Assessment of Environmental Impact of the Addition of Photocatalytic Nanoparticles to Cementitious Materials

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Use of photocatalytic titanium dioxide (TiO₂) in cementitious materials is increasing due to its novel capabilities, including smog abatement, hydrophobicity/philicity, and self-cleaning. However, the contributions of TiO₂ nanoparticles to the overall environmental impacts of photocatalytic cementitious materials have not been thoroughly considered. That is, the balance between their potential beneficial long-term use and the environmental costs associated with their production should be considered. In the first part of this study, the potential influence of TiO₂ nanoparticles on early hydration kinetics of major components in portland cement are measured and these data compared with hydration models. Results, which showed nanoparticle acceleration of calcium silicate hydration, are used to assess whether cement fractions may be reduced when nanoparticles are included, while retaining similar concrete properties. The second part of this study examined the environmental impact of the photocatalytic cement, analyzed by SimaPro Life Cycle Assessment (LCA) software. The LCA study indicates that even though the introduction of nanoparticles increases the initial environmental impact of photocatalytic cement as compared to ordinary portland cement, the long term NOx binding capabilities of TiO₂-modified cements could result in a lower environmental impact. The contributions to sustainability can be further enhanced by reductions in cement fraction, based upon the results of the first part of this investigation.

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INTRODUCTION

Use of photocatalytic titanium dioxide (TiO$_2$) in cementitious materials is increasing due to its strong oxidizing capability. One of the major applications of photocatalytic cement-based materials is on the nitrogen oxides (NO+NO$_2$=NO$_x$) oxidation. Nitrogen oxides are classified as one of the major air pollutants, mostly stemming from mobile sources such as cars, planes, and trains. NO$_x$ participates in the formation of photochemical smog and ozone (O$_3$), as well as threatening human health. Use of photoactive TiO$_2$ is considered one way of passively mitigating this problem. However, although this TiO$_2$-cement composite is effective in NO$_x$ oxidation, the effect of addition of these TiO$_2$ nanoparticles to cement substrate is relatively undocumented.

In this paper, the overall objective is to examine the global environmental impact of TiO$_2$-bearing cement-based materials. This is accomplished by first examining the influence of these chemically inert nanoparticles on cement hydration, to determine if cement factors may be reduced, reducing then the well-known environmental impact associated with cement. Commercially appropriate compositions are then analyzed and compared by life cycle assessment (LCA).

Prior work by these authors have shown that in alite (tricalcium silicate, C$_3$S) pastes where TiO$_2$ nanoparticles are added [1, 2], the early hydration is accelerated. The boundary nucleation (BN) model [3], which presumes surface nucleation and takes into account the cement and TiO$_2$ particle surface areas, provided a better fit to the hydration behavior than conventionally used Avrami model, which presumes heterogeneous nucleation in pore solution-filled space. Thus, the C$_3$S acceleration was ascribed the high surface area of the chemically inert nanoparticles of TiO$_2$. The work performed here will build upon the previous work by authors such that belite (dicalcium silicate, β-C$_2$S), the second major component of portland cement after alite, is examined. C$_2$S requires less energy to produce than C$_3$S but its use is limited due, in part, to its slower hydration rate [4]. Here, the hydration rate of C$_2$S in the presence of TiO$_2$ nanoparticles is measured and compared to two mathematical models, the BN model and the Avrami model.

Further, the potential global environmental impact of TiO$_2$-bearing cementitious materials is examined through a lifecycle analysis (LCA). While the NO$_x$ abatement capability of photocatalytic materials is a potential environmental benefit, a comprehensive investigation that includes all factors including embodied energy, embodied CO$_2$, transportation, cost, among other factors, is required to truly appreciate the impact of their usage on a commercial scale. In this study, SimaPro LCA software is used to perform a life cycle analysis on compositions of photocatalytic cementitious materials which are appropriate for field use.

