

Nanotechnology in construction and demolition: what we know, what we don't

Report submitted to the IOSH Research Committee

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Abstract

Nanomaterials¹ can be found in everyday products such as electronics, foods and sun protection creams. They are also found in construction products, primarily in surface coatings, concrete, window glass, insulation and steel. Usage rates appear to be relatively low but are expected to increase considerably. Academic and manufacturers' literature was reviewed and interviews conducted with industry representatives: it was difficult to identify which products definitely contain nanomaterials, and what these materials might be. The legislation which applies to construction products (such as COSHH, REACH and CLP) does not make specific requirements in relation to nanomaterials or nanoparticles, and such products rarely carry detailed labels which describe their composition. This is of concern as some nanomaterials, such as certain types of carbon nanotube, are reported as being potentially harmful, although other nanomaterials and nanoparticles are considered much less problematic.

Work activities in construction and demolition release dust and may therefore also release engineered or manufactured nanoparticles, if these are present - for example, cutting, drilling and sanding during construction, and explosive methods and concrete crushing at demolition. Current evidence suggests that nanoparticles (or other nano-objects such as fibres) released through such activities are generally still attached to fragments of the underlying matrix (and are therefore less likely to be toxic), but the number of studies in this area is too small to draw firm conclusions.

Dust is a very significant hazard for those working in construction and demolition. The use of almost all currently available nano-enabled construction products is unlikely to add significantly to the risks already present. The priority is to manage existing risks robustly. This should ensure that the majority of unknown risks are also controlled. However, it is important to ask questions of material suppliers regarding the exact content of unfamiliar products, particularly those which may contain nanoscale fibres. There is also a responsibility on manufacturers and those developing new products to ensure that these are designed and manufactured with the health risks of those using and installing the products in mind.

¹ Nanomaterials – This report uses the ISO definition of nanomaterials, which includes materials with particles, structures, or spaces at the nanoscale, i.e. 1–100 nm

List of definitions and glossary as used in this review

Aggregate: particle comprising strongly bonded or fused particles where the resulting external surface area may be significantly smaller than the sum of calculated surface areas of the individual components (1)²

Agglomerate: collection of weakly bound particles or aggregates or mixtures of the two where the resulting external surface area is similar to the sum of the surface areas of the individual components (1)

BIM: Building Information Modelling

The process of developing information-rich object-oriented models. The term is sometimes used to denote the models themselves.

Bulk form/parent substance: a chemical substance which is not a nanomaterial, being discussed in comparison to a substance of the same chemical composition which is at the nanoscale

CDM: The Construction (Design and Management) Regulations (2015)

These are UK regulations which set out the processes and duties to ensure construction projects are carried out in a way that secures health and safety

CLP: Classification, Labelling and Packaging of substances and mixtures Regulation

This EU Regulation came into force in January 2009. It adopts the United Nations' Globally Harmonised System on the classification and labelling of chemicals (GHS) across all European Union countries, including the UK

COSHH: Control of Substances Hazardous to Health Regulations (2002)

COSHH Regulations require employers within the UK to control substances that are hazardous to health

CNT: Carbon nanotube

Carbon nanotubes are hollow structures with a diameter between 1 and 100 nm, and a length of several microns or longer e.g. (3). They may have a single wall (SWCNT) or may consist of several tubes inside each, multiwalled carbon nanotubes (MWCNT) e.g. (4)

CPC: Condensation particle counter (see also OPC)

This instrument measures particle release over time. It cannot differentiate between particles of different sizes, but it will include particles which are extremely small (5,6)

ENM: Engineered nanomaterial

A nanomaterial designed for a specific purpose or function (1)

Fluid nanodispersion: heterogeneous material in which nano-objects or a nanophase are dispersed in a continuous fluid phase of a different composition (7)

In vitro: A term applied to any study carried out in isolation from the living organism in an experimental system (literally in glass) (8)

In vivo: A study carried out within a living organism (8)

² Numbers in parentheses relate to definition sources, as listed in the References

MNM: Manufactured nanomaterial

A nanomaterial intentionally produced for commercial purpose to have specific properties or specific composition (1)

Nanocomposite: solid comprising a mixture of two or more phase-separated materials, one or more being nanophase (7)

Nanodispersion: material in which nano-objects or a nanophase are dispersed in a continuous phase of a different composition (7)

Nano-enabled: exhibiting function or performance only possible with nanotechnology (1)

Nano-enhanced: exhibiting function or performance intensified or improved by nanotechnology (1)

Nanofibre: nano-object with two similar external dimensions in the nanoscale and the third dimension significantly larger (7)

Nanomaterial: material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale (1)

Nanomaterial, EU definition: A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm (9)

Nano-object: discrete piece of material with one, two or three external dimensions in the nanoscale (1)

Nanoparticle: nano-object with all three external dimensions in the nanoscale (7)

Nanoplate: nano-object with one external dimension in the nanoscale and the two other external dimensions significantly larger (The smallest external dimension is the thickness of the nanoplate; the two significantly larger dimensions are considered to differ from the nanoscale dimension by more than three times; the larger external dimensions are not necessarily in the nanoscale) (7)

Nanoporous material: solid material with nanopores (the solid may be either amorphous, crystalline, or a mixture of both); the definitions of solid nanofoam (where most of the volume is occupied by pores) and nanoporous material (also materials with a small fraction of pores covered) are overlapping (7)

Nanoscale: size range from approximately 1 nm to 100 nm (1)

Nanostructure: composition of inter-related constituent parts in which one or more of those parts is a nanoscale region (1)

Nanostructured material: material having internal nanostructure or surface nanostructure (1)

Nanostructured powder: powder comprising nanostructured agglomerates nanostructured aggregates, or other particles of nanostructured material (the term “powder” is used in the sense of an assembly of discrete particles, usually less than 1 mm in size) (7)

Nanotechnology: application of scientific knowledge to manipulate and control matter predominantly in the nanoscale to make use of size- and structure-dependent properties and phenomena distinct

from those associated with individual atoms or molecules, or extrapolation from larger sizes of the same material (1)

NIOSH: The National Institute for Occupational Safety and Health

This is part of the U.S. Centers for Disease Control and Prevention, and has specific responsibility for workplace health and safety in the United States

OECD: Organisation for Economic Co-operation and Development

This is an international government forum which seeks solutions to common problems which affect the economic and social wellbeing of its members

OELs: Occupational exposure limits

These are the highest accepted levels for particular toxic substances, generally set by national or international bodies. They often relate to the atmospheric concentration of a substance, measured in the personal breathing zone of workers, but they can also be set in terms of the permissible levels in biological samples (for example in blood tests) (10)

OPC: Optical particle counter (see also CPC)

This is an instrument sometimes used to measure airborne nanoparticles, although it is also good for larger particles. It uses laser light scattering to count the number of particles per litre of air over time. Some types can categorise the particles according to their size (within particular bands) as well (5,6)

REACH: Registration, Evaluation, Authorisation and Restriction of Chemicals (2006)

This is a European Union Regulation which came into force initially in June 2007, with the final stage of implementation due in 2018

Solid nanofoam: solid matrix filled with a second, gaseous phase, typically resulting in a material of much lower density, with a nanostructured matrix, for example having nanoscale struts and walls, or gaseous nanophase consisting of nanoscale bubbles [closed nanofoam], or both (7)

Ultrafine particle: A particle with an equivalent diameter less than 100 nm (8)

In essence, this is another term for nanoparticles, but is usually used in relation to substances which arise as a by-product such as pollutants

WELs: Workplace exposure limits

WELs are British occupational exposure limits and are set in order to help protect the health of workers. WELs are concentrations of hazardous substances in the air, averaged over a specified period of time, referred to as a time-weighted average (TWA) (11)

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Executive Summary

Introduction

Nanomaterials are those which have one or more dimensions in the range 1–100 nm. They can occur naturally, can arise as a by-product of human activities such as the use of engines, or can be manufactured. The use of nanomaterials which have been intentionally produced is growing (engineered nanomaterials, ENM, or manufactured nanomaterials, MNM) but it can be difficult to identify exactly where they are and how widely they are used.

The aim of this research is to provide some clarity regarding the current use of nanomaterials in the built environment and the potential benefits and risks arising for those working in the construction and demolition sectors.

Desktop study, including review of academic and manufacturers' literature, has been the main method employed in this research. In addition, interviews have been conducted with individuals (n = 59) working in various parts of the construction, demolition and materials supply sectors. Email exchanges and visits to construction, demolition and recycling sites have yielded further data. Data from the different sources have been integrated throughout the report to provide an overview of the current situation with regard to nanomaterials in the built environment.

A second part of this research, published separately and available from a.g.gibb@lboro.ac.uk, has involved laboratory testing of samples of nano-enabled construction products. Some outputs from this have been used in this report to illustrate the nature of the materials involved. Additionally, a summary of the findings from this part of the research can be found in the appendix.

Background

There are thousands of different nanomaterials, varying in chemical composition, size, shape and many other characteristics. Adding nanomaterials to a product can alter the way that the product performs, sometimes significantly increasing performance or providing additional functionality.

Nanomaterial use has grown in recent years, and they are used in coatings, electronics, textiles, foods and many other areas. In construction they are used, for example, in concrete to provide additional strength, abrasion resistance, or to reduce the need for steel reinforcement. However, there is little readily accessible information on the extent or scope of their usage. To complicate matters further, the term 'nanomaterial' is used in different ways by different authorities. For example, the ISO definition, which is used in this report, includes all substances which have one or more dimensions at the nanoscale – even if these are internal dimensions. It includes, therefore, nanoscale films, and nanostructured materials which contains no nanoparticles. However, the European Commission (EC) definition is narrower, using the term 'nanomaterial' only in relation to those substances which contain nanoparticles, plates or fibres – collectively known as nano-objects. This definition, intended to underpin any regulation to manage health risks, reflects the concern that increased health risk might arise as a consequence of smaller particle size. However, toxicity varies widely depending on a number of characteristics; for example particular shapes of nano-objects such as long, thin tubes (or rods or wires) are considered to be potentially problematic. Other substances, however, may not be significantly more toxic than non-nanomaterials.

