

# Influence of Nano-Anatase Titanium Dioxide on Cement Hydration: Experiments and Modeling



### Introduction

Researchers have noted that the addition of fine fillers to Portland cement can change the early hydration reaction of cement with potential implications relating to setting time, dimensional stability and strength development.

An acceleration in the hydration reaction has been observed when fine fillers were added to cement [1]. However, the addition of fine fillers could also affect the dimensional stability of a cement mix by increasing shrinkage of the cementitious material [2]. The particle size of the filler could be optimally selected, so that the filler could increase the hydration reaction but not significantly affect the dimensional stability of the cement system.

Addition of a fine non-reactive filler to cement modifies the hydration reaction primarily due to dilution, modification of particle size distribution and heterogeneous nucleation [3]. Most of the fine fillers previously examined react chemically to some extent in the cement hydration process.

There is an increasing interest in the addition of inert additives to cement. Titanium dioxide (TiO<sub>2</sub>) is added to cement for its photocatalytic activity, which can impart biocidal, self-cleaning, and smog-abating functionality to cement-based materials. Research has shown that the photocatalytic activity is superior in nano-crystalline anatase TiO<sub>2</sub> [4].

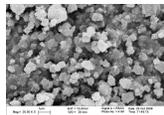


Figure 1. Scanning Electron Microscope (SEM) image of anatase Titanium Dioxide (magnification 20000X)

The objective of this research was to study the effect of the TiO<sub>2</sub> nanoparticles on the rate of hydration and dimensional stability during early stages of cement hydration.

### Avrami Model

The Avrami model was first developed by Avrami [5] to explain the kinetics of phase change of metals. The main assumptions of Avrami model are

- the new phase is nucleated by germ nuclei
- the grain centers of the new phase are randomly distributed throughout the matrix.

The theory has then been widely adapted for C<sub>3</sub>S hydration [6]. The hydration rate of C<sub>3</sub>S has been modeled according to the following equation

### Avrami Model – continued

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

where R is the hydration rate,  
A is a normalization constant,  
n is a dimensionality parameter,  
k<sub>avr</sub> is the effective rate constant and  
t<sub>0</sub> is the time between mixing and the start of nucleation and growth kinetics.

### Boundary Nucleation Model

The boundary nucleation (BN) and growth model was first developed by Cahn [7], to describe the nucleation kinetics and growth of polycrystalline materials. The key assumption is that nucleation is permitted to occur only on internal boundaries. For the BN model, the transformed volume fraction as a function of time, X, is given by:

$$X = 1 - \exp\left[-2O_v^G \int_0^{Gt} (1 - \exp(-Y^r)) dY\right] \quad (2)$$

where G is the linear growth rate  
O<sub>v</sub><sup>B</sup> is the boundary area per unit volume and  
I<sub>0</sub> is the nucleation rate per unit area of untransformed boundary

For applying the BN model for C<sub>3</sub>S hydration [8], a scaling and time delay parameters were introduced and the hydration rate was obtained by numerically differentiating equation 2. Two parameters were also introduced.

$$k_G = O_v^B G \quad k_B = (I_0 O_v^B)^{0.25} G^{0.75} \quad (3)$$

where k<sub>G</sub> is transformation rate in the bulk matrix and  
k<sub>B</sub> is transformation rate on internal boundaries (on the surface of particles).

### Materials and Methods

Three TiO<sub>2</sub> samples of different surface areas, obtained from various commercial manufacturers were used for the tests (Table 1). Ordinary Portland cement and pure C<sub>3</sub>S were supplied by Lafarge. T1 and T2 were used for cement tests and T3 was used for tests on C<sub>3</sub>S.

	Crystal Size (nm)	Agglomerate Size (µm)	Surface Area (m <sup>2</sup> /g)	pH	Purity (%)
T1	20-30	1.5	45-55	3.5-5.5	>97
T2	15-25	1.2	75-95	3.5-5.5	>95
T3	6	2.5	280	6-8	93

Table 1. Properties of Anatase TiO<sub>2</sub> (manufacturers data)

Effect of addition of various percentages of TiO<sub>2</sub> on the hydration of ordinary Portland cement and pure C<sub>3</sub>S at a water-to-solids ratio of 0.5 was examined. Isothermal calorimetry was conducted on triplicate samples. Chemical shrinkage tests were conducted according to the ASTM C 1608-07. Modeling of C<sub>3</sub>S hydration was conducted according to Avrami model and Boundary Nucleation (BN) model.

