

Use of nanomaterials in the European construction industry and some occupational health aspects thereof

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Abstract In the European construction industry in 2009, the use of engineered nanoparticles appears to be confined to a limited number of products, predominantly coatings, cement and concrete. A survey among representatives of workers and employers from 14 EU countries suggests a high level of ignorance about the availability and use of nanomaterials for the construction industry and the safety aspects thereof. Barriers for a large-scale acceptance of products containing engineered nanoparticles (nanoproducts) are high costs, uncertainties about long-term technical material performance, as well as uncertainties about health risks of nanoproducts. Workplace measurements suggest a modest exposure of construction workers to nanoparticles (NPs) associated with the use of nanoproducts. The measured particles were within a size range of 20–300 nm, with the median diameter below 53 nm. Positive assignment of this exposure to the nanoproduct or to additional sources of ultrafine particles, like the electrical equipment used was not possible within the scope of this study and requires further research. Exposures were below the nano

reference values proposed on the basis of a precautionary approach.

Keywords Nanomaterials · Construction industry · Awareness · Risk assessment · Exposure measurements · Nano reference values · Occupational health · EHS

Introduction

Nanotechnology creates possibilities to produce construction materials with novel functionalities and improved characteristics. An overview of current nanotechnologies research for the construction industry has been presented (NICOM3 2009; Lee et al. 2009; Ge and Gao 2008). Applications of nanotechnology have been described for cement, wet mortar and concrete, paints, and coatings (NICOM3 2009), insulation materials (Insulcon 2009; Relius 2009; Aspen 2009), glass (Econtrol 2009; 3M 2009; Saint-Gobain 2009) and infra-structural materials (Eurovia 2008; Bijl 2008). Nanoparticles (NPs) have been claimed to reduce the weight of concrete by using silica fume (an aggregate of amorphous SiO₂ nanoparticles), to increase strength and elasticity of concrete, to save energy consumption of houses by improved performance of isolation materials, to improve weathering properties for exterior surfaces, as self cleaning coatings for interior and exterior surfaces and window glass, as traffic exhaust

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purification coatings for infrastructural works, to provide better crack resistance of polymer materials, as biocidal surfaces for walls of surgery rooms, to improve fire resistance of materials, etcetera. Nano-TiO₂ in concrete is explored with the aim to enhance its' durability and to maintain whiteness throughout the entire lifetime of the construct. It is claimed that organic pollutants, microorganisms and NO_x are broken down by the photo-catalytic activity of TiO₂. The efficient performance of nano TiO₂ for road coating systems or coating of acoustic fencing along motorways has not been substantiated in practice, though (van Ganswijk 2009).

More advanced, "smart" developments have been reported, including building materials containing nano-sensors, and nanoparticulate self-repairing materials (Koleva 2008; Yang et al. 2009). Some of the applications of nanotechnology have already reached the market; many are still under development. Actual uses of these applications in buildings have been described (Hessen Agentur 2007; Leydekker 2008).

Occupational exposure to NPs may have an impact on health. Indications for human health hazards have been reported by many research groups showing oxidative stress, fibrosis, cardiovascular effects, cytotoxicity, and possibly carcinogenicity as effects of nanoparticle exposure (Renwick et al. 2004; Borm et al. 2006; Schneider 2007; Schulte et al. 2008; Borm et al. 2008; Trouiller et al. 2009; Knol et al. 2009; Stone et al. 2010, b). Findings, e.g., suggest that metal oxide nanoparticles affect the cardiovascular system and may inflict DNA damage. The pulmonary response to nanoparticulates in general has been demonstrated to be inflammogenic in nature, with epithelial damage, oxidative stress and cytotoxicity, driven by particle mediated ROS (reactive oxygen species) production, being common findings.

At present there is only very limited information about the availability and actual use of nanoparticulate products and about possible exposures to NPs released from these products at the workplace. To date, exposure to engineered NPs in practice is limitedly reported in scientific literature for research activities and to an even lesser extent for workers in NPs manufacturing or nanoproducts' use.¹ Reports on

the exposure of downstream use workers to NPs are rare (Schneider 2007; Berges 2009; Brouwer et al. 2009; Plitzko 2009; Methner et al. 2010a; Methner et al. b). Insight in exposure to NP in practice when NPs are emitted from products, which contain a solid matrix, is limited. Mechanical abrasion tests quantifying the nanoparticle release into air from dried surface coatings show that there is no significant correlation to nanoparticle content. NPs remain embedded in the coarse wear particles (Vorbau et al. 2009; Göhler et al. 2010). Also, Koponen et al. (2010) were not able to detect a clear effect of ENPs on dust emissions from sanding "nanopaints" in a standardized testing situation.

Against this background this paper addresses the following questions:

1. Which nanoparticulate products are used in the European construction industry?
2. Are employers and employees aware of the nanoparticulate character of those products and of its implications for occupational health?
3. What are actual exposures to nanoparticles in a limited number of working environments where workers deal with nanoproducts?
4. How do these exposures compare with preliminary nano reference values for workplace exposure based on a precautionary approach?

In the characterisation of nanoparticles a distinction is made between engineered nanoparticles (ENPs) and ultrafine particles (UFPs). Both are in the same size range, but ENPs are nanoparticles that are industrially manufactured and used in products to add a specific functionality. UFPs are nanoparticles with a natural origin or nanoparticles with an anthropogenic origin generated as by-product of human activities, such as burning fuel or drilling. If no distinction is being made between these two types the term "nanoparticles" (NP) is used.

Concerning the nanoparticle size the draft definition, as published by the European Commission (2010) for "nanomaterial" is used. This definition considers three different possibilities, of which the first is used in this study: Nanomaterial means a material that meets the following criteria: consists of particles, with one or more external dimensions in the size range 1–100 nm for more than 1% of their number size distribution.

¹ In this article, a nanoproduct is considered to be a product in which engineered nanoparticles are used to influence the specific properties and to improve the performance.

