NANOTECHNOLOGY: EXCITING FACILITATOR OR WORRYING INNOVATION

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ABSTRACT: Nanotechnology is an important feature of concrete technology and innovation in the 21st century. Nanoparticles are enabling concrete technologists to make significant steps forward in terms of concrete performance. However, there is some evidence suggesting health concerns from nanoparticles. Much of this has focussed on the manufacturing processes but there remains a potential health risk for construction in the bioavailability of nanoparticles through working of the products during installation, maintenance and in particular demolition. This paper introduces some new research funded by IOSH to investigate this issue.

Keywords: Nanotechnology, health and safety, cement, concrete, micro silica

INTRODUCTION

Nanoparticles are not a single group of objects but a multiplicity of shapes, sizes and compounds – the definition for a nanoparticle is that one of its dimensions must be less than 100nm. Similarly, nanotechnology is the "engineering of materials at the nano-scale to manipulate the fundamental properties resulting in new bulk properties and capabilities" Teizer et al [22]. Nano-modification of concrete involves introducing reactive modification agents with a very small particle size, hence possessing very large surface areas.

In 2006, an organisation called Nanologue published a report called: The future of nanotechnology: we need to talk (Nanologue, 2006) in which they present their view of the progress of nanotechnology up until 2006:

1959	"The word nanotechnology first appears in Richard Feynmann's lecture. 'There's plenty of room at the bottom'
1964	Precedent set for patenting at the matter level – Glenn Seaborg "invented" americium 95 and acquired US patent #3,156,523
1965-71	Russell Young develops technology that is later used in the first Scanning Tunnelling Microscope (STM)
1985	Buckyballs (C60) discovered
1986	The Nobel Prize in Physics is awarded for the discovery of atomic resolution in scanning tunnelling microscopy
	'Engines of creation' published by Eric Drexler
	Development of the Atomic Force Microscope (AFM)
	Foresight Nanotech Institute founded – fi rst organisation to educate society about the benefits and risks of nanotechnology
1989	IBM scientist Don Eigler used an STM to spell out IBM in xenon atoms as an illustration of engineering capability at nano-scale
1991	Carbon nanotubes discovered
1996	Nanotechnologist Richard E Smalley of Rice University awarded the Nobel Prize in Chemistry for his discovery of buckminsterfullerenes
2000	Bill Joy's vision of the nano-assembler switched attention to the topic, which, in turn, raised public funding
	President Clinton announces the formation of the (US) National Nanotechnology Institute
2002	'Prey', science fiction book on nanotechnology by Michael Crichton
2003	President Bush signs Bill authorising US nanotechnology programme
2004	'Nanotechnology: Small matter, many unknowns' report published by Swiss Re
	'Nanoscience and nanotechnologies: opportunities and uncertainties' report published by the Royal Society
	Prince Charles article speaks out against nanotechnology
2005	European Commission adopts Action Plan that defines a series of linked actions for the "implementation of a safe, integrated and responsible strategy for nanosciences and nanotechnologies"
	Research finds that Buckyballs may deform DNA
	Glass-treating spray containing nanoparticles recalled in Germany" (Nanologue, 2006)

Nanologue go on to paint three alternative scenarios for 2015: *disaster recovery; now we're talking;* and *powering ahead*.

In the first scenario, *disaster recovery*, Nanologue argued that "public institutions had been slow to plan for the possibility of health or environmental risks related to nanotechnology and private enterprise had been reluctant to self-regulate. This lack of regulation contributed to a major accident at a manufacturing plant in Korea in 2012. Public concern about nanotechnologies escalated and a cautious approach to technology development was adopted. Although the technology was still being used and the science was still developing, the term nanotechnologies was used less, and the prefix nano had all-but disappeared" (Nanologue, 2006).

Nanologue named the second scenario *now we are talking* and suggested that, by 2015, "regulation of new technologies had been standardised internationally and strong accountability systems were in place, enabling transparent development of nanotechnology. Public sector incentives had directed research towards products that explicitly benefitted society, supported by public participation. Local stakeholder forums were debating issues that were arising from the use of technology (such as privacy) and were making decisions for their local area. The strong regulatory regime, especially around issues of toxicity, meant that health and safety risks were spotted early on and were well-managed. The focus on products that benefit society and reduce environmental impact had paid off: growing resource stress meant demand for these products was increasing around the world" (Nanologue, 2006).

