HYDRATION OF PORTLAND CEMENT PASTE

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Abstrakt:
During hydration and hardening, the concrete is gaining mechanical strength, resistibility and chemical stability, while physical and chemical reactions are in progress. Workability of concrete belongs to the crucial parameters. Concrete should be workable, but not segregate or bleed excessively. Knowledge of the rate of reaction between cementing materials and water (hydration) is important to determine setting time and hardening. An electrical measurement technique has been used to measure the electrical resistivity of cement paste at various temperatures. The different hydration periods were identified from the electrical resistivity curve, where inflex points mark the beginning and the end of a certain period.

INTRODUCTION

Application of cement-based materials is extremely wide, ranging from stomatology to civil engineering. Incubation time represents one of major parts of the so-called workability corresponding to a time when hardening cement-based materials is formable and transportable to required locations. Recent effort is oriented to prolongation of the incubation time (and, thus, also of the workability) in terms of various types of additives retarding process of hardening. The study of early stages of hardening of cement-based materials may give a clue.

As a typical example, an indispensable material in civil engineering - Portland cement - can be considered. Portland cement is the most used and best known type of cement, it is a mixture of calcium silicates (mainly tricalciumsilicates $\rightarrow$ 3CaO.SiO2 $\rightarrow$C3S). If water is added to the cement, the process of silicate hydration is triggered and the products are calcium-silicate-hydrate gel (the so called CSH gel) and dihydroxide calcite are produced.

The process of hydration (see Fig. 1) starts with the addition of water. In the very beginning liquid and cement grains are present, shortly after addition of water the so-called chemical stage is in process. Ions from Portland cement are released into the solution and the coating gel appears around the grains.
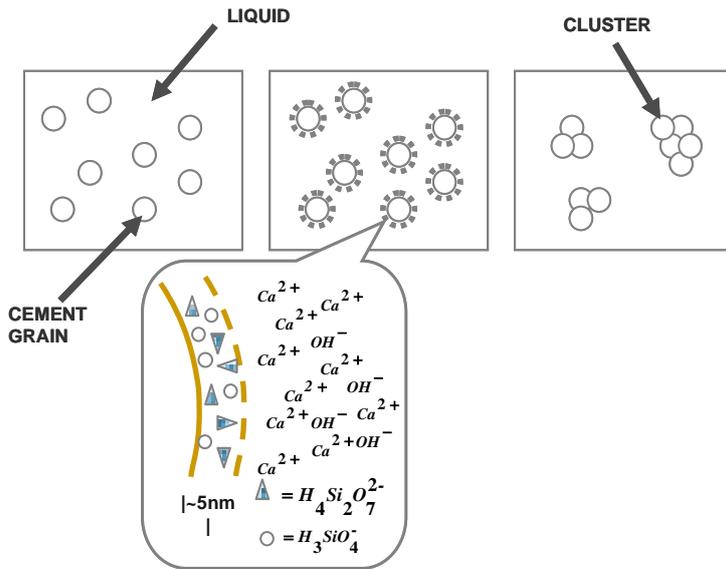
Figure 1.
Hydration of Portland cement.

Next stage is the so-called induction period, the value of pH is increasing steadily and the concentration of calcium ions together with CSH gel on the surface of grains is responsible for decrease in the solubility of phases of Portland cement. The formation of ettringit is developed and the hardening of cement is initiated. Finally, the fibrils of hydrated calcium silicate grow into a cluster (for details, see, e.g. [3]).

HEAT EVOLUTION

Heat evolution of the hydration of cement may be divided into three stages – chemical stage, nucleation and growth.
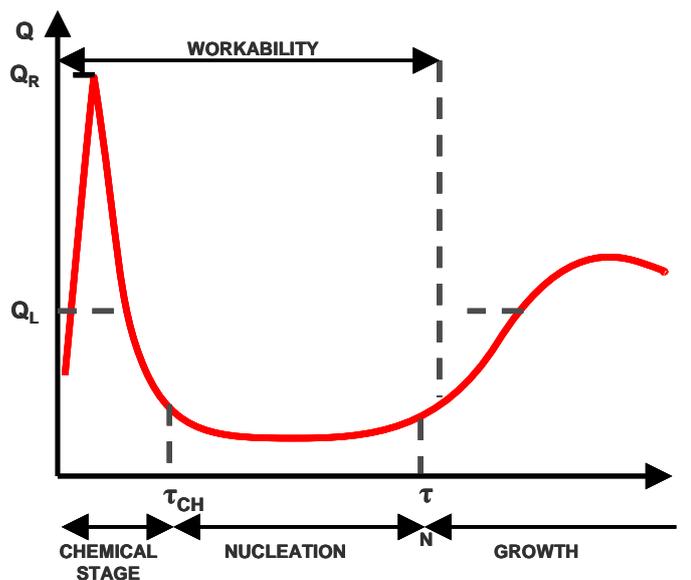

Figure 2.
Heat evolution of hydration of cement paste (schematically).

