Cement Research. Paper 1700138 Received 03/08/2017; revised 29/09/2017; accepted 29/09/2017

Mix ID	CEM I	Slag	Limestone	Anhydrite	Water	Aggregates		
						Fine	10 mm	20 mm
C1	320·3	—	—	—	160·2	651·8	237·7	950·8
C2S	162·3	150·8	—	7·2	160·2	648·8	236·6	946·4
C2S-L	163·9	121·8	27·4	7·2	160·2	648·1	236·4	945·5





Starting point before freeze-thaw tests.

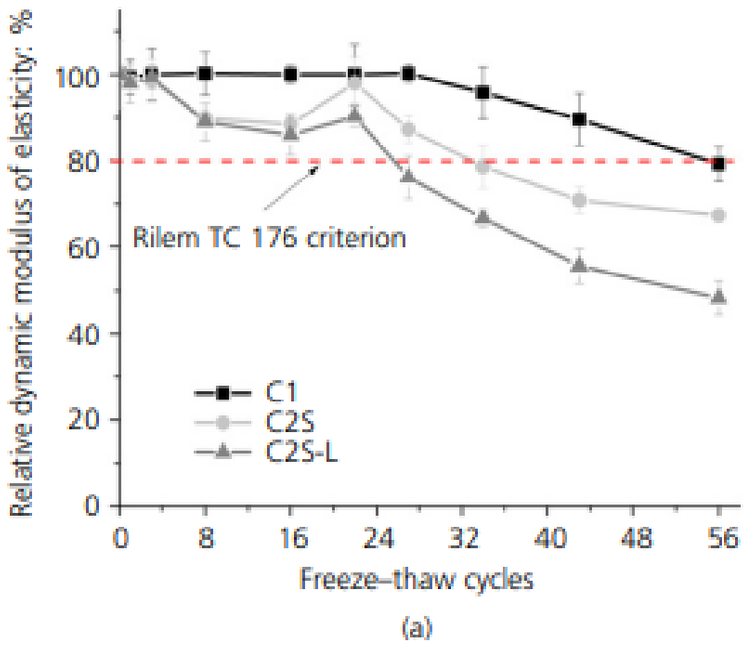
7 d in water and 21 d in RH 65%. 0·5 w/b ratio without air entrainment.

Carbonation and freeze damage. (AK)

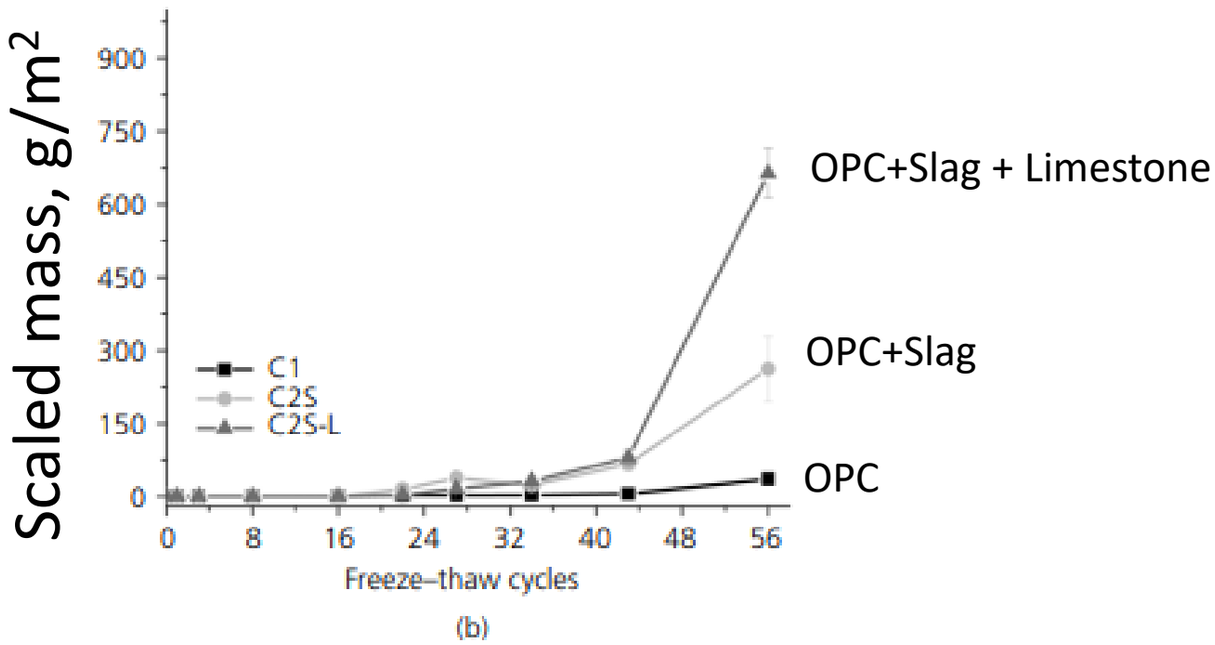
Relationship between cement composition and the freeze–thaw resistance of concretes (2/3)

Adu-Amankwah, Zajac, Skocek, Ben Haha and Black. Advances in Cement Research. Paper 1700138 Received 03/08/2017; revised 29/09/2017; accepted 29/09/2017

Rel. dyn. modulus of elast. %



Scaled mass, g/m^2



"A probable explanation for the reduced freeze–thaw resistance includes the porosity differences and the lower portlandite content compared to CEM I concrete."

"Differences in the carbonation resistance of the investigated mixes have important implications for the suction characteristics of the affected regions and the overall performance, including strength and freeze–thaw resistance"

"It is probable that the mechanism controlling scaling is common for the cement types studied and associated with a decalcification process."

"It is thus imperative that existing standards and test methods take into account the lower portlandite content, as well as the reduced carbonation resistance, of composite cement concretes. Prolonged curing is one alternative to achieve this."

Relationship between cement composition and the freeze–thaw resistance of concretes (3/3)

Adu-Amankwah, Zajac, Skocek, Ben Haha and Black. Advances in Cement Research. Paper 1700138 Received 03/08/2017; revised 29/09/2017; accepted 29/09/2017

- Before freeze–thaw testing, compressive strengths were similar but the composite cements were slightly more susceptible to carbonation.
- However, the scaling and internal damage resistance decreased in the order of CEM I, binary and limestone ternary blended cements.
- The composition of the scaled material differed from the bulk, revealing an absence of portlandite and a marked reduction in AFm and ettringite contents.
- A probable explanation for the reduced freeze–thaw resistance includes the porosity differences and the lower portlandite content compared to CEM I concrete.

The improved microstructure associated with blended cements … but yet reduced freeze–thaw resistance cannot be explained entirely by the existing freeze–thaw mechanisms (Fagerlund, 1997; Powers, 1945; Setzer et al., 2004).

The objective of this paper is to initiate a discussion on the fundamental mechanism of freeze–thaw by comparing the microstructure of concretes before and after freeze–thaw damage.

Carbonation causes freeze damage. (AK)

Hydration and Carbonation of Alternative Binders (1/3)

Kraft, B.; Achenbach, R.; Ludwig, H.-M.; Raupach, M. Corros. Mater. Degrad. 2022, 3, 19–52.

Table 1. Overview of the binders investigated and w/b ratios.

Group	Identifier	Description	w/b
Reference	Ref I	CEM I 42.5 N	0.50
SCMs	CC I	30% Metaillite, 70% Ref I	0.50
	CC II	30% Metakaolin, 70% Ref I	0.50
	LD	30% LD slag, 70% Ref I	0.49
$C\bar{S}A$	$C\bar{S}A$	$C\bar{S}A$ with tartaric acid as retarder	0.50
C-S-H	C-S-H	Celitement®	0.40
AAMs	Geo MK	Metakaolin activated by potassium silicate	0.50
	Geo FA	Fly ash activated by NaOH and sodium silicate	0.34
	AAS I	GGBFS 1 activated by sodium silicate	0.38
	AAS II	GGBFS 2 activated by CEM I and Na_2SO_4	0.39

Linz-Donawitz (LD) process, also referred to as basic oxygen furnace (BOF) process.