EXPERIMENT AND MODELING

Materials

Pure belite (β-C$_2$S) powder was obtained from CTLGroup in Skokie, IL. C$_2$S powder was stabilized by boron trioxide (B$_2$O$_3$) and was ground to 100% passing No.325 sieve (45µm). Purity of C$_2$S was 100.00%, examined by quantitative X-ray diffraction under Cu-Kα radiation. Anatase TiO$_2$ that was used for this study was AMT-100 (Tayca Corp., Osaka, Japan), that is 93% pure, has average crystal size of 66nm, and pH of 7.0, as specified by the
manufacturer. Particle size distribution was measured by Zetasizer Nano (Malvern Instruments, UK) after ultrasonicating TiO$_2$-water-superplasticizer solution for 1 hour for better dispersion (Figure 1). Nitrogen BET surface area of the powders were determined by Micromeritics ASAP 2020 (Micromeritics, Norcross, GA) accelerated surface area and porosimetry analyzer. The BET surface area was measured to be 2.81 m$^2$/g and 611.54 m$^2$/g for C$_2$S and TiO$_2$ respectively.

**Calorimetry and Hydration Modeling**

For isothermal calorimetry, TiO$_2$ containing C$_2$S sample pastes were prepared at 0%, 5%, and 10% addition of TiO$_2$ by mass of C$_2$S with the addition of 2% calcium chloride (CaCl$_2$) in an attempt accelerate the reaction. CaCl$_2$ solution was first prepared, and TiO$_2$ powder was added to the solution and mixed for 1 min, then C$_2$S powder was added. Water-to-cement ratio (w/c) was constant at 0.50. The heat of hydration was measured by isothermal calorimetry (TAM AIR, TA instruments, New Castle, DE) at 20°C up to 90 days.

The two models, Avrami model [5-7] and BN model [3], are applied to the experimental results. The model curves are fitted to the experimental data through an iterative process. Detailed model derivation and equations can be found from the previous work performed with pure C$_3$S powder [1].

**LCA Methods**

To examine the overall impact of the TiO$_2$-containing cement to the environment in comparison to ordinary portland cement, a life cycle assessment (LCA) was performed. This analysis is a technique that incorporates environmental impact of all the stages of a product from raw material through disposal or recycling. For this study, SimaPro software was used and the Eco-Indicator 99E [8] was selected as the calculation method for impact assessment. A generalized processing of TiO$_2$ based on data from manufacturer was considered for the material information in the analysis. Once the data for the different materials were input into the program, SimaPro conducted the life cycle impact analysis (LCA) that includes classification, characterization, normalization and weighting. In the classification step of
LCIA, SimaPro and Eco-Indicator 99E categorized the impacts of the materials into the following eleven impact categories based on ISO 14040 standard endpoints [9]: carcinogens, respiratory organics, respiratory inorganics, climate change, radiation, ozone layer, ecotoxicity, acidification/eutrophication, land use, minerals and fossil fuels. In this study, weighting factors for each of these eleven categories were selected based on Eco-Indicator 99 method [8]. Once the appropriate weights were applied by the program, a single indicator was generated and reported as “points,” where one point is equivalent to one thousandth of the environmental load by an average European inhabitant. The final “single score” was used to compare the environmental impacts of the TiO\textsubscript{2}-cement compared to ordinary portland cement. Also, further investigation was performed that takes into account the NOx oxidizing capability of TiO\textsubscript{2}-cement. This offsets a part of the environmental impact of TiO\textsubscript{2}-cement. The time required to offset the initial NOx emissions from material is calculated.

For this analysis, it was assumed that cement paste is replaced with 5% of TiO\textsubscript{2} by mass. Results were then compared to ordinary portland cement paste, where the cements were considered to be equivalent. The environmental impacts of both of the cases are discussed. Further, a case when additional “inert” filler is added is analyzed. This “inert” filler is assumed to have negligible life cycle cost, but is envisioned as having similar accelerating properties to the TiO\textsubscript{2} nanoparticles. As a result, inclusion of an additional filler material, with the TiO\textsubscript{2}, could further contribute to reductions the life cycle cost of the entire photocatalytic cement, while retaining similar performance.

