HYDRATION KINETICS AND EFFECT ON PERFORMANCE OF CONCRETE

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ABSTRACT

The cement matrix acts as a binding material for aggregates and its properties influence the overall behavior of the material. In concrete, cement matrix exists in two forms, namely the bulk paste and the interface. The two phases have the same chemical composition but differs in particle size distribution (PSD) and the water-cement ratio. The distinction between the two phases is made on the basis of wall effect exhibited on distribution of cement grains due to the presence of aggregate. The properties of both the phases are influenced by the chemical composition, PSD, water cement ratio and so on. The PSD governs the reaction mechanisms and hence the time required for complete hydration. The PSD along with the water cement ratio strongly governs the strength development in concrete. For the present work, a numerical approach is adopted to emphasize the role of PSD in strength development. The interlocking of hydration products as a function of the degree of hydration is adopted as a measure of strength. The influence of reduction in pore sizes and the available water content is accounted using correction factors.

INTRODUCTION

Cement is a composite material consisting of inclusions in the form of coarse and fine aggregates embedded in the cement matrix. Due to wall effect exhibited by the presence of inclusions, the arrangement of cement grains in the region closer to inclusion gets disturbed leading to the formation of a zone with uneven PSD [1]. This region of uneven PSD is often referred as interfacial transition zone (ITZ) and is also accompanied by a higher water cement ratio [2]. The smaller size particles along with the higher water cement ratio leads to early hydration and lesser embedment of particles thus leading to reduced strength for the interface. However, the process of hydration remains same for both the bulk matrix and the interface and is governed by the similar parameters. Hence the properties of bulk matrix and interface can be derived from the same model (numerical or analytical). Analytical modeling of hydration behavior is difficult due to the existence of various simultaneously operating mechanisms [3]. Hence the observed hydration behaviour in concrete is often described using numerical approaches [3-6]. Prior to the discussion on numerical approaches on hydration, a brief overview on hydration process is presented.

Immediately after coming in contact with water, cement grains release the calcium ions thus making the solution rich in calcium concentration [7]. The concentration of calcium ions in the solution and the deficiency of it on the surface of cement grains lead to initiation of hydration reaction. The hydration reaction is accompanied by the deposition of reaction products either on the surface of the grain or in the free space available in the system [7]. The deposition of hydration product namely Calcium hydroxide (CH) takes place in the free space thus reducing the pore volume. The deposition of Calcium silicate hydrate (CSH) takes place outside the original grain boundaries leading to interlocking of hydration products thus developing a skeleton of hydration products [3,7]. With the progress of hydration, the merging of hydration products grows more intense thus making the concrete strong enough to sustain heavy loads. This process of hydration is influenced by particle size distribution (PSD), water cement ratio, temperature, pore size distribution and so on. Apart from this, shape of the particle also plays a dominant role in controlling the reaction mechanism and hence the time required for hydration. Several theories have been proposed to describe the hydration process and the associated mechanisms [3]. Owing to this theories number of numerical approaches have been development to explain the process of hydration and the influence of various parameters on strength development [3,5,8,9,10,11].

The numerical models for hydration can be used for quantification of the material behaviour. Once the accuracy of the numerical model is established with standard results, efforts can be made to develop new materials with enhanced performance [12,13]. The mechanism of hydration and structure development is complex and the contradictory theories describing hydration behaviour is also reported in the literature [3,12]. Any attempt to model the hydration behavior with intrinsic details is either not feasible or may lead to huge computational effort. Hence a
compromise is to be made so as to achieve practically meaningful results on one hand and a reduced computational effort on the other. In order to reduce the computational effort and achieve meaningful results, several assumptions are made to describe the process of hydration. The assumptions often used for modeling hydration behaviour of cement are mentioned in literature [3]. A numerical hydration model can be considered acceptable if it is able to account for and predict the various physical, chemical and mechanical properties of hardened cement paste with reasonable accuracy. Several empirical hydration models are mentioned in the literature.

