Engineered Calcium-Silicate-Hydrates for Applications

Up-scaling production of controlled hydrates

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1. OBJECTIVES

Individual project objectives

- engineer materials with optimised microstructure for transport properties
- materials composed of C-S-H manufactured using industrial products
- verify the findings from microstructure as understood from ESR projects 1 to 8
- develop means by which hydrates can be scaled-up to an industrial production

Expected results

Month 12

Screen of suitable methods for large scale production

Month 21

Up-scaled samples with variable composition

Month 30

Characterisation of transport properties of different hydrated systems

Month 39

Link made between chemical composition and microstructure of hydrates and transport properties

Designing and studying C-S-H

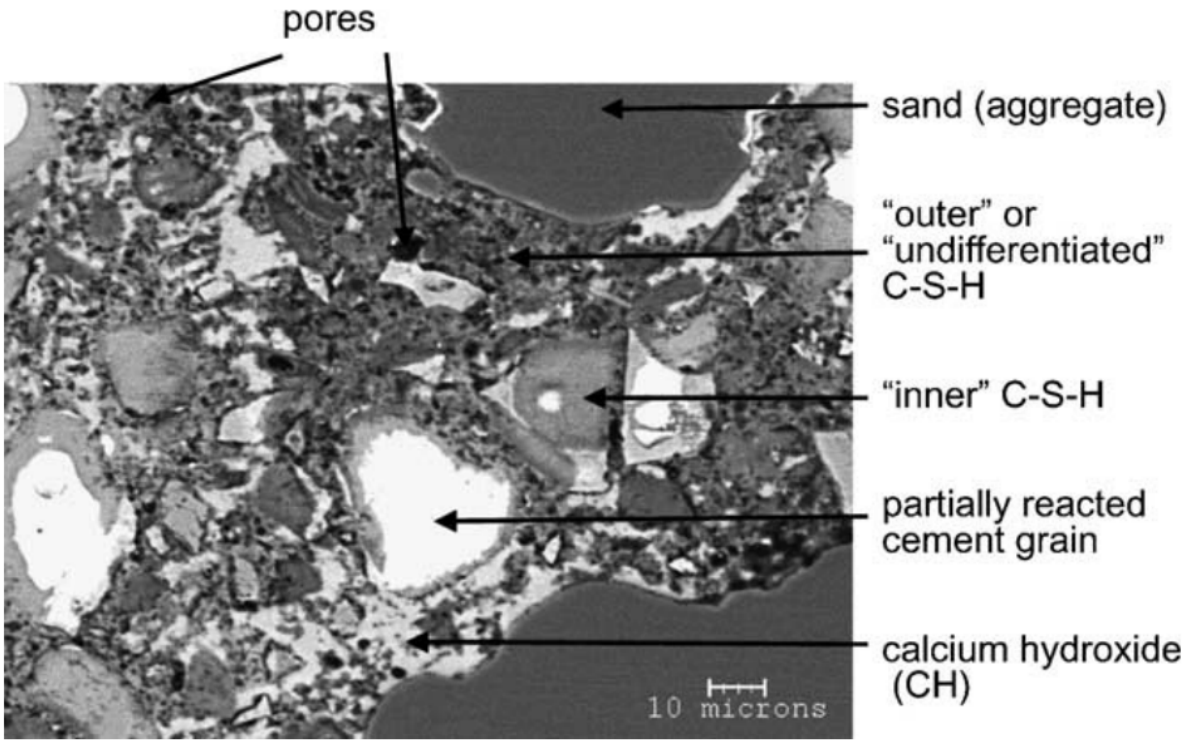
-> chemical processes: very versatile, but not easy to obtain hardened microstructure
-> most common approach, hydrating ordinary Portland cement (OPC)

Clinker phases

C_3S
C_2S
C_3A
C_4AF

+ H_2O ⇨

C-S-H
CH
Aft
Afm
.....



Aim: produce hydrated microstructure with homogenous C-S-H.

