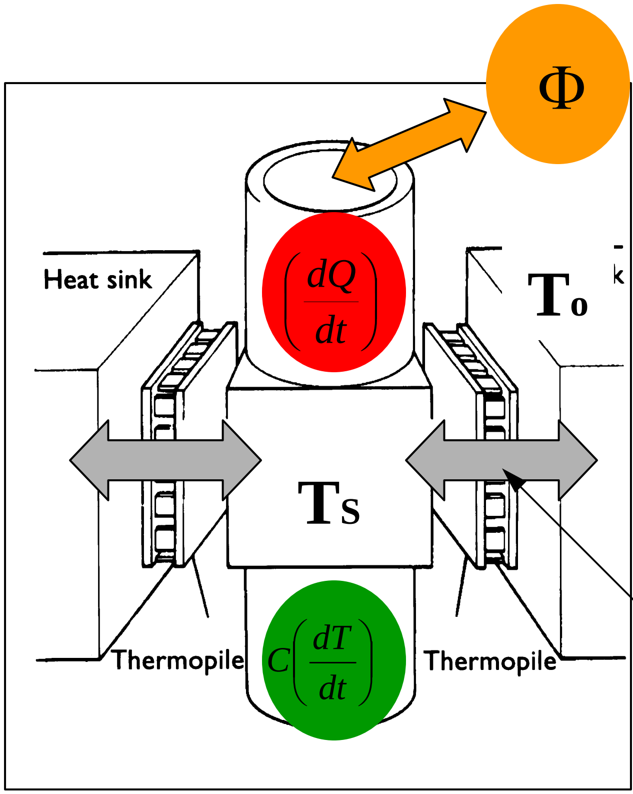
Isothermal Calorimetry of Cement

TAM Air

- 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.

Calorimetric Unit



General Heat Balance Equation

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

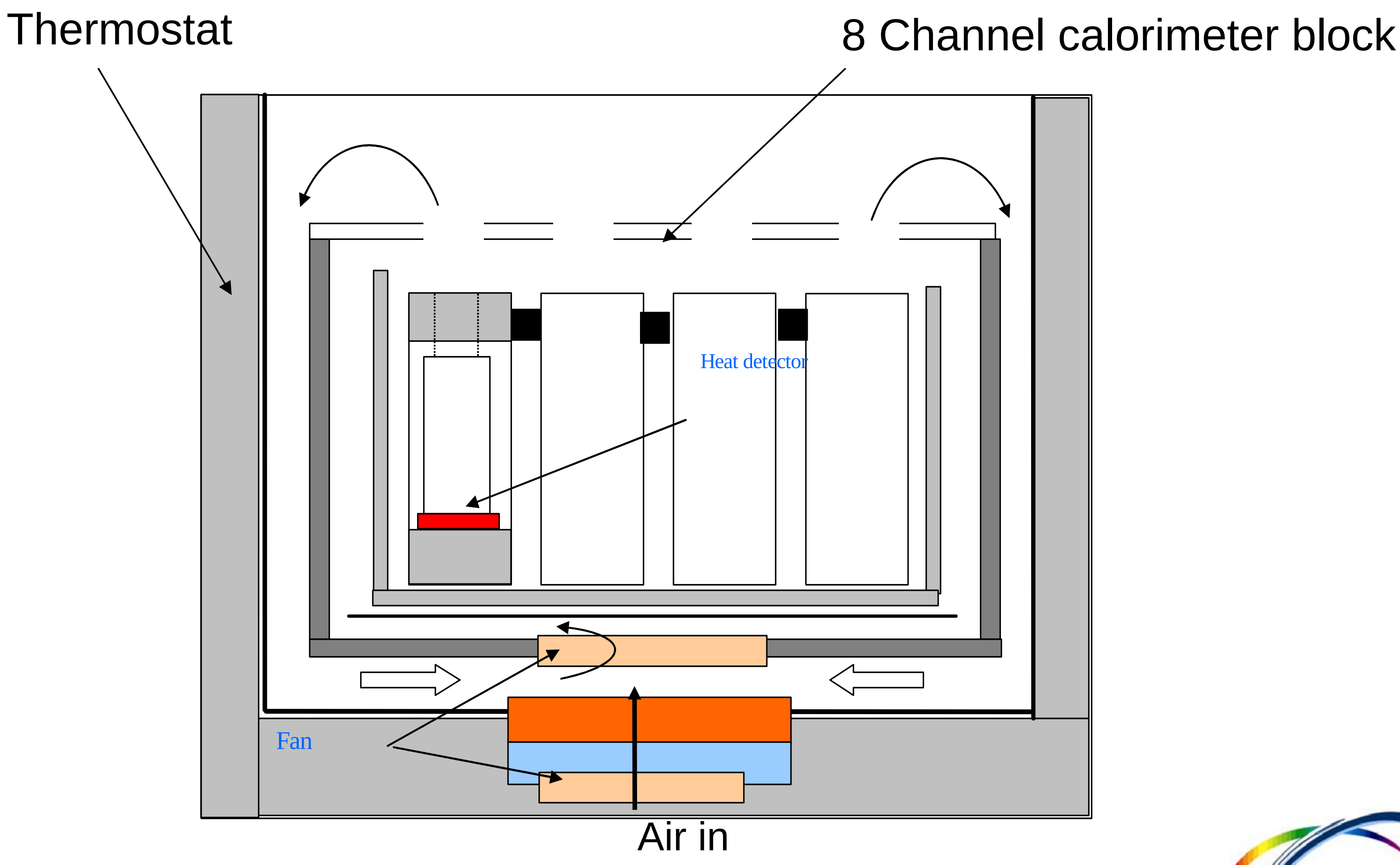
Rate of Heat Production = **Rate of Heat Exchange** + **Rate of Heat Accumulation**

