Influence of TiO$_2$ Nanoparticles on Early C$_3$S Hydration


Synopsis: The effect of nano-anatase titanium dioxide (TiO$_2$) powder on early age hydration kinetics of tricalcium silicate (C$_3$S) was investigated. Isothermal calorimetry was performed on C$_3$S pastes with 0, 10, and 15% of TiO$_2$ addition by weight, and two mathematical models—the Avrami model and the boundary nucleation model (BN model)—were fitted to the data. The addition of TiO$_2$ accelerated the rate of hydration, increased the peak reaction rate, and increased the degree of hydration at 12 and 24 hours. The model fits demonstrate that the BN model better captures the kinetics of the reaction, particularly in the deceleration period, than the Avrami model. The increase in the ratio of rate parameters ($k_B/k_G$) of the BN model with TiO$_2$ addition suggests that hydration product is formed on or near the surfaces of TiO$_2$ particles, as well as on the C$_3$S surface. These results demonstrate that the addition of TiO$_2$ nanoparticles accelerates the early hydration by providing additional nucleation sites, forming the foundation for future optimization of photocatalytic and other nanoparticle-containing cements.

Keywords: Avrami model; kinetics; modeling; nucleation; titanium dioxide.
ACI member **Bo Yeon Lee** is a PhD Candidate in the School of Civil and Environmental Engineering at Georgia Institute of Technology, Atlanta, GA, where she also received her MS. She received her BS in architectural engineering from Yonsei University in Korea.

**Jeffrey J. Thomas** is a Research Associate Professor in the Department of Civil and Environmental Engineering at Northwestern University. His research interests include modeling of the nanostructure and hydration kinetics of cement-based materials.

**Matthew Treager** is an undergraduate in the School of Civil and Environmental Engineering at Georgia Institute of Technology in Atlanta, GA.

ACI member **Kimberly E. Kurtis** is Associate Professor in the School of Civil and Environmental Engineering at Georgia Institute of Technology. She is Chair of ACI Committee 236, Materials Science of Concrete, and is a member of ACI Committee 201, Durability of Concrete; E802, Teaching Methods and Educational Materials, and the Educational Activities Committee.

INTRODUCTION

Tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$ or $\text{C}_3\text{S}$) comprises about 50 to 70% of ordinary portland cement, and it hydrates to form calcium silicate hydrate ($\text{C}_3\text{S}-\text{H}$) gel, the primary binding constituent in ordinary concrete. It is of primary importance to understand the hydration kinetics of $\text{C}_3\text{S}$ to predict the hydration kinetics of Portland cement (Fujii and Kondo 1974; Tarrida et al. 1995; Berliner et al. 1998; Damasceni et al. 2002). There have been attempts to approximate the kinetics of $\text{C}_3\text{S}$ hydration mathematically, and several mathematical models have been developed. The Avrami nucleation and growth model (Avrami 1939, 1940, 1941) is the most widely used model to predict the early age hydration rate (Brown et al. 1985; FitzGerald et al. 1998; Thomas and Jennings 1999).

Recently, Thomas (2007) suggested that the boundary nucleation model (BN model), developed by Cahn (1956) to describe a solid-solid phase transformation in a polycrystalline material, could better approximate the process of $\text{C}_3\text{S}$ hydration than the Avrami model. While the Avrami model assumes that nucleation occurs randomly throughout the transforming volume, the BN model assumes that nucleation is favored at grain boundaries, similar to the observation that $\text{C}_3\text{S}$ hydration occurs by the outward growth of hydration products from the surface of the hydrating grains into the surrounding water-filled porosity. The BN model takes into account the effect of the surface area of the starting material, which, in the case of hydrating cement or $\text{C}_3\text{S}$, is known to have a strong effect on the hydration kinetics.

In this research, early hydration of $\text{C}_3\text{S}$ was examined with two different addition levels of insoluble, nano-anatase titanium dioxide ($\text{TiO}_2$) particles along with a control $\text{C}_3\text{S}$ without $\text{TiO}_2$. The anatase form of $\text{TiO}_2$ is known for its photocatalytic smog-abating, self-cleaning, and biocidal capacities, which are especially efficient in nanocrystalline form (Carp et al. 2004; Fujishima and Zhang 2006). The addition of $\text{TiO}_2$ to cement-based materials is increasingly being researched and has been used in applications in various parts of the world (Beeldens 2007; Kawakami et al. 2007; Poon and Cheung 2007; Jayapalan et al. 2009). The objective of this research is to verify whether the surface area provided by nano-sized $\text{TiO}_2$ affects the cement hydration rate and whether such an effect can be captured by mathematical modeling. The model fit results from both the Avrami model and the BN model will be compared, and the role of $\text{TiO}_2$ in early age cement hydration will be discussed.

