Influence of water-to-cement ratio on hydration kinetics: Simple models based on spatial considerations

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Abstract

Based on simple spatial considerations, models to describe the hydration kinetics of portland cement are developed and compared to existing experimental data, particularly in terms of the influence of the starting water-to-cement ratio (w/c) on hydration rates. The conceptual basis for the models is to relate the instantaneous hydration rate to local probabilities for the dissolution and precipitation of the cement phases. In the simplest model, hydration kinetics are strictly a function of the volume fraction of local (global) water-filled porosity, as computed based on Power's model for cement hydration. While this simplest model is inadequate to quantitatively describe the observed hydration behavior in real cement pastes with various w/c, a more complicated version of the model that considers both the water-filled porosity and the unhydrated cement volume fractions appears to provide an adequate description. Finally, the models are extended to consider the influence of the replacement of a portion of the cement by an inert filler on the resulting hydration kinetics.
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1. Introduction

Cement hydration is recognized as a complex physico-chemical process and many attempts have been made to describe and quantify the kinetics of hydration. Many of the developed models explicitly consider the effects of cement particle size distribution (PSD) and curing temperature on kinetics. However, considerably less consideration has been given to the influence of the starting water-to-cement mass ratio (w/c) on the developing hydration. From a practical viewpoint, predicting the change in degree of hydration at specific points in time due to a change in the starting w/c would be extremely useful to field engineers, researchers, and ready-mix concrete producers.

Computer models have definitively demonstrated the importance of spatial considerations in influencing hydra-tion kinetics [1,2]. An example would be the influence of w/c on achieved degrees of hydration. At ages of 1 day and beyond, higher w/c cement pastes generally exhibit a higher degree of hydration than lower w/c pastes [2]. At least partially, this is due to the fact that in a higher w/c paste, there is more space available for the dissolution of reactants and the nucleation/precipitation of hydration products. More specifically, according to Power's model for cement hydration [3], for w/c less than about 0.36, there is insufficient capillary pore space available for the complete hydration of the cement. In this case, the maximum achievable degree of hydration can be estimated as $(w/c)/0.36$. This in turn implies that at later ages, pastes with $w/c > 0.36$ will achieve a higher degree of hydration (e.g., 1.0) than those with $w/c < 0.36$, and the ratio of the higher w/c paste degree of hydration to that of the lower one will approach some asymptotic value greater than 100%. For example, in comparing the relative degree of hydration of a $w/c = 0.4$ cement paste to a $w/c = 0.3$ paste, both under saturated curing conditions, one should find an

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asymptotic value of (1.0/(0.3/0.36))*100=120%. Conversely, pastes with two different $w/c > 0.36$ cured under saturated conditions can both achieve a degree of hydration approaching 1.0 at infinite time, and thus the ratio of their degrees of hydration should asymptote to a value of 100%. These same spatial considerations will surely influence the ratios of degrees of hydration at intermediate ages.

In this paper, simple models for the kinetics of cement hydration based on spatial considerations will be presented and compared to available experimental data. The basic approach taken is to consider the hydration kinetics from a local perspective, but using global parameters. The probability for any given "unit" of cement within the cement paste volume to react is related to an instantaneous hydration rate. The resulting differential equations are then solved to yield functions that represent the degree of cement hydration vs. time, $\alpha(t)$. Solutions to these equations are graphically compared to experimental data, both in terms of individual cumulative degree of hydration vs. time curves and in terms of the influence of w/c on achieved hydration.

2. Models

2.1. Capillary porosity and unhydrated cement phase fractions

The models to be presented in this section depend critically on the volume fractions of water-filled and total capillary porosity ($\phi_W(t)$ and $\phi_T(t)$) and unhydrated cement ($\gamma(t)$), as a function of time, t. Based on Power's model for cement hydration, for an ordinary portland cement paste, these quantities are given by [3,4]:

$$\phi_W(t) = \frac{\rho_{cem}(w/c) - (f_{exp} + \rho_{cem}CS)\alpha}{1 + \rho_{cem}(w/c)} \quad (1)$$

$$\phi_T(t) = \frac{\rho_{cem}(w/c) - f_{exp}\alpha}{1 + \rho_{cem}(w/c)} \quad (2)$$