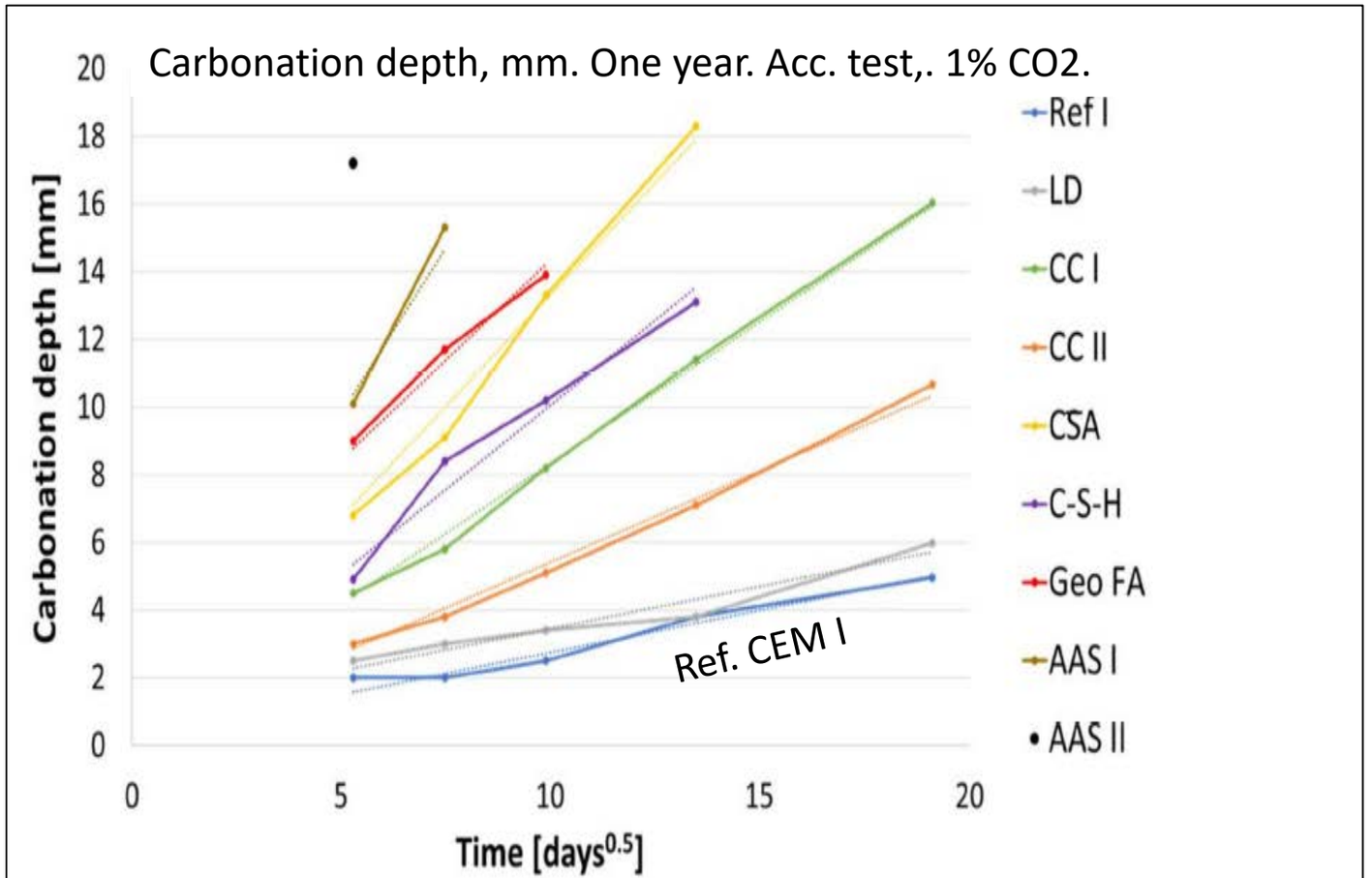


Figure 8. Carbonation depths at cement lime specimens over one year from accelerated test (1 vol.-% CO_2) and regression.

SMCs increase capillary porosity and accelerate carbonation. (AK)

Hydration and Carbonation of Alternative Binders (2/3)

Kraft, B.; Achenbach, R.; Ludwig, H.-M.; Raupach, M. Corros. Mater. Degrad. 2022, 3, 19–52.

Table 1. Overview of the binders investigated and w/b ratios.

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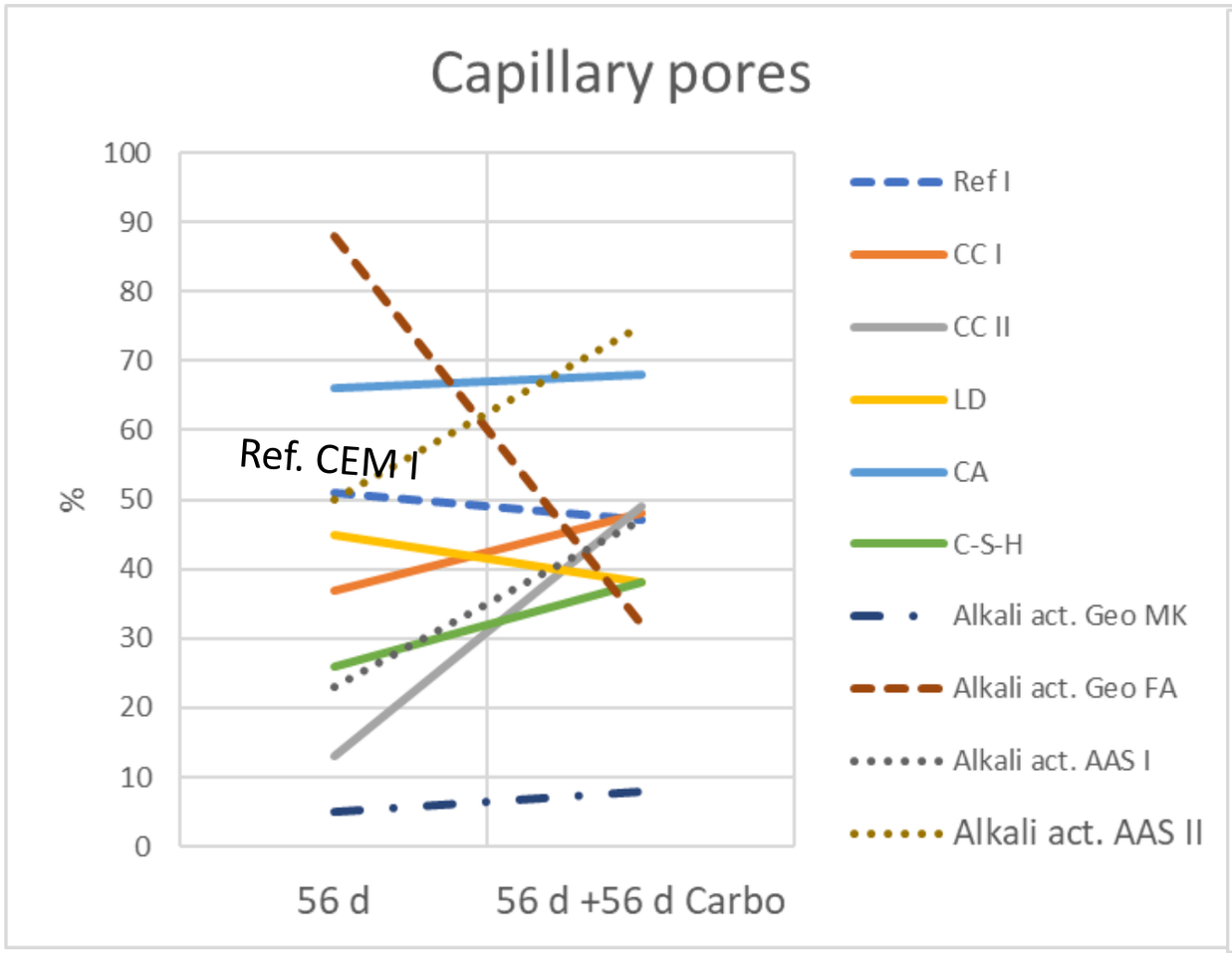
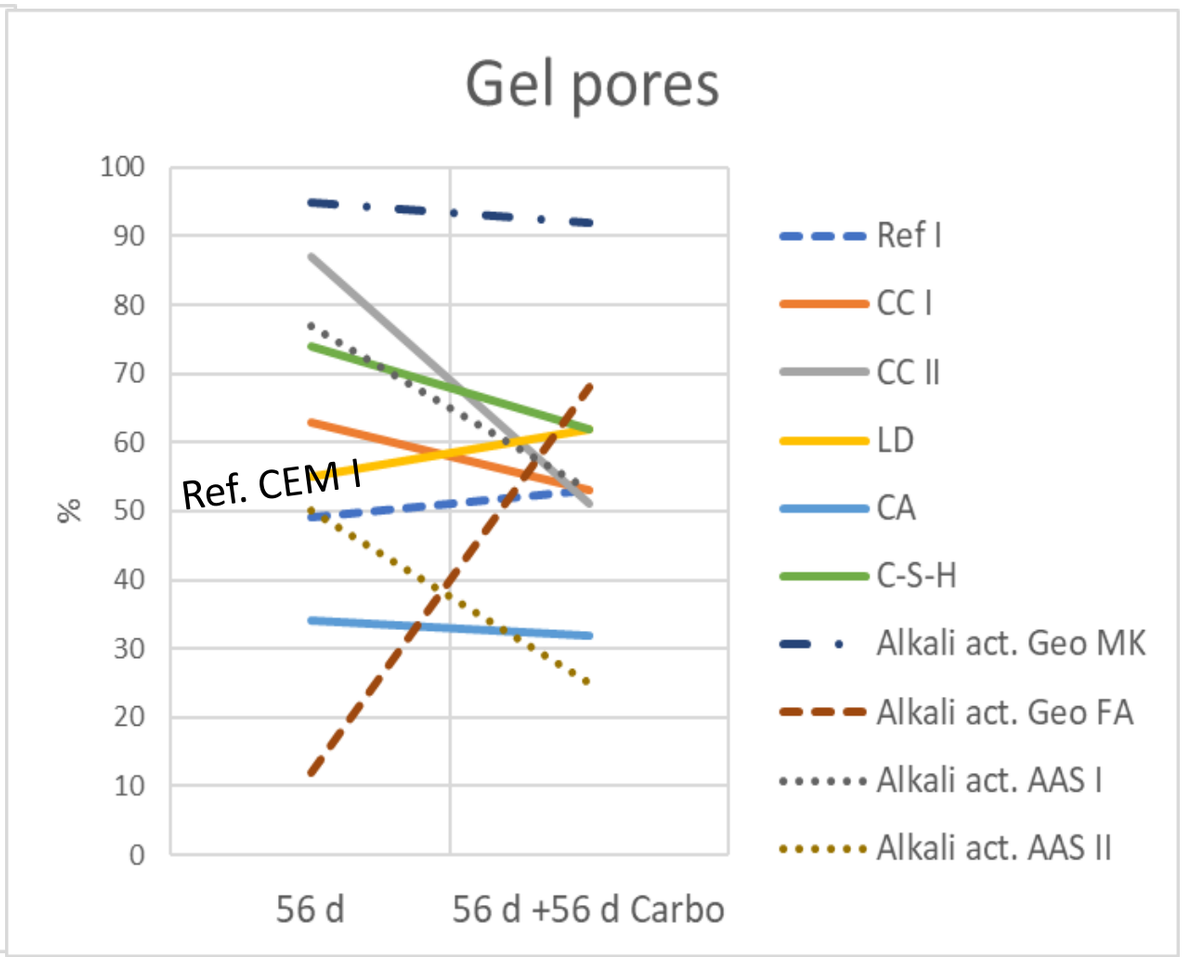




