

DETERMINATION OF INTENSITY OF HYDRATION HEAT DEVELOPMENT OF SILICATE BINDERS

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ABSTRACT

Chemical mineralogical reactions taking place during hydration of silicate binders display by thermal manifestation qualified as hydration heat. Knowledge of time behavior of intensity of hydration heat development is important for judging properties of binder mixtures and their thermal technical behavior during hydration process. Besides, on the basis of intensity course of hydration heat development, it is possible to conclude a degree of effect on properties of binder mixtures when adding chemical additives. This paper describes possibilities of utilization of isoperibolic calorimeters for assessment of intensity of hydration heat development for cement pastes and possibilities of practical application of these measurements in building practice.

Keywords: Hydration heat, Binder, Cement, Calorimeter, Temperature

1. Introduction (hydration heat)

Hydration heat is thermal demonstration of hydration of cement. Hydration is an exothermic reaction during which heat liberates. Liberated heat is defined as summation of heats from various physical and chemical processes proceeding simultaneously. There is no simple way to resolve them but observing their summation. They are these heat amounts:

- Wetted heat of cement
- Solvent heat of clinker minerals
- Reactive heat of hydrosilicates and aluminates
- Crystalline and recrystalline heat
- Adsorptive heat of water on hydration products.

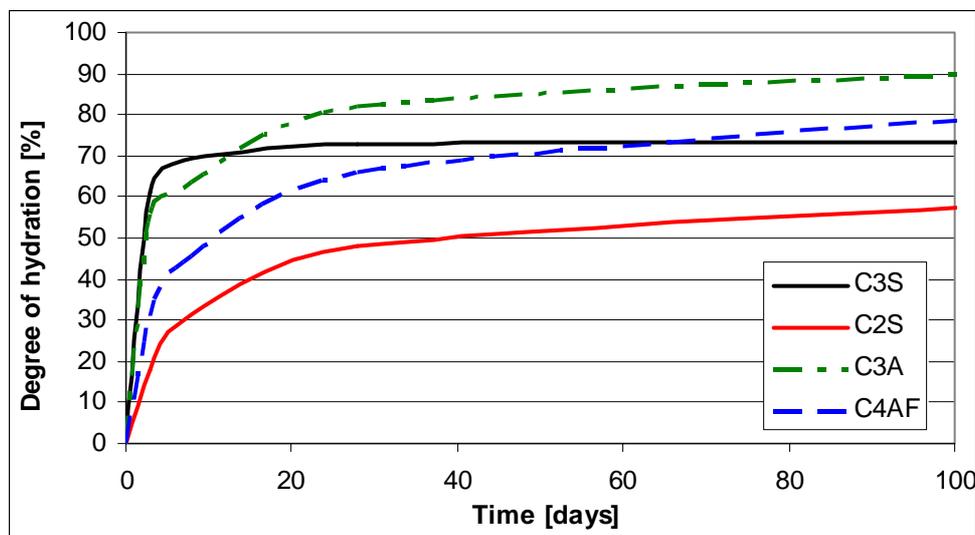
Increased temperature of mixture caused by heat liberated during hydration process acts reversely to acceleration of hydration processes. However, temperature rise of hydrating cementing compound may also induce adverse strain up to cracking which decreases strength and particularly durability of concrete. Development of hydration heat is thus an important quantity worth observing during hardening of concrete in particular during concreting of large volumes. Such events often occur in structures of stopes, hydraulic engineering etc. There arise great thermal differences on surface and in centre of concrete block as result of relatively low thermal conductivity during hardening of concrete. This difference is the greater the more massive is concrete block and the greater is temperature difference between temperature of embedded batch and environment. Such temperature difference invokes strain leading to fissuring. Extensive development of hydration heat during concreting in summer period leads

together with raised temperature of surrounding environment to overheating of concrete. Potential boiling of water induce again formation of undesirable cracking with all of its consequence. On the contrary, during concreting at summer period, extensive development of hydration heat is desirable for heating of concrete mixture which basically enables process of hydration reactions. Knowledge of value of hydration heat may be utilized for quality estimation of stored cement.

