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TiO_2 Nanoparticles in Portland Cement: A Life Cycle Inventory Analysis (LCI)

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The use of engineered nanoparticles (ENPs) in concrete has been gaining steady popularity over the past decade and a half. ENPs in concrete provide enhanced engineering properties. Titanium Dioxide (TiO_2) nanoparticles are used in concrete, especially pavements because of their self-cleaning and photocatalytic properties. However, these nanoparticles may pose health and environmental hazards and therefore it is important to conduct life cycle studies in terms of applications in cement and concrete. In this paper an attempt has been made to develop a life cycle inventory analysis (LCI) of TiO_2 nanoparticles specifically in cement and concrete applications. The results of this study may be potentially used to create a life cycle analysis (LCA) of TiO_2 nanoparticles and pave the way for studies of other ENPs used in the cement and concrete industry.

Keywords: Engineered Nanoparticles, TiO_2, LCI, Cement, Concrete.

Introduction

From the invention of the wheel and the discovery of fire, humankind has come far in developing technology by constant and inter-disciplinary innovation. The construction industry has been open to the incorporation of new ideas, one of the most notable being the use of engineered nanoparticles (ENP) in building materials such as concrete. ENPs are produced by restructuring matter on the order of nanometers (~10^{-9} meter), thereby creating materials with fundamentally new properties and functions (Sanchez & Sobolev, 2010). The concept of nanotechnology was introduced by Richard Feynman in a famous lecture in 1959 titled "There's Plenty of Room at the Bottom" (Feynman, 1960). Nanotechnology has since taken many disciplines by storm, including physics, chemistry and biology. The construction field (particularly in cementitious materials) is likewise also embracing the benefits of nanotechnology. This is due to potential improvements from the use of ENPs, including improved strength, durability, and such environmentally sustainable functions as self-cleaning, pollution reduction, anti-microbial ability by photocatalytic processes, anti-fogging, and self-sensing capabilities (Sanchez & Sobolev, 2010; Singh, Karade, Bhattacharyya, Yousuf, & Ahalawat, 2013) Notably, Titanium Dioxide (TiO_2) nanoparticles are used in cement and concrete for various self-cleaning benefits of structures.

However, such use of nanoparticles may have potential environmental impacts (Jayapalan, Lee, & Kurtis, 2013). The exposure of nanoparticles can be during their manufacture as well as application phases (Wiesner, Lowry, Alvarez, Dionysiou, & Biswas, 2006). Considering TiO_2 nanoparticles specifically, the small size of these nanoparticles make it ideal for uptake into cells as well as trancytosis across epithelial cells into blood and lymph circulation, thereby affecting the central nervous system. These TiO_2 nanoparticles can enter cell micro-organelles such as, nuclei and mitochondria and disrupt vital functions (Gheshlaghi, Riazi, Ahmadian, Ghafari, & Mahinpour, 2008). Thus, TiO_2 nanoparticle exposure to biological systems can lead to various diseases. Therefore, it is important to quantify the amounts of such nanomaterials flowing in and out of concrete structures. One of the important tools to quantify the flow of such materials is Life Cycle Analysis (LCA). The first step to conduct an

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LCA requires a compilation of input parameters and their quantities, called Life Cycle Inventory analysis (LCI) (International Standard, 1997). The research gap lies in the limited number of published studies pertaining to LCA and LCI of TiO_2 nanoparticles for cement and concrete applications. In this paper, an attempt has been made to perform a life cycle inventory analysis of TiO_2 nanoparticles in cement and concrete applications. This information may potentially help in developing an LCA to assess impacts such as Global Warming Potential (GWP) due to these nanoparticles in concrete.

Background

In the field of cement and concrete research, nano-engineering refers to the techniques by which structure is manipulated at the nanometer scale to develop "a new generation of tailored, multifunctional, cementitious composites with superior mechanical performance and durability potentially having a range of novel properties such as low electrical resistivity, self-sensing capabilities, self-cleaning, self-healing, high ductility, and self-control of cracks" (Sanchez & Sobolev, 2010). Different nanoparticles have been used with cementitious materials to achieve superior engineering properties of cement mortar and concrete (fresh and hardened) by achieving a higher rate of cement hydration. This is possible because ENPs have a higher surface area to volume ratio as compared to their bulk counterparts. Out of the many ENPs studied with cement and concrete, nano silica (SiO_2) has been used the most, as mentioned in prior literature where the incorporation of nano SiO_2 into the cementitious system significantly improves the compressive strength of the concrete (Singh et al., 2013). This is because of the high pozzolanicity of nano SiO_2 due to higher specific surface area, leading to an increased rate of calcium silicate hydrate (C-S-H) and calcium hydroxide (CH) production. Other nanoparticles used with concrete include iron nanoparticles (nano-Fe_2O_3), nano-alumina (nano-Al_2O_3), nanoclays, nanosized cement particles (ultrafine cement), and titanium dioxide nanoparticles (nano-TiO_2) (Jayapalan et al., 2013; Singh et al., 2013).

