TAM Air

An Eight Channel Isothermal
Heat Flow Calorimeter
for
Cement / Concrete Research and
Production Control
use in the mW range

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Outline

- Isothermal calorimetry – fundamentals/theory
- TAM Air - Details
- Calibration
- Cement basics / Main applications
- Software and Hands on

TAM Air Cement

Isothermal calorimetry -fundamentals

- TAM Air measure the heat flow associated with physical processes and chemical reactions continuously.
- The heat flow reflects the rate of the process/reaction.
- The heat evolved reflects the extent of the process/reaction.

Calorimetric data

- Heat flow $\dfrac{dQ}{dt}$ $\left[\dfrac{\mathrm{J}}{\mathrm{s}}\right]$
- Heat Q $[\mathrm{J}]$
- Heat capacity C_P $\left[\dfrac{\mathrm{J}}{\mathrm{g}\cdot\mathrm{K}}\right]$
- Non-specific $\dfrac{dQ}{dt}=\sum_{i=1}^{n}\left(\dfrac{dc}{dt}\right)_i\cdot\Delta H_i\cdot k_i$

Isothermal Heat flow Calorimeters of Twin Type

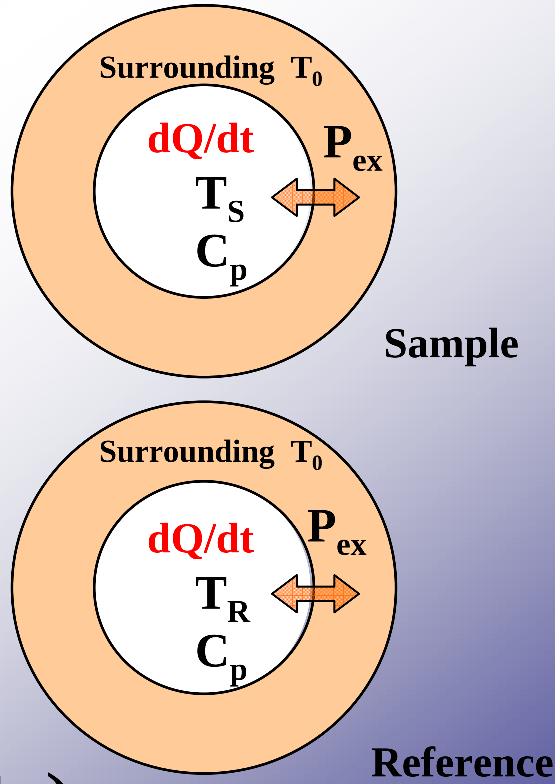
- Heat flow calorimetry
  - The heat produced/consumed by a sample will be exchanged with the surroundings.
  - The heat flow caused by the sample is measured by sensitive heat detectors utilising the Seebeck effect (thermoelectric modules).
  - IMPORTANT: The temperature will maintain essentially constant during a measurement.

- Twin type calorimeter
  - One sample and one reference calorimeter
  - Minimises any disturbances of the thermostat, reduces the noise and increases the sensitivity.
  - Reference: inert/stable material and similar c_p-value compare to the sample.

The heat conduction principle
- *steady state*

$$dQ/dt = dQ/dt_{measured} + C_p \cdot dT_s/dt$$

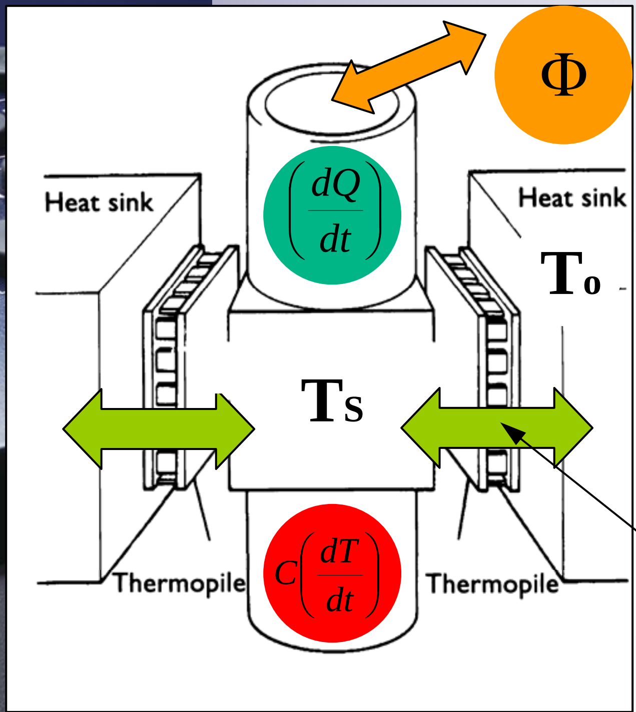
$$dQ/dt_{measured} = k \cdot (T_s - T_o)$$



Differentially:

$$\Rightarrow \quad dQ/dt = k \cdot (T_s - T_R)$$

Heat Balance Equation



General Heat Balance Equation

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

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

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

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

Theory

$$\underbrace{dQ/dt}_{\text{Change in heat production rate in the sample}} = \underbrace{k\cdot(T_S - T_{HS})}_{\text{Measured heatflow}} + \underbrace{C\cdot dT_S/dt}_{\text{Heat accumulation in the sample}}$$

