Environmental exposure to TiO₂ 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, TiO₂, CNT and SiO₂) and types of products (mainly paints, textiles and coatings). 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 (TiO₂-NM) is currently among the most highly produced NMs in Europe (ca. 10,000 t/year) (Keller et al., 2013; Piccinno et al., 2012; Tian Yin 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 TiO₂-NM release from paints (Al-Kattan et al., 2014, 2013; Kaegi et al., 2008a; Shandilya et al., 2015), sunscreens (C 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 TiO₂-NMs, these studies have revealed the exclusive particulate release of TiO₂-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. TiO₂-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; T. Y. Sun et al., 2014), because of their very low solubility.

Among TiO₂-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. (Sun et al., 2014) and Piccinno et al. (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 remove residual cutting dust. Precise mass and external surface were measured for each pellet before leaching test.

2.2 Mineralogical analysis

Synchrotron X-ray diffraction (SXRD) data of the anhydrous and hydrated cements loaded in 1 mm Kapton capillaries were collected at beamline 11-ID-B ($\lambda = 0.2114 \text{ \AA}$) at the Advanced Photon Source, Argonne National Laboratory (APS-ANL, Argonne, IL). An amorphous Si area detector system (Perkin Elmer) was used for data collection (Chupas et al., 2003). A CeO_2 standard (NIST diffraction intensity standard set 674a) was used to calibrate the sample-to-detector distance and the non-orthogonality of the detector relative to the incident beam. 2D to 1D data conversion was performed using Fit2D (Hammersley et al., 1996). The background intensity measured for a blank (empty) capillary was subtracted from the data.

2.3 Particulate and soluble Ti release

Leaching batch tests were performed for 168 h (7 days) at a mass liquid-to-solid ratio (L/S) of 100 with ultra-pure water (UPW). A classical batch protocol was adapted to differentiate the particulate and soluble released fractions. Although far from typical realistic conditions, the purpose of our protocol was to generate a “worst case scenario” and to test our initial question: Is the porosity gradient that develops during cement leaching the primary driver of TiO_2 -NM release? Cement pellets were placed inside a dialysis membrane (10 kDa cutoff, about 2.5 - 4 nm) containing 50 mL of UPW (V_{in}) and immersed in a beaker filled with UPW (V_{out}). The total leaching solution volume ($V_{\text{out}} + V_{\text{in}}$, about 600-800 ml) was precisely determined for each test to reach an L/S ratio of 100 and was stirred with a magnetic polytetrafluoroethylene (PTFE) bar. Released Ti detected in the solution outside the membrane was exclusively assigned to soluble Ti based on the assumption that all released particulate Ti remains trapped inside the membrane.

The three types of hardened cement paste (cement 30, 40 and 50%) were leached in triplicate. pH and conductivity were monitored in the solution outside the dialysis membrane (see values in Fig. S1). TiO_2 -NM particulate release rates were determined by collecting and replacing both the dialysis bag and the solution inside the dialysis bag (V_{in}) at various leaching times (1, 3, 7, 24, 48, 72, 96, 120, 144 and 168 h). Less than 10% of the leaching solution volume was replaced at each time point, thus minimizing the disturbance potentially

generated due to concentration gradient between the cement pores and leaching solutions (i.e. negligible pH and conductivity variations measured during the sampling procedure).

Chemical analyses of the sampled leaching solutions and dialysis membranes were performed by ICP-AES. All samples were digested in a nitric (67-69 vol.%) and sulfuric (96 vol.%) acid solution at 200°C for 4 h in ceramic vial. All chemicals were reagent grade. The digestion method was validated by dissolution of pure TiO₂-NMs (P25). The resulting limit of quantification (LQ) was calculated by addition of the blank value ($\approx 5 \mu\text{g/l}$) and 10 times the SD of blank and was about 10 $\mu\text{g/l}$.

Particulate and soluble Ti released at each time point, expressed in mg of Ti/m² cement, were then calculated using the following equations:

$$m_{Ti\ particulate} = m_{Ti\ membrane} + m_{Ti} \times V_{in} - m_{Ti} \times V_{out}$$

$$m_{Ti\ soluble} = m_{Ti} \times V_{out}$$

$m_{Ti\ membrane}$ is the amount of particulate Ti adsorbed on the dialysis membrane, $m_{Ti} \times V_{in}$ is the amount of Ti in the solution inside the membrane and $m_{Ti} \times V_{out}$ is the amount of Ti in the solution outside the membrane.

