www.LC3.ch

Hydration monitoring techniques

7th Doctoral School – 22nd to 25th of November, 2021
Laboratory of Construction Materials, EPFL

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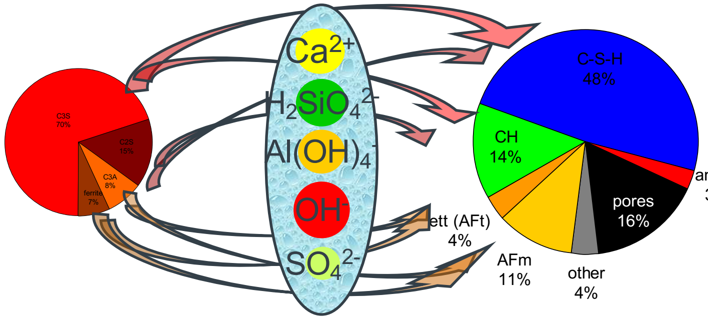
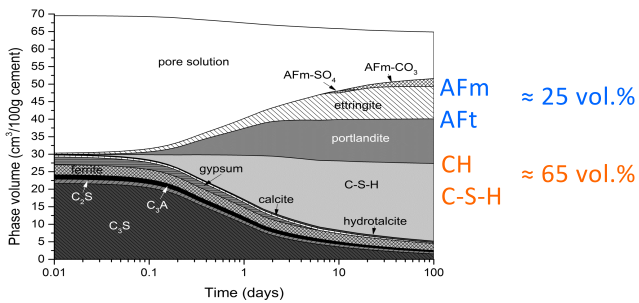
From anhydrous cement to hydrated cement paste



Based on slide by K. Scrivener

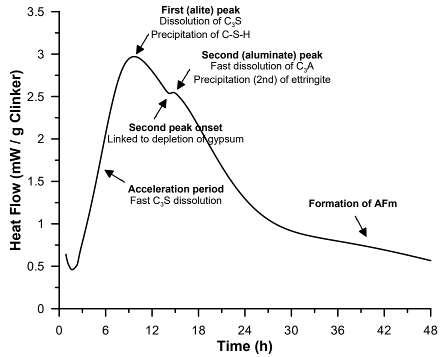
From anhydrous cement to hydrated cement paste



Thermodynamic simulation from Lothenbach

Based on slide by K. Scrivener

Hydration kinetics



- How can we measure this curve?
- What can we learn from it?
- What we cannot learn from it?

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Isothermal calorimetry

Widely adopted technique to measure the heat release over time of cement

- Precise
- Reproducible
- Small sample required
- Versatile (can be performed at different temperatures)
- Easy to interpret results (in general)

Isothermal = Temperature is kept constant

The machine measures the heat extracted (positive) or supplied (negative) to the sample in order to keep the set temperature constant over time

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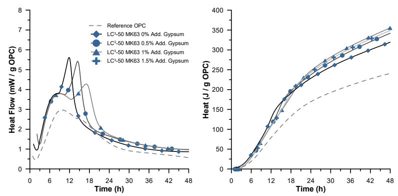
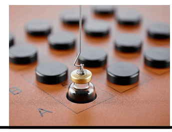
Jeong et al, 2014

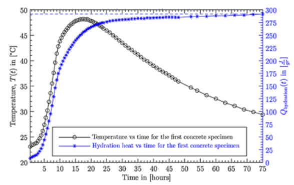
Isothermal calorimetry

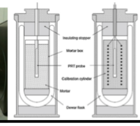
Isothermal





Semi-adiabatic





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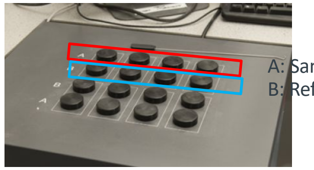
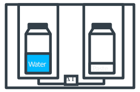
Isothermal calorimetry – the device



C_{water} = 4.18 J/g
C_{cement} = 0.75 J/g



Substance used as reference should have similar heat capacity as the sample and no heat production
e.g. water, quartz