When the starting cementitious material is mixed with water (but also other kinds of liquids may be used, for example in stomatology) a set of chemical reactions produces a significant amount of heat released due to exothermal reactions and this amount of heat can be measured (for example, using various modifications of calorimetric methods – see, e.g. [5]). Duration of these chemically based reactions may be affected by different types of retarders (e.g. [6]). Beside of heat released also a number of various charged objects (dominantly calcium ions, resp. hydroxyl groups [3]) are intensively produced during this reaction kinetics. These ions play essential role in subsequent, nucleation stage of evolution and form the so-called monomers – the building units from which the product, solid phase is successively built up.

Indeed, the chemical stage of evolution is followed by the so-called incubation (or dormancy) period when the pure chemical processes are slowly terminated and the first-order phase transformation (solidification) starts within the metastable system. At a very first stage of cementitious paste hardening, the sub-nanosized domains of a new, solid phase are formed via sufficiently large fluctuations (the monomers are already present as a consequence the chemical stage).

Number density of these newly-forming clusters is too low in order to influence the magnitude of practically negligible total heat release within hardening system, which is clearly visible in the heat evolution – no observable peaks or increases in Q. Thus, the calorimetry methods are, in fact, inapplicable to obtain useful information on processes occurring in the cement paste during incubation period. Nevertheless, the fact that the building units are charged with various levels of mobility can be usefully utilized. Hence, time-change of electrical conductivity may be straightforwardly related to the immediate stage of system evolution.

The beginning of macroscopic growth (and, thus, termination of incubation period) can be characterized by dramatical change in the time-dependency of electrical resistance because of appearing of the massive clusters with relatively low mobilities. This process is accompanied by increasing release of the latent heat Q_L.

MODEL

Duration of incubation period, τ_N, can be estimated using following path. Due to chemically based process of solvation of the cementitious material in water, various types of charge carriers (monomers Ca^{2+}, OH^-, etc.) are released and free to move within the system. Due to chemical reaction and physical processes occurring within hardening cementitious paste, a number density of ions changes with time logically followed also by the change of electric properties of the system. In particular, temporal dependency of electrical resistance (resp. conductivity) may be closely related to τ_N.

For this purpose, we have measured electrical resistance of hardening cement paste. We used the cement CEM type II 32,5 produced by HeidelbergCement Group (chemical composition of cement paste is collected in Tab. 1). There exist many methods how to measure electrical resistance in cement-based materials (e.g. [7] - [10]).

Tab. 1. Chemical composition of cement paste

Chemical	weight
SiO_2	2.27
Fe_2O_3	0.62
Al_2O_3	25.36
CaO	4.12
MgO	6.90
SO_3	55.40

We used a relatively simple set-up for measuring electrical resistance (see Fig. 3). Typical data obtained by the set-up are shown in Fig. 4, where time-dependency of resistance was measured for cement paste with water to cement ratio 0.5 at temperature 21.8 °C (water to cement ratio is amount of water related to the amount of cement).
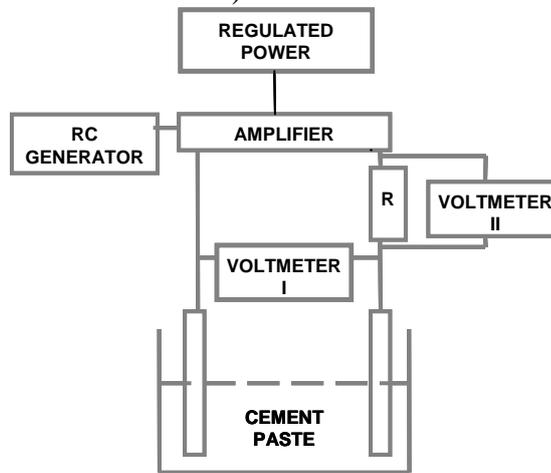