SMCs increase capillary porosity and accelerate carbonation. (AK)

Hydration and Carbonation of Alternative Binders (3/3)

Kraft, B.; Achenbach, R.; Ludwig, H.-M.; Raupach, M. Corros. Mater. Degrad. 2022, 3, 19–52.

Multistep curing before natural carbonation for 1 year in 20 ◦C, RH 65% .

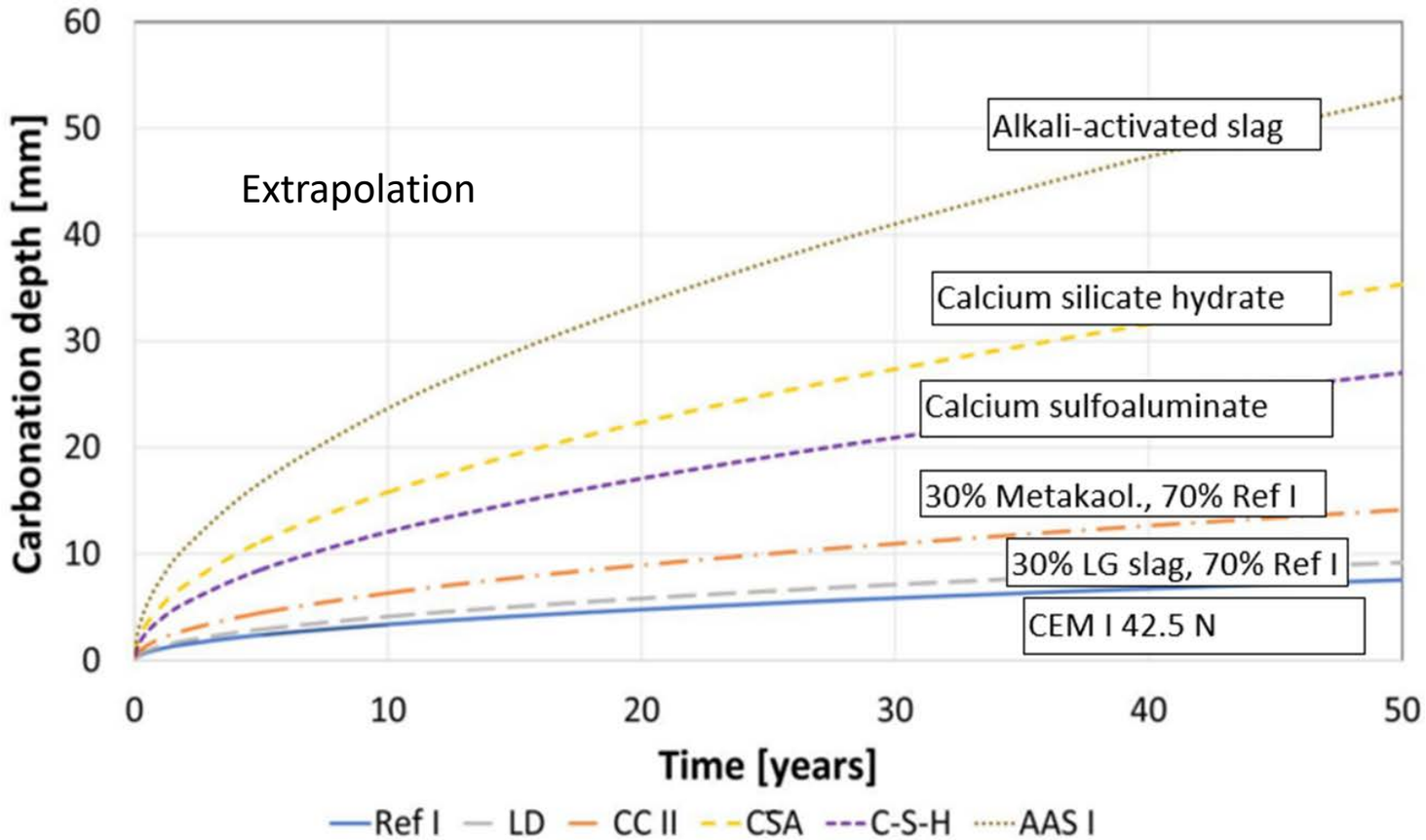


Figure 10. Extrapolation of the natural carbonation depths, calculated from accelerated test.

For the binder types, where the accelerated carbonation testing seems to be suitable, an extrapolation of the carbonation depths for 50 years based on the calculated KNAC values….

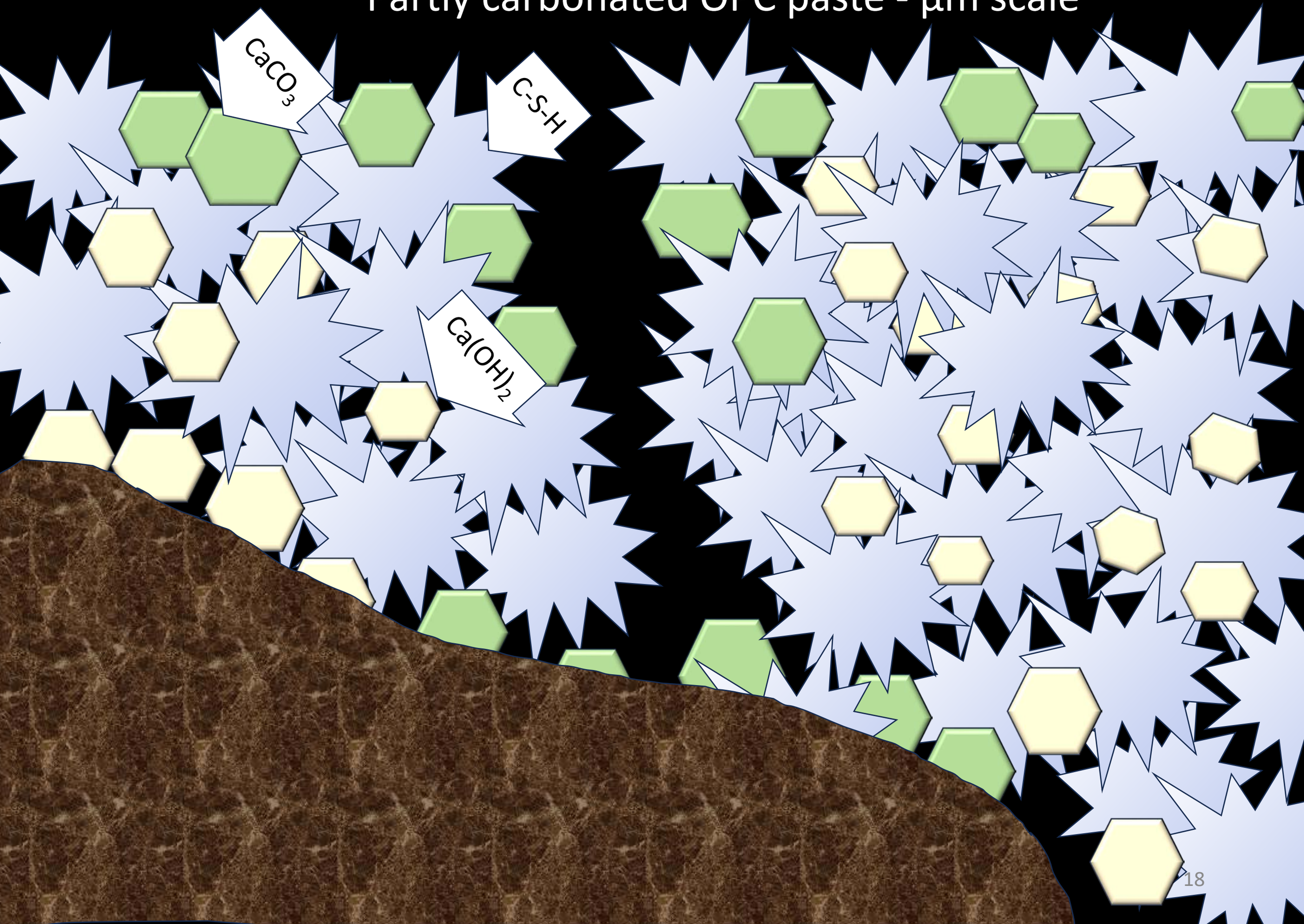
However, this is just a first theoretical estimation, based on models developed on OPC binders.