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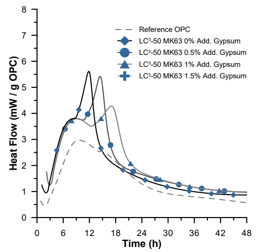
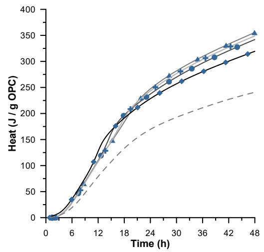
Isothermal calorimetry – data output





- Reaction kinetics
- Enhancement, filler effect

- DoH of the system
- Slow reactions at later age

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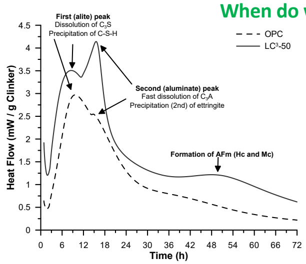
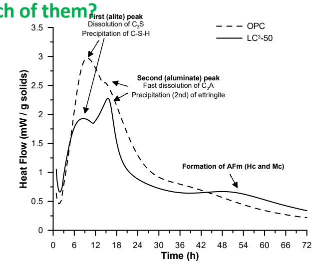
Isothermal calorimetry – data normalization

When do we use each of them?

Output per gram of Clinker (or OPC)



Output per gram of solids (binder)



- Compare the filler effect contribution of different SCMs
- Analyze the effect of accelerators / activators
- Observe the enhancement / reduction of a particular reaction (peak)

- Get an idea of the relative thermal output of systems
- Observe the dilution effect of fillers (or SCMs) on OPC

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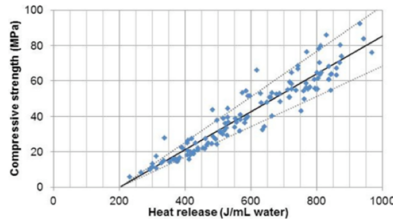
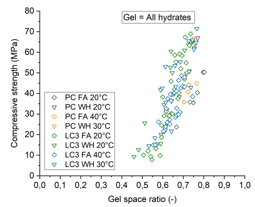
Isothermal calorimetry – Heat v/s strength

Bentz et al., 2012



Strength is proportional to the amount of hydrates formed in the system (implicit reference to the concept of gel-to-space ratio)



Data normalized per volume of initial water (account for different w/b ratios in volume based design)

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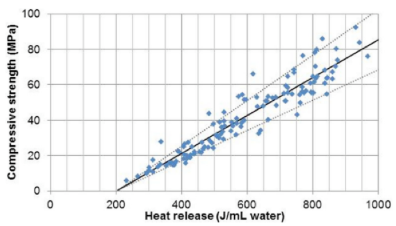
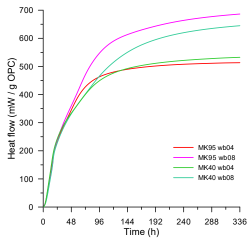
Isothermal calorimetry – Heat v/s strength

Bentz et al., 2012



Strength is proportional to the amount of hydrates formed in the system (implicit reference to the concept of gel-to-space ratio)



Data normalized per volume of initial water (account for different w/b ratios in volume based design)

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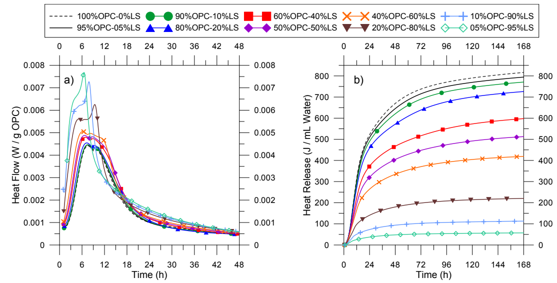
Isothermal calorimetry – Filler effect