The measured property

<u>After calibration the following holds:</u>

Rate of Heat Production (dQ/dt) = **Heat flow Monitored by TAM**

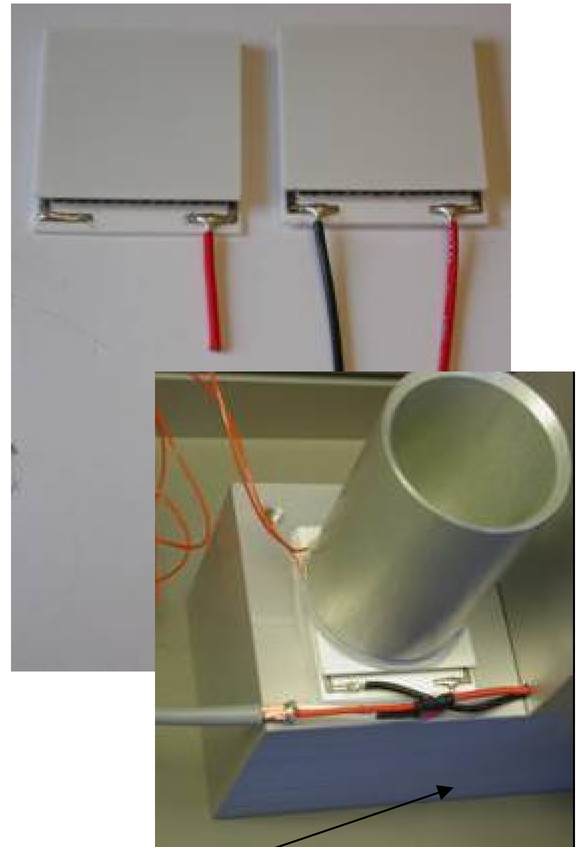
TAM Air



Thermostat
8 Channel calorimeter block
Heat detector
Fan
Air in

TAM Air Heat Detectors

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

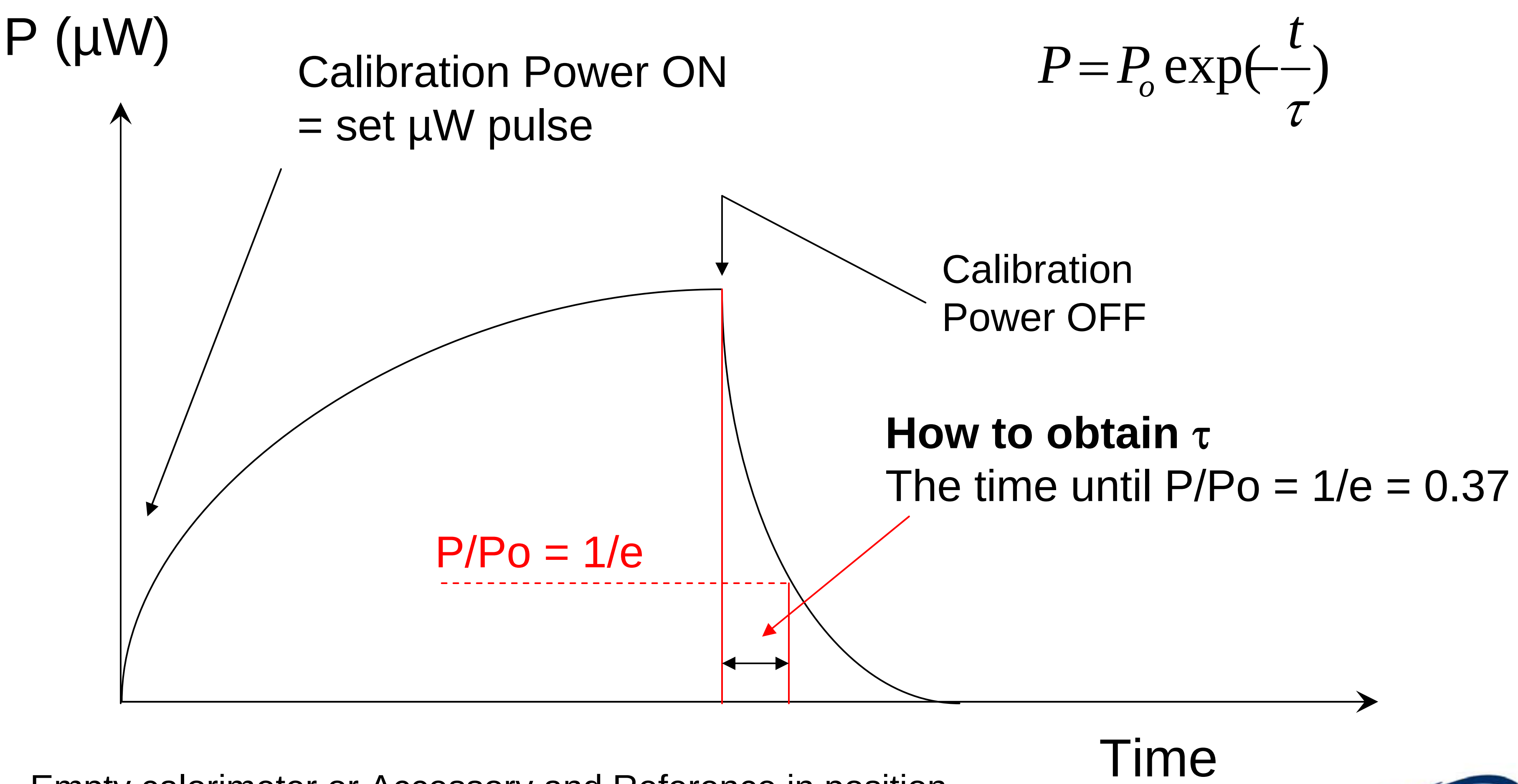


Heat sink in contact with the air thermostat

Static Calibration

Exponential heat exchange

$$P = P_o \exp(-\frac{t}{\tau})$$



Empty calorimeter or Accessory and Reference in position.

Heatflow and Dynamically Corrected Data

- For reactions where the slope of the heat flow time curve (dP_{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_{Raw}) using the following formula. For fast reactions an additional term is used to calculate P_{Dyn}.

$$P_{HF} = P_{Raw} + \tau \frac{dP_{Raw}}{dt}$$

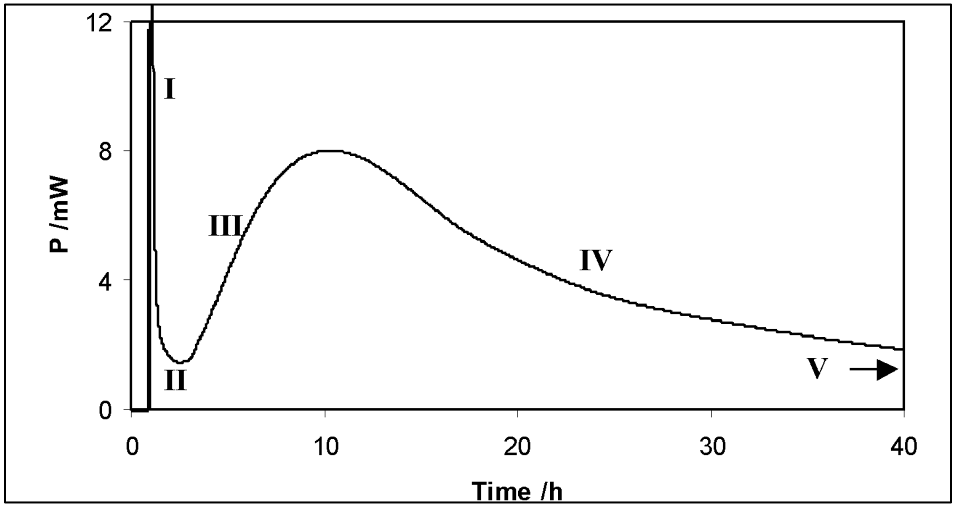
$$P_{Dyn} = P_{Raw} + (\tau_1 + \tau_2)\frac{dP_{Raw}}{dt} + \tau_1 \cdot \tau_2 \frac{dP^2_{Raw}}{dt^2}$$