Materials and methods

Inventory European nanoproducts market

Within the European social dialogue in the construction industry the association of employers organisations FIEC² and the association of trade unions EFBWW³ together did set up an inventory of the current availability and use of nanomaterials and nanoproducts at European construction sites. This inventory aimed to provide insight into barriers and drivers for the use of nanoproducts in this sector and to identify related occupational health and safety issues. The FIEC represents 34 national member Federations in 29 countries (27 EU and EFTA, Croatia and Turkey), construction enterprises of all sizes, i.e., small and medium-sized enterprises as well as “global players”, carrying out all forms of building and civil engineering activities. The EFBWW is the European Industry Federation for the construction industry, the building materials industry, the wood and furniture industry and the forestry industry. The EFBWW has 75 affiliated unions in 31 countries and represents a total of 2,350,000 members.

Part of the inventory was a questionnaire set out by the FIEC and the EFBWW among their members in 24 European countries (hereafter called the 2009-survey). A strategic selection of 144 well-informed FIEC and EFBWW contact persons in the Member States resulted in 28 completed questionnaires from 14 European countries. Completeness was not pursued, as this would require a much more elaborate approach. The aim was to get an impression of the actual use of nanoproducts in the European construction industry and of the communication about technical performance and health and safety issues regarding nanoproducts in the sector.

Literature research and an extensive web search generated further insight in the use of nanomaterials and communication about potential related occupational health risks.

The insight gained in the development and use of nanoproducts in the construction industry was further deepened by in-depth interviewing of construction employers and workers, architects, raw material, and product manufacturers as well as R&D scientists, in total ca 45 interviewees from Western European countries and 5 from the USA and Canada.

Preliminary exposure measurements

Exposure to NPs dispersed during use of nanoproducts was measured at two different companies for a total of four different working situations: 1 spraying a liquid window coating, 2 and 3 applying a cement repair mortar and 4 nano-concrete drilling.

All exposure measurements are carried out with an Aerasense NP monitor (NanoTracer): a portable aerosol sampler of Philips Aerasense, Eindhoven, and The Netherlands. The NanoTracer provides real time information about the number concentration (particles per cm³), number-averaged particle diameter and surface area. The apparatus detects NP's within a range of 10–300 nm, as an arithmetic mean in time intervals of 16 s or less, depending on the selected modus. The accuracy is considered to be ca. 10%. The apparatus technical details of the Aerasense NP monitor were described by Marra et al. (2007; 2010).

On board data logging capabilities were utilized for the Aerasense NP monitor. A laptop computer with software was used for both control and data acquisition (NanoReporter 1.0.2.0, Philips Aerasense, Eindhoven, The Netherlands) and data analysis (NanoReporter 1.0.2.0 and MS Excel, Microsoft Corporation, United States). All aerosol NP monitors used were time synchronized with the laptop prior to commencement of sampling. Statistical analysis was carried out with the statistics programme Stata.

Personal exposure assessment and source identification measurements were carried out during all described activities. Personal monitoring was carried out with a NanoTracer fixed at the belt of the worker. Natural background concentrations were measured at the workplace preceding the activities using nanomaterials. Near-field emission (within 1–2 metres from activities) measurements were carried out with a second NanoTracer operated hand-held by one of the authors. During all observed activities, the workers wore FFP3 protection masks.

² FIEC Fédération de l'Industrie Européenne de la Construction.

³ EFBWW European Federation of Building and Wood Workers.

Working situation 1

Company 1 specialised in the application of water based self-cleaning and antibacterial coatings for exterior and interior hard surfaces: walls, windows, and horizontal surfaces. According to the technical data of the product the active nano-component is TiO_2 (anatase) with an initial particle diameter of <8 nm and a BET 160 ± 30 m^2/g .⁴ For application a paint spraying system is used (Wagner W850F). The actual activities concerned the application of the self-cleaning coating on the exterior windows (approx. 75 m^2 glass) of a small rural detached house (see Fig. 1). One worker applied the coating, during 1 h. The activities carried out were the filling of the spraying system with 1 L pre-mixed coating dispersion, followed by the spraying activities. In total ca 250–330 mL coating was used, with an estimated use of 17 mg nano- TiO_2 . The electric generator of the spraying system was placed at approximately 1.5 meter distance of the personal monitoring equipment. The weather conditions were dry with a mild wind (approximately 3 Beaufort).



Fig. 1 Spraying the self-cleaning coating on a window (Company 1)

Working situation 2

Company 2 is specialised in concrete repair in civil works situated in or nearby water, especially bridges and viaducts. The company uses concrete mortar with nano-filler for repairing large damaged surfaces and for applying a concrete covering on reinforced steel (rebar). The mortar material used is Emaco Nano-Crete R4. According to the supplier, the product contains “applied nanotechnology” that provides elasticity to the mortar, and prevents the development of cracks. Neither the technical data sheet, nor the Material safety data sheet (MSDS) provide information on the exact nature of the nanomaterial present. However, according to direct information from the manufacturer, the nanocomponent in NanoCrete is highly agglomerated fumed silica with a size of > 100 nm (BASF 2009, personal communication). The MSDS does not mention any nano-related measures. The actual work concerned the manual repair of a limited surface area at the underside of a concrete bridge (see Fig. 2). Deteriorated concrete parts were pneumatically removed, after which



Fig. 2 Manual concrete repair at the underside of a bridge (Company 2, location 1)

⁴ Technical product information of the product Environ-X, provided by the supplier NanoServices.

NanoCrete was applied manually. The total amount NanoCrete used was 25 kg, which was mixed with water, resulting in ca 11 L mortar. The mixing itself had a duration of 3 min; the period used to apply the mortar was 35 min. Electric power for the equipment used was generated by a diesel generator, which was situated at approximately 15 metres from the construction site. The weather conditions were dry with a mild wind (approximately 2 Beaufort).