To gain knowledge on the possible corrosion rates in carbonated material, further research is needed for all of the investigated binder types

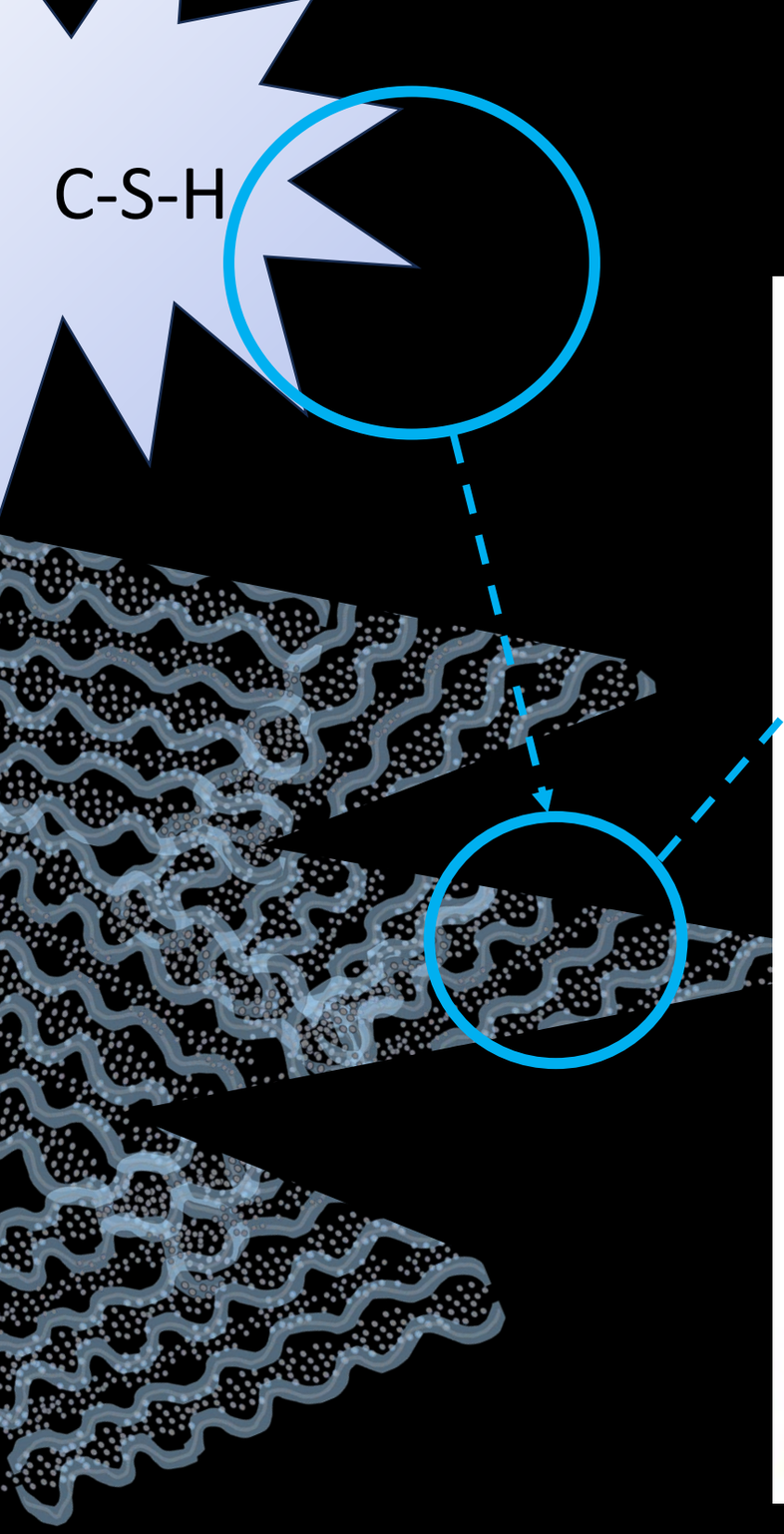
We do not know, how much SMCs accelerate carbonation. (AK)

Carbonation in nanoscale.
First with OPC, then with SCM.

Partly carbonated OPC paste - µm scale



C-S-H nanostructure



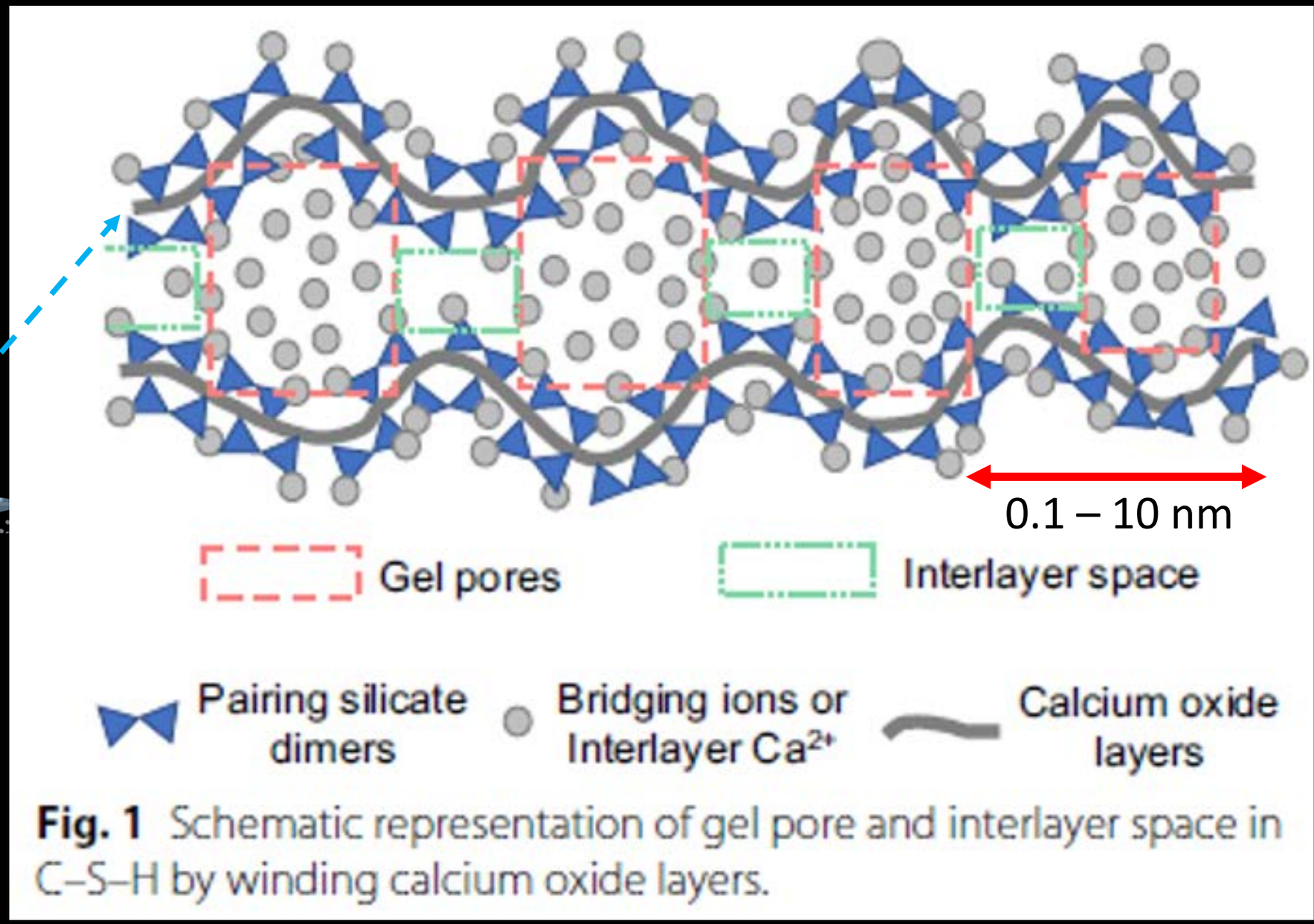


Fig. 1 Schematic representation of gel pore and interlayer space in C–S–H by winding calcium oxide layers.