In a second step, the leaching protocol was slightly modified to simulate the transfer of NDRs into natural aquatic media and specifically evaluate the speciation of TiO₂-NMs i.e. embedded or not in cement matrix and as single particles or forming aggregates/agglomerates. Cement pellets (cements 30% and 40 %) were maintained in suspension by a nylon thread and immersed in UPW for 168 h (L/S of 100). No dialysis membrane was used in order to avoid interactions between released TiO₂-NMs and the membrane. A shaker table was used to avoid any contamination resulting from abrasion of the PTFE stir bar.

After 168 h of leaching, the cement pellets were then removed and the collected NDR-containing solutions were neutralized at pH 7 using an HNO₃ solution at 0.5 mol./L. The objective was to simulate the behavior of TiO₂-NMs when reaching natural neutral aquatic media. One sample was dedicated to electron microscopy observations (see details below). Aggregation/agglomeration state of TiO₂-NMs in neutralized solution cannot be rigorously estimated from electron microscopy observation as artifacts can occur during sample preparation (e.g. aggregation of particles during drying step). And note that size measurement by dynamic light scattering was not possible because of the low particle concentrations. Thus the neutralized solutions were filtered at 0.45 μm using a frontal filtration system with a nitrate cellulose filter and Ti was quantified in both size fractions according to the above-described procedure (acid digestion and ICP-AES analysis).

2.4 Electron microscopy observations (SEM and TEM)

The morphology and size of TiO₂-NMs incorporated in anhydrous cement was assessed by transmission electron microscopy (TEM, model CM 12, Philips). The microscope was operated at 120 kV accelerating voltage and was equipped with a coupled energy-dispersion spectrometer (EDS, X-max Oxford Instruments) for elemental analyses. Sample was deposited onto copper mesh grids, previously treated by plasma to be hydrophilic ((0.1 mbar and 45 mA for 3 min, model *K100X*, Quorum Technologies Ltd.).

NDRs in neutralized solution were observed by scanning electron microscopy (SEM, Zeiss GeminiSEM 500 ultra-high resolution FESEM) and analyzed with EDX (Energy Dispersive X-Ray) system (EDAX SSD EDS). The microscope was operated at 10 kV accelerating voltage and was equipped with multiple detectors (In-lens SE and Energy Selective Backscattered detector). A drop of sample was deposited onto silicon wafer and dried at 40°C. Prior to deposition, the neutralized leaching solution was dialyzed to remove Ca⁺ ions (1000 Da cutoff) and reduce precipitation of calcite during the drying step.

2.5 Altered layer formation kinetics

The extent of leached cement paste degradation was first estimated by measuring the altered layer thickness after 3, 11, 24, 72 and 168 h of leaching for the three hardened cement pastes. At the end of the leaching time, cement pellets were removed from the dialysis membrane, then immediately dried in a nitrogen atmosphere to avoid secondary calcite precipitation at their surface and embedded in resin (araldite).

Hyperspectral mapping analyses were carried out using an X-ray micro-fluorescence spectrometer (μ -XRF; model XGT-7000, HORIBA Jobin Yvon) equipped with an X-ray guide tube producing a finely focused beam with a 10 μ m spot size (Rh target, accelerating voltage of 30 kV, 1 mA). Chemical maps (256 x 256 pixels with a 10 μ m pixel size) showing the spatial distribution of Ti and Ca were obtained from their respective K α emission lines with a total counting time of 20000 s/map. Mapping areas were selected from a cross-section of embedded leached cement pellet including the non-altered core, the altered layer and the cement-water interface. The altered layer thickness was measured from the μ -XRF intensity profile along the x-axis (from the cement surface to the non-altered core) of the Ca map while integrating a minimum of 100 pixels along the y-axis. The Ca intensity profile decreases in the altered layer due to cement aging and non-congruent dissolution of Ca-bearing primary cement phases. Thus, the calcium alteration front is generally used as a marker of the extent of cement degradation. The interface between the non-altered core and altered layer was considered to be at the point where the Ca intensity dropped in the profile (decrease from the

average intensity observed in the non-altered core), as detailed in Fig S2. The error in the altered layer thickness is evaluated at $\pm 20 \mu\text{m}$ (± 2 pixel size). Ca profiles were obtained using ImageJ freeware (Schneider et al., 2012). Ti maps were used to determine the TiO_2 -NM dispersion in the hardened cement paste at a spatial resolution of $10 \mu\text{m}$.