Nano-enabled construction products (i.e. those which have improved functionality as a consequence of the addition of nanomaterials) are rarely precisely labelled. Thus a product which describes itself as 'nano' may contain nanoparticles or other nano-objects; may be highlighting the fact that it is nanostructured (e.g. has nanoscale holes), contains nanoscale films or was developed using nanotechnology; or may be using the term solely in order to make the product seem new and different. Other products may be nano-enabled but choose not to declare this. Consequently, it is difficult to

identify those which contain nanomaterials or to determine the exact material involved, and this makes it difficult to assess exposure potential and health risk for those working in construction and demolition.

Nanomaterials within the United Kingdom and Europe are covered by the same regulations as other chemicals and toxic substances, such as COSHH, REACH and CLP, but there are no specific nano-related requirements except those relating to cosmetics and use in foodstuffs. There are ongoing discussions within the European Commission to refine the definition of nanomaterials and to strengthen requirements under REACH so that better data can be gathered regarding the production and use of nanomaterials which contain nano-objects.

France, Belgium and Denmark have each produced their own regulations requiring the registration of nanomaterials, although the exact requirements vary between them. In the United States, specific reporting requirements for existing and new nanomaterials have recently been approved. Both Canada and Australia manage nanomaterials through their existing registration systems, although the Canadian system makes higher demands, including the classification of a nanomaterial as 'new' even if the bulk (non-nano) form has previously been registered. These regulations generally apply only to nanomaterials which contain nanoparticles or other nano-objects.

The use of nanomaterials in construction

Research objective

to identify products used in the built environment which contain nanomaterials, and the type of nanomaterials involved

Research findings

The main nano-enabled products available are surface coatings, concrete, window glass, insulation and steel. However, there is a lack of evidence regarding which products definitely contain nanomaterials, and what these materials might be. Current usage rates for nano-enabled products in construction are difficult to assess but appear to be relatively low.

Concrete: Nanosilicas with various particle sizes can be added to concrete (e.g. silica fume, fumed silica) to produce materials which are stronger, achieve strength earlier or are self-compacting. These have been available for many years but usage in the UK is relatively low.

Titanium dioxide particles provide concrete with self-cleaning properties due to photocatalysis and can also reduce atmospheric pollution. Usage appears to be very limited at present.

CNTs can be added to concrete to improve strength and potentially allow electrical conductivity. CNTs are expensive and difficult to work with: only one CNT-enhanced concrete appears to be commercially available, launched recently following large scale field trials in the United States.

Window glass: Nanoscale film coatings can be added to glass during production to provide special properties for windows. Glass with improved insulation properties (low-e) is quite widely used, especially in the construction of commercial buildings. Coatings can also reduce the amount of solar gain within a building. 'Smart' windows allow solar gain to be varied to accommodate changes in the weather, although these products are currently installed only rarely.

Self-cleaning glass has a nanoscale film of titanium dioxide which breaks down dirt through photocatalysis and is quite widely used, for example in conservatory roofs. Fire safety glass with an intumescent layer of nanosilica has been available for many years but is only used in high-risk situations. When exposed to high temperatures, the nanosilica swells and forms a resilient barrier, absorbing the energy of the fire.

Surface coatings are the most numerous and readily available nano-enabled products for use in the built environment, being marketed for both professional and DIY use as well as being applied to products during manufacture. Many coatings contain silica (either as particles or in polymers) and are marketed for waterproofing or for their easy clean/dirt repellent properties. Coatings may also contain titanium dioxide nanoparticles, providing self-cleaning properties through photocatalysis; or antimicrobial silver nanoparticles.

CNTs and graphene are novel carbon nano-objects which offer strength, corrosion resistance and conductivity for coatings but only a very small number of such products are commercially available. Carbon black is a much more commonly used (and familiar) material used, for example, for shielding against radio waves.

Insulation materials are generally based on silica aerogels, which can be used in insulation blankets, translucent windows or vacuum insulated panels. These materials are highly effective insulators but are expensive and currently not very widely used outside of specialist projects.

Steel can be improved through the use of nanotechnology which modifies the grain structure to improve strength, wear resistance and corrosion resistance. There is some limited use of nano-enabled steels e.g. in reinforcement for road building, although most applications are targeted at the automotive and airline industries.

Health risks from nanomaterials

Research objective

to summarise the literature regarding the health risks of the nanomaterials most likely to be used in the built environment

Research findings

Potential health risks from nanomaterials are generally associated with the presence of nanoparticles and other nano-objects: the smaller particle size results in increased surface area and therefore increased reactivity. However, the size of objects is not the only factor which influences risk and there are wide variations between different materials in terms of their toxicity. This can be influenced by many factors including size, aggregation and agglomeration (how particles stick together), solubility and electrical charge. Particle shape is of key importance: there are particular concerns about fibre-shaped materials such as long, thin and rigid carbon nanotubes (CNTs) and other fibre or wire-shaped nano-objects. In some cases, these can behave in the same way as asbestos fibres which are able to travel down to the deepest parts of the lungs but are then too long for the normal clearance mechanisms to remove successfully.

Information currently available about the health risks from nanomaterials is based on laboratory research rather than on cases of ill-health in workers. The results of studies are often inconsistent or inconclusive due to variations in the methods and exact materials used.

Carbon nanotubes are reported to be potentially toxic due to their high aspect ratio and their biopersistence – they are long and thin, and thus similar to asbestos fibres. However, some shapes of CNTs appear to cause no problems; for example CNTs which are short or tangled and non-biopersistent are less likely to be toxic than those which are long, stiff and biopersistent.

Graphene is another carbon-based nanomaterial; it exists as flat sheets or plates. There is relatively little published literature regarding its health effects. In principle it could be toxic as some forms are able to penetrate deep into the lungs; smaller plates are likely to present a lower risk as they are easier for the body to clear. **Carbon black** is a particulate nanomaterial which has been used for decades, for example in tyre manufacture. It is classed as a possible carcinogen based on animal studies, although there is no clear epidemiological evidence of this effect. There is some evidence

from the literature that carbon black causes irreversible respiratory ill-health, and may be the causative agent behind smoking related ill-health.

Silver is reported to be effective as an antimicrobial in both its nano and non-nano forms. Reports on the health effects of nanosilver particles are inconclusive. There is relatively little evidence to show it is toxic but neither is there sufficient evidence to confirm it as safe.

There is evidence to suggest that **nanotitanium dioxide** particles may be toxic when inhaled. NIOSH (National Institute for Occupational Safety and Health) in the United States has recommended a maximum workplace exposure level which is one eighth of the exposure level for titanium dioxide which is not nanoscale. There is insufficient evidence to exclude it being carcinogenic. Nanotitanium dioxide is generally considered to be safe for dermal application (e.g. in sun protection creams) although there is limited evidence regarding the impact of pre-existing skin damage on this.

Nanosilica is usually amorphous. This is a different form of silica from the crystalline silica which is recognised as a major hazard in the construction industry, particularly as a dust. Amorphous nanosilica particles are acknowledged in most of the literature as being relatively low risk, with any ill effects being largely reversible. However, there is insufficient evidence to declare nanosilica as 'safe', particularly as there are so many different forms of it in use.

Exposure to nanomaterials

Research objective:

to explore the potential for exposure to nanomaterials during construction and demolition

Research findings

The findings presented in this section are based on review of the academic literature and on interviews with demolition and recycling managers and workers and visits to their sites.

Assessment of nanomaterial risk is difficult due to the uncertainties over the toxicity of particular nanomaterials and the lack of information on which nanomaterials are contained in which products.

There is some evidence that exposure to nanoparticles from engineered nanomaterials is likely to be low during demolition and construction processes as nanoparticles remain attached to fragments of the underlying matrix. However the evidence base is small and material ageing might also influence this, particularly in the demolition context. Additional exposures may occur as nano-enabled products are recycled and incorporated into new materials.

Measurement of exposure to nanomaterials is complex and data are currently limited. Qualitative assessments methods can be useful as they allow assessments to be made without such measurements, for example categorising activities as low, medium or high risk based on general principles. Such methods tend to reach relatively cautious conclusions, specifying higher levels of protection than expert assessment. Nanomaterial risk may not add substantially to existing construction health hazards (for example silica dust), and commonly used protective methods are likely to be appropriate in many cases.

Building on the findings of this research

Research objective:

to produce guidance for IOSH practitioners and industry stakeholders on nanotechnologies in the built environment

Research findings

Parallels have been drawn between asbestos and some nanomaterials, particularly certain CNTs which have similar needle like dimensions and bio persistence. In addition, the fact that nanomaterials, like asbestos before, are heralded as being a new 'miracle' solution raises anxieties in some quarters. However, CNTs in particular, and other nano-objects and nanomaterials in general, are very varied in terms of their functionality and their health risk potential. The question 'are nanomaterials hazardous?' is therefore difficult to answer given the wide variability between different substances. The rapid development of materials and new uses for these, and the limited availability of published information from manufacturers further complicates the situation.

It is unlikely that legislative change will have a major impact on this in the short term. Improved clarity will only occur if manufacturers take action to share information more readily and to follow voluntary guidance to provide greater detail in safety data sheets regarding any nano-objects. Action by manufacturers to design products and materials which are intrinsically safer is the best route to minimise any risks to workers in the long term (for example, CNTs which are non-biopersistent and are short or tangled) and research is ongoing to explore this; as well as to better understand the toxicity of nanomaterials and the specific factors which influence this. Further research is needed to assess the potential for worker exposure from nano-objects in construction and demolition and to consider the impact of secondary nanomaterials.

The use of most currently available products which contain nanomaterials is unlikely to add substantially to the risks already present for those working in construction and demolition. In the absence of detailed information, the following steps are recommended:

- robust management of existing health risks, which continue to be significant, notwithstanding any novel risks from nanomaterials;
- the use of a precautionary approach, extending the control measures already taken to protect against known risks to reduce exposures to those where less is known about toxicity;
- asking questions of suppliers and manufacturers regarding the exact content of new products. This is particularly important where fibres may be present as the size and shape of these can influence risk profiles substantially; and
- recording the materials/products used (for example in the CDM file or through the Building Information Model - BIM) to facilitate decision making during subsequent refurbishment or demolition.