Basics of Cement Calorimetry

Dr. P. Sandberg, Grace Construction Products, US (**2002**)

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_3A , lower C_4AF 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

*Dr. P. Sandberg, Grace Construction Products, US **(2002)***

Sample Handling

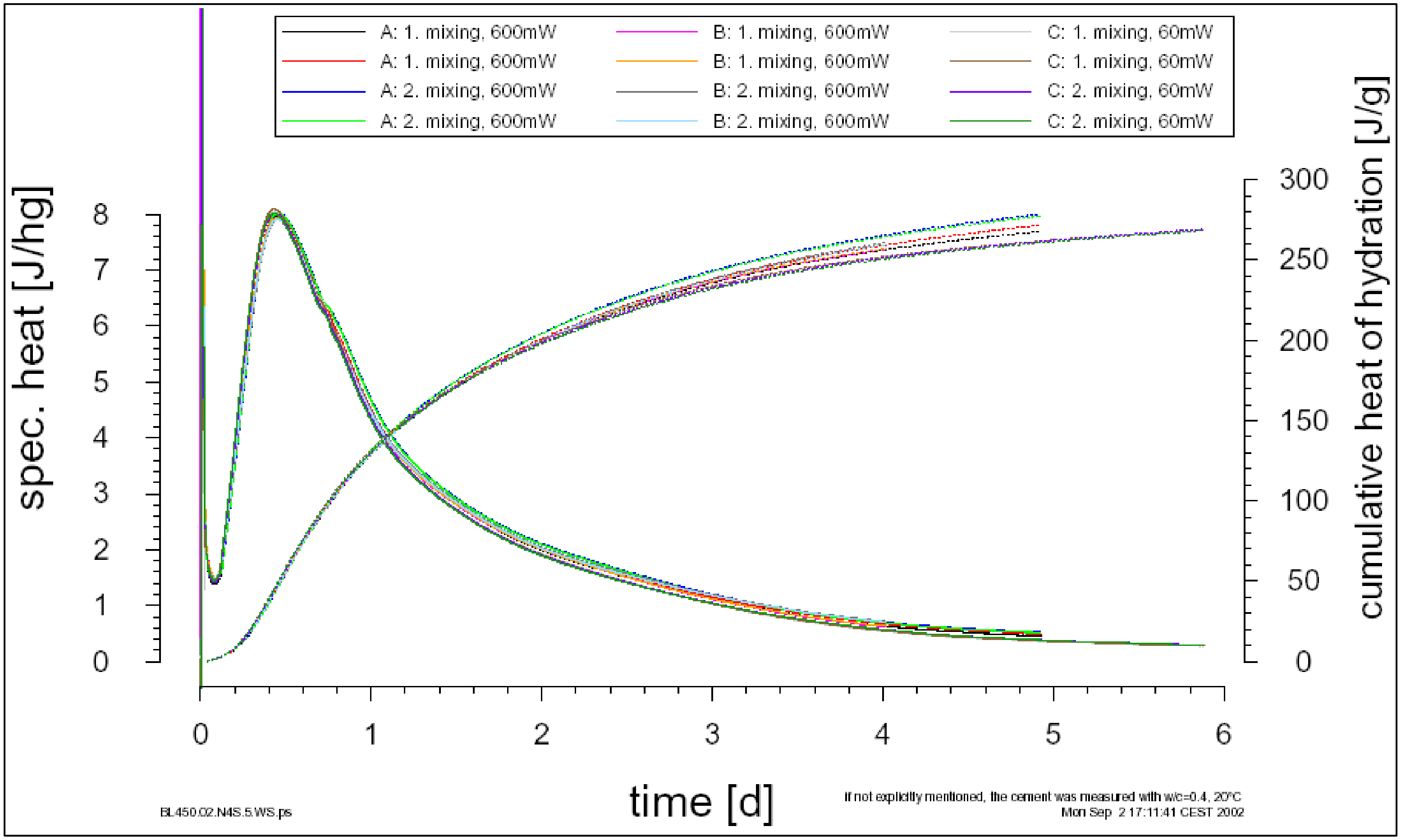
- Closed ampoules for long term reactions.
- Admix ampoule for early reactions i.e. first 30-45 minutes.
  - Refer to EN 302 (Lars Wadsö)

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)**

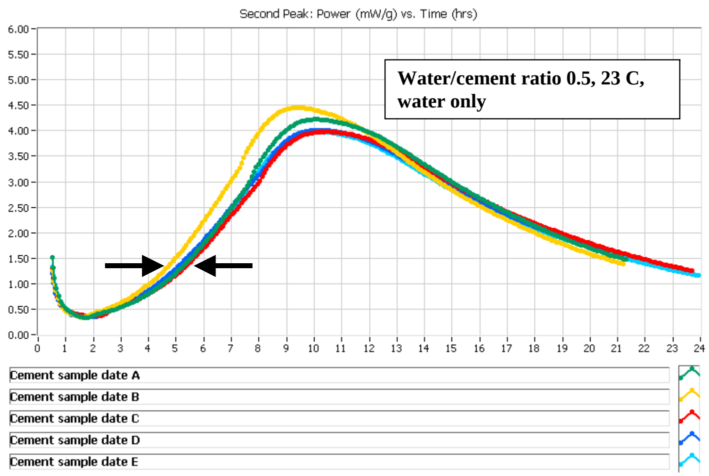
Isothermal Calorimetry Reproducibility



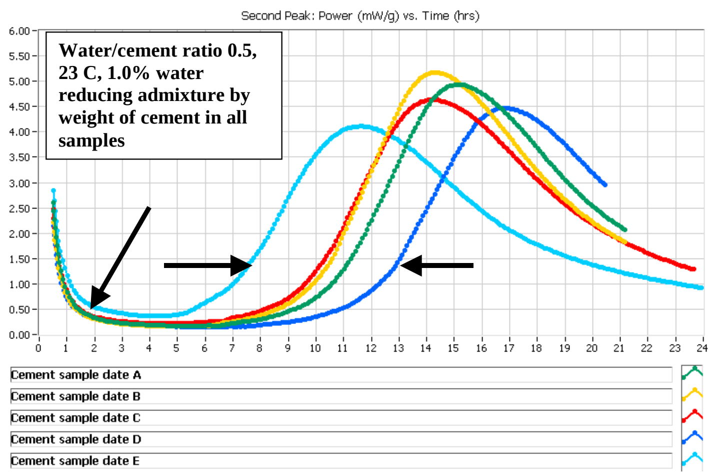
Dr. Moro , Holcim Group Support, Switzerland ***(2002)***