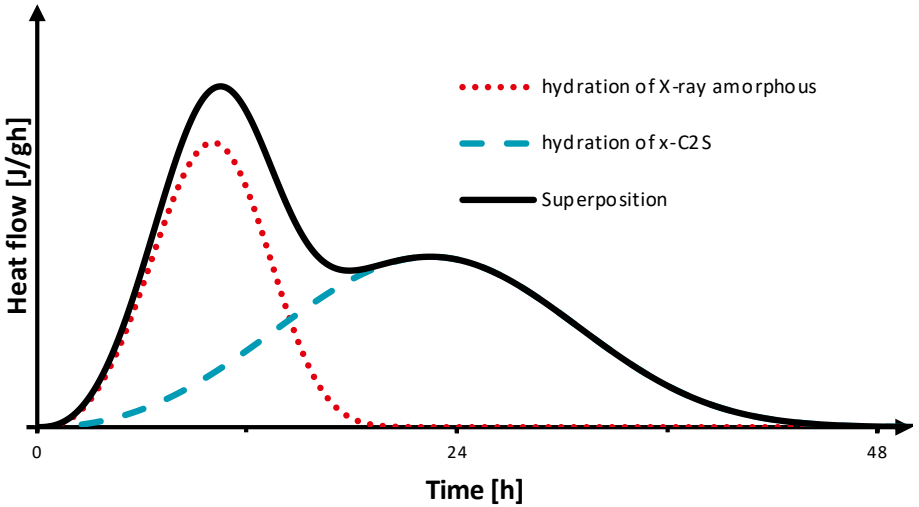
Reactive C_2S binder

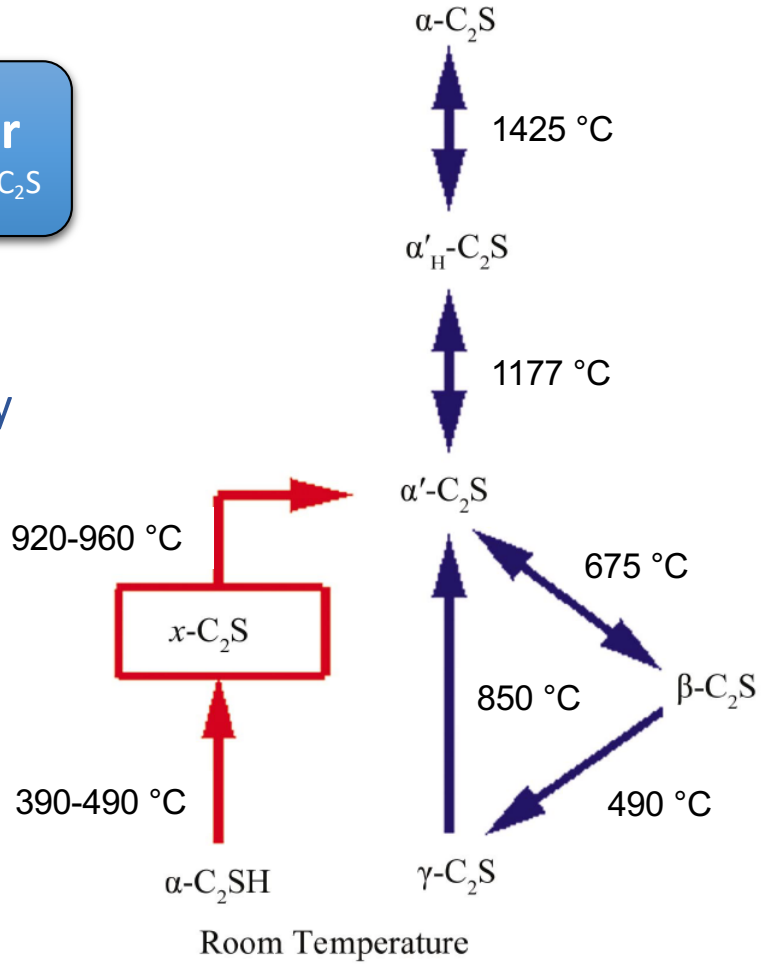
Based on HC previous project

Hydrothermal α-C_2SH → **annealing < 500 °C** → **Reactive binder**
x-ray amorphous, *x*-C_2S, γ-C_2S

- Resulted binder is a mixture of phases, reactivity decreases in the order:

X-ray amorphous > x-C_2S > β-C_2S > γ-C_2S





Phase relationship of the present new phase with the established C_2S system (Toraya et al, 2002)

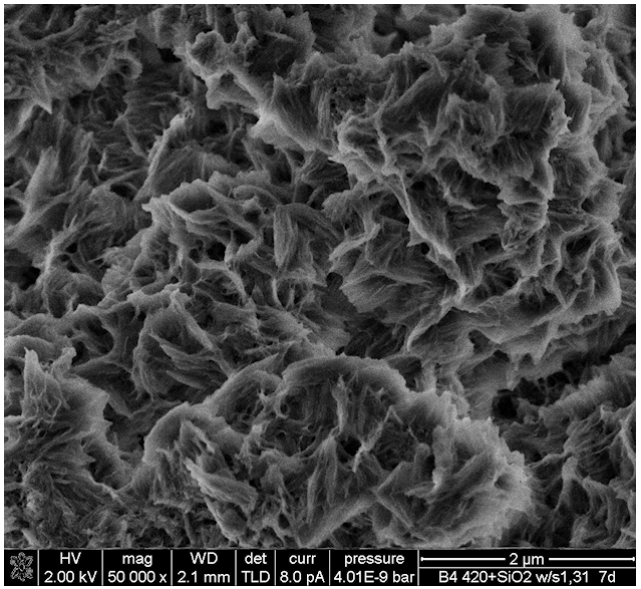
Reactive C_2S binder

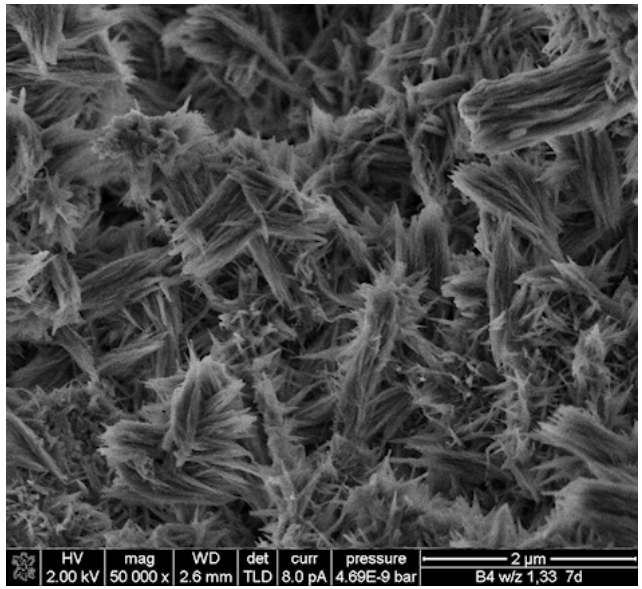
Reactive belite binder

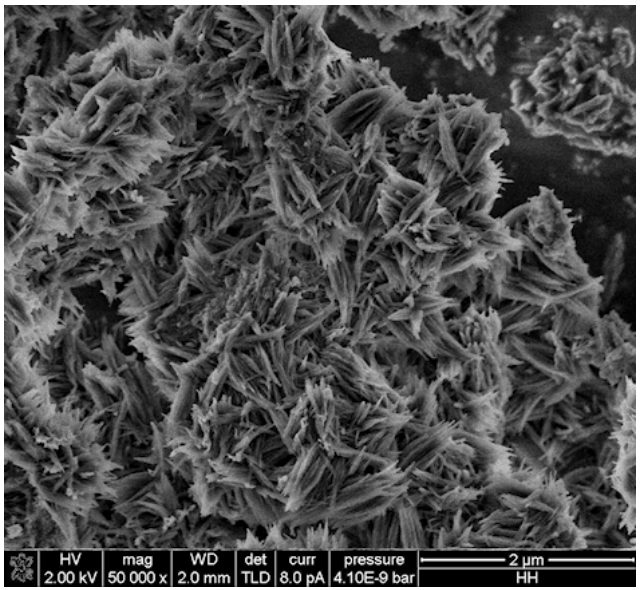
mixtures with 10 % nano-silica before hydration