Titanium dioxide (TiO_2) is a naturally occurring oxide of titanium which has three crystal arrangements: anatase, rutile, and brookite (Hassan, Dylla, Mohammad, & Rupnow, 2012). Fujishima and Honda (Fujishima & Honda, 1972) discovered the potential of TiO_2 as a photocatalyst in 1972 and research has been conducted encompassing its photochemistry ever since (Folli, Pade, Hansen, De Marco, & Macphee, 2012). The application of TiO_2 nanoparticles in the field of construction started towards the late 1980s (Folli et al., 2012). Global warming due to greenhouse gases is the cause of a global average temperature rise of 0.74°C in the last 100 years, and a major atmospheric air pollutant is nitrogen dioxide (NO_2) (Lee, 2012). NO_2 is produced by combustion processes such as heating, power generation, and vehicle operation (Folli et al., 2012). Under high-temperatures, nitrogen and oxygen combine to form nitric oxide (NO) which in turn reacts with ozone and oxygen to produce nitrogen dioxide (NO_2), which again under photolysis converts to NO. Both of these gases coexist in equilibrium in the atmosphere and their sum is known as NO_X (Lee, 2012), one of the major air pollutants of recent times and responsible to a large extent for photochemical smog (Harrison, 2001). The interaction of sunlight with already present pollutants creates photochemical smog and, when this mixture of hazardous chemicals comes in contact with Sulphur oxides (SO_X), generates acid rain (Harrison, 2001) The entire ecosystem is affected by acid rain or vapor and their adverse effects on lung tissues in human beings and the metabolism of plants (Harrison, 2001). Nano-TiO_2 by virtue of its photocatalytic properties can cause NO_X oxidation (Lee, 2012). Moreover, nano-TiO_2 can help in the removal of volatile organic compounds, and has self-cleaning (Lee, 2012) and biocidal characteristics (Giannantonio, Kurth, Kurtis, & Sobecky, 2009). Photocatalytic oxidation of NO_X is one of the most popular depollution alternatives (Folli et al., 2012) and, due to high efficiency of TiO_2 nanoparticles in the process, many products are increasingly made available in the market that include nano-TiO_2- containing cement (Folli et al., 2012) and photocatalytic pavement blocks (Murata, Tawara, Obata, & Murata, 2003). Since TiO_2 is a semi-conductor when energy from UV irradiation (hv) is incident upon TiO_2, oxidizing holes (h+) and photo-generated electrons (e-) are formed which in turn react individually to create hydroxyl radicals and super oxides. These hydroxyl radicals and super oxides take part in oxidation and reduction reactions (Fujishima, Rao, & Tryk, 2000; Hassan et al., 2012) to cause the photo degradation of NO_X.

$$TiO_2 + hv \rightarrow h^+ + e^-$$
$$OH^- + h^- \rightarrow OH^*$$

$$O_2 + e^- \rightarrow O_2\text{-}$$
$$NO + OH \xrightarrow{TiO_2} NO_2 + H^*$$
$$NO_2 + OH \xrightarrow{TiO_2} NO_3 + H^*$$

The photocatalytic abilities of TiO_2 nanoparticles have inspired construction professionals and scientists to promote the use of these nanoparticles in cement and concrete. The use of TiO_2 in concrete initially stemmed from its white color and versatility but, with increasing awareness of the photocatalytic properties of TiO_2 nanoparticles, there are more applications in photocatalytic pavements. TiO_2 nanoparticles, like many other ENPs, can however be hazardous to health and the food chain in general (Shi, Magaye, Castranova, & Zhao, 2013), and it is important to understand the exposure limits of these nanoparticles in construction. Additionally, the use of such nanoparticles may increase the carbon footprint of concrete, as can be assessed through its Global Warming Potential (GWP). The use of nanoparticles in the field of construction is an upcoming area of research. However, efforts need to be made to understand implications of such construction inclusions on the environment. It is therefore important to perform life cycle exposure and flow studies of these nanoparticles that encompass cement and concrete related applications. Life cycle assessment (LCA) is defined as the process of analyzing the life cycle of a particular product from its inception to its disposal. According to ISO 14040 (International Standard, 1997), an LCA consists of a life cycle inventory analysis (LCI) phase and a life cycle impact assessment (LCIA) phase. LCI involves "compilation and quantification of inputs and outputs for a product throughout its life cycle".

