



Effect of relative humidity decrease due to self-desiccation on the hydration kinetics of cement



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ABSTRACT

Hydration rate of cement decreases at reduced relative humidity (RH) and hydration virtually ceases below about 80% RH. Until now, this problem has been studied by means of determining the hydration degree only at later ages on hydrated samples continuously stored under fixed, reduced RH, or based on theoretical considerations. Here, the effect of reduced RH on hydration rate was studied in the course of the process during initial days of hydration. Isothermal calorimetry was applied to study the evolution of the heat of hydration in cement pastes with low water-to-binder ratio, either in water-saturated or sealed conditions. In parallel, RH evolution was measured on sealed, companion samples with water-activity stations. The sealed samples show considerably lower rates of hydration when the RH is reduced due to self-desiccation. The coefficient describing the reduction of hydration rate as a function of RH was determined for different water-to-binder ratios and different cements.

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1. Introduction

Hydration of cement slows down at reduced relative humidity (RH) and practically ceases below about 80% RH [1]. This phenomenon is of paramount practical importance for concretes exposed to drying at early ages, or, on the contrary, for cements that need to be stored for longer times without prehydrating. Due to desaturation and the corresponding reduction of the internal RH in the pores of a cementitious material, even though a significant amount of water is still present, hydration may almost come to a halt and the development of material properties may be hampered. This problem was recognized already by Powers [1] and the underlying mechanisms have been extensively analyzed, both experimentally and theoretically [2–5]. Nevertheless, the available experimental data, in particular regarding modern cements and concrete, is still very scarce [5–8].

Whereas providing external curing to the concrete surfaces allows to eliminate the RH reduction and to prolong cement hydration in ordinary concretes, this solution cannot be applied to high-performance concrete (HPC) with low water-to-binder ratio (w/b) and fine fillers or supplementary cementitious materials that densify the microstructure. In such concretes, chemical shrinkage causes desaturation of fine pores and due to formation of capillary menisci the internal RH decreases even without loss of moisture to the environment; this phenomenon is referred to as self-desiccation [9–12]. A further reduction of internal RH by about a couple of % occurs due to reduction of water

activity caused by the ions in the pore solution [9,10,13]. When internal RH decreases, hydration proceeds at slower rates and ultimately reaches a lower degree in such mixtures. This remains true even when external curing water is provided, because during typical curing times of a few days water can penetrate only a couple of mm into HPC with fine microstructure [14–16]. A natural consequence of hydration stopping below 80% RH is that self-desiccation, which is a process driven by hydration, cannot reduce the RH in pores below this level [4]. The approximate limiting level of 75–80% RH will vary depending on the cement composition, since the reactivity of different clinker minerals is expected to show different sensitivity to reduced RH [5]. Jensen [4], based on a thermodynamic analysis, suggested that the reaction of belite is most sensitive to reduced RH. In a further experimental study [2], it was found that the reactions of alite, belite, and tricalcium aluminate stop below 85, 90, and 60% RH, respectively. Similar levels were obtained in the experimental study by Patel et al. [5].

Different mechanisms have been considered responsible for the hindered hydration at reduced RH. According to Powers [1], the mechanism was of purely physical nature—reduced RH corresponds to a partial desaturation of pores, and therefore hydration products cannot form in the absence of water. Jensen suggested in [2] that the mechanism may be related to the kinetics of the hydration process. According to this mechanism, at reduced RH (or similarly at reduced temperature), the length of the induction period of cement hydration increases and therefore the onset of hydration is delayed. Flatt et al. [3] showed based on thermodynamic modeling that ceasing of hydration of alite below 80% RH is due to reduced water activity, caused primarily by the action of capillary tension in pore fluid. The reduced water activity shifts the solubility of alite so that it stays in equilibrium with pore fluid.

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In the experiments performed until now, samples of hydrating cements or clinker minerals were usually exposed to reduced, constant RH and the extent of hydration was determined after a certain exposure time, e.g. [1,2,5]. Such static tests only allow to observe the effect on the final degree of hydration after a certain, usually very long time. This leads to a high level of uncertainty related to the accuracy of experimental methods for determining hydration degree and, together with the limited amount of RH levels studied, does not allow to obtain a finely resolved function of hydration dependence upon RH. A further issue regards modeling of the effect based on such experimental data. In modeling (see e.g. [6,7,17]), a coefficient that reduces the hydration rate based on RH is usually applied. Such approach is based on the implicit assumption that the *hydration rate* depends upon the dynamically changing RH at short time scale (minutes to hours) in the same way as the *hydration extent* depends on the RH that is kept constant over the long period (usually days to several months). In fact, this may not be correct, since the reaction kinetics may also play a role in the process (see [2]).

The alternative method proposed in this paper allows to observe in situ the effect of reduced RH on the kinetics of hydration, while the cement paste samples are continuously measured with isothermal calorimetry. This is possible thanks to comparing the rate of heat liberation of thin cement paste samples (about 1 mm thick) hydrating in two conditions:

- with a layer of water on top (so-called *open system* [18], here also referred to as *saturated*);
- without any additional water on top, where self-desiccation takes place (so-called *closed system*, here also referred to as *dry*).

