Isothermal Calorimetry of Cement
The hydration process of cement is highly exothermic and is typically measured in the milliwatt (mW) range.

TAM Air was originally designed for use in cement calorimetry research.

TAM Air combines eight channels with a sensitivity of about ±4 µW.
After calibration the following holds:

General Heat Balance Equation

\[
\frac{dQ}{dt} = \Phi + C\left(\frac{dT}{dt}\right)
\]

Rate of Heat Production = Rate of Heat Exchange + Rate of Heat Accumulation

The measured property

Heat flow Monitored by TAM
TAM Air
TAM Air Heat Detectors

- Consist of small plates with thermopiles (Seebeck Modules)
- When the two sides of the plate are exposed to different temperatures, heat will flow from the warm to the cold side
  - Same principle as TAM III
- Sensitivity in µW-mW range

Heat sink in contact with the air thermostat
Static Calibration

P (µW)

Calibration Power ON
= set µW pulse

\[ P = P_0 \exp\left(-\frac{t}{\tau}\right) \]

Calibration Power OFF

Empty calorimeter or Accessory and Reference in position.

How to obtain \( \tau \)
The time until \( \frac{P}{P_0} = 1/e = 0.37 \)
For reactions where the slope of the heat flow time curve \( (dP_{\text{Raw}}/dt) \) is changing slowly the first part of the following formula can be used to calculate the true response in heat flow \( (P_{HF}) \) from the heat flow monitored by the heat detector \( (P_{\text{Raw}}) \) using the following formula. For fast reactions an additional term is used to calculate \( P_{\text{Dyn}} \).

\[
P_{HF} = P_{\text{Raw}} + \tau \frac{dP_{\text{Raw}}}{dt}
\]

\[
P_{\text{Dyn}} = P_{\text{Raw}} + (\tau_1 + \tau_2) \frac{dP_{\text{Raw}}}{dt} + \tau_1 \cdot \tau_2 \frac{dP^2_{\text{Raw}}}{dt^2}
\]
The hydration process undergoes a number of phases (Young, 1985)

- (I) Rapid initial processes
- (II) Dormant period
- (III) Acceleration period
- (IV) Retardation period
- (V) Long term reactions

The phases have been described in more detail (Sandberg, 2002)

- (I) Dissolution of ions and initial hydration
- (II) Formation of ettringite
- (III) Initiation of silicate hydration
- (IV) Depletion of sulphate
Portland Cement Basics

- Silicates hydrate to give strength giving gel, “glue”
- Aluminate and ferrite phases necessary to get a molten phase during production of cement
- Aluminates react rapidly, interact with admixtures, workability, set, early strength development
- Gypsum added during grinding to slow down aluminate hydration rate
  - Higher C_{3}A, lower C_{4}AF generally more reactive
  - Different sulfate forms have different solubility
- ASTM Standard Method drafts available in 2008
  - C1679 (kinetics)
  - WK 4922 (heat of hydration)

*Dr. P. Sandberg, Grace Construction Products, US (2002)*
Isothermal Calorimetry for Cements

- Isothermal calorimetry is sensitive and versatile tool for studying the hydration process of cement.
  - The shape of the heat flow versus time curve reflects the hydration process(es) of cement
  - The effect of an admixture is reflected in a change of the hydration curve
  - The integrated heat flow time curve, i.e. the energy evolved is related to the extent of hydration
- Excellent experimental reproducibility.
Typical Cement Applications for Isothermal Calorimetry

- Setting time and premature stiffening
- Effect of contaminations
- Effect of admixtures
- Temperature dependency of cement hydration
- Quality control
- R&D

Sample Handling

- Closed ampoules for long term reactions.
- Admix ampoule for early reactions i.e. first 30-45 minutes.
  - Refer to EN 302 (Lars Wadsö)
How to Perform Cement Hydration Measurements

- Weigh ampoule and/or lid
- Weigh cement powder (1-10g) and water (1-10g)
- Mix well and mix for a consistent time (~1-3min)
  - Stirring rate can be important
  - Time zero important
  - Load and weigh cement paste into the ampoule
- Load into TAM Air and come back in a few days
  - Most common test is 72 hour (or 3 day) hydration
  - Cement hydration completion after 28 days
- ASTM Methods in 2008 - WK4922 or C1679 (kinetics)
Isothermal Calorimetry Reproducibility