Working situation 3

At another location of company 2, at another day, measurements were carried out during mixing of shotcrete repair mortar at a repair work at a concrete bridge. The product used was the same concrete repair mortar as used in working situation 2. The dry mortar was dosed from 25 kg bags into a vessel, and mixed with water by means of a long-stemmed mixer (see Fig. 3). Subsequently, the wet mortar was pumped through a hose and pneumatically projected at high pressure onto the surface of the bridge. The actual spraying activities were not monitored. During mixing and spraying, the workers wore P3-dust protection masks. During all activities the weather conditions were dry, with a relatively strong wind of approximately 5 Beaufort. In addition to the measurements of activities involving nanomaterials, to



Fig. 3 Mixing concrete repair mortar (Company 2, location 2)

measure NPs generated by the electrical equipment, measurements were carried out immediately next to the idle running mixer. Electric power for the equipment used was generated by a diesel generator, which was situated at approximately 25 metres from the construction site, adjacent to the workers canteen. Cigarette smoking workers generated an additional source of exposure to UFPs (ultrafine particles).

Working situation 4

At location 3 the same company 2 re-enacted drilling activities in cured concrete mortar. Measurements were carried out during drilling work in a concrete wall in the open air, at the companies' headquarters. Measurements were carried out during drilling in conventional concrete as well as in a wall that that was constructed with NanoCrete mortar. In addition to the measurements during drilling, a measurement was carried out immediately next to the drill, while it ran idle, to measure NPs generated by the electric equipment. During all activities the weather conditions were dry, with a relatively strong wind, approximately 5 Beaufort. In all cases (drilling and idle- running) one NanoTracer was located 'upwind' and one 'downwind' at approximately 0.5 metres from the employee.

Results

Market survey

In Table 1 an overview is given of typical nanomaterials offered at the market for actual use in the European construction industry in 2009, as identified in the interviews and the inventory. In total 94 different products were identified (Broekhuizen et al. 2009).

Table 1 shows that only a few types of NPs dominated the use of NPs in construction materials in 2009. Nano- TiO_2 , ZnO , aluminium oxide, Ag, and SiO_2 are predominant. No evidence was found for the use of carbon nanotubes (CNT) in construction materials neither in coatings nor in cementitious or concrete products; this despite the intensive ongoing research and the claimed high potential of CNT to positively influence the specific performance of products.

Coating products were identified to dominate the market, being 68% of the total number of the

Table 1 Nanomaterials actually applied in construction materials (2009)

Material	Functionality introduced	Nanoparticle	Type of introduction
Concrete	Self-cleaning surface (photo-catalytic)	TiO ₂	Surface layer
	Increased durability		
	Ultra strong concrete	SiO ₂ (silica fume)	Mixed in matrix, filler to improve material strength
Insulation material	Corrosion reduction		
	Improved insulating properties against heat, cold, fire or a combination thereof	Nanoporous material [#]	Aerogel, often SiO ₂ or carbon based
Coatings ^{##}	Improved surface penetration, coverage	Nano-sized dispersions	
	Reduced layer thickness		
	Transparent coatings	Nano-sized ingredients	
	Photo-catalytic, self-cleaning, hydrophobic properties	TiO ₂ , ZnO, SiO ₂	Additive in the coating
	Anti-bacterial	TiO ₂ , ZnO and Ag	Additive in the coating
	Scratch resistance	SiO ₂ , Aluminium oxide	Additive in the coating
	Easy-to-clean surfaces	Carbon fluorine polymers	Additive in the coating
	Fire retardant	TiO ₂ , SiO ₂ and nano-clays	Additive in the coating
	UV-protection of wood	TiO ₂ , ZnO, CeO ₂ ,	Additive in the coating
	Decolourisation of wood by tannin	Nano-clays	Additive in the coating
Glass	IR-reflection	Tungsten oxide	Surface coating
	Non-reflective glass	Nano-porous surface SiO ₂	Surface structure
			Surface coating
	Fire or heat protection	Metal oxides SiO ₂	Surface coating
			Transparent silica gel inter-layer between two glass panels
	Easy-to-clean properties	Ag, SiO ₂ , carbon fluorine polymers	Surface coating
Infrastructure	Photo-catalytic self cleaning properties	TiO ₂	Surface coating
	UV active air pollution reduction on asphalt, road pavement blocks, sound barriers and tunnels	TiO ₂	Surface coating

[#] The internal structure consists of nano-bubbles (nano-holes)

^{##} Coatings with similar functionalities are developed for many different material surfaces like wood, plastic, metal, concrete, glass, ceramics and natural stone

The inventory of nanomaterials applied in the European construction industry is the result of a questionnaire held under 144 members of FIEC and EFBWW in 24 EU-countries. The response was 28 answers from 14 countries. To this inventory data were added from in-depth interviews with 50 manufacturers and end-users in the EU and an extensive web search on nanoproducts that are marketed in the European construction industry

identified nanoproducts. Coatings also included products like a top coating for road pavement or a top coating for concrete products. Concrete and cement products and insulation products made up for 12 and 7% of all the identified products.

According to the interviews, silica fume-based cement (amorphous silica) appears to be a successful nano-niche. Silica fume does improve the particle packing of the concrete matrix resulting in improved

mechanical properties, reduced water permeability and a higher durability (NICOM3 2009). However, its production process and the high demands placed on the equipment to handle silica fume cement cause silica fume to be more expensive for use than alternative cement types. As a result, silica fume is only applied on specific customer demand or if regulation does require so.