Review of Several Experimental Methods for Characterization of Micro- and Nano-Scale Pores in Cement-Based Material

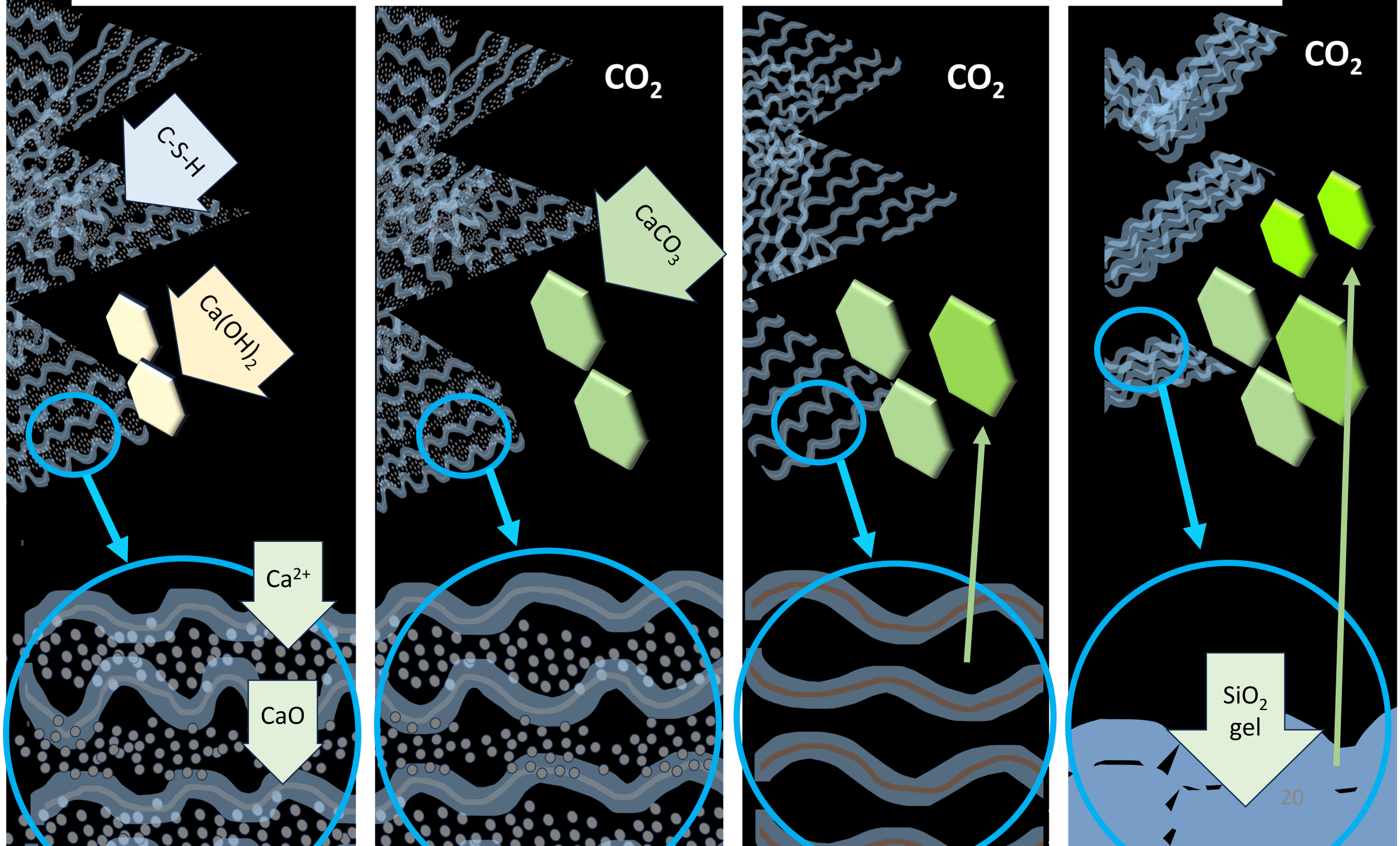
Aili and Maruyama *Int J Concr Struct Mater (2020) 14:55*

Carbonation of OPC paste (AK)

Understanding the carbonation of concrete with supplementary cementitious materials: a critical review by RILEM TC 281-CCC.

Materials and Structures (2020) 53:136. (Received: 13 July 2020 / Accepted: 18 September 2020 / Published online: 22 October 2020 (The Author(s) 2021, corrected publication 2023)

Simplified presentation by A. K.



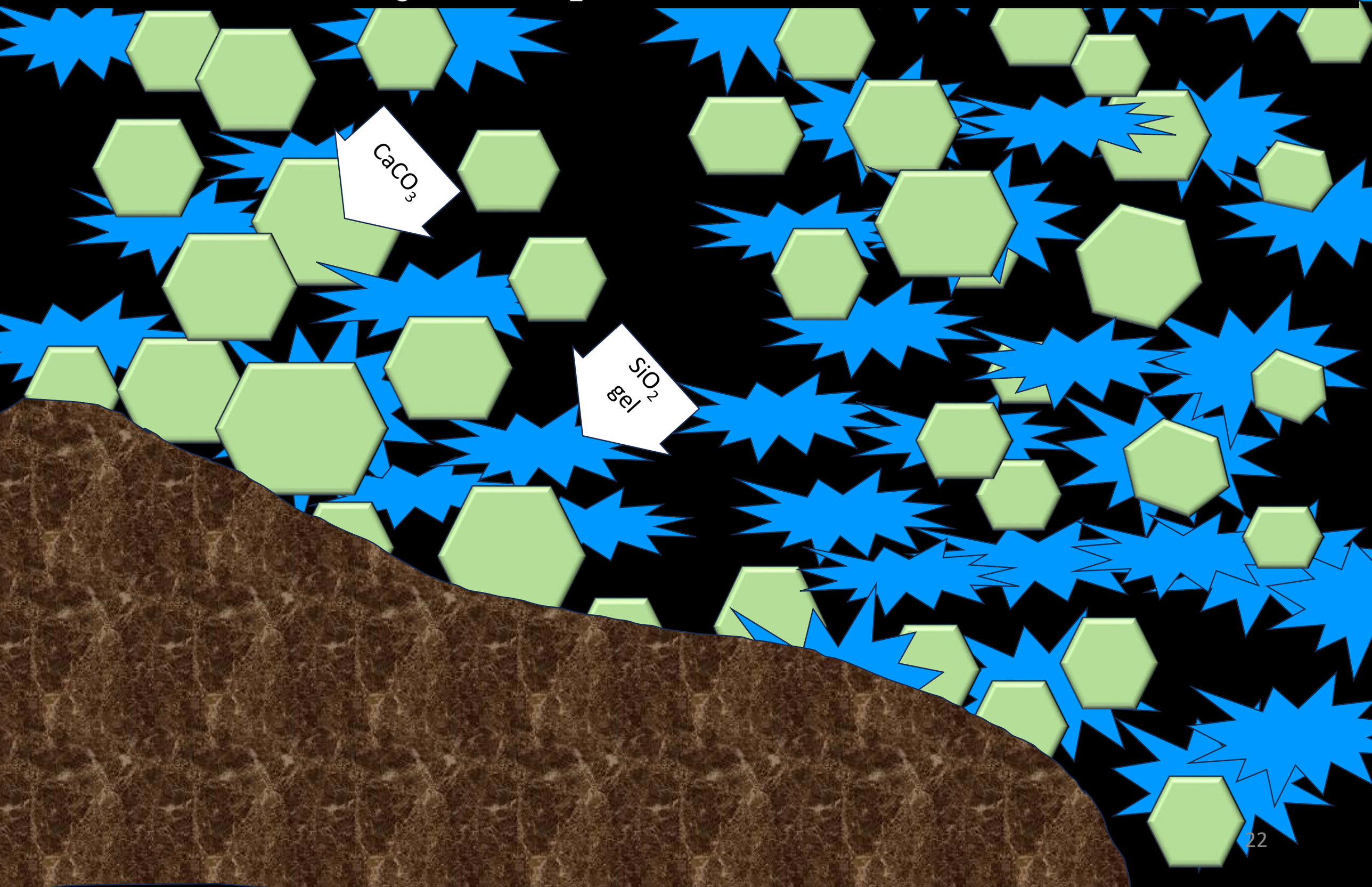
Understanding the carbonation of concrete with supplementary cementitious materials: a critical review by RILEM TC 281-CC. Materials and Structures (2020) 53:13 Simplified presentation by A. K. (1/3)

OPC Porosity densification due to portandite CO_2 reaction in early carbonation					
Thermodyn. modelling				Reality	
OPC	Ca/Si to	pH to	Vol of product	Consequence	Kinetic constrains
$Ca(OH)_2$ + CO_2 → $CaCO_3$ + H_2O	…1.7	13,5 … 12.5	↗	$CaCO_3$ and H_2O fills pores	Porosity reduction. $CaCO_3$ grows over $Ca(OH)_2$. Water fills pores limiting reaction rate.
C-S-H reaction. CaO removed from interlayer.	…1.3	…12.5	→	Reaction product fills larger pores. Pore size becomes smaller. H_2O produced.	Denser porosity limits carbonation rate
C-S-H reaction. CaO removed from C-S-H layers.	…0.75	…11	→	Destabilisation of C-S-H. The structure begins to collapse. Pore size becomes larger.	Porosity coarsening accelerates carbonation rate.
C-S-H and Ettr. reaction	…0.67	…10	↘	C-S-H destabilization continues. Porosity increases.	Porosity increase and coarsening continues.
End of Carbonation	…0	…8	↘	All C-S-H forms $CaCO_3$ SiO_2–gel. Total of 40 … 50 g CO_2 bound to 100 g OPC	

SMCs accelerte carbonation but kinetics is important. (AK)

De-calcified OPC paste.Fully carbonated.