Nanomaterials have much to offer the construction industry, and their use is expected to grow substantially in the future. If good practice and the right controls are in place and used correctly, for all existing hazardous substances, then the introduction of most currently available nanomaterials is unlikely to significantly increase the risk or require additional control measures. Nevertheless, it is important that we balance the benefits and the opportunities for improved functionality with a degree of caution. This includes an ongoing research agenda to improve understanding; challenge to manufacturers and suppliers to improve clarity and transparency; and a questioning approach by the industry. This will enable us to continue making well informed judgements to protect the workforce in the longer term.

1. Introduction

Nanomaterials are those which have one or more dimensions in the range 1–100 nm. They can occur naturally, arise as a by-product of human activities such as the use of engines, or can be manufactured. The use of nanomaterials which have been intentionally produced (engineered nanomaterials, ENM, or manufactured nanomaterials, MNM) is growing but it can be difficult to identify exactly where they are and how widely they are used.

The aim of this research is to provide some clarity regarding the current use of nanomaterials in the built environment and the potential benefits and risks arising for those working in the construction and demolition sectors.

1.1. What are nanomaterials?

Nanomaterials have one or more dimensions in the range 1–100 nm, and have particular properties or characteristics that are a consequence of this. To give some context to these dimensions, consider that the thickness of a human hair is around 100 μm (i.e. 100 000 nm). Figure 1 shows a carbon fullerene which is around 1 nm across – the ratio between this and a small grapefruit being similar to the ratio between the grapefruit and the world.

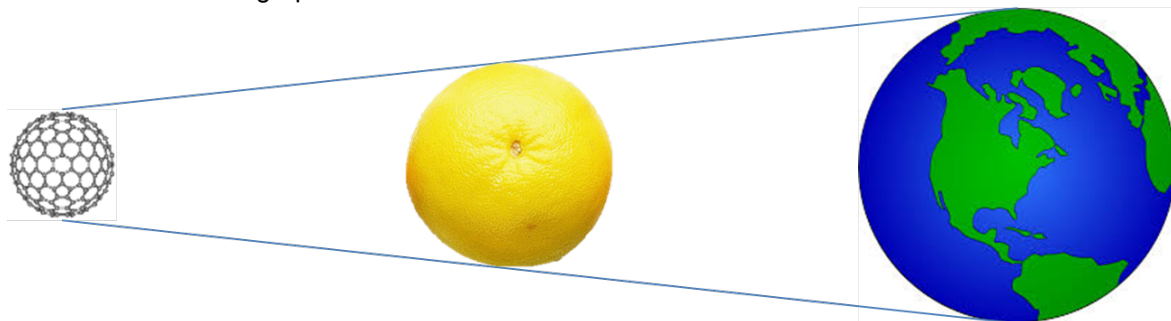


Figure 1 A carbon fullerene, a grapefruit and the world

Objects at the nanoscale can occur naturally, including viruses, volcanic debris and the crystals on some leaves which enable them to shed water easily. They can also be formed as an unintentional consequence of human activity such as the use of car engines, aeroplanes and incinerators (12): these are more commonly referred to as ultrafine particles and are recognised to have adverse health effects (13,14).

The use of nanoscale materials and processes is not new. Steel production has been based on nanotechnological methods for over 200 years (15) and paints have included nanoscale pigments since the earliest cave paintings (16). Some materials which are widely used in manufacturing are also made up of nanoscale particles – examples include carbon black, used in rubber and tyre manufacture; and synthetic amorphous silicon (SAS) used in tyres as a filler and also in foodstuffs, toothpaste etc. However, other nanomaterials have been developed, designed or discovered more recently. Particularly exciting examples include graphene, a sheet of carbon which is only one atom thick (17); and carbon nanotubes (CNTs), essentially the same sheet rolled into a tube (18). These are being used, for example, in computer components and batteries; and have been used to create Vantablack, the darkest manmade substance and reportedly the closest thing to looking into a black hole.³ Nanomaterials which have been intentionally created for their novel properties are often

³ <https://www.surreynanosystems.com/vantablack>

referred to as engineered nanomaterials (ENM) or manufactured nanomaterials (MNM) to distinguish them from naturally or accidentally occurring nanomaterials.

Nanotechnology is reported to be a growing industry – there is, for example, a progressive increase in the number of nanotechnology patents registered, and the number of academic papers published relating to it (19). However, such developments do not always translate into useable products – the European Commission observed several years ago that, *“presentations about the potential benefits of nanotechnologies predict an almost infinite diversity of future applications of nanomaterials, but fail to provide reliable information about current uses”* (20, page 2).

The limited availability of information is an issue in the construction industry – use of nanomaterials is reportedly increasing (21) but it is difficult to identify exactly where they are. This is of particular concern to those working in demolition, as they use dynamic methods to break down materials, with an associated risk of dust and particle release, but often have limited information on the exact content of the materials involved. There is also a lack of clarity regarding the potential health impact of nanomaterials. For example, parallels have been drawn between CNTs and asbestos, as both are needle shaped and have low solubility, and this is clearly of concern to those working in the construction and demolition industries. However, some forms of CNTs appear to be much less toxic than others, and many other nanomaterials may also be unproblematic.

It is important to consider these risks in context. Developing our understanding of hazard from nanomaterials (which may be only rarely used) must not detract from managing the very real risks already recognised in the industry. Silica, for example, is a cause of substantial ill-health in construction and very widely used, and robust efforts to manage it must remain a priority.

1.2. The aim of this research

The aim of this research is to provide greater clarity regarding the use of nanomaterials in the built environment and the potential benefits and risks arising for those working in the construction and demolition sectors. The objectives of the research are as follows:

- to identify products used in the built environment which contain nanomaterials, and the type of nanomaterials involved;
- to summarise the literature regarding the health risks of the nanomaterials most likely to be used in the built environment;
- to explore the potential for exposure to nanomaterials during construction and demolition; and
- to produce guidance for IOSH practitioners and industry stakeholders on nanotechnologies in the built environment.

A separate strand of this research has tested samples of nano-enabled building products to explore the likelihood of particle release when buildings are demolished and the materials recycled. These findings are published separately from a.g.gibb@lboro.ac.uk. A summary can be found in the appendix.

1.3. Terminology in this report

There is some variation and misunderstanding around the use of many terms in the field of nanotechnology. The terms nanomaterial, nanoparticles and nanotechnology are often used synonymously (22) or are conceptualised differently by different authors or bodies. The International Standards organisation (ISO) defines nanomaterials as *“Materials with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale”* (1).

Within this, there is differentiation between

- a) nano-objects: particles or fibres which have external dimensions at the nanoscale; and

- b) nanostructured objects which have internal dimensions at the nanoscale (i.e. they may have pores, or spaces that are smaller than 100 nm).

There are further divisions within these categories, and Figure 2 gives an overview of how the various terms are used by ISO.

The term 'nanotechnology' is broader as it covers '*application of scientific knowledge to manipulate and control matter predominantly in the nanoscale*' (7). Therefore it can include materials which have been created or investigated using equipment which operates at the nanoscale, even though the material is not itself 'nano'. Thus, nanotechnology has improved our understanding of the structure of ordinary concrete, through study at the molecular level (23).

Within this report, the ISO definitions will be used. Where appropriate, specific terms such as 'nanoparticle' or 'nanofibre' will be used, with 'nano-objects' as an umbrella term. 'Nanomaterial' will be used as a generic term and will be used where the exact nature of the substance is not known (which is a very common scenario). This will include products which are labelled as being 'nano' by manufacturers, even if there is no definitive evidence as to whether nanomaterials are actually contained. 'Nano-enabled' will be used in reference to construction products which are reported or believed to have some nanomaterial elements which influences their function, even if there is little certainty what these elements may be.

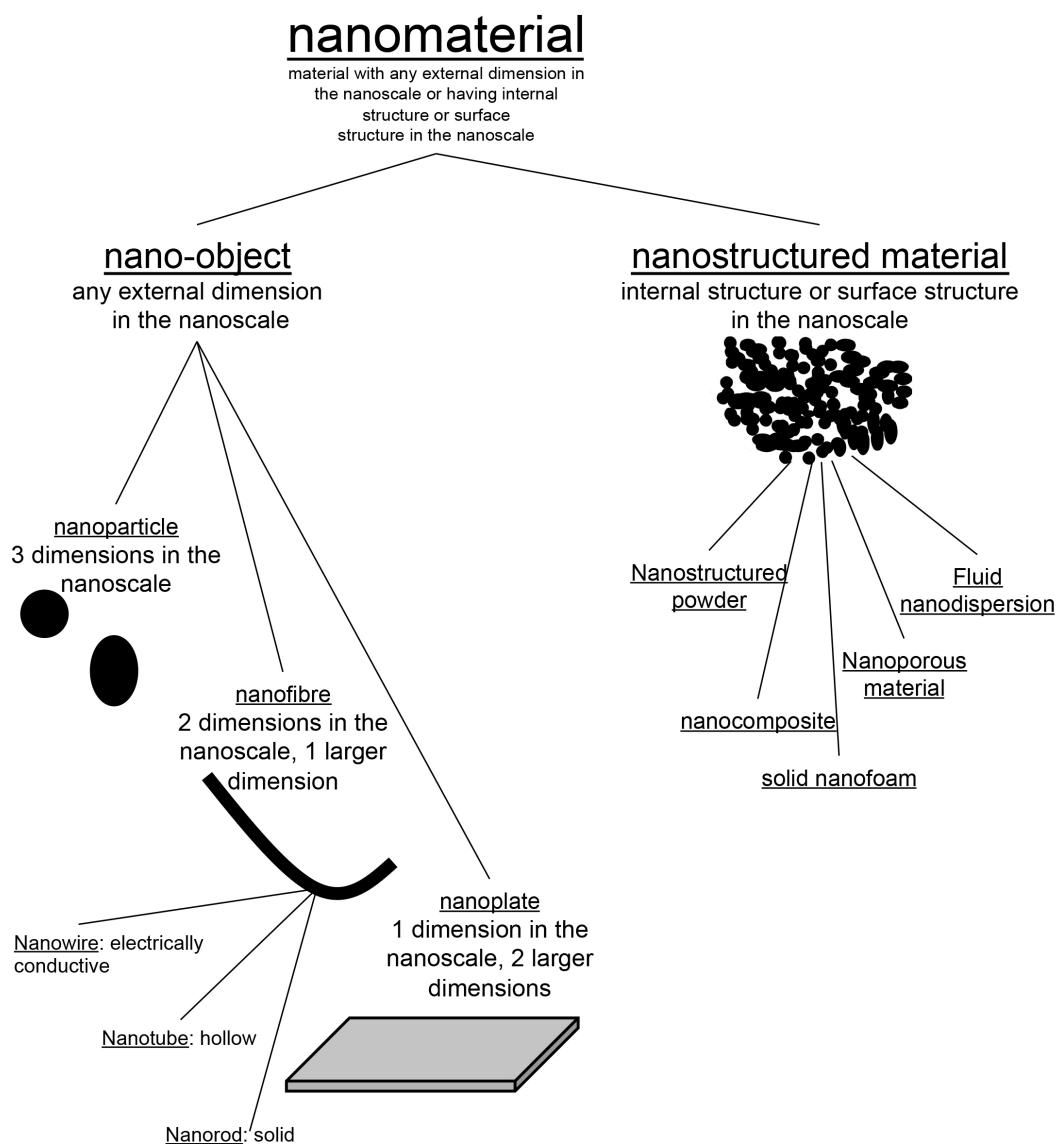


Figure 2 Nanomaterial categories from ISO definitions, as used in this report

2. Background

There are thousands of different nanomaterials, varying in chemical composition, size, shape and many other characteristics. Adding nanomaterials to a product can alter the way that the product performs, sometimes significantly increasing performance or providing additional functionality.

