NATIONAL TRANSPORTATION SAFETY BOARD
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Materials Laboratory Division
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MATERIALS LABORATORY STUDY REPORT Report No. 19-037

A. ACCIDENT INFORMATION

Place	:	Miami, FL
Date	:	March 15, 2018
Vehicle	:	FIU UniversityCity Pedestrian Bridge
NTSB No.	:	HWY18MH009
Investigator	:	Robert Accetta (HS-20)

B. COMPONENTS EXAMINED

Literature review of the use of titanium dioxide (TiO_2) nanoparticles in concrete structures.

C. DETAILS OF THE STUDY

Cement is a mineral mixture that when ground into powder and mixed with water can form a stone-like mass. The hardening is due to chemical reactions that occur when the crystalline constituents hydrate. When it was re-discovered in the 1700s, cement consisted of volcanic ash, lime, and clay that hardened when wet. Cement with improved hardness was patented in 1824 as "portland cement'.[1] Current production Portland cement is a combination of a calcareous material (e.g., a calcium-rich oxide like limestone, chalk, or oyster shells) and an argillaceous material (e.g., a combination of silica and alumina, such as from clay, shale, and blast furnace slag). Today portland cement is one of the most widely used construction materials in the world. The use of portland cement concrete is so pervasive that unless stated otherwise, 'concrete' is assumed to refer to portland cement concrete.[2]

Concrete is a composite material that in the most basic form combines cement, aggregates (both coarse and fine), water, air voids, and, frequently, admixtures. Admixtures are substances added to impart a specific quality to the concrete, either in its freshly mixed state or its hardened condition. Admixtures are typically classified by their chemical and functional physical characteristics, such as air entrainers, water reducers, retarders, accelerators, and others.[3]

[1] J.R. Davis, Technical Brief 8: Cement, *ASM Materials Engineering Dictionary*, ASM International, 1992, p 67.
[2] M. S. Mamlouk and J. P. Zaniewski, *Materials for Civil and Construction Engineers*, Addison Wesley Longman, Inc., 1999, p 140.
[3] P.C. Hewlett, *Concrete Admixtures: Use and Applications*, The Construction Press, 1978.

One specific use of admixtures is to increase the durability of the concrete. Over time, concrete in older bridges, roads, and other structures can allow water and other aggressive elements, for example applied de-icing substances and sea salt effects, to enter the structure, eventually resulting in corrosion problems.[4] Permeability of substances can be affected by the internal structure of the concrete. An addition of nanoparticles to concrete can act as nanofillers that result in tighter pore structure and better packing condition, as well as better consolidation during construction.[5,6] Experiments have shown reduced depth of chloride penetration into a concrete structure with nanoparticles as compared to one without, which would reduce the ability of the chloride to cause corrosion in the inside of the structure.[5]

Photolysis is the phenomenon where UV-radiation from sunlight decomposes air pollutants, which helps get rid of smog in cities. Photolysis proceeds slowly but can be accelerated by a catalyst; the process is then called photocatalysis.[7] Photocatalysts can be admixtures used in concrete to reduce atmospheric pollution and make structures so-called 'self-cleaning'. Titanium dioxide (TiO_2) is the photocatalyst most widely added to concrete due to its high activity, competitive cost, and because it is produced at a large scale. However, photocatalytic activity resulting from TiO_2 reactions only 'clean' the external surface of the structure that is in the presence of sunlight.[8] Thus, the amount of photocatalytic activity can vary depending on parameters like wall orientation and solar radiation.[9] Comparisons between such variables are difficult because there is no standardized test for measuring photo-degradation of organic pollutants in cement-based materials.[10]

The use of nano-TiO_2 is preferred over normal TiO_2 because it has increased reactivity due to its higher specific surface area.[7] While there is added cost associated with nano-TiO_2, it is often offset by only needing a small amount in the surface layer of the structure to produce the self-cleaning effect. However, there is a balancing act to get the level of TiO_2 correct, as a lower amount of TiO_2 may be insufficient to ensure self-cleaning and air purification at longer times as the structure ages.[8]

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[4] E. Mohseni, M. M. Ranjbar, and K. D. Tsavdaridis, "Durability Properties of High-Performance Concrete Incorporating Nano-TiO_2 and Fly Ash", *American Journal of Engineering and Applied Sciences*, 2015, Vol. 8, No. 4, 519-526.

[5] M. Jalal, "Durability Enhancement of Concrete by Incorporating Titanium Dioxide Nanopowder Into Binder", *Journal of American Science*, 2012, Vol. 8, No. 4, 289-294.

[6] K. Behfarnia, A. Keivan, and A. Keivan, "The Effects of TiO_2 and ZnO Nanoparticles on Physical and Mechanical Properties of Normal Concrete", *Asian Journal of Civil Engineering*, 2013, Vol. 14, No. 4, 517-531.

[7] P. Bílý, "Exploitation of TiO_2 Nanoparticles in Concrete Industry", *Proceedings of the 9th fib International PhD Symposium in Civil Engineering*, July 22-25, 2012, 425-430.

[8] A. Rehman, A. Qudoos, H. G. Kim, and J. S. Ryou, "Influence of Titanium Dioxide Nanoparticles on the Sulfate Attack Upon Ordinary Portland Cement and Slag-Blended Mortars", *Materials*, 2018, Vol. 11, No. 3, 356.

[9] A. Esteban-Cubillo, R. Pina-Zapardiel, J. Vera-Agullo, and J. Santarén, "Concrete Benefits from New Nanoparticles: Sepiolite Carrier Enhances Photocatalytic Activity of TiO_2", *European Coatings Journal*, 2013, No. 11, pp 5-9.