$$\gamma(t) = \frac{1 - \alpha}{1 + \rho_{cem}(w/c)} \quad (3)$$

where (w/c) is the water-to-cement mass ratio, α is the degree of hydration (reacted fraction) of the cement at time t, ρ_{cem} is the specific gravity of cement (here taken to be 3.2), f_{exp} is the volumetric expansion coefficient for the "solid" cement hydration products relative to the cement reacted (here taken to be (2.15−1)=1.15) [2,4], CS is the chemical shrinkage per gram of cement (here taken to be 0.07 mL/g), and a density for water of 1.0 g/cm³ has been assumed. The $\rho_{cem}CS\alpha/(1 + \rho_{cem}(w/c))$ term in Eq. (1) represents the empty porosity created under sealed curing conditions by the chemical shrinkage occurring during hydration. Under saturated curing conditions, the chemical shrinkage is assumed to be exactly compensated for by the

imbibition of external curing water (i.e., CS=0), and the total and water-filled porosities are thus equivalent.

2.2. Simple models for hydration kinetics

Most models for cement hydration kinetics start at the particle level and derive rate equations for an individual particle as a function of its radius [for example [1,5–7]]. This derivation is then often extended to considering a complete realistic PSD. Here, a different approach is taken conceptually. Since all hydration products must form in the available water-filled porosity, it is first assumed that the hydration rate is simply proportional to the volume fraction of this water-filled porosity (first-order "physical" kinetics):

$$\frac{\partial \alpha}{\partial t} = k_1 \phi_W(t) \quad (4)$$

where k_1 is analogous to a first-order rate constant and will vary with the specific cement composition, PSD, curing temperature, etc. In this first model, the hydration rate is dependent only on the space available for the deposition of hydration products and not even on the amount of cement present in the hydrating system. It is equivalent to assuming that the local probability of dissolution (or precipitation) of a cement compound is directly proportional to the local (and global) water-filled porosity. Substituting Eq. (1) into Eq. (4), the result is easily integrated and solved with the boundary condition that $\alpha(0)=0$ to yield:

$$\alpha(t) = \text{Min}\left\{ 1, \frac{\rho_{cem}(w/c)}{(f_{exp} + \rho_{cem}CS)} \right.$$
$$\left. \times \left[1. - \exp\left(\frac{-(f_{exp} + \rho_{cem}CS)k_1 t}{1 + \rho_{cem}(w/c)} \right) \right] \right\} \quad (5)$$

The minimum function has been added to Eq. (5) to assure that the degree of hydration of the cement does not exceed 1, a physical impossibility. Although derived from a different perspective, Eq. (5) is similar in form to kinetics equations often derived considering nucleation and growth kinetics for cement hydration (so-called Avrami behavior) [8]. In the "Avrami" form, the t (time) term in Eq. (5) is often raised to a power n and an induction time t_i is often subtracted from the t term. Substituting the various parameter values into Eq. (5), the dependence of hydration rates on w/c can be easily computed. Eq. (5) can be applied to both saturated and sealed curing conditions, using values for CS of 0.0 and 0.07 (or the equivalent chemical shrinkage determined for a specific cement), respectively.

At the next level of complexity, one can make an analogy to a bimolecular-type reaction for cement hydration, where the hydration rate has a first-order dependence on both the volume fractions of available water-filled porosity and available unhydrated cement. Based on an analogy to the sol–gel process in producing ceramics, Wojcik et al. have presented such an equation where the hydration rate of the

binder components is a function of both the binder component and water *molar concentrations* [9]. Here, instead, it is assumed that the local probability of reaction of the cement is linearly proportional to both the available water-filled porosity and the available unhydrated cement *volume fractions*. In terms of these phase fractions, one thus has:

$$\frac{\partial \alpha}{\partial t} = k_2 \phi_W(t)\gamma(t) \tag{6}$$

Substituting Eqs. (1) and (3) into Eq. (6), the result can still be solved analytically as [10]:

$$\alpha(t) = \frac{p\{\exp[R(1-p)t] - 1\}}{\{\exp[R(1-p)t] - p\}} \tag{7}$$

with $p = \rho_{cem}(w/c)/(f_{exp} + \rho_{cem}CS)$ and $R = k_2(f_{exp} + \rho_{cem}CS)/[1 + \rho_{cem}(w/c)]^2$. For the special case where $p = 1$, application of L'Hopital's rule gives the solution as [10]: $\alpha(t) = Rt/(Rt + 1)$.