Seebeck effect: $V = g\cdot(T_S - T_{HS})$

$$dQ/dt = k/g(V + C/k\cdot dV/dt)$$

Calibration constant, ε = k / g

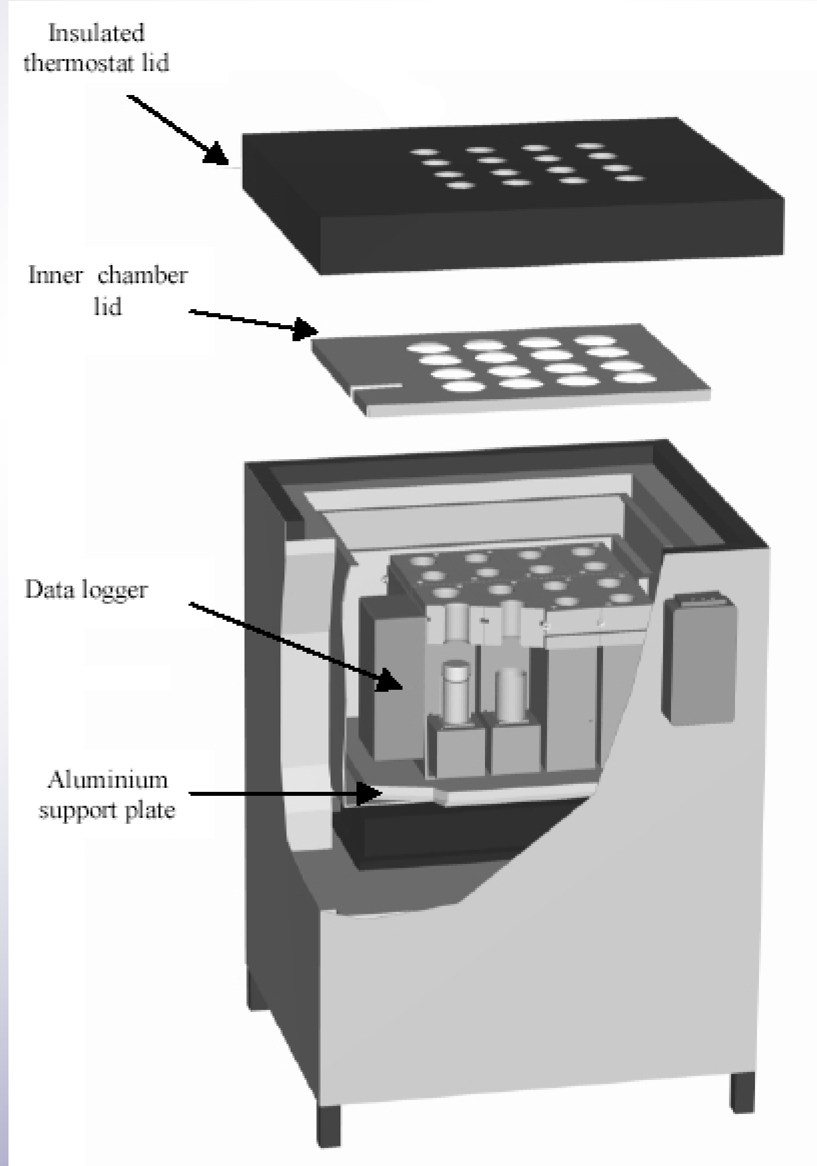
Time constant, τ = C / k

Heat exchange coefficient, k

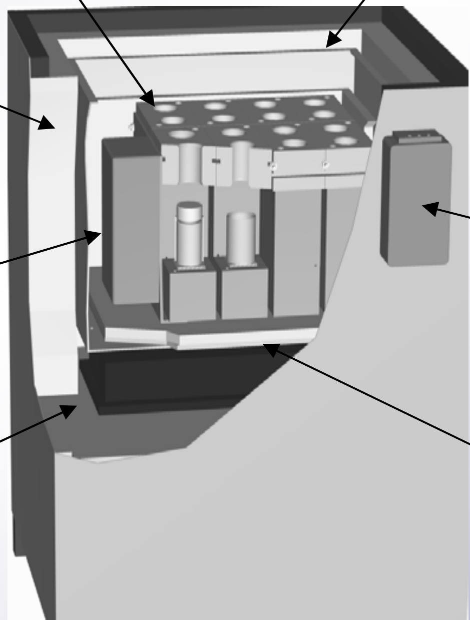
Seebeck coefficient, g

$\boxed{\text{Tians equation: } dQ/dt = e\cdot(V + t\cdot dV/dt)}$

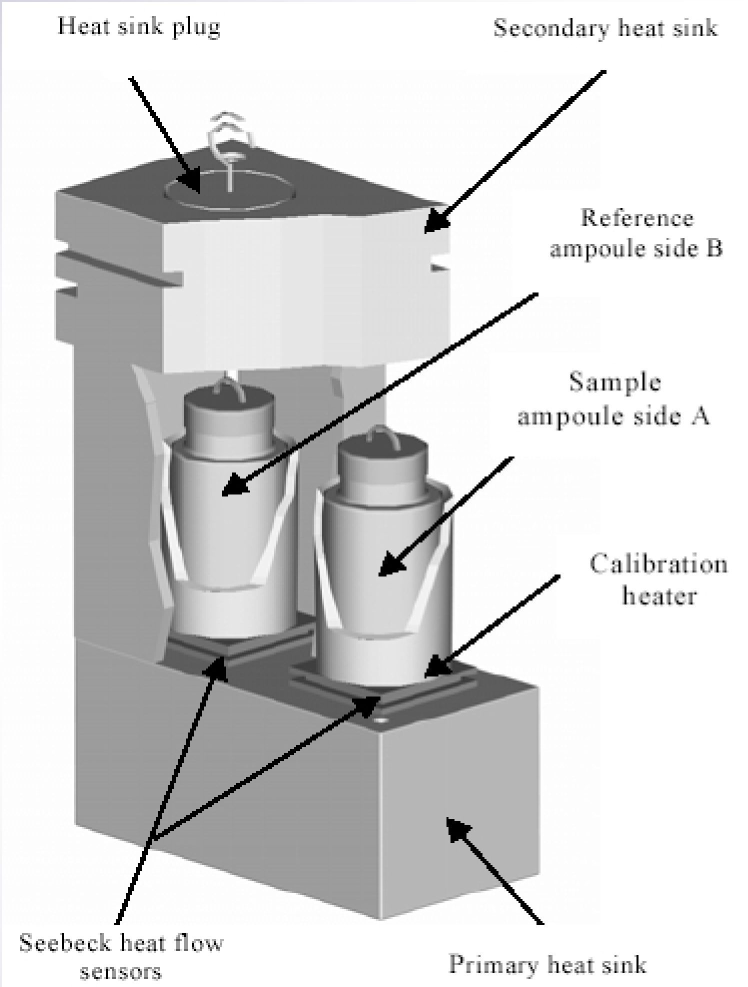
TAM Air - Details



Functional description



TAM Air - a twin calorimeter



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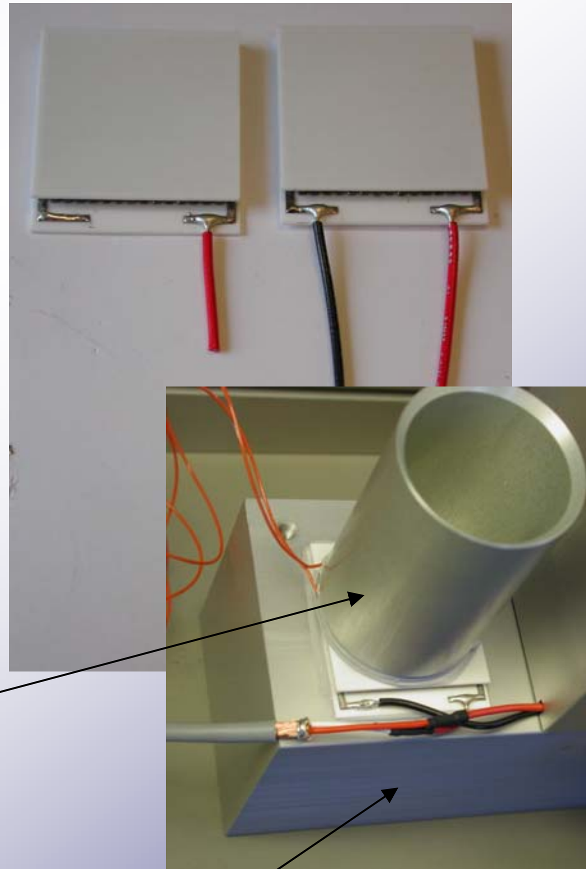
Heat detector of TAM Air

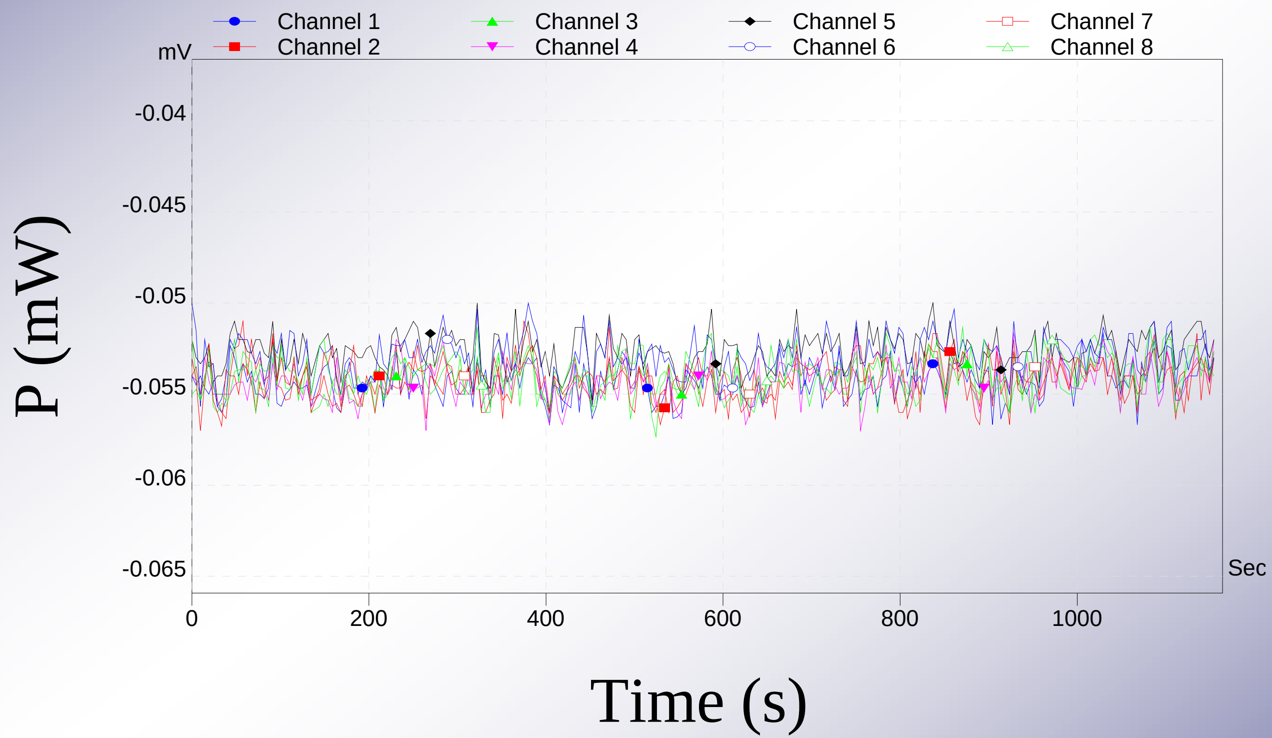
- Consist of small plates with thermopiles (semi conducting materials)
- When the two sides of the plate are exposed to different temperatures, heat will flow from the warm to the cold side



Sample
Exothermic ➔ heat is produced
Endothermic ➔ heat is consumed

Heat sink (surroundings) in contact with the air thermostat

Performance



Short term noise:	± 4 µW
Drift	40 µW/24 hr

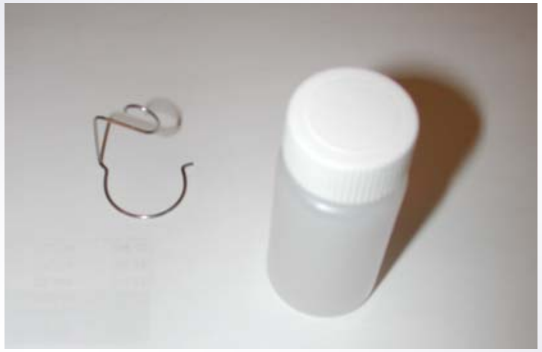
Specifications

Number of calorimetric channels	8
Operating temperature range	5/15 – 90±1 °C
Thermostat type	Air
Thermostat accuracy	±0.02°C
Limit of detectability	4 µW
Precision	±20 µW
Baseline over 24 hours Drift Deviation Error	 < 40 µW < ± 10 µW < ± 23 µW