Effect of Admixtures

*Dr. P. Sandberg, Grace Construction Products, US (**2002**)*



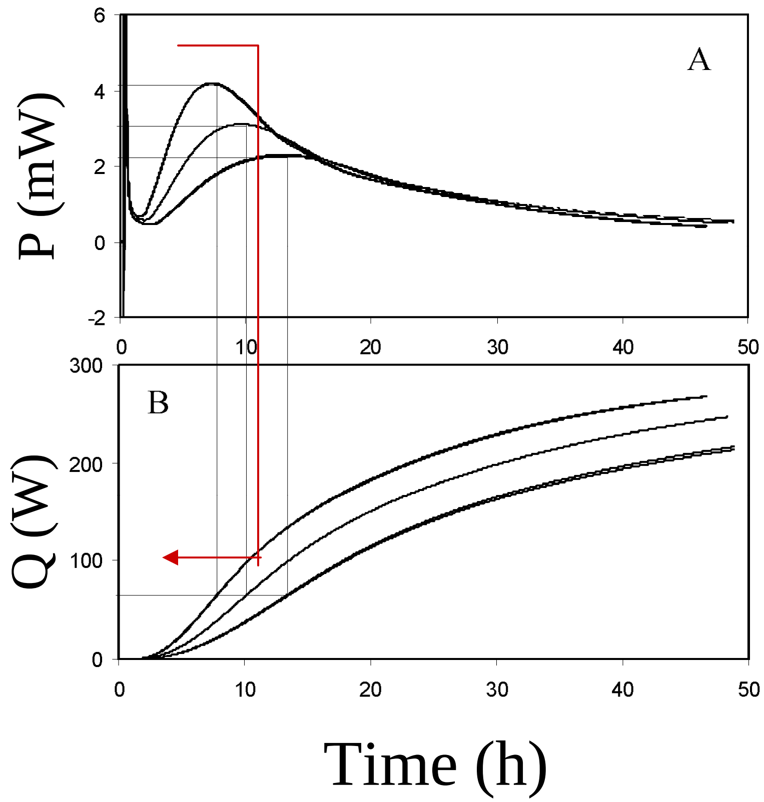
- Only small differences between cement lots when tested <u>without</u> admixture



- Very large differences between cement lots when tested <u>with</u> same admixture!!!