- Bound water: 25.1 % ↗ 29.9 %
- Portlandite: 8.2 % ↘ 0
- Ca/Si ratio: 1.7 ↘ 1.5
- Morphology: needle-like ➔ foil-like

addition of sulfate leads to a formation of finer needle-like hydrates

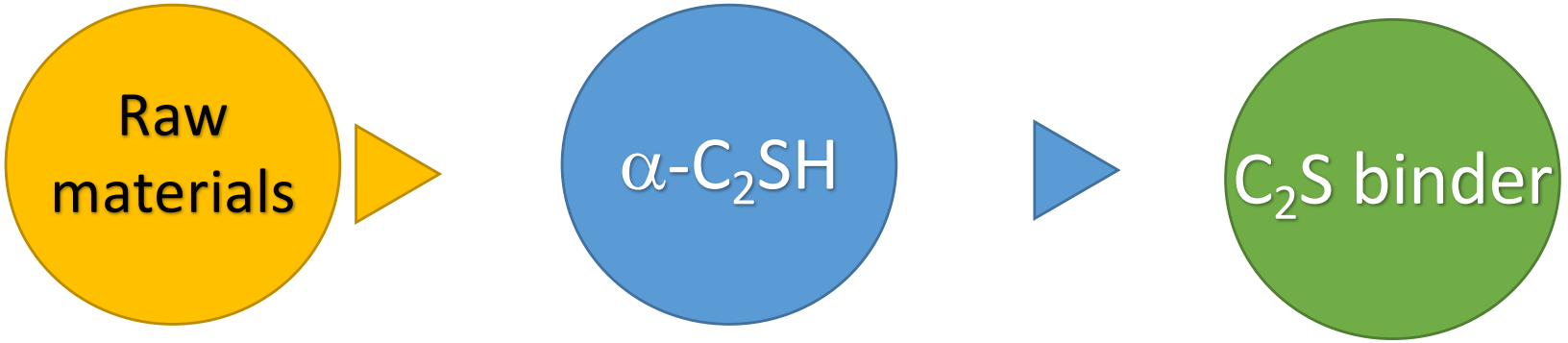






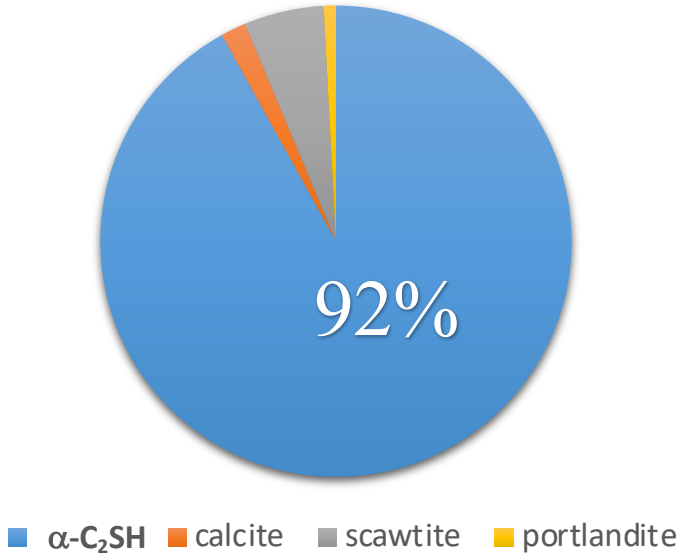
*Link, 2017

2. PRODUCTION OF BINDER


Raw materials
α-C2SH
C2S binder

Raw materials → α-C_2SH → C_2S binder

Industrial product from Kronau plant



Sample	α-C_2SH
CaO	**56.83 %**
SiO_2	**30.78 %**
MgO	0.53 %
K_2O	0.14 %
Al_2O_3	0.03 %
Na_2O	0.00 %
Fe_2O_3	0.00 %
MnO	0.01 %
TiO_2	0.00 %
SO_3	0.04 %
P_2O_5	0.03 %
LOI (1050°C)	11.48 %
TOTAL	99.87 %

Raw materials

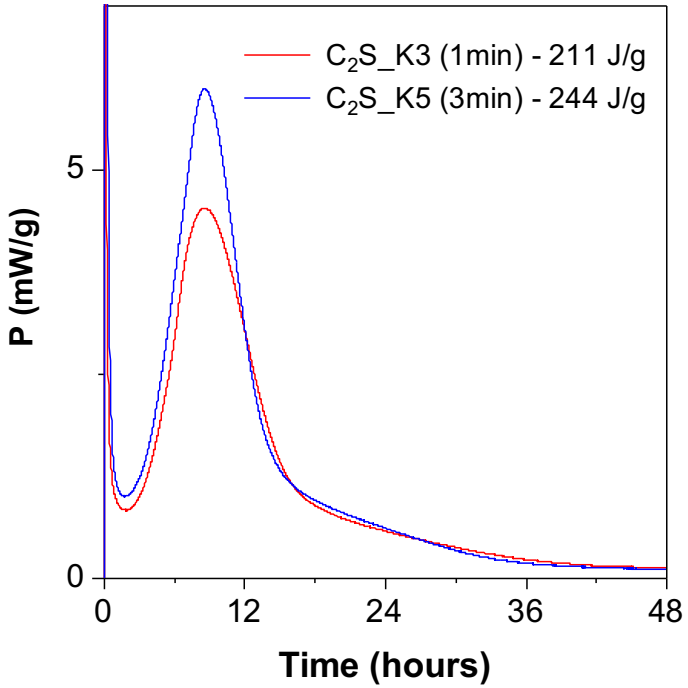
α-C_2SH

460°C

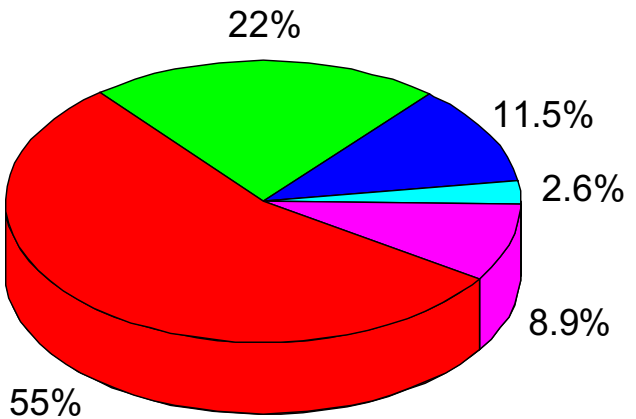
(2 h)

