Hydration monitoring techniques

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Laboratory of Construction Materials, EPFL

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» Summary of cement hydration
» Isothermal calorimetry
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» Case study: the third peak of hydration in LC3
» Conclusion

From anhydrous cement to hydrated cement paste

Based on slide by K. Scrivener

Hydration products in cement hydration

Based on slide by K. Scrivener

From anhydrous cement to hydrated cement paste

Ordinary Portland cement hydration (CEMI, containing 2 % CaCO₃)

AFm
AFt
≈ 25 vol.%

CH
C₃S
C₃A
Ferrite
C₃S-H
C₂S-H
AFm
AFt
≈ 65 vol.%

Thermodynamic simulation from Lothenbach

Based on slide by K. Scrivener
to the sample in order to keep the set temperature constant over time. The machine measures the heat extracted (positive) or supplied (negative) to the sample in order to keep the set temperature constant over time.

Hydration kinetics

- First exothermic peak: Dissolution of C3S
- Second (exothermic) peak: Formation of C3AH6
- Acceleration period: Formed the C3A of ettringite
- Formation of AFm

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

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 – the device

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

Isothermal calorimetry – data output

- Reaction kinetics
- Enhancement, filler effect
- Diff of the system
- Slow reactions at later age

Isothermal calorimetry – data normalization

- Compare the filler effect contribution of different SCMs
- Analyze the effect of accelerators / activators
- Get an idea of the relative thermal output of systems
- Observe the enhancement / reduction of a particular reaction (peak)

Isothermal calorimetry – Heat v/s strength

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

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

Alternative approaches:
- Compare the total heat release at 24 hours (in J/g)
- Compressive strength test at 24 hours
We learned that XRD can help us to study phase assemblage

- 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?

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 (preparation of external XRD and XRF)
- Timing of discrete 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
- 1/2° slit, PMT 200 scan, step size 0.0167° 2θ
- Disc cut at the moment of the measurement, surface polished with #2000 sand paper

**In-Situ**
- Bragg-Brentano configuration, Cu source, 45 kV/40mA
- 1° slit, PMT 200 scan, step size 0.0167° 2θ
- Sample mounted on sample holder and covered with Kapton film
- Temperature controlled with Peltier plate and A/C at 20°C
- Scan taken every 30 min

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

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

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).
Calorimetry and in-situ XRD complement each other!

![Graphs showing hydration time vs. peak area for OPC, OPC + Limestone, and LC3 samples.](image)

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1H Nuclear Magnetic Resonance

- 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

![Diagram showing relaxation times for different types of water.](image)


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

» Cement hydration

\[
\text{Anhydrous cement} + \text{Water} \rightarrow \text{Hydration products}
\]

» Reduction of porosity by filling space occupied by water

» But final volume < initial volume

» Bound / adsorbed water occupies less space than free water

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Strength development of LC\textsuperscript{3} 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
Reactions involving MK and/or limestone

1. Calcined clay (metakaolin) with portlandite
   \[ \text{AS} + 3\text{CH} + 6\text{H} \rightarrow \text{C-A-S-H}_x \]

2. Limestone reaction with clinker aluminates
   \[ \text{CA} + \text{C}_c + 11\text{H} \rightarrow \text{C}_c\text{AH}_x \]
   \[ \text{CA} + 0.5\text{C}_c + 0.5\text{CH} + 11.5\text{H} \rightarrow \text{C}_c\text{Al}_4\text{H}_8 \]

3. Limestone reaction with aluminates from calcined clay
   \[ \text{AS} + 0.5\text{C}_c + 3.5\text{CH} + 8.5\text{H} \rightarrow \text{C}_c\text{Al}_4\text{H}_8 \]

Decoupling the aluminates from OPC and MK

Factors influencing the reaction of MK and LS

1. In the third peak, the MK (aluminates and/or silicates) from calcined clay are participating
2. The occurrence of the third peak requires the presence of both MK and limestone
3. The heat released during the 3rd peak and the amounts of Hc + Mc observed are correlated.
4. During the first hydration days, more MK leads to higher amounts of Hc + Mc formed. Afterwards this trend is not longer seen.
Factors influencing the reaction of MK and LS

Metakaolin content of the calcined clay

- 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

Sulfate content

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

Factors influencing the reaction of MK and LS

Mesh content of the calcined clay

- 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
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

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

Questions?

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