End products $CaCO_3$ and SiO_2 gel. Incearsed porosity. Poor strenghth.



Carbonation of SCM (slag) + OPC and AAM (AK)

Understanding the carbonation of concrete with supplementary cementitious materials: a critical review by RILEM TC 281-CCC.

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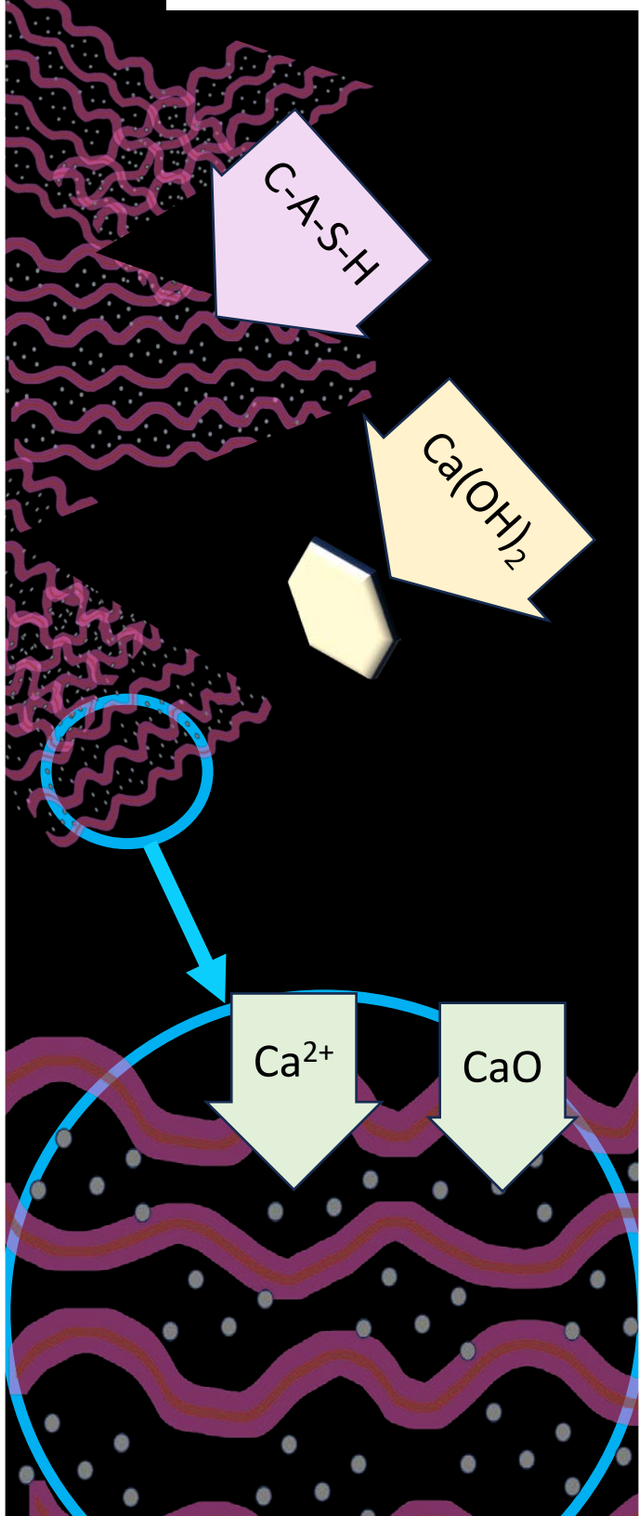
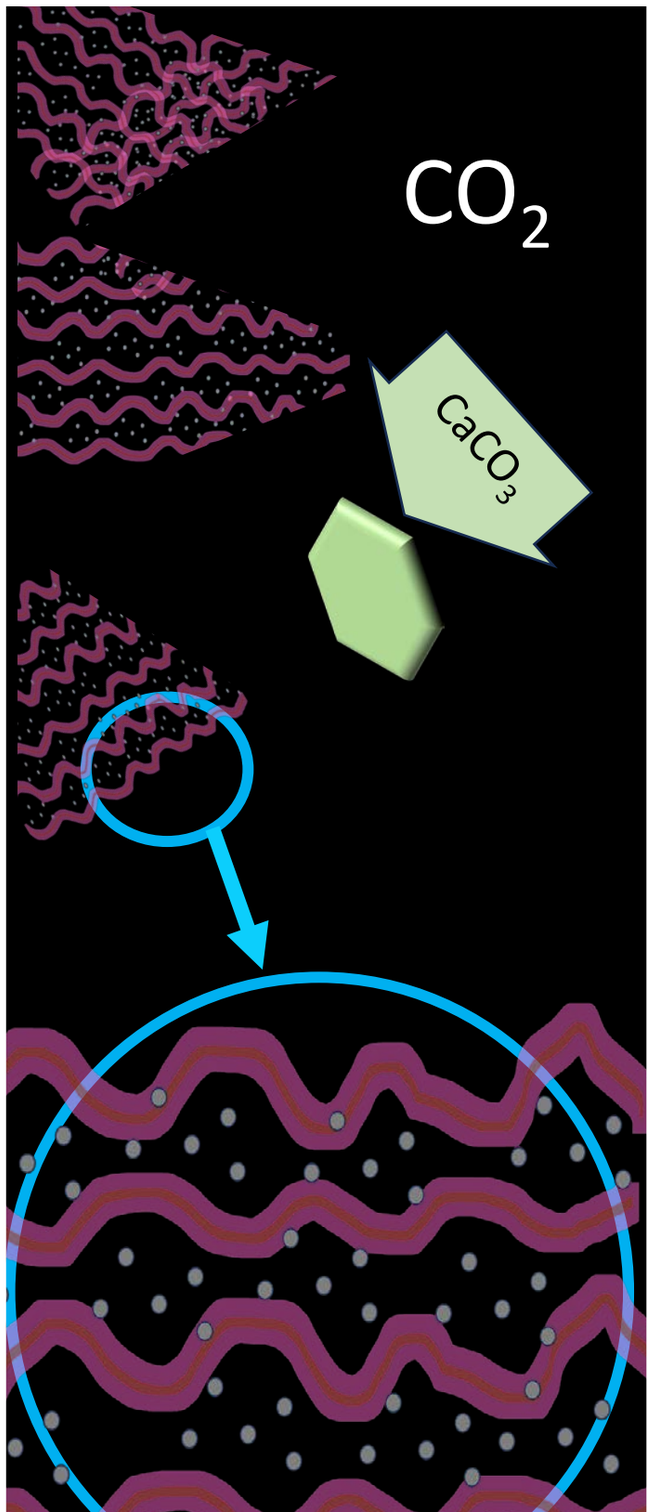
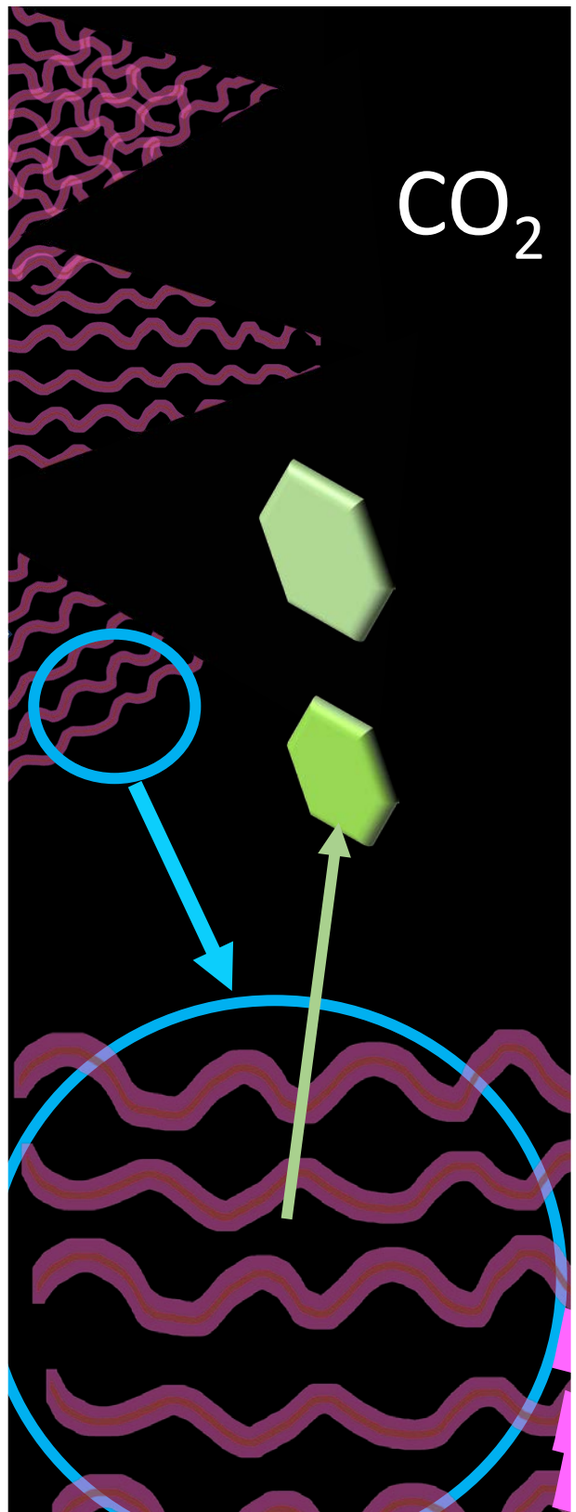
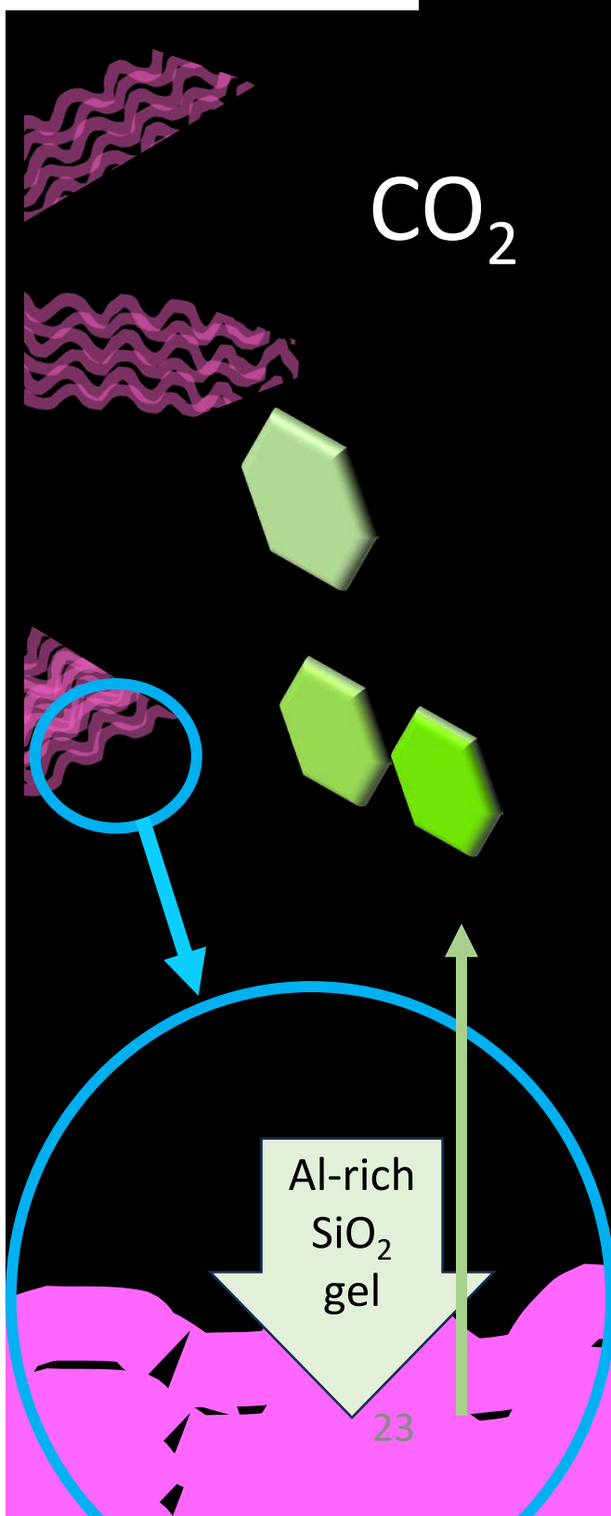