RESEARCH SIGNIFICANCE

Photocatalytic cementitious materials hold promise in the construction industry due to their potential for smog-abatement, self-cleaning abilities, and biocidal applications (Carp et al. 2004; Fujishima and Zhang 2006). However, while practical use of these materials continues to grow, little has been published describing the influence of photocatalytic nanoparticles on early age behavior of such cementitious materials (Jayapalan et al. 2009). This research examines the influence of photocatalytic titanium dioxide dosage rates on early age hydration of $\text{C}_3\text{S}$ by isothermal calorimetry, and compares it with two existing models on hydration kinetics. The aim is to better understand the influence of the nanoparticles on hydration of Portland cement, forming the basis for anticipating the influence of these nanoparticles on setting time, rate of strength gain, and durability.

THEORETICAL BACKGROUND

For the purpose of this research, it is useful to first review the hydration models considered.
Avrami nucleation and growth model

The theory was first treated by Kolmogorov (1937), Johnson and Mehl (1939), and Avrami (1939, 1940, 1941) to explain the kinetics of phase change of metals. The main assumptions made were that the new phase is nucleated by germ nuclei and that the grain centers of the new phase are randomly distributed throughout the matrix. Due to its simple mathematical form, the theory has been widely adapted for C\textsubscript{3}S hydration (Brown et al. 1985; FitzGerald et al. 1998; Thomas and Jennings 1999). Only the final forms of the equations will be introduced here.

The transformed volume fraction \( X \) as a function of time can be written as,

\[
X = 1 - \exp \left[ -\left( k_{avr} t \right)^n \right]
\]  

where the effective rate constant \( k_{avr} \), as proposed by Avrami, is a function of constant linear growth rate, \( G \), and either of the rate of nucleation per unit of untransformed volume, \( I_v \), or the number of nuclei per unit volume, \( N_v \), and \( n \) is an exponent that depends on the dimensionality of the product that forms.

The hydration rate, which can be obtained by differentiating Eq. (1) with respect to time, can be written as,

\[
R = A n k_{avr}^n (t - t_0)^{n-1} \exp(-[k_{avr}(t - t_0)]^n)
\]  

where \( R \) is the hydration rate, \( A \) is a normalization constant to match isothermal calorimetry data, and \( t_0 \) is the time delay between the time of mixing and the start of nucleation and growth kinetics. Note that there are four parameters varying, which are \( A, k_{avr}, t_0 \) and \( n \). While the Avrami model has been used widely to describe C\textsubscript{3}S hydration, the heterogeneous nucleation process that occurs during cement hydration may not be best described by a homogeneous nucleation assumption (Garrault et al. 2006; Thomas 2007).

Boundary nucleation model

The boundary nucleation and growth model (BN model) was first developed by Cahn (1956), to describe the kinetics of nucleation and growth of a polycrystalline material. The key assumption is that nucleation is permitted to occur only on internal boundaries, unlike the Avrami model which assumes that nucleation occurs at randomly distributed locations everywhere within the untransformed volume. For the BN model, the transformed volume fraction as a function of time, \( X \), is given by

\[
X = 1 - \exp \left[ -2 O_v^{\beta} \int_0^t \left( 1 - \exp\left( -Y^\beta \right) \right) \, dt \right]
\]

where

\[
Y^\beta = \frac{4 \pi}{3} G^2 t^3 \left[ 1 - \frac{3y^2}{G^2 t^2} + \frac{2y^3}{G^4 t^4} \right] \quad \text{(if } t > y/G) \]

\[
Y^\beta = 0 \quad \text{(if } t < y/G) \]

Note that \( y \) and \( Y^\beta \) are temporary variables that disappear after integration. In Eq. (3), \( X \) depends on just three well-defined physical parameters: \( G \), the linear growth rate of transformed phase, \( I_v \), the nucleation rate per unit area of untransformed boundary, and \( O_v^{\beta} \), the boundary area per unit volume.