Eq. (7) should be directly applicable to saturated systems, with $CS = 0$. For sealed curing conditions, an additional complication may be that the creation of empty porosity may effectively "inactivate" a portion of the unhydrated cement (surfaces) [11], as well as reducing the amount of water-filled capillary porosity (e.g., $CS = 0.07$). To a first approximation, the fraction of *active* unhydrated cement could be estimated as the total fraction of unhydrated cement multiplied by the ratio of water-filled to total porosity. In this case, Eq. (6) would be extended to:

$$\frac{\partial \alpha}{\partial t} = k_3 \phi_W(t)\gamma(t)\frac{\phi_W(t)}{\phi_T(t)} \tag{8}$$

When Eqs. (1), (2), and (3) are substituted into Eq. (8), upon reduction one obtains an equation of the form:

$$\frac{\partial \alpha}{\partial t} = A\frac{(B - \alpha)^2(1 - \alpha)}{C - \alpha} \tag{9}$$

with

$$A = \frac{k_3(f_{exp} + \rho_{cem}CS)^2}{f_{exp}[1 + \rho_{cem}(w/c)]^2}$$

$$B = \frac{\rho_{cem}}{f_{exp} + \rho_{cem}CS}\left(\frac{w}{c}\right)$$

$$C = \frac{\rho_{cem}}{f_{exp}}\left(\frac{w}{c}\right)$$

While Eq. (9) is solvable in an analytical fashion only for very limited cases such as $C = 1$, it can be solved numerically using a graphical symbolic manipulation package.

The models developed above (Eqs. (5), (7), and (9)) will be evaluated in comparison to data sets available from the literature and measured recently at NIST. Two types of comparisons will be presented, a direct comparison of the $\alpha(t)$ vs. t behavior for a set of two w/c values for a specific

cement and a comparison of the predicted dependence of degree of hydration on w/c to the experimentally observed trends for a variety of cements. These comparisons will be conducted for both saturated and sealed curing conditions.

3. Experiments

Cement and Concrete Reference Laboratory portland cement proficiency sample 152 [12], issued in January of 2004, was used to assess the hydration rates of cement pastes cured under saturated and sealed conditions. Portland cement pastes with $w/c = 0.35$ and $w/c = 0.45$ were prepared by mixing the water and cement in a temperature-controlled high speed blender for several minutes at 20 °C. For the water-to-solids mass ratio (w/s) of 0.45, cements were also blended with either a fine or a coarse limestone powder replacing 20% of the cement by mass. The fine and coarse limestone were obtained by classifying a commercially available material with a cutoff diameter of approximately 30 μm [13]. Based on its measured loss on ignition, the limestone powder was estimated to be 97% $CaCO_3$. Wafers (about 3 g to 5 g) of cement paste were placed in small capped plastic vials and cured under either saturated (water ponded on top) or sealed conditions at 20 °C. At ages of (1, 3, 7, 28, and 92 days), specimens were removed from their vials, crushed to a fine powder, flushed with methanol, and divided between two crucibles. The non-evaporable water content (w_n) of each crucible sample was determined as the mass loss between 105 °C and 1000 °C divided by the mass of the ignited sample, corrected for the loss-on-ignition of the unhydrated cement (or of the unhydrated cement blended with limestone). Previously, the expanded uncertainty in the calculated w_n has been estimated to be 0.001 g/g cement, assuming a coverage factor of 2 [2]. w_n values were converted to estimated degrees of hydration based on the calculated Bogue composition of the cement and published coefficients for the non-evaporable water contents of the various cement clinker phases [14]. Further experimental data on the influence of w/c on the degree of hydration of cement pastes was taken from the literature [2,4,15–17].