The third scenario, *powering ahead*, explained that by 2015 "scientific progress had been faster than expected and nanotechnology-related products were making a real impact on society and the economy. For example, there had been dramatic improvements in the efficiency of solar photovoltaic (PV) cells, with the result that applications expected to come into the market in the 2020s were already a reality. Long-term investments in fossil fuel resources were progressively losing value and new market entrants were growing quickly. The speed of change had left regulation behind. Although there had been discussion around the risks of novel materials, as far as public debate was concerned the benefits so far outweigh the risks" (Nanologue, 2006).

So, what has been happening since 2006. Perhaps unsurprisingly it would appear to be a combination of parts of all three scenarios. Thankfully, there has not been a major disaster, certainly the proliferation of nano-enabled products is continuing, but, our evidence suggests that regulation is not keeping up with developments and people are certainly not talking. Despite thousands of research studies (including many on health and safety issues) and a significant number of reports produced focussing on health and safety aspects, even specifically dealing with construction (e.g. Tiezer et al, [22]) the majority of construction practitioners are still unaware of the nature or extent of nanotechnology in the built environment. In a survey of more than 330 designers in 2012 by the author (Gibb et al, [23]), all but a few of them believed that they had not specified products that contained nanotechnology and expressed considerable surprise when a list of typical nano-enabled products was revealed and they realised that they were indeed designing buildings and facilities that incorporated such technologies on a regular basis.

In the last few years many Governments around the world have published reports on nanotechnology, focussing on health and safety aspects (e.g. HSE 2004 [9]; EC 2005 [5]; EEA 2013 [6]; HSE, 2013 [10], NIOSH, 2014 [15]). There general advice is that there is research suggesting that some nanoparticles may have negative implications for health and that a 'prudent approach' (ref HSE) should be adopted. The Oxford English Dictionary defines prudence as 'acting with or showing care and thought for the future'. The authors argue that you cannot take a prudent approach without knowledge and, despite extant publications, most knowledge that does exist is not being accessed by those who have the opportunity, and responsibility, to do something about it. There appears to be no pragmatic evidence-based advice on the hazards and on what precautionary measures would be effective. We do not know which materials contain nanoparticles; we do not know which particular nanoparticles are present; we do not know how easily they could become bio-available; and we do not know what to do if they do become bio-available.

NANOPARTICLES AND CONCRETE

Concrete has been enhanced using additives and special techniques for many years. Figure 1 has been adapted from Birgisson [3] to show the relative particle size of concrete constituents.

Nanoparticles have also been used to produce very significant changes in concrete performance. Sobolev et al [21] studied mechanical properties of cement based materials with nano-SiO_2, TiO_2 and Fe_2O_3. They claim that "experimental results demonstrated an increase in compressive and flexural strength of mortars containing nano-particles. Based on the available data, the beneficial action of the nano-particles on the microstructure and performance of cement based materials can be explained by the following factors:

- Well-dispersed nano-particles increase the viscosity of the liquid phase helping to suspend the cement grains and aggregates, improving the segregation resistance and workability of the system;
- Nano-particles fill the voids between cement grains, resulting in the immobilization of "free" water (a "filler" effect);
- Well-dispersed nano-particles act as centres of crystallization of cement hydrates, therefore accelerating hydration;
- Nano-particles favour the formation of small-sized crystals (such as $Ca(OH)_2$) and small-sized uniform clusters of Calcium-Silicate-Hydrate (C-S-H);
- Nano-SiO_2 participates in the pozzolanic reactions, resulting in the consumption of $Ca(OH)_2$ and formation of extra C-S-H;
- Nano-particles improve the structure of the aggregates' contact zone (the interfacial transition zone), resulting in a better bond between the aggregates and cement paste;
- Crack arrest and interlocking effects between the slip planes provided by nano-particles improve the toughness, shear, tensile and flexural strength of cement based materials" (Slobolev et al, [21]).