Nanomaterial use has grown in recent years, and they are used in coatings, electronics, textiles, foods and many other areas. In construction they are used, for example, in concrete to provide additional strength, abrasion resistance, or to reduce the need for steel reinforcement. However, there is little readily accessible information on the extent or scope of their usage. To complicate matters further, the term 'nanomaterial' is used in different ways by different authorities. For example, the ISO definition, which is used in this report, includes all substances which have one or more dimensions at the nanoscale – even if these are internal dimensions. It includes, therefore, nanoscale films, and nanostructured materials which contains no nanoparticles. However, the European Commission (EC) definition is narrower, using the term 'nanomaterial' only in relation to those substances which contain nanoparticles, plates or fibres – collectively known as nano-objects. This definition, intended to underpin any regulation to manage health risks, reflects the concern that increased health risk might arise as a consequence of smaller particle size. However, toxicity varies widely depending on a number of characteristics; for example particular shapes of nano-objects such as long, thin tubes (or rods or wires) are considered to be potentially problematic. Other substances, however, may not be significantly more toxic than non-nanomaterials.

Nano-enabled construction products (i.e. those which have improved functionality as a consequence of the addition of nanomaterials) are rarely precisely labelled. Thus a product which describes itself as 'nano' may contain nanoparticles or other nano-objects; may be highlighting the fact that it is nanostructured (e.g. has nanoscale holes), contains nanoscale films or was developed using nanotechnology; or may be using the term solely in order to make the product seem new and different. Other products may be nano-enabled but choose not to declare this. Consequently, it is difficult to identify those which contain nanomaterials or to determine the exact material involved, and this makes it difficult to assess exposure potential and health risk for those working in construction and demolition.

Nanomaterials within the United Kingdom and Europe are covered by the same regulations as other chemicals and toxic substances, such as COSHH, REACH and CLP, but there are no specific nano-related requirements except those relating to cosmetics and use in foodstuffs. There are ongoing discussions within the European Commission to refine the definition of nanomaterials and to strengthen requirements under REACH so that better data can be gathered regarding the production and use of nanomaterials which contain nano-objects.

France, Belgium and Denmark have each produced their own regulations requiring the registration of nanomaterials, although the exact requirements vary between them. In the United States, specific reporting requirements for existing and new nanomaterials have recently been approved. Both Canada and Australia manage nanomaterials through their existing registration systems, although the Canadian system makes higher demands, including the classification of a nanomaterial as 'new' even if the bulk (non-nano) form has previously been registered. These regulations generally apply only to nanomaterials which contain nanoparticles or other nano-objects.

This section will summarise what is currently known about nanomaterials, their uses in the built environment and elsewhere and their potential to cause harm. It will also highlight the lack of clarity in this field. As outlined in the introduction, this report will use the ISO definition of nanomaterials which

includes those which are nanostructured as well as those which contain nanoparticles or other nano-objects.

It is important to remember that nanomaterials may be defined in other ways. For example, the European Commission (EC) has defined nanomaterials as, *A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm* (9). This definition, which focusses on materials which contain particles rather than those which are nanostructured without containing nano-objects, is intended to underpin future regulation and is subject to ongoing debate. The EC also has other definitions which are used within existing nano-specific legislation such as that used to regulate cosmetics and foodstuffs.

Definitions vary in other aspects also (24), such as whether they include naturally occurring or incidental nanomaterials: the EC definition does (because health effects may arise from these), whilst the ISO definition focusses only on engineered nanomaterials (ENMs) or manufactured nanomaterials (MNMs). There are also variances in how many particles (or alternatively, what mass of particles) must be present to qualify for the definition; and whether specific novel properties must be present which are attributable to the nanoscale particle size.

A further area of discussion is around the term 'nanoscale'. Most definitions including ISO define this as approximately 1-100 nm, as this is where novel properties are mostly likely to occur as a consequence of size. However, dimensions as small as 0.1 nm are technically nanoscale (25). There is also an argument that the 100 nm cut off point is arbitrary: particularly in health terms, as it has no value in distinguishing clearly between materials which might be safe and those which are less so (12,26,27). For example the International Agency for Research on Cancer (IARC) includes titanium with a particle size of 150 nm in its discussions on the risks of nanotitanium, even though this would fall outside many definitions, including the EU one.

2.1. Use of nanomaterials

There is widespread agreement that the use of nanomaterials has grown extensively in recent years both in terms of the volumes of materials produced and the range of application and sectors which use them.

- The largest fields of use by volume are in coatings and pigments; electronics; and cosmetics. There is also extensive use in automotive and aeronautical industries, textiles, food and medical applications (28).
- 97% of nanomaterial use arises from just two substances (20, page 10): carbon black (9.6 million tonnes globally), most of which is used as a reinforcer in rubber such as that used in tyres (29); and synthetic amorphous silica (1.5 million tonnes) which is also used in rubber as well as being a filler or flow agent in powders, foods, toothpaste etc.
- Titanium and zinc have been used in sunscreens in their nanoform since the 1990s (30). They provide a high level of protection against UV light, but appear transparent, making them more desirable to users than traditional non-nano versions which appear white on the skin. Annual volumes of titanium and zinc produced (for sunscreens and other uses such as in coatings) are of the order of 10 000 tonnes and 8000 tonnes respectively (20).
- Nanosilver is used as an antimicrobial in medical applications but also in consumer goods such as socks, washing machines and hair dryers.⁴ It is estimated that around 20 tonnes are marketed annually (20).

⁴ www.silverdoctors.com/silver/silver-news/samsung-introduces-washing-machines-using-patented-nano-silver-ions/

Information on the range of products available is being collated on a number of public-access websites. These include the Nanodatabase (31), a Danish inventory of consumer products that contain nanomaterials or are marketed with the word 'nano'; and the Project on Emerging Nanotechnologies (32) in the United States. However, there is limited detail available on the exact nanomaterials involved – the Nanodatabase currently lists around 1400 products, and for 920 of these the nanomaterial contained is listed as 'unknown'. Similarly, the PEN site lists 1810 products, but only 159 of these have provided any evidence regarding the nature of the nanomaterials contained.

2.2. Use of nanomaterials in construction

Nanotechnology in construction is reported to be an important and expanding market, with data from market research companies predicting substantial growth. Teizer et al (21) quote Freedonia data which anticipates an increase in the market from \$100M in 2011 to \$1.75 billion by 2025. Bill Looney of AECOM has suggested that “By 2025, over 50 percent of building materials are expected to contain nanomaterials as more take advantage of these lighter, stronger, and more energy efficient materials” (33).

The reason for this anticipated growth is that nanomaterials offer tangible benefits to the industry. For example, improvements attributable to their use in concrete include higher compressive and tensile strength, improved abrasion resistance, reduced cement consumption and associated environmental benefits (34). In addition there is potential for the use of nano-enabled concretes to reduce the need for steel reinforcement which carries risks of corrosion and oxidation.⁵ Nanomaterials also offer improved thermal efficiency of windows and insulation materials.

The literature on the use of nanomaterials in construction includes a number of summary reports outlining the products which might be most useful. However these often focus on the underlying research, and on the useful properties of these materials, but fail to “*distinguish between what is available now and what is theoretically possible in the future*” (35). Examples include papers by Hanus et al (35), Teizer et al (21), and Mann (36).

Other resources have attempted to focus more explicitly on construction products which are available commercially, but have found limited evidence regarding the specific materials used. For example, a substantial and well referenced report by van Broekhuizen and van Broekhuizen (37) lists over 80 product names which are believed to contain nanomaterials and which are ostensibly used in construction. However, for many of these, the specific nanomaterial used is not identified; and many of the brand names which do carry nano-specific detail relate to product additives (such as adhesives or flow agents), and are difficult to link to named products (such as coatings or concretes) which might be used in construction projects.

Similar difficulties have been encountered by the eLCOSH nano website (www.nano.elcosh.org), a resource which was first published sometime after the current project began. This lists over 450 construction related products which are believed to contain nanomaterials in some form. However, for less than half of these are clear statements available regarding what nanomaterial is involved, despite the website owners collecting safety data sheets for all products included. The journal paper which describe the development of the eLCOSH website observes that, ‘a lack of transparency regarding the use of nanotechnology in construction products appears to be the norm’ (38). This conclusion echoes similar comments made elsewhere in the literature regarding the incomplete labelling of nano-enabled products (37,39).

A consequence of this incomplete labelling is that those working in construction have no easy way of knowing whether or not they are working with nano-enabled products, and an associated lack of

⁵ www.cement.org/learn/concrete-technology/concrete-design-production/ultra-high-performance-concrete

awareness has been confirmed in several surveys (37,38,40). Where there is discussion in the field it tends to focus on the higher profile materials such as carbon nanotubes. A study by Arora et al (40) identified these as the nanomaterials which construction stakeholders were most aware of, and there is certainly substantial research on their development. However, CNTs are expensive and difficult to work with and in reality are used only in specialist applications. This highlights the difficulty of assessing the extent to which nano-enabled products have penetrated the built environment. Despite the prediction that around 50% of building products will be nano-enabled by the year 2025 (33), current usage estimates are much smaller – for example market penetration of coatings has been estimated at around 1% (41).