Means and Methods

Life Cycle Inventory Analysis (LCI)

A life cycle inventory analysis (LCI) was conducted to assess the input parameters for potential life cycle assessment (LCA) studies of TiO_2 nanoparticles in concrete pavements. Figure 1 shows the flow scheme of TiO_2 nanoparticles from manufacture to disposal. Data used have been based on previous literature (DaNa; Keller, McFerran, Lazareva, & Suh, 2013; Loijos, Santero, & Ochsendorf, 2013; Piccinno, Gottschalk, Seeger, & Nowack, 2012), and the global annual production rates have been estimated from previously published data (DaNa; Piccinno et al., 2012). High and low estimates of annual production of TiO_2 nanoparticles have been used upon which, further calculations have been based.

Out of the total TiO_2 nanoparticles produced annually, an estimated 1% is used for cement and concrete applications (Piccinno et al., 2012), and it has been assumed that all of this amount is used in concrete pavements and bridges. During manufacture some release of the nanoparticles is estimated into various compartments. High and low estimates of 2% and 0.1% respectively have been considered for release of the TiO_2 nanoparticles into the environment (Keller et al., 2013). These releases have been considered specifically for that part of nanoparticles manufactured for cement and concrete applications. Both scenarios of high and low annual production estimates have been considered in case of 2% and 0.1% release estimates.

The nanoparticles released during manufacture will be released into three different compartments: Landfill, Waste Water Treatment Plant (WWTP) and Air (Keller et al., 2013). The TiO_2 nanoparticles then flow into the application/use phase. This paper is focused on the application of TiO_2 nanoparticles in cement and concrete and their use in self-cleaning and photocatalytic pavements and bridges. High and low release estimates of 5% and 1% respectively have been assigned. These estimates in turn are considered for high and low annual global production estimates, and 2% and 0.1% release estimates during manufacture. The release estimates into the different compartments (Soil, WWTP and Air) are calculated. Finally, the nanoparticles flow to the rehabilitation and disposal phase.

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Considering two instances of repair and rehabilitation of pavements over a 40-year period and a replacement and discarding of 4% of the pavement slab (Loijos et al., 2013) into a landfill, the global annual weights of TiO_2 nanoparticles released into landfill during disposal phase have been estimated. These estimates are based on the assumption that the nanoparticles are uniformly distributed throughout the depth of the pavement. As in earlier phases, estimates are made for high and low global annual production, 2% and 0.1% release estimates during the manufacture phase, and 5% and 1% release estimates during application phase.

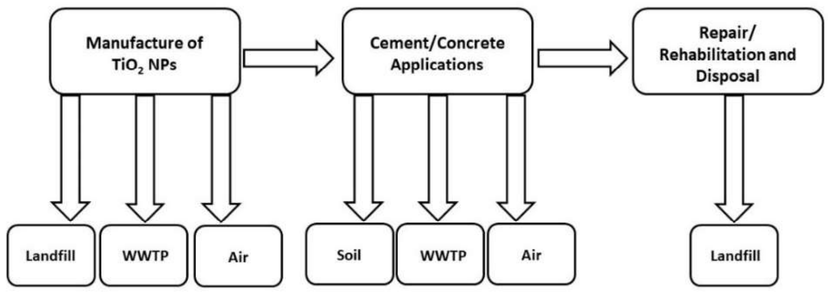

Figure 1: Life Cycle of TiO_2 Nanoparticles in Cement and Concrete

Results and Discussion

Tables 1-3 show the results of estimates for the life cycle inventory analysis conducted for the use of TiO_2 nanoparticles in cement and concrete applications in pavements and bridges. These results can be potentially used for generating life cycle analysis studies specifically for the use of TiO_2 nanoparticles in cement and concrete applications. It should be noted that there are not many published studies on the global release and flow of nanoparticles in cement and concrete applications, and these results can pave the way for further such studies conducted on other ENPs apart from TiO_2 nanoparticles. The release of these ENPs into the environment may prove to be toxic and therefore it is important to understand the limits of exposure.