TAM Air – Batch ampoules

- 20ml disposable glass ampoules with crimp cap
- 20ml disposable PE ampoules with screw cap

Mixing of solid/liquid outside calorimeter



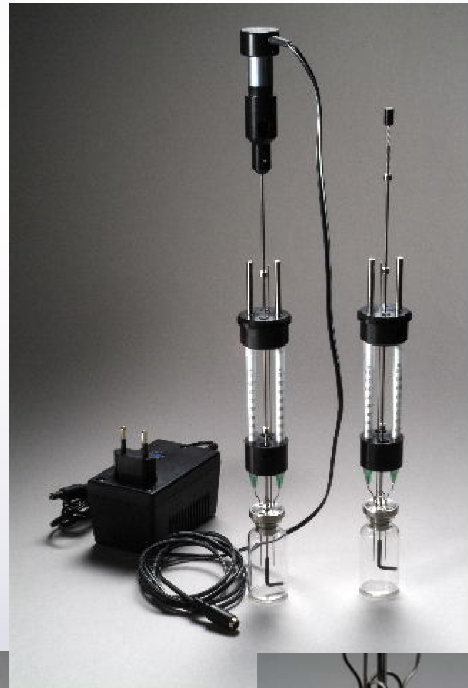
TAM Air Cement

TAM Air Cement

TAM Air 20 ml Admix ampoule

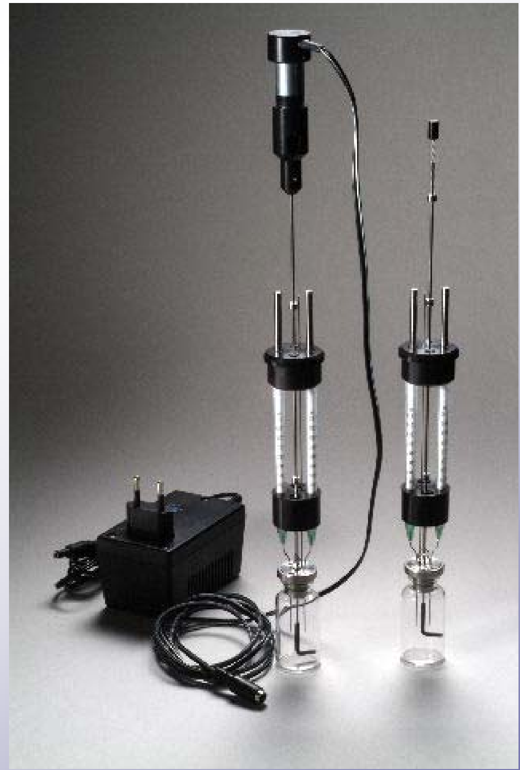
- The Admix Ampoule is available with or without a motor.
  - For suspensions such as mixtures of cement/water we recommend manual stirring.
  - For liquid systems it might be more convenient to use a motor for stirring.

- 1 - 4 syringes (1 ml)
- Materials
  - polypropylene, silicon stopper, stainless steel



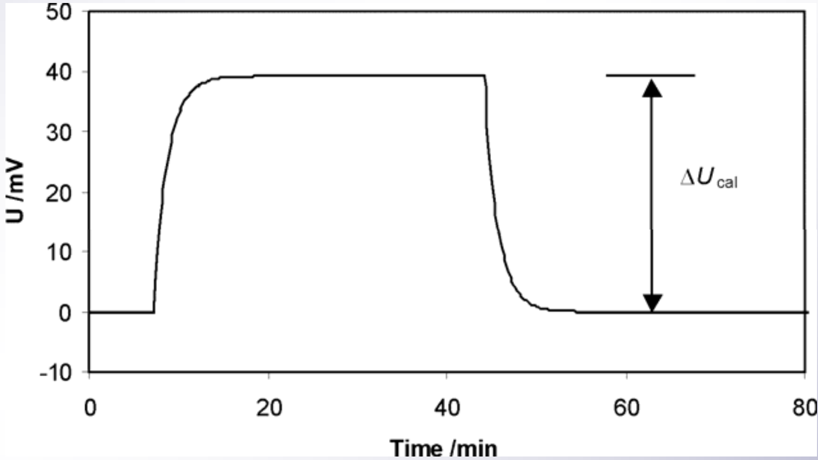
20 ml Admix ampoule

- Designed for mixing a cement sample inside the calorimeter under thermal equilibrium conditions.
- Dry cement is added to a 20 ml glass ampoule which is attached to the admix ampoule.
- In addition, up to three syringes are filled with a known volume of distilled water which also are attached in the admix ampoule.
- The complete unit is loaded into TAM Air and allowed to reach thermal equilibrium (approximately one hour).
- Then, water/admixture is injected to the sample under stirring (automatically or manually).



Calibration

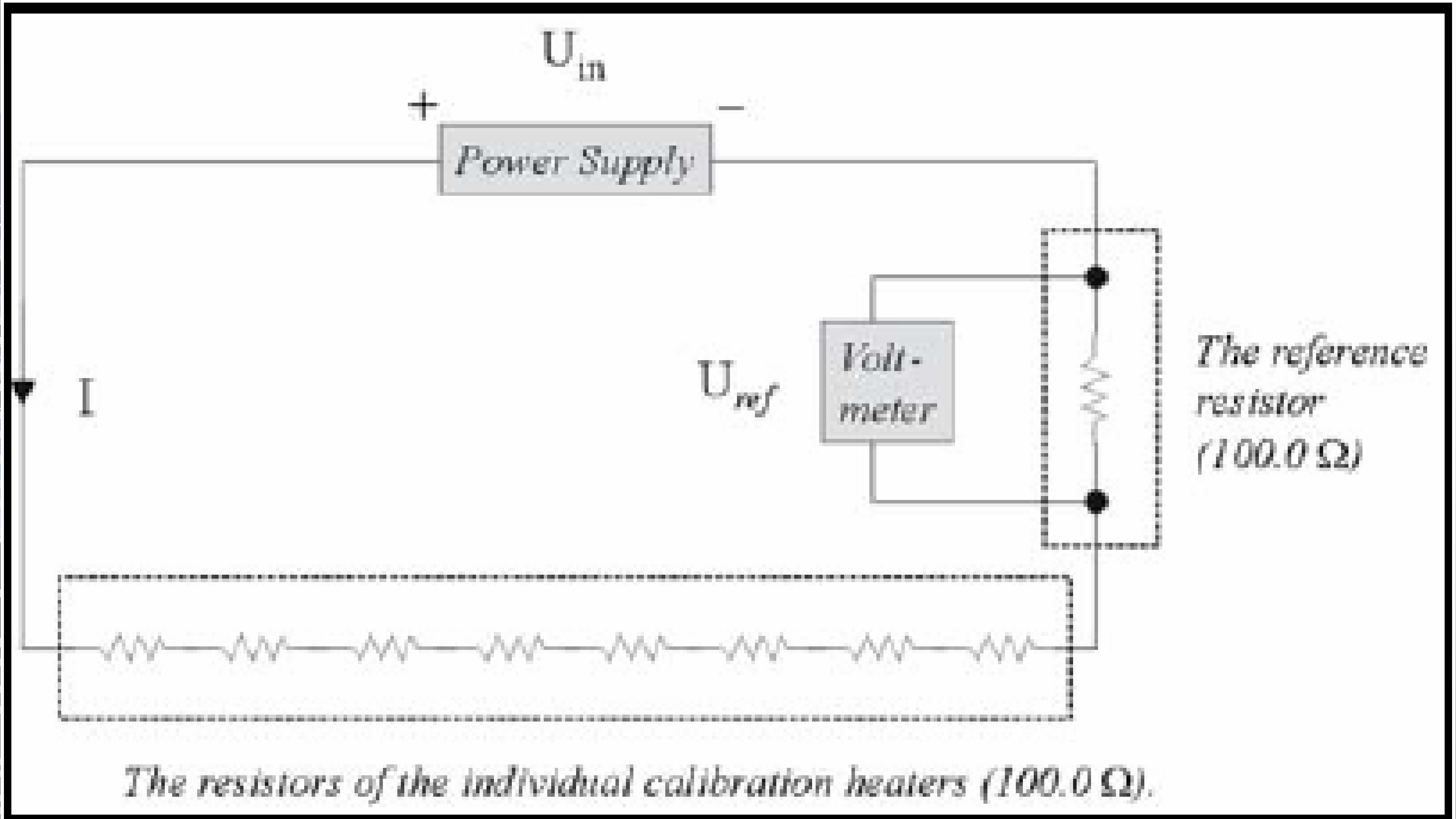
Calibration is usually made electrically by an internal heater



A number of chemical calibration/ test reactions exists for isothermal calorimeters