C_2S binder

Influence of grinding time on reactivity



Phase quantification by QXRD



amorphous

calcite, scawtite, portlandite

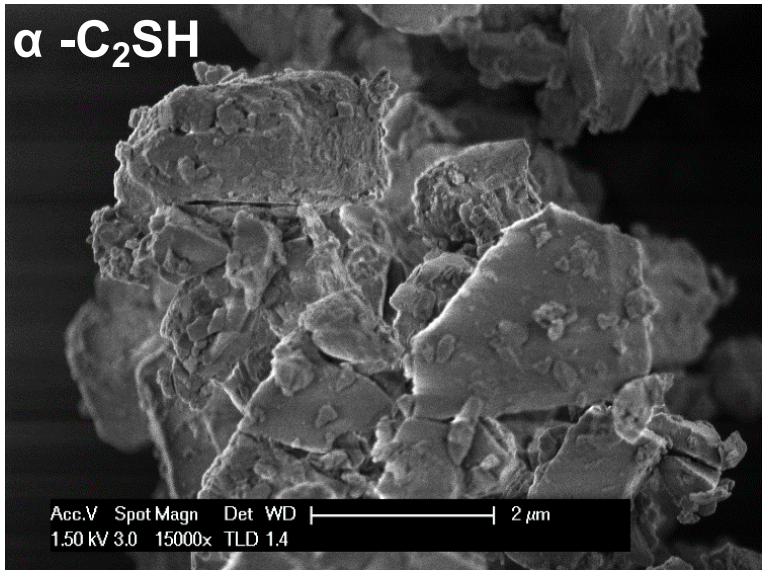
x-C_2S

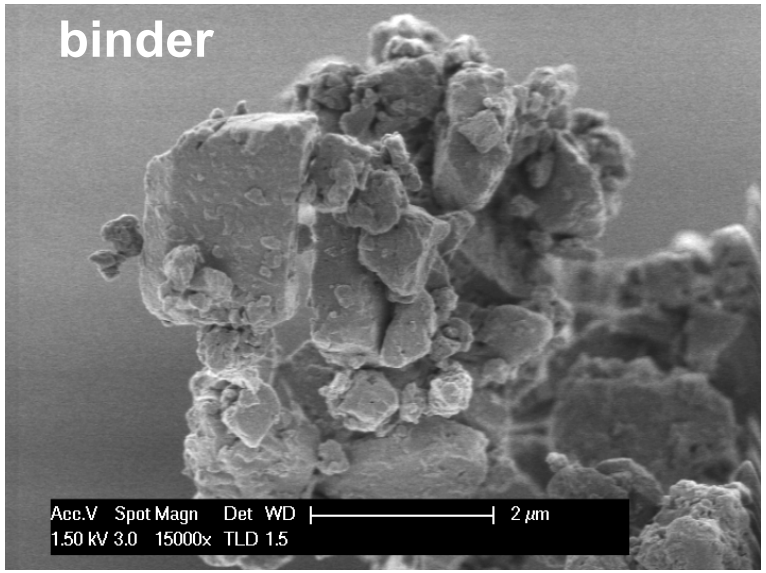
γ-C_2S

β-C_2S

Raw materials → α-C_2SH → 460°C (2 h) → C_2S binder

Morphology of particles before and after annealing



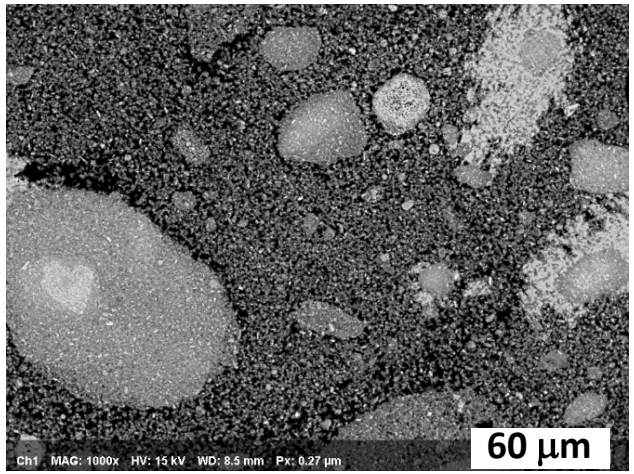


3. HYDRATION AND MICROSTRUCTURE

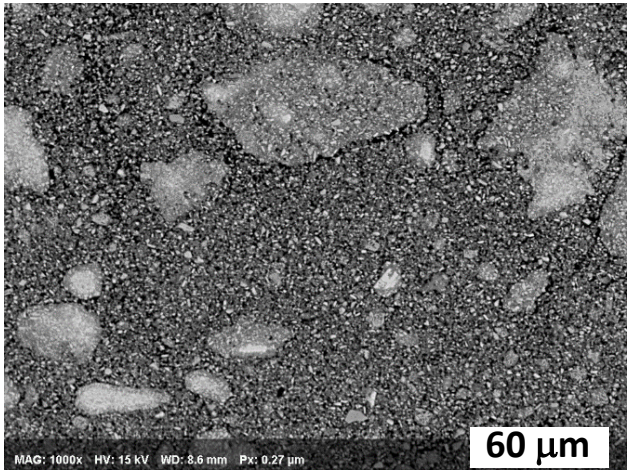
Microstructure for w/b = 0.8 … 0.35

- BSE images on pastes cast with different w/b ratio and sealed cured.
- DoH > 90 % at 1 day, > 99 % at 7 days