2.6 Variations in the hardened cement paste porosity during aging experiments

The extent of leached cement degradation was also evaluated by measuring the porosity in specific regions of each sample, i.e. non-altered core and altered layer, using micro and nano X-ray computed-tomography (micro-CT and nano-CT, respectively) systems (microXCT-400 and UltraXRM-L200, Zeiss XRadia). Nano-CT (63 nm isotropic voxel size, field of view (FOV) of $65 \mu\text{m}$ side) and micro-CT ($1.81 \mu\text{m}$ isotropic voxel size, FOV of 1.85 mm side) were combined to obtain statistical pore network information for cement pore sizes ranging from 130 nm to $500 \mu\text{m}$. Although this pore size range corresponds to only a fraction of the total cement pore volume probed by mercury intrusion porosimetry (MIP) (i.e. pore volume ranging from a few nm to $375 \mu\text{m}$) (Bossa et al., 2015; Raymond A. Cook and Hover, 1999b), the main advantage of CT compared to MIP is that it is spatially resolved and thus provides information on the porosity gradient formed in the altered layer during cement leaching.

Micro-CT was used to image pore sizes ranging from $3.62 \mu\text{m}$ to about $500 \mu\text{m}$, corresponding to a part of the cement capillary pores and air trapping pores, in a large FOV (mm range). A large FOV enables scanning of a representative volume, including the non-altered core, the altered layer and the resin. Nano-CT scans were recorded at the altered cement surface, focused at the cement/water interface. Its unique spatial resolution at the lab-scale provides a description of the pore size ranging from 130 nm to about $10 \mu\text{m}$, named capillary pores in cement. Additional details regarding sample preparation, combined micro- and nano-CT analysis and data treatment (pore network quantification) were published previously (Bossa et al., 2015).

3 Results

3.1 TiO_2 -NMs in anhydrous photocatalytic cement: content, mineralogy and size

The chemical compositions of the cements determined by ICP-AES are summarized in Table S1. These cements were mainly composed of Ca and Si ($\approx 66 \text{ wt.}\%$ CaO and $\approx 23 \text{ wt.}\%$ SiO_2).

The TiO_2 content in anhydrous photocatalytic cement was $2.85 \pm 0.08 \text{ wt.}\%$, including a small fraction of Ti detected as an impurity in the main cement minerals ($0.18 \text{ wt.}\%$ TiO_2

content in the control cement). The SXRD pattern of the photocatalytic cement exhibited a peak at 3.52 Å, corresponding to the (101) reflection of anatase (Fig. S3). The average crystallite size estimated using the Scherrer line broadening equation (Patterson, 1939) was 76 nm.

TEM size analysis of TiO₂-NMs in anhydrous photocatalytic cement revealed the presence of individual and aggregates/agglomerates containing Ti-rich roundish like particles with the presence of faced with individual sizes between 55 to 270 nm (mean size = 138 ± 53 nm, N=35) (Fig. 1A). These average values were slightly higher than the average crystallite size range estimated by SXRD (Fig. 1A). Note that the TEM observations were not necessary representative of the whole sample. Consistent with the SXRD results, the Fourier transform of single TiO₂ particle images revealed the presence of interplanar distances characteristic of anatase (Fig. 1B).

3.2 Hardened photocatalytic cement pastes: mineralogy, initial porosity and TiO₂-NM distribution

The SXRD analyses showed that the three hardened photocatalytic cement pastes (cement 30%, 40% and 50%) consisted of similar mixtures of hydrated minerals (portlandite, calcium-silicate-hydrates, ettringite) and residual anhydrous minerals (alite and belite) (Fig. S4). The peak characteristic of the (101) reflection of anatase observed for anhydrous photocatalytic cement was maintained after hydration.