### Results

Addition of nano-TiO<sub>2</sub> accelerated hydration (Fig. 2). At 10% dosage, T1 & T2 accelerated hydration by ~80 and ~180 minutes respectively. Acceleration increased with increasing dosage and decreasing particle size. Nucleation effect was found to be dominant compared to dilution.

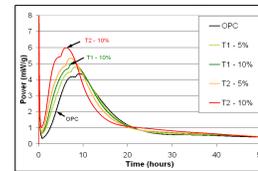


Figure 2. Rate of hydration reaction of ordinary Portland cement and TiO<sub>2</sub>-blended cements

Total energy evolved and the degree of cement hydration at a certain age were directly proportional to the TiO<sub>2</sub> dosage and surface area (Fig. 7), reinforcing the significant effect of heterogeneous nucleation reaction on hydration.

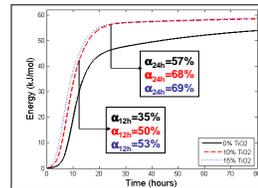


Figure 3. Cumulative energy released by mixes with pure C<sub>3</sub>S and C<sub>3</sub>S blended with 10% and 15% TiO<sub>2</sub>

Addition of TiO<sub>2</sub> particles results in an increase in the chemical shrinkage of the cement paste and shrinkage increased with increasing dosage of TiO<sub>2</sub>.

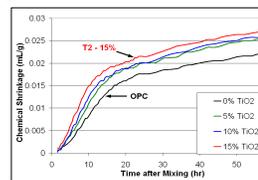


Figure 4. Chemical Shrinkage of TiO<sub>2</sub>-blended cements

### Results – continued

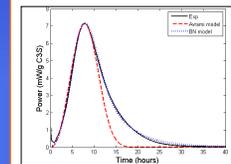


Figure 5. Results of modeling using Avrami and Boundary Nucleation Model for 10% TiO<sub>2</sub>-C<sub>3</sub>S mix

The hydration data of C<sub>3</sub>S and TiO<sub>2</sub>-C<sub>3</sub>S mixes was used to fit the Avrami and BN models (Fig. 5). BN model was found to give a better fit for all the mixes tested. Nucleation effect which increases with increasing surface area of solids phases (C<sub>3</sub>S and TiO<sub>2</sub>) was found to be the dominant effect.

TiO <sub>2</sub> (%)	t <sub>0</sub> (h)	k <sub>B</sub> (h <sup>-1</sup> )	k <sub>G</sub> (h <sup>-1</sup> )	k <sub>B</sub> /k <sub>G</sub>
0	1.2	0.103	0.0624	1.25
10	-1.0	0.099	0.0734	1.3488
15	-1.8	0.1043	0.0656	1.5899

Table 2. Fit parameters for Boundary Nucleation Model

An increase in the k<sub>B</sub>/k<sub>G</sub> ratio in the BN model suggests that additional surface area provided by the increasing amounts of TiO<sub>2</sub> promotes hydration, according to the model assumptions. The negative t<sub>0</sub> found in the BN fits suggests that the TiO<sub>2</sub> particles have an effect of promoting the nucleation rate at a very early age

### Conclusions

TiO<sub>2</sub> of different particle sizes accelerated and increased the peaks of hydration reaction. The increase was also proportional to the dosage of TiO<sub>2</sub> added to cement/C<sub>3</sub>S.

Chemical shrinkage test results indicate that the addition of nanoparticles increase the shrinkage in cement paste and the increase in shrinkage is proportional to the percentage replacement of the cement.

The Boundary Nucleation model is capable of better representing the kinetic behavior of C<sub>3</sub>S paste mixed with TiO<sub>2</sub> nanoparticles better than the Avrami model. Heterogeneous nucleation effect was found to be dominant compared to the dilution effect.

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