Kinetics of Cement Hydration

Measurements at 20, 25 and 30 °C

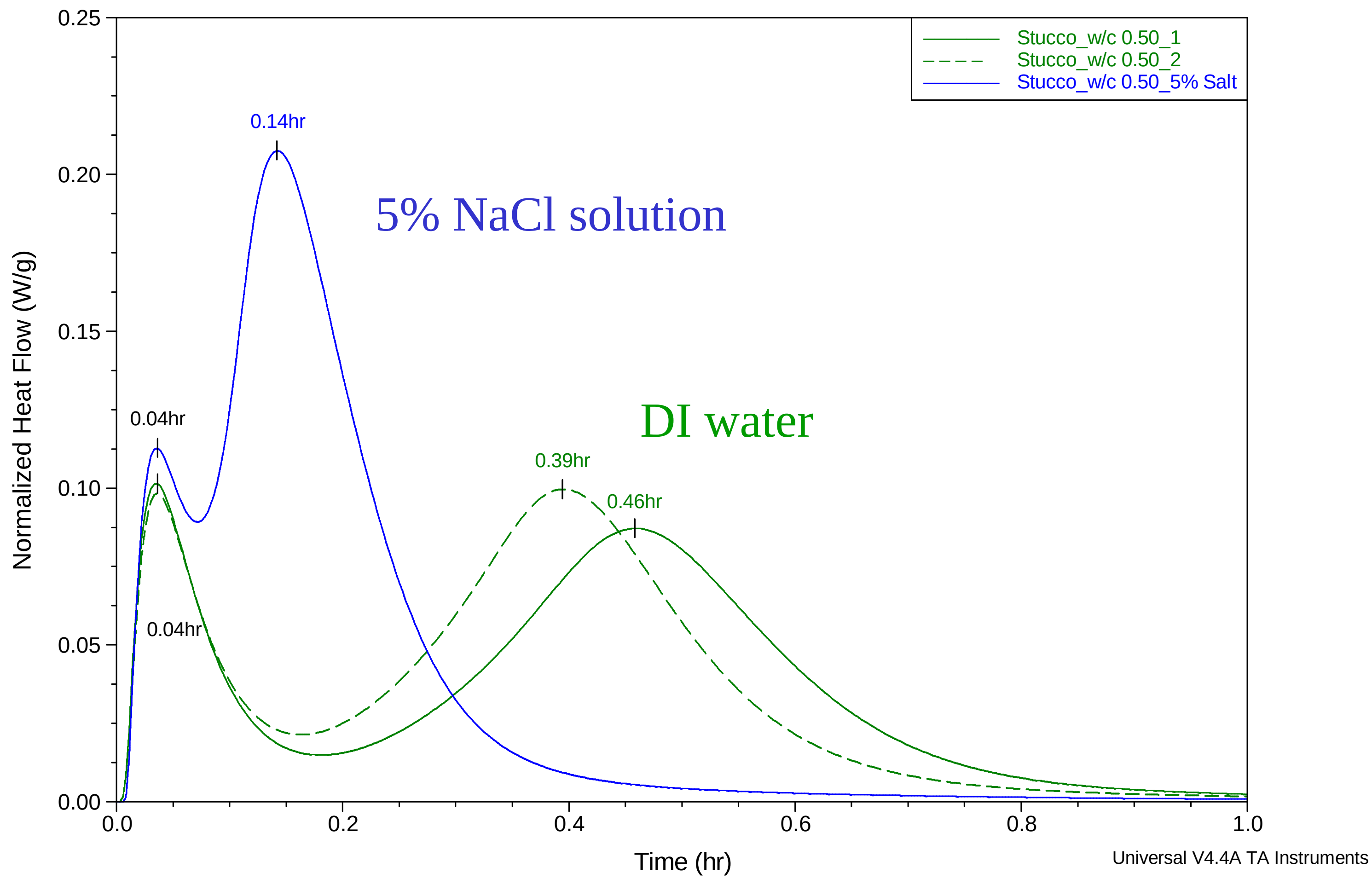


P reflects the rate of the process

Q reflects the extent of the process

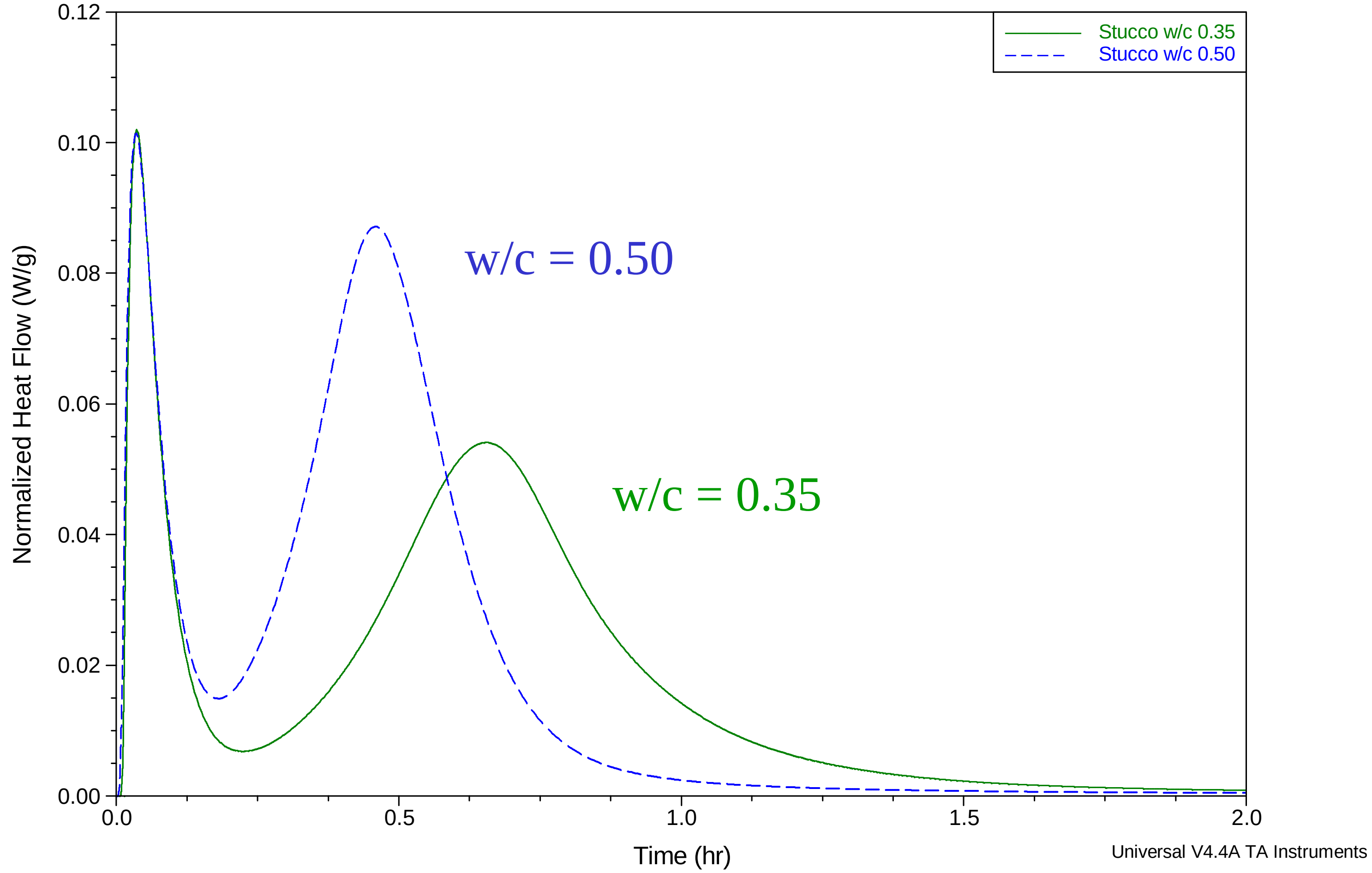
Dr. P. Vikegard, Thermometric AB, Sweden (**2002**)