Dr. Moro, Holcim Group Support, Switzerland (2002)
Effect of Admixtures


- Only small differences between cement lots when tested without admixture

- Very large differences between cement lots when tested with same admixture!!!
Kinetics of Cement Hydration

Measurements at 20, 25 and 30 °C

$P$ reflects the rate of the process

$Q$ reflects the extent of the process

Dr. P. Vikegard, Thermometric AB, Sweden (2002)
Admix Ampoule Experiment Reproducibility

Calcium Sulfate Hemihydrate 1-2 g powder mixed at w/c 0.50
Admix Ampoule Experiment

Calcium Sulfate Hemihydrate 1-2 g
mixed with DI water at w/c 0.50 and 0.35
Mix ~2.85 g cement solid with 1.38 mL water

Differences in the heat of wetting/mixing observed for two different cement powders. Mixed with DI water at w/c 0.48. Hydration plot shown on next slide.
Mix ~2.85 g cement solid with 1.38 mL water

Differences in the cement hydration profile observed. Mixed with DI water at w/c 0.48.
Normalized Heat

Mix ~2.85 g cement solid with 1.38 mL water

Differences in the cement hydration profile observed. Mixed with DI water at w/c 0.48.
Mortar – Normalized Heat of Wetting

1 g cement: 2.75 g sand: 0.475 mL water

Injected DI water
Mortar – Normalized Heat of Hydration

1 g cement: 2.75 g sand: 0.475 mL water

Cement 1 w/ Sand A

Cement 1 w/ Sand B
Repeatability

Three different samples

Relative specific heat flow vs. Time (weks)
Microhygrostat

Glass tube with pure solvent or a solvent saturated by a salt (e.g. sat. NaCl (aq))

Solid sample

Developed independently by: Angberg, Uppsala University and Byström, Astra Zeneca (1992)
Other Calorimetric Methods for the Study of Cement

- Adiabatic calorimetry or semi-adiabatic calorimetry
  - Sample is placed in insulation made of polystyrene. One example of a semi-adiabatic calorimeter is the Nordic “hökassen” that was investigated in NORDTEST-studies: NT 821 and NT Build 388.

- Solution calorimetry
  - ASTM C186
  - Total heat of hydration at a certain time is determined as the difference between the liberated heat when an un-hydrated sample and the sample under investigation is dissolved in a mixture of hydrofluoric acid and nitric acid.
  - This old measurement technique is described in ASTM C186, prEN 196-8, and SS B1 1960.
  - This method is time-consuming, costly and dangerous, but still in use.
Isothermal Calorimetry (heat flow) versus Semi-Adiabatic

- Isothermal calorimeters directly measure the heat production rate that is proportional to the rate of the reaction
  - adiabatic calorimeters measure temperature change and that is recalculated to give heat produced
  - Heat capacity of the sample is required for adiabatic calorimetry and not for isothermal
- Isothermal calorimeters are very stable and need not be calibrated more than a few times a year
  - adiabatic calorimeters are often calibrated before each run.
- The temperature never increases to unrealistic temperatures in an isothermal calorimeter. The structure and thus the properties of the hardened cement paste depend on the temperature of hydration.
- A main benefit of isothermal calorimetry is that the hydration process of the cement is monitored *continuously* with multiple samples from the start of the measurements.
 Isothermal Calorimetry

- Analysis in laboratory environment
- Multiple channels (sample and reference) for parallel analysis
- Built in calibration heaters for automated calibrations
- Sample temperature can be assumed isothermal
- Very sensitive calorimeter(s) with the ability to load up to 20 mL volume samples
  - Compare heat flow stability/sensitivity.
- Admix accessory to study initial hydration.
  - Software includes data analysis
Suggested Readings

- AN 22014 Hydroscopic powders – a microcalorimetric assessment of cement
- AN 314-01 The Study of Cement Hydration by Isothermal Calorimetry
- AN 314-05 Optimization of sulfate - Part I without admixture
- AN 314-06 Optimization of cement sulfate Part II with admixture
- AN 314-07 Effect of carboxylic acids on the hydration of calcium sulfate hemihydrate pastes
- EN 302 Using the Admix ampoule for cement hydration measurements

- ASTM Methods in 2008 - WK4922 or C1679 (kinetics)

- Applications of an eight-channel isothermal conduction calorimeter for cement hydration studies. By Lars Wadsö, Cement International 2005