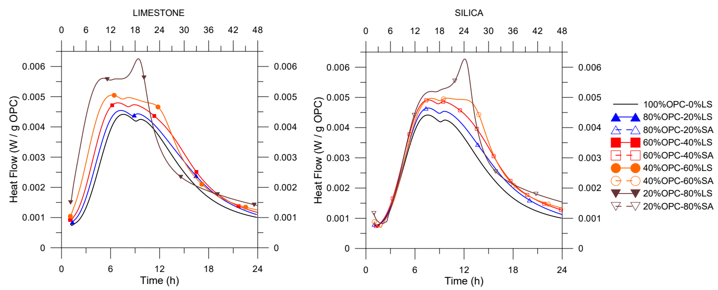


Normalization per gram of OPC useful to see enhancement of OPC hydration
Normalization per mL of water useful to get an idea of relative strengths

Bentz et al., 2017

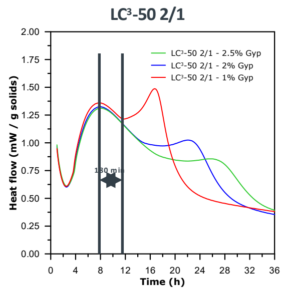
Isothermal calorimetry – Filler effect

Comparison between limestone and quartz



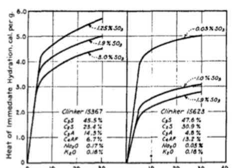
Bentz et al., 2017

Isothermal calorimetry – Sulfate balance



Alternative approaches:

- Compare the total heat release at 24 hours (in J/g)
- Compressive strength test at 24 hours



Lerch, 1946

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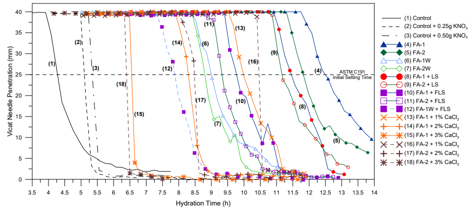
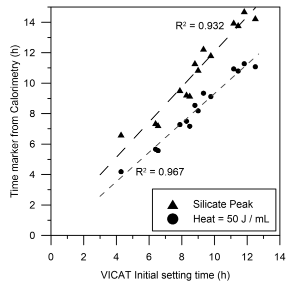
Isothermal calorimetry – Setting time





Zunino et al., 2018

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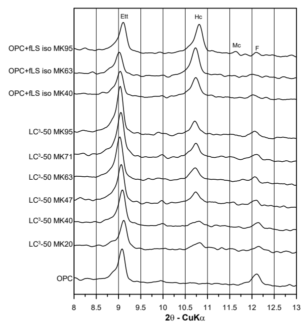
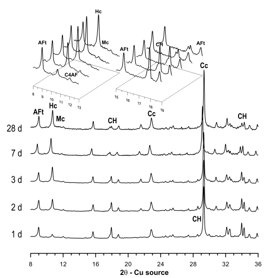
We learned that XRD can help us to study phase assamblage





- Fresh discs are very reliable, we can use them for quantification
- We still need a solid…. can we do better to study hydration before 24h?

Zunino and Scrivener, 2019

In-situ XRD

Place the sample of fresh paste inside the diffractometer, scan continuously to monitor phase precipitation/dissolution

XRD Measurements – Pros and Cons

Fresh Disc
Unaltered sample (preservation of sensitive AFt and AFm)
Testing at discreet times
Risk of carbonation

In-Situ
Continuous monitoring of phase assemblage
Strong Kapton film background to be accounted
Preferred orientation on Kapton's film surface

Diffractometer and scan configuration

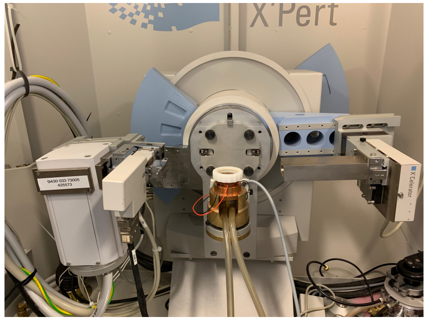
Fresh Disc
Bragg-Brentano configuration, Cu source, 45 kV/40mA
1/2º soller slit , 7º-70º 2θ scan, step size 0.0167º 2θ
Disc cut at the moment of the measurement, surface polished with #1200 sand paper