Understanding the carbonation of concrete with supplementary cementitious materials: a critical review by RILEM TC 281-CC. Materials and Structures (2020) 53:13 Simplified presentation (AK)

OPC Porosity densification due to portandite CO_2 reaction in early carbonation						OPC + SCM Porosity densification due to pozz. reaction prior to carbonation		
Thermodyn. modelling				Reality			Reality	
OPC	Ca/Si to	pH to	Vol of product	Consequence	Kinetic constrains	OPC + SCM	Consequence	Kinetic constrains
$Ca(OH)_2$ + CO_2 → $CaCO_3$ + H_2O	…1.7	13,5 … 12.5	↗	$CaCO_3$ and H_2O fills pores	Porosity reduction. $CaCO_3$ grows over $Ca(OH)_2$. Water fills pores limiting reaction rate.	$Ca(OH)_2$ C-S-H C-A-S-H	Paste and ITZ porosity densification.	Smaller and denser porosity reduces carbonation rate
C-S-H reaction. CaO removed from interlayer.	…1.3	…12.5	→	Reaction product fills larger pores. Pore size becomes smaller. H_2O produced.	Denser porosity limits carbonation rate	C-A-S-H	Carbonation shrinkage, autogegenous shrinkage and micro cracking. H_2O produced.	Faster carbonation rate
C-S-H reaction. CaO removed from C-S-H layers.	…0.75	…11	→	Destabilisation of C-S-H. The structure begins to collapse. Pore size becomes larger.	Porosity coarsening accelerates carbonation rate.	C-A-S-H and Ettr.	The structure begins to collapse. Pore size becomes larger.	Faster carbonation rate. Increasing RH decrases carbonation rate. Assesment on carbonation rate of a blend is difficult. Fig. 5.
C-S-H Ettr. reacti…								
End of Carb.	…0	…8	↘	All C-S-H forms $CaCO_3$ SiO_2–gel. Total of 40 … 50 g CO_2 bound to 100 g OPC		End of carb.	$CaCO_3$ and SiO_2-Al_2O_3 - gel	

SMCs accelerte carbonation but let's not forget kinetics. (AK)

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

Seppo Matala
Dissertation for the degree of Doctor of Technology
Espoo 1995

In OPC mixes the increased capillary porosity is caused by a decrease in the finest gel porosity. In contrast, in GBFS blends reduction of the coarsest gel pores brings about a very clear increase in coarse capillaries.

Due to the lower amount of CH, GBFS compositions are more disposed to carbonation of the CSH gel, which transforms the initially relatively dense gel to a more porous silica hydrate gel.

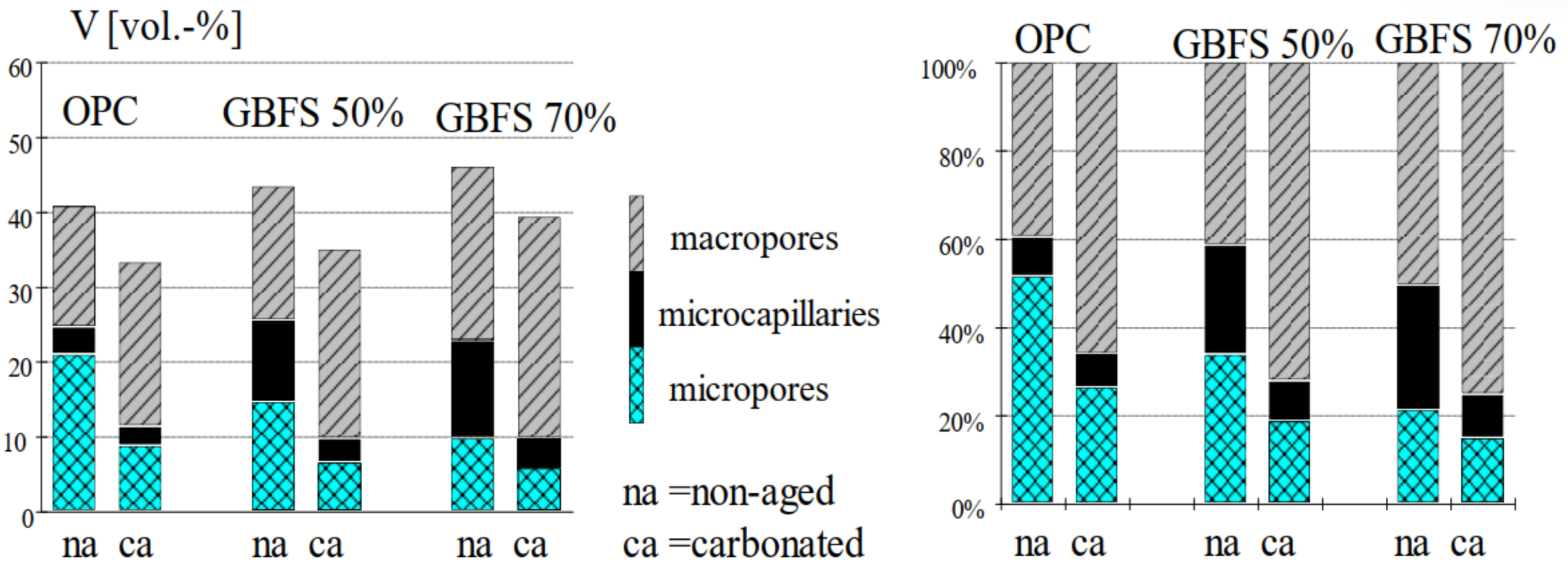
A high level of carbonation affects transformation of the CSH gel to SH gel in the inner slag hydrate.