EU wide rough estimates, made by interviewed experts, suggest that silica fume UHPC (Ultra High

Table 2 Exposure measurements to NPs at some construction sites

Working situation	ENP	Measurement Location	Workers exposure to nanoparticles						Diameter nanoparticles			
			N						Min (nm)	Max (nm)	Median (nm)	AM (nm)
			Min (Np/cm ³)	Max (Np/cm ³)	Median (Np/cm ³)	AM (Np/cm ³)						
1	Company 1: Spraying self-cleaning coating	TiO ₂ (anatase) Background	83	9,512	16,337	11,832	12,219	34	174	53	59	
2	Company 2, location 1 Mixing mortar	SiO ₂ (amorphous) NanoCrete R4 Background	23	45,429	641,074	123,931	199,508	23	173	47	62	
3	Company 2, location 2 Mixing and handling repair mortar	SiO ₂ (amorphous) NanoCrete R4 Background Background in workers canteen Direct emission mixer	26	6,177	73,928	11,412	20,763	27	65	47	41	
4	Company 2, location 3 Drilling cured concrete mortar	Up-wind location Down-wind location	52	6,107	71,519	10,985	13,983	21	300	51	69	
		Drilling in NanoCrete concrete, near field	107	5,964	13,310	8,738	8,844	20	184	47	57	
		Drilling in normal concrete, near field	24	59,957	115,011	80,450	79,619	25	70	44	43	
		Drilling machine idle-running	5	6,896	114,962	9,318	49,978	19	94	47	48	
		Drilling in NanoCrete concrete, near field	11	7,416	52,732	35,966	29,545	22	223	51	107	
		Drilling in normal concrete, near field	7	7,886	20,068	18,549	15,960	34	48	44	42	
		Drilling machine idle-running	13	9,743	83,545	43,460	39,033	21	59	40	32	
		Drilling in NanoCrete concrete, near field	11	7,043	164,424	55,865	70,981	19	97	43	51	
		Drilling in normal concrete, near field	9	10,075	66,079	12,319	22,889	24	40	37	32	
		Drilling machine idle-running	9	10,656	572,410	88,688	195,616	19	300	44	74	
		Background	12	5,611	11,346	7,643	7,605	34	54	48	45	

N amount of measurements, Min lowest measured value, Max highest measured value, AM arithmetic mean
 Np/cm³ number of nanoparticles/cm³, nm nanometres

Measurements at four outside locations in the construction industry were carried out using two NanoTracers, one for personal monitoring and one to measure the concentration of NP in the near field (as in situation 4, respectively the down- and up-wind concentration). The near field is defined as a distance of 1–2 m from the activities with dispersive use of nanomaterials. The background for situations 1, 2 and 3 was measured preceding the activities using ENPs. The background for situation 4 was measured at larger distance in up-wind position. Direct emissions from idle-running electrical equipment were measured without the use of products containing ENPs. The nanomaterial used in situation 1 concerns a waterborne suspension of Nano-TiO₂, while situations 2 and 3 concern the mixing of dry nanomaterial. Situation 4 concerns release of NPs from drilling activities in cured concrete

The NanoTracer detects NP's within a range of diameters of 10–300 nm as an arithmetic mean in time intervals of 16 s

Table 3 Background-corrected 8-h TWA exposures to NPs. The 8-h TWA exposure was calculated based on the actual working period with products containing NP at the days of the

measurements, and corrected for the local background concentration (see Table 2)

Working situation	Measurement location	Exposure time (h)	AM (N_p/cm^3)	Mean 8-h TWA (N_p/cm^3)	
1	Company 1, Spraying self-cleaning coating	Personal exposure during spray activities	1.25	12.219	50
		Background		11.898	
2	Company 2, location 1 Mixing mortar	Personal exposure: (NanoCrete mixing)	0.05	199.507	1.117
		Background		20.763	
3	Company 2, location 2 Mixing and handling repair mortar	Personal exposure: (Nanocrete mixing)	0.5	13.983	321
		Background		8.844	

Table 4 IFA proposed benchmark levels

Description	Density	Benchmark level (Nano reference value) (8-h TWA)	Type NP
1 CNT with a high aspect ratio (>3:1), length > 5.000 nm, insoluble		0.01 fibres/cm ³ (10.000 fibres/m ³)	• CNT, for example asbestos-like SWCNT or MWCNT <u>without</u> specific toxicity information of the manufacturer
2 Metals and metal oxides and other biopersistent granular nanomaterial in the range of 1 and 100 nm	>6.000 kg/m ³	20.000 particles/cm ³	• Ag, Au, CeO ₂ , CoO, Fe, Fe _x O _y , La, Pb, Sb ₂ O ₅ , SnO ₂ ,
3 (Metals and metal oxides and other) biopersistent granular nanomaterial in the range of 1 and 100 nm	<6.000 kg/m ³	40.000 particles/cm ³	• Al ₂ O ₃ , nanoclay, SiO ₂ , TiN, TiO ₂ , ZnO • Carbon Black, C ₆₀ , dendrimers, polystyrene • CNT with explicitly <u>excluded</u> asbestos-like effects
4 Ultrafine liquid and soluble particles		Applicable OEL	• e.g., fats, hydrocarbons, siloxanes, NaCl

Performance Concrete; ~4w/w% silica fume) makes up for 5% of the concrete market, which comes down to approximately 3.6 Mtons of silica fume concentrated in relatively few special construction projects. Raw material silica fume generally is highly agglomerated (Evonik Rheinfelden 2008, personal communication; BASF 2009, personal communication).

The interviews indicate further that the actual use of titanium dioxide NPs in concrete is limited, typically reserved for those types of concrete that can be manufactured as bi-layer systems and for which a relatively high unit price can be asked (2009, personal communication). Photo-catalytic cement products like concrete blocks, bricks, tiles or roof

tiles are just about to appear on the market, their actual use is still small. Because of its lower costs and similar, but less reactive characteristics, microcrystalline TiO₂ (particles > 100 nm) is used more frequently than the nano-TiO₂ (Heidelberg Technology Center Germany 2009, personal communication).

Other TiO₂ containing products are photo-catalytic cement products for the construction of exterior walls, facades and tunnels (Heidelberg Technology Center Germany 2009, personal communication; ItalCementi 2009), binders for coating materials for concrete floors, paving blocks, tiles, roof tiles, road marking paints, concrete panels, plaster, and cementitious paints (ItalCementi 2009), and coating for natural stone and concrete surfaces (Nanogate 2009).