The initial cement porosities measured by micro-CT reached 0.5, 2.5 and 1.8% for cement 30, 40 and 50%, respectively. Nano-CT indicated higher porosity values of 4.1, 14.3 and 17.0%, respectively (Fig. 2), confirming that the cement pore volume was mainly occupied by small pores not detectable by micro-CT (Bossa et al., 2015).

These porosity values were smaller than the previously reported cement pore volume determined by MIP, which probes the volume of pores in a larger size range (as mentioned above) (Cook and Hover, 1999; Gallé, 2001). In accordance to the literature, the initial porosities of hardened cement pastes measured at the nanometer-scale increased with the initial w/c ratio (Fig. 2) (Haga et al., 2005b) confirming we were able to test our initial hypothesis.

The spatial distribution of TiO₂-NMs in the hardened cement pastes was determined by μ-XRF (Fig. 1C). With a 10 μm pixel size, the Ti map suggested that Ti was relatively homogeneously dispersed in the hydrated cement matrix, with the exception of a few larger areas (around 50 μm) that were relatively concentrated in Ti. In accordance to ICP-AES chemical analysis results (Table S1) and μ-XRF sensibility, no significant Ti signal

(significantly higher than background signal) was detected in the control cement (Fig. 1D). The Ti signal measured by μ -XRF could therefore be attributed to TiO_2 -NMs. However, the μ -XRF spatial resolution was not sufficient to precisely identify the behavior of TiO_2 -NMS during cement hydration and a potential speciation variation. As for anhydrous cement, electron microscopy observation would be requested but TiO_2 identification into cement matrix was too challenging.

3.3 Extent of cement degradation as a function of the w/c ratio

The thickness of the altered layer at the cement surface, measured from the μ -XRF Ca profiles, increased with the leaching time and reached 370 ± 20 , 600 ± 20 to 860 ± 20 μm for cement 30, 40 and 50%, respectively (Fig. 3) after 168 h of leaching.

The porosity gradients in the altered layers of each sample were determined by micro- and nano-CT, as presented in Figure 2. At both scales and for the three photocatalytic cements, the porosity increased in the altered layer, thus confirming that mineral partial dissolution occurred during leaching. At the micro-scale, the porosity was 4.4 ± 0.2 , 3.6 ± 0.2 and $6.1\pm 0.3\%$ in the altered layer, for cement 30, 40 and 50%, respectively. At the nano-scale, the altered layer porosity was 13.7 ± 0.2 , 28.4 ± 0.4 and $58.0\pm 1.2\%$ for cement 30, 40 and 50%, respectively. These values revealed an increase of 9.6, 14.1 and 41%, respectively, compared to the initial porosity measured in unaltered cement paste. Taken together, the latter results (porosity and thickness of the altered layer) suggest that the extent of cement degradation increased with the w/c ratio of cement hydration, as initially expected.

3.4 Particulate TiO_2 -NM release kinetics

The Ti contents in solutions outside the dialysis membrane were below the ICP-AES quantification limit of 10 $\mu\text{g/L}$. The Ti concentrations measured in solutions inside dialysis membranes were ranging from 10 to 200 $\mu\text{g/L}$. The concentrations were then attributed to particulate Ti (size > 10 kDa cutoff, about 2.5 - 4 nm) released during the leaching test, as no dissolved Ti species was detected. The total particulate Ti release (expressed in mg Ti/m^2 of external surface of cement pellet exposed to water during leaching) was plotted as a function of the leaching time for each hardened cement type (cement 30, 40 and 50%) (Fig. 4.A).

Ti particulate release was detected for the three cement types as of 1 h of leaching. No significant difference in total particulate Ti release was measured between 1 h and 96 h of leaching for the three hardened cement pastes. After 96 h, the three cement types exhibited two distinct release trends. The total amounts of particulate Ti released from cement 40 and 50% were similar, but significantly higher than the total amount of particulate Ti released from cement 30%. After 168 h of leaching (7 days), the total particulate Ti release was

18.7±2.1, 33.5±7.4 and 33.3±5.1 mg Ti/m² of cement for cement 30, 40 and 50%, respectively. Note that Ti particulate release did not reach a plateau even after 168 h of leaching.