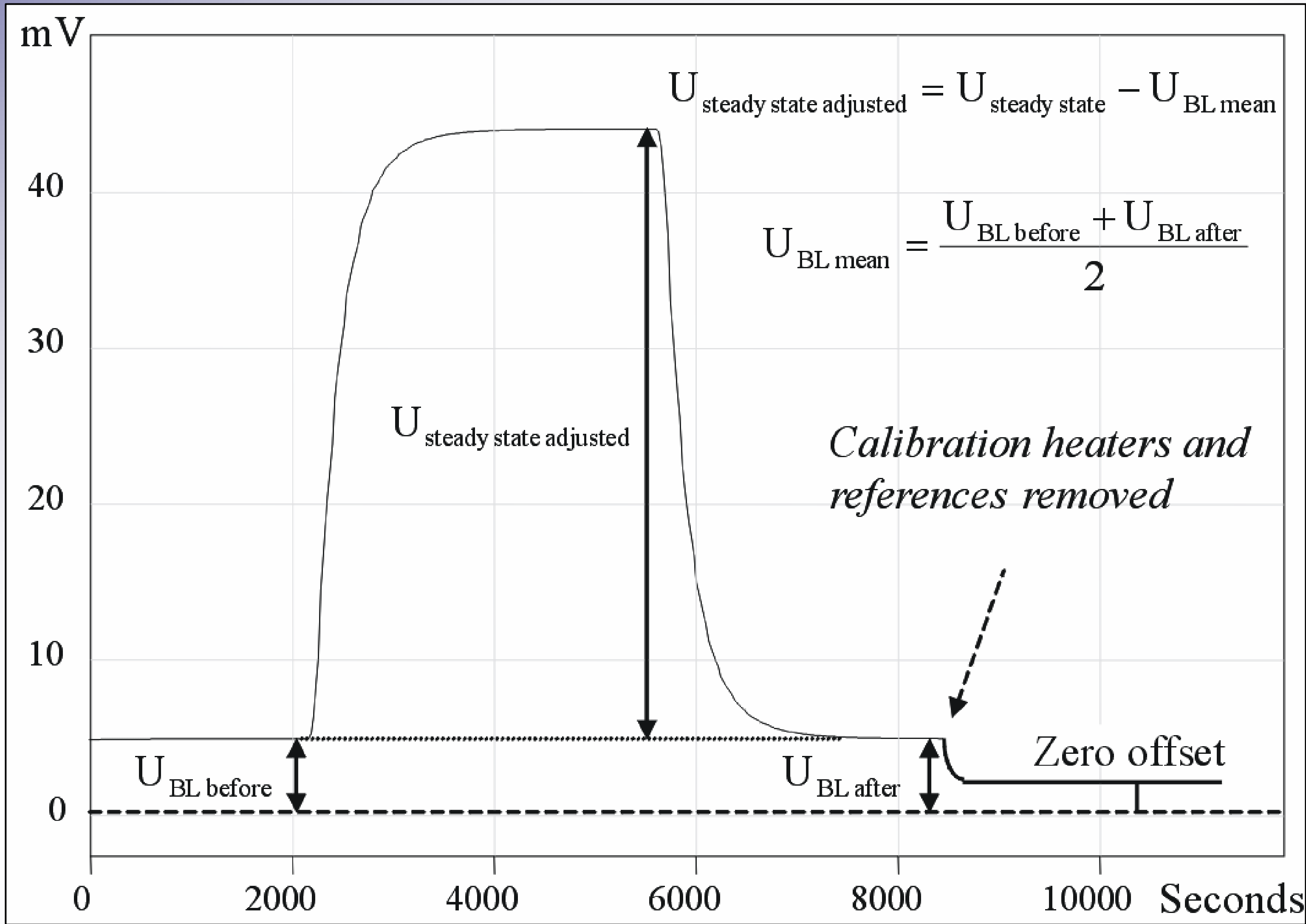
*I. Wadsö and R.N. Goldberg (**2001**), Standards in isothermal microcalorimetry, IUPAC technical report. Pure. Appl. Chem., 73(10) 1627.*

Calibration



$$P_{Heater} = U_{ref}^2 / R$$

Calibration



Applications / Results

- Interpretation of data provided by TAM Air on Portland cement
- Repeatability
- Effects of admixtures
- Effects of contaminations
- Temperature dependency of cement hydration
- Final conclusions

Portland Cement Basics

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

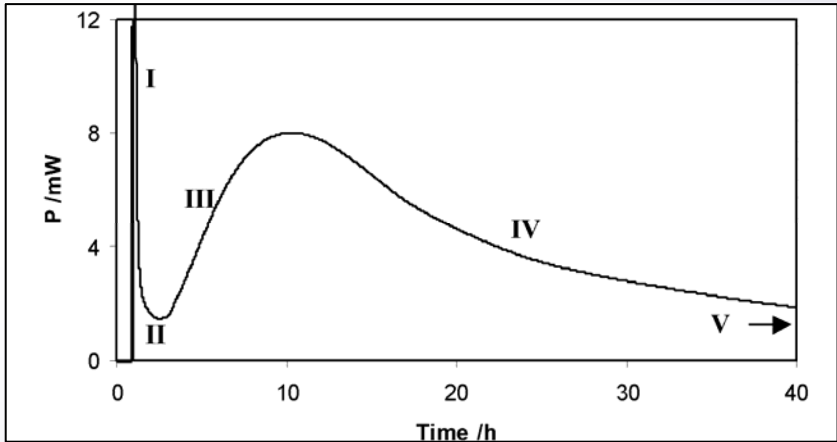
- Silicates hydrate to give strength giving gel, “glue”
- Aluminate and ferrite phases necessary to get a molten phase during production of cement
- Aluminates react rapidly, interact with admixtures, workability, set, early strength development
- Gypsum added during grinding to slow down aluminate hydration rate
  - Higher C_3A , lower C_4AF generally more reactive
  - Different sulfate forms have different solubility

Portland cement basics

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

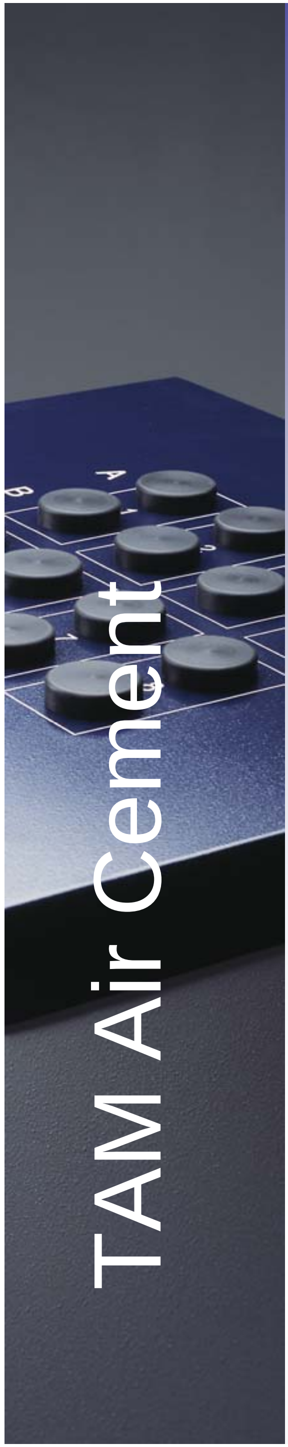
The hydration process undergoes a number of phases (*Young*, 1985)

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



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

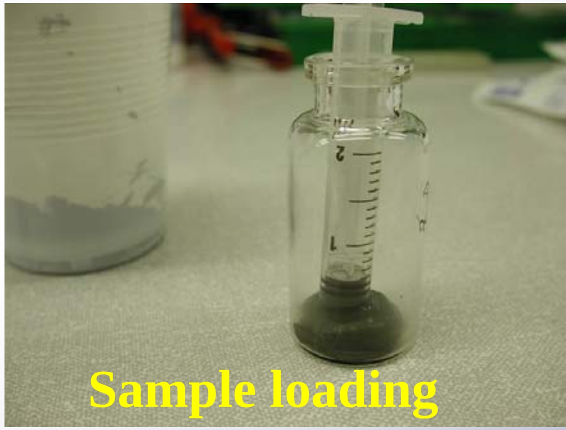
- (I) Dissolution of ions and initial hydration
- (II) Formation of ettringite
- (III) Initiation of silicate hydration
- (IV) Depletion of sulphate