RESULTS AND DISCUSSION

Effect of TiO\textsubscript{2} Nanoparticles on Early Hydration

The rate of hydration per gram of dry C\textsubscript{2}S is shown in Figure 2(a) for the first 90 days after mixing for each of the pastes examined. Corresponding cumulative heat data is presented in Figure 2(b). The effect of addition of chemically inert nanoparticles can be examined by comparing the C\textsubscript{2}S samples containing 0%, 5%, and 10% TiO\textsubscript{2}. From Figure 2(a), addition of nano-TiO\textsubscript{2} particles noticeably accelerated the hydration reaction. The 5% and 10% case clearly shows induction period at ~3 days, reaching rate peak at ~40 days. Comparing to 0% case where rate peak is observed at ~60 days, hydration of C\textsubscript{2}S was accelerated by ~20 days with the addition of TiO\textsubscript{2} nanoparticles. This acceleratory effect of addition of chemically inert nano TiO\textsubscript{2} was also observed in authors’ previous work performed with pure C\textsubscript{3}S paste [1, 2]. On the other hand, not much difference is shown between 5% and 10% case. It could be that the rate of nuclei or hydration product formation is slow enough in the case of C\textsubscript{2}S, that the added surface area of TiO\textsubscript{2} beyond the level of 5% does not have a noticeable effect on acceleration. Additional effects may be due to minor amount of sulfate ions on the TiO\textsubscript{2} stemming from its production; the sulfates at greater, but still minor, concentration at the higher dosage rates could interfere with the acceleration due to the additional surface area, as described in [10].

Cumulative heat of hydration plot in Figure 2(b) suggests that degree of hydration of TiO\textsubscript{2} containing C\textsubscript{2}S pastes surpass that of pure C\textsubscript{2}S paste at about 20 days, and reaching 49% at 90 days as compared to 34% in case of pure C\textsubscript{2}S paste. This is a 47% increase in degree of hydration. The degree of hydration was calculated by dividing the total heat of hydration at a given time by the enthalpy of reaction of C\textsubscript{2}S (ΔH=45kJ/mol) [11]. Detailed description of C\textsubscript{2}S hydration and Figure 2(a) and (b) can be found from elsewhere [10].
Overall, from these calorimetry data, it was found that method of isothermal calorimetry can be used to capture the hydration rate of C$_2$S, and TiO$_2$ nanoparticles accelerate the rate of C$_2$S hydration.

![Figure 2](image.png)

Figure 2  (a) Hydration rate of TiO$_2$-blended C$_2$S pastes  
(b) Cumulative heat of hydration of TiO$_2$-C$_2$S pastes

**Model Fits**

The Avrami model and the BN model were fitted to the rate of hydration data for the C$_2$S pastes with 0%, 5%, and 10% TiO$_2$ addition. The initial rate peak that occurs immediately after mixing as a result of initial dissolution of C$_2$S was not considered for the model fit. Fitting was performed by manually adjusting model parameters: A, t$_0$, k$_{avr}$, and n were...
adjusted in case of Avrami model, and A, \( t_0 \), G, IB were adjusted in case of BN model. The \( O_v^B \) value for the BN model, which represents surface area of powder, was calculated by dividing the total surface area per gram of mixed powder by the volume occupied by the hydration products after complete hydration. The hydration volume of C\(_2\)S is 0.5694 cm\(^3\)/g C\(_2\)S and the volume of TiO\(_2\) was incorporated based on the density of 4.23 g/cm\(^3\). The increase in \( O_v^B \) as more TiO\(_2\) is added represents the increasing surface area due to addition of nanoparticles. The values are presented in Table 1. Curve fitting was iteratively done until the model fit best approximates the experimental data. The finalized model fits are presented in Figures 3(a), 3(b), and 3(c), and the model parameters are presented in Table 1 and Table 2 for the Avrami model and the BN model, respectively.