4. Results and discussion

Fig. 1 presents the experimental data along with the model results for the simplest model based on Eq. (5). The source of the experimental data is indicated by either the last name of the first author on the corresponding reference [4,15–17] or by the proficiency sample cement number for CCRL proficiency sample cements C116 [2,18] and C152 [12]. The value of k_1 was chosen to provide a reasonable agreement to the experimentally measured degrees of hydration for the $w/c = 0.35$ and $w/c = 0.45$ cement 152 pastes at an age of 7 days. It is observed that this simplest
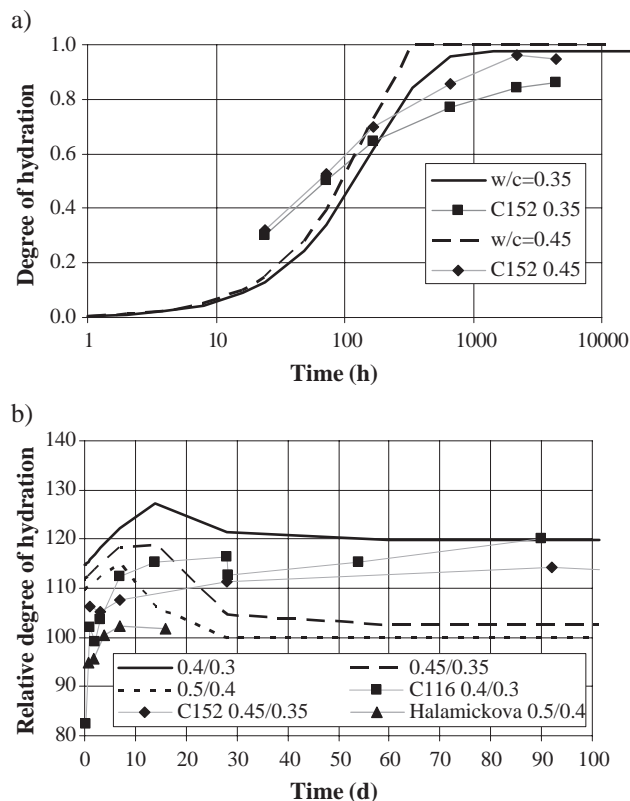
a)

b)

Fig. 1. Predicted (a) degree of hydration vs. time and (b) relative degree of hydration vs. time for kinetics model based on Eq. (5) for saturated curing conditions with $k_1=0.011$ h^{-1}. Dark lines (solid, dotted, and dashed) represent model results and symbols connected by grey lines represent experimental data. In panel (b), legend indicates the two w/c for which the ratio of their degrees of hydration is being determined.

model underpredicts the early hydration rate, overpredicts the later age hydration rate, and only qualitatively captures the relative degree of hydration trends in Fig. 1b. The fits are slightly better for the case of sealed curing, as shown in Fig. 2, but still far from adequate. Relating the hydration kinetics only to the volume fraction of available porosity, while providing a general indication of the influence of w/c on degree of hydration, does not provide an adequate quantitative description of the available experimental data.

However, when the kinetics models are extended to include both the volume fractions of available water-filled porosity and unhydrated cement, a significant improvement between model predictions and experimental data is observed. Fig. 3 shows the results for the case of saturated curing conditions utilizing the model based on Eqs. (6) and (7). Now, the agreement between model and experimental degree of hydration data for cement 152 is much more reasonable and the measured relative degrees of hydration for various w/c pairs are captured adequately by the model predictions, as shown in Fig. 3b. Basing the hydration kinetics on a bimolecular basis that involves both of the reactants (cement and water) results in the simple derivation of a model for hydration kinetics that reasonably represents the observed data.