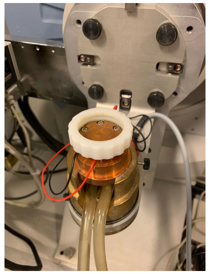
In-Situ
Bragg-Brentano configuration, Cu source, 45 kV/40mA
1º soller slit , 7º-70º 2θ scan, step size 0.0167º 2θ
Sample mounted over sample holder and covered with Kapton film
Temperature controlled with Peltier plate and A/C at 20ºC
Scans taken every 30 min

Limestone Calcined Clay Cement LC3 — LOW CARBON · LOW COST · LOW CAPITAL

In-situ XRD

Bragg-Brentano configuration with a Peltier plate to keep temperature constant





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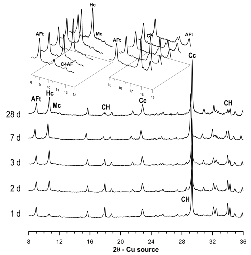
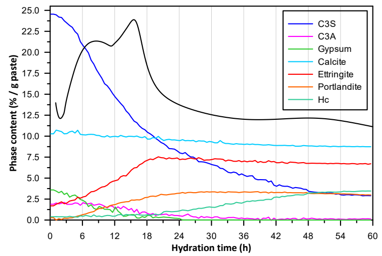
Limestone Calcined Clay Cement LC3 — LOW CARBON · LOW COST · LOW CAPITAL

In-situ XRD vs fresh slices





Scans at discrete times from 24 h onwards

Very precise, possible to perform quantification

Scans every 30 min from 6 min of hydration onwards

Not so precise, a lot of background effects, evaporation, temperature

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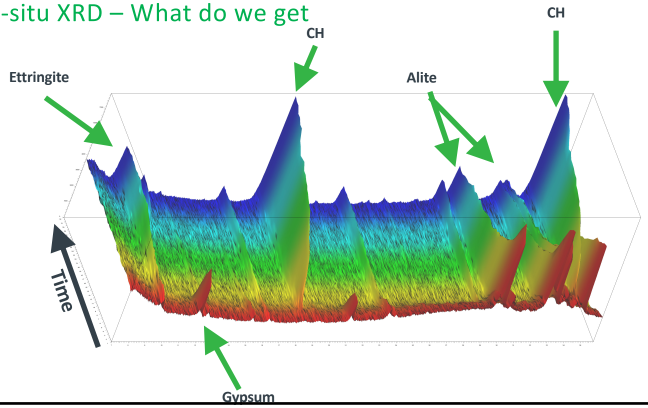
Limestone Calcined Clay Cement LC3 — LOW CARBON · LOW COST · LOW CAPITAL

In-situ XRD – What do we get



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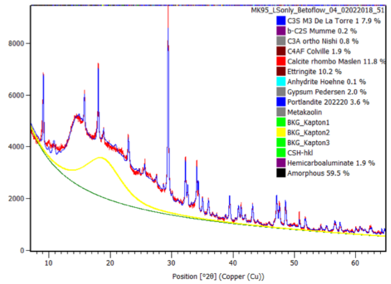
Limestone Calcined Clay Cement LC3 — LOW CARBON · LOW COST · LOW CAPITAL

In-situ XRD – What do we get



- Background effects of cover film and free water need to be accounted
- Some rapid appearance/disappearance of peaks are difficult to catch with automatic routines
- Some minor phases may be difficult to detect
- Sealing is good only until 24-48 h
- Sample shrinks upon hydration….. Variation of vertical displacement!

To improve results, it is a good idea to calibrate the obtained values with the results of one fresh slice (for example, at 24 h).

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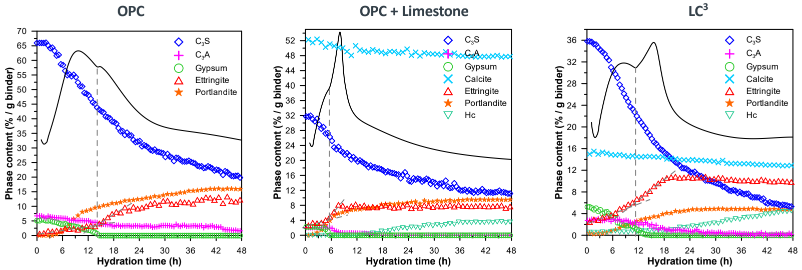
Calorimetry and in-situ XRD complement each other!