In order to apply the BN model to C\textsubscript{3}S hydration rate data, some slight modifications must be made (Thomas 2007). Eq. (3) must be numerically integrated to obtain the transformation rate, \( dX/dt \). Also, the scaling parameter \( A \) and the time constant \( t_0 \) described above in conjunction with the Avrami model (Eq. (2)), are introduced. The three physical parameters \( O_v^{\beta} \), \( I_v \), and \( G \) are correlated such that the kinetic profile is described by two independent rate constants \( k_a \) and \( k_g \) as proposed by Thomas (2007):

\[
k_a = (I_v O_v^{\beta})^{1/4} G^{3/4}
\]

\[
k_g = O_v^{\beta} G
\]

Thus fits made with the BN model have four varying parameters: \( A, t_0, k_a \), and \( k_g \). If any one of the physical parameters in Eq. (4) are known independently, then the other two can be calculated from the fitted values of the rate constants. For the case of a hydrating C\textsubscript{3}S paste, the value of \( O_v^{\beta} \) can be calculated by dividing the measured surface area of the C\textsubscript{3}S powder by the calculated volume occupied by the hydration products after complete hydration, allowing \( G \) and \( I_a \) to be determined from the fits.
Each of the rate constants represents different physical behavior: \( k_g \) describes the rate of transformation on the internal boundaries (the surface of particles), whereas \( k_s \) describes the rate of transformation in the bulk matrix (the pore space between the particles). The ratio of these two rate constants \( (k_g/k_s) \) can be used to identify the type of kinetic behavior. If \( k_g/k_s \) is very large, then the hydrated products will be densely populated on or very near the nucleation sites (i.e., the C\( _3 \)S surface in the case of C\( _3 \)S hydration). If \( k_g/k_s \) is very small, then the hydrated products will form evenly throughout the paste, approaching the condition of the Avrami model.

**EXPERIMENTAL PROCEDURE**

**Materials**

Pure tricalcium silicate (C\( _3 \)S) powder was obtained from the Lafarge Research Center in Lyon, France. The chemical composition of C\( _3 \)S was analyzed by quantitative x-ray diffraction (QXRD) using Cu-K\( \alpha \) radiation, which gave C\( _3 \)S = 98.43\%, C\( _2 \)S = 1.46\%, and CaO = 0.10\% by mass fraction (Fig. 1). Particle size distribution was measured in ethanol slurry using Microtrac X-100 laser particle analyzer (Fig. 2). The median diameter of the C\( _3 \)S sample was measured to be 7.754 \( \mu \)m. Using an empirical relationship between surface area of cement and particle size distribution developed by Zhang and Napiermunn (1995), the surface area of C\( _3 \)S was found to be 0.291 m\(^2\)/g (1420 ft\(^2\)/lb).

The anatase titanium dioxide (AMT-100, Tayca Corp.) used was 93\% pure with an average crystal size of 6 nm and a pH of 7. The manufacturer-provided surface area was 280 m\(^2\)/g (1.37 \times 10^6 ft\(^2\)/lb).

**Experiment**

Three different C\( _3 \)S pastes were prepared at 0\%, 10\%, and 15\% addition rate of TiO\(_2\) by mass; note that the TiO\(_2\) was dosed in addition to, not by weight replacement, for cement. This approach keeps the cement content constant among the different pastes, which simplifies interpretation of calorimetry data. The water to cement ratio (w/c) was kept constant at 0.50, which resulted in a stiffer mix as more of the high surface area TiO\(_2\) was added.

The rate of hydration was measured by isothermal calorimetry (TAM AIR, TA instruments) at 20°C (68°F), which has precision of \( \pm 20\% \) when compared to pure C\( _3 \)S paste. The total heat of hydration (Fig. 3) shows the rate of hydration per gram of C\( _3 \)S for the first 40 h after mixing for each of the pastes examined; corresponding cumulative heat data for the first 80 hours is presented in Fig. 4. Recall that the C\( _3 \)S content and w/c for each paste remains constant, while the dosage of TiO\(_2\) nanoparticles varies among 0\%, 10\%, and 15\%.

As the addition level of TiO\(_2\) nanoparticles increased, the rate of hydration was accelerated. For example, the rate peak (or greatest power evolved with time) occurs 123 min. earlier for the 10\% TiO\(_2\) paste and 200 min. earlier for 15\% TiO\(_2\) compared to the peak for the ordinary paste (Fig. 3). Furthermore, the peak heights in the rate curve occurring at 6.5, 7.7, and 9.8 hours after mixing, were increased by 11.0\% and 11.9\%, respectively, for 10 and 15\% TiO\(_2\) paste, when compared to pure C\( _3 \)S paste. The total heat of hydration (Fig. 4) data demonstrate that the pastes containing TiO\(_2\) experience higher heat evolution than the ordinary paste in the first 20 hours before the energy evolved begins to slow. In comparison, the 0\% TiO\(_2\) (pure C\( _3 \)S) paste releases energy more slowly initially, but continues to steadily increase through the 80 hours of data collected. These data suggest that the addition of TiO\(_2\) particles to cement paste may affect early age hydration by decreasing the time to set and increasing the rate of early strength development.