Intensity of heat development is not constant in time. Considerable part of heat releases due to hydration of C_3A at start of hydration and then by its reaction with gypsum. Only afterwards heat liberates from hydration of the other clinker minerals. Hydration kinetics may be expressed as a series:



It has been also proven that hydration rate of pure (synthesized) clinker minerals is rather distinct in comparison with compounds included in cement.



Graph 1: Process of hydration of minerals of Portland clinker.

Kinetics and intensity of hydration processes is affected by many factors:

- external conditions (particularly temperature and moisture content),
- cement composition,
- fineness of grinding,
- water cement ratio,
- additives and admixtures,
- crystal size,
- type and amount of ions in crystalline structure,
- degree and type of crystalline defects and relation to phase content of clinker (e.g. hydration rate of belite is higher at presence of alite),
- type of hydration product.

Research objective was, of all things, to follow influence of additives and admixtures on change of intensity of hydration heat for modified cement mortars. Generally, it is valid that practically all substances being added to binder mixture influence hydration process in certainly less or much significant way and hereby intensity of hydration heat (rate and intensity of hydration) as well.

- **ADDITIVES** – Chemically active substances: substances reacting with binder grain, absorbing onto their surface, influencing binder solubility in water, altering electrostatic potential of mixture.

- **ADMIXTURES** – Physically active substances: substances initiating change in thermal conductivity of mixture, change of heat capacity, transformation of surface of solid portion of mixture, etc.

2. Calorimetric methods for study of kinetics of hydration reactions

Development of hydration reactions and processes in qualitative respect may be followed with aid of monitoring of development of hydration heat by direct and indirect calorimetric methods.

- Direct methods** – technically works on assumption of temperature change of testing sample under exactly defined marginal conditions
- Indirect (solvent) methods** – Hydration heat assessed from solvent heat of hydrated testing samples (after 7 and 28 days) in mixture of acids

Indirect methods are relatively accurate but they can assess only total value of hydration heat in certain phase of hydration. In case that hydration heat is being assessed by means of this way, it is necessary to wash a testing sample in ethyl alcohol and exsiccate. This method can therefore theoretically determine total hydration heat of testing sample in various stage of hydration and interpolate a curve of development of intensity of hydration heat from observed dependence, however, this procedure is empirically extensively demanding.

On the contrary, by means of indirect methods we follow dynamically quantities that are proportional to intensity of development of hydration heat and then total value of liberated hydration heat can be assessed by integration of this intensity. There exist three most used types of indirect methods such as:

- Adiabatic methods** (semi-adiabatic) – there is no heat exchange between a testing sample and surrounding environment. This method is widely considered very inaccurate and little corresponding as enormous temperature rise often up to ≈ 100 °C of a testing sample comes up affected by hydration heat liberation during measurement. This causes strong acceleration of reaction kinetics therefore measured values of development of hydration heat strongly differ from real ones. Further, it is mostly very problematic to prevent heat exchange between testing sample and environment.
- Isothermic methods** – The testing sample at these methods is being tempered on a certain constant temperature and thermal flow between the testing sample and surrounding environment is being measured
- Isoberibolic methods** – Hydration of testing sample proceeds under exactly defined conditions similar to those ones under which concrete mixture hydrates in situ in practice. Using this process, it is, for example, possible to assess effect of additives and admixtures on development of intensity of hydration heat of concrete very objectively. Hydration of a testing sample proceeds in given case under exactly defined conditions in isoperibolic calorimeter with known exact thermal characteristics (loss heat flow Φ_z [W]):

$$\Phi_z = f(U_c, (T_i - T_e), T_i, T_e)$$

Testing samples are imbedded into calorimeters after they are mixed and their interior temperature is being recorded. Then, intensity of development of hydration heat may be defined from these values according to relation:

$$\dot{Q}_{hyd} = \frac{\frac{\Delta T_i}{\tau} m c_s - \Phi_z S}{m_c}$$

where: \dot{Q}_{hyd} – intensity of development of hydration heat [$\text{J} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$], m – mass of a testing sample [kg], m_c – mass of cement [kg], c_s – specific heat capacity [$\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$], τ – time [s], Φ – loss heat flux density [$\text{J} \cdot \text{s}^{-1}$], T_i – temperature of a testing sample [K], T_e – external temperature [K], U_c – heat transfer coefficient of body of calorimeter [$\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$], S – equivalent utility surface of calorimeter [m^2].

3. Assessment of intensity of hydration heat development by means of isoperibolic calorimeter

A set of isoperibolic calorimeters has been developed for observing of hydration heat development at Brno University of Technology, Faculty of Civil Engineering. The body of calorimeter is made of paper board impregnated with color (due to presence of moisture and potential of getting soaked during handling). Space between container and measuring cell is filled with loose polystyrene to ensure shielding of time-local variations of temperature of surrounding environment but also to prevent effecting of reactions in reaction cell by extensive temperature rise of observed set.

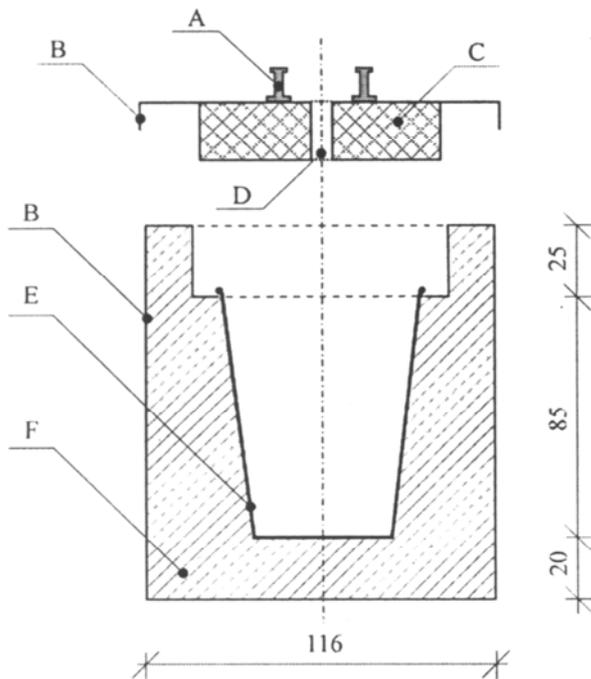


Fig. 1: Transversal section of calorimeter's body

Description

- A ... Latchets easing handling with a lid
- B ... Cover from hard paper coloured with paint
- C ... Thermal insulation from foam polystyrene
- D ... Opening for a thermal probe
- E ... Reaction cell form plastic crucible
- F ... Thermal insulation from loose foam polystyrene

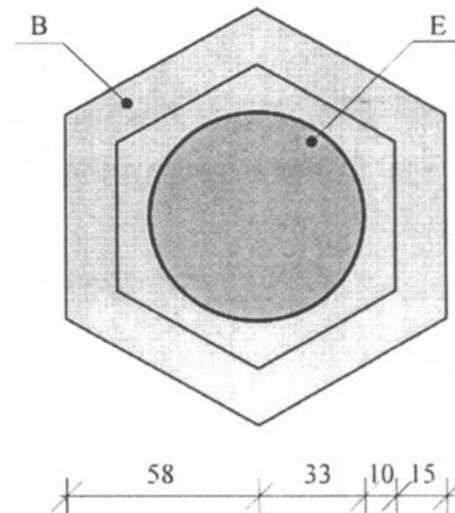


Fig. 2: Plan of calorimeter's body

Thermal probes with pulse-modified digital output for monitoring of temperature inside a calorimeter, insensitive to humidity. Probes are protected with metal cover (stainless steel) – see the following figures:



Fig. 3: Images of measuring set of isoperibolic calorimeters for assessment of intensity of hydration heat development.