The instantaneous Ti release rate was measured at each time point t for the 3 cements using the following formula: $((m_{t+1})-(m_t))/\Delta t$, with m_t being the TiO₂-NM release quantity at time t expressed in mg of Ti/m² of cement (Fig. 4.B). Kinetic curves of TiO₂-NM release revealed two behaviors (Fig. 4.B). Similar trends were observed for the three cement types.

A first release behavior characterized by high variability and heterogeneity in the Ti particulate release rate was observed between 0 and 7 h of leaching. The proposed mechanism associated with this first release behavior is cement surface washing and the detachment of poorly attached TiO₂-NMs from the cement surface. This first release behavior represented 1.9, 2.7 and 5.5% of the total TiO₂ release measured after 168 h for cement 30, 40 and 50% respectively. It could therefore be considered as a minor release mechanism mainly due to sample preparation artifacts and is therefore not the focus of further discussions.

Contrary to the first, the second regime was identified by a release rate that gradually increased with the leaching time (between 7 and 168 h). Indeed, the Ti release rate increased from 0.05±0.04, 0.07±0.06 and 0.05±0.02 mg of Ti/(m² of cement.h) at 24 h of leaching to 0.19±0.10, 0.30±0.05 and 0.48±0.20 mg of Ti/(m² of cement.h) at 168 h of leaching for cement 30, 40 and 50%, respectively. The second behavior was considered to be the major behavior controlling TiO₂-NM release (up to 94.5% of total TiO₂ release) and will be correlated with the extend of the altered layer as well as the increase of cement porosity in the discussion part.

3.5 Speciation of TiO₂-NMs in neutralized leaching solution (pH 7)

Leaching solutions collected after 168 h of leaching with the adapted batch protocol were neutralized at pH 7 to simulate the transfer of NDRs into natural aquatic media. A significant amount of released Ti was detected in these solutions (cem 30%, 18,1±3.8 mg/m² after 168 h), in accordance with the findings for the first set of batch leaching (Fig. 4.A).

SEM observations of the NDRs in the neutralized leaching solutions (Fig. 5) revealed the presence of aggregate/agglomerates containing TiO₂ particles with individual sizes between 70 and 312 nm (average size of 148 ±41 nm, N=120) in accordance with individual initial size. TiO₂ particles present as bright spot on the image. The description of TiO₂ morphology is limited by the analysis resolution and the aggregation state. However, the faced morphology observed on TiO₂ particles in the anhydrous cement is still visible on some

particles. Some aggregate/agglomerates show a high concentration of TiO_2 particles (Fig.5.D).

Ti-containing particles were observed aggregated/agglomerated with Si-Al particles, present as linear intermix chains (Fig. 5. A and B). Some aggregate/agglomerates show a high concentration of TiO_2 particles (Fig.5.D). Ti was mainly detected in neutralized solution size fraction larger than $0.45\ \mu\text{m}$ ($89\pm3\%$ of total released Ti, cem 30%, 168h, N=3), confirming the SEM observation. Only one free TiO_2 particle was observed Fig.5. C.

4 Discussion

4.1 Particulate release of TiO_2 -NMs during photocatalytic cement aging based on a worst case scenario

The importance of obtaining data on NM release has been recently recognized for consumer and environmental exposure assessment. Indeed, NM release from consumer products is a relevant risk assessment factor. This study provides the first quantitative results on TiO_2 -NMS release from photocatalytic hardened cement pastes during aqueous weathering. After 168 h of batch leaching, the total particulate Ti release was 4.12 ± 0.38 , 8.72 ± 1.35 and $9.21\pm1.95\ \mu\text{g TiO}_2/\text{g}$ of photocatalytic cement for cements 30, 40 and 50%, respectively. These values corresponded from 0.015 to 0.033% of the total TiO_2 -NM mass initially present in the photocatalytic cement pellets subject to leaching. If we consider that the total released TiO_2 -NM only originated from the altered layer, it corresponded to less than 0.2% of the TiO_2 -NM mass initially present within the altered layers.

