Occupational Issues of Cementitious Materials with Nano-Oxides

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Abstract
The modification of concrete materials with oxides nanoparticles usually leads to quite fair improvements on mechanical and barrier properties and to cement consumption reduction. The construction sector has normally the highest numbers of occupational diseases and accidents; with the indiscriminate use and application of nanomaterials these numbers can turn higher. This small review aims to analyse the possible safety impacts of the use and incorporation of nano-oxides during the cementitious materials production, with basis mainly on the published literature from 2005 to 2013. The literature examination was achieved using search engines (e.g. MetaLib) and directly in databases. Until now there is no direct knowledge about health implications in humans except to caution against ingestion of large amounts of nano-oxides. Current knowledge about the nano-oxides is insufficient, thus more research is needed to fill the existing gaps. Until then precautionary/prevention measures should be taken in the workplaces.

Keywords: concrete; construction; nano-oxides; safety.

1. INTRODUCTION
Globally, around 11,5 million tonnes of nanomaterials are annually marketed, with a market value of roughly 20 billion euros. The nano-oxides are among the most used nanomaterials in the industry, especially in the construction sector (EC, 2012; Lee, Mahendra, & Alvarez, 2010). These nanoparticles already showed the ability to improve the global performance of the most widely material used in construction, the concrete. The modification of concrete materials with oxides nanoparticles usually leads to a micro-and nanostructure densification, improving the mechanical performance of the final material (Table 1) (Jo, Kim, Tae, & Park, 2007; Li, Zhang, & Ou, 2006; Oltulu & Şahin, 2011).

Table 1 – Some changes made by the nano-oxides addition in cementitious based materials

Nano-oxide			Binder	
Type	**SSA[a] (m^2/g)**	**ϕ^b (ηm)**	**Content (wt. %)**	**Changes**
Al_2O_3	100 ± 15	13	0,5-2,5	Affect the fresh and hardened properties. The powder types and ratios which ↗ compressive strength the most in single, binary and ternary (Al_2O_3, Fe_2O_3 and SiO_2) combinations are those which ↘ the capillary permeability the most. The interaction between powders combinations leads to certain negative effects (Oltulu & Şahin, 2011).
Fe_2O_3	60	20-60	0,5-2,5	
SiO_2	200	12	0,5-2,5	
	60	40	3-12	↗ Microstructure densification (Jo et al., 2007).
	640 ± 50	10 ± 5	1-3	↗ Abrasion resistance of concrete (Li et al., 2006).
	300	9	1-2.5	↘ Amount of lubricating water available in the mixture, the apparent density and ↗ the air content (Senff, Labrincha, Ferreira, Hotza, & Repette, 2009).
TiO_2	240 ± 50	15	1-5	The abrasion resistance is better than that containing the same amount of nano-SiO2. ↗ Abrasion resistance of concrete (Li et al., 2006).
	50 ± 15	20-50	2-5	More superplasticizer dosage was required to help the dispersion. ↗ Compressive strength. ↗ Trend of nitrogen oxide removal accompanied by an ↗ in nanomaterial content (Guo, Ling, & Poon, 2012).

[a] Specific surface area; [b] Average diameter;

Cementitious materials have large quantities of CO_2 emissions associated to the cement production. It is unlikely that in the near future we can live without concrete; though, it is possible to reduce the cement consumption through nanotechnology, but at what price? The construction sector involves a considerable number of workmen, presenting normally the highest records of occupational diseases and accidents. With the increasing use of nanomaterials (NM) these figures can become higher.
The present work is aimed at resuming the status of worldwide research in the possible safety impacts of the inclusion of oxide nanoparticles in the cementitious materials production.

2. METHODOLOGY
It was performed a holistic and a systematic review based on diverse bibliography concerning nano-oxides in cementitious materials, mainly on the literature from 2005 to 2013. The literature examination was achieved using search engines, like the MetaLib - Ex Libris and other databases. The search was conducted with the following search strategy: combination of the keywords and sub-keywords; selection of the relevant articles by reading the title and abstract; and full text reading of the selected articles. Additionally, a search was carried out in the revised documents in order to ensure that there were not conflicts of interests. After selecting the items, a critical reading was conducted. At

last, it was flowed the PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) guidelines to select the most relevant information.