For the decorative paints industry, the following high performance construction coatings and coatings with specific nano-modified properties can be identified on the market: anti-bacterial coatings (Bioni 2008), photo-catalytic *self cleaning* coatings (Clou 2009), UV and IR reflecting or absorbing coatings (BASF 2009 personal communication; Byk 2009), fire retardant coatings and scratch resistant coatings. Nanoclay (i.e., hydrotalcite) is used in wood coatings to prevent wood “bleeding” by tannins that, in time, decolorize the wood surface (Byk 2009). Coating applications for glass and wood benefit especially from the transparency of NPs to visible light. In the case of glass, one finds “baked-on coatings” applied during the glass production process and sprayed-on coatings applied on-site.

Insulation materials called ‘nano’ are often made out of a nano-foam (or aerogel), containing nano-size holes (Insulcon 2009). On the market are: nano-structured fluoro polyurethane products (combined with a photo catalytic iron oxide top layer) for heat and cold protection (BASF 2009, personal communication; Relius 2009). There are also nano-porous silica structure insulation materials produced for fire protection (Aspen 2009), as well as materials for sound isolation (BASF).

Awareness

The 2009-survey indicates that 80% of the workers’ representatives and 71% of the employers’ representatives were not aware of the availability of nanomaterials and were ignorant as to whether they actually use nanomaterials at their workplace.

This high level of ignorance makes that no strong conclusions can be drawn from the survey results alone with respect to the market penetration of nanoproducts in construction. Nevertheless, combining the responses from workers and employers that did work with nanomaterials, with several comments

received from respondents (see Box 1) and statements obtained from the in-depth interviews does indicate that the actual market penetration anno 2009 is still low and limited to a rather few niche products.

Interviewees state that high costs and uncertainties about long-term technical material performance of nanoproducts are a barrier for large-scale acceptance (BASF 2009, personal communication; Heidelberg Technology Center Germany 2009, personal communication; Skanska 2009, personal communication).

Interviewees emphasize further that health and safety issues remain barriers to be overcome prior to market application (Makar 2009, personal communication; NanoCyl 2009, personal communication; BASF 2009, personal communication; Bayer 2009, personal communication). Not only the toxic (asbestos-like) effects identified for specific long multi wall carbon nanotubes (Poland et al. 2008a, b; Takagi et al. 2008) trigger end-users to postpone the use of nanomaterials. Also the uncertainty about the toxicity of spherical shaped nanomaterials influence this attitude (2009, personal communication).

Information supply

The primary source of hazard information for downstream users is the MSDS. However, from the respondents 37% answered that general hazard information was provided via the MSDS or the product label, but that very limited, if any, information was supplied on the nano-additive in the product. Kittel (2009) describes comparable findings for the situation in Austria.

Current legislation does not oblige manufacturers and suppliers to report the level of NPs contained in the product to the downstream user, but as in-depth interviews point out, there is also confusion about the definition of NPs, nanomaterials and nanoproducts, resulting in conflicting opinions about characterizing the supplied material as “nano” or not. As was

Box 1 Citations from the 2009-survey on awareness

“...I have spoken to a number of companies regarding this subject and no one is aware of any materials containing these products. I have also spoken to a number of people from the Health and Safety Executive and they are also not aware of the existence of these products. I would be happy to receive further information regarding this issue so that I can investigate further (UK),”

“...we tried to get information from several construction-subsectors, but until today we didn’t receive useful indications. The problem (and we are not very surprised) is still unknown (CH),”

“...the subject is simply too abstract and too unfamiliar to respond to the survey at all (NL)”

stressed in the interviews, the time that a “nano-tag” was a good product selling argument is over; uncertainty about possible health or environmental effects prevails. As a consequence, to prevent a negative impact on the sales, products are now predominantly marketed without referring to the nano-size. In industry the terms ultrafine (Stone et al. 2010a, b) and sub-micron particles (Sprietersbach 2010) are frequently used. The market may now face a growing number of downstream users who are not informed about the type and content of NPs in the products they use.

Exposure measurements

Results from the exposure measurements are presented in Table 2. From the measurements in the four working situations it is evident that sources of UFPs such as the electric mixer, the drill, the diesel aggregate or cigarette smoke may well dominate over ENPs exposure at the construction site as generated by the use of nanoproducts. It is uncertain whether the NPs released from the NanoCrete R4 in the mortar are ENPs. Due to the claimed highly agglomerated state of the silica fume in the NanoCrete R4 in situations 2, 3, and 4, the amount of free ENPs in the prepared mortar may be very limited. Nevertheless release (de-agglomeration) of ENPs might occur under the high-energetic activities like drilling, but confirmation as this can only be given by chemical analysis of the particles and a more thorough analysis of the particle size distribution.

At all measured outside locations there is a large variation in the airborne concentrations. The minimum and maximum concentration may differ by a factor 50, as measured for the idle-running drilling machine at location 3 of company 2. An explanation for this strong variation might be the strong influence of turbulences in the outside air on the airborne NP-concentration. The short, sometimes very high peak exposures generated by short-term activities like adding nanosized mortar and the subsequent mixing, are quickly diluted by the outside air turbulence.