2.3. Health risks from nanomaterials in construction

A key reason to develop a better understanding of which nanomaterials are used and where is that nanomaterials, particularly those which contain nano-objects, may have adverse health effects. Nanoscale pollutants (arising mostly from vehicle emissions, and more commonly referred to as ultrafine particles) have been associated with increased morbidity and mortality (13,14). The effects may arise in part from increased reactivity, consequent on their higher surface area for a given mass (42). In addition, particular particle shapes have been identified as problematic. Some carbon nanotubes, for example, have been suggested to have health risks similar to those from asbestos fibres due to their high aspect ratio (i.e. the fact that they are long and thin) and their low solubility (43). This is clearly of particular concern to those working in the construction industry, given the ongoing harm from the use of asbestos in the early and middle 20th century. Any building constructed before 2000 may still contain asbestos (44), which was widely adopted as a building material without full understanding of its inherent risks. Despite legislative controls and information campaigns, exposures continue: some are a result of lack of knowledge, others a consequence of intentional disregard of the law. Every year, around 5000 workers in the UK die as a result of past exposure to asbestos and new cases continue to be diagnosed.

However, there is substantial uncertainty around the toxic potential of engineered nanomaterials with little, if any, epidemiological evidence of harm (45). It has been argued that simply being 'nanoscale' is not in itself a predictor of harm (27), and risk will vary between materials according to chemical composition, as it does for non-nano substances. Additionally, nanomaterials are highly variable, with multiple forms often existing for each chemical substance. For example nanosilica can be crystalline (similar to the hazardous non-nano silica forms found in cement-based construction materials) but more commonly has an amorphous structure. This changes its behaviour and function and also its hazard profile (with amorphous silica having much lower toxicity). Similar differences exist for other materials, with variations relating to particle size, shape, surface charge, whether particles aggregate or agglomerate (stick together), the rate at which they dissolve, and the presence of other elements (46), and all of these factors can influence toxicity. There is, consequently, a lack of certainty: an expert panel of the WHO has noted that the current data and evidence on the effects of nanotechnology on health is 'far from conclusive' (47).

In addition to uncertainties around the toxicity of nanomaterials, there is very limited information available regarding possible exposures to them (48-50). There are also factors in construction which make exposure assessment and management especially challenging (compared to, for example, laboratory work). These include the highly varied and rapidly changing nature of the work environment, where tasks may take place in confined or poorly ventilated areas, or outside, often in inclement weather. These are factors that the industry already has to deal with in its management of familiar hazards such as silica.

Additional concerns relate to the potential for nanomaterial exposure during demolition. The energetic and dynamic processes used here can release respirable particles, and again the sector has for many years faced the challenge of demolishing buildings containing toxic asbestos. Additional risks arise

where the provenance of materials is unknown, a likely occurrence by the time a building is demolished or refurbished 10, 50 or 100 years after its construction.

2.4. Legislation in Europe and other countries

The management of nanomaterials within the United Kingdom and Europe falls under general chemical legislation such as COSHH (Control of Substances Hazardous to Health), REACH (Registration, Evaluation, Authorisation & Restriction of Chemicals) and CLP (Classification and Labelling of Products, which is derived from the Global Harmonisation System (GHS)), the contribution of each is shown in Table 1. Nanomaterials which are known to be hazardous will be covered under these regulations in the same way as non-nanomaterials which are hazardous. However, these particular regulations and the wider legal framework in Europe (and most other countries) do not require most nano-enabled or nano-enhanced products to be labelled as such (with the exception of cosmetic products and foodstuffs). This results in limited information often being available regarding the nanomaterial content of products. There are ongoing discussions at the United Nations regarding the GHS for labelling products and whether it needs to be revised to improve its applicability to nanomaterials (51).

Guidance has been published by the EU on best practice when registering nanomaterials under the existing legislation (52), and the International Organization for Standardization has published guidance on how to complete safety data sheets for nanomaterials (53). However many nanomaterials are not explicitly registered under REACH, and in other cases the dossiers which have been submitted are reported to be inadequate (54). There is also evidence that safety data sheets are often incomplete or incorrect, making it difficult for those working with materials to conduct adequate risk assessments (55).

There is a commitment within Europe to review the current regulatory arrangements with regard to nanomaterials, and in recent years the EC has undertaken a public consultation and an impact assessment of various options. There are a number of ongoing discussions.

First, there is ongoing review of the European definition of nanomaterials, to ensure that it is suitable to underpin future regulation. Discussion is focussing, for example, on the proportion of particles which must be nanoscale to require a designation as a nanomaterial; how nanostructured materials might be dealt with (i.e. those which do not contain nanoparticles); and how aggregated particles (nanoparticles which are strongly bound to form particles which are effectively larger than nanoscale) should be considered under the regulations. A decision is anticipated soon, based on reports produced by the Joint Research Centre (56).

Secondly, a review is under way to consider how to regulate nanomaterials within Europe. A study to assess the impact of regulation has explored a range of options including the establishment of a specific nanomaterials registry, or the establishment of a database, populated by data drawn from existing registries (57). The EC has not reached a formal conclusion on how to proceed but has indicated that it anticipates any change to be introduced through modifications to the REACH annexes rather than through the introduction of new nano-specific legislation (58). It is looking unlikely that a specific nanomaterial register will be produced at a European level.⁶

In the absence of specific regulation of nanomaterials in the EU, several countries have produced their own legislation, each with different mandatory reporting requirements (59) and others are in the process of discussion or development. Examples of these and of arrangements for some countries outside of Europe are shown in Table 1. The impact of these regulations on the availability of information regarding nanomaterials is difficult to judge, as they are largely aimed at improving

⁶ https://chemicalwatch.com/48058/nano-registers-improving-information-along-supply-chain#utm_campaign=47992&utm_medium=email&utm_source=alert

government awareness. For example the French regulations allow for publication of a register of which chemical substances are used, what they are used for and in what quantity. However, this is in general terms and would not allow identification of individual products which contained nanomaterials. Nor do any of the current regulations require products to be labelled or stipulate the provision of nano-specific information to the product user.

Table 1 Examples of current legislation relating to nanomaterials

Country	Current arrangements	Date of introduction	Comments
EU/United Kingdom	Under REACH, all chemical substances imported or manufactured in quantities greater than one tonne must be registered. There is an optional 'nano' box on the submission form Under CLP manufacturers or importers must supply a safety data sheet for all hazardous materials (as determined by the manufacturer/importer, based on criteria set out in CLP, largely arising from the outcomes of animal testing). Registration is also required for substances which are Persistent, Bio accumulative or Toxic; or are Substances of Very High Concern Under COSHH in the UK, those who use materials including nanomaterials must carry out risk assessment, usually based on the information contained in the safety data sheet (52,54)	June 2018. Volumes greater than 100 tonnes have been registerable since June 2013 and particularly hazardous substances since June 2010 1989, current version dates from 2002	A review of REACH is underway to consider how it might be modified (through its Annexes) to regulate nanomaterials (which contain nano-objects) more closely (58,60)
France	Nanoscale substances or mixtures supplied to professional users must be registered by the manufacturer, importer and/or distributor (61) The regulations apply to materials which contain nanoparticles/nano-objects (including those which are aggregated or agglomerated), of which 50% or more are at the nanoscale The registration must include details such as size, shape, aggregation, electrical charge etc.	January 2013 (registration for substances used/imported from 2012)	A high proportion of reported substances relate to nanomaterials that have been in common use for many years (such as carbon black and amorphous silica) (60) There are reports that the high costs of registration act as a disincentive to companies to develop nano-enabled products
Belgium	Nanomaterials which are supplied to professional users must be registered in advance of being placed on the market (59,62) As with the French regulations, registration applies to substances and mixtures which contain nanoparticles/nano-objects. The registration must include size, shape, aggregation	January 2016, for substances Mixtures will fall under a second phase, which has	Common substances such as carbon black, amorphous silica and pigments are excluded from the requirement

Country	Current arrangements	Date of introduction	Comments
	etc.	currently been delayed and is likely to be implemented in 2018	
Denmark	Consumer products which contain nanomaterials must be registered (59,63) Again, this applies to nanoparticles/nano-objects and their aggregates and agglomerates. The registration must include chemical content. Further detail such as size, shape etc. are voluntary	June 2015 (at registration for substances used since 2015)	Common substances such as carbon black, amorphous silica and pigments are excluded from the requirement Registration is not required if nanomaterial release is not expected. For example, self-cleaning coatings for windows must be registered, but windows which incorporate such coatings need not (63)
Norway	All hazardous materials must be notified, including whether they are nanoscale or not (64)		Being a nanomaterial does not in itself trigger a need to report if the substance is not considered to be hazardous
US	Under the Toxic Substances Control Act, all existing new chemicals must be notified in advance of manufacture to allow determination of their risk potential. An amendment which is due to come into force during 2017 will require all existing nanomaterials (which contain nano-objects) to be reported including chemical identity, use and data regarding health effects. All new material will need to be reported prior to manufacturing or processing (65).		A proposed requirement on manufacturers or importers of nanomaterials to declare these met with a negative reaction from industry (66,67)
Canada	All new materials produced above 1000 kg must be registered. This includes new nanomaterials (those with unique structures or molecular arrangements) even if the previous non-nano version is already registered (68,69).		
Australia	All new materials must be register under NICNAS. This includes nanomaterials, but a new nanomaterial does not have to be reported if the bulk form has previously been recorded (70)		

3. Methods used

Methods used in this research have included review of academic and manufacturers' literature; interviews with individuals working in construction, demolition and materials supply; and visits to construction, demolition and recycling sites.

Initial laboratory tests have been performed on samples of nano-enabled construction products and some results are included in this report to illustrate the nature of the materials. The majority of laboratory testing is described in a separate report (available from a.g.gibb@lboro.ac.uk).

Data from the different sources have been integrated throughout the report to provide an overview of the current situation with regard to nanomaterials in construction and demolition.

The primary method used in this research was a desktop study based on academic literature and manufacturer's data. This was supplemented with interviews and site visits and with preliminary laboratory testing of products and samples. The key types of data used and further details on the methods used to collect them are summarised below.