Figure 3.
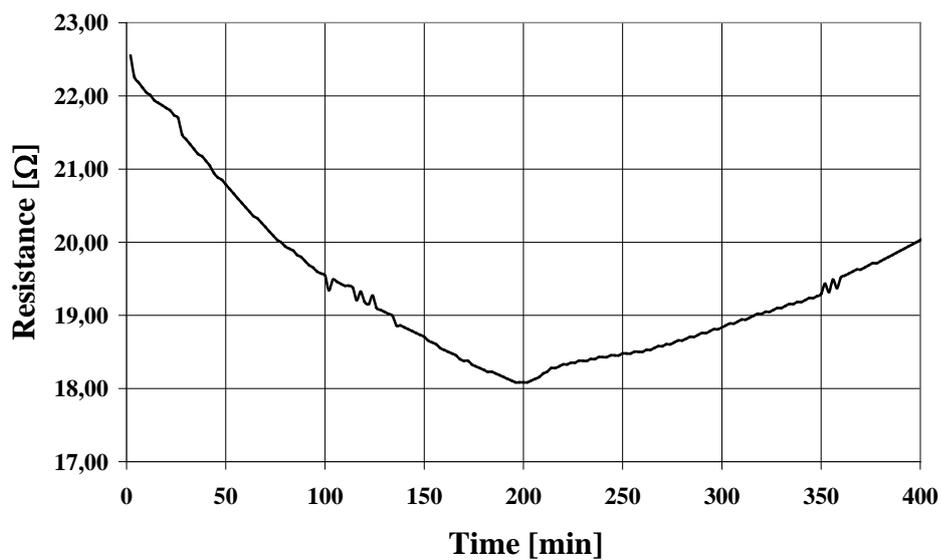*Scheme of applied electric set-up.*

Figure 4.
Typical temporal dependency of electrical resistance of cement paste (w/c = 0.5; T= 23.8°C).

Formation of clusters in material is a consequence of fluctuations. If the classical Boltzmann theory from statistical physics is applied to the process of cluster formation, it can be found out that the probability of appearing of a cluster consisting of n-building units can be expressed as follows:

$$\Pr(n) \approx \exp\left[-\frac{\Delta G(n)}{kT}\right], \qquad (1)$$

where k is Boltzmann constant, T is the temperature, and the ΔG is the change of Gibbs potential given by (see, e.g. [4])

$$\Delta G = -n \cdot \ln \mathscr{S} + \gamma \cdot \sigma \cdot n^{2/3}, \qquad (2)$$

where n is number of monomers in the newly-forming cluster, $\mathscr{S}$ is given supersaturation of the system (water + cement), σ represents surface energy between cluster and its environment and γ expresses geometrical shape of the cluster (plot of ΔG versus n is on Fig. 5). ΔG reaches maximum at the moment when the newly forming clusters have the critical size n_C. When the cluster consists of n particles and n is less than n_C, then dissolution takes place; otherwise, the cluster tends to grow.
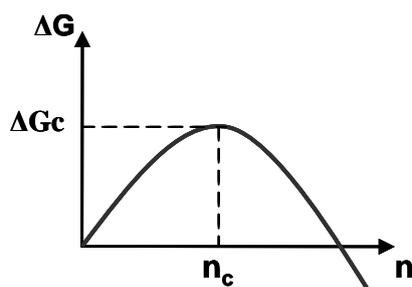

Figure 5.
Plot of ΔG versus n.

The critical size of cluster can be derived from extremum condition for ΔG to be:

$$n_c = \left[\frac{2\gamma\sigma(T)}{3\ln\mathscr{S}}\right]^3 . \qquad (3)$$

RESULTS AND DISCUSSION

Crucial quantity entering above relationship, dividing the unstable (undercritical) and stable (supercritical, growing) regimes of evolution via nC is temperature dependent surface energy $\sigma(T)$ between solid cluster and original liquid phase. It can be found in standard books on physical chemistry [3] that surface energy σ usually decreases with increasing temperature and vanishes at equilibrium temperature TM. Dependency of nC versus temperature can be derived from formula for the critical size of cluster. Since σ decreases with increasing temperature, taking into account eq. (3), following behavior of nC (as a function of T) may be assumed for given supersaturation:
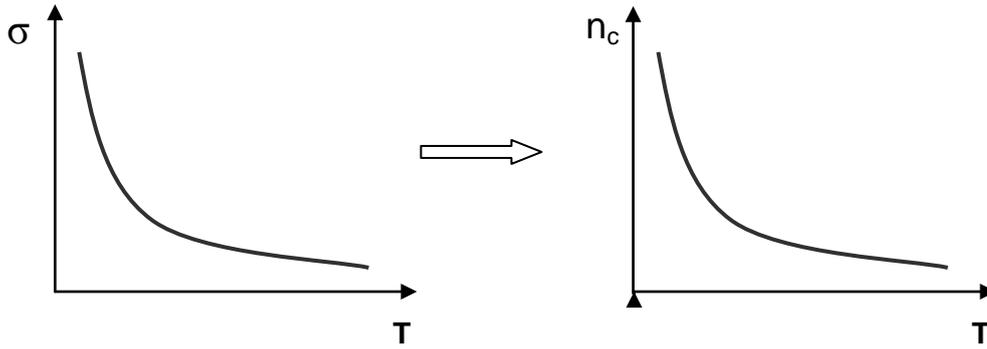
Figure 6.
Dependencies of σ , resp. n_C on temperature T.