Zunino and Scrivener, 2019

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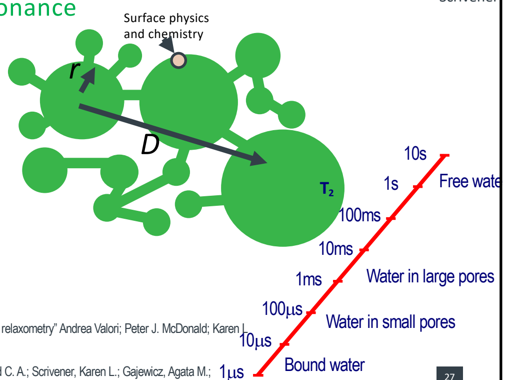
¹H Nuclear Magnetic Resonance

Scrivener

- a unique technique which can analyse porosity using water as a probe
- no drying is necessary
- in fact the pores must contain water to give a signal
- many, in-situ measurements on same sample



"The morphology of C-S-H: Lessons from 1H nuclear magnetic resonance relaxometry" Andrea Valori; Peter J. McDonald; Karen L. Scrivener, Cem. Conc. Res. 49, 65-81, 2013

"Densification of C-S-H Measured by H-1 NMR RelaxometryMuller, Arnaud C. A.; Scrivener, Karen L.; Gajewicz, Agata M.; McDonald, P.M" J Phys. Chem. C 117 (1) 403-412 2013

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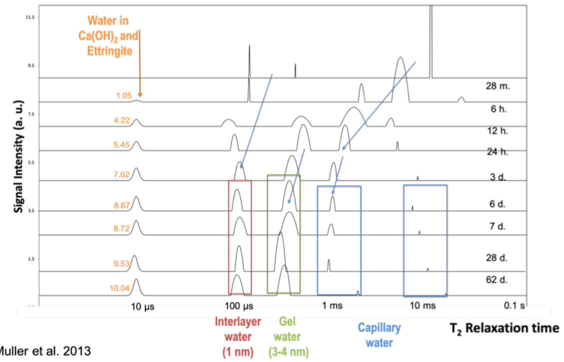
¹H Nuclear Magnetic Resonance



Muller et al. 2013

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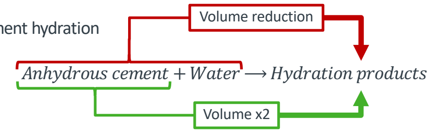
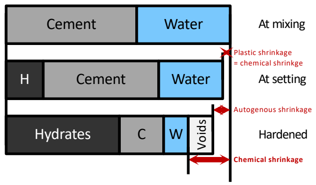
Chemical shrinkage

» Cement hydration



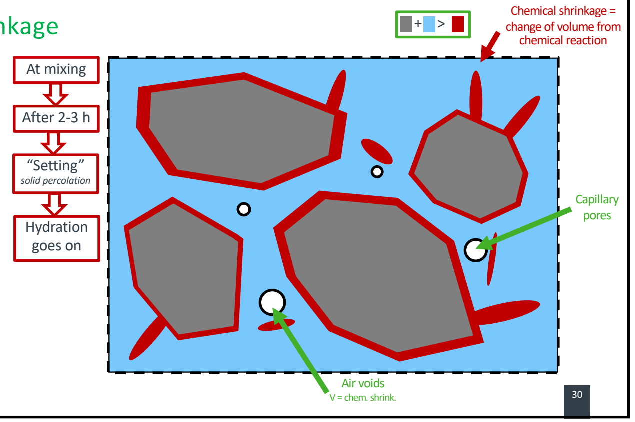
» Reduction of porosity by filling space occupied by water

» But final volume < initial volume
  » Bound / adsorbed water occupies less space than free water



