



# Hydration kinetics modeling of Portland cement considering the effects of curing temperature and applied pressure

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## ABSTRACT

A hydration kinetics model for Portland cement is formulated based on thermodynamics of multiphase porous media. The mechanism of cement hydration is discussed based on literature review. The model is then developed considering the effects of chemical composition and fineness of cement, water–cement ratio, curing temperature and applied pressure. The ultimate degree of hydration of Portland cement is also analyzed and a corresponding formula is established. The model is calibrated against the experimental data for eight different Portland cements. Simple relations between the model parameters and cement composition are obtained and used to predict hydration kinetics. The model is used to reproduce experimental results on hydration kinetics, adiabatic temperature rise, and chemical shrinkage of different cement pastes. The comparisons between the model reproductions and the different experimental results demonstrate the applicability of the proposed model, especially for cement hydration at elevated temperature and high pressure.

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## 1. Introduction

The hydration of cement and the accompanying phenomena such as heat generation, strength development and shrinkage are the results of interrelated chemical, physical and mechanical processes. A thorough understanding of these processes is a critical prerequisite for modeling hydration kinetics of cementitious materials.

The advances of computer technology made it possible for a branch of computational materials science to develop rapidly in the past twenty years, i.e., the computer modeling of hydration and microstructure development of concrete. Noteworthy studies include those of Jennings and Johnson [1], Bentz and Garboczi [2], van Breugel [3], Navi and Pignat [4], and Maekawa et al. [5]. Among these, the NIST model, referred to as CEMHYD3D [6], and the HYMOSTRUC model [3] appear to be the most advanced and widely used ones. These models attempt to simulate cement hydration and microstructure formation on the elementary level of cement particles, which is the most rational way, as long as the chemical, physical and mechanical characteristics of cement hydration are properly taken into account.

However, there exist certain applications for which simpler mathematical models describing and quantifying hydration kinetics are necessary. In fact, numerous attempts have been undertaken with that objective and many such simplified formulations can be found in

the literature, e.g., Byfors [7], Knudsen [8], Freiesleben Hansen and Pedersen [9], Basma et al. [10], Nakamura et al. [11], Cervera et al. [12], Schindler and Folliard [13], and Bentz [14]. In contrast to the aforementioned microscopic models, most of these simplified models are empirical in nature, based on experimental observations of macroscopic phenomena, and they capture the effects of curing temperature, water–cement ratio, fineness, particle size distribution and chemical composition of cement with different degrees of accuracy. The range of curing temperature in these models is usually small and does not exceed 60 °C, and none of them include the effect of applied pressure. However, elevated temperatures and high pressures are frequently encountered in oil wells where they must be addressed.

In this study, a hydration kinetics model is formulated based on the thermodynamics of multiphase porous media, which was first proposed by Ulm and Coussy [15]. The hardening cement paste is known to be a multiphase porous material and the thermodynamics theory of [15] is an ideal framework to model hydration kinetics. Cervera et al. [12,16] proposed an equation to describe hydration kinetics using this theory, but it needs to be elaborated and reformulated to take into account the experimental observations of cement hydration, especially curing temperature and applied hydrostatic pressure. This paper presents the theoretical formulation of a new model. The model parameters are calibrated and related to the chemical composition of cement through simple but explicit equations; the model is then used to predict the experimental results of different investigators, including those on hydration kinetics, adiabatic temperature rise, and chemical shrinkage of cement pastes.

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## 2. Literature survey on hydration of Portland cement

Before a mathematical model can be developed that properly considers the various influencing factors, the known facts of Portland cement hydration should be thoroughly surveyed. A comprehensive study on cement hydration was conducted by van Breugel [3]. However, during the past decades, many new findings, mostly experimental, regarding cement hydration have been reported. Therefore, the most recent findings and their relevance to understand Portland cement hydration will be addressed herein.

### 2.1. Influence of chemical composition of cement

The composition of cement is the most important influencing factor of all. There exist two forms in which to describe the composition of cement, i.e. the oxide composition and the chemical composition. The latter is usually determined using the compound stoichiometries and the values of the former. The Bogue calculation [17] is the most frequently quoted mathematical procedure among such indirect methods and thus is used in the present study.

Experimental results show that the four major clinker phases of cement, viz.  $C_3S$ ,  $C_2S$ ,  $C_3A$  and  $C_4AF$  have different reaction rates with water [18–20]. It is well known that  $C_3A$  reacts the fastest, followed by  $C_3S$  and the other two. However, whether the individual constituent phases hydrate independently from one another or at equal fraction rates is still not resolved [3]. Because of different reaction rates of the clinker phases and their interactions, it is generally accepted that the so-called degree of hydration of cement is just an overall and approximate measure. Due to the difficulty of identifying and simulating the complicated interactions, the overall degree of hydration, denoted as  $\alpha$ , is still widely used [1–16] and will be employed in this study.