Berlage [8] developed the model to simulate the hydration process in concrete. The model was used to quantify the development of inter-particle and effect of particle interaction on the rate of hydration. Effect of water reducing mechanism, shielding of surface to prevent water access were developed. Van Breugel [3] improved the model of Berlage and addressed the issues of temperatures rise and reaction changing mechanism. The influence of various parameters on morphology of reaction products was discussed. However the development of both models rest on a large set of experimental data. Tomosowa et al. [9] proposed a hydration model to predict the heat of hydration and the adiabatic temperature rise in concrete. A single particle hydration model with four different rate reducing mechanisms is proposed. Bentz [5] proposed a 3D numerical cement hydration model to describe the process of micro-structure development. A set of cellular automata rules was applied to starting microstructure to model the chemical reactions for all major phases during the evolving hydration process. Maruyama [10] developed the model to describe hydration kinetics and phase composition of Portland cement using experimental data. A hydration model for concrete incorporating fly ash or slag was developed by Wang et al [11]. The above described models are mostly empirical in nature and hence cannot be used to study the influence of various parameters on strength development. Also the accuracy of the model depends on quality and quantity of experimental data. In the present work, analytical model developed earlier to describe the hydration of a single isolated grain is adopted to describe the influence of PSD on strength development [14]. This is discussed in next section.

DEVELOPMENT OF NUMERICAL MODEL FOR HYDRATION OF CEMENT

In order to determine the time required for hydration of a single isolated cement grain, it is assumed that the reaction products are deposited directly on the surface of anhydrous grain. The distinction between different hydration products is ignored and also the expansion of grain outside the original grain boundaries is considered to be controlled by the expansion coefficient. A modified shrinkage core model to account for the expansion characteristics of hydrating grain is used to obtain the time required for complete hydration of an isolated grain. The time required for complete hydration is given as in Eq. (1)

$$t = \frac{\rho_c \phi_c R_0^2}{2.025C D_{Ab} \log \left( \frac{1+0.6625y_{A0}(t)}{1+0.6625y_{A0}(t)} \right)} \left( 1 - \frac{R(t)}{R_0(t)} \right)^2 + \left( \frac{R(t)}{R_0(t)} \right)^3. \tag{1} $$

Where,

- $C =$ Total concentration = \frac{\text{No of moles}}{\text{Volume}}
- $D_{Ab} =$ Effective diffusivity
- $y_{A0} =$ Molar fraction of water
- $y_{As} =$ Molar fraction at interface of hydrated and unhydrated core
- $R_0 =$ Outer radius of hydrating grain at time $t$
- $\rho_c =$ Molar density of cement
- $\phi_c =$ Volume fraction of cement

The detailed derivation of the above equation is given in literature [14]. In order to obtain the degree of hydration at any instant of time $t$, the above equation is rearranged to obtain the radius $R(t)$ of a hydrating grain at that time instant. The modified form in terms of cubic expression in $R(t)$ is given in Eq. (2)
\[2R(t)^3 - 3R_0(t)R(t)^2 + R_0(t)^3 = \left(\frac{R_0(t)}{\rho_c \theta_c}\right) 2.025c(t) D_{ab} \log \left(\frac{1 + 0.6625y_{A0}(t)}{1 + 0.6625y_{As}(t)}\right)\left(\frac{1 + y_{Ar}(t)}{1 + 0.6625y_{Ar}(t)}\right)\]  

In order to obtain the rate of hydration, the cubic expression in Eq. (2) is solved at time instant \(t_1\) and \(t_2\). The difference in radius of the particle at two time instants can be used to determine the rate of hydration for a particle with initial radius \(R_0\). The rate of hydration can be determined using Eq. (3)

\[
\frac{dR}{dt} = \frac{R(t_1) - R(t_2)}{t_2 - t_1}
\]