Admix Ampoule Experiment Reproducibility



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

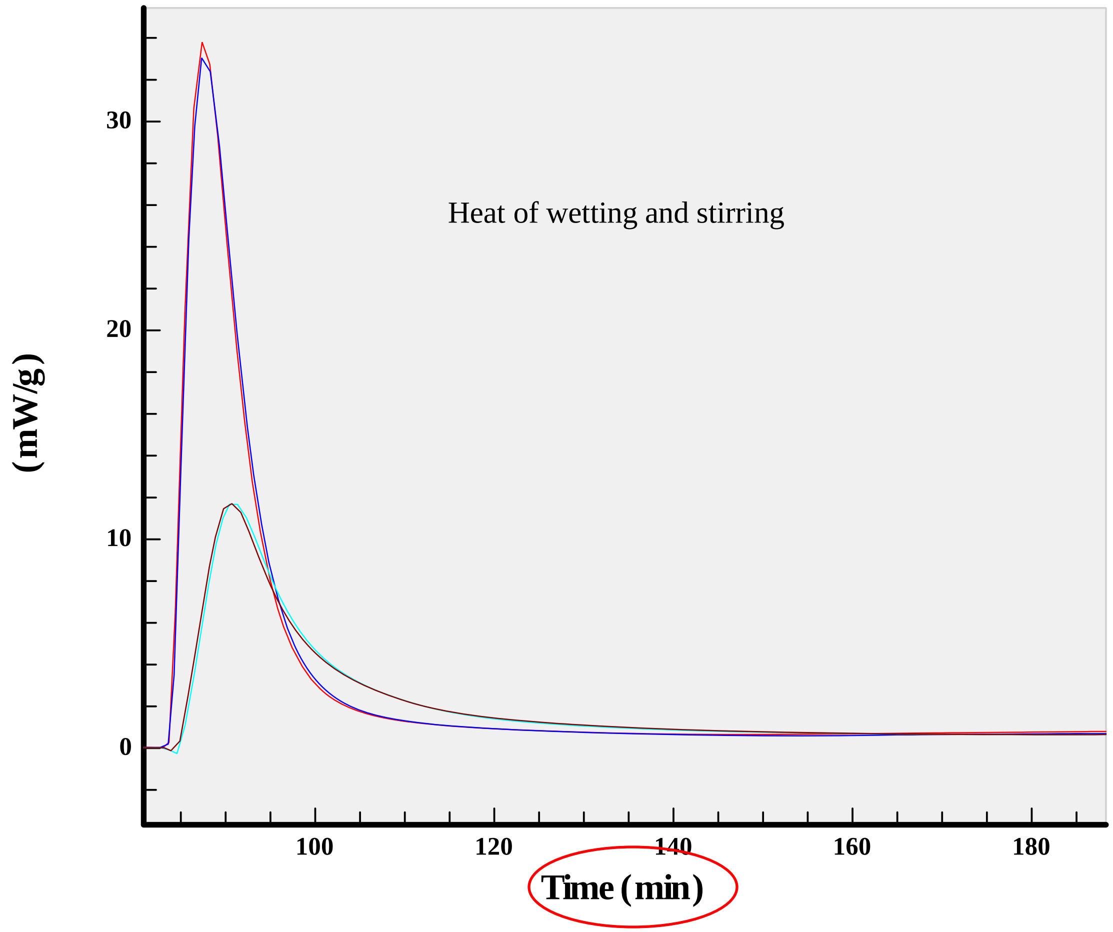
Admix Ampoule Experiment



Calcium Sulfate Hemihydrate 1-2 g
mixed with DI water at w/c 0.50 and 0.35

Normalized Heat of Wetting/Mixing

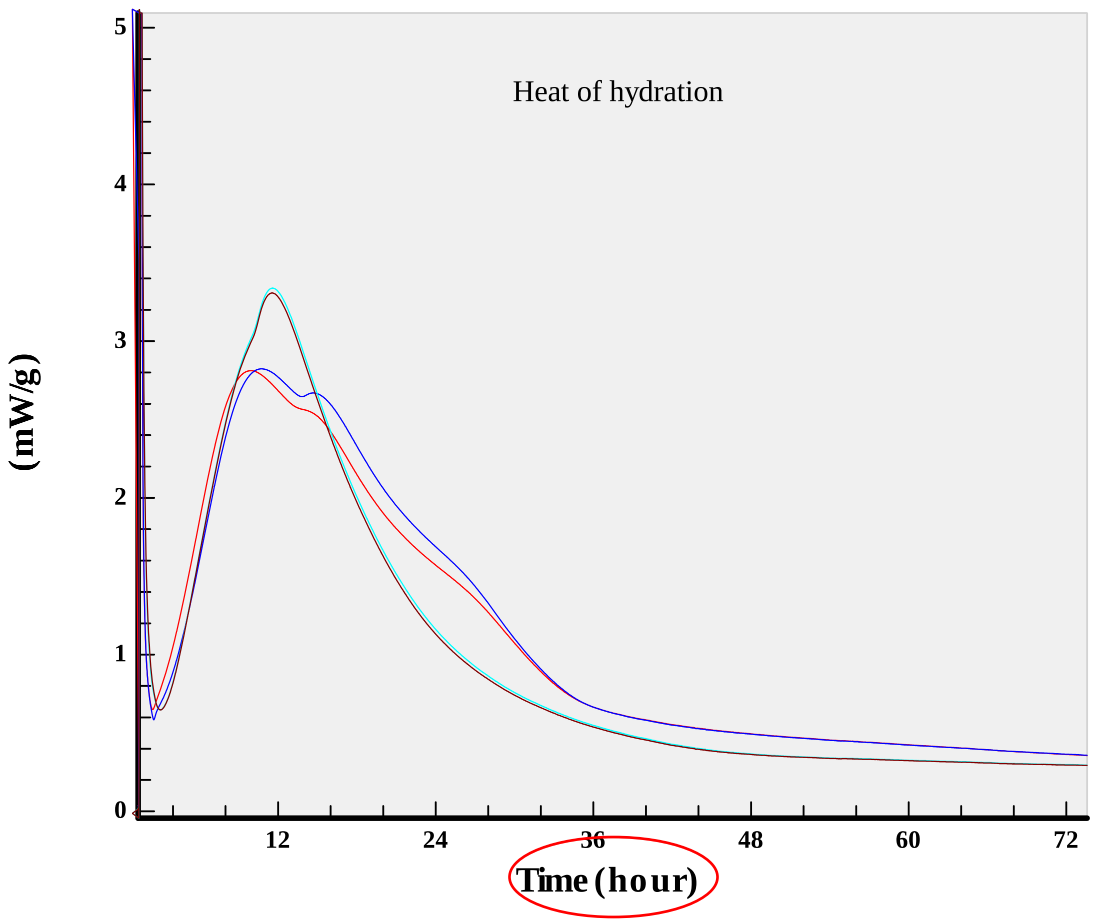
Mix ~2.85 g cement solid with 1.38 mL water



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.

Normalized Heat of Hydration

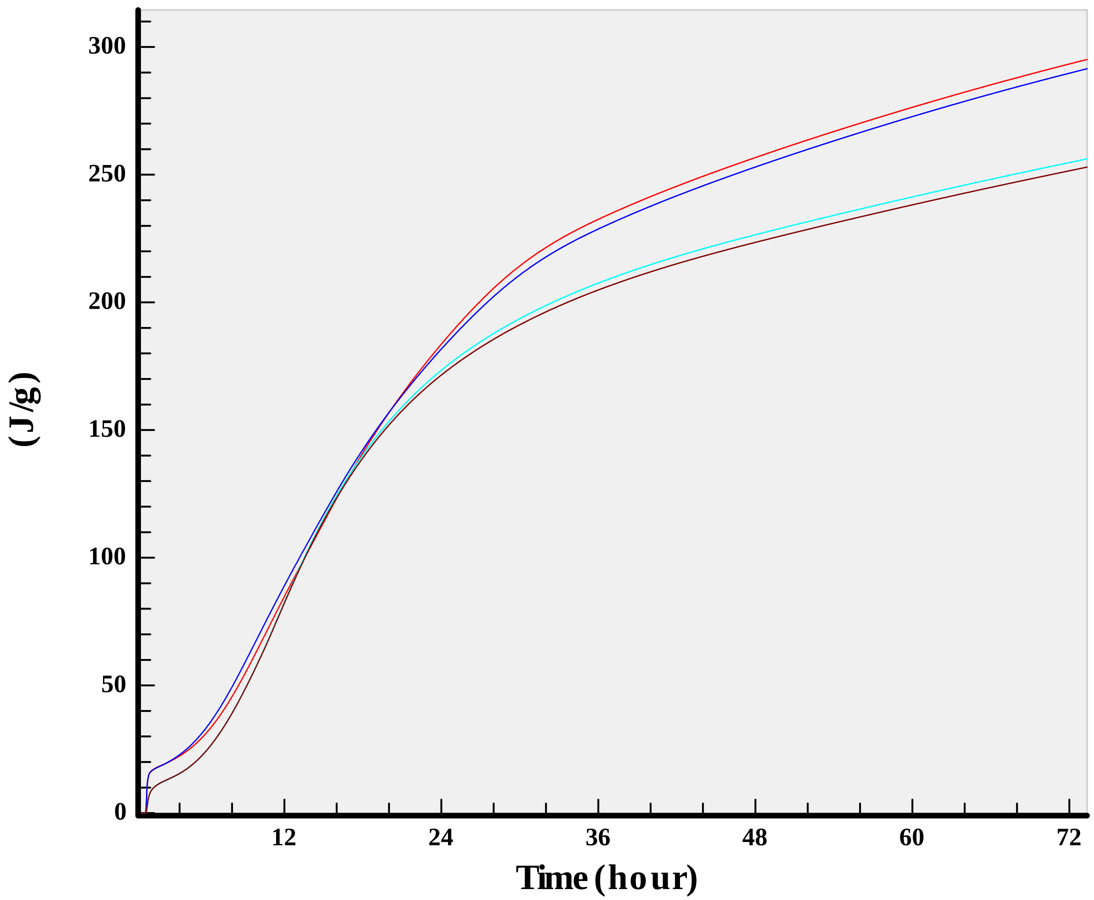
Mix ~2.85 g cement solid with 1.38 mL water



