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Environmental exposure to TiO_2 nanomaterials incorporated in building material☆

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ABSTRACT

Nanomaterials are increasingly being used to improve the properties and functions of common building materials. A new type of self-cleaning cement incorporating TiO_2 nanomaterials (TiO_2-NMs) with photocatalytic properties is now marketed. This promising cement might provide air pollution-reducing properties but its environmental impact must be validated. During cement use and aging, an altered surface layer is formed that exhibits increased porosity. The surface layer thickness alteration and porosity increase with the cement degradation rate. The hardened cement paste leaching behavior has been fully documented, but the fate of incorporated TiO_2-NMs and their state during/after potential release is currently unknown. In this study, photocatalytic cement pastes with increasing initial porosity were leached at a lab-scale to produce a range of degradation rates concerning the altered layer porosity and thickness. No dissolved Ti was released during leaching, only particulate TiO_2-NM release was detected. The extent of release from this batch test simulating accelerated worst-case scenario was limited and ranged from 18.7 ± 2.1 to 33.5 ± 5.1 mg of Ti/m^2 of cement after 168 h of leaching. TiO_2-NMs released into neutral aquatic media (simulate pH of surface water) were not associated or coated by cement minerals. The TiO_2-NM release mechanism is suspected to start from freeing of TiO_2-NMs in the altered layer pore network due to partial cement paste dissolution followed by diffusion into the bulk pore solution to the surface. The extent of TiO_2-NM release was not solely related to the cement degradation rate.

1. Introduction

The rapid development of new nano-enabled products (nano-products) is raising concerns about potential environmental impacts associated with unintended release of engineered nanomaterials (NMs) (Wiesner et al., 2006). Release into the environment may occur during each stage of a nano-product life cycle (i.e. production, manufacturing, use, disposal or recycling) (Gottschalk and Nowack, 2011; Mitrano et al., 2015; Nowack et al., 2012).

Environmental exposure can be estimated by quantifying the extent of NMs released during the usage and end-of-life stages of the product life cycle, and determining their environmental fate. Several papers recently reviewed the literature on NMs release mainly estimated from lab-test. (i.e Caballero-Guzman and Nowack, 2016; Froggett et al., 2014; Mackevica and Foss Hansen, 2016). Over the past 5 years, an increasing number of studies have reported NMs release from nano-products. However, those studies focused only on a limited number of NMs (Ag, TiO_2, CNT and SiO_2) and types of products (mainly paints, textiles and coatings).

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Moreover, only a limited number of relevant release scenarios (machining, weathering) were investigated. More in-depth knowledge on potential NMs release in a wide range of matrices is crucial to come up with reliable risk assessments.

Titanium dioxide nanomaterial (TiO_2-NM) is currently among the most highly produced NMs in Europe (ca. 10,000 t/year) (Keller et al., 2013; Piccinno et al., 2012; Sun et al., 2014). It is used for a variety of applications, including in manufacturing cosmetics (mainly sunscreens), plastics, paints and cements (Macwan et al., 2011; Robichaud et al., 2005). Studies on TiO_2-NM release from paints (Al-Kattan et al., 2014, 2013; Kaegi et al., 2008a; Shandilya et al., 2015), sunscreens (Botta et al., 2011; Gondikas et al., 2014), and textiles (von Goetz et al., 2013; Windler et al., 2012) have focused mainly on the usage stage of the product life cycle. In accordance with the high chemical stability of TiO_2-NMs, these studies have revealed the exclusive particulate release of TiO_2-NMs present mostly as agglomerates and/or aggregates in nano-product degradation residues (NDRs). These experimental data obtained at lab-scale provide a first quantitative basis for real scenarios emission estimations. They are used to validate models recently developed to predict NM release as well as the fate and distribution of these materials in environmental compartments. TiO_2-NMs are assumed to be present in all environmental compartments, with preferential accumulation in soils and landfills (Gottschalk et al., 2010, 2009; Mueller and Nowack, 2008; Sun et al., 2014), because of their very low solubility.

Among TiO_2-NM applications, their incorporation in construction materials is considered as an emerging market (Broekhuizen et al., 2011; Hincapié et al., 2015; Lee et al., 2010; Sanchez and Sobolev, 2010). The NMs incorporation (i.e. carbon nanotube, fly ash, silica etc.) in building materials is referenced in the purpose to increase their durability, hydration degree and resistance (Bolyard et al., 2013; Makar, 2011; Nochaiya et al., 2010). Unlike, TiO_2-NMs are incorporated in cement for their photocatalytic properties to confer newly self-cleaning and air purifying properties (Cárdenas et al., 2012; Demeestere et al., 2008; Folli et al., 2012; Maggos et al., 2007). TiO_2-NMs incorporated in the cement matrix are usually non-coated anatase with a mass concentration ranging from 0.3 to 10 wt% (Ruot et al., 2009). Photocatalytic cement is now used in paving blocks, concrete roads, glass-reinforced cements, wall panels, floor plates, covering panels, etc. According to Sun et al., (2014) and Piccinno et al., (2012), TiO_2-NMs incorporated in photocatalytic cement represent about 0.1 and 1% of the European TiO_2-NM production, i.e. a total of about 10.2 and 102 t of TiO_2-NMs, respectively. These masses are equivalent to an annual production of 204–340 and 2400–3400 t of cement, respectively (with a mean TiO_2-NM concentration in photocatalytic cement of 3–5 wt%). These estimates are in close agreement with the total production volume given by some photocatalytic cement producers, estimated at 4000 t/year in Europe (Guerrini, 2012). This represents a minor, but not negligible, fraction of the total European cement production (235.5 million t in 2014) (CEMBUREAU, 2014).

