Modeling the coupled effects of temperature and fineness of Portland cement on the hydration kinetics in cement paste

Pipat Termkhajornkit *, Rémi Barbarulo

Lafarge Research Centre, 95 Rue de Montmurier 38290 St-Quentin-Fallavier, France

ABSTRACT

This paper revisits the coupled impacts of fineness and temperature on the kinetics of Portland cement hydration. The approach consists in i) modeling the impact of fineness on cement dissolution through the hypothesis that the surface dissolution rate of cement particles is independent of their size, in order to, in a second step, ii) model the impact of temperature on the kinetics of cement dissolution. The analysis of the experimental results shows that the effect of cement fineness on the hydration kinetics can be captured by a simple hypothesis: for any age, the reacted thickness of cement grains can be considered independent of the initial cement particle size. In addition, the analysis of the results at different temperatures shows that a constant activation energy can account for the effect of temperature on the hydration kinetics, with an Arrhenius equation applied to the kinetics of surface dissolution. The results from the model give a good agreement with the experimental results in a significant number of combinations (different Portland cements, water/cement ratio from 0.5 to 0.6, cement Blaine fineness from 3500 to 6600 cm^2/g, temperature histories between 20 and 60 °C).

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Increasing the rate of hydration of cement is one of the most common ways (with reducing the water/cement ratio) to increase the rate of development of the mechanical properties of concrete. Both temperature and cement fineness change the kinetics of cement hydration. For instance, in the precast concrete industry, thermal treatment is often used to accelerate cement hydration and consequently accelerate compressive strength development — thus increasing the productivity. On the other side, for ready-mix applications, low temperature can lead to low rates of strength development. Another way to increase productivity is to use a more reactive (e.g. finer) cement. Both factors (fineness and temperature) have been studied extensively, but rarely within a same study.

The originality of this work is to propose a simple model that can estimate simultaneously the effects of both temperature and fineness on degree of hydration. The model is based on simple geometrical and physical considerations. It was evaluated on the basis of specific experiments performed on cement pastes, designed to explore the impact of the main parameters considered: cement fineness, temperature history and water/cement ratio.

1.1. Effect of temperature on the kinetics of hydration

The most obvious impact of temperature on concrete properties is the fact that a higher temperature increases early compressive strength and lowers long term compressive strength. This phenomenon was the reason for many studies on the impact of temperature on cement hydration [1–6].

It is largely admitted that at early ages, temperature increases the rate of cement hydration [1,2,4,7–12], justified by the fact that temperature induces faster kinetics of the chemical phenomena (faster dissolution, nucleation or precipitation rates) and faster diffusion through the hydrates assemblage around unreacted cement grains. Many authors have used the Arrhenius equation in order to capture the effect of temperature on the kinetics of hydration; this modeling approach will be detailed further in this paper (Section 2.1).

At later ages, the lower final compressive strength of concretes cured at higher temperature has led some authors to propose that the kinetics of hydration was slowing down after the initial acceleration [1,11,13]. The denser layer of hydration products observed at higher temperature [14,15] or an increased polymerization rate of C–S–H [16] was considered as the reason for a slow down of the diffusion process. However, it is quite largely admitted today that final degrees of hydration are similar at late ages, regardless of temperature of hydration [4,10–12], while the observed lower final strength for concretes cured at higher temperature is induced by a coarser microstructure with denser hydrate layers around the anhydrous products [1,4,8,9,17].

* Corresponding author. Tel.: +33 4 74 82 83 87; fax: +33 4 74 82 80 11.
E-mail address: pipat.termkhajornkit@lafarge.com (P. Termkhajornkit).

1.2. Effect of cement fineness on the kinetics of hydration

The impact of fineness on cement hydration is more straightforward. Fineness of cement is known to increase significantly the compressive strength, particularly at early ages, and to a lesser extent at later ages [18,19]. This acceleration of strength development is considered to be the result of a faster hydration of cement [20] due to a higher specific surface. The impact of fineness on Portland cement hydration has been studied intensively (e.g. [19–24]) and modeled in many ways [20,25–35].

However, not many experimental and modeling studies focusing on the coupled effects of cement fineness and temperature on cement hydration can be found. The present study was designed to evaluate and model the simultaneous effects of fineness and temperature.

2. Theoretical considerations

2.1. Modeling impact of temperature on hydration kinetics

The impact of temperature on the kinetics of cement hydration is often modeled by an Arrhenius equation, which can be written in a simplified form as:

$$\left(\frac{d\alpha}{dt}\right)^{T=T_2}_{\alpha=\alpha_0} = \left(\frac{d\alpha}{dt}\right)^{T=T_1}_{\alpha=\alpha_0} \times \exp\left\{-\frac{E_a}{R} \times \left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right\} \quad (1)$$

where α is the degree of hydration, E_a is the apparent activation energy (J/mol), R is the gas constant (8.31243 J.mol^{-1}.K^{-1}) and T is the absolute temperature (Kelvin). It should be noted that here the degree of hydration and the apparent activation energy E_a integrate all effects of temperature on the processes of cement hydration, including chemical reactions, diffusion of ions and water, plus restrictions such as space limitation, lack of water, etc.