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

Normalized Heat

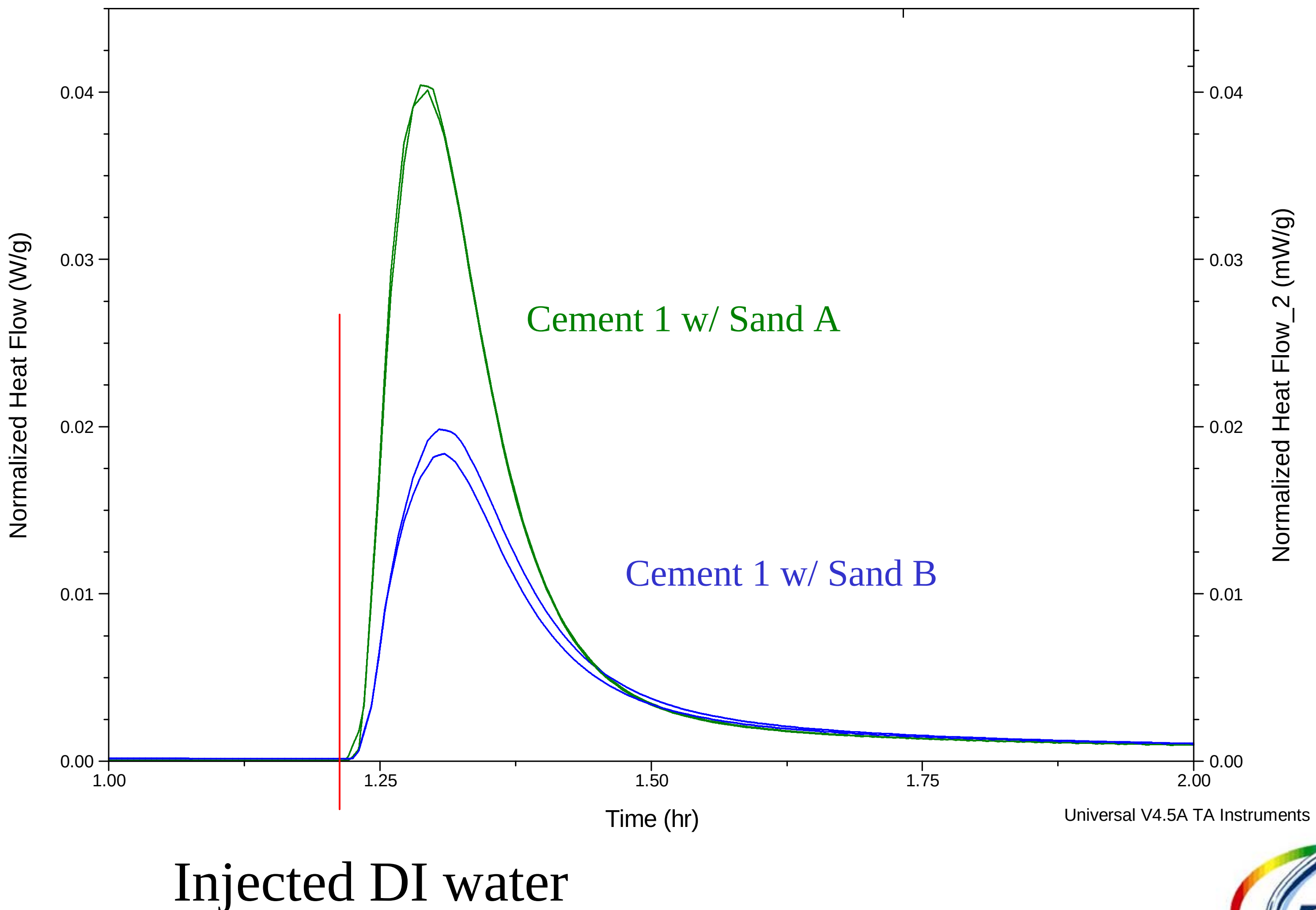
Mix ~2.85 g cement solid with 1.38 mL water