3.1. Literature review of academic papers

The aim of the literature review was to gain an understanding of the current situation with regard to nanomaterials in the built environment, rather than to conduct a systematic critical review. The starting point was a number of key papers which have summarised nanotechnology in construction and the built environment in recent years. These papers (21,35-37,71-74) provided an initial overview of the field, and individual references were followed up. These papers also provided some details of products available and product manufacturers.

In addition, specific searches were conducted in relation to:

- the health effects of nanomaterials, using search terms such as
NANO + SILVER + HEALTH + REVIEW
CNT + HEALTH + REVIEW; and
- the development of particular construction products using search terms such as
WINDOWS + BUILDING + REVIEW
CONCRETE + NANOTECHNOLOGY + REVIEW
CONCRETE + CNT + REVIEW.

The literature on nanotechnology has grown substantially in recent years. For example, around 2500 papers are published each year on nanotoxicity (75), and a similar number are published annually on 'concrete and CNTs'. Review papers were therefore used in order to make the literature manageable initially. Individual papers were then followed up and a combination of backward and forward searching used to explore areas of particular relevance.

3.2. Web-based information

Three databases of nano-enabled products were used to identify the scope of nanomaterial use in consumer and construction products. Two of these are targeted at consumers - the Consumer Product Inventory run by the Project on Emerging Nanotechnologies (32) and the Nanodatabase in Denmark (31). The third database is eLCOSH Nano, an inventory of nano-enabled construction products hosted by the CPWR (The Center for Construction Safety and Training)⁷ in the United States

⁷ <http://www.cpwrr.com/>

(76). Development of this started around the same time as the current project and has provided good opportunities for information sharing.

Manufacturers' product sites were also studied, including review of Safety Data Sheets (SDS) where these were available. Relevant sites were identified from the academic and web-based literature above, and from promotion of products which were identified as 'nano' or as having novel properties which might indicate nano-enablement.

3.3. Interviews

Unstructured interviews (face to face or telephone) were conducted with individuals working in the construction industry or involved in the development, production or sales of building materials or products (n =59). These interviews were used to understand the current use of nano-enabled construction products, and to explore how it might differ from that portrayed in the academic literature. In some cases, interviews were conducted at construction sites or other workplaces and included observation of the site, providing opportunities to take many of the photographs included in this report. Interviews were the main source of data on demolition and recycling methods.

Interviewee selection was partly purposive (e.g. approaching members of a particular job family such as architects or site managers), and partly selective (e.g. approaching individuals who worked for specific manufacturers). Four of the interviewees had specific health and safety (H&S) responsibilities as H&S manager or similar. Several others had H&S responsibilities within their overall role e.g. in small companies. Table 2 and Table 3 summarise the interview cohort in terms of the job role of the interviewee and the industry they were employed in.

Table 2 Industry sectors represented by interviewees

Industry	Number of interviewees (n=59)
Coatings	8
Concrete	5
Construction	9
Demolition	10
Glass	8
Architecture and design	6
Research	3
Recycling	4
Other	6

Table 3 Job roles of interviewees

Job role	Number of interviewees (n=59)
Project or site manager	20
Research or development	10
Product sales	15
Other professional (e.g. architect, designer, engineer)	11
Other	3

3.4. Email exchanges

Email discussions were conducted to gather further information. These were largely with representatives of companies which sold nano-products and were aimed at, for example, gathering

further information about the materials involved, securing samples, or obtaining safety data sheets. Emails were also used to share/seek information with researchers working in related fields.

3.5. Networking and context

Links were established with others working in similar fields including:

- the CPWR in the United States, who run the eLCOSH Nano website and are conducting research on nanomaterial exposure during construction activities. Contact included frequent email exchanges to identify new nano-enabled products and to discuss research findings.
- Scaffold⁸, a large European project looking at nanomaterials in construction. Contact included attendance at two workshops conducted as part of their research.
- visits to trade shows and academic conferences to provide additional context and ensure that the research team were abreast of current developments in the field. This included the following:
 - Surfex – coatings exhibition/trade show, May 2014
 - FIT, UK window and door trade show, June 2014
 - Plantworx – construction trade show, June 2015
 - EU workshop on transparency measures for nanomaterials June 2014
 - Nanosafe conference, November 2014
 - Senn International Congress on Safety of Engineered Nanoparticles and Nanotechnologies April 2015
 - UK Nanosafety group conference, September 2015

3.6. Laboratory testing

Samples of a range of construction products were obtained: some were purchased, and in other cases samples were provided by manufacturers (who were advised of the aims of the research). A total of 44 samples were acquired, including 19 coating materials (some in liquid form, some applied to a substrate as part of the manufacturing process); 6 concrete samples; 7 pieces of window glass; 1 steel sample; and 5 other products (including a ceiling tile and flooring materials)

From these samples, candidate materials were chosen and samples were analysed using a variety of scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques to determine the chemical content and nanoparticle size and loading quantity in each case.

A brief summary of the findings from this work is given in the appendix. More comprehensive details regarding the laboratory testing methods and findings are included in the companion report (77). For access to this report, contact a.g.gibb@lboro.ac.uk.

3.7. Integration

Data from the different sources have been integrated throughout the report to provide an overview of the current situation with regard to nanomaterials in construction and demolition. Each section or subsection includes a note of which methods have informed that particular theme.

⁸ <http://scaffold.eu-vri.eu/>

4. Findings

4.1. The use of nanomaterials in construction

This section addresses the research objective:

to identify products used in the built environment which contain nanomaterials, and the type of nanomaterials involved

It is based on a review of the academic literature, and manufacturer's literature; and on interviews with representatives of nanomaterial manufacturing and sales, and construction managers, designers and architects. It is illustrated using preliminary findings from laboratory testing.

Key points

The main nano-enabled products available are surface coatings, concrete, window glass, insulation and steel. However, there is a lack of evidence regarding which products definitely contain nanomaterials, and what these materials might be.

Current usage rates for nano-enabled products in construction are difficult to assess but appear to be relatively low.

A review of the academic and manufacturers' literature identified 156 construction products currently available which are believed to be nano-enabled. These are summarised in Table 4.

Table 4 A summary of the construction product types which are most commonly nano-enabled (based on literature and web review and interviews with industry representatives)

<i>Product type</i>	<i>Construction products n=156 (further explanation in body text)</i>	<i>% of total nano-product list</i>
<i>Surface coatings</i>	<i>70</i>	<i>45%</i>
<i>Glass</i>	<i>23</i>	<i>15%</i>
<i>Concrete</i>	<i>22</i>	<i>24%</i>
<i>Steel</i>	<i>11</i>	<i>7%</i>
<i>Insulation</i>	<i>10</i>	<i>6%</i>
<i>Composites</i>	<i>1</i>	<i>1%</i>
<i>Other (roofs, flooring)</i>	<i>19</i>	<i>12%</i>

- Most of the products included in Table 4 are available in the United Kingdom. However, some products are also included which are widely available elsewhere e.g. in Europe or the US.
- Products are included if they have the word 'nano' in the title or advertising literature; if it is reported in the academic literature that a nanomaterial is present; or if the product literature reports special properties (such as photo catalysis or super hydrophobia) which are likely to be related to the presence of a nanomaterial. Hence the summary reflects products which are presumed or believed to be nano-enabled, although in many cases the evidence to support this conclusion is incomplete.
- Where products have multiple variants (for example coatings for different substrates such as glass, metal or concrete) these have been counted as a single product.
- Only end-use products are included in the summary, e.g. coatings, concretes, rather than products which may feature as ingredients in these.

- New products are being released on an ongoing basis and others are disappearing from the market or changing their names. Hence, the table is illustrative rather than definitive.

Rather than publishing a detailed list of the 156 products, the information has been converted into summary tables relating to specific construction products, presented later in this chapter. This has been done to make it a more useful resource for those working in the industry than a simple list might be. It also helps to overcome the uncertainties in the data set related to poor labelling of products and changeability of product names.

There are uncertainties regarding how widely and how frequently these products are used. Hincapié et al (41), based on a survey of Swiss construction experts, estimated 1% of coating products to be nano-enabled, supporting the conclusions of van Broekhuizen and van Broekhuizen (37) who found nano-enabled products to be a 'niche market'. Interviews for the current research support this evidence for low market penetration, confirming the construction industry to be a relatively conservative sector, with a very strong focus on perceived cost effectiveness (at least based on 'first-cost') and historical precedence. Projects generally include the cheapest materials which will fulfil a particular requirement and, as one manager observed, *'they just want us to put bricks on top of bricks.'* This contrasts with the prediction that 50% of construction products will be nano-enabled in 10 years' time (29,31), suggesting that the industry is still at an early stage of the predicted growth curve. However, it is also possible that it is approaching a tipping point where the use of new products will increase rapidly for financial, practical or environmental reasons. For example, interviews with those working in the glazing sector found that the use of nano-enabled glass has increased rapidly in the UK in recent years as it is the most effective way of fulfilling the thermal efficiency requirements of the most recent updates of the 2010 Building Regulations (78).

As Table 4 shows, the main product areas for nanomaterials in construction are concrete, glass, surface coatings, insulation material and steel. The next section will consider these applications in more detail, identifying in each case:

- the nanomaterials commonly involved;
- the purpose/benefits/properties of these materials to the product;
- how long the material has been nano-enabled, and how widely it is used;
- examples of product names, drawn from the product list described above; and
- what is likely in the future.

4.1.1. Concrete

Nanosilicas with various particle sizes can be added to concrete (e.g. silica fume, fumed silica) to produce materials which are stronger, achieve strength earlier or are self-compacting. These have been available for many years but usage in the UK is relatively low.

Titanium dioxide particles provide concrete with self-cleaning properties due to photocatalysis and can also reduce atmospheric pollution. Usage appears to be very limited at present.

CNTs can be added to concrete to improve strength and potentially allow electrical conductivity. CNTs are expensive and difficult to work with: only one CNT-enhanced concrete appears to be commercially available, launched recently following large scale field trials in the United States.

Sanchez and Sobolev (23) observe that nanotechnology has contributed to concrete technology in two ways. First, the development of equipment which can characterise cement-based materials at the

nanoscale has greatly advanced understanding of the science of concrete, in particular the nature of C-S-H⁹ bonds and the ways this influences material properties.