The degree of hydration, \( \alpha \), of a C\( _3 \)S paste can be calculated by dividing the heat of hydration at a given time by the enthalpy of reaction of C\( _3 \)S, which has been reported to be \( \Delta H = -121 \text{ kJ/mol} \) (Thomas et al. 2009). The values of \( \alpha \) at 12 and 24 hours for each paste are listed in Table 1. The increasing \( \alpha \) with higher levels of TiO\(_2\) shows that these pastes have achieved greater degrees of hydration by 12 and 24 hours, as suggested by the faster hydration rate described above. In particular, increases in \( \alpha \) at 12 hours of 42.86 and 51.43\%, respectively, for 10 and 15\% TiO\(_2\), when compared to the reference paste are notable. By 24 hours, the acceleratory effect of the TiO\(_2\) is less than at 12 hours; increases in \( \alpha \) at 24 hours are 19.30 and 21.05\%, respectively, at 10 and 15\% TiO\(_2\), when compared to the reference C\( _3 \)S paste. It should be recalled that the TiO\(_2\) particles added to these pastes are not known to react with water or calcium silicates. Therefore, an alternative explanation for the observed increase in early age C\( _3 \)S reaction in the presence of these nanoparticles must be sought.
Both the Avrami model and the BN model were fit to the experimental data for each of the samples (see Fig. 5 to 7). Fitting was performed manually using least mean square error to obtain the closest fit around the rate peak. The two rate parameters $k_0$ and $k_b$ for the BN model were first derived with a fixed $O_6^0$ calculated from the surface area of the $C_3S$ powder ($O_6^0 = 0.44 \text{ m}^2/\text{cm}^3$ [72.6 ft$^2$/in.$^2$]) and then $G$ and $I_0$ for different pastes were calculated using the relationships in Eq. (4). The fit parameters are listed in Table 2 for the Avrami model and in Table 3 for the BN model. Figures 5 to 7 show the rate of hydration data with both fits for each of the three pastes examined.

For the $C_3S$ paste, the BN model clearly provides a better fit than the Avrami model to the hydration rate behavior, as was previously shown for $C_3S$ hydration under different conditions by Thomas (2007). While both models closely approximate the early hydration reaction of $C_3S$ in the acceleration period (for all of the pastes), the BN model more closely captures the hydration behavior of the deceleration period after the rate peak. The divergence with the Avrami model occurs in the deceleration period and suggests that the conditions of random nucleation assumed by that model do not apply to pure $C_3S$ hydration. The BN model also better represents the early age hydration of $C_3S$ mixed with TiO$_2$ than the Avrami model. Again, the improvements in the fit are especially notable in the down slope region. This suggests that nucleation is spatially nonrandom and is likely related to the surface area of the solid phases available for product nucleation and growth.

Further, an increase in the $k_i/k_0$ ratio of the BN model is found as the TiO$_2$ dosage (and solid surface area) increases (Table 3). This suggests that the presence of additional surface area, provided by the increasing amounts of TiO$_2$, promotes hydration product formation, which occurs on or near the surfaces of the particles according to the model assumptions. This implies that the addition of TiO$_2$ powder supplied additional nucleation sites to accelerate the hydration. It is also proposed that by providing additional nucleation sites away from the reacting $C_3S$ particles, the start of diffusion-controlled hydration kinetics is delayed, increasing the amount of early nucleation and growth hydration, as has been proposed for other nucleating materials (Thomas et al. 2009). Such behavior would account for both the acceleration in reaction rate and the increase in peak height observed in the presence of TiO$_2$ nanoparticles.

The $t_0$ parameter in both the Avrami model and the BN model graphically shifts the curves either to the right or to the left, depending on the sign. A positive $t_0$ value can be interpreted as an induction period, shifting the curves to the right. On the other hand, a negative $t_0$ found in the BN model suggests that the TiO$_2$ particles have an effect of promoting the nucleation rate at a very early age. Note that the differences seen in $t_0$ between the 0% paste and the 10 and 15% pastes in the case of the BN model are 2.2 and 3.0 hours, respectively, which are on the order of magnitude of the acceleration noted previously with respect to the peak heights seen in Fig. 3.