J. Ston

Chemical shrinkage



J. Ston

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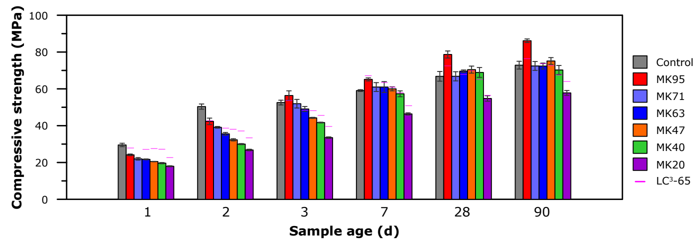
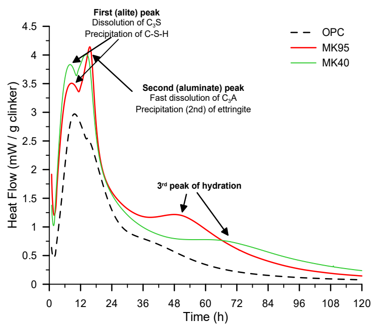
Strength development of LC³ as function of MK content



➢ At 1 day, there is no direct relationship of the strength with the calcined kaolinite content, being only function of the clinker DoH (which is influenced by the filler effect)
➢ At later ages, strength is a function of calcined kaolinite content

The correlation is more clearly observed at 2 and 3 days of hydration

Hydration kinetics of LC[3]



Reactions involving MK and/or limestone

1. Calcined clay (metakaolin) with portlandite

$$AS_2 + 3CH + 6H \rightarrow C\text{-}A\text{-}S\text{-}H + C_2ASH_8$$

metakaolin; strätlingite

2. Limestone reaction with clinker aluminates

$$C_3A + Cc + 11H \rightarrow C_4AcH_{11}$$

limestone; monocarboaluminate

$$C_3A + 0.5Cc + 11.5H \rightarrow C_4Ac_{0.5}H_{12}$$

limestone; hemicarboaluminate

3. Limestone reaction with aluminates from calcined clay

$$AS_2 + 0.5Cc + 3.5CH + 8.5H \rightarrow C_4Ac_{0.5}H_{12}$$

metakaolin; hemicarboaluminate

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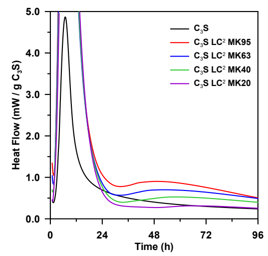
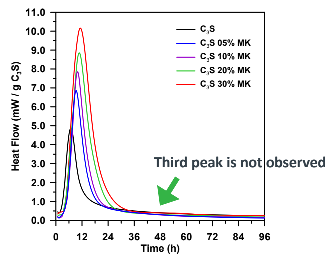
Decoupling the aluminates from OPC and MK

$C_3S + LC^2$



$C_3S + MK$



- In the third peak, the MK (aluminates and/or silicates) from calcined clay are participating
- The occurrence of the third peak requires the presence of both MK and limestone

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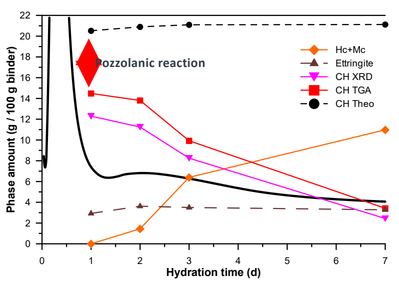
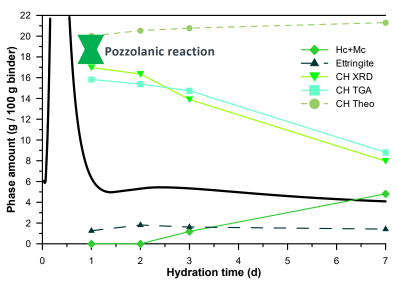
Decoupling the aluminates from OPC and MK

$C_3S + LC^2$ MK95



$C_3S + LC^2$ MK40



- The phase precipitated during the third peak is hemicarboaluminate (i.e., synergetic reaction)

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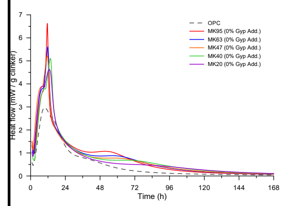
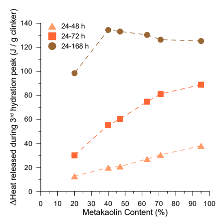
Factors influencing the reaction of MK and LS