Repeatability
- four different cement samples

Sample preparation


External mixing


Sample loading


Ampoule loading into TAM Air

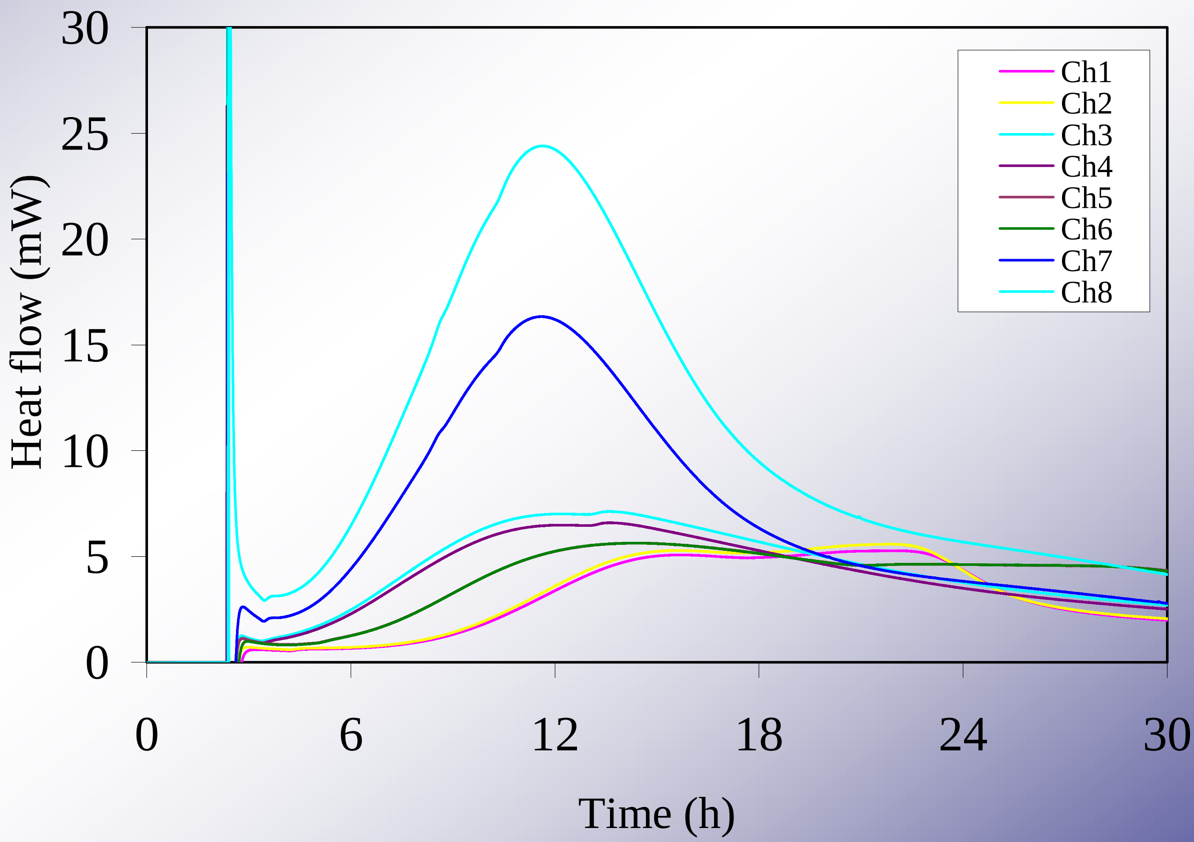
TAM Air Cement

Sample preparation -details

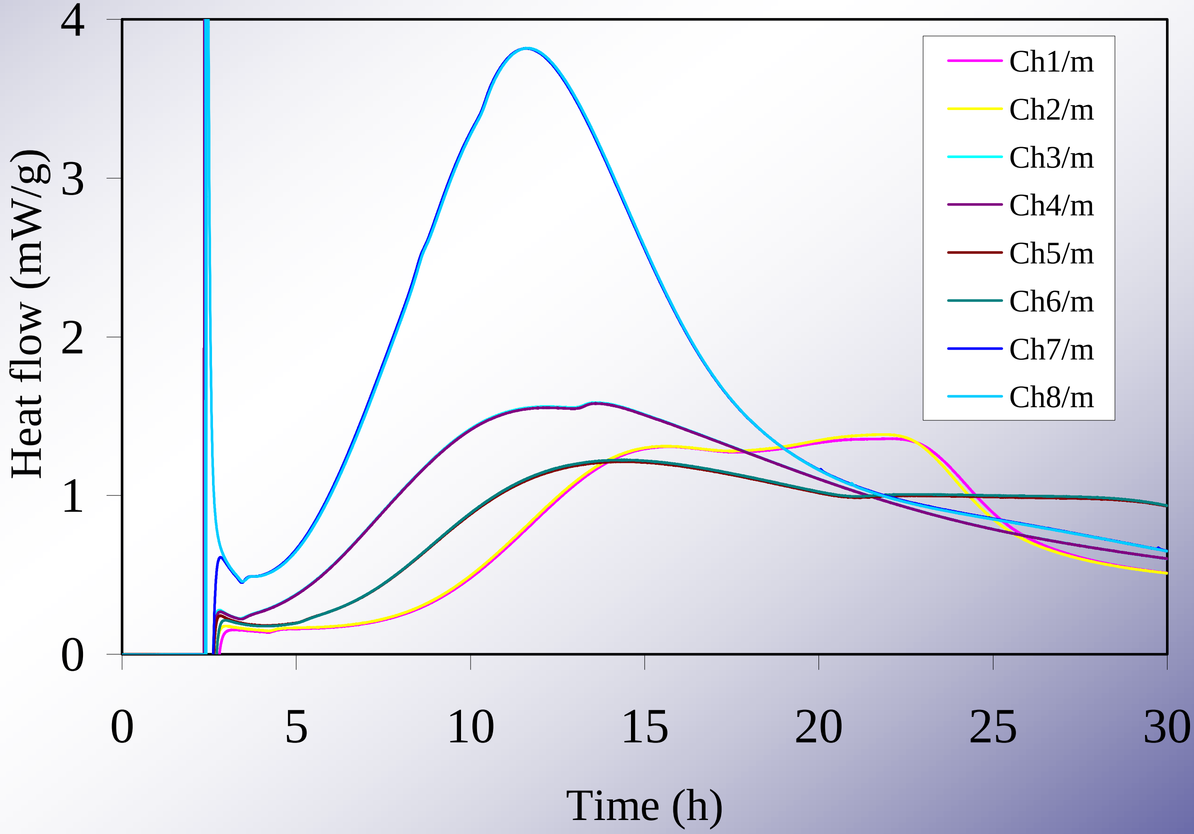
- External mixing for 3 minutes
- Water/cement=0.4

  (25 g cement / 10 g water)
- Syringe (without tip)
- Closed 20 ml glass ampoules (m = 4 – 6 g)
- Reference ampoule with 4 – 6 g of water
- All samples prepared after each other and then loaded into TAM Air at the same time
- Measuring temperature: 20 ± 0.1°C