Secondly, and more pertinent to the current work, it has enabled the development of new materials, which provide improved functionality such as concrete with improved strength, early strength or self-compacting properties. Limiting factors to the widespread adoption of these materials include the production costs, the difficulties of producing enough for large construction projects (37) and the need to demonstrate that the materials are reliable in large scale applications and resistant to long term environmental challenges such as moisture and temperature changes (79,80).

Silica in concrete

Micro and nanoscale silica particles can be added to concrete to fill the voids between cement grains, increasing the packing density of concrete so that it is stronger and has reduced capillary porosity. They also promote pozzolanic reactions, increasing the number of C-S-H bonds and the speed with which they develop (34).

Two different forms of nanosilica are typically used. The first is silica fume, which has been used as a concrete additive since the 1970s (81). Although it has an average particle size of around 150 nm, the high proportion (by number) of particles which are less than 100 nm in size leads to its classification as a nanomaterial (although these particles account for only a small proportion of the material by mass). Silica fume is typically added as 5-10% (by weight) of the cement mix. The inclusion of these small spherical particles enable concrete to be produced which is stronger and denser with improved plasticity and reduced porosity (82); although very few actual particles will remain in the finished product, as they will take part in the concretion reaction on contact with water. Figure 3 shows a sample of silica fume concrete, examined under SEM. Most of the major concrete producers include microsilica-enabled concretes in their portfolio, although these are rarely labelled as such. Interviews with industry professionals for the current research suggest that microsilica concretes account for only a small proportion of the concrete market in the UK (probably less than 5%), largely because there are many other additives which provide similar properties and are cheaper or easier to use. Silica fume appears to be largely confined to use in high specification buildings where it provides a high quality finish or allows pumping of concrete upwards for high rise building. However, interviews have also found it to be used on occasion for ground works for new homes, as it is self-levelling and thus eliminates the need for vibrating or floating of the surface. Silica fume is also reported to be an ingredient in Reactive Powder Concrete (RPC), a very expensive material which uses fine sands in place of aggregate and achieves high strength without the need for steel reinforcement in roads and bridges.¹⁰

⁹ Calcium-Silicate-Hydrate: this is the main product arising from the reaction between cement and water, and the main source of its strength (74)

¹⁰ www.cement.org/learn/concrete-technology/concrete-design-production/ultra-high-performance-concrete

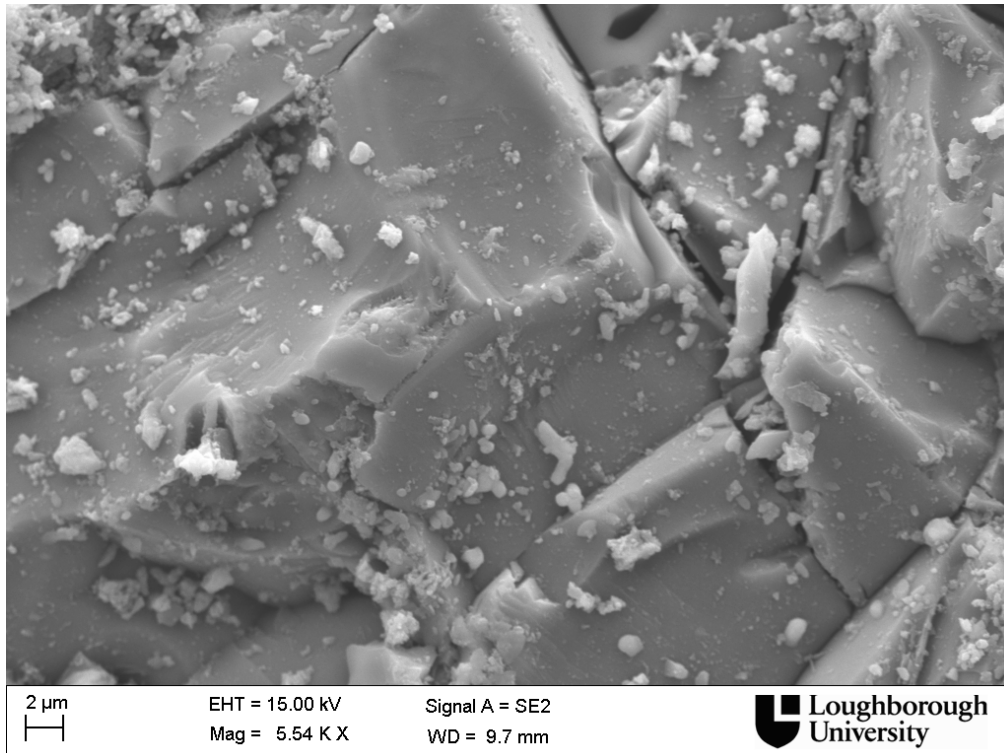


Figure 3 Silica fume concrete: very few nanoscale particles can be seen in the finished product, although they were added to the concrete mix¹¹

(Illustration previously published in (83))

A second silica additive which can be used in concrete is Nanosilica (also known, confusingly, as fumed silica). It has a particle size about 10 times smaller than silica fume (84) (see Figure 4) and can be used to produce ultra-high performance concretes (UHPC). These are typically extremely dense and enable production of concrete slabs which are thin but very strong (85). UHPC can also be used to improve the quality of concretes which contain waste materials such as fly ash or sludge, with financial and environmental benefits (86,87).

Both silica fume and fumed silica are based on amorphous silica. This is a material with lower toxicity than crystalline silica (quartz) which is more familiar in construction. Further explanation regarding this difference is given in section 4.2.3.

¹¹ The scale bar on this illustration is 2 μm, which is 2000 nm. Therefore, nanoscale particles (100 nm or smaller) are those seen to be about one twentieth of the size of the scale bar. Other illustrations in this report may be shown at a different scale.

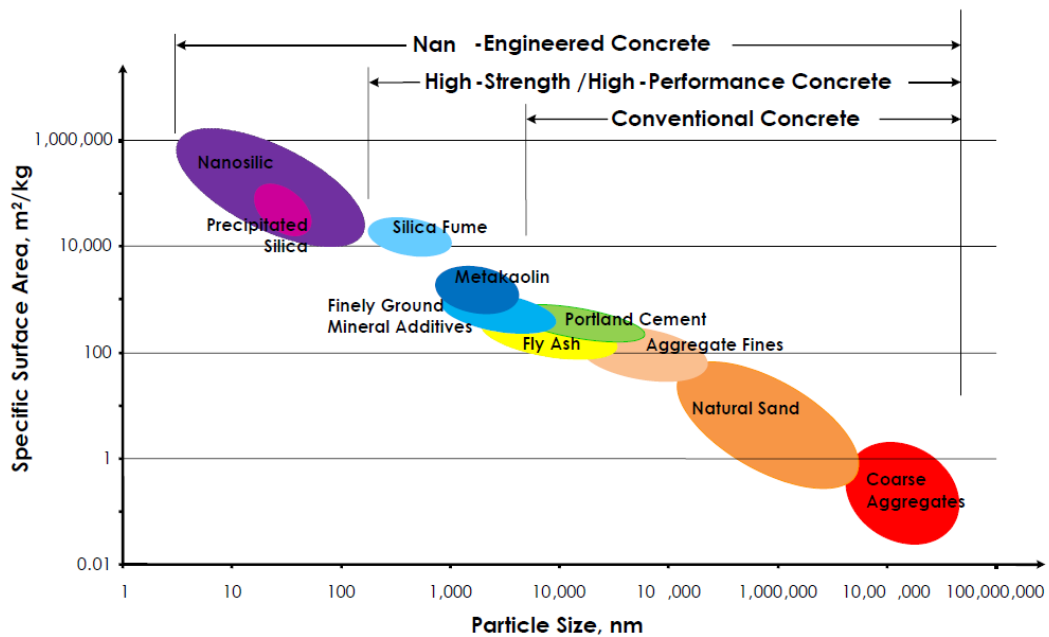


Figure 4 Particle size and specific surface area related to concrete materials (23,84,88)
(illustration used with permission of The American Ceramic Society)

Titanium dioxide in concrete

A second additive which can be used in its nano form in concrete is titanium dioxide. This material has photocatalytic properties, which offers two useful functions. The first is to produce concrete surfaces which are 'self-cleaning' i.e. which retain their light colour for longer. A commonly given example of this is the Jubilee Church in Rome (73). A second associated property is that nanotitanium acts as a catalyst to enable the removal of airborne toxins, particularly the various nitrogen oxides. Thus it can be used on pavements, roads, and walls to convert pollutants from traffic into water, carbon dioxide and harmless nitrates (89) (see Figure 5).

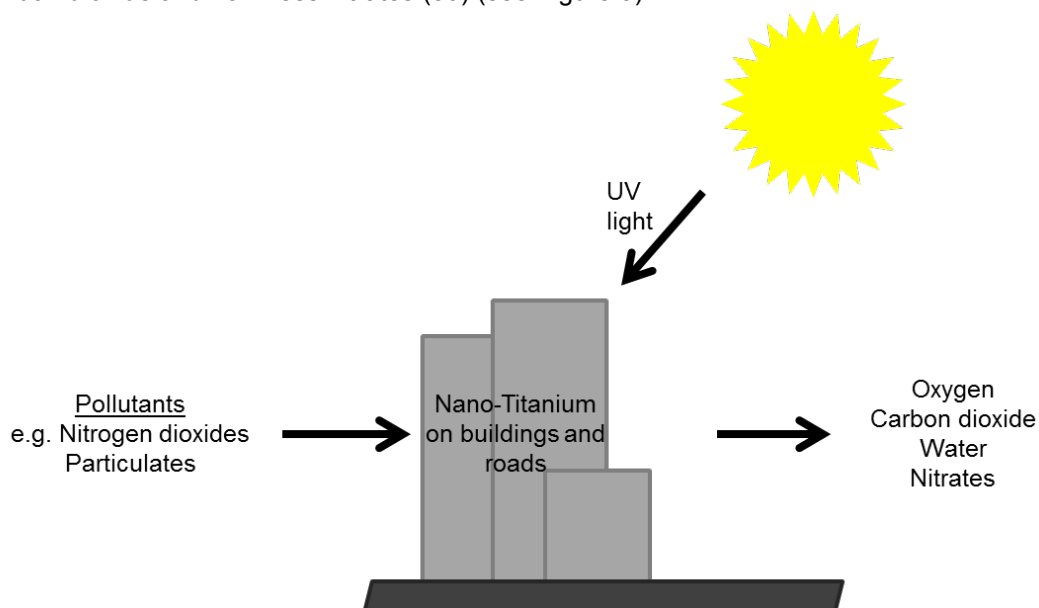


Figure 5 Breakdown of pollutants by sunlight, using titanium dioxide as a catalyst

To be effective, the nanotitanium needs to be at the 'interface' of the concrete, i.e. at the point where it can react with sunlight and organic debris (which then breaks down to CO₂ and water). For this

reason, and also to reduce cost, it is more usefully added as a surface coating or thin slurry rather than being mixed into construction concrete. Because the titanium dioxide is acting as a catalyst it is non-sacrificial, and should therefore be long lasting. However there are suggestions that its effectiveness might be relatively short-lived in some cases, and particularly that it can be reduced by weathering and accumulation of dirt (89,90). Titanium dioxide is also photocatalytic in its non-nano form which is considerably cheaper than nanotitanium, and potentially less toxic (37). This may explain why the use of nanotitanium in concrete is currently extremely limited: although Bartos (91) has suggested that lack of awareness of its benefits and of properly applied research are also contributory factors to the construction industry lagging behind other fields in its adoption of this nanomaterial. It is difficult to know how much nanotitanium concrete is being used – no examples have been found in the construction projects viewed during the current project.