Eqs. (6) and (7) were also applied to the case of sealed curing (results not shown), but a better fit to the available experimental data for this curing condition was obtained by the application of the hydration kinetics model based on Eqs. (8) and (9). The model predictions and experimental results for this case are provided in Fig. 4. With the most complicated of the three models, a quite reasonable agreement with experimental data is observed. But, it should be noted that each of the three models described by Eqs. (5)–(9) is based on only one free parameter (the rate constant k_i). This can be contrasted against other models currently available in the literature where as many as six free "fitting" parameters may be employed [19]. In the models presented here, the parameter k_i will vary with cement composition, PSD, and curing temperature, so that a calibration will be required to obtain the best fit for each particular cement and curing temperature. However, when determining the relative degrees of hydration, such as those shown in Fig. 4b, etc., the model results are relatively insensitive to the chosen value of k_i. For this reason, the model predictions are observed to adequately fit experimental data obtained for different cements [2,4,15–17]. Thus, the model predictions in Figs. 3b and 4b could be used to predict
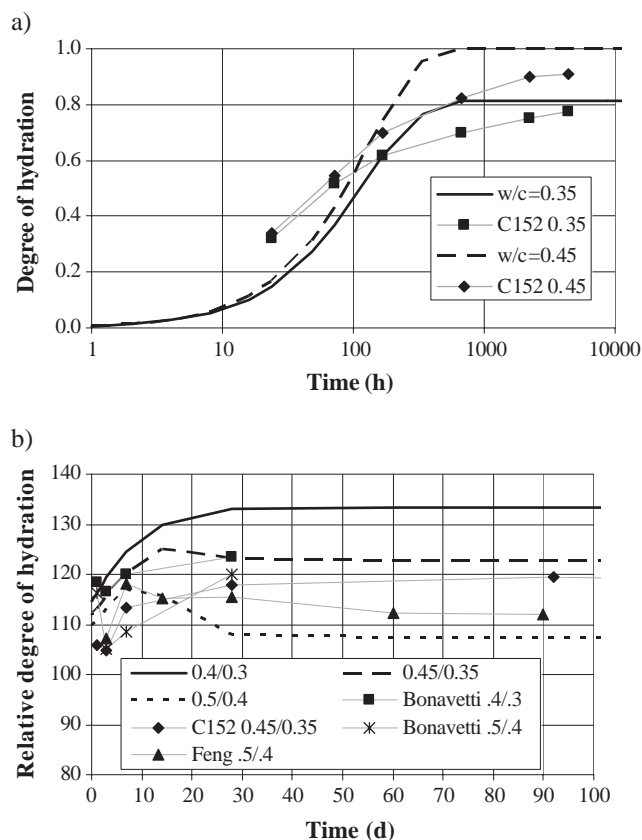
a)

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Fig. 2. Predicted (a) degree of hydration vs. time and (b) relative degree of hydration vs. time for kinetics model based on Eq. (5) for sealed curing conditions with $k_1=0.013$ h^{-1}.
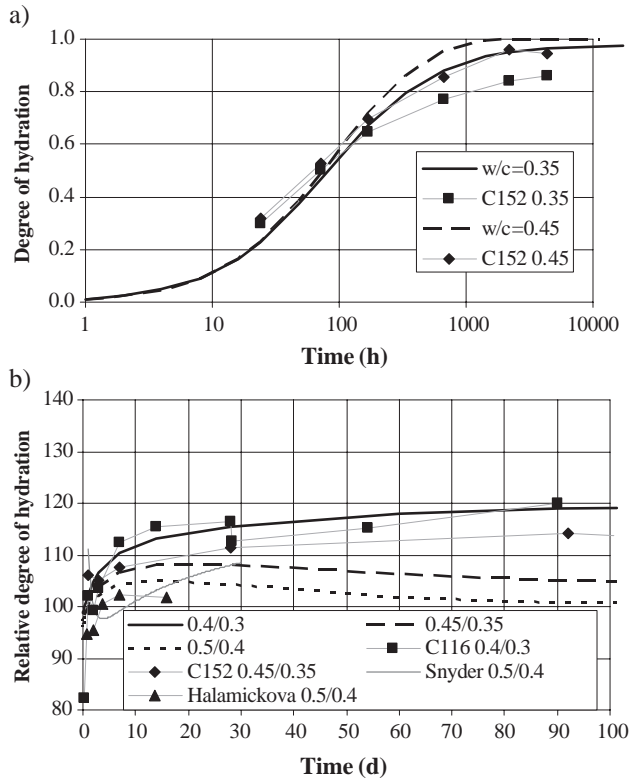
a)

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Fig. 3. Predicted (a) degree of hydration vs. time and (b) relative degree of hydration vs. time for kinetics model based on Eq. (7) for saturated curing conditions with $k_2 = 0.05$ h^{-1}.

the influence of w/c on achieved degree of hydration for portland cements in general, when cured near 20 °C.