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

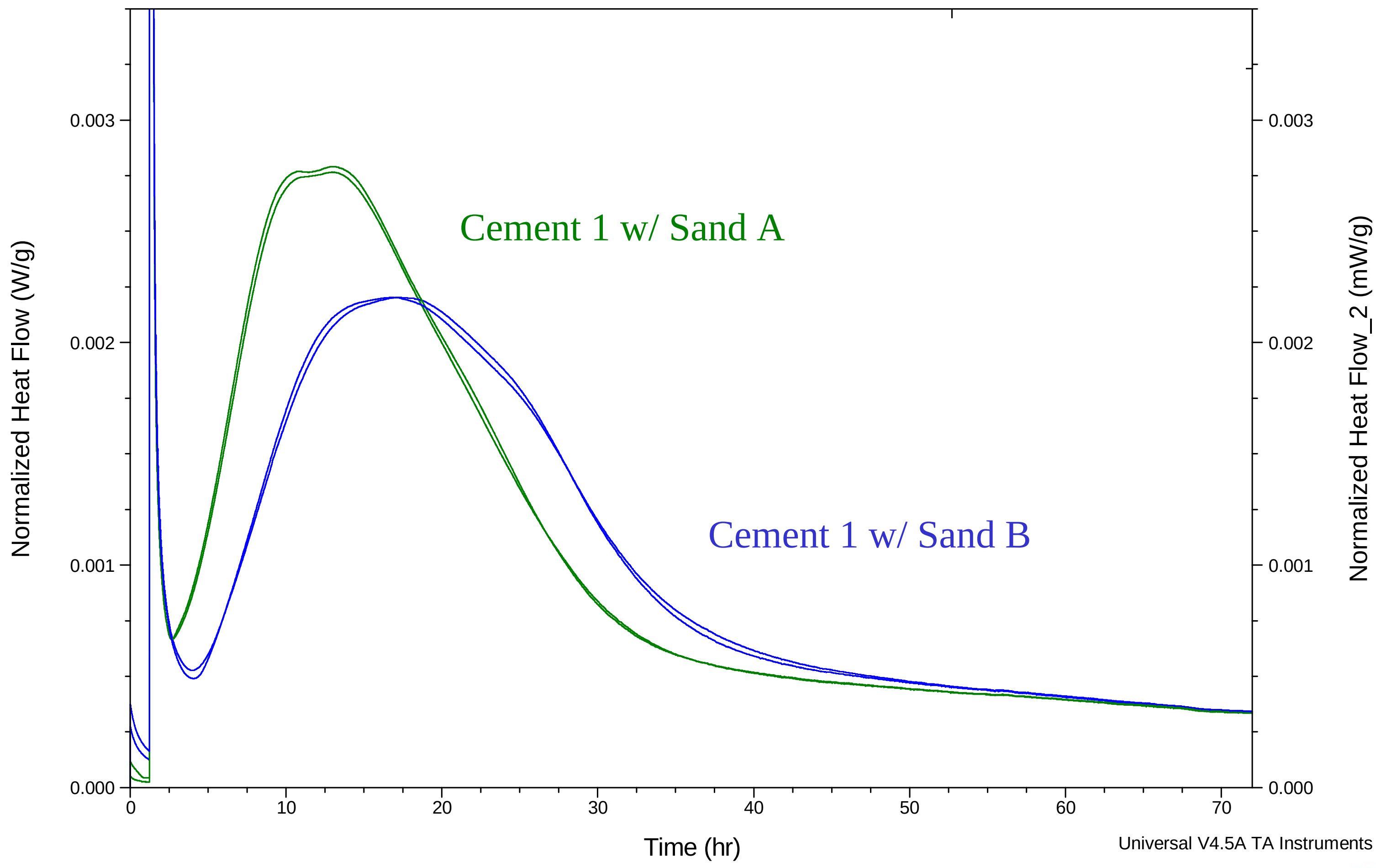
Mortar – Normalized Heat of Wetting

1 g cement: 2.75 g sand: 0.475 mL water

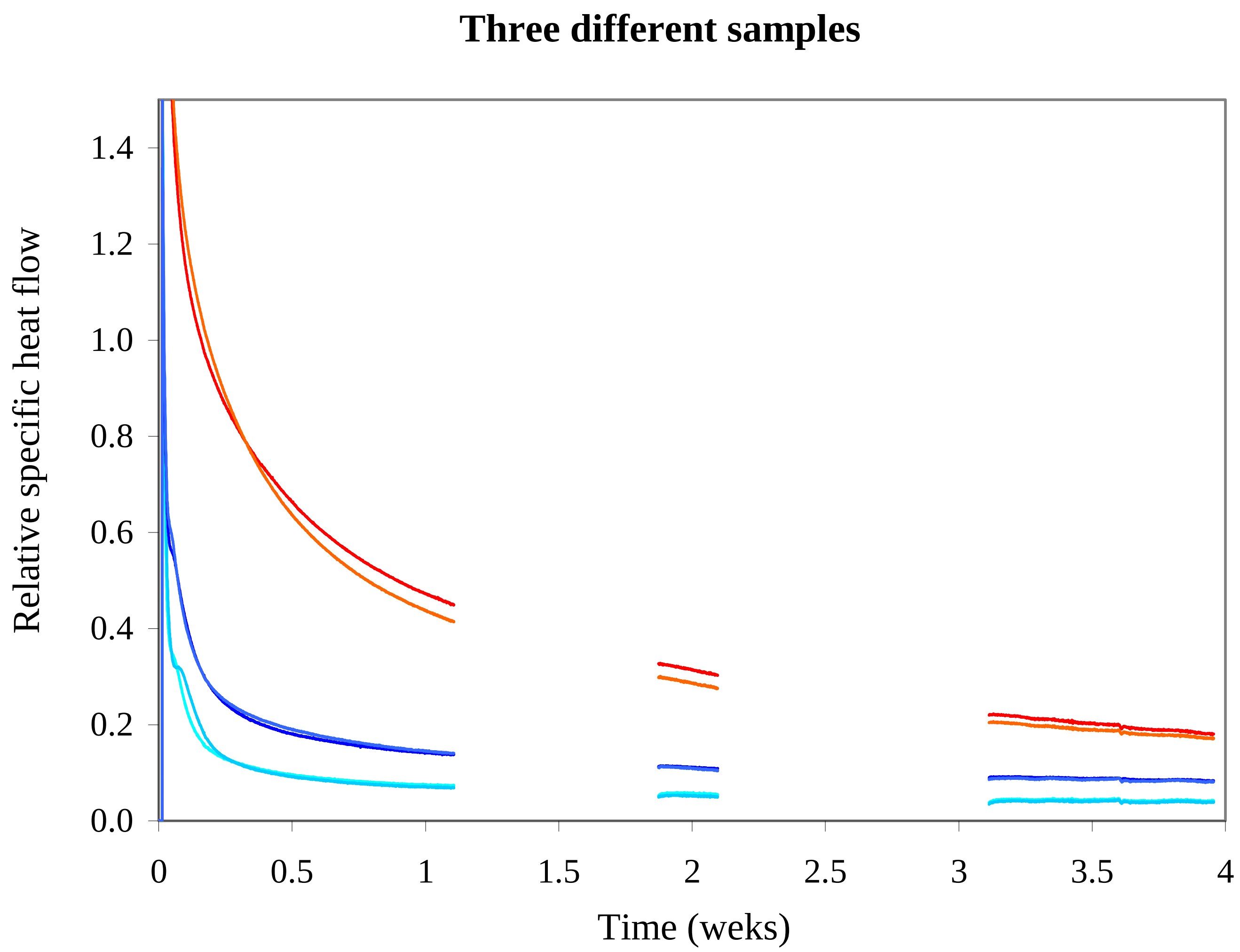


Mortar – Normalized Heat of Hydration

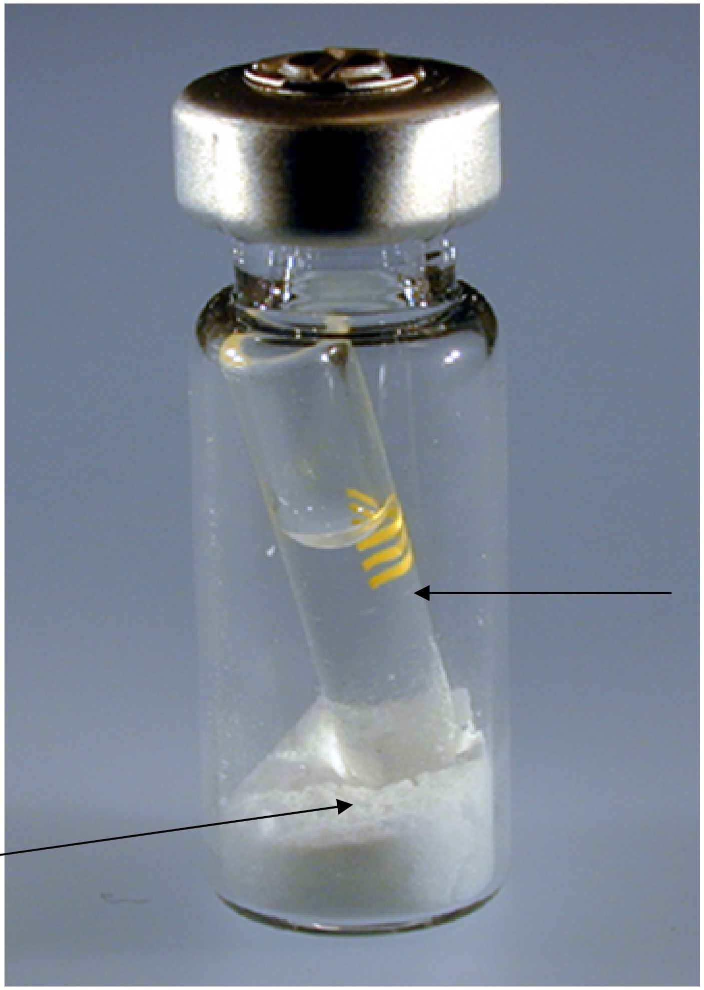
1 g cement: 2.75 g sand: 0.475 mL water



Repeatability



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 <u>assumed</u> 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