Only particulate Ti release was detected by ICP-AES, indicating that there was no TiO_2 -NM dissolution. Indeed, the solubility product of TiO_2 mineral (anatase) enables modeling of the dissolved Ti concentrations at equilibrium (using the PHREEQC thermodynamic model (Halim et al., 2005) and expressed as $\text{Ti}(\text{OH})_4$). The calculations indicated that the dissolved Ti concentration at equilibrium was constant from pH 7 to 13.5 at $2.7\times10^{-9}\ \text{mol/L}$ for an initial TiO_2 concentration $\geq 2.92\times10^{-9}\ \text{mol/L}$. However, considering the specific character of cement (basic pH and high calcium concentration), partial TiO_2 -NMs dissolution and precipitation into calcium titanate forms such as CaTiO_3 or $\text{CaTi}_2\text{O}_5(\text{OH})_2$ could occur as detailed elsewhere (Crocker et al., 2009, Lencka and Riman, 1995). Calcium titanate was not detected by XRD in hydrated or altered cement and neither by XPS in RDN (data not show). Then no strong evidence of nano- TiO_2 morphology evolution along TiO_2 life cycle (cement hydration, cement aging, and nano- TiO_2 release) was observed by microscopy. This Ti speciation is supposed to be limited and at least below tools detection limits to TiO_2 -NM surface.

Most experimental studies investigating NMs release from nano-products are based on a scenario, performed at the lab-scale under controlled conditions, with a high release potential (Céline Botta et al., 2011; Mackevica et al., n.d.; Schlagenhauf et al., 2015). The weathering scenario is then generally simulated using more or less complex methods and accelerated aging protocols. Such protocols do not perfectly reflect the realistic aging conditions. This was the case in our study, as weathering was simulated at the lab-scale with accelerated leaching tests. The cements were completely immersed for 7 days in a solution with a L/S ratio of 100, corresponding to a very high water volume and a minimal time as compared to the life span of cement under real conditions. Such weathering cannot realistically reproduce rainfall of outdoor building walls. In addition, some factors were not reproduced, such as the saturation/desaturation cycle that induces cement surface carbonation, acid rain, wind, UV and salt attacks that could prevent (e.g. cement carbonation) or induce heavy damage to the cement.

However, as previously mentioned, the aim of this static leaching test was to focus on understanding the water effect using a worst-case scenario and to provide an opportunity to identify the mechanisms controlling NM release and also to quantify the amount of released nano-TiO₂. This aim required the characterization of cement matrix alteration and thus a relatively thick altered layer. Such thick layer can be obtained at lab-scale in a reasonable time at such high L/S ratio. Moreover, analytical methods for NMs characterization are currently very limited and not adapted for detection in complex media at very low concentrations. So it is a substantial challenge to come up with a realistic description of NM release, particularly in the case of nano-products with a long life cycle (several decade of years for cement). In this context, lab-scale approaches offer an interesting alternative to conduct a so-called “worst case assessment of NM release”, provided that the obtained results are adequately and carefully interpreted and extrapolated.

The extrapolation of these results to long-term environmental aging is challenging. Indeed, to our knowledge, no data on long-term cement aging at field-scale under environmental conditions are available. This extrapolation can then be estimated from published modeling data. Adenot et al. (Adenot, 1992; Adenot and Buil, 1992) estimated that the altered layer thickness of cement aged 300 years (in contact with demineralized water) would reach 40 mm following a kinetic law function of square root of time. Based on these considerations, the altered layer thickness measured for cement 40% after 168 hours of lab-scale leaching (680 µm) is estimated to be equivalent to about 2 years of real-scenario aging. We can roughly estimate that our leaching test performed at lab-scale simulate between of few years and 10 years of cement aging during use stage.

In 2011, a cement producer estimated that there was an active surface of over 2 million m² of photocatalytic cement in Europe (Guerrini, 2012). By extrapolation of release data for cement 30% after 168 h of lab-scale leaching, over 37.4 kg of TiO₂-NMs could be potentially released from this photocatalytic cement surface into the environment. Although based on these “worst case estimations”, photocatalytic cements are predicted to be a minor source of TiO₂-NMs released into the environment. However, the entire long cement life cycle should be investigated, so additional research closer to real-life conditions is still required. In particular, the cement building disposal and especially the demolition stage should be considered as a high potential source of TiO₂-NM release in aerosols.