Carbonation coarsens the densest part of the gel spaces in GBFS concretes, changing the gel porosity toward coarser capillaries, where water becomes freezable at moderate temperatures.

Seppo´s dissertation available.

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

Seppo Matala

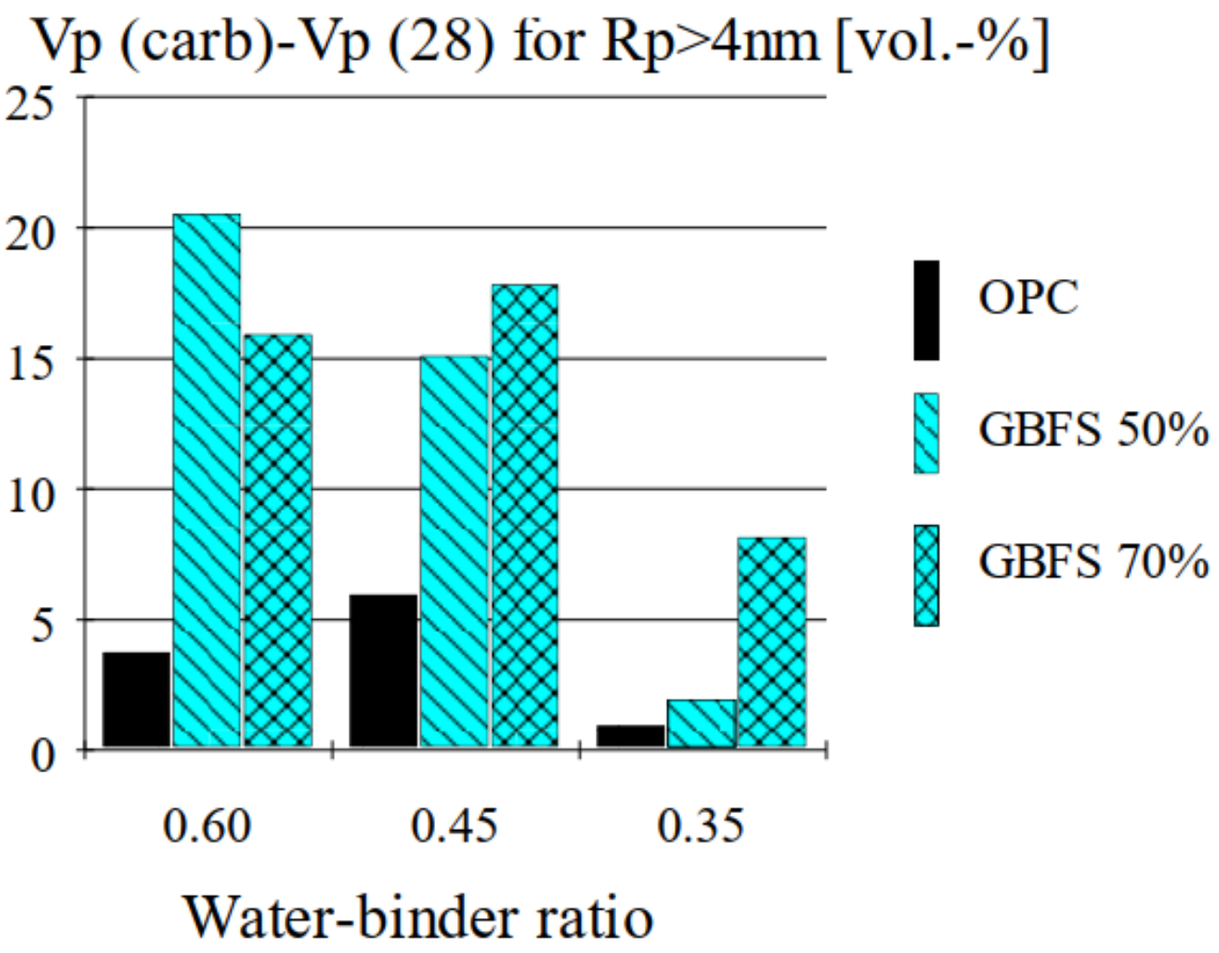


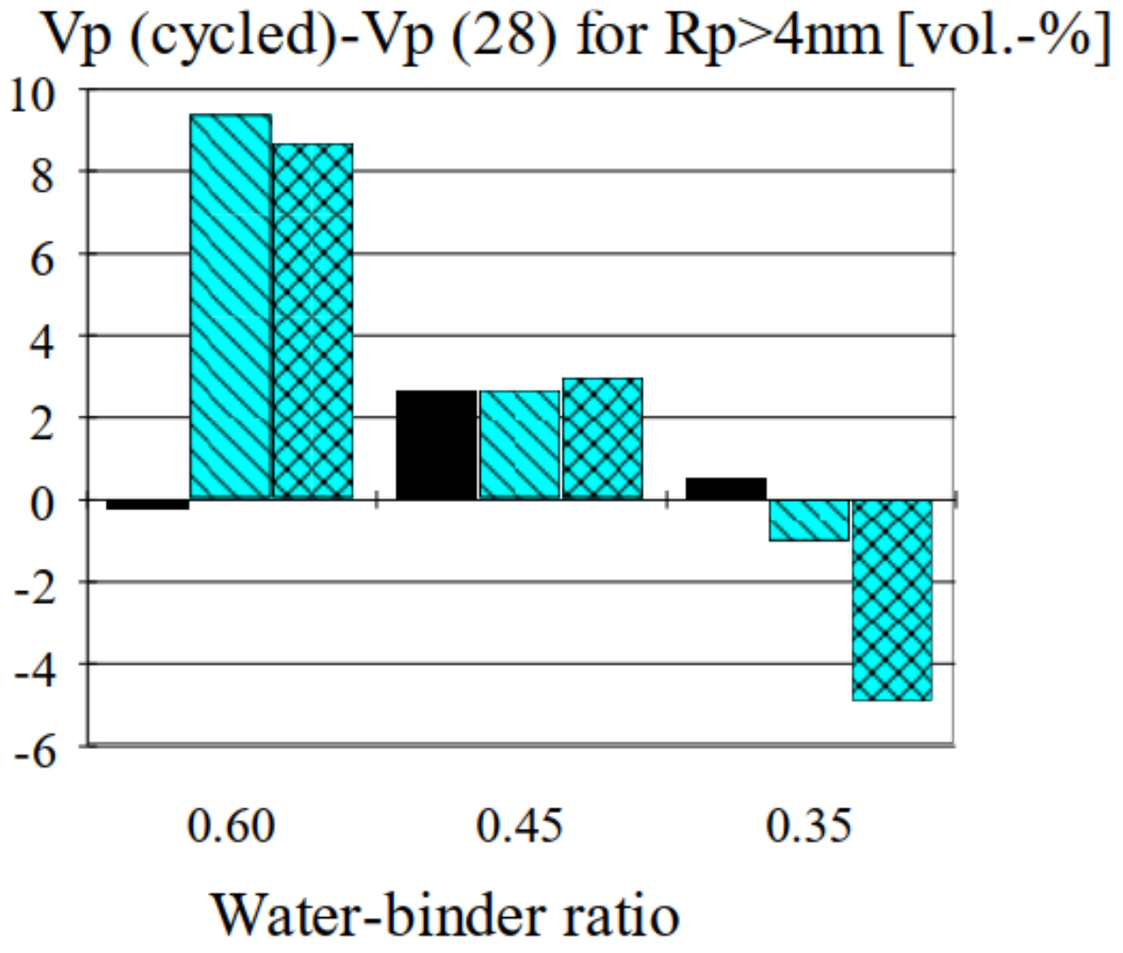
Absolute and relative redistributions in pore ranges of different binder compositions due to carbonation.

- "…gel pores divided into micropores and microcapillaries which can be measured by the LTC method…"
- "The capillary pores are called here as macrocapillaries or macropores ranging from 4 nm to a few microns. Capillary pores are detectable in the MIP and LTC method. "

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

Seppo Matala





Difference in macroporosity values after carbonation and cycled treatments.

We will return to this later.

Thank you !