Table 2 also shows the diameters of the measured nanoparticles, measured as the arithmetic mean of the particles diameter averaged over time intervals of 16 s. Measured particles vary in minimum and maximum diameter between 19 and 300 nm (probably larger than 300 nm as well, which is the detection limit of the

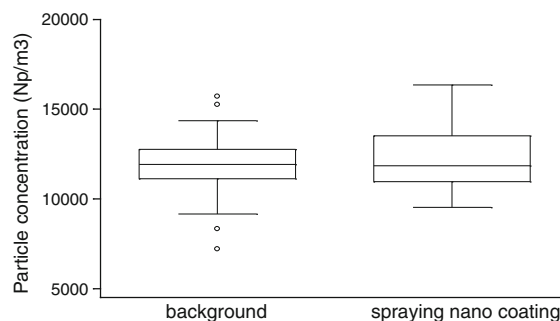


Fig. 4 Boxplot of the particles concentration measured during application of the self-cleaning coating. The plot shows the minimum, the 25% percentile, the median value, the 75% percentile and the maximum particles concentrations. The background and the spraying activities are in the same order, although the amount of measured NPs for the spraying activities is slightly higher

used equipment). Larger NPs are likely to be formed by agglomeration. The arithmetic mean of the particles' diameter in the personal exposure measurements varies from 59 to 69 nm. For the drilling activities a larger arithmetic mean is measured, but the median is comparable. The median for the different situations varies between 37 and 54 nm.

The measurements carried during the spraying of the self-cleaning coating are presented in boxplot (see Fig. 4). A slightly elevated particles concentration is observed during these activities. A distinction between exposure to ENPs derived from the coating and those NP possibly generated by the electrical motor of the spraying equipment cannot be made at this stage.

During the mixing of mortar a high emission of NP is possible, as is shown with a peak exposure of $> 600.000 \text{ N}_p/\text{m}^3$ for the single use of one 25 kg bag of NanoCrete at the location 1 of company 2. At the second location the measured exposures, during the mixing of 6 bags, were much lower, probably largely influenced by the weather conditions. These measurements are shown in Fig. 5 of which a boxplot is presented in Fig. 6. In this situation, with a relatively strong wind, peak exposures did not exceed $72.000 \text{ N}_p/\text{cm}^3$. Independently, a peak exposure of almost $115.000 \text{ N}_p/\text{cm}^3$ is measured for an idle running mixer (see Table 2). For the series of short peak exposures no distinction can be made between exposure to ENPs dispersed from the mortar-mix and UFPs generated by the electrical mixer equipment.

At the same location separate measurements were carried out of the exposure to NPs in the workers

Fig. 5 Exposure to NPs during mixing mortar in company 2, location 2. The figure shows the results of personal monitoring of the adding of 6 NanoCrete bags and the consequential mixing of the mortar (time is represented in seconds). The actual mixing activities took place in the time interval between 565 and 2493 s. Just before this period, in the time interval between 235 and 565, a smoking colleague visited the working site, which resulted in a short peak exposure of the worker of $60.000\text{N}_p/\text{cm}^3$

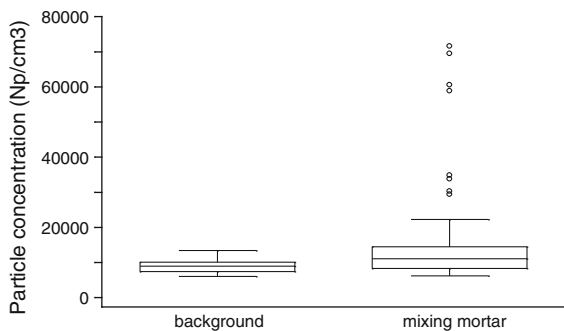
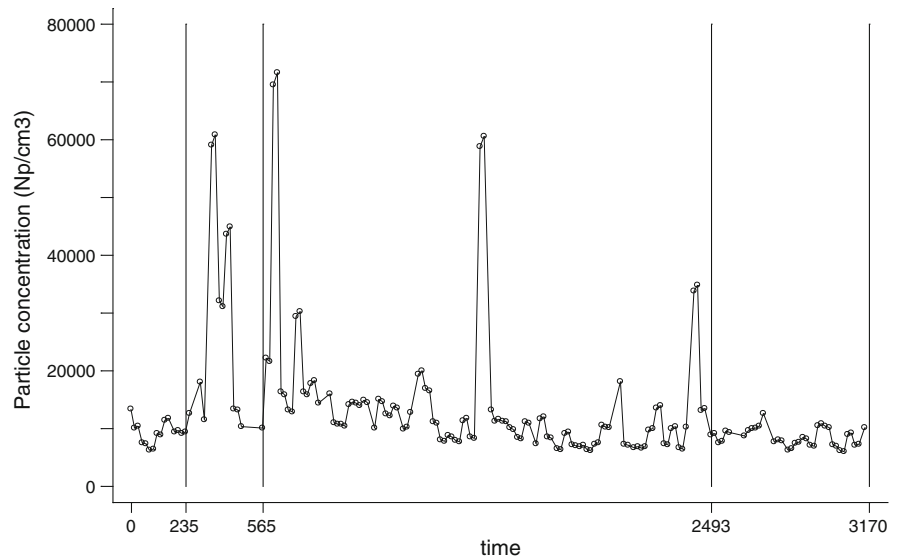


Fig. 6 Boxplot of the particles concentration during mixing of mortar at company 2, location 2. The plot shows the minimum, the 25% percentile, the median value, the 75% percentile and the maximum particles concentrations, including outliers representing the short-term peak exposures during the actual mixing of NanoCrete. The exposure during mixing of mortar is clearly distinguishable from the background

canteen and of the emission of NPs of the diesel aggregate (see Table 2). The workers' exposure in the canteen shows a high average personal exposure to NPs, of nearly $80.000\text{N}_p/\text{cm}^3$, with peak exposures of $> 110.000\text{N}_p/\text{cm}^3$, likely to be generated by (indoor) smoking workers. A contribution to the indoor NP concentration, however, may also be generated by the diesel aggregate that was standing adjacent the canteen.