The results in Figs. 1–4 indicate that hydrating under sealed conditions as opposed to saturated conditions increases the inherent hydration rate (k_i) by about 20%. This could be due to the presence of a pore solution with higher concentrations of alkali ions and a correspondingly higher ionic strength for the case of sealed curing conditions. This effect is beyond the scope of the current spatial-based models, so that k_i must be determined for each curing condition, similar to the manner in which it must be determined for each curing temperature. Of course, as more experimental data becomes available, it may well be that k_i can be represented as a (Arrhenius) function of temperature and saturation.

An interesting application of the kinetics equations presented above is to consider the influence of the additions of "inert" fillers, such as limestone, on achieved degree of hydration. In the literature, as summarized by Hawkins et al. [20], mixed results are reported; sometimes significant acceleration in the presence of the limestone is observed, while at other times, no significant effect is noted. Often, the experiments are difficult to interpret due to the fact that the limestone may be interground with the cement, changing the cement's PSD and introducing a confounding factor into the interpretation of any measured degree of hydration data.

From the viewpoint of Eqs. (6) and (7), for example, there are at least three different manners for incorporating a limestone substitution into the model. The simplest approach might be to essentially ignore the limestone and consider only that the w/c is changed by the replacement of cement by limestone. With a 20% mass substitution at a constant w/s ratio, for instance, the true w/c would change from 0.45 to 0.5625. Second, one could consider that in a constant volume system, the local porosity and cement volume fractions both are reduced by the presence of the inert filler. In this case, Eqs. (1) and (3) become:

$$\phi_W(t) = \frac{\rho_{cem}(w/c) - (f_{exp} + \rho_{cem}CS)\alpha}{1 + \rho_{cem}(w/c) + \frac{\rho_{cem}}{\rho_{fil}}(s/c)} \quad (10)$$

$$\gamma(t) = \frac{1 - \alpha}{1 + \rho_{cem}(w/c) + \frac{\rho_{cem}}{\rho_{fil}}(s/c)} \quad (11)$$

where ρ_{fil} is the specific gravity of the inert filler (2.71 for limestone present as calcite) and (s/c) is the filler-to-cement mass ratio (0.25 for a 20% limestone substitution). Third, the possibility of the limestone filler providing nucleating surfaces for the precipitation of
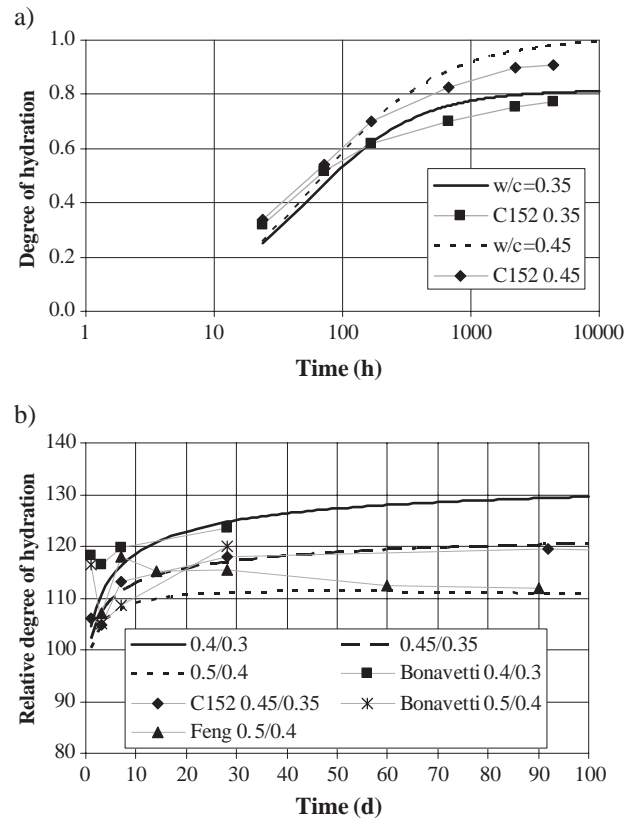
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Fig. 4. Predicted (a) degree of hydration vs. time and (b) relative degree of hydration vs. time for kinetics model based on Eq. (9) for sealed curing conditions with $k_3 = 0.061$ h^{-1}.
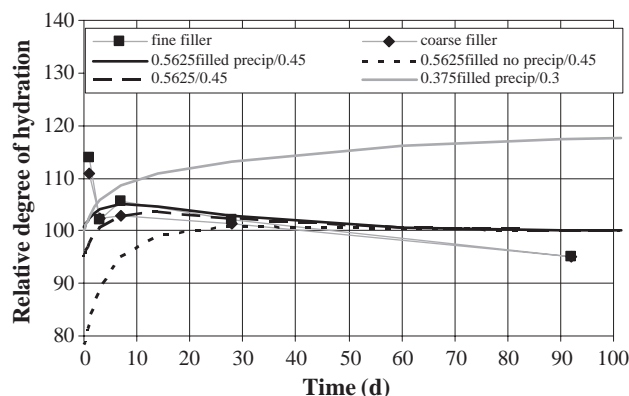
Fig. 5. Predicted and measured influence of 20% by mass (fine and coarse) limestone filler substitution on relative degree of hydration in an original $w/c=0.45$ cement paste (CCRL cement 152) hydrated under saturated curing conditions at 20 °C, with $k_2=0.05$ h^{-1}.