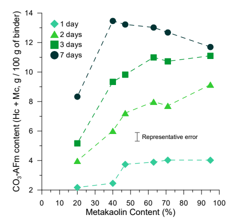
Metakaolin content of the calcined clay



Heat released 3[rd] peak



Hc + Mc measured by XRD



- The heat released during the 3[rd] peak and the amounts of Hc +Mc observed are correlated.
- During the first hydration days, more MK leads to higher amounts of Hc + Mc formed. Afterwards this trend is not longer seen.

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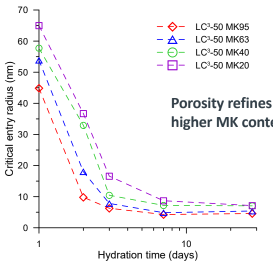
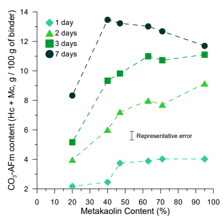
Factors influencing the reaction of MK and LS

Metakaolin content of the calcined clay



Porosity refines earlier in systems with higher MK content

Hc + Mc measured by XRD

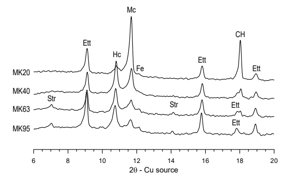


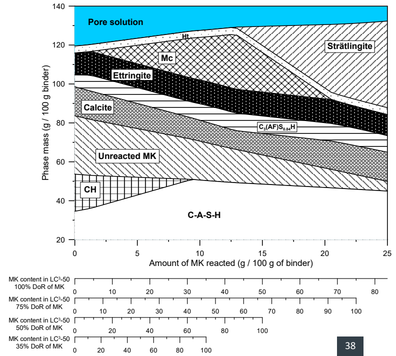
- Precipitation of Hc + Mc leads to refinement of the porosity.
- The reaction slows down (space limitation) earlier in systems that refine their porosity before (high MK content) → lower amounts of Hc + Mc seen at later ages.

Factors influencing the reaction of MK and LS

Metakaolin content of the calcined clay

XRD patterns of LC³ samples cured in sealed conditions for 3 years



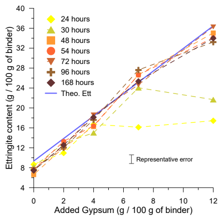


- The reaction kept going, slowly, after 90 days
- It is likely that space availability poses a kinetic limitation, rather than a stoppage of the reaction

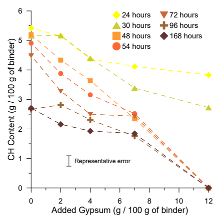
Factors influencing the reaction of MK and LS

Sulfate content

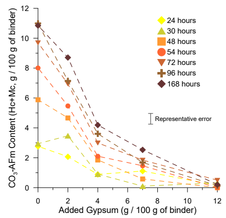
Ettringite is formed until sulfate is depleted



Consuming calcium from the system (CH)



And reducing the amount of Hc + Mc formed



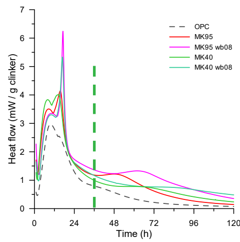
$$C_3A + 3C\$H_2 + 26H \rightarrow C_6A\$_3H_{32}$$

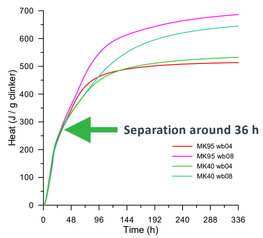
If aluminates come from MK (AS_2) the reaction requires another Ca source

$$AS_2 + 3CH + 3C\$H_2 + 23H \rightarrow C_6A\$_3H_{32}$$

Factors influencing the reaction of MK and LS

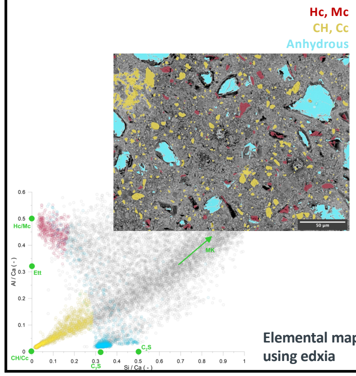
w/b ratio (initial space available)