Signals from thermal probes of calorimeters are transferred to thermal logger where a pulse modulated digital signal from measuring sensors is transformed by microprocessor, measured quantities are transferred by means of RS 232 protocol to PC unit for interpretation and archiving.



Fig. 4: Image of a measuring logger with connected thermal probes.

Calorimeters are imbedded in air-conditioning case with a constant temperature (due to demands of measurement) during measuring time. Complete scheme of measuring apparatus is represented on following figure:

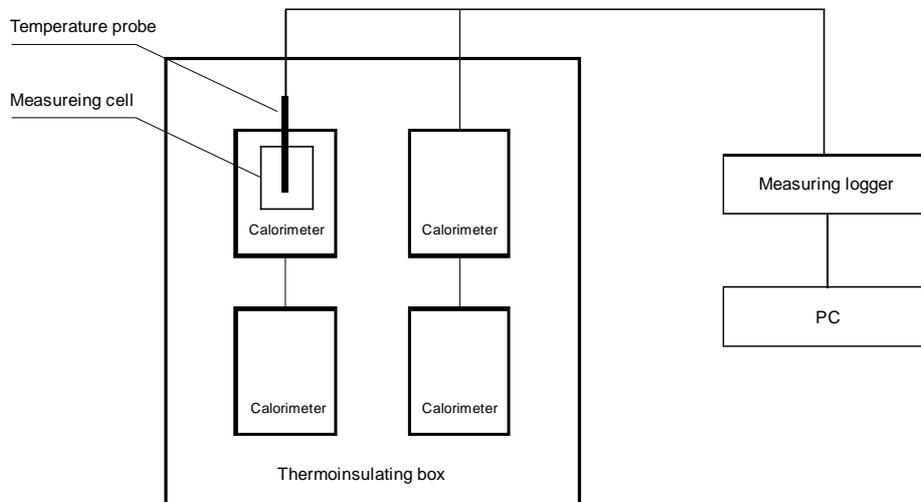


Fig. 5: Scheme of measuring device for assessment of development of hydration temperatures of cement pastes.

When comparing effects of addition of additives and admixtures to modified cement mortars, it is not essential to calculate intensity of development of hydration heat but it is possible to use directly measured heat behavior while observing the following parameters:

- Temperature behavior in time,
- Time for achieving maximum temperature,
- Achieved relative maximum temperatures – θ_{\max} .