cement hydration products could be considered by including the filler volume fraction in the "$\gamma(t)$" term in Eq. (6), e.g.:

$$\gamma(t) = \frac{\left[1 + \frac{\rho_{cem}}{\rho_{fil}}(s/c)\right]*(1-\alpha)}{1 + \rho_{cem}(w/c) + \frac{\rho_{cem}}{\rho_{fil}}(s/c)} \qquad (12)$$

In Eq. (12), the simplifying assumption is being made that the fraction of filler surfaces available for precipitation is reduced in direct proportion to the degree of hydration of the cement. This assumption has been observed to provide a better overall fit to the available experimental data than the alternative of considering that all of the limestone surfaces are always available for the precipitation of hydration products. The latter case only provided a better fit to the 1 day relative degree of hydration experimental data, while vastly overestimating the experimentally measured relative degrees of hydration for 3 days and beyond.

As indicated by the comparison to the measured experimental results shown in Fig. 5, the first and third methods both seem to provide reasonable fits to the experimental data for hydration times of 3 days and beyond. Since the two provide predictions that are basically indistinguishable for ages of 28 days and beyond, no conclusive preference can be established at this time. As would be expected, experimentally, the higher surface area fine limestone is seen to generally accelerate the hydration slightly more than its coarser counterpart, and to provide a better agreement with the third model where precipitation of hydration products on the limestone surfaces is directly considered. Finally, as indicated by the solid grey line in Fig. 5, it is projected that for lower w/c values (such as 0.3), the influence of filler additions on achieved degree of hydration will be much more pronounced [13]. In this case, since there is insufficient space for complete hydration of the cement in the original unfilled paste, the increase in effective w/c due to the replacement of cement by filler provides a substantial increase in the relative volume of

water-filled capillary pore space available for the precipitation of hydration products. A similar heightened influence of silica fume additions on chloride ion diffusivities at lower w/c has been previously noted [21].

5. Conclusions

Models for hydration kinetics based on simple spatial considerations show promise in describing the hydration behavior of ordinary portland cements and cements blended with inert fillers. Particularly, the dependence of relative degrees of hydration on w/c appears to be well characterized by a model where the instantaneous hydration rate is linearly dependent on the volume fractions of both the water-filled porosity and the remaining unhydrated cement (and filler). For sealed conditions, a further adjustment of the unhydrated cement volume fraction to reflect the probable remaining "active" cement provided the best fit to the limited available experimental data. The models are easily extended to consider the influence of the replacement of a portion of the cement by relatively inert fillers such as limestone powder. Because the achieved hydration is critically dependent on the starting w/c, the influence of filler replacement on relative hydration rates is equally dependent on the w/c of the original unfilled cement paste. Filler replacement may thus accelerate cement hydration much more for an initial $w/c=0.3$ cement paste than for a $w/c=0.45$ one.

Acknowledgements

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