The hydration process in terms of heat flow time curves

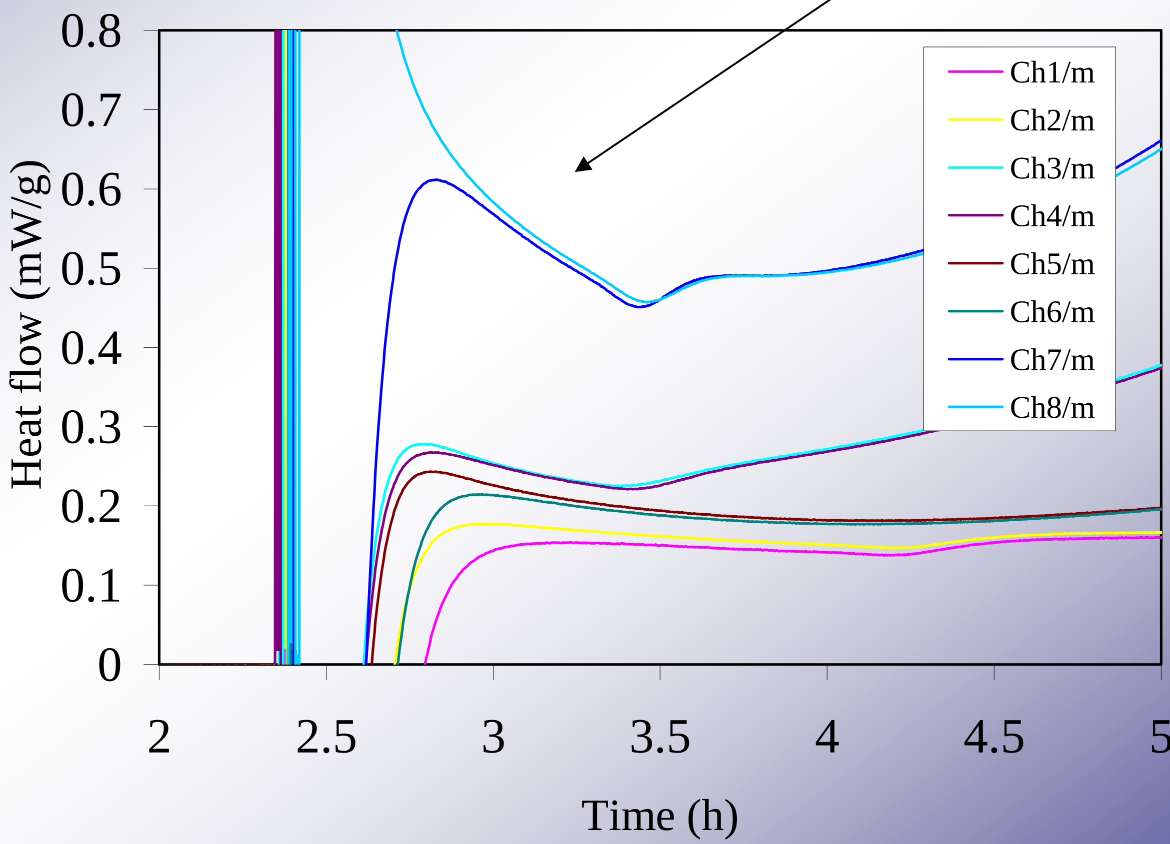


Normalized heat flow time curves -excellent reproducability

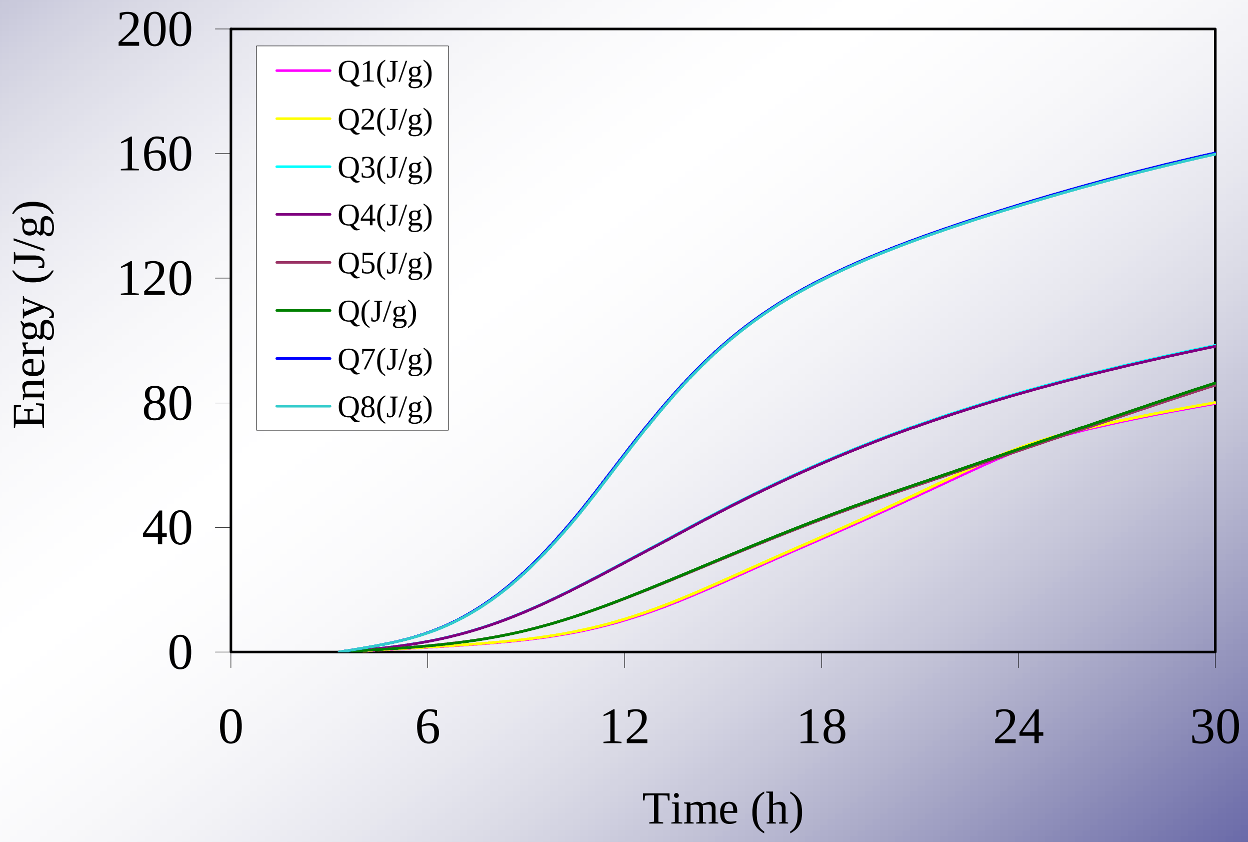


The hydration process -initial stage

Thermal disturbances



Energy time curves
- reflects the extent of hydration



Conclusion

1. The hydration process of cement is exothermic and can be studied with TAM Air in terms of heat flow and energy.

2. The heat flow time curves of the four cement samples studied were different indicating differences in the hydration process of the individual samples.

3. TAM Air has a high measuring capacity – up to eight samples can be studied simultaneously.

4. The repeatability of TAM Air is excellent.

TAM Air Cement

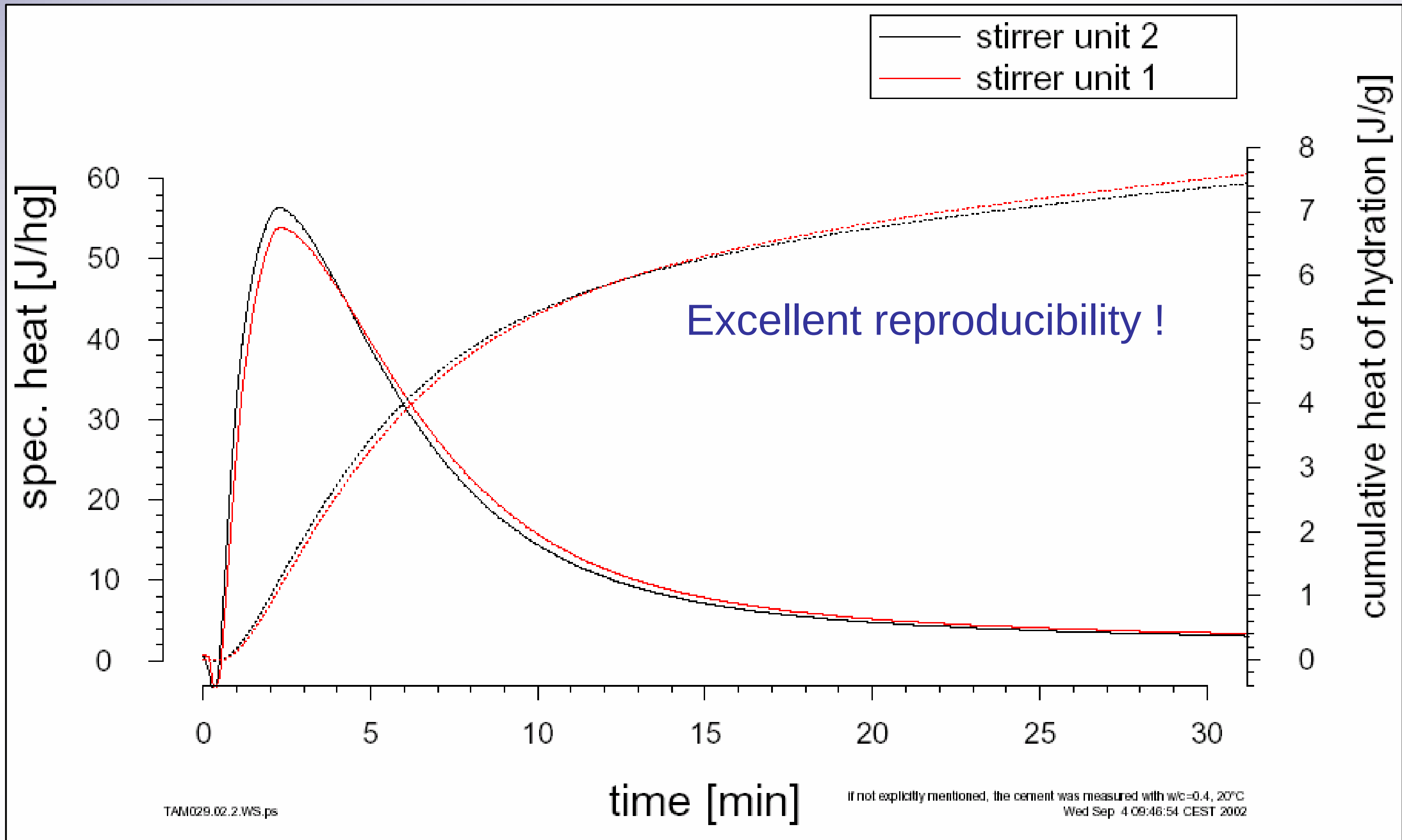
Application areas: A few examples

- Assessment of setting time and early stiffening
- Influence of concrete admixtures
- Influence of glass fillers, waste products, slags etc.
- Influence of contaminants, e.g. in water
- Assessments of the efficiency of mixing

Admix ampoule

-two identical ampoules

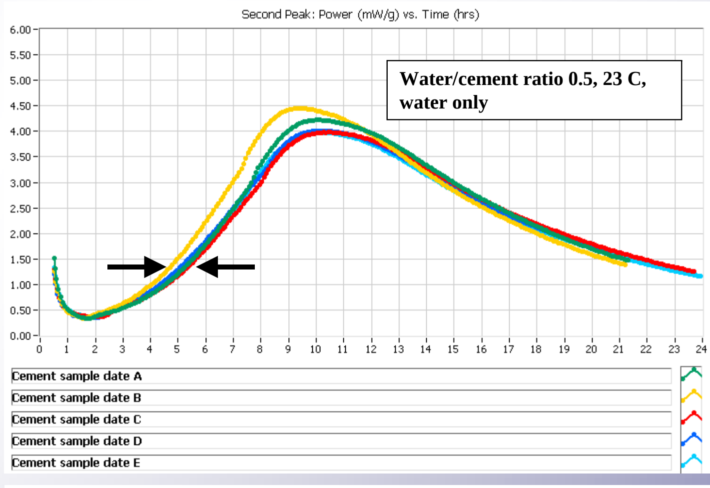
*Dr. Moro , Holcim Group Support, Switzerland **(2002)***