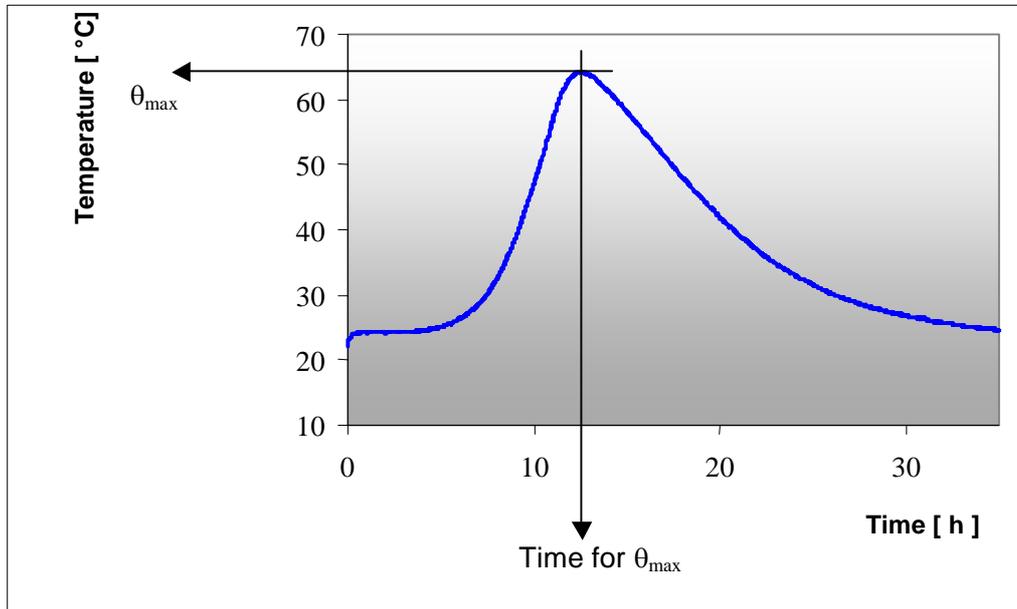


Fig. 6: Schematic representation of monitored quantities.

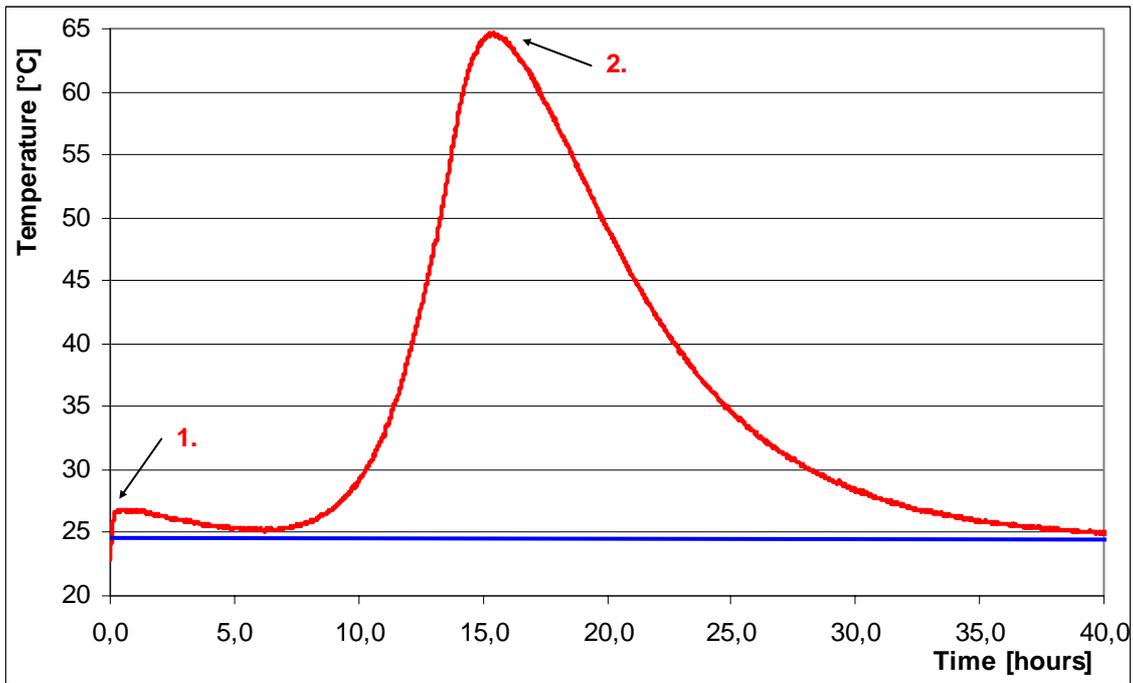
4. Utilization of calorimetry for assessment of properties of modified cement pastes

When considering usability of chemical additives or during technical thermal calculations, we need to know the curve of intensity of hydration heat development in time dependence. This curve is possible to be obtained from a direct measurement of temperature change of a testing sample, thus by assessment of hydration heat development by means of isoperibolic calorimeter (when neglecting thermal accumulation component of a testing sample, it is possible to define a proportionality between temperature of testing sample during hydration and intensity of hydration heat development).