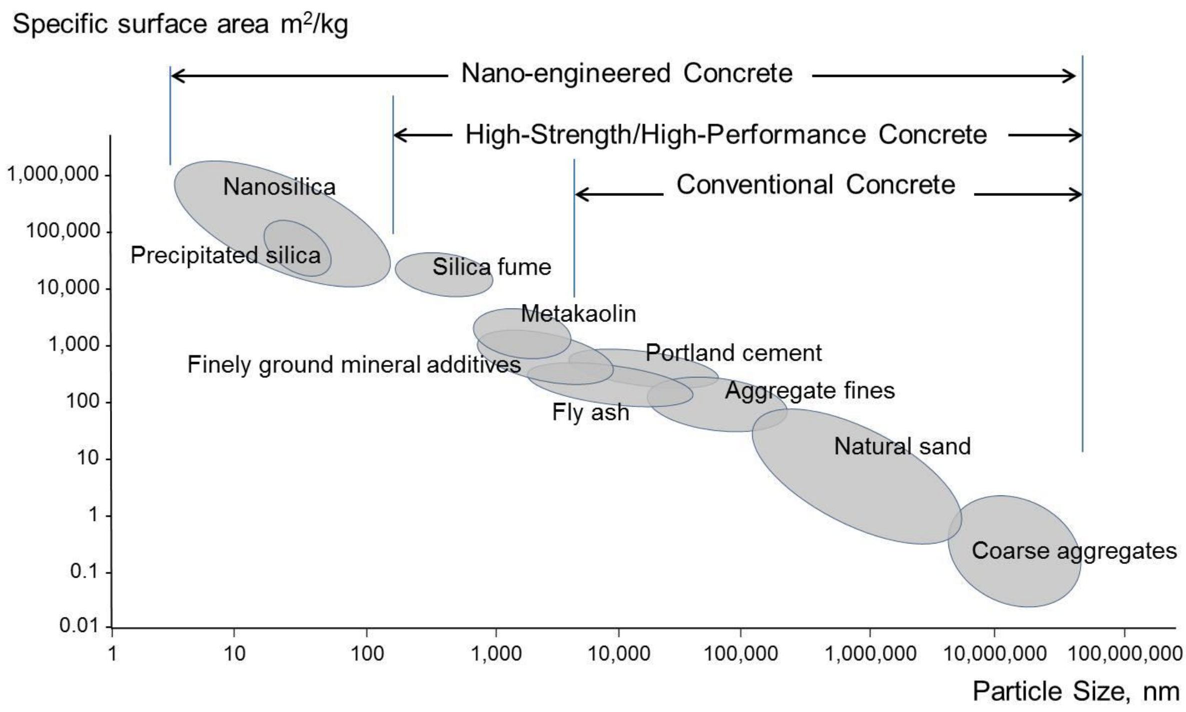

Figure 1 Particle size-scale related to concrete (adapted from Birgisson [21])

Teizer et al [22] in a report for the Construction Industry Institute in North America, describe current and proposed applications of nano-modified cement and concrete. These include:

- Strength and fracture properties
    - Ultra high compressive strength and improved tensile strength
    - Controlled triggering and setting
    - More efficient cement hydration
    - Increased aggregate paste bond strength
    - Control of cracks and self-healing
- Improvement in ductility
    - Reduced permeability
    - Freeze/thaw resistant
    - Chloride / sulphate resistant
- Volume change characteristics
    - Minimise shrinkage
    - Minimise pavement curling / warping
- Sustainability and safety
    - Self-cleaning /smog eating
    - Less CO2 emission clinkers
    - Longer life pavements / structures
    - Recycling concrete and using recycled components
- Sensing technologies
    - Self-powered long lasting material based sensors, warning and communication systems
    - Vibration harvesting for power (Teizer et al[22]

A Note on Microsilica

Microsilica (silica fume) is sometimes discussed as nanotechnology. However, if a nanoparticle is defined as being less than 100nm, then microsilica just misses out on this classification (Figure 1). Microsilica is a highly pozzolanic material, consisting essentially of silica in non-crystalline form with a high specific surface area, thus demonstrating significant pozzolanic activity. Nano silica is a more recently available synthetically produced pozzolanic material, often in the form of water emulsion of ultra-fine amorphous colloidal silica (UFACS). Compared to microsilica it has a higher content of amorphous silica (> 99%), as well as a smaller particle size (1-50 nm). The 28-day compressive strength water permeability resistance of normal concrete has been shown to be improved by using nanosilica

(Ji[12]), as has the strength of high-strength concrete (Li[14]), and the mechanical properties and durability of self-compacting concretes (Quercia et al[18]). In addition, the inclusion of both microsilica and colloidal nanosilica together has been shown to improve compressive strength and diminish capillary absorption, over and above what can be achieved with just microsilica (Nili et al[16]).

Much progress in the continued enhancement of the compressive strength and other structural properties of concrete is expected in the near to medium future, with commercial concretes such as Lafarge's Ductal providing indications of what might be achievable. Though not marketed as nano-technology as such, Ductal is advertised as possessing "nano-meter sized non-connected pores throughout its cementitious matrix", which aid imperviousness and durability (Ductal [4]).