To account for the continuous RH reduction due to self-desiccation in the *closed* systems, the internal RH is measured on companion sealed samples. This method is similar to the method used by Gerstig and Wadsö [19], who first applied isothermal calorimetry for observing the effect of RH on the hydration rate. In their measurements, however, a reduction of RH was imposed only at certain time points by means of drying the samples directly within the calorimeter with a flow of dry nitrogen gas. In the method proposed here, the reduction of hydration rate takes place continuously only due to self-desiccation and is further referenced to the samples kept under water. Taking advantage of self-desiccation as the mechanism causing RH reduction instead of imposing external drying has the following main advantages: 1) it allows for observing continuously the effect of dynamically changing RH on hydration kinetics and 2) it allows to avoid RH gradients in the sample, which in turn enables using larger samples with resulting better accuracy.

A coefficient, β_{RH} , that can be conveniently used for reducing the hydration rate in the framework of e.g. the equivalent age approach [17] is next determined as a function of internal RH. This coefficient is obtained by comparing the heat evolution rate of the saturated and dry samples at the same equivalent ages, i.e. the ages at which the same cumulative heat was released by the two systems. The tests have been performed on cement pastes prepared with different cements (grey and white ordinary Portland cements with and without silica fume, blast furnace slag cement, and composite cement) and with different w/b in the range 0.16–0.35.

2. Materials and methods

2.1. Raw materials and mixing

Cement paste samples (about 100 ml) were mixed for 2 min in a vacuum mixer. Deionized water was used as mixing water. A polycarboxylate-based superplasticizer was incorporated in the mixing water. The w/b reported refer to the mass of water plus the mass of superplasticizer (excluding the solid content). Where applied, cements were manually premixed with silica fume (Microsilica 968-u by Elkem)

before mixing with water. Mix compositions and cement properties are summarized in Tables 1 and 2, respectively.

2.2. Isothermal calorimetry

Directly after mixing, the cement paste was poured into glass vials with an internal diameter of 24.9 mm. Depending on the type of test (*dry* or *saturated* system), either only cement paste was poured into the vials, or additionally 1 ml of purified water (Milli-Q) was poured over the cement paste layer, respectively. Rigorously speaking, the samples of cement paste without any additional water on top would not exactly correspond to a *closed system* as described in [18], due to the presence of water vapor in the whole glass vial above the thin layer of cement paste. However, at saturation vapor pressure, the total amount of water in the gaseous phase above the sample would be at most about 0.2% of the water contained in the cement paste, which is negligible. The vials were then sealed with a tight rubber cap and placed in an isothermal conduction calorimeter TAM Air (Thermometric) capable of measuring 8 samples in parallel. The temperature in the calorimeter was maintained at 20 ± 0.02 °C.

Different amounts of paste, from 0.5 to 4.5 g, were used in different calorimetry tests. The nominal thicknesses of the samples were estimated by measuring several samples with a caliper after the tests. The small differences in thickness that may occur between different mix compositions with different densities can be considered negligible if one compares them with the variations of thickness within an individual sample. The latter one was resulting from the bottom of the glass sample holders, which was not perfectly flat. Another reason was that the cement paste layer was not perfectly level. The precision of the estimated nominal thicknesses reported here was around ± 0.25 mm.

In addition to the main series of measurements on cement paste with or without purified water, single tests were performed with lime-saturated water and with extracted pore solution. The pore solution was extracted 15 min after mixing from the same w/c 0.30 CEM I paste as used in calorimetry. Extraction was performed with compressed air applied on a sample placed on a 0.45 μ m nylon filter.

The amount of water or other liquid poured on the sample should be possibly small to limit artifacts due to e.g. increased heat capacity of the specimen. On the other hand, a thin water layer should cover the sample over the whole measurement time. No difference in heat evolution between the three different amounts (0.5, 1.0, and 2.0 ml) of water poured over w/b 0.30 CEM I paste could be observed. In all further tests, 1 ml was used, corresponding to a layer of water of thickness of approximately 2 mm. This amount was substantially larger than the chemical shrinkage, which is estimated as ~ 0.2 ml for the 4-mm-thick sample of w/b 0.30 CEM I paste at complete hydration.

Due to external mixing, the initial heat peak could not be measured. All the heat measurements were zeroed at the time of 1 h from mixing. Each curve presented here is the average of two samples measured simultaneously in separate cells of the calorimeter, prepared from the same mixing. The results were logged at 1 min intervals. The difference in cumulative heat release between duplicate samples at the end of each test (about 7 d) was on average below 1 J/g and it never exceeded 5 J/g. All results are given per mass of binder (considered as the sum of cement, fillers and silica fume, where applied).

2.3. RH measurements

The RH evolution was measured with AW-DIO and HC2-AW water activity stations by Rotronic. The nominal trueness of the sensors was 1.0 and 0.8% RH, respectively. However, the actual trueness was improved by means of calibrating the sensors before and after each measurement with 4 saturated salt solutions with equilibrium RH in the range 75–98% RH. Fresh cement pastes after mixing were poured into hermetic plastic containers. At different ages, from few hours up to 2 d, the pastes were crushed into pieces of 2–5 mm and enclosed

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