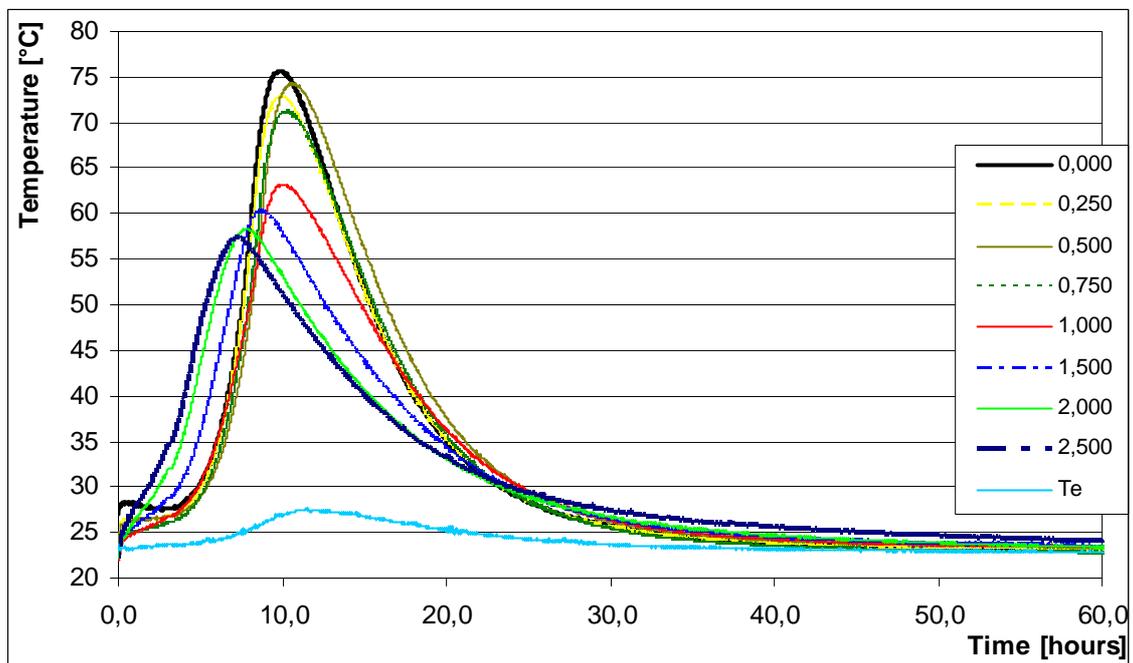
As evident from the graph 2, a relatively significant release of thermal energy arises immediately after mixing of cement with water (point 1) and it is possible to find a strong relationship between intensity of hydration heat development and rheology of cement paste in this period (approx. 2 hours). The next extreme in development of hydration heat is possible to be recorded approximately in period 8-24 hours when exact time and value of hydration heat development are dependent on the following factors:

- Type of cement and its grinding fineness
- Water cement ratio
- Type and amount of chemical additives
- Type and amount of reactive admixtures (gypstone)
- Type and amount of admixtures with latent hydraulic properties

Measure of influence of used chemical additives to hydration behavior is possible to be assessed by means of isoperibolic calorimeter (see graphs 2 and 3).