TABLE 1: LCI OF TIO_2 NANOPARTICLES IN CEMENT AND CONCRETE: MANUFACTURE

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Level of Estimate	Total Production (ton/year)	Application in Cement and Concrete (%)	Manufacture					
			Weight of ENM in Concrete (ton/year)	Release During Manufacture (%) High/Low	Release During Manufacture (ton/year) High/Low	Release into Landfill @20% for High Estimate and 80% for Low Estimate (ton/year)	Release into WWTP @40% for High Estimate and 10% for Low Estimate (ton/year)	Release into Air @40% for High Estimate and 10% for Low Estimate (ton/year)
High Estimate	46800	1.0	468	2.0	9.36	1.87	3.74	3.74
				0.1	0.47	0.37	0.05	0.05
Low Estimate	3000	1.0	30	2.0	0.60	0.12	0.24	0.24
				0.1	0.03	0.02	0.00	0.00

As shown in Figure 1, the flow of TiO_2 nanoparticles during their life cycle can be categorized into such different phases as manufacture, application/use, rehabilitation/repair, and disposal. During manufacture, there may be potential release routes of these nanoparticles into different compartments: landfill, WWTP and air. For the sake of this paper, only those TiO_2 nanoparticles have been considered which are manufactured for use in the cement and concrete industry. Other applications such as cosmetics, healthcare, coatings, and paints have been dealt with in life cycle assessment or inventory analysis studies by earlier researchers (Keller et al., 2013; Piccinno et al., 2012). Figure 2 shows release estimates during manufacture into different compartments and under different levels of estimation. The following notations have been used throughout the following figures: High and low estimates are designated HE and LE respectively; the accompanying percentage indicates the percentage of release.

TABLE 2: LCI OF TIO_2 NANOPARTICLES IN CEMENT AND CONCRETE: APPLICATION

Level of Esti	Total Production	Application in	Application	
			High Estimate for Release During Manufacture (2%)	Low Estimate for Release During Manufacture (0.1%)

mate	(ton/year)	Cement and Concrete (%)	Release During Use (%) High/Low	Release During Use (ton/year) High/Low	Release into Soil @80% for High Estimate and 90% for Low Estimate (ton/year)	Release into WWTP @5% for High Estimate and 5% for Low Estimate (ton/year)	Release into Air @15% for High Estimate and 5% for Low Estimate (ton/year)	Release During Use (%) High/Low	Release During Use (ton/year) High/Low	Release into Soil @90% (ton/year)	Release into WWTP @5% (ton/year)	Release into Air @5% (ton/year)
High Estimate	46800	1.0	5.0	22.93	18.35	1.15	3.44	5.0	23.38	21.04	1.17	1.17
			1.0	4.59	4.13	0.23	0.23	1.0	4.68	4.21	0.23	0.23
Low Estimate	3000	1.0	5.0	1.47	1.18	0.07	0.22	5.0	1.50	1.35	0.07	0.07
			1.0	0.29	0.26	0.01	0.01	1.0	0.30	0.27	0.01	0.01

TABLE 3: LCI OF TiO_2 NANOPARTICLES IN CEMENT AND CONCRETE: DISPOSAL					
				Disposal into Landfill	
				2% Release in Manufacture	0.1% Release in Manufacture
Level of Estimate	Total Production (ton/year)	Application in Cement and Concrete (%)	Release During Use (%) High/Low	Rehabilitation (Twice over 40 years) @4% replacement (ton/year)	Rehabilitation (Twice over 40 years) @4% replacement (ton/year)
High Estimate	46800	1.0	5.0	0.87	0.89
			1.0	0.91	0.93
Low Estimate	3000	1.0	5.0	0.06	0.06
			1.0	0.06	0.06

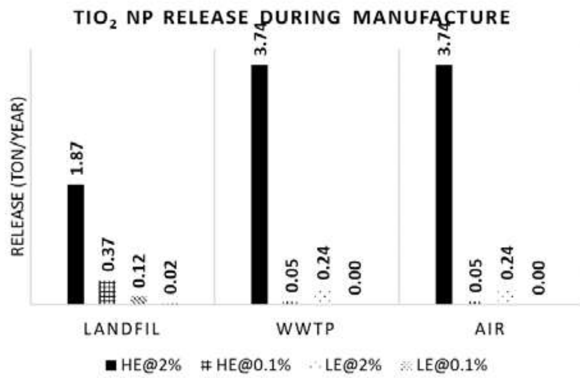

Figure 2: Release During Manufacture

For higher estimates of release during manufacture (2%) WWTP and Air compartments have higher estimated release of TiO_2 nanoparticles as compared to landfill, as a spill of bigger volume will tend to end up more into runoff and eventually into a waste water treatment plant, and atmosphere as these are easier exits for lightweight nanoparticles, rather than settling into a landfill. However, this behavior is reversed in case of lower estimate of release during manufacture (0.1%) due obvious ease of handling a smaller spill. The next phase in the life cycle of the TiO_2 nanoparticles is application/use. Since this paper is focused on the use of TiO_2 nanoparticles in cement and concrete high and low estimates have been assigned accordingly. While calculating releases into the different compartments (Table 2) Soil, WWTP, and Air, the difference between production estimates and release during manufacture has been considered. The calculated estimates have been shown in Figures 3 and 4.

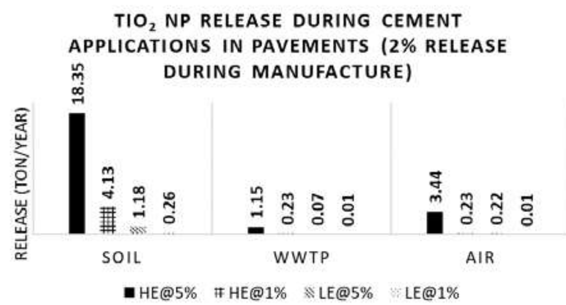

Figure 3: Release During Application/Use for 2% Release During Manufacture

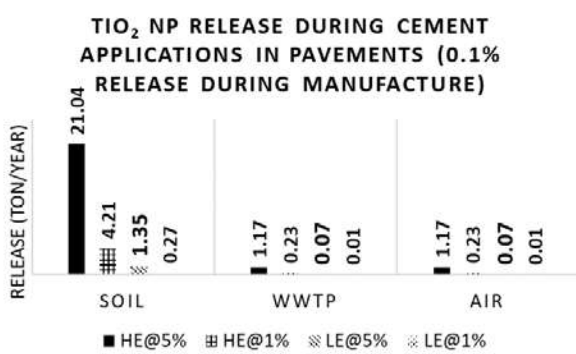

Figure 4: Release During Application/Use for 0.1% Release During Manufacture

Usually ENPs are applied in colloidal form while mixing with concrete and therefore the risks of exposure into air and water compartments are considerably lower. Therefore, higher releases are observed in the case of Soil, rather

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than WWTP and Air compartments. However, in the case of a high release estimate, exposure into air is comparatively higher than that in the case of lower release estimate. This is because nanoparticles are difficult to contain in soil when exposure levels are high due to acute weightlessness.

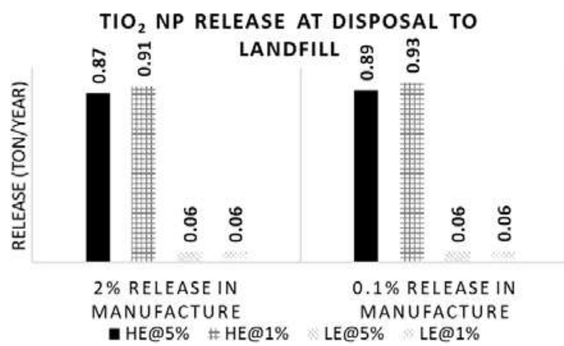

Figure 5: Release During Disposal

The last phase in the life cycle of TiO_2 nanoparticles is disposal. Over a 40-year period, pavement may be repaired or rehabilitated an estimated two times, including replacement of approximately 4% of the pavement slab (Loijos et al., 2013). Therefore, the annual release of TiO_2 nanoparticles at disposal has been calculated by multiplying the difference of the initial production amount of the nanoparticles with 0.08 (4x2/100), and dividing it by 40.These estimates have been shown in Figure 5. It may also be mentioned that the removal of pavement slabs creates chunks of solid concrete and it is assumed that 100% of the nanoparticles contained in the removed concrete ends up in the landfill.

Conclusion

This paper attempts to develop a life cycle inventory analysis (LCI) of Titanium Dioxide (TiO_2) nanoparticles used in cement and concrete for pavement and bridge construction. An LCI can provide for the input parameters of a life cycle analysis (LCA) as per ISO 14040 (International Standard, 1997). The use of nanoparticles in concrete can have numerous benefits due to which their effects on the engineering properties of concrete have been studied extensively. Such benefits may include better durability, higher pozzolanicity, self-cleaning ability etc. of concrete. The photocatalytic properties of TiO_2 nanoparticles are beneficial for self-cleaning concrete. However, in spite of the many benefits of engineered nanoparticles (ENPs), their use in concrete may lead to unwanted emissions in the form of carbon dioxide emissions or particulate matter. There is also the risk of eco-toxicity due to introduction of ENPs into the food chain. This study paves the way for further research on exposure studies of ENP in concrete applications. This is a new area where little work has been done in the past. Toxicity potential of ENPs such as Global Warming Potential (GWP) vis-à-vis cement and concrete applications can also be explored by future researchers by making use of this LCI and developing an LCA.

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