### 2.2. Influence of water–cement ratio

The water–cement ratio,  $\frac{w}{c}$ , also influences hydration kinetics. Experimental results have shown that a higher water–cement ratio leads to a higher hydration rate after the middle period of hydration, but only has a small effect on the hydration rate in the early stage [21,22]. The water–cement ratio also determines the ultimate degree of hydration  $\alpha_u$ . Theoretically, a water–cement ratio of about 0.4 is sufficient for the complete hydration of cement (i.e.  $\alpha_u = 1.0$ ). In other words, a water–cement ratio higher than 0.4 will lead to full hydration given enough time. However, cement hydration is retarded at low internal relative humidity, and the theoretical water–cement ratio of about 0.4 is not sufficient for full hydration [23]. The hydration products around the anhydrous cement particles prevent further hydration if there is insufficient free water in the macro-pores. From experimental observations, the relationship between the ultimate degree of hydration  $\alpha_u$  and the water–cement ratio can be described by a hyperbola with  $\alpha_u \leq 1.0$ . Mills [24] conducted a series of tests and derived the following equation for  $\alpha_u$ ,

$$\alpha_u = \frac{1.031 \frac{w}{c}}{0.194 + \frac{w}{c}} \leq 1.0 \quad (1)$$

This equation has been used frequently in hydration kinetics modeling [13]. However, it does not consider the effects of cement fineness and curing temperature and may underestimate the ultimate degree of hydration in some cases.

### 2.3. Influence of fineness of cement

The fact that fineness of cement influences the ultimate degree of hydration  $\alpha_u$  as well as the hydration rate has been observed in experiments and numerical simulations [25,26]. The finer the cement particles, the higher  $\alpha_u$ , and the higher the hydration rate. However,

Bentz and Haecker [26] also found that at low water–cement ratios, the influence of cement fineness on  $\alpha_u$  diminishes. A finer cement, or cement with a larger surface area, provides a larger contact area with water and hence causes a higher hydration rate. Also, at the same degree of hydration, a larger surface area corresponds to a smaller thickness of hydration products around the anhydrous cement particles, which increases the ultimate degree of hydration. Apart from fineness, the particle size distribution of cement also influences the hydration rate [3,8,27,28].

### 2.4. Influence of curing temperature

The effects of curing temperature on hydration kinetics have been shown to be twofold. On the one hand, the reaction rate  $\alpha$  increases with the increase in temperature [29–31]. On the other hand, the density of hydration products at higher temperature is higher [32], which slows down the permeation of free water through the hydration products. Therefore, during the late period, the hydration rate is lower at elevated temperature and the ultimate degree of hydration may thus also be lower. Based on the experimental results in [32], van Breugel [3] proposed the following equation for the volume ratio between hydration products and the reacted cement at temperature  $T$  [K]:

$$v(T) = \frac{\text{Volume of Hydration Products at } T}{\text{Volume of Reacted Cement at } T} = v_{293} \exp[-28 \times 10^{-6}(T - 293)^2] \quad (2)$$

Generally,  $v_{293} \approx 2.2$  according to Powers and Brownyard [33].

It should be pointed out that the available experimental results regarding the effects of elevated curing temperature on hydration kinetics are still very limited. Very few publications can be found that consider curing temperatures higher than 60 °C (333 K). Chenevert and Shrestha [34] and Hills et al. [35] are the two studies worth mentioning.

An issue related to the effects of curing temperature is the apparent activation energy  $E_a$ . Because cement is a mixture of different chemical components rather than a pure material, its activation energy is merely phenomenological and can only be referred to as the apparent one. Different and conflicting conclusions regarding the value of the apparent activation energy have been drawn based on experiments and theoretical analysis. Xiong and van Breugel [3,36] argued that  $E_a$  is a function of chemical composition of cement, curing temperature and the degree of hydration. Freiesleben Hansen and Pedersen [37], on the other hand, suggested that  $E_a$  is only a function of curing temperature. Schindler [38] proposed an equation for  $E_a$  that considers the chemical composition and fineness of cement. Among these studies, the work of [38] is found to be most convincing because of its applicability to a wide range of cements and simplicity.

### 2.5. Influence of applied pressure

The experiments to investigate the influence of applied pressure on hydration kinetics are even scarcer than those involving curing temperatures. Roy et al. [39,40] studied strength development of cement pastes at high temperature and high pressure, but did not address hydration kinetics. Bresson et al. [41] conducted hydration tests on  $C_3S$  subject to hydrostatic pressure up to 85 MPa and found that a higher pressure increases hydration rate. Zhou and Beaudoin [42] also found that applied hydrostatic pressure increases the hydration rate of Portland cement, but has only a negligible effect on the pore structure of hydration products when different cement pastes at similar degrees of hydration are compared. The finding of [42] is important since it implies that the density of the hydration products is not considerably affected by the applied hydrostatic pressure, at least not up to 6.8 MPa, which is the pressure they used.

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