In all the cases considered, the BN model approximates the experimental data better than the Avrami model, especially in the deceleration period. This is due to the unsymmetrical shape of the rate curve that could only be represented by the BN model. The Avrami model is capable of representing only a symmetrical bell shape while the BN model can present a skewed bell shape depending on the \( k_B/k_G \) ratio. As \( k_B/k_G \) ratio approaches zero, the shape gets symmetrical, and the model essentially is identical to the Avrami model. The \( k_B/k_G \) ratio also reflects the effect surface area, where nucleates are expected to form. In this study, the \( k_B/k_G \) ratio of C\(_2\)S hydration is determined to be around 1~2. Model fit parameters are summarized in Table 1 and Table 2 for the Avrami model and the BN model, respectively.

The \( t_0 \) parameter in both the Avrami model and the BN model shows a negative value, indicating that the curves are shifted to the left. This suggests that enough starting nucleates exist which accelerated the hydration reaction. There is no obvious trend in \( t_0 \) for the Avrami model, but for the BN model \( t_0 \) is decreasing (growing more negative) at higher nanoparticle dosage rates. That is, 450 hours of acceleration was observed for the 5% case in comparison to the 0% case, and additional 50 hours of acceleration was observed for the 10% case in comparison to the 5% case. This suggests that the additional surface area provided by the nanoparticles of TiO\(_2\) accelerated the early C\(_2\)S reaction. The G parameter, which represents the linear growth rate of hydrated phases, is decreasing and the IB parameter, which represents nucleation rate per unit area of total surface area, is increasing as more TiO\(_2\) nanoparticles are added. These suggest that hydration products are forming on a larger surface area, which is increased due to TiO\(_2\) addition. This trend was also observed in case of C\(_3\)S paste [1, 2]. However, the order of magnitude is 2-3 times lower in case of C\(_2\)S paste, indicating slower hydration reaction is occurring, as expected.

The \( k_B/k_G \) ratio shows an increase from 0% case to 5% and 10% case; increase of 81% from 0% case to 5% case and 61% from 0% case to 10% case was observed. Interestingly, an 11% decrease in the \( k_B/k_G \) ratio was observed between 5% case and 10% case. The authors believe that this could be the result of “diminished returns” as stated previously [10], which resulted in the very similar curves despite the higher addition rate. Also, the sensitivity of the fitting parameters according to little changes in the shape, and unsmooth experimental data can be the reason for the drop \( k_B/k_G \) ratio. Nevertheless, the significant increase of the ratio after adding TiO\(_2\) imply that the acceleration is due to the added surface area by TiO\(_2\) nanoparticles, although other factors may also contribute the behavior observed. Certainly, additional research is needed to better understand the applicability of the BN model to belite hydration and the mechanism(s) of nanoparticle-derived acceleration.
Figure 3  Rate of hydration: Experiment versus Avrami and BN models (a) 0% TiO₂, (b) 5% TiO₂, and (c) 10% TiO₂
Table 1  Fit parameters \( A, t_0, k_{avr} \) and \( n \) for Avrami model

<table>
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<tr>
<th>( \text{TiO}_2 ) (%)</th>
<th>( A ) (kJ/mol)</th>
<th>( t_0 ) (h)</th>
<th>( k_{avr} ) (h(^{-1}))</th>
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Table 2  Fit parameters \( O_v^B \), \( A \), \( k_B \), \( k_G \), and \( k_B/k_G \) for boundary nucleation model

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<th>( t_0 ) (h)</th>
<th>( G ) (( \mu m/h ))</th>
<th>( I_B ) (( \mu m^2/h )) (^{-1})</th>
<th>( k_B ) (h(^{-1})*10(^4))</th>
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**Life Cycle Analysis**

The life cycle analysis of ordinary portland cement, cement containing 5% of TiO\(_2\), and cement containing 5% TiO\(_2\) and an additional inert filler were performed using SimaPro. The results for 1000kg of each mixture are presented by a single point score as shown in Figure 4. Ordinary portland cement resulted a single point score of 22.14 points and TiO\(_2\)-modified cement resulted 40.47 points. This analysis considers only the materials production, including raw material acquisition and processing of the components used in the cement mixes. (Analysis of the TiO\(_2\)-modified cement with filler is described subsequently.) As the higher value designates greater detriment to the environment, the TiO\(_2\)-modified cement negatively impacts the environment 83% more than ordinary portland cement when only the material production is considered.

