

Science for Environment Policy

Nanoparticle release from self-cleaning cement: new study considers how much escapes into the environment, and how

New figures on how much titanium dioxide nanomaterial (TiO₂-NM) could be released into the environment from photocatalytic cement — a new type of self-cleaning cement — are presented in a recent study. Based on experimental test results, the researchers estimate that between 0.015% and 0.033% of photocatalytic cement's TiO₂-NM content could potentially escape over several years of cement use, depending on the level of cement porosity. The study could help inform environmental risk assessment of TiO₂-NM, as well as safer design of nano-products (i.e. commercialised products incorporating nanomaterials).

Photocatalytic cement containing TiO₂-NM is used in a number of construction products, including paving blocks, road surfaces and wall panels, and there is an emerging market for it. The nanomaterial gives the cement self-cleaning and air-purifying properties. In 2012 it was estimated that 4 000 tons of photocatalytic cement are produced in Europe each year — a minor, but not insignificant, fraction of Europe's total cement production (235.5 million tons in 2014).

The potential environmental risks of this cement need to be considered alongside its promising benefits. Studies have suggested that TiO₂-NM may have toxic effects on aquatic animals, for example¹.

To shed new light on how the cement's design could affect such risks, this study investigated how TiO₂-NM is released from the material during its use as a building material, how much is released, and the characteristics of TiO₂-NM when released. Indeed, cement is not a stable material and is subjected to degradation and weathering when exposed to harsh environmental conditions (rain, freezing/thawing cycle, etc.).

Specifically, the researchers were interested in how the porosity of the cement (the number of tiny holes it contains) affects the release. The researchers performed tests at the laboratory scale to simulate cement-accelerated weathering. They placed pellets of three types of white Portland cement (the most common type of cement used around the world) containing TiO₂-NM in water for seven days. They then chemically analysed the water to quantify the presence of TiO₂-NM which had leached out of the cement. They found that TiO₂-NM was exclusively released as a particle, as no dissolved Ti was detected.

The three cements differed in their initial porosity, which was determined by X-ray 3D imaging. This cement porosity is related to the water content used during cement paste cure² (water to cement ratio (w/c) of 30, 40 and 50% in this study): the higher the water content in the initial cement paste, the more porous the hardened cement. The researchers assumed the hypothesis that the higher the cement porosity, the higher the TiO₂-NM release.

As expected, the cements degraded over the seven days and their surface layer became even more porous. The degradation and porosity increased at higher rates for cements with higher water content. Importantly, the surface layer of the cement, which may play a key role in releasing the particles, increased in porosity by 9.6%, 14.1% and 41% for the 30%, 40% and 50% cements, respectively.

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1. See, for example: Fouqueray, M., B. Dufils, B. Vollat, *et al*, (2012). Effects of aged TiO₂ nanomaterial from sunscreen on *Daphnia magna* exposed by dietary route. *Environmental Pollution*, 163: 55–61.

2. Cement curing is the process of maintaining moisture levels inside cast concrete so that hydration can continue. The typical curation time is 28 days.

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After seven days of accelerated ageing, the total release of TiO₂-NM was calculated to be 18.7, 33.5 and 33.3 milligrams per square metre of cement (or 4.12, 8.72, 9.21 micrograms of TiO₂-NM per gram of cement) — for the 30%, 40% and 50% cement mixes, respectively. These figures represent 0.015–0.033% by weight of the total TiO₂-NM initially contained in the cement.

The release rate of TiO₂-NM gradually increased with time spent in the water — the researchers believe that this may be related to the changes in the altered surface layer and increasing cement porosity. However, it is interesting to note that the 50% and 40% cements released similar quantities of particles — despite the higher degradation and porosity of 50% cement. Further research to identify the mechanisms behind this apparent blockage/retention of nanoparticles in the 50% cement could help manufacturers design safer nano-products, the researchers suggest.

In a second set of experiments, the researchers adapted the initial tests to analyse the form of released TiO₂-NM under conditions that simulate the real world a little more closely. The pH level of the water was neutralised to pH 7 (from around pH 10 in the first set of experiments), to resemble natural surface water, such as river water. At this lower pH, the residual cement, potentially surrounding released TiO₂-NM, is more likely to dissolve.

TiO₂-NM detected in the water in these second experiments was nearly all in clusters with silicon (Si) and aluminium (Al); only one 'free' (non-clustered) TiO₂ particle was detected. These clusters are not found in the cement itself, and the researchers comment that even if the TiO₂-NM can be released with cement surrounding layers, the layers were chemically transformed at pH 7. This brings the free TiO₂-NM and TiO₂-NM Si-Al clusters into direct contact with the environment and thus may increase its toxic risk to wildlife. Individually, the released TiO₂ particles were between 70 and 312 nanometres (nm) in size (average size of 148 nm).

The study's experimental conditions, designed at a laboratory scale, were intended to represent a 'worst-case scenario' of cement degradation by water. While they are unrealistic conditions (as the researchers themselves write), the study was designed to provide new data on the mechanisms controlling the TiO₂-NM release, which could also act as a 'starting point' for risk assessment and computer models, which predict the fate and transport of nanoparticles.

However, the researchers estimate that the seven days of submersion in water simulated from a few years to a decade of real-world ageing of cement during use. They suggest that this represents a minor source of TiO₂-NM to the environment, but stress that research into the release of TiO₂-NM over the cement's entire life-cycle is needed. They emphasise that specific attention is required at the end of life stage (building demolition, waste management/storage, etc.), as there is potential for a higher release of TiO₂-NM.