The rate of hydration (rate of reduction in grain size) obtained using Eq. (3) is influenced by the presence of particles in the neighborhood of central hydrating grain with radius \(R_0\). Also the rate of hydration is known to be influenced by the reaction temperature and reduction in pore size. The effect of these factors on the rate of reaction can be taken into account using correction factors and is given in Eq. (4)

\[
\left(\frac{dR}{dt}\right)_{\text{mod}} = \left(\frac{dR}{dt}\right) F_1 \Omega_1 \Omega_2
\]

Where,

- \(F_1\) = Temperature function to account for the effect of temperature.
- \(\Omega_1\) = Correction factor to account for effect due to embedding of fully or partially hydrating cement grain [14].
- \(\Omega_2\) = Correction factor to account for reduction in pore sizes[3].

The rate of hydration obtained using Eq. (4), can be used to obtain the hydration thickness (\(\delta\)) upto time \(t\) and is given in Eq.(5)

\[
\delta(t) = R_0 - R(t)
\]

Where,

- \(R_0\) = Initial radius of grain
- \(R(t)\) = Radius of partially hydrated grain at time instant \(t\)

The hydration thickness obtained using Eq. (5) can then be used to determine the degree of hydration (\(\alpha\)) and is given in Eq. (6)

\[
\alpha(t) = 1 - \left[1 - \frac{\delta(t)}{R_0}\right]^3
\]

The total degree of hydration for an assembly of grains with different particle sizes can be obtained using Eq. 7

\[
\alpha_s(t) = \sum_{i=1}^{n} W(i) \alpha(i,t)
\]

The degree of hydration obtained using eqs. (6) and (7) depends on radius \(R(t)\) of partially hydrated grain at time instant \(t\). From Eq. (2) it is quite clear that the radius \(R(t)\) depends on various factors namely the total concentration \((c)\), molar fraction of water \((y_{Ao})\), and so on. These factors and their determination are discussed in details in subsequent section.

**DETERMINATION OF PARAMETERS GOVERNING TIME REQUIRED FOR HYDRATION**

Several parameters as mentioned in Eq. (2) influence the radius of un-hydrated core at time instant \(t\). These parameters are influenced by the chemical composition of cement and the available water cement ratio. The outer radius of a hydrating grain is a function of initial outer radius \(R_0\) and the expansion coefficient \((\upsilon)\). Thus Eq.1 and Eq.2 represents the time required for complete hydration and the radius of un-reacted core at time \(t\). Both these parameters are influenced by physical and chemical aspects of a problem. The determination of these input parameters in Eq. (2) and their dependence on physical and chemical composition are discussed in the further subsections.
Determination of Outer Radius of Hydrating Grain

The deposition of reaction products takes place directly over the surface of anhydrous grain. Due to the expansive characteristics of cement, the deposition takes place even beyond the original grain boundaries (see Fig. 1). This leads to increase in length \( \Delta \delta = R_{\text{out}} - R_{\text{in}} \) over which the diffusion will take place thus increasing the time required for hydration. Thus the outer radius is not constant but is a function of the degree of hydration and needs to be determined. Also the expansion of hydrating grain outside the original grain boundaries leads to embedment of particles smaller than \( R_0 \) which are either partially or fully hydrated (see Fig. 1). This causes reduction in quantity of water available for the hydration of central particle thus causing reduction in rate of hydration. The effect due to embedment of particles on rate of hydration is accounted using correction factor \( \Omega_1 \). The procedure to determine \( \Omega_1 \) is discussed in literature [14].

