Isothermal calorimetry

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Doctoral School – EPFL Lausanne
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Calcined Clay for Sustainable Concrete
Agenda

- Introduction
- Device
- Training – sample preparation, experiments
- Conclusions
- References
INTRODUCTION
What does calorimeter measure?

Why do we need calorimetry measurements?
Heat released and Kinetics

![Graph showing heat flow over time](image_url)
Cement hydration is divided into several stages:

1. **Stage 1**: Dissolution
2. **Stage 2**: Induction period
3. **Stage 3**: Acceleration period
4. **Stage 4**: Deceleration period
5. **Stage 5**: Slow down period

A graph illustrates the heat flow over time, with a peak around 20 hours and a slow decline after 28 days.
Dissolution – induction periods

Stage 1: Dissolution
Stage 2: induction period

>28 days

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Dissolution

Equilibrium curve of cement

Precipitation

Equilibrium curve of hydrate

Dissolution
Dissolution rate controls the kinetics

P. Juillard, Cem. Conc. Res. 2010
Which parameters can affect the induction period?

- Density of crystal defects
- Fineness
- Temperature
- Admixtures
Crystal defects affect the dissolution rate

P. Juilland, Cem. Conc. Res. 2010

Etched pits
Step retreat

AFM on alite surface
Which parameters can affect the induction period?

- Density of crystal defects

After grinding:
- Many defaults
  - C₃S

After grinding + annealing:
- No defaults
  - C₃S

Less crystal Defects
Longer induction period

Acceleration period

Stage 3 Acceleration Period

>28 days
Acceleration rate controled by N+G C-S-H

Growth of C-S-H
Quartz Cement paste 4h

Cement paste 4h

Heat Flow (mW/g of cement)

0 1 2 3 4 5

Time of hydration (hours)

0 10 20 30 40

Cement paste w/s 0.4
Quartz-cement paste w/s 0.4

More nuclei, steeper slope

Which parameters can affect the acceleration period?

- Mixing
- Fineness
- Temperature
- Admixtures
- Supplementary Cementitious Materials
Which parameters can affect the acceleration period?

- **Mixing**


Which parameters can affect the acceleration period?

- Fineness
Which parameters can affect the acceleration period?

- Supplementary Cementitious Materials


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Which parameters can affect the acceleration period?

- Supplementary Cementitious Materials

- Pozzolanic reaction (Silica fume)

A. Muller, Thesis 2014
Cement hydration is divided in several stages

Stage 4
Deceleration Period

>28 days
Sulfate adjustment

Figure 4.14: Isothermal calorimetric curves plotted for blends systems at 45% substitution with different gypsum contents.
Later age

Stage 5
Slow down
Period

>28 days
Impact of SCMs at later age

Reaction of the SCMs

Heat release (J/g of cement) vs. Hydration time (hours)

- 40% Quartz
- 40% Slag
- 40% Fly ash
- OPC

Heat flow (mJ/g cement) vs. Time (hours)

Plain cement

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DEVICE
Substance used as reference should have similar heat capacity as the sample and no heat production e.g. water, quartz! NO old hydrated cement samples
Water reference

Which quantity of water?

The amount of water is calculated to have same specific heat capacity than the relative cement paste sample (A channel).

\[ C_{\text{water}} = 4.18 \text{ J/g} \]
\[ C_{\text{cement}} = 0.75 \text{ J/g} \]

Calculate the water reference for a sample of 10g of cement paste w/c 0.4
STEPS for calorimetry experiments at EPFL

1. Baseline 1 day before
   1. Check temperature of the calorimeter
   2. Preparation of water reference
   3. Insertion of water references in the calorimeter
   4. Start baseline

2. Sample preparation
   1. Preparation of the anhydrous component (Blender)
   2. Preparation of the water to add

3. Experiment
   1. Check end baseline
   2. Mixing of the paste and record time
   3. Insert

!!! Dependent on the calorimeter brand !!!
Experimental conditions

Standard EPDL protocol
- 80g solids
- Mixing 2 minutes at 1600 rpm with blades
- Samples of 10g

Other protocols

Vibrating protocol

Cement and water directly in bottle

800 rpm
CONCLUSIONS
Influence of Protocol

N. Myers, Master thesis 2011
A Practical Guide to Microstructural Characterisation of Cementitious Materials – Chap. 2 Calorimetry published soon!!


References