Other products incorporate nanotechnology more blatantly, for example Emaco's Nano-crete[7]. Confusingly however, they state that "nanotechnology does not mean nano-sized particles", but that their "better understanding of cement hydration has allowed us to improve the quality and density of the nanostructures in cement paste" (Emaco, [7]). Other cementitious products available include Nanosilent, from PCI Augsburg GmbH, a BASF subsidiary company, a tiling mortar incorporating rubber granules for noise suppression. The nano-technology however, refers to formulating the cementitious matrix on a nano scale to improve essential material characteristics, such as bond (BASF [2]).

POTENTIAL IMPLICATIONS FOR OCCUPATIONAL HEALTH

There are three main questions relating to health implications for nanoparticles:

1. Which of the nanoparticles are hazardous to health?
2. How do the nanoparticles affect (or enter) the body to affect it?
3. How do the nanoparticles become bio-available?

The first two aspects are common to all nanotechnologies and are dependent on epidemiological research. This is outside the scope of this paper, but, to aid the reader's understanding, Table 1 has been adapted from Som et al (2011), which brings together the various health challenges and identifies the extent to which evidence exists to link them to particular nanoparticles (based on published results).

Table 1 Assessment of different engineered nanomaterials in relation to their biological effects (health) based on published results in respect to different biological endpoints (adapted from Som et al [24])

HEALTH	Sliver Ag	Zinc ZnO	Titanium TiO_2	Silica SiO_2 (amorphous)	Aluminium Al_2O_3	Montmorillonite	Carbon nanotubes CNT	Carbon Black CB
Overall implications for health	a	c	a	a	b	b	b	c
Specific health aspects								
Acute toxicity	–	+	– –	– –	–	– –	+/-*	+
Chronic toxicity (long term effects to be expected)	+	+	+/-	–	n.a.	– –	+*	++
Impairment of DNA	–	+	–	–	n.a.	n.a.	–	+
Crossing and damaging tissue barriers	n.a.	n.a.	+	+	–#	n.a.	–	+
Brain damage: damage of the central nervous system	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Skin	– –	– –	– –	– –	n.a.	n.a.	–	–
Gastrointestinal tract	–	+/-	–	–	n.a.	–	–	–
Respiratory tract	–	+	–	–	–	n.a.	+	+

Legend:

a) rather safe[1]; b) uncertain due to weak evidence; c) biological effects detectable

+ applies to; +/- weak evidence available; – does not apply to; n.a. no data available (high uncertainty)

** depends often on contaminants in the samples (especially transition metals such as iron, nickel, cobalt etc)*

 # AlOOH was explored in the lungs

[1] 'Rather safe' is the description used by Som et al and so has been retained here. However, as a principle, the authors of this paper would choose not to use this term.

Notwithstanding the potential health problems of specific particles, it is the bioavailability of the particles that is of particular interest and relevance to built environment stakeholders. Considering the lifecycle of a nano-enabled product, the authors have developed Table 2 showing the stages that should be considered:

Table 2 Implications from the stages in the production and use of nano-enabled products

Stage	Examples	Workers at risk	Existing research and guidelines
The manufacture of the nanoparticles	e.g. Carbon nanotubes	Nano manufacturers	Significant research and guidelines
The incorporation of the nanoparticles into the construction material	e.g. cement or steel reinforcement	Material manufacturers / suppliers	Some research and guidelines
The use of the material in its incorporation into the product	e.g. in creating precast or insitu concrete elements	Product manufacturers / suppliers	Little research or guidelines
The installation of the product into the building/facility	e.g. installation of precast elements; or bending, cutting and fixing of reinforcement steel	Construction: steel fixers; concrete gangs; PC installers	No research and no guidelines
The use of the product as part of the building or facility	Including maintenance and degradation over time	Building users; cleaners; maintenance	Little research and no guidelines
The demolition of the products		Demolition contractors	No research and no guidelines
The re-use or recycling of products or of the arisings from products		Demolition / recycling contractors	Some research but few guidelines
The eventual disposal of the product or arisings from the product	Including environmental impacts e.g. to ground water	Waste contractors; wider society	Some research and some guidelines

The likelihood of nanoparticles or nanotubes being released from products in which they have been fixed or embedded (e.g. composites) is expected to be low, but it is recommended that manufacturers assess this potential exposure risk throughout the product lifecycle and make their findings available to the regulatory bodies (RS-RAEng[19]). There appears to be little evidence of this happening. Led by the biomedical and electronic industries, construction is seeking ways of improving the performance of conventional materials using nanomaterials to improve strength, durability and lightness, endow useful properties (e.g. heat-insulating, self-cleaning and antifogging) and function as key sensing components to monitor construction safety and structural health (Lee et al[11]). The term "greater risk than previously thought" is now appearing in articles concerning production and use of products containing nanoparticles. Kipen and Laskin [13] refer to studies suggesting that workers exposed at the current permissible exposure level may risk developing pulmonary fibrosis.