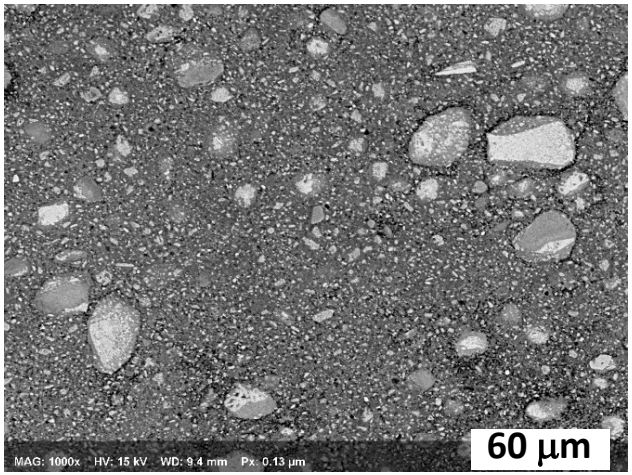
w/b = 0.8; 14 d



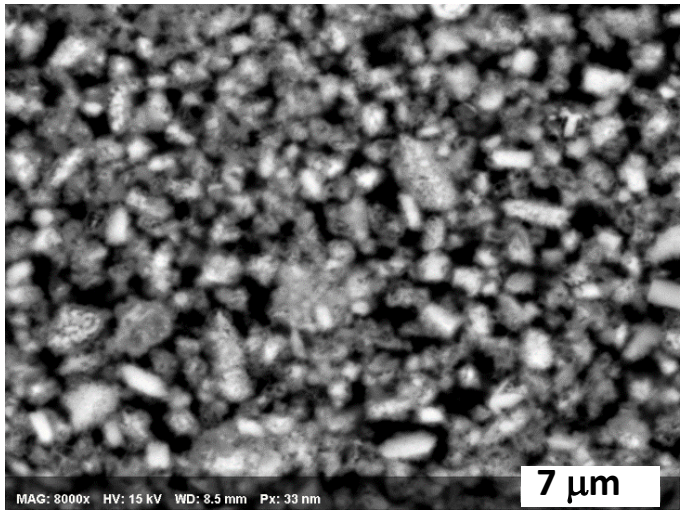
w/b = 0.5; 7d

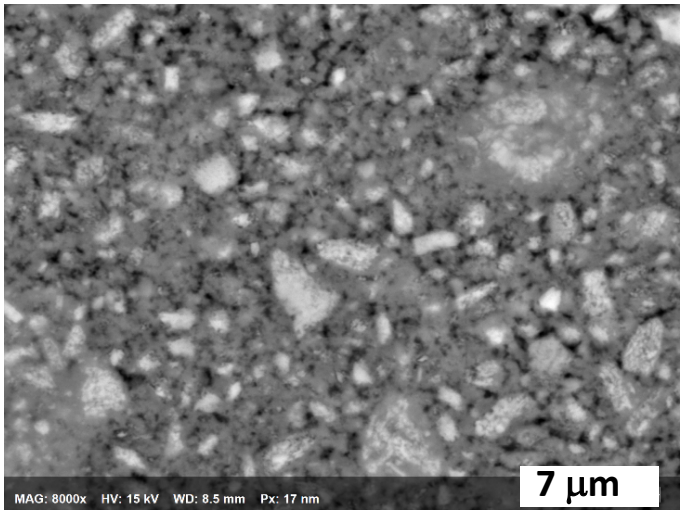


w/b = 0.4; 14d



w/b = 0.5
1d

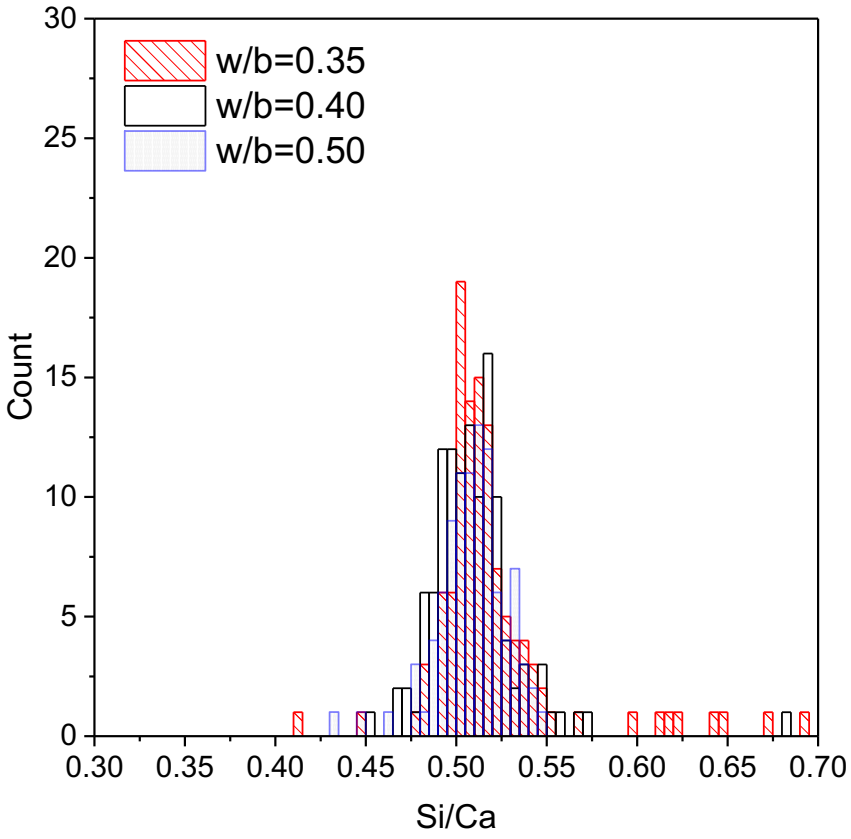


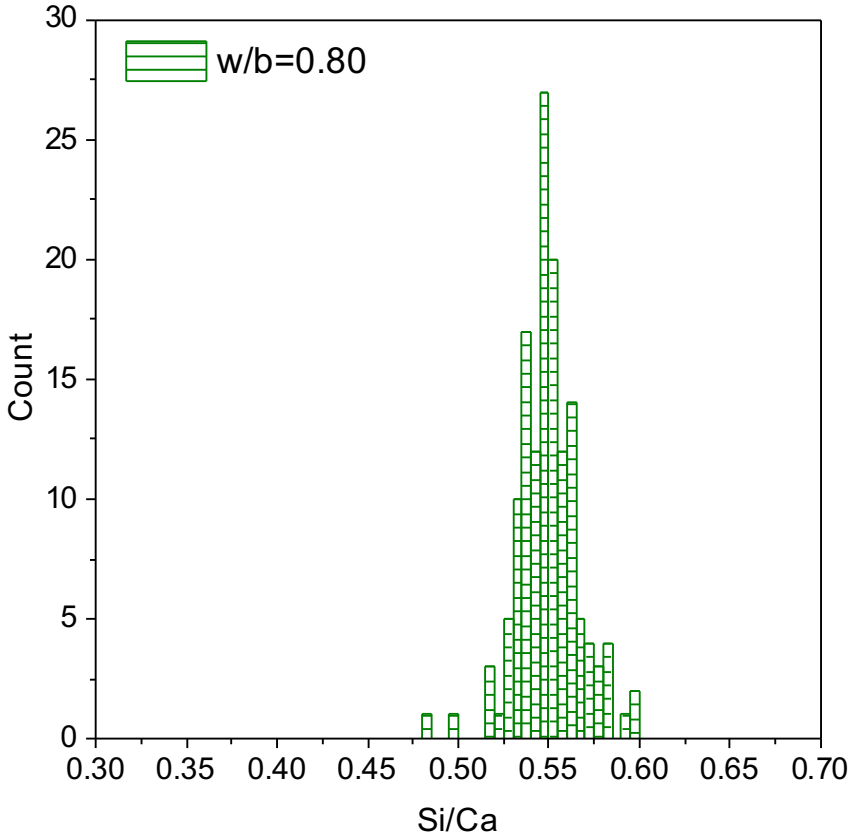


w/b = 0.35
1 d

Pastes with w/b=0.35 & 0.40

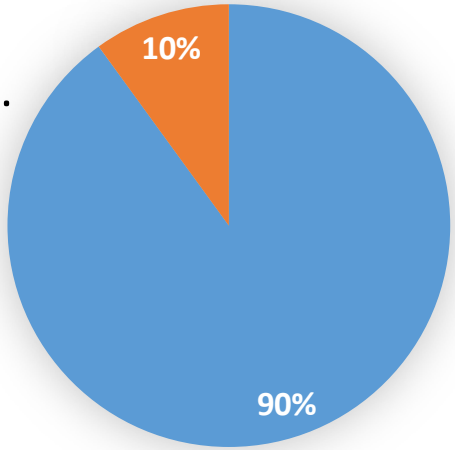
- SEM EDS point analysis on hydrated pastes => Si/Ca ratio
- systems cast with w/b = 0.5, 0.4, 0.35 => Ca/Si ratio ~ 2.0
- system cast with w/b = 0.8 => Ca/Si ratio ~ 1.8
- SEM EDS mapping => Ca and Si distribution is homogenous.