The environmental benefits of incorporating TiO_2-NMs in cement should be assessed along with the potential release of TiO_2-NMs into the environment at each stage of the cement life cycle. Indeed during its usage stage, cement is subjected to alteration and dissolution when exposed to water (Faucon et al., 1996; Jain and Neithalath, 2009). Cement leaching leads to the formation of an altered layer at the cement-water interface, where primary mineral dissolution and secondary mineral precipitation occur. Recent literature reviews have highlighted the lack of investigations on NMs release from cement during the usage stage (Caballero-Guzman and Nowack, 2016; Froggett et al., 2014; Mackevica and Foss Hansen, 2016).

Many variables can potentially control the extent of TiO_2-NM release, such as: (i) chemical stability and morphology of NMs, (ii) physico-chemical properties and stability of the cement, and (iii) specific NM-matrix interactions (Foss Hansen et al., 2007). As previously mentioned, TiO_2-NMs exhibit high chemical stability, leading to exclusive particulate release from nano-products. In photocatalytic cement subjected to alteration during its usage stage, we expected that the porosity gradient at the cement leaching front would drive TiO_2-NM release into the environment. Indeed, increased porosity due to partial cement dissolution can lead to TiO_2-NM leaching out of the cement.

In the literature, cement porosity is mainly determined on the basis of mercury porosimetry (MIP) results. Cement pores are commonly divided into gel and capillary pores, with sizes of 1–3 nm and 3 nm-30 μm, respectively. Cement porosity ranges from 17 to 58% depending on the water-to-cement mass ratio (w/c ratio) and curing (Raymond A. Cook and Hover, 1999a; Faucon et al., 1998; Haga et al., 2005a). A longer curing time and lower w/c ratio result in a smaller total porosity and smaller threshold pore width. The altered layer formed at the cement surface during leaching is characterized by increased porosity, mainly due to the partial dissolution and diffusion of calcium ions in the pore solution, thus generating a new pore volume. The volume of pores with larger diameter pores, as well as volume of pores with a diameter of less than 0.1 μm increase in this altered layer (Haga et al., 2005b). The w/c ratio, i.e. the initial porosity, strongly influences the extent of cement degradation (Haga et al., 2005b), i.e. the larger the initial porosity the faster the dissolution kinetics.

This study was aimed at identifying the main TiO_2-NM release mechanisms. We specifically focused on determining whether the porosity gradient that develops during cement leaching was the primary driver of TiO_2-NM release into the environment. To this end, hardened cement pastes with different initial porosities were subjected to an accelerating leaching protocol (batch test) designed at the lab-scale to differentiate particulate and soluble Ti release. TiO_2-NM release kinetics during cement aging were investigated. In parallel, the cement matrix was characterized in detail before and after leaching to measure the altered layer thickness (X-ray μ-fluorescence (μ-XRF)), and the porosity (micro and nano X-ray computed tomography (X-ray CT)). TiO_2-NM release was quantified by ICP-AES. Moreover, the neutralization of leaching solutions was performed to simulate the transfer of NDRs in natural media such as rivers and specifically study TiO_2-NM speciation (i.e. identify potential TiO_2-NM aggregation/agglomeration, heteroaggregation and any embedding/coating).

2. Materials and methods

2.1. Cement preparation

White Portland cement (called control cement) and photocatalytic white Portland cement incorporating TiO_2-NMs were provided by an industrial partner. Total Ti content in both anhydrous cements was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; model Ultima C, Horiba Jobin Yvon) after cement alkaline fusion. Three types of hardened cement paste were obtained by mixing anhydrous cement powder with ultrapure water (UPW) at water to cement ratios (w/c) of 0.3, 0.4 and 0.5 to create a range of initial porosity. Cement pastes were cured in a cylindrical container (diameter about 2 cm) under water-saturated atmosphere at room temperature for 28 days. The hardened cement pastes are referred to cement 30%, 40%, and 50%, respectively. Cylindrical pellets (thickness about 1 cm) of hardened cement paste were obtained by micro-cutting with a diamond wire saw. Pellet's edges were polished to remove specific border surface crystal orientations and then were flushed with compressed air to