Eq. (1) implies that knowing the hydration kinetics $\left(\frac{d\alpha}{dt}\right)^{T=T_1}_{\alpha=\alpha_0}$ at degree of hydration α_0 and temperature $T=T_1$, one can compute the hydration kinetics $\left(\frac{d\alpha}{dt}\right)^{T=T_2}_{\alpha=\alpha_0}$ at temperature $T=T_2$, for degree of hydration α_0. The apparent activation energy E_a should be independent of temperature, but is often considered to be dependant on the degree of hydration α in order to fit the experimental data (e.g. [11,36,37]). Some authors report that E_a as defined by Eq. (1) also depends on cement mineralogy and fineness (e.g. [38,39]).

It is worth noting that the Arrhenius equation can be used to estimate the impact of temperature on the rate of a given chemical reaction [40]. Cement hydration involves many different mechanisms (dissolution of cement phases, precipitation of hydrates, diffusion of ions and water) and by such the impact of temperature on the kinetics should not be modeled by a simple Arrhenius equation. But it is rarely mentioned that one of the major reasons why this should not be done is because cement is a powder with a broad particle size distribution [26]. Indeed, as will be demonstrated in Section 2.4, if the surface dissolution rate follows an Arrhenius law, the overall dissolution rate (as measured through degree of hydration) may not follow an Arrhenius law.

2.2. Introduction of the 'uniform reacted thickness' concept

Blaine surface area is probably the simplest and the most classical way to characterize cement fineness. However, such a simple parameter is inadequate for a precise evaluation of the influence of fineness on the degree of hydration. Indeed, a parameter representative only of the initial surface area (such as Blaine or BET) can account only for the very first moments of hydration; the impact of the initial surface area on the kinetics of cement is not relevant anymore once the reactive surface has started decreasing. Similarly, mean diameter such as D50 cannot capture how dissolution affects the reactive surface area. More sophisticated models have also been proposed, that take into account the particle size

distribution of cement and in some cases the mineralogy of cement grains [31–34].

In the present work we consider an intermediate approach that takes into account the whole particle size distribution of cement, but with simple hypotheses for what concerns the mechanisms of cement dissolution. Let us consider a mineral which dissolves, at instant t, with a rate $k(t)$ expressed in quantity of matter per unit of surface area and unit of time, so that the quantity of matter dissolved during a small time increment dt is:

$$dn = k(t).S(t).dt \quad (2)$$

where $S(t)$ is the surface area of the mineral at time t. Note that no hypothesis is made concerning the mechanisms that determine the dissolution rate $k(t)$. The variation of volume of the dissolving mineral during time dt is:

$$dV = -V^m.dn = -V^m.k(t).S(t).dt \quad (3)$$

where V^m is the molar volume of the mineral considered.

Now, let us consider a spherical particle of the said mineral, of initial radius $r(0)$. At time t, the radius of the particle $r(t)$ varies of value dr during time dt, and its surface area is $S(t)$, so that $dV = S(t).dr$. By combining this equality with equation Eq. (3), we get:

$$dr = -V^m.k(t).dt. \quad (4)$$

By integrating the previous equation over time, the radius of the particle at time t is given by:

$$r(t) = r(0) - V^m \int_{\theta=0}^{\theta=t} k(\theta).d\theta. \quad (5)$$

We now introduce the notion of 'dissolved depth' or 'reacted thickness' $h(t) = r(0) - r(t)$, i.e. the distance of the dissolving surface from the original surface of the particle, that can be expressed as:

$$h(t) = r(0) - r(t) = V^m \int_{\theta=0}^{\theta=t} k(\theta).d\theta. \quad (6)$$

One can see that, if the dissolution rate $k(t)$ does not depend on the radius of the particle, the right-hand side of equation Eq. (6) is not a function of the initial particle size. Consequently, the reacted thickness at time t should be identical whatever the initial particle size. This hypothesis, referred to as 'uniform reacted thickness' concept in this study, and illustrated in Fig. 1, will be discussed later on in this paper. Note that we also assume that the cement particles are spherical and monophasic, which are clear oversimplifications of the complexity of cement nature.
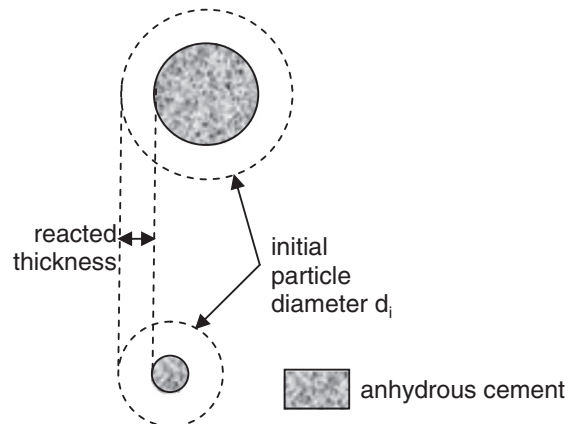

Fig. 1. Schematic representation of the 'uniform reacted thickness' concept.