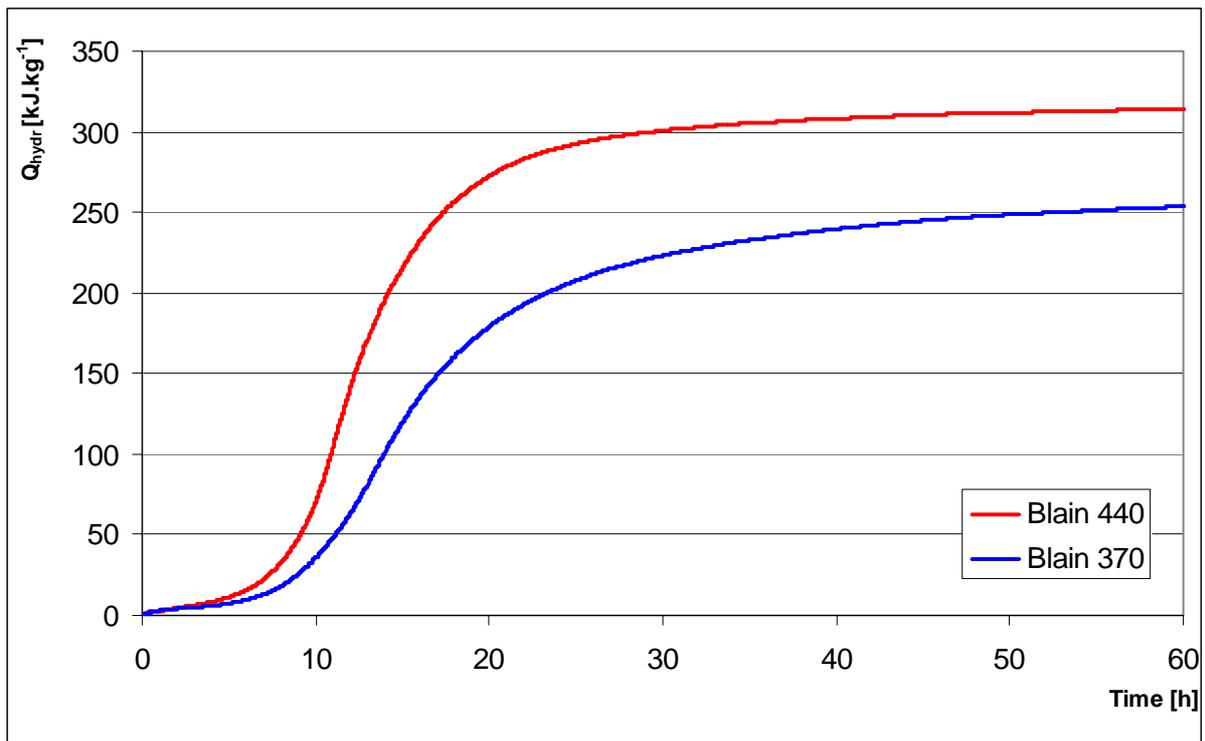


Graph 2: Temperature behavior in calorimeter during hydration of specimen CEM I 42,5R Mokra with addition of super plasticizer on basis of polymelamins (1.5% part by weight).



Graph 3: Behavior of hydration temperature of hydrating cement paste (CEM I 42,5 R, $w = 0,38$) with variable addition of accelerating additive on basis of calcium nitrate

Further, it is possible to verify quality of binder, its activity and grinding fineness. Dependence of hydration temperature behavior of cement pastes (CEM I) with variable specific surface is captured in the following graph:



Graph 4: Development of hydration heat for cement of CEM I class with variable specific surface dependent on time.

5. Conclusions

Knowledge of time behavior of hydration process thus contributes to a design of concrete mixture that will best meet the given conditions. Considering all effects during building performance is not always simple but hydration heat development is a process that ought not to remain neglected. As evident from above mentioned results, hydration process of concrete may have completely distinct behavior in dependence on its composition and surrounding conditions. Affects by temperature rise inside concrete massive during hydration and negative temperature gradients may cause failures in structure and degradation of utility properties and durability.

The results of this work conclude the following recommendations for concrete design:

- Always, if it is possible, verify composite action of considered additive with used cement from point of view of hydration heat development or temperature behavior.
- It is better to monitor temperature behavior of hydrating structure even straight in situ during concreting of large-volume elements and concreting in summer months
- Try to replace at least part of fine compounds in concrete with increased amount of these compounds with inert type of additive. In case that all fine compounds will form cement grains, there is a danger of overheating of cement
- It is better to combine a package of precautions for concreting under lower temperatures. It is convenient to test interaction of additive and cement. The most appropriate combination that allows safe concreting even in winter, will be preheating of water, use of Portland cements, use of accelerators on basis of calcium nitrate and suitable curing of concrete.

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