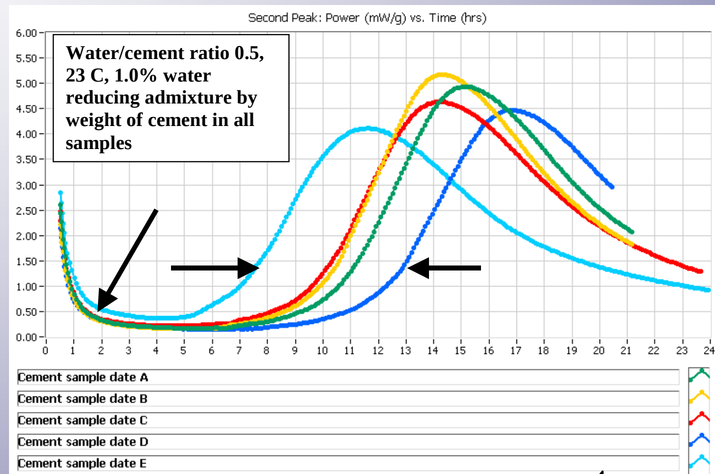
Effects of admixtures

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

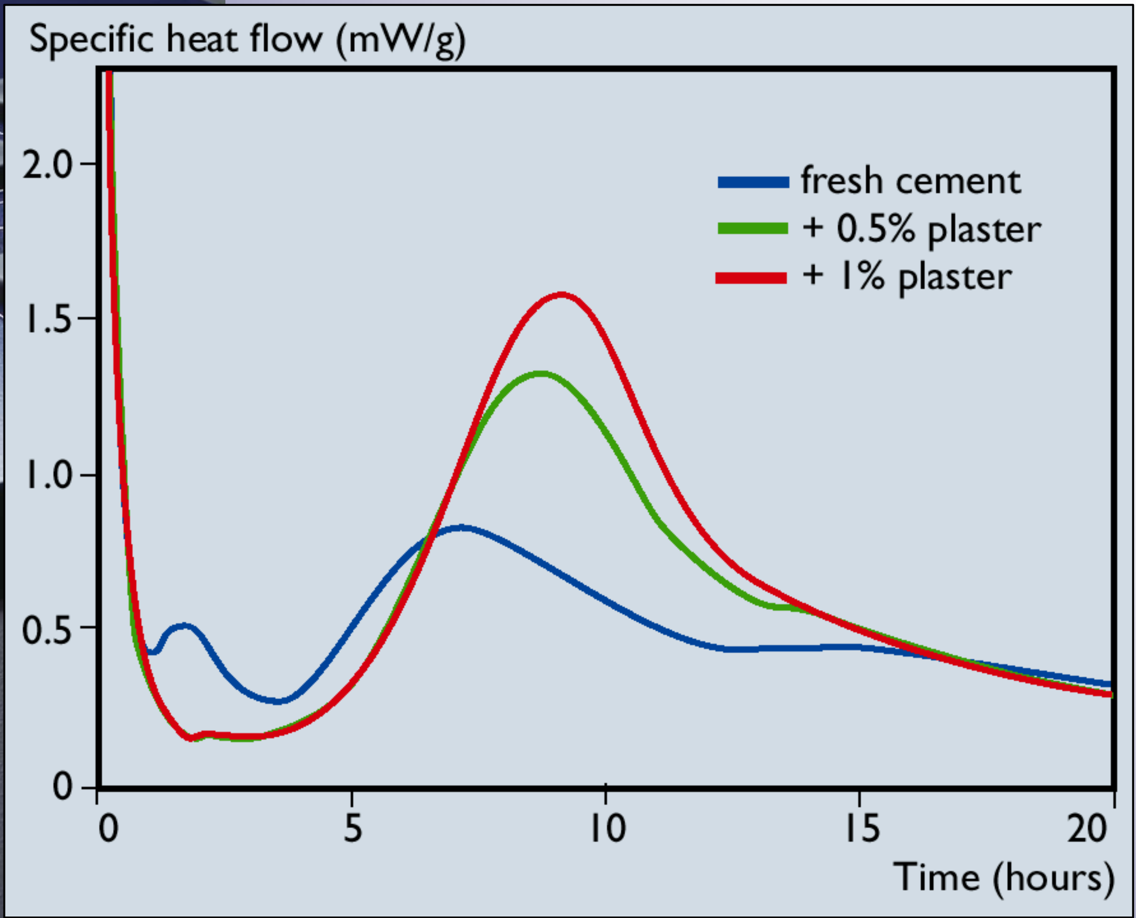
- Only small differences between cement lots when tested without admixture



- Very large differences between cement lots when tested with same admixture!!!



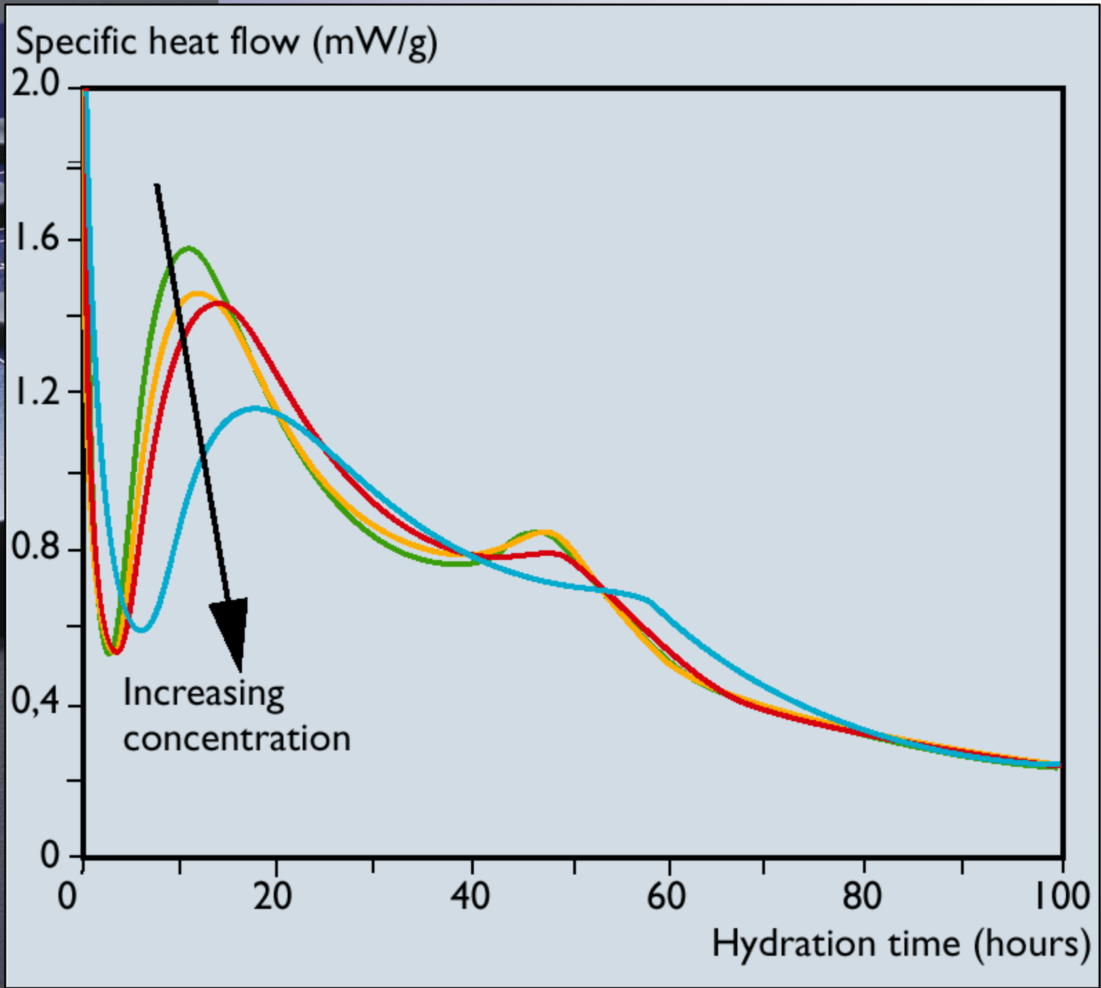
Effect of calcium sulphate hemi-hydrate on the hydration of cement



Heat flow per mass unit of dry cement at 23°C for cement samples containing 50% water.

Data by Dr. Paul Sandberg, WR Grace & Corporation, Cambridge, USA.

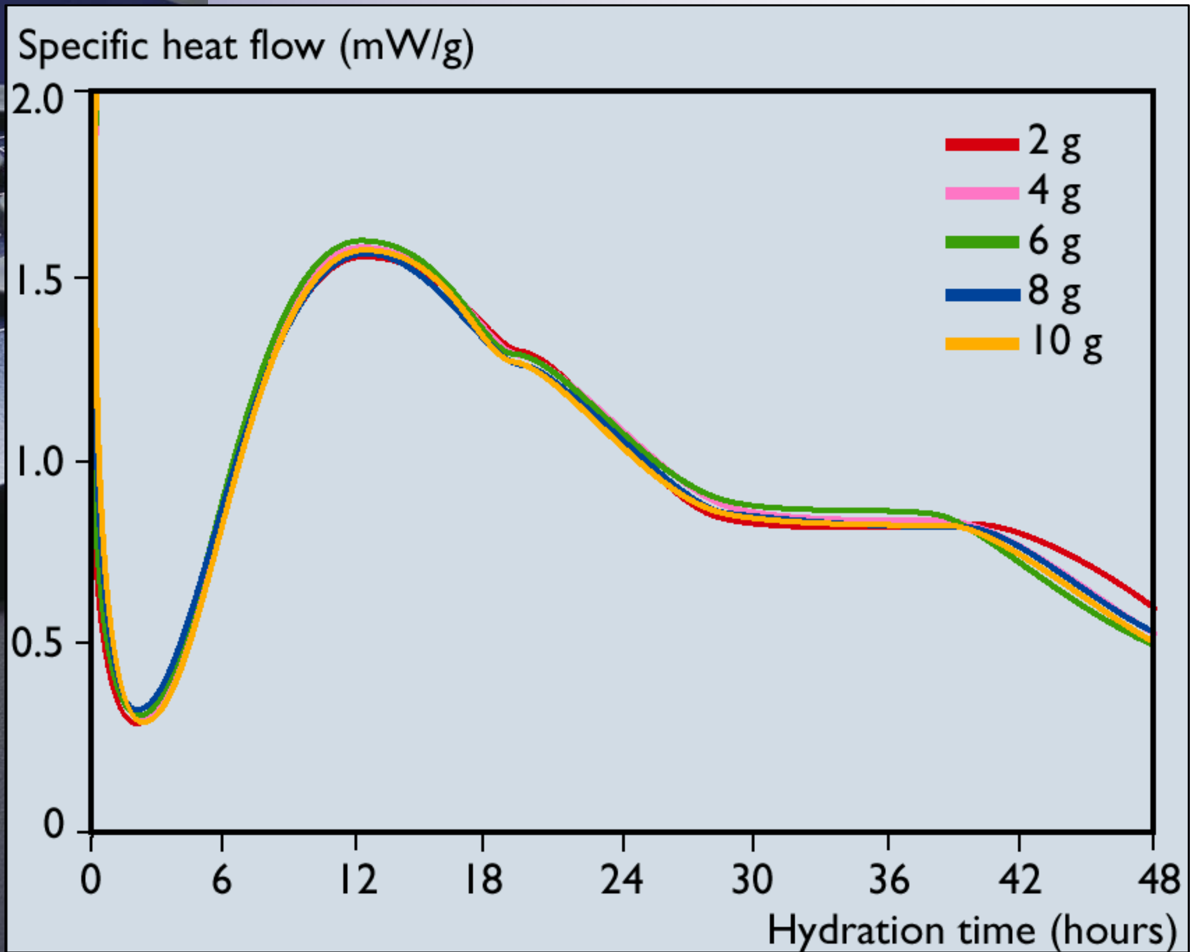
Effect of contaminated aggreagate on the hydration of cement



Influence on hydration rate of a mixture of *soil and sawdust* (0; 0.9; 2.5 and 5.9% of w/c=0.6 cement mortar).

Data by Dr.Lars Wadsö, Building Materials, Lund University, Lund, Sweden.

Influence of the amount of sample on the response of TAM Air



Influence of the amount of a cement sample. The overlapping curves indicate that the hydration process is homogeneous and that the repeatability and reproducibility of TAM Air is excellent.

Data by Gerd Bolte, Heidelberger Zement Group, Technology Center GmbH, Leimen,Germany.

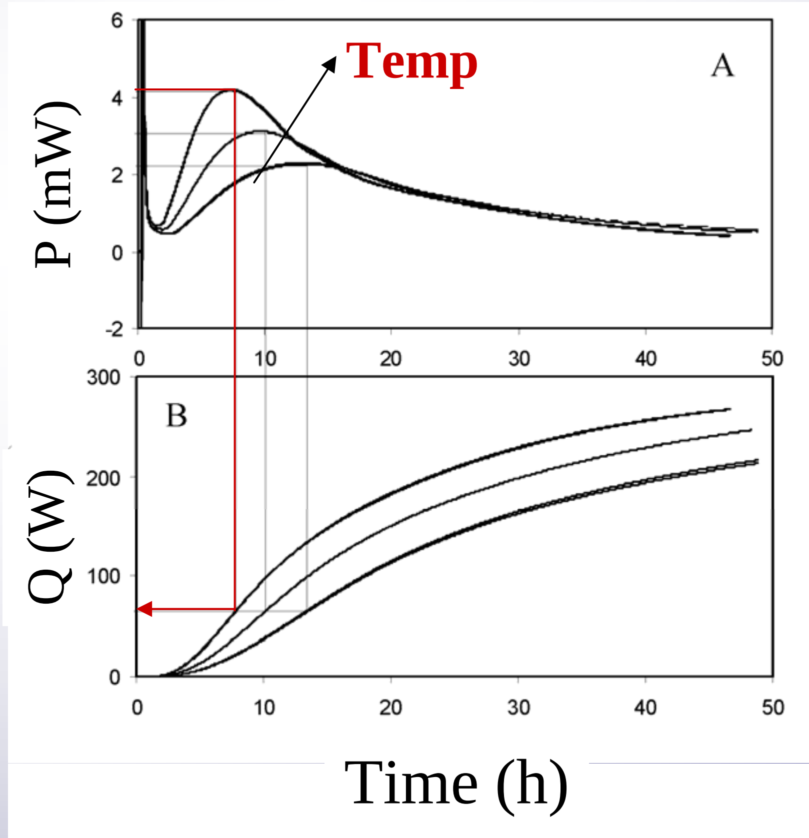
Temperature dependency of cement hydration

*Dr. Johansson , Thermometric AB, Sweden (**2002**)*

Measurements at 20, 25 and 30 ◦C

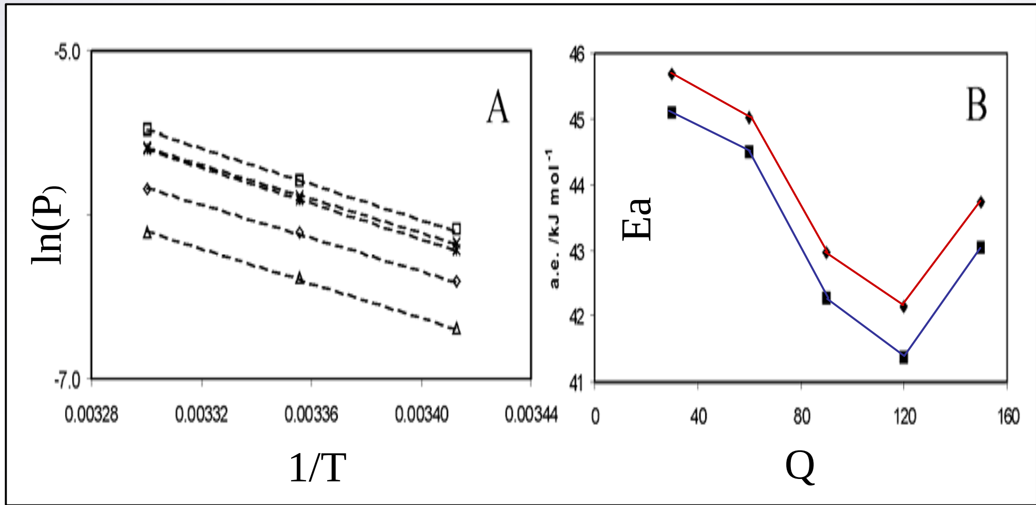
P reflects the rate of the process

Q reflects the extent of the process



Apparent activation energies

Q **– values were taken at 30, 60, 90, 120 and 150 J/g for two independent sets of measurements**



Arrhenius plots for the five cases described in the text (left) and the corresponding apparent activation energies for two repetitive measurements.

Conclusion: *Cement hydration is a complex process with multiple activation energies*

Final Conclusions

- The shape of the heat flow time curve reflects the hydration process of cement
- The integrated heat flow time curve, i.e. the energy evolved is related to the extent of hydration
- Large heat flow values indicates a fast hydration process
- A well defined quality should result in a heat flow time curve of a well defined shape

TAM Air Cement

Final Conclusions

- The effect of ad-mixtures is reflected in a change of the hydration curve
- The influence of various ad-mixtures can effectively be studied
- TAM Air is sensitive and versatile tool for studying the hydration process of cement
- The reproducibility of TAM Air is good