Despite these limitations, the data obtained in this study provided a valuable starting point for fate and transport modeling and risk assessment frameworks. They could serve as a useful benchmark for the state of knowledge on TiO₂-NM release from photocatalytic cement.

4.2 Fate of released TiO₂-NMs reaching natural aquatic media

Environmental exposure assessment requires quantification of TiO₂-NM release, as well as the identification of TiO₂-NM speciation in NDRs reaching natural aquatic media, such as rivers. Indeed, this feature partially controls the fate of TiO₂-NMs in the environment.

TiO₂-NMs released from cement are potentially free or embedded in cement matrix. Because of the pH gradient at the cement/water interface (pH 10-11) and in natural media (pH 7), secondary degradation of NDRs, particularly of cement matrix is expected once they reach media such as rivers. A filtration experiment of neutralized NDRs revealed that TiO₂-NM are mainly associated to NDRs larger than 0.45 µm. In neutralized NDRs (at pH 7), TiO₂-NMs were found to be associated with Si-Al intermix chains (Fig. 5). This mineral is not identified as initial cement matrix. The Si is expected to come from the highly degraded CSH (decalcification) and the Al come from the ettringite mineral dissolution. Si-Al chains are supposed to be geopolymers stable at pH 7 resulting from secondary precipitation during the pH neutralization process, as described elsewhere (Fraival et al., 1997). In natural conditions, i.e. considering a dynamic system with slower release kinetics, the system will be under-saturated with respect to the precipitation of these Si-Al chains. The release into the environment of TiO₂-NMs not embedded in the cement matrix is thus suspected, in accordance with the high chemical stability of TiO₂-NMs and the high degradability of the cement matrix in aquatic media.

This result differentiated the photocatalytic cement from other nano-products with matrices as paint, textile or polymer. Indeed previous studies (Al-Kattan et al., 2013; Kaegi et

al., 2008b; Windler et al., 2012) have revealed that the release of dissociated NMs (i.e. not embedded in the product matrix) is infrequent. In most studies, while degradation occurs, NMs were found to remain tightly bound to the matrix of the nano-product or were released still embedded in the matrix rather than as bare particles.

This result was cement matrix dependent, not scenario dependent and could thus be extrapolated to the entire cement life cycle stage (i.e. demolition, machining), where the release of cement degradation residues containing TiO₂-NMs might occur. This point should be taken into consideration regarding the photocatalytic cement categorization in terms of environmental risk. Data obtained in previous studies on bare TiO₂-NMs (anatase) could thus be used to extrapolate the behavior and toxicity of TiO₂-NMs released from photocatalytic cement in the environment.

4.3 Influence of the extent of cement degradation on the rate of TiO₂-NM release

In accordance to the literature (Haga et al., 2005b) and as expected, the three leached cements exhibited an initial porosity and extent of degradation that increased with the w/c ratio. Leached cement 30% showed a lower extent of degradation than leached cement 40%, which in turn exhibited a lower extent of degradation than cement 50%.

A relationship between the extent of cement degradation and the amount of TiO₂-NMs released during leaching was initially suspected. Indeed, the suspected cascade release scenario was (i) partial dissolution of cement matrix in contact with leaching solution, (ii) pore volume increase at cement altered surface (ii) transfer of cement-embedded TiO₂-NMs into the pore solution, (iii) diffusion of suspended TiO₂-NMs through the altered layer pore network to the surface and (iv) release into the environment.

Ti particulate release measured for cement 30% was lower than for cements 40% and 50%, but similar release kinetics and amounts were observed for cement 40% and 50%.