Carbon nanotubes (CNT) in concrete

Carbon nanotubes (CNTs) are widely discussed within the academic literature with reference to construction e.g. (21,35,36,72), identifying that they have the potential to enable concretes which are particularly strong or self-healing. These benefits are thought to accrue from the ability of individual CNTs to fill spaces between C-S-H phases, and also to form bridges across cracks in the structure, preventing their propagation (4). Additionally, CNTs are electrically conductive and hence have the potential to act as sensors within concrete, transmitting information regarding the state of deterioration of the material. Figure 6 illustrates the presence of CNTs in a sample of cement, visible as individual fibres.

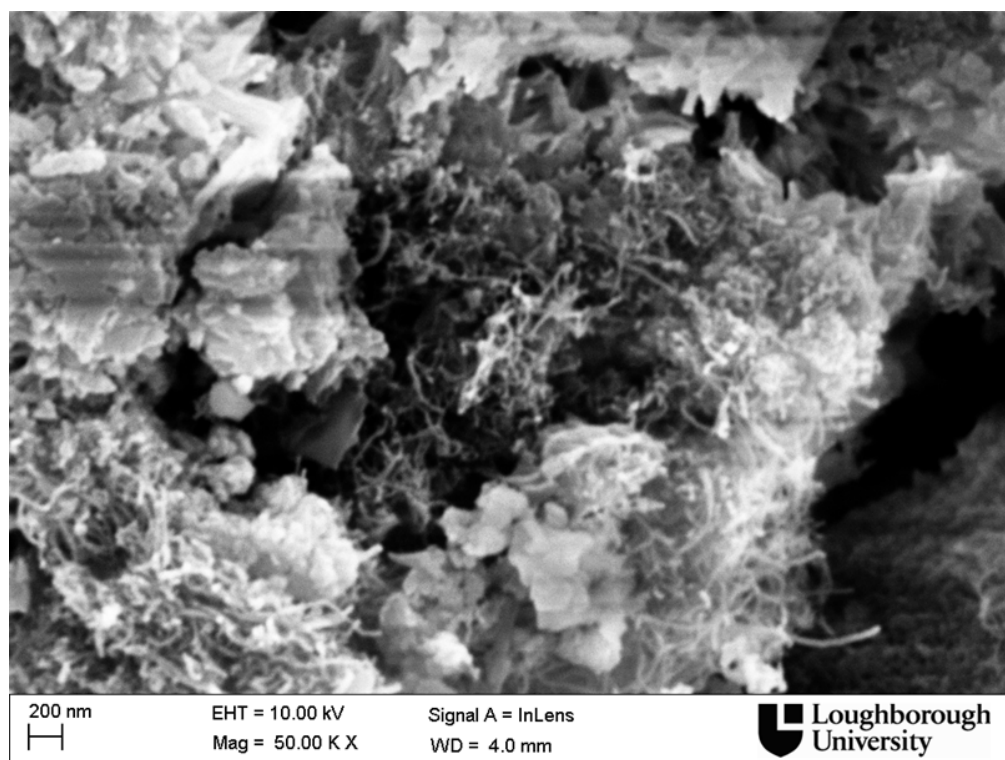


Figure 6 Cement which is enhanced with CNTs. The CNTS are visible as fine strands protruding from the concrete

The papers which summarise the use of nano in construction generally refer to the benefits of adding 1% CNTs to concrete, although it is not clear what the source of this figure is. For example, Chaipanich et al (92) identify 1% of CNTs (by weight) as the ideal proportion to compensate for the addition of fly ash to concrete, ensuring that strength remains as good as that attained with pure Portland cement; but the wider literature explores the effectiveness of a variety of concentrations as

well as many different shapes and sizes of tube. A review by Sobolkina et al (93) concludes that the impact of CNTs on compressive or flexural strength of concrete is extremely variable, influenced by the type of tubes used, the quantity, and fibre length, particularly in the finished product. For example multiwalled CNTs (MWCNTs) are less well understood than single walled CNTs (SWCNTs) and are more likely to have defects, but they are also cheaper and more readily available (4).

There are, therefore, uncertainties regarding the best types and concentrations of CNTs to use in concrete. The literature also recognises that there are commercial difficulties with these developments. This is partly due to high cost and low availability, although it is widely acknowledged that production capacity for CNTs is currently increasing rapidly and prices falling (4). There are also practical challenges of working with the materials, for example, dispersing tubes effectively. Carbon nanotubes have a high tendency to agglomerate (stick together), and unless the tubes can be effectively dispersed, there is an impact on the qualities of a finished product (94).

No examples have been found in the construction projects viewed during the current project. However, recent developments have seen the emergence of CNT-enhanced concrete being trialled in the United States, including laying a stretch of highway. The product has now been approved for use by the Georgia Department of Transport¹² and is reportedly being supplied to a European company also.¹³ The company report that the addition of CNTs to concrete increases tensile strength by 46% and in compressive strength by 41%, allowing structural integrity to be achieved with smaller quantities of concrete.¹⁴ It has not been possible to identify the details of the CNTs being used in the product.

Examples of commercial nano-enabled concretes

Table 5 gives examples of products currently available which might be nano-enabled. These are drawn from the product list summarised in Table 4. This is not an exhaustive list, and in some cases there is a lack of robust evidence regarding the nature of the nanomaterials used.

¹² www.edencrete.com/case-studies/georgias-highways/

¹³ www.proactiveinvestors.com.au/companies/news/170503/eden-innovations-wins-european-order-for-concrete-additive-170503.html

¹⁴ www.edencrete.com/strengths/

Table 5 Examples of commercially available concretes containing nanomaterials

Nanomaterial	Property(ies) attributable to nanomaterial	Concrete brand names (Manufacturer) which may be nano-enabled	What the manufacturers' literature says	Comments
Micro silica (Silica fume)	Self-compacting, high strength, rapid strength gain	Agilia, Ductal, Chronolia (Lafarge), Rapidcrete (Breedon) Diamondcrete (Aggregate industries) Evolution, Microtech, Promptis (Cemex) Emaco nanocrete (BASF) Easy Flow, Fasttrack (Hanson)	"Chronolia® represents a major technological advance for the building sector. The result of extremely advanced research in nanotechnologies" ¹⁵	The properties of these concretes suggest they might contain silica fume at production although this is not stated overtly and some (e.g. Emaco nanocrete) state that they do not contain nanoparticles. It is likely that most of the added nanoparticles will be reacted with the alkalis during the curing process so that a relatively small number of particles remain in the final product
Nanosilica (Fumed silica)	High strength, absorbs vibration	Nanodur UHPC (Dyckerhoff)		Personal communication with the manufacturers suggests that these materials contain nanosilica particles at the point of production. However, the particles agglomerate strongly and are also consumed by the cement reaction
Titanium dioxide	'Self-cleaning' absorbs pollution	NOxer (Eurovia) TioCem (Hanson) Ti Active (Italcementi)	"This nano-crystalline titanium dioxide is a photocatalyst" ¹⁶ (TioCem product brochure) "Portland Cement ...with the addition of nano-sized particles of titanium dioxide" ¹⁷ (TX Active product brochure)	The manufacturers' literature confirms that these products contain nanotitanium dioxide

¹⁵ www.lafarge-na.com/wps/portal/na/en/5_2_B_2-Aggregate_Concrete_&_Asphalt

¹⁶ www.heidelbergcement.com/NR/rdonlyres/28528B72-3125-4370-B657-616609415500/0/TioCem_Broschuere_englisch.pdf

¹⁷ www.essroctech.com/browse/essroc_data_files/bak/tpds/TX%20Active%20Data%20Sheet.pdf

Nanomaterial	Property(ies) attributable to nanomaterial	Concrete brand names (Manufacturer) which may be nano-enabled	What the manufacturers' literature says	Comments
Carbon Nanotubes	Increased strength and abrasion resistance	EdenCrete (Eden Innovations)	".... a carbon nanotube enriched liquid additive that elevates concrete structures to new levels of strength and toughness. ... It boosts surface abrasion resistance and produces extremely low permeability." ¹⁸	The manufacturer's literature states that this concrete is produced with 0.5% MWCNT This product appears to be currently in transition from development to commercial use

¹⁸ www.edencrete.com/resources/

4.1.2. Windows

Nanomaterials can be added to glass in the form of a very thin film during production to provide special properties for windows. Glass with improved insulation properties (low-e) is quite widely used especially in the construction of commercial buildings. These nanofilms can also reduce the amount of solar gain within a building. 'Smart' windows allow solar gain to be varied to accommodate changes in the weather, although these products are currently very rarely installed.

Self-cleaning glass has a film of nanoscale titanium dioxide which breaks down dirt through photocatalysis and is quite widely used, for example in conservatory roofs.

Fire safety glass with an intumescent layer of nanosilica has been available for many years but is generally only used in high risk situations.

Nanomaterials in window glass are most commonly used in the form of nanofilms, added during manufacