Draft operating protocol to determine the level of heat released during cement hydration on a concrete specimen placed in quasi adiabatic calorimeter designed for concretes (QAB) : Note technique

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GENERAL REMARKS

Purpose

This operating protocol is intended to specify the method for determining the quantity of heat released over time (quantity of heat at time *t*, plus the kinetics) during cement hydration for a concrete specimen placed into a quasi-adiabatic calorimeter specially designed for concretes (QAB). This operating protocol enables determining, at regular intervals, the quantity of heat produced, from just after specimen fabrication extending over several weeks. This quantity is expressed in Joules.

Scope of application

This operating protocol is applicable regardless of the type of hydraulic binder, with the exception of quick-setting cements.

Testing principle

The QAB calorimeter method consists of placing a specimen Ø 16 cm × 32 cm high at the center of a heat-insulated box in order to determine the quantity of heat released. At any given time, the heat released by hydration equals the cumulative heat input into both the calorimeter and specimen plus the heat that has dissipated to the outside since the initial time.

REFERENCES

Semi-adiabatic calorimeters are calibrated according to a protocol established within the network of LCPC Laboratories, indicated by the code Pro Q-E (Langavant-type calorimeters, verification). This protocol makes reference to the following documents:

– Pro Q-S1 (Metrological function)
– Pro Q-S2 (Langavant calorimeters, means of verification)
– Standard NF EN 196-9 (Cement test methods - Part 9: Heat of hydration - semi-adiabatic method)
– MET E2-1-4-3 (Metrology of digital thermometers: Calibration).

QAB calorimeters are calibrated according to a procedure analogous to that of the Langavant calorimeters **[1]**.

INSTRUMENTATION AND DEVICE CHARACTERISTICS

Calorimeter

The calorimeter is composed of a PVC box, insulated using polyurethane foam. The specimen housing, located at the center of the box, has been designed for placement inside an intermediate steel cylinder. An insulated cover provides access for the cable connecting the temperature probe.

The calorimeter diagram is included in Appendix 1. To ensure adequate test reproducibility, the thicknesses of polyurethane foam insulating layers need to be compliant to the greatest extent possible. Rubber type joints provide the necessary seal. The calorimeter bases are essential for ventilation beneath the device, so that the temperature of the sidewall is determined by the ambient air. Without this precaution, the heat loss coefficient derived through calibration might have to be modified. It has even been recommended to install the calorimeter on a table at a height that allows for stirring on the under-surface, yet low enough to easily place the specimen inside the device (i.e. a height of 40 ± 5 cm).

To conduct a test, two calorimeters are introduced; a control specimen is positioned inside a QAB calorimeter identical to the calorimeter holding the fresh concrete specimen. The control specimen's internal temperature is close to ambient temperature and evolves with fluctuations in ambient temperature according to a time constant that is nearly the same as for the fresh concrete specimen.

Temperature measurement instrumentation

The temperature probes required to conduct measurements contain platinum resistors (100 Ω at 0°C), which are to be calibrated according to standard procedure. The probes are connected to their conditioning box, which in turn is connected to a data storage system.

The power dissipated by the Joule effect of this platinum probe must not exceed 1 mW (with a maximum current of 1.5 mA). It is recommended that this current only be applied when conducting measurements.

The maximum cross-section of wires running through the cover must remain less than 0.2 mm^2 per conductor for the thermocouples and 0.25 mm^2 per conductor for the platinum probes.

The expanded uncertainty (expansion factor $k = 2$), which is applicable to the entire temperature measurement chain, must be less than 0.2°C.

The temperature probes are calibrated according to the procedure specified in the "References" section.

EXPERIMENTAL CAMPAIGN

In the vicinity of the calorimeters, air temperature must be within ±1°C of the initial test temperature. The ambient air temperature probe is used to control test room settings; this probe needs to be positioned at the center of an aluminum block that serves to limit rapid temperature fluctuations caused by air (sized as Ø 20 mm × 80 mm high). An active calorimeter receives the specimen to be tested while an identical one is used as the control device. A chemically-inert concrete specimen (aged for more than 3 months) is placed inside the control device.

Test requirements include:

– 2 QAB calorimeters featuring identical heat loss coefficients and heat capacities to within 5%;
– a compensation specimen fabricated with a concrete similar to the tested design (i.e. equivalent specific heat capacity values), yet remaining in its cardboard mold;
– three calibrated temperature probes;

– a data acquisition system;

– a cardboard mold along with its plastic cover.

Prior to conducting the test, room temperature is set at the initial test temperature value. The calorimeters are laid out in the test room, then opened so as to remove the control specimen from its calorimeter. This configuration allows placing the calorimeters and control specimen at the proper test temperature.

Note: The user may elect to collect multiple control specimens (between 2 and 5), under the premise of being able to respond to all types of situations. As an example, a concrete mix design that contains limestone aggregates and a large quantity of water offers a higher specific heat capacity than that of a design containing siliceous aggregates with little water. This aspect of the test protocol is left up to the operator to implement.

The temperature probes are routed through the cover cable gland of both calorimeters and then through the steel mold cover opening. The plastic cover of the control specimen is perforated exactly at the center with an 8-mm diameter. A copper tube (170-mm length, 10-mm outside diameter, 1-mm thickness), fitted with a flared nipple (or a plastic, quick-clamping collar) at one end and hermetically closed at the other end, is run through the mold cover opening (it is assumed that the same conditions have been adopted for the control specimen).

The mold is then weighed, to within the nearest gram, along with its cover and the copper tube.

The concrete is mixed. The date and time of adding water are carefully recorded. At the mixer output, the concrete temperature ($T_{concrete}(0)$) is measured and recorded as well. The concrete is placed into the mold using state-of-the-art practices. Once the mold is nearly filled, the copper tube is penetrated, under the effect of vibration (either internal or external to the mold), until the cover is readjusted onto the top of the specimen. This assembly is then weighed to know the actual concrete mass (m_b) being set. An adhesive tape is wrapped around the cover in order to minimize evaporation and condensation inside the calorimeter. Next, the specimen is transported into the test room.

The calorimeters are placed on the low table, as outlined in the section "Calorimeter". Specimens are inserted inside the calorimeter steel shell and covered by the steel cap. The temperature probes are positioned inside the copper tubes. Oil is poured into these tubes up to the rim. Modeling putty is applied around the steel cap opening. The calorimeter covers are installed and attached; additional putty is applied where the cable gland gets inserted.

The data acquisition system is activated. The measurement frequency interval is set at 10 to 15 min (for between 96 and 144 measurements/day). A display of temperature deviation between the test specimen and control specimen is desirable. The data recorded are: date and time of reading (format: dd/mm/yy hh:mm:ss), temperatures $T_{concrete}$, $T_{control}$ and T_{amb}.

Both the hydration kinetics and duration of complete concrete hydration are highly variable. No rule has ever been adopted to dictate when these measurement recordings are to be terminated. At a certain point in time, depending on temperature measurement performance, heat release can no longer be detected; in this case, it is assumed that the bulk of the hydration reaction has already occurred. As of this point, continuing to record temperatures is of no further utility. If the test is stopped before reaching this point, then the test result consists of the value of heat released at this stop time. Choosing when to halt measurements is thus incumbent upon the operator. The indication of temperature deviation derived from the data acquisition chain offers a useful control value for this particular purpose. It is possible, for example, to determine the stop point once this deviation value declines to less than twice the expanded uncertainty of the temperature measurement.

DETERMINATION OF HEAT OF HYDRATION

Notations

Let's denote the following:

– $C_{concrete}$ [in J/°C]: heat capacity of the concrete alone (product of mass times specific heat capacity),
– C_{cal} [J/°C]: heat capacity of the calorimeter, obtained from the calibration step,
– C_{tot} [J/°C]: total heat capacity = $C_{concrete} + C_{cal}$
– t [hours]: time elapsed during the QAB test,
– $T_{concrete}$ [°C]: temperature of the fresh concrete specimen,
– T_{ext} [°C]: exterior temperature,
– $T_{control}$ [°C]: temperature of the hardened concrete control specimen,
– $q(t)$ [J]: heat release at time t
– $\theta(t)$ [°C or K] = $T_{concrete} - T_{control}$: deviation in temperature between the fresh concrete specimen and the control specimen at time t
– α[J/h/°C]: heat conduction coefficient, which can be expressed as a function of θ ($\alpha = a + b\,\theta$), where coefficients a and b are obtained by calibration,
– m_b: mass of concrete poured into the cardboard mold.

Spreadsheet-based calculation of heat released

In the QAB calorimeter, a proportion of the heat released by cement hydration increases specimen temperature, while another proportion increases the calorimeter temperature and the final proportion is discharged to the outside. Such a breakdown can be expressed as follows:

$$q(t) = C_{tot}\left(T_{concrete}(t) - T_{concrete}(0)\right) + \alpha \int_0^t \theta(t)\ \mathrm{d}t \qquad (1)$$

The protocol for using this expression in a spreadsheet application on a set of discrete data is described below.

Initially a row, containing the date and time of casting, mixer output temperature $T_{concrete}(0)$, control specimen temperature (set equal to the first temperature measured on this specimen) and a similarly-treated ambient temperature value, is added on top of the actual measurement recordings.

A column entitled "concrete age" or time t is added as well. This time parameter is calculated in hours, as the date and time of each measurement minus the date and time recorded when casting first took place.

C_{tot} is the sum of heat capacities of both the concrete ($C_{concrete}$) and calorimeter (C_{cal}). The calorimeter heat capacity is given in the calibration report; its order of magnitude for the dimensions shown in the **figure** in Appendix 1 equals 3,400 J/°C. The heat capacity of concrete is calculated according to the following expression:

$$C_{concrete} = \mu_s\,(m_c + m_s + m_g) + \mu_l\,m_e \qquad (3)$$

• μ_s is the specific heat capacity for solids in the mix (cement, sand and aggregates) and equals approx. 800 J °C^{-1} kg^{-1}.

• μ_l = is the average specific heat capacity[1] for the mixing water and equals 3,800 J °C^{-1} kg^{-1}.

• m_c, m_s, m_g, and m_e are respectively the masses of cement, sand, aggregates and water of the specimen itself.

[1] *The specific heat capacity of water equals 4,180 J °C-1 kg-1, yet this value differs for water combined with hydrates.*

These masses are obtained from both the concrete composition and specimen mass. With this set-up, the first step consists of determining the mass proportion of each concrete component (component mass per m^3 of concrete divided by the total mass of all components per m^3 of concrete). To ascertain the masses of all specimen components, the next step simply requires multiplying the mass proportions of each component by the specimen mass.

The last term of **Equation (1)** is calculated from the initial time 0, i.e. when it is considered that zero heat has been released (heating due to anhydrate dissolution is neglected during the first few instants). For each subsequent step of rank k, the basic energy loss is calculated as follows:

$\Delta q(k) = \alpha \dfrac{T_{\text{concrete}}(k) - T_{\text{control}}(k) + T_{\text{concrete}}(k-1) - T_{\text{control}}(k-1)}{2} \Delta t$, which is then added to the value obtained for rank $k-1$.

The $q(t)$ curve then yields the expected result.

Other information can also be drawn from this curve (see **[2, 3, 4]**).

UNCERTAINTIES IN THE HEAT RELEASE DETERMINATION

The parameters exerting significant influence on this result are the specimen and control temperature measurements, as well as the heat loss coefficient of the calorimeters.

With a set of elementary uncertainties u_{xi}, such as those listed in the table below, the standard uncertainty on heat release equals approx. 5% of the release through four weeks of testing **[2]**.

Parameter	Nominal value	u_{xi}	Units
Mass of the empty mold	0.346	0.0002	kg
Mass of the filled mold	15.262	0.005	kg
Cement mass	2.171	0.005	kg
Water mass	1.176	0.0002	kg
Sand mass	4.722	0.005	kg
Gravel mass	6.846	0.005	kg
C_{cal}	3266	32.66	J/°C
α	369.8	3.2	J/°C/h
Solid specific heat capacity	750	7.5	J/°C/kg
Liquid specific heat capacity	3760	37.6	J/°C/kg
T_{concrete}	$T_{\text{concrete}}(t)$	0.1	°C
$T_{\text{control}}(t)$	$T_{\text{control}}(t)$	0.1	°C

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APPENDIX 1:

Scaled diagram of a QAB calorimeter