Currently, legislation is aiming at a moving target as technology accelerates. It is important to catch up with new innovations in product design and manufacture. The 2013 European Environment Agency report (EEA [6]) states that "there remains a developmental environment that hinders the adoption of precautionary yet socially and economically responsive strategies in the field of nanotechnology."

The OECD (Organisation for Economic Cooperation and Development [17]) lists 729 recent research projects in the field (http://webnet.oecd.org/nanomaterials). However, whilst a number refer to health concerns, very few world-wide are starting to consider implications on construction. One example is the EU's 'Scaffold' initiative: innovation strategies, methods and tools for occupational risks management of manufactured nanomaterials in the construction industry (http://scaffold.eu-vri.eu). This relatively new initiative is still to 'gather steam', but they acknowledge that "occupational exposure to these emerging risks may be accidentally or incidentally produced at different stages of the construction industry life cycle". They also concur that scientists are only just starting to understand the risks and that "detailed information about the product composition and their possible nano-specific health and safety issues is generally lacking… as a consequence, for the average construction company it will be very difficult to conduct a proper risk assessment and organise a safe workplace for its employees" (Scaffold [20]). However, interest is growing rapidly, evidenced by the attendance of more than 100 construction professionals at the webinar on the subject organised by the Institution of Occupational Safety and Health. A recording of this is available at www.iosh.co.uk/nanowebinar.

The 'elephant in the room' in terms of nano-health is asbestos and, whilst serious researchers are reluctant to make too much of the similarities between nanotechnologies and the emerging health concerns in the first part of the last century, the potential connection should at least be acknowledged.

IOSH-funded Research Project on Managing Nanotechnology in Construction

It was mentioned previously that there has been little nano research relating to the built environment. However, the Institution of Occupational Safety and Health (IOSH), that represents OSH practitioners across all industry sectors, has recently commissioned the authors to research into nano and the built environment, focussing on demolition and recycling activities. This research is timely and relevant for the built environment in the 21st century. It will start to take a step forward in an area that has massive potential but also significant risks that are largely going unnoticed or ignored across the world.

The project will:

1. Catalogue products used in the built environment that incorporate nanoparticles
2. Catalogue the type(s) of nanoparticle in each product
3. Equate the types of nano with the relevant hazard and risk based on published data
4. Establish the likely demolition and recycling techniques for such products
5. Test selected samples of such products to establish the bioavailability of the nanoparticles from likely demolition and/or recycling techniques.
6. Produce guidance for IOSH practitioners and industry stakeholders on nanotechnologies in the built environment

CONCLUSIONS

As mentioned previously, nanotechnologies are a reality for the built environment, including cement and concrete. Nano silica, both with or without microsilica, has been proved to have the ability to improve the mechanical and durability properties of structural concrete, and is increasingly being introduced, either visibly or more surreptitiously, into commercially available mortars, concretes and other cementitious products.

The issue for the safety and health of both workers and the public however, is one of effective management of the materials and applications. If the comparison with asbestos is valid only in a minor way or only with reference to part of the nanotechnology spectrum, then the research introduced here will be making a massive step in the improvement of safety and health and in the saving of many lives.

Even if the research does no more than identify the significant products that incorporate nanoparticles then this, in itself, will provide the opportunity for these items to be noted and their location recorded, for instance in facility building's health and safety file. This will enable future maintenance, demolition and recycling workers to take appropriate precautions, remembering that, with asbestos, the most difficult situation is when its location is unknown.

It may even be possible through the use of technological advances using nanotechnology to improve occupational health for countless number of workers worldwide. However, according to Bauer et al[1], unless life cycle thinking is used to assess the environmental impact of the improvements the advantages cannot be reliably promoted. By considering the demolition stage of the construction process and the likely release of nanoparticles this work will enable others to complete life cycle assessments on the introduction of the increasing number of opportunities for novel products and technological solutions using nanomaterials.

This research will assist in the understanding of exposure of workers to engineered nanoparticles by providing a catalogue of materials used in the construction process containing the particles together with information pertaining to the release of the particles through typical operations used in the demolition and recycling processes. This would then be able to be incorporated into research by people such as Gibson et al[8] who are assessing the occupational health effects of engineered nanomaterials and arguing for a clear need to gather experimental, clinical and epidemiological data for the purpose of characterizing the relationship between exposure and health outcomes.

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