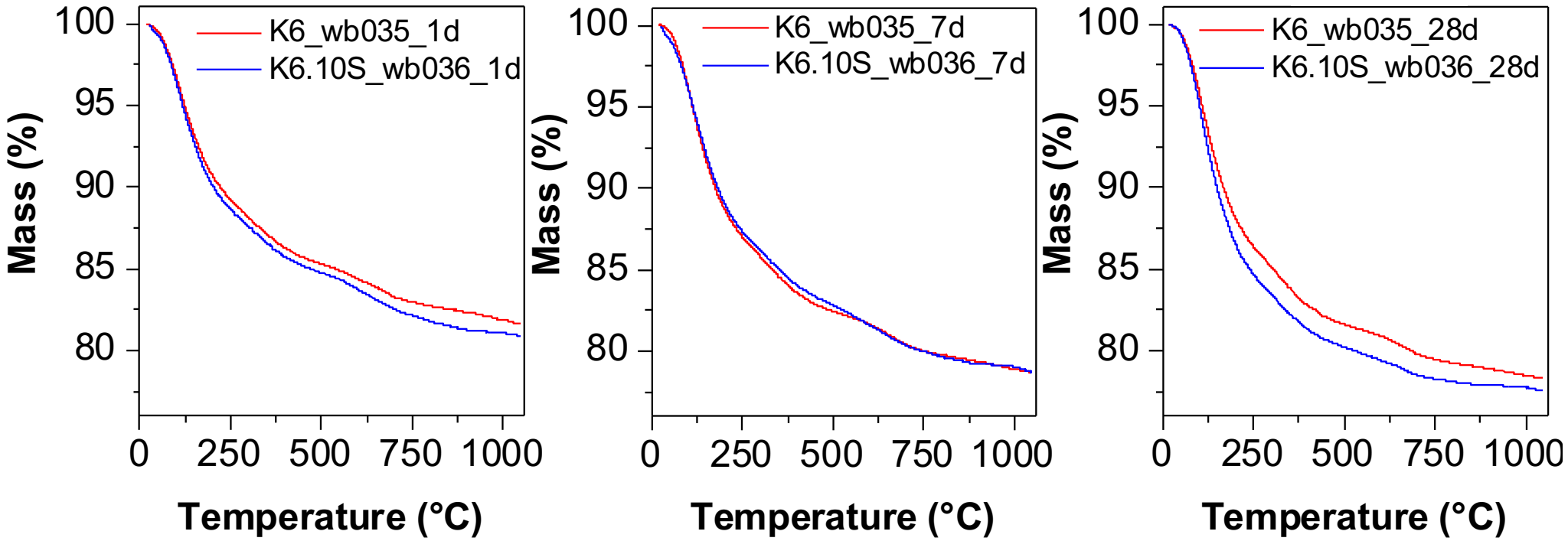




Addition of 10 % silica

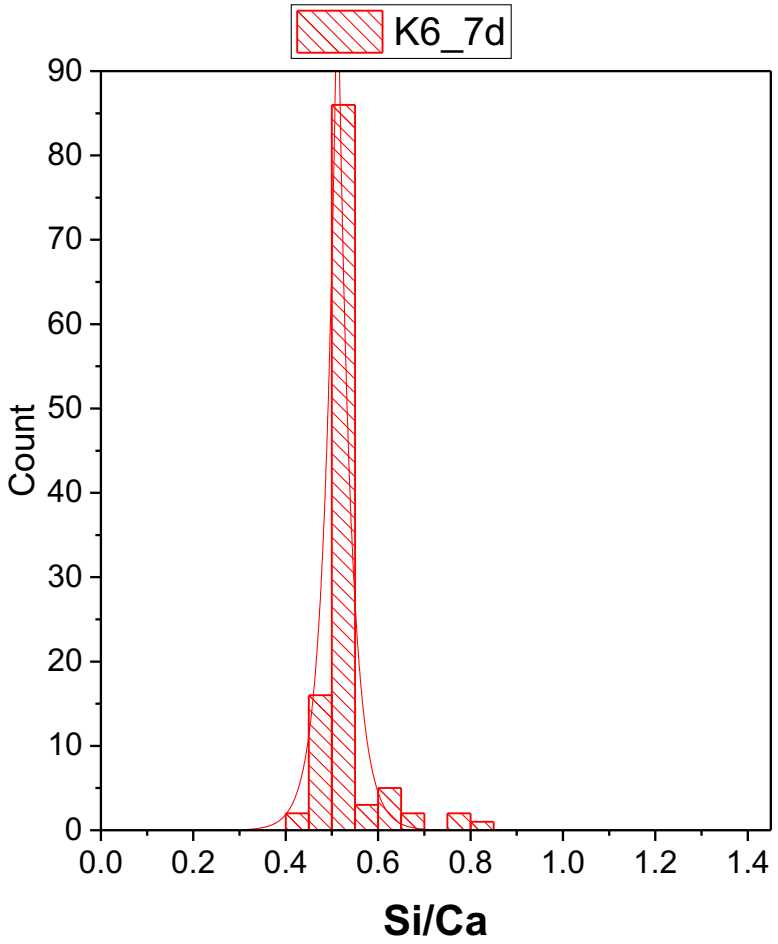
- Mixture with 10 % micro-silica from ELKEM was cast (d_{50} < 500 nm).
- w/b = 0.36, workability was poor compared to plain system.
- After demolding at 1 day, samples were kept in lime water.
- TG curves show higher mass loss at almost all ages for pastes with silica.

