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Discussion of best practice for heat of hydration using isothermal calorimetry

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Heat of hydration (HoH) = the total heat produced from mixing of cement and water until a certain time (typically, 1 d, 2 d, 3 d or 7 d)

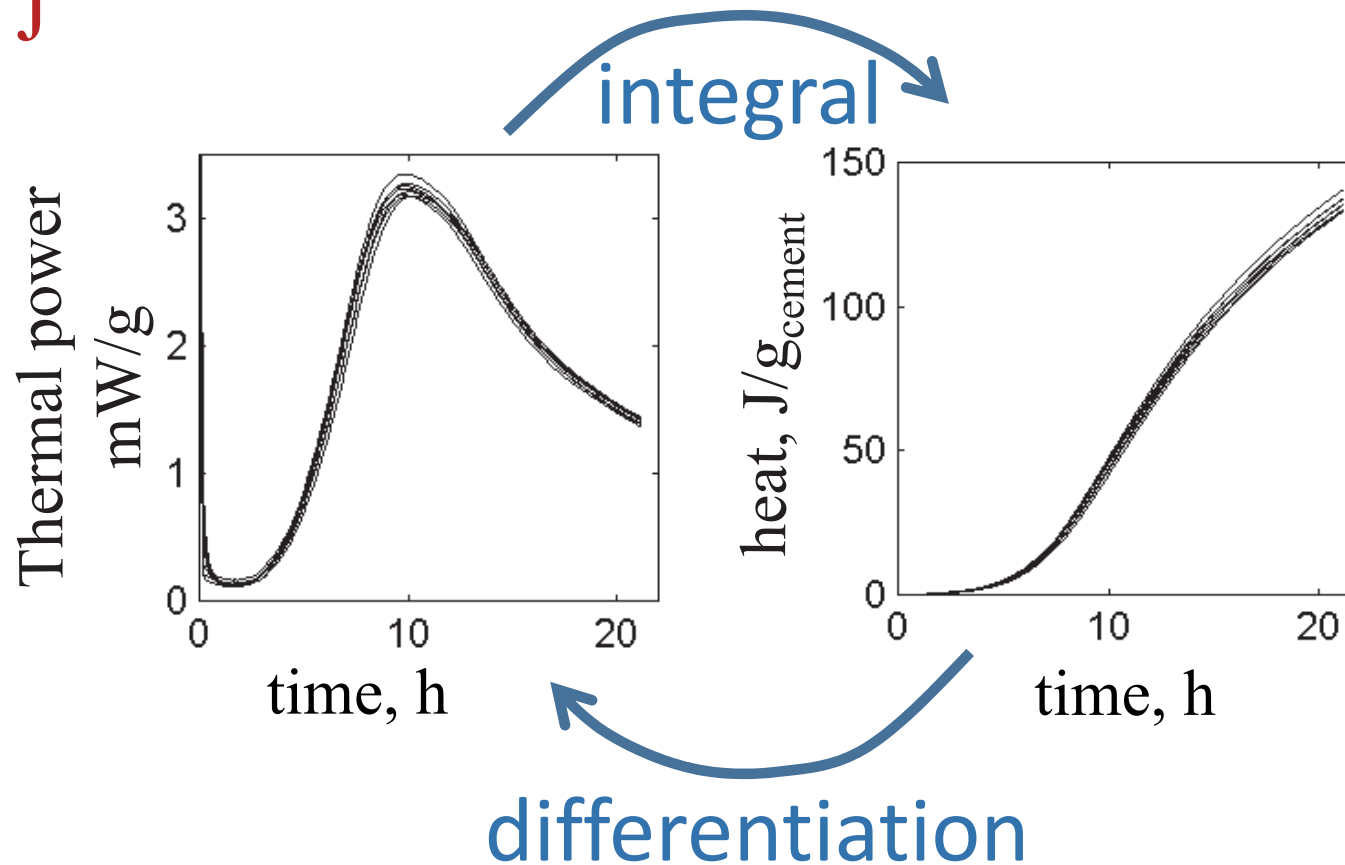
Why measure heat of hydration?

- Classification of cements into low heat cements etc. (ASTM 1702, EN 106-11)
- General measure of cement reactivity (QC)
- Correlating heat with other measurables (strength etc)

Thermal power, heat production rate,
heat flow, heat rate

$$\text{J/s} = \text{W}$$

Heat J





Designation: C1702 – 14

**Standard Test Method for
Measurement of Heat of Hydration of Hydraulic
Cementitious Materials Using Isothermal Conduction
Calorimetry¹**

Fpr EN 196-11 Methods of testing cement. Part 11. Heat of hydration. Isothermal Conduction Calorimetry method

17/30361318 DC

BS EN 196-11. Methods of testing cement. Part 11. Heat of hydration.
Isothermal Conduction Calorimetry method

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EN 196-11 will be similar to ASTM C1709, but there are a few things that I would like to comment on:

- water/binder-ratio=0.4 (to comply with EN 196-10, solution calorimetry)
- very tight temperature demands on calorimeter (± 0.2 K)
- complex correction procedure
- may lead to unnecessary complex calibration and evaluation procedures
- sample size
- external mixing large batch

Water/binder-ratio shall be 0.4 (requirement)

It is difficult or impossible to mix finely ground slag and composite cements in an internal mixer using $w/b=0.4$, i.e., internal mixing cannot be used for some of the cements for which the standard is intended.



- ▶ Requirements – shall, shall not
- ▶ Recommendations – should, should not
- ▶ Permission – may, need not
- ▶ Possibility and capability – can, cannot

<https://www.iso.org/files/live/sites/isoorg/files/archive/pdf/en/how-to-write-standards.pdf>

Temperature demands (4.3 and 7.1)

EN 196-11 has two writings on the temperature stability of the calorimeter. In 4.3 it is written (note that the word *should* is used; see the preceding paragraph):

4.3 Thermostat

Although the driving force of heat flow is a temperature gradient, the overall temperature in the calorimeter (heat sink) during test should be essentially constant (isothermal). For this purpose the calorimeter should be equipped with a thermostat. The temperature instability of the thermostat should not exceed 0,2°C. The working temperature of the apparatus should be at 20 °C ± 0,2.

In section 7.1 it is written (note that “has to be” in the last sentence denotes a requirement):

Before starting the test, the calorimeter equipment has to be in temperature equilibrium. This means the temperature stability of the heat sink and the baseline noise has to comply with threshold limits specified in 3.2 and 4.4. The temperature stability has to be checked by using a reference external thermometer.

There are three statements on the temperature here (written as they appear above):

1. The instability of the thermostat **should** not exceed 0.2 °C.
2. The working temperature of the apparatus **should** be at 20 °C ± 0.2.
3. The temperature stability **has to be** checked by using a reference external thermometer.

recommendation

recommendation

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2. The working temperature of the apparatus **should** be at 20 °C ± 0.2.
3. The temperature stability **has to be** checked by using a reference external thermometer.

requirement

What does this mean?

Complex correction procedure (required for external mixing)

The heat Q produced from time of mixing until the 72 h can be written as follows:

$$Q = Q_i + Q_a + Q_T. \quad (1)$$

Here, Q_i is the heat integral from the start of the integration t_i to 72 h, Q_a is the heat produced before time t_i , and Q_T is the effect of the Tian correction for the time lag. The time t_i , from which the integration is made, is in this study 60 s after the initial peak caused by charging of a sample. All the heats are expressed in units of J/g (cement).

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An international round robin test on isothermal (conduction) calorimetry for measurement of three-day heat of hydration of cement

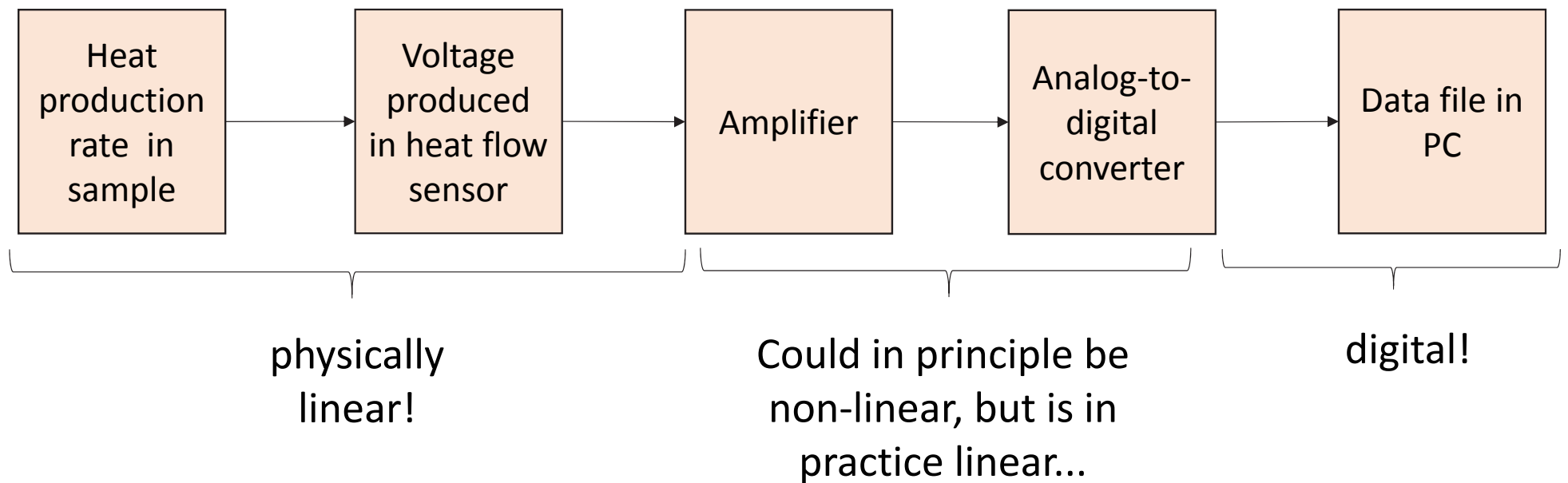


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"There are evidences of the fact that the response of sensors could be no linear below a limit threshold of thermal power"



Sample size

In EN 196-11 it is recommended to use samples with 3-10 g of cement, but it is also written:

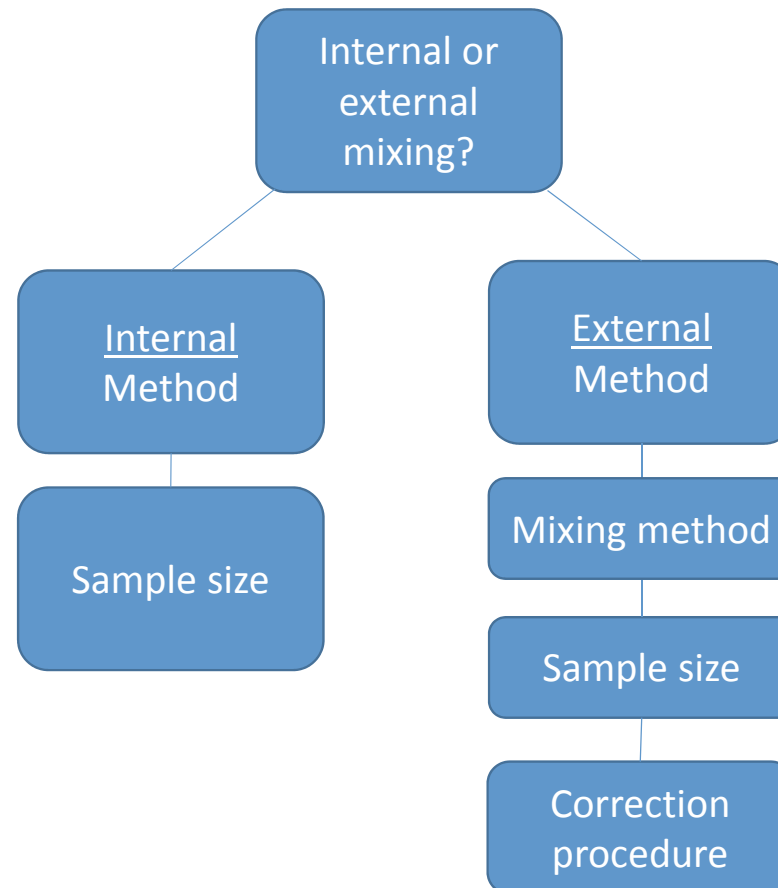
Always taking into account the indication of the apparatus supplier.

The 3-10 g range is proper for the smaller ampoules of the I-Cal Flex/Ultra, but for the I-Cal 2000 HPC significantly larger samples can be used (for example 50 g cement). The reason is that the latter calorimeter has a larger heat flow sensor and thus loses heat at a higher rate than the smaller calorimeters.

External mixing of a large batch (7.2)

The standard allows for different types of mixing, but exemplifies with a mix of 50 g cement and 20 g water from which a small sample is taken. It is our experience that it is better to use smaller amounts that are weighed into the ampoules. The reason is that if a small sample is taken from a large mix it may be difficult to get a representative sample (with the correct proportion of cement).

There are some decisions that have to be made by those that will use EN 196-11:



Some good alternatives (EN 196-11)

For fluid mixes and if the kinetics of the first peak are of interest: internal mixing.

Using large samples (50 g cement), water thermostated in the calorimeter, quick manual external mixing and charging. Correction procedure (a second measurement needed*).

External vortex mixing in small vials (a few gram). Correction procedure (a second measurement needed*).

* Required, but not specified. A. Internal mixing with high w/b for very early heat. B. Temperature increase in large mix of cement and water (Wadsö and Arndt 2016)