3. RESULTS AND DISCUSSION

The nano-oxides (either at powder or enclosed into the cement binder) can create potential exposure during the cementitious materials production. Laboratory-based studies, using various animal models as well as cell-culture-based in vitro experiments, have shown an increase in pulmonary inflammation, oxidative stress, inflammatory cytokine production, apoptosis in response, and other symptoms to exposure to ultrafine particles (Oberdorster et al., 2005). Several studies already demonstrated that nanoscale oxide particles have harmful effects to the aquatic ecosystem health when they were released into the aquatic environment (Aruoja, Dubourguier, Kasemets, & Kahru, 2009; Blaise, Gagné, Férard, & Eullaffroy, 2008; Zhu et al., 2008). In vitro studies have demonstrated degrees of cytotoxicity for a variety of manufactured nano-oxide materials (Table 2). These studies give a preliminary understanding of the potential harmful effects of airborne nano-oxides in the human respiratory system. Quantitative toxicity studies on engineered NM are still relatively sparse, and the published data on nanoscale oxides support the need to carefully consider how NM are characterized when evaluating potential biological activity. Until now there are no direct implications of the health effects in humans except to caution against ingestion of large concentrations of NM (Jeng & Swanson, 2006; Oberdorster et al., 2005; Soto, Garza, & Murr, 2007).

Table 2 – Nano-oxide use: potential negative impacts to health and safety

Nanomaterial	**SSA[a] (m^2/g)**	**ϕ[b] (ηm)**	**Impact**
Al_2O_3	35-43	40-47	Moderately toxic (Jeng & Swanson, 2006).
CuO	23	42	Cytotoxicity, DNA damage, and oxidative DNA lesions (Karlsson, Cronholm, Gustafsson, & Mőller, 2008).
$CuZnFe_2O_4$	18	29	Potent in inducing DNA damage (Karlsson et al., 2008).
Fe_2O_3	-	20-30	Low toxicity (Karlsson et al., 2008).
Fe_3O_4	40	29	Low toxicity (Karlsson et al., 2008).
	50-245	25	Slight toxicity (Jeng & Swanson, 2006).
SiO_2	-	20 -50	Cytotoxicity (F. Wang et al., 2009).
	268,01	15 ± 5	Higher cytotoxicity (Lin, Huang, Zhou, & Ma, 2006).
	52,48	46 ±12	
TiO_2	-	6,57	Genotoxicity and cytotoxicity (J. J. Wang, Sanderson, & Wang, 2007).
	50	30	DNA damage (Kang, Kim, Lee, & Chung, 2008).
	24	63	Cytotoxic or DNA damage (Karlsson et al., 2008).
	20-40	<40	Slight toxicity (Jeng & Swanson, 2006).
	-	25-85	No obvious acute toxicity (J. Wang et al., 2007).
ZnO	15	71	Cytotoxic or DNA damage (Karlsson et al., 2008).
	15-25	50-70	Highly toxic (Jeng & Swanson, 2006).

[a] Specific surface area; [b] Average diameter

4. CONCLUSIONS

The construction sector is one with higher number of workers and its workplace is in continuous mutation; once the nano-oxides are increasingly applied into cement concrete materials, it is imperative to establish guidelines to handle nano-oxides during the cementitious materials production. Nano-oxides at powder and "liquid" (enclosed into the fresh cement binder) state are more dangerous and could lead to NM exposure. An obvious step to mitigate possible risks related to NM exposure is to take preventive measures. Eliminating the risk at source, by replacing the NM by more safe materials is one solution at first sight. However, this may be difficult to be implemented given the unique and singular characteristics of NM. The more effective solution is to design the process and preventing the risks at upstream, downstream and during manufacturing process (isolation of production systems, especially when the nano-oxides in powder or in solution state are added into the water or superplasticizer of the ready-mixed concrete or dry concrete). Organizational procedures should also be taken, such as employee training and good working practices, with regular updates according to the existing knowledge about "nano safety" (the knowledge of majority of the construction employers and employees about the safety procedures is very low, so any improvement on the awareness on safer use of nano-oxides is important (Broekhuizen, Broekhuizen, Cornelissen, & Reijnders, 2011)). Recently the Commission of the European Communities indicated that the legal basis to work with NM does exist; however, there is still a long way to go through in terms of safety rules regarding the handling of these nanoparticles. Current knowledge about the nano-oxides is insufficient; thus more research work is needed to fill existing gaps. Until then precautionary/prevention measures should be taken in the workplaces.

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