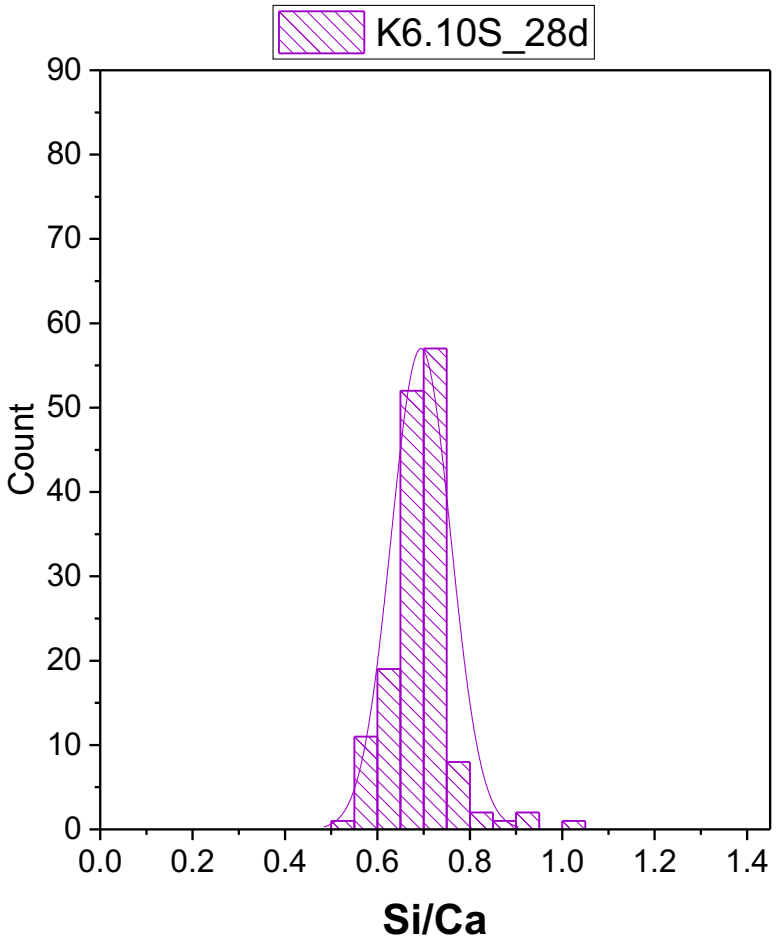




C-S-H composition

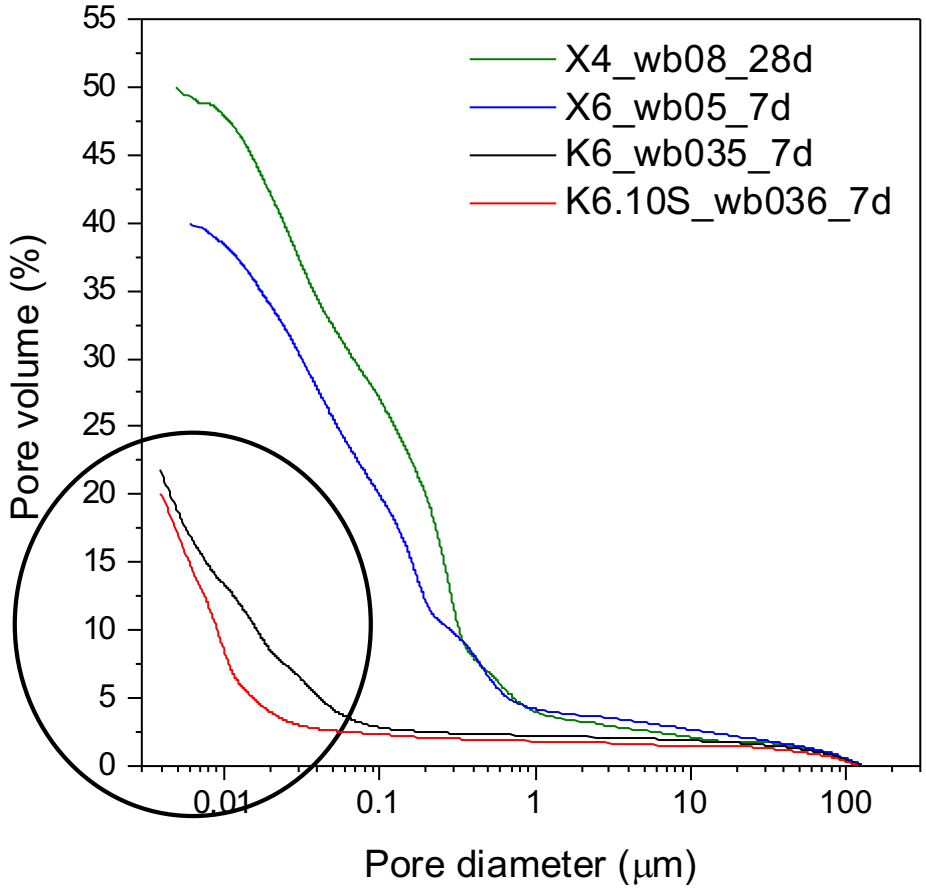
- Hydrated C_2S binder: Ca/Si ratio 2.0
- System C_2S/silica: Ca/Si ratio 1.4

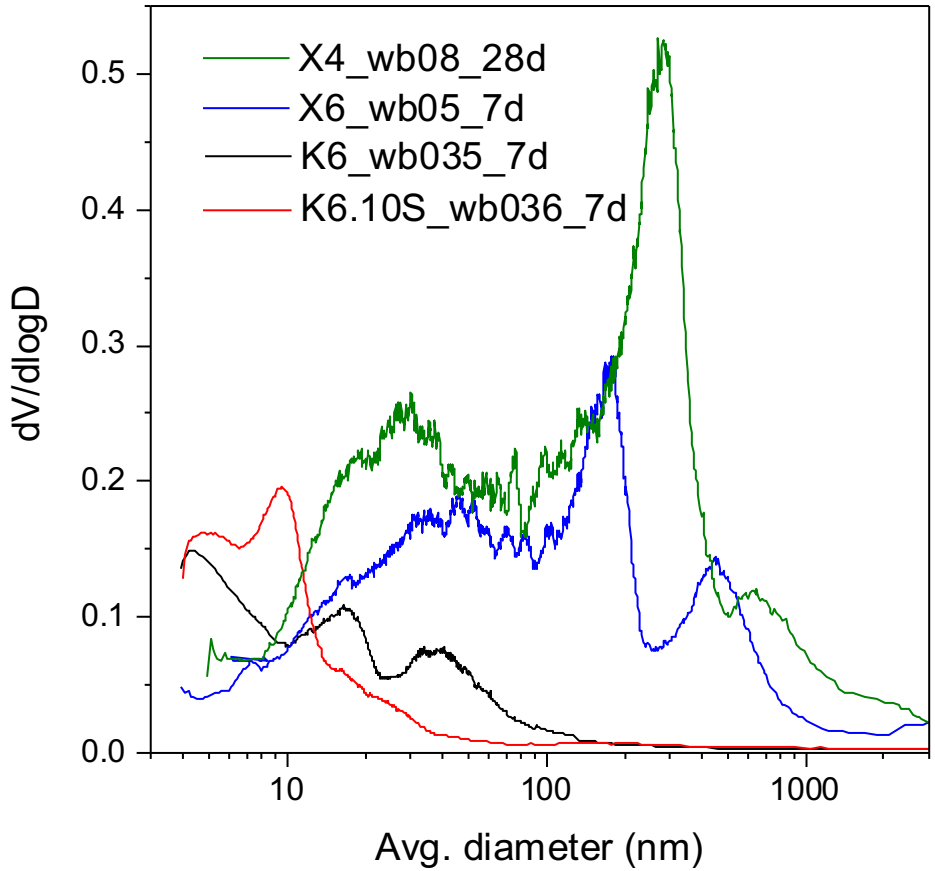




Porosity

- Samples analyzed by MIP after solvent exchange.
- Total pore volume and critical pore entry radius are reduced.





4. CONCLUSIONS AND PERSPECTIVES

- C-S-H samples in dense hardened microstructures can be easily obtained with high DoH at low w/b from reactive C_2S.
- Microstructure is formed only by homogenous outer C-S-H.
- On-going work: C-S-H with different chemical composition (Ca/Si ratio) are being synthesized and also with different ions (Al^{3+}, SO_4^{2-}, alkali).
- Transport tests – more insight on interaction of chloride with C-S-H and migration through pore network.
  - electro-migration test
  - bulk diffusion test

- **SECONDMENTS OVERVIEW AT EPFL**

2018	2019	2020	2021
2 months (April – May)	1 month (August)	1 month (January – June)	2 months (September-October)
Characterization of hydrated microstructure	Chloride transport tests on C-S-H and ^{1}H NMR relaxometry	Chloride transport tests on different C-S-H systems	Thesis preparation for submission

- **OUTREACH ACTIVITY**

Romania, Politehnica University of Bucharest: session with bachelor students about ERICA Project and main research directions in the cement science field, during the current university year.

THANK YOU!