Due to the expansion of hydrating grain, the volume of reaction products outside the original grain boundaries can be determined using Eq. 8

\[
V_{\text{outer}}(R_0, \alpha) = (\nu - 1) \alpha(R_0, t) V(R_0)
\]  

(8)

Where,
\( \nu = \) Expansion coefficient
\( \alpha(R_0, t) = \) Degree of hydration for a particle with radius \( R_0 \) at time \( t \)
\( V(R_0) = \) Volume of cement with particle radius \( R_0 \)

Due to increase in volume of reaction product, the outer radius of the hydrating grain is increased and can be determined using Eq. 9

\[
R_{\text{out}}(\alpha) = \left(\frac{V(R_0) + V_{\text{outer}}(R_0, \alpha)}{4\pi} \right)^{\frac{1}{3}}
\]  

(9)

Determination of Total Concentration

The time required for complete hydration of a cement grain also depends on total concentration as seen in Eq. 1. The total concentration of a hydrating cement system is a function of chemical composition of cement and water. It also depends on the degree of hydration and chemical composition of reaction products. In general, the total concentration for any reacting system is defined using Eq. 10
The number of moles and also the total volume of a hydrating cement system depend on degree of hydration and the chemical composition. The number of moles of a hydrating cement system with water cement ratio less than 0.4 and that with water cement ratio more than 0.4 is given using Eq. 11 and 12

\[
\text{Number of moles} (\alpha) = (1-\alpha)n_{\text{water}} + (1-\alpha)n_{\text{ce}} + n_{\text{prod}}
\]  \hspace{1cm} (11)

\[
\text{Number of moles} (\alpha) = (1-\alpha)n_{\text{water}} + (n_{\text{water}} - 0.022) + (1-\alpha)n_{\text{ce}} + n_{\text{prod}}
\]  \hspace{1cm} (12)

Where,

\[n_{\text{water}} = \text{Initial number of moles of water}\]
\[n_{\text{ce}} = \text{Initial number of moles of cement}\]
\[n_{\text{prod}} = \text{Number of moles of product after hydration}\]

The number of moles for any given system can be determined using equation 13.

\[
n = \frac{\text{Mass}}{\text{Molecular weight}}
\]  \hspace{1cm} (13)

In order to determine the number of moles for various components of a hydrating cement system, the mass of the system is known and the molecular weight can be determined from the molecular weight of individual components by using the principle of superposition. The molecular weights of individual components are given in Tables 1 and 2.

Table 1: Molecular weight and phase fraction of cement compounds

<table>
<thead>
<tr>
<th>% Fraction</th>
<th>H_2O</th>
<th>C_3S</th>
<th>C_2S</th>
<th>C_3A</th>
<th>C_4AF</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/c *100</td>
<td>18.02</td>
<td>228.32</td>
<td>172.24</td>
<td>270.2</td>
<td>485.98</td>
</tr>
</tbody>
</table>

Table 2: Molecular weight and phase fraction of hydration products

<table>
<thead>
<tr>
<th>% Fraction</th>
<th>CSH</th>
<th>CH</th>
<th>ETTRINGITE</th>
<th>MONOSULPHATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>360.48</td>
<td>25</td>
<td>05</td>
<td>10</td>
</tr>
<tr>
<td>100</td>
<td>74.02</td>
<td>1255</td>
<td>602.6</td>
<td></td>
</tr>
</tbody>
</table>

Determination of Molar Fraction of Water

The dependence of water cement ratio on time required for hydration and the influence on associated mechanical properties is quite well-known. However, such dependence is not quite directly evident in Eq.1 which represents the time required for complete hydration. The dependence on water cement ratio comes through the influence of total concentration (c) and the mole fraction of water \(y_{A0}\). The total concentration as discussed in earlier subsection depends on the number of moles of water. Apart from this, mole fraction of water will be influenced by the water cement ratio. However, the influence of water cement ratio on mole fraction of water is stronger than its influence on total concentration. The molar fraction of water for a hydrating cement system is defined using Eq. 14

\[
y_{\text{water}} = \frac{\text{No. of moles of water}}{\text{Total number of moles}} = \frac{n_{\text{water}}}{n_{\text{water}} + n_{\text{ce}} + n_{\text{prod}}}
\]  \hspace{1cm} (14)
Due to consumption of water during hydration process, the molar fraction of water decreases with increasing degree of hydration and hence is a function of the degree of hydration. The molar fraction of water as a function of the degree of hydration is given in Eq. 15

\[
y_{water} = y_{A0} = \frac{(1-\alpha)n_{water}}{(1-\alpha)n_{water} + (1-\alpha)n_{ce} + \alpha n_{prod}}
\]