A theoretical release could be calculated based on the initial hypothesis that TiO₂-NM release is exclusively driven by the extent of cement degradation and increased porosity in the altered layer. The mass of TiO₂-NMs suspended in the cement pore network during leaching was estimated from the TiO₂-NM content in cement, altered layer thickness and porosity gradient at the leached cement surface revealed by nano-CT (i.e. pore volume created by matrix dissolution). In the calculation, we assumed that the theoretical TiO₂-NM release corresponded to all TiO₂-NMs suspended in the pore volume and diffusing to cement surface. The calculations are detailed in SI. The theoretical values obtained were 2.1, 5.3 and 21.6 g of TiO₂/m² of cement for cement 30, 40 and 50%, respectively, and they were 72- to 377-fold higher than the experimental data.

These results challenged our initial hypothesis and revealed that the parameters controlling TiO_2 -NM release during photocatalytic cement leaching appeared to be more complex than simply considering the extent of cement degradation and increased porosity in the altered layer. Very low experimental data in term of TiO_2 -NMs release quantification suggest that blockage/retention mechanisms are involved. These mechanisms seem to retain the TiO_2 -Nms in the altered cement matrix even if high degradation level is evidenced.

Diffusion of TiO_2 -NMs within the pore network could be slowed down or inhibited through additional mechanisms such as chemical retention due to the affinity of TiO_2 -NMs for the cement matrix and/or physical retention due to the porous network morphology (e.g. low pores connectivity or narrow bottleneck between two pores).

5 Conclusion

This experimental study addressed the issue of TiO_2 -NM release from photocatalytic cement using a static leaching test (L/S 100) simulating a worst-case water weathering scenario. Less than 0.04 w.% of initial TiO_2 -NMs were released from cement pellets. Considering this first worst-case scenario based approach and the current estimated photocatalytic cement market, photocatalytic cements are predicted to be a minor source for the release of TiO_2 -NMs into the environment. And interestingly, when released in surface water, TiO_2 -NMs appeared to be dissociated from the cement matrix because of the low chemical stability of cement minerals in neutral natural media. This point should be taken into consideration regarding the photocatalytic cement categorization in terms of environmental risk

The next step would be to perform more realistic aging protocol (e.g. instrumented outdoor cement-wall submitted to long-term weathering and natural climatic conditions (rain, temperature and radiations cycle)) for a more precise quantification of this TiO_2 -NMs release.

The parameters controlling TiO_2 -NM release appears to be more complex than expected, i.e. simply considering the extent of altered layer and increased of porosity in the altered layer. Physical and/or chemical blockage/retention mechanisms are suspected and more detailed investigations are now required to precisely define them. Although these are preliminary findings, this approach could be useful to: i) improve the parameterization of nanomaterial release models so as to get closer to a mechanistic description and develop mechanistic equations for systemic release assessments, and ii) to provide information to manufacturers to enable them to design safer nano-products.

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752 **Figure 1: A- TEM image of TiO₂-NMs incorporated in anhydrous photocatalytic cement.**
 753 **B- Fourier transform image of the TEM image. C- Ti map obtained by μ-XRF on a cross**
 754 **section of hydrated photocatalytic cement (cement 30%) and D- Ti profile extracted**
 755 **from the D map along the x-axis, integrating five pixels along the y-axis (referred to as**
 756 **black rectangle on D), compared to a similar profile obtained from a Ti map of the**
 757 **control cement.**

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Figure 2: Porosity measured by micro- and nano-CT, in the non-altered core and in the altered layer of cement 30%, 40% and 50% leached for 168 h in a batch test.

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Figure 3: Variations in the altered layer thickness over the leaching time for leached cement 30, 40 and 50%. Inset: Typical Ca map obtained on a leached cement cross section by μ -XRF (top left), used for Ca profile extraction and for Ca alteration front determination (i.e. altered layer thickness).

Figure 4: (A) Total amount of particulate Ti released during leaching of hardened cement 30, 40 and 50% over a time course. Released amounts are normalized by the cement external surface. (B) Ti particulate release rates calculated from (A). The two TiO₂ particulate release behaviors over the leaching time are indicated as (1) and (2).

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782 **Figure 5: Figure 5. Representative SEM images (secondary electron detection mode)**
783 **of NDRs in neutralized eluate (pH 7) obtained after 168 h of leaching of cement 40%.**
784 **Chemical compositions of selected region of interest were determined by EDS**
785 **analysis. “Si-Al” refer to Si-Al linear intermix chains.**

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Photocatalytic cement (porous cement)

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