**CONCLUSIONS**

The early hydration behavior of pure $C_3S$ was measured and compared to that of $C_3S$ pastes containing 10% and 15% additions of high surface area TiO$_2$. Two nucleation and growth models—the Avrami model and boundary nucleation model—were applied to the experimental data. Based on the results of this study, the following conclusions are drawn:

- The addition of high surface area TiO$_2$ powder accelerates the early age hydration of $C_3S$ by ~2.0-3.3 hours and increases the rate peak height by ~11-12%, an effect that is attributed to its ability to stimulate nucleation of hydration product.
- The BN model is capable of representing the kinetic behavior of $C_3S$ paste mixed with TiO$_2$ nanoparticles and provides a better fit to the rate data than the Avrami model for all pastes tested.
- The increase in the ratio of the rate constants from the BN model ($k_i/k_0$) with addition of TiO$_2$ suggests that the formation of hydration products is linked to the increase in available nucleation sites (i.e., increase in solid surface area) provided by the TiO$_2$ nanoparticles.

Observations such as these which show that the early rate of hydration can be altered through the addition of unreactive TiO$_2$ particles suggest that the setting behavior, strength development, and permeability of photocatalytic and other Portland cements can be optimized by controlling compositional variables and particle size.

**ACKNOWLEDGMENTS**

This material is based upon work supported by the National Science Foundation under Grant No. CMMI-0825373. The authors are grateful to Lafarge for providing the $C_3S$ used. The authors thank Matthew Treager and Sarah Fredrich for their help. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation.
REFERENCES


<table>
<thead>
<tr>
<th>TiO2 added (%)</th>
<th>Cumulative heat (12 h), kJ/mol</th>
<th>α (12 h)</th>
<th>Cumulative heat (24 h), kJ/mol</th>
<th>α (24 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>42.65</td>
<td>0.35</td>
<td>68.76</td>
<td>0.57</td>
</tr>
<tr>
<td>10</td>
<td>60.15</td>
<td>0.50</td>
<td>82.13</td>
<td>0.68</td>
</tr>
<tr>
<td>15</td>
<td>64.70</td>
<td>0.53</td>
<td>83.85</td>
<td>0.69</td>
</tr>
</tbody>
</table>
Table 2—Fit parameters $A$, $t_0$, $k_{avr}$ and $n$ for Avrami model

<table>
<thead>
<tr>
<th>TiO$_2$, %</th>
<th>$A$, kJ/mol</th>
<th>$t_0$, h</th>
<th>$k_{avr}$, h$^{-1}$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>56.718</td>
<td>2.700</td>
<td>0.1190</td>
<td>2.90</td>
</tr>
<tr>
<td>10</td>
<td>64.116</td>
<td>0.180</td>
<td>0.1144</td>
<td>2.97</td>
</tr>
<tr>
<td>15</td>
<td>59.184</td>
<td>0.042</td>
<td>0.1320</td>
<td>2.80</td>
</tr>
</tbody>
</table>

Table 3—Fit parameters $A$, $t_0$, $k_B$, $k_G$ and $k_B/k_G$ for boundary nucleation model

<table>
<thead>
<tr>
<th>TiO$_2$, %</th>
<th>$A$, kJ/mol</th>
<th>$t_0$, h</th>
<th>$k_B$, h$^{-1}$</th>
<th>$k_G$, h$^{-1}$</th>
<th>$k_B/k_G$</th>
<th>$l_B$ (μm$^{-2}$·h)$^{-1}$</th>
<th>$G$, μm/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>71.514</td>
<td>1.2</td>
<td>0.1030</td>
<td>0.0824</td>
<td>1.2500</td>
<td>0.0390</td>
<td>0.1871</td>
</tr>
<tr>
<td>10</td>
<td>85.488</td>
<td>-1.0</td>
<td>0.0990</td>
<td>0.0734</td>
<td>1.3488</td>
<td>0.0471</td>
<td>0.1666</td>
</tr>
<tr>
<td>15</td>
<td>87.954</td>
<td>-1.8</td>
<td>0.1043</td>
<td>0.0656</td>
<td>1.5899</td>
<td>0.0811</td>
<td>0.1490</td>
</tr>
</tbody>
</table>

Fig. 1—Diffraction pattern for cement sample compared to reference pattern for C$_3$S.

Fig. 2—Particle size distribution and cumulative particle size of C$_3$S powder examined.
Fig. 3—Hydration rate of TiO$_2$-blended C$_3$S pastes.

Fig. 4—Cumulative heat of hydration of TiO$_2$-blended C$_3$S pastes.
Fig. 5—Rate of hydration with 0% TiO$_2$ – Experiment versus Avrami and BN models.

Fig. 6—Rate of hydration with 10% TiO$_2$ – Experiment versus Avrami and BN models.
Fig. 7—Rate of hydration with 15% TiO$_2$ – Experiment versus Avrami and BN models.