RELATIONSHIP BETWEEN STRENGTH AND EMBEDDED CEMENT VOLUME

As already discussed, with the progress of hydration expansion of cement grains takes place beyond the original grain boundaries thus leading to the merging or embedding of hydration products. The merging of hydration products becomes intense with increasing degree of hydration thus allowing the material to sustain heavy loads. Thus it is quite obvious to believe that the strength of hardened paste can be related to the volume of embedded cement. This relationship between the volume of embedded cement and that of the strength of paste is given by Eq. 16 [14, 15]

\[
\sigma_f = \sqrt{0.77E_{eff}G_0(1-\phi)^2(\pi - 4\phi)^{0.37}}
\]

\[
\pi l' \left( 1 + \frac{a}{b} \right)^{0.37}
\]

Where,

- \( E_{eff} \) = Effective modulus of elasticity of hydrated cement paste
- \( G_0 = G_d + G_p \) = Fracture toughness of hydrated cement paste
- \( G_p = E_f \left( \frac{CH\%V_{embT}}{1.696} \right) \)
- \( E_f \) = Energy dissipated for pull-out of one CH crystal
- \( CH\% \) = Percentage fraction of Calcium hydroxide (CH)
- \( l' = 0.5(1 + r_{CH}) \) = Critical crack length
- \( \phi \) = Pore volume fraction
- \( \frac{a}{b} \) = Ratio of major to minor axis of the void (= 1 for present case)
- \( r_{CH} \) = Radius of the largest CH crystal

The contribution of \( G_d \) in fracture toughness (\( G_0 \)) is insignificant and hence can be ignored.

NUMERICAL STUDY TO UNDERSTAND THE EFFECT OF PSD ON STRENGTH OF PASTE

In order to understand the influence of PSD on process of hydration, different PSD are considered for numerical study. The process is carried out at constant reaction temperature and hence the influence of temperature function is not discussed. Fig. 2a shows the influence of PSD on degree of hydration. For an increasing PSD, the degree of hydration attained at any given instant of time decreases. The influence of PSD on degree of hydration is evident right from the initiation and is continued till the cessation of hydration process. The influence of these varying hydration degrees for different PSD will influence the volume of embedded cement and hence will influence the strength of cement paste as shown in Eq. 16. The embedded cement volume for different gradations is shown in Fig. 2b. For different PSD, the degree of hydration attained at a given instant of time is different and hence has different volume of embedded cement. At a given instant of time, when PSD with \( R_0 \) ranging from 0.5-60 \( \mu \)m attains complete hydration, the volume of embedded cement attains its maximum value for \( R_0=0.5-80 \mu m \) and for further increase in PSD the volume of embedded cement decreases. The complete hydration for the increased PSD may lead to higher embedded cement volume but the time required for complete hydration of cement with such PSD may not be realistic.
The information obtained about the influence of PSD on embedded cement volume and the effect of water cement ratio can be used to understand the mechanical properties of matrix and interface. The influence of PSD and water cement ratio on the properties of matrix and interface are discussed in the next section.

![Fig. 2 Influence of PSD on a) degree of hydration and b) volume of embedded cement](image)

PROPERTIES OF MATRIX AND INTERFACE FROM THE HYDRATION MODEL

In order to understand the properties of interface, it is assumed that the gradation of aggregates and water cement ratio decreases as we move away from the aggregate surface. Five different ranges of PSD and water cement ratio are considered and its effect on the embedded cement volume is studied. The decrease in range of PSD and increase in water cement ratio is considered to represent the decreasing distance from the aggregate surface. The PSD 0.5-100 µm represents the distribution of grains in bulk matrix whereas the remaining PSD represents the variations in interfacial transition zone (ITZ).