![Figure 4](image-url)

Figure 4  Single point LCA score for cement mix, TiO\(_2\)-blended cement mix and theoretical cement mix with TiO\(_2\) and inert filler additives
Isothermal calorimetry has shown that 5% replacement of TiO$_2$ nanoparticles for cement increases the cumulative heat evolved by 21% at 48 hours of hydration (Figure 5), as compared to ordinary portland cement; similar results are also reported in [12]. This can directly be related to degree of hydration. This indicates that to some extent, cement can be replaced with other “inert” filler to achieve a similar degree of hydration as that of ordinary portland cement paste, thus decreasing cement content. Inert filler could be selected such that the life cycle cost of the filler be negligible compared to the cement or TiO$_2$, such as waste product or fine aggregate. If such “optimum” inert filler were added to TiO$_2$-blended cements to reach similar degrees of hydration as ordinary portland cement at 48 hours, the maximum replacement rate is calculated to be approximately 17%. For this mix (labeled cement+5% TiO$_2$+filler in Figure 4), the single point score according to LCA is 33.29 points. This is 50% higher than ordinary portland cement but results in 18% lower environmental impact than 5% TiO$_2$-cement due to the decreased cement content. Thus addition of inert (according to life cycle cost) filler decreases the total LCA single point score of the TiO$_2$-blended cement.

![Figure 5](image.png)

Figure 5  Cumulative heat of hydration of ordinary portland cement (OPC) mix and TiO$_2$-blended cement pastes

On the other hand, taking into account the photocatalytic NOx oxidizing effect of TiO$_2$-cement, a part of this impact – the initial NOx emissions - can be offset with time. Further analysis was performed based on the conditions in Atlanta, Georgia, USA to calculate the time required for the TiO$_2$-cement to offset the NOx from its production. Atlanta, USA with an average sunshine per day of 7.25 hours was selected because of the location where this research was conducted as well as its relevance to urban environmental conditions. The annual NO$_2$ concentration in Atlanta was reported 17.0 ppb in 2004 [13]. When 5% of TiO$_2$ was used as a replacement of cement by mass and 5mm thick layer is applied to a surface, 2.12 years are required to offset the initial NOx emissions by the TiO$_2$-modified cement. If the surface is frequently washed, as with rainfall, as is expected during the life of TiO$_2$-cement surfaces, the photocatalytic activity could be renewed and hence these surfaces should perform well throughout the life of the structure. The direct benefit of the use of this TiO$_2$-modified cement is reduction of pollutant gas (NOx) concentration and thereby positively impact the air quality and decrease of smog creation, especially in urban applications. Thus in the long term, TiO$_2$ modified cement could be beneficial to decrease the
initial higher environmental impact because of production and thereby resulting in a sustainable construction product.

CONCLUSIONS

Nanoparticles of TiO$_2$ were found to accelerate the rate of C$_2$S hydration and increase peak height with increasing percentage mixed with C$_2$S pastes. Similar acceleratory behavior with nanoparticle additions was noted from prior studies on C$_3$S and ordinary portland cement. The model fits for the C$_2$S hydration data indicated that these kinetics be described by the two models, with the BN model giving a better fit especially in the deceleration period than the Avrami model. Because the increased C$_2$S rate of hydration was not necessarily related to the $k_B/k_G$ in the boundary nucleation model, other acceleratory mechanisms should be investigated to more fully understand the behavior.

The results from LCA show that initially the TiO$_2$-modified cement has higher environmental impact compared to ordinary portland cement. This can partly be ameliorated by adding up to 17% of inert filler without compromising the degree of hydration, due to the acceleratory effect of the nanoparticles on portland cement hydration. Also, it is likely that the negative environmental effect from production can be offset in the long term by the photocatalytic NOx oxidation of TiO$_2$, ultimately turning into more beneficial to the environment than ordinary portland cement.

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