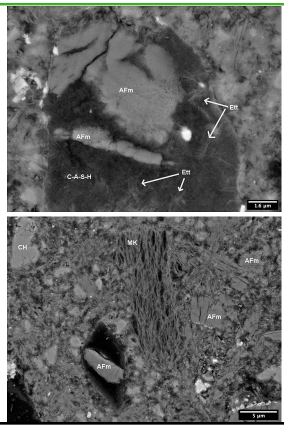


- More (initial) space prolongs the period where the reaction between MK and LS can proceed in "fast mode" (broader 3rd peak observed at high w/b).

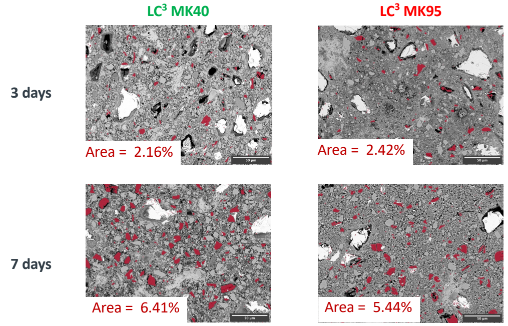
Microstructure of LC³ at early ages



Elemental map analysis using edxia

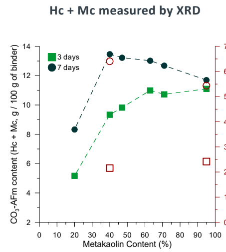


Microstructure of LC³ at early ages



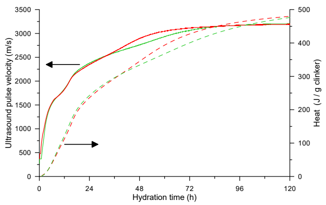
BSE

CO₃-AFm masked in red

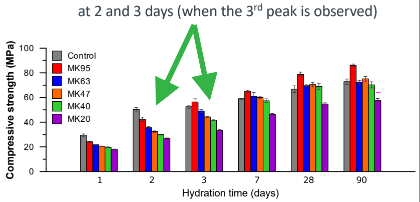


The role of the 3rd peak on mechanical properties

In-situ ultrasound pulse velocity measurement



Strongest correlation of MK content and strength is seen at 2 and 3 days (when the 3rd peak is observed)

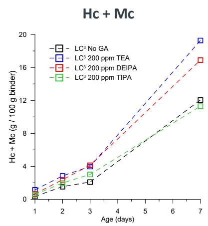


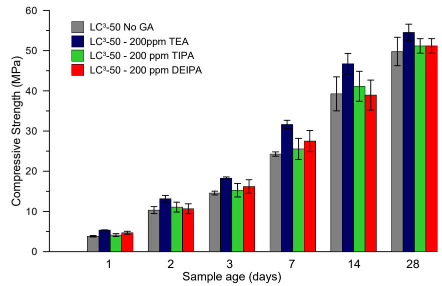
- Precipitation of Hc and Mc contribute to pore refinement and strength of LC³ systems at early age.

If we can increase the amount of Hc + Mc, we can likely increase the strength as well.

The influence of alkanolamines in LC³ properties

Compressive strength





Limestone Calcined Clay Cement LC3

LOW CARBON LOW COST LOW CAPITAL

Contents

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Conclusions

- ✓ Isothermal calorimetry is a powerful technique to study hydration kinetics in cement based materials
- ✓ Depending on the type of data normalization that we use, we can follow different types of effects in our material
- ✓ In-situ XRD complements calorimetry providing direct evidence of phases dissolving and precipitating over time
- ✓ Calorimetry can be complemented with proton NMR and chemical shrinkage

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Limestone Calcined Clay Cement LC3

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Questions?

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