The PSD and the associated water cement ratio for an increasing distance from the aggregate surface is given in Table.3. It can be said that with an increasing PSD and decreasing water cement ratio, the time required for complete hydration increases. This is possibly due to two reasons, one the PSD of cement grains and the other due to higher water cement ratio. The distribution of capillary pores as a function of the degree of hydration for various PSD is shown in Fig 3b. The size of capillary pores decreases substantially in the initial stages of hydration and the rate of decrease reduces with the progress of hydration. The rate of decrease in size of capillary pores is an indication of an increase in strength of hardened paste. The variation of embedded cement volume with increasing degree of hydration is shown in Fig. 3a. For the present study, the theoretical formulation described earlier is used to determine the tensile strength. The tensile strength of hardened cement is seen to decrease with decreasing aggregate gradation and increasing water cement ratio. From Table 3, it can be said that the properties of matrix and interface is not a constant but varies as a function of PSD and the water cement ratio.

<table>
<thead>
<tr>
<th>Property</th>
<th>PSD µm</th>
<th>w/c</th>
<th>α</th>
<th>V_{emb} (µm³)</th>
<th>Φ_0</th>
<th>E_0  (GPa)</th>
<th>G_0  (N/m)</th>
<th>σ_t (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>0.5-100</td>
<td>0.38</td>
<td>0.983</td>
<td>1.3284*10^{11}</td>
<td>0.0346</td>
<td>21.647</td>
<td>36</td>
<td>31.158</td>
</tr>
<tr>
<td>Interface-I</td>
<td>0.5-80</td>
<td>0.438</td>
<td>0.9803</td>
<td>6.92*10^{10}</td>
<td>0.0748</td>
<td>21.647</td>
<td>25.868</td>
<td>29.353</td>
</tr>
<tr>
<td>Interface-II</td>
<td>0.5-60</td>
<td>0.497</td>
<td>0.9895</td>
<td>4.36*10^{10}</td>
<td>0.111</td>
<td>21.647</td>
<td>19.02</td>
<td>9.4007</td>
</tr>
<tr>
<td>Interface-III</td>
<td>0.5-40</td>
<td>0.555</td>
<td>0.9899</td>
<td>3.2726*10^{10}</td>
<td>0.142</td>
<td>21.647</td>
<td>15.70</td>
<td>5.0345</td>
</tr>
<tr>
<td>Interface-IV</td>
<td>0.5-20</td>
<td>0.6133</td>
<td>1.000</td>
<td>2.0614*10^{10}</td>
<td>0.1709</td>
<td>21.647</td>
<td>11.53</td>
<td>2.985</td>
</tr>
</tbody>
</table>

CONCLUSIONS

The rate of change of radius of particle is found by knowing the time required for hydration of a single particle. The embedded cement volume influences the tensile strength and is therefore important to be defined. Knowing the volume of embedded cement and the pore volume fraction, the tensile strength is determined. The PSD is shown to have significant influence on the embedded cement volume and hence will affect the tensile strength. For the present study, the PSD of the matrix has been varied. It is understood that finer particles are closer to aggregate while as the distance increase they become coarser.
Four different PSD of cement in the interface region is considered for the present study, one to represent the particle closest to the aggregate and the other closest to the matrix i.e., farthest from interface-I. The water cement ratio is also influenced and is highest at interface-IV i.e., closest to the aggregate and is lowest at the interface-I i.e., farthest from the aggregate. Because of variation in water cement ratio, strength is also lowest for interface-IV and highest for interface-I. Therefore it can be conjectured from the present study that if these variation is made more uniform it reduces the stress concentration around the aggregate and thus provides the higher strength.

REFERENCES