For the drilling of cured concrete (company 2, location 3) the near field concentration of NPs was measured in an up-wind and a down-wind position,

both at a distance of 0.5–1 meter from the drilling worker (see Table 2). For drilling in cured NanoCrete concrete the arithmetic mean NP concentration for the downwind position exceeds the concentration in the up-wind position by $40,000\text{N}_p/\text{cm}^3$. For drilling in 'normal' concrete this difference is ca. $16,000\text{N}_p/\text{cm}^3$. The median values for these situations differ $20.000\text{N}_p/\text{cm}^3$ and $6.000\text{N}_p/\text{cm}^3$, respectively. The NPs emission generated by drilling in NanoCrete concrete is 2–3 higher than the emission of drilling in "traditional" concrete, suggesting a higher release of NPs from the NanoCrete concrete. At the same time a control measurement shows that the emission of NPs from the idle-running drill in this situation may be as high as $> 600,000\text{N}_p/\text{cm}^3$ in the downwind position, indicating that the higher emission during the NanoCrete-concrete drilling may as well be caused by engine-generated NPs from the higher drilling intensity in the denser NanoCrete concrete.

Personal exposure 8-h TWA

A mean 8-h TWA (time weighted average) personal exposure to NPs, corrected for the background concentration of NPs, can be calculated assuming that no other activities with this nanomaterial are carried out during the working day. For working situation 1 this means no further spraying activities, for situation 2 and 3 no further mixing of NanoCrete containing mortar. For working situation 4, the

drilling in concrete, no 8-h TWA was calculated because this was specifically arranged to test the generation of NPs and does not represent a real-life drilling activity. In all cases the calculated 8 h-TWA exposures to ENPs (including engine-generated NPs) are an estimate of the apportionment of workplace-emitted particles to the total particles concentration.

The calculations are presented in Table 3.

For the situation 2 and 3, in company 2, the level of the background corrected 8 h-TWA exposure to workplace-generated NPs is largely determined by the short-term peak exposures of handling the nanoparticle. The exposure may be a mix of ENPs released from the nanoparticle and UFPs generated by the electrical equipment.

Comparison of measured values with nano reference values

Based on what is known today tools have been published to help to design a safe nano-workplace (Schulte et al. 2008; VCI 2007; Borm et al. 2008; NanoSafe 2008; NanoSmile 2010), including the use of control banding tools (Paik et al. 2008; Höck et al. 2008).

Ignorance about possible risks and the lack of essential health and safety information of the downstream user might be argued to call for a precautionary approach in risk assessment and risk management. Building blocks for a precautionary approach were adopted by the construction employers' organization and the trade unions (Broekhuizen and Reijnders 2010; FIEC-EFBWW 2009). The question, which arises in this context, is *what is an acceptable precautionary exposure level?* As for ENPs HBR-OELs⁵ or DNELs⁶ are not available, temporarily precautionary reference values are being developed in The Netherlands, called nano reference values (NRV) (Dekkers and Heer 2010). A NRV is defined as a warning level and refers to the ENP-concentration in the workplace atmosphere, corrected for the background NP concentration. It is intended to be a warning level to trigger a thorough assessment of nanoparticles

at the workplace. When exceeding this level the source of the nanoparticles' emission(s) should be thoroughly identified and possibilities to reduce the emission of nanoparticles must be assessed. The NRVs are based on the benchmark levels as proposed by (IFA 2009; Schulte et al. 2010) and quantified as 8-h TWA (time weighted average), corrected for the background concentration as shown in Table 4:

For the measured workplace situations 1–3 in which nano-TiO₂ or fumed silica may be emitted, both metal oxides with a density of <6.000 kg/m³, the values in Table 4 would imply a (background corrected) level of the NRV of 40.000 particles/cm³. All the calculated 8-h TWA exposures (see Table 3) remain well below the NRV level, suggesting that for the specific workplaces of this study and their actual conditions no extra measures would have been necessary additional to the measures that were already required based on the risk assessment of the other (bulk and molecular) materials used.

Discussion

The high expectations for nanotechnological products for the construction industry, as mentioned in scientific literature and market studies (Freedonia 2007), are as yet not reflected by practice. Limited communication in the production chain about technical and health and safety aspects of these products is observed. Costs and the present uncertainty regarding long-term technical performance of nanoproducts are factors that limit the use of nanoproducts in the European construction industry. At the moment nanomaterials and thus nanoproducts are significantly more expensive than their non-nano alternatives. Manufacturers of construction materials are reluctant to develop nanoproducts, especially when the performance of existing non-nanoproducts is believed to be sufficient. This holds in particular for the larger volume products like concrete or mortar and for construction coatings. Nanoproducts, as a result, remain niche products that are only applied upon specific request.

A larger potential in the future is expected for insulation materials, architectural and glass coatings that have the improvement of the energy performance of the construct as their main objective. These are currently niche markets, but the current focus of

⁵ HBR-OEL Health-based recommended occupational exposure limit. (maximum permissible concentration of a given gas, vapor, fiber or dust in the air at the workplace).

⁶ DNEL Derived no-effect level. (Within REACH the level above which humans should not be exposed).

society on the improvement of energy management in the context of climate change and the reduction of greenhouse gasses does stimulate an increased market share (Broekhuizen et al. 2009).

Risk avoidance is another drawback for use. Potential users seem to wait with using nanomaterials, until more evidence for a safe use comes available. Advocates for more openness of the industry about the type of nanomaterials used in the products, have taken up this point (IG DHS 2008; ETUC 2008; EEB 2009; Broekhuizen and Reijnders 2010; FIEC, EFBWW 2009) and have suggested openness about health risks, advice on how to use nanomaterials safely and information about the so far unknowns. However, it is questionable if voluntariness alone would suffice to generate more openness in the communication. Voluntary initiatives to increase openness of industry about their nanoproducts have been only limitedly successful (Berger 2007; Helland et al. 2008; DEFRA 2008; Breggin et al. 2009; US EPA 2009), which in some countries did lead to initiatives to develop legal instruments to enforce more openness (e.g., The Netherlands, France, Austria).