[10] A. Maury and N. De Belie, "State of the Art of TiO_2 Containing Cementitious Materials: Self-Cleaning Properties", *Materiales de Construcción*, 2010, Vol. 60, No. 298, pp 33-50.

One other consideration when relying on TiO_2 as a cleaning agent is that it is specifically vulnerable to sulfate attack. If sulfates penetrate the structure then microcracking can result, particularly at the aggregate/cement paste interface.[8] Since the aggregate/cement paste interface is typically the weakest location within concrete, additional cracking in this area can effect the strength of the structure overall.[11] Consequently, it is best to design structures that include TiO_2 additions to be sulfate resistant.

While the addition of nano-TiO_2 is only prudent in the outer layers of a structure when focusing exclusively on atmospheric pollution reduction, the addition of nanoparticles in general can affect the physical properties of the concrete. Since nano-TiO_2 was added not just to the outer layer but within the concrete mix used for the structure from the referenced investigation, the effect specifically of nano-TiO_2 to concrete structures was researched.

The addition of nanoparticles to concrete can accelerate cement hydration, which has a positive effect on the microstructure of concrete, which directly correlates with durability.[12] Concrete microstructure that has accelerated hydration due to nanoparticles is denser due to their ultrafine size and high surface area to volume ratio.[13] Early age hydration rate can be beneficial due to the potential influence on setting time, dimensional stability, and strength development.[7] Use of nanoparticles can also minimize the strength loss associated with using low-cost supplementary cementitious material, such as fly ash, though the effect is mostly confined to the early stages of curing.[4]

Similar to how interstitial elements can fill space in the crystalline structures of metals, nanoparticles can fill smaller spaces with a concrete microstructure. Porosity will therefore decrease, which can correlate to a deterioration in the workability of the concrete mix.[14] While not all have observed this effect, in general the addition of further amounts of TiO_2 added to a concrete mix directly decreases the workability of fresh concrete.[12,15,16] However, this effect can be offset and the workability improved with the addition of superplasticizers to the concrete mix.[4]

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[11] M. S. Mamlouk and J. P. Zaniewski, *Materials for Civil and Construction Engineers*, Addison Wesley Longman, Inc., 1999, p 193.

[12] P. Niewiadomski and D. Stefaniuk, "The Effect of Adding Selected Nanoparticles on the Mechanical Properties of the Cement Matrix of Self-Compacting Concrete", *Applied Mechanics and Materials*, 2015, Vol. 797, pp 158-165.

[13] L. Wang, H. Zhang, and Y. Gao, "Effect of TiO_2 Nanoparticles on Physical and Mechanical Properties of Cement at Low Temperatures", *Advances in Materials Sciences and Engineering*, 2018, Vol. 2018, Article ID 8934689, 12 pages.

[14] P. Niewiadomski, "Short Overview of the Effects of Nanoparticles on Mechanical Properties of Concrete", *Key Engineering Materials*, 2015, Vol. 662, pp 257-260.

[15] M. Jalal, A. A. Ramezanianpour, and M. K. Pool, "Effects of Titanium Dioxide Nanopowder on Rheological Properties of Self Compacting Concrete", *Journal of American Science*, 2012, Vol. 8, No. 4, pp 285-288.

[16] J. Sorathiya, S. Shah, and S. Kacha, "Effect of Addition of Nano "Titanium Dioxide" (TiO_2) on Compressive Strength of Cementitious Concrete", *ICRISET2017 International Conference on Research and Innovations in Science, Engineering & Technology*, Kalpa Publications in Civil Engineering, 2017, Vol. 1, pp 219-225.

Due to their size, nanoparticles have high surface energy, which causes them to agglomerate. This agglomeration then reduces their activity and hinders their incorporation and homogeneous dispersion. Nanoparticles thus can end up grouped into larger aggregates in the microstructure.[9] Such grouping can lower the compressive strength of concrete by preventing a uniform, compact pore structure.[6] Additionally, a non-uniform, weakened pore structure can result in increased chloride penetration, and thus accelerate degradation.[5]

Many researchers have found that the addition of small amounts of nano-TiO_2 can result in higher compressive strength of concrete. Higher compressive strength of concrete can lead to a reduction in the necessary amount of steel reinforcement within a structure, which would be a significant cost savings.[4] Addition of nanoparticles has also been shown to result in higher elastic modulus, bond strength, and corrosion resistance, as well as increased abrasion resistance, which can prolong the service life of a structure.[12,17,.18]

However, there is a tipping point (experimentally around 1.0-1.5 wt. %) at which adding higher amounts of nano-TiO_2 will have a detrimental effect and further additions will lead to a decrease the compressive strength of the concrete, as well as other beneficial mechanical properties.[4,8,16,17,19,] While many agree this is true, there is no definitive conclusion on the optimum amount of TiO_2 nanoparticles to add for the greatest benefit to physical properties.[14] Additionally, little is known about cyclic loading, fracture mechanics, and behavior in freeze-thaw conditions of TiO_2 nanoparticle enhanced concrete structures. These areas provide suggested directions of further research.

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[17] M. M. Sadawy and E. R. Elsharkawy, “Effect of Nano-TiO_2 Addition on Mechanical Properties of Concrete and Corrosion Behavior of Reinforcement Bars”, *International Journal of Engineering Research and Application*, 2016, Vol. 6, No. 10, pp 61-65.

[18] H, Li, M. Zhang, and J. Ou, “Abrasion Resistance of Concrete Containing Nano-Particles for Pavement”, *Wear*, 2006, Vol. 260, pp 1262-1266.

[19] A. S. Kushwaha, R. Saxena, and S. Pal, “Effect of Titanium Dioxide on the Compressive Strength of Concrete”, *Journal of Civil Engineering and Environmental Technology*, 2015, Vol. 2, No. 6, pp 482-486.