The newly-forming cluster becomes stable and growable when overcross the so-called nucleation barrier ΔG_C (corresponding to ΔG_C at critical size n_c) that can be determined from relationships (2), resp. (3) to be:

$$\Delta G_C = \frac{4\gamma^3}{27(\ln \mathscr{S})^2}\sigma^3(T),\qquad (4)$$

Or, with given supersaturation

$$\Delta G_C = const.\,\sigma^3(T).\qquad (5)$$

Consequently, with increasing temperature T the nucleation barrier decreases (as it follows from the Fig.6 and formula (4)). Thus, the boltzmannian probability (1) defining, in fact, a boundary separating unstable and growable states strongly depends on temperature dependent surface energy of cluster.

$$\Pr(n) \approx \exp\left[-\frac{const.\,\sigma^3(T)}{kT}\right].\qquad (6)$$

In other words, the higher temperature T, the higher probability of formation of a new, growable cluster (usually called nucleus [11]).

In standard nucleation theory, the number density of supercritical nuclei formed within unit volume per unit time corresponds to nucleation rate (see, e.g. [12]-[15]), while time-integral of this quantity (integral flux) expresses "intensity" of early stage of the phase transformation and becomes time-independent from a certain time defining incubation time of nucleation [15]. From this moment, intensive growth of a new phase begins and critical (resp. supercritical) clusters present in system dramatically increase their sizes. Moreover, due to change of viscosity (as a consequence of increasing density of solid phase within liquid one!) the mobility of charge careers (Ca^{2+}, reps. OH^- ions) markedly decreases resulting in dramatical increasing of electrical resistivity of hardening cement paste. We relate this moment to incubation time of nucleation. Then, utilizing our measurements of temporal dependency of electrical resistance at various temperatures (but for fixed w/c ratio) we obtain from inflex points of these curves the following influence of temperature on induction period τ_N of nucleation:
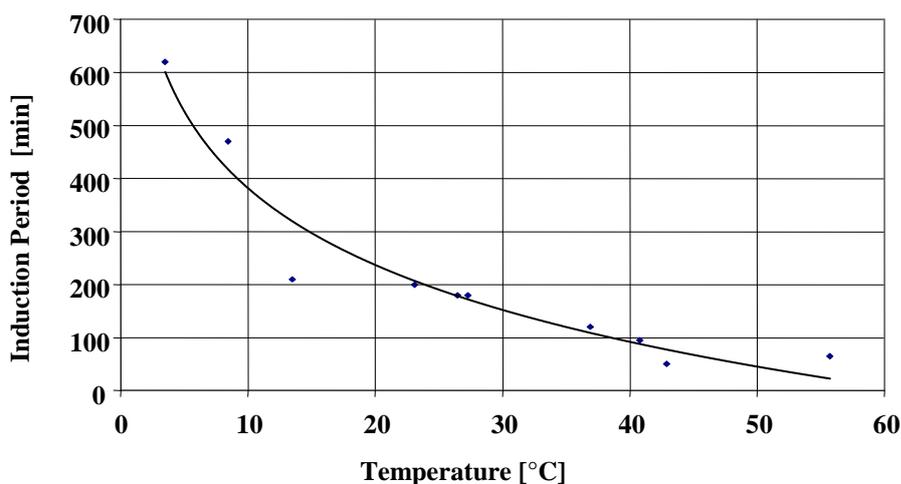
Figure 7.
Temperature dependency of induction period (w/c=0,5).

Summarizing, in terms of temporal behavior of electrical resistance the rate of evolution of a very first stage of solidification (i.e., nucleation) within cementitious materials can be indirectly estimated. The crucial role is played by surface energy of newly-forming cluster which modulates the height of nucleation barrier and separates the unstable and growable regimes of system.

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