Measuring the personal exposure to ENP at industrial workplaces is subject to several factors which influence the level of NP exposure, as presented here, and merit discussion. The first one is the size range of the measured nanoparticles concentration. The NanoTracer measures in the range from 10 to 300 nm, meaning that in principle an over-estimation of the amount of nanoparticles is possible. For risk assessment this is not necessarily a problem since there seems not to be a sharp limit for effects at the 100 nm size, as is shown for example by Barnard (2010) for TiO_2 for the potential of generating of ROS as a function of the nanoparticles size. Furthermore, the measurements show that the major part of the measured particles is in the range <100 nm.

Especially the background concentration, the use of electrical equipment, heaters, diesel aggregates, and smoking are identified in this study as potential confounding factors in ENP measurement. The use of electrical equipment is of specific interest. This study indicates that the use of electrical mixers and drilling machines may contribute significantly to the workers NP exposure. For instance, the difference measured between drilling traditional and NanoCrete concrete in the near field might relate to an emission of NPs from the Nanocrete concrete, but it may also be that

the denser concrete structure of the NanoCrete provokes a higher drilling intensity, resulting in an increase in engine-generated NPs. As anticipated by Maynard and Zimmer (2002) and shown by Szymczak et al. (2007) electric equipment is a source of NP-exposure that cannot be neglected. In a test system Szymczak found a significant emission of Cu NPs up to 3.0×10^{11} particles/m³, generated by universal motors as used in domestic and do-it-yourself electrical equipment, including a drilling machine. Chen et al. (2006) and Meng et al. (2007) have reported about the high reactivity and acute toxicological effects of copper nanoparticles. This emphasizes the need to take Cu-NP exposure also into consideration when making a risk assessment.

The emission of NPs from the electrical equipment shown here and reported elsewhere (Szymczak 2007) is of the same order of magnitude as, or larger than the measured on-site exposures. Consequently one could suggest that the exposures to nano- TiO_2 or nano- SiO_2 may well be lower than the measurements presented in Table 3 suggest. Uncertainty about the origin and relative contribution of measured NP calls for more elaborate sample analysis to quantify exposure to ENPs.

The claimed highly agglomerated state of the SiO_2 NP's in the cement mortar used and the possible contribution to the exposure of electrical equipment-generated NPs, are arguments for further physical/chemical analysis of the samples. EDX/SEM analysis might be a good option.

Notwithstanding the need for further analysis of the NPs, comparing the 8 h-TWA exposure (Table 3) with the proposed NRVs (Table 4) suggests that the use of NRVs may provide a valuable tool for a first workplace risk assessment. The calculated 8-h TWA exposures to NPs (possibly as a mix of different types of NPs) remain well below the proposed NRVs and to date there is no indication that for the prevention of adverse effects of the concerned nanoparticles the use of a ceiling value is advisable. In view thereof no further specific nano-risk related measures would be necessary. However, given the observed exposure pattern additional assessment of the peak exposures seems appropriate (van Broekhuizen 2011). This might lead to a 15 min-TWA and a short-term peak exposure level should be leading in the risk assessment and suggests the need for additional short-term nano reference levels, for example in analogy

with the rule of thumb for a 15min chemicals' exposure, used by Labour Inspectorates, $NRV(15 \text{ min-TWA}) = 2 \times NRV(8 \text{ h-TWA})$ and for peak exposures $NRV\text{-peak} = 10 \times NRV(8 \text{ h-TWA})$ (van Broekhuizen 2011). For most of the cases presented here, this would mean an exposure well below the proposed $NRV\text{-peak}$ and the 15min-TWA. Only for the mortar mixing in situation 2 the $NRV\text{-peak}$ might be exceeded, which might lead to an advice to apply risk mitigating measures during the adding actual mixing of the NanoCrete.

Carbon nanotubes (CNT) were not found to be used in the European construction industry. In the case that this changes it is useful to point out that the suggested NRV for CNT of $10,000 \text{ fibres/m}^3$ (see Table 4) is analogous to the established OEL for asbestos. It should be mentioned that this asbestos OEL has recently come under debate. The Dutch Health Council published an advice to lower the OEL for chrysotilic asbestos to $2,000 \text{ fibres/m}^3$ and amphibolic asbestos to 420 fibres/m^3 , in line with an acceptable yearly fatality risk level of 4.10^{-5} (Dutch Health Council 2010). One might argue that the levels suggested by the Dutch Health Council should be adopted in setting the level for nano reference value of long CNTs for which the toxicity is not specifically established, in line with findings that exposure to long CNTs triggers responses that are similar to the effects of asbestos (Poland et al. 2008a, b).

Conclusion

In 2009, the use of nanoproducts in the European construction industry was at a relatively low level. Within the as yet small nanomarket in the construction industry, primarily coatings and cement and concrete dominate. The most important NPs in these applications seem to be nano-TiO₂ and silica-fume.

A major barrier is the high price of nanoproducts used in bulk amounts, limiting the use to situations where the customer specifically requests their use. A higher use is foreseen for nanoproducts with energy saving properties. Another barrier is the uncertainty of potential manufacturers and end-users about adverse occupational risks of ENPs leading to reluctance in selecting these materials. The production of nanoproducts and their use is postponed until more evidence comes available.

The awareness of majority of the end-users, construction employers and employees about the existence of nanoproducts and about their actual use appears to be very low. It is concluded that communication about product performance and health risks of nanomaterials has to be improved in the production chain.

Real-time exposure measurements in a limited amount of exterior workplaces show a low 8 h-TWA workers' exposure to dispersed airborne NPs, if compared with $NRVs$, but it is difficult to distinguish ENPs from a NPs' background exposure and from NPs generated by the electrical machining equipment. Short-term peak exposures seem to be characteristic for the workplaces investigated. Further chemical analysis of airborne workplace nanoparticulate samples is needed to elucidate the product-related contribution to the measured nanoparticle exposure. Comparison of the exposure with $NRVs$ shows a limited exposure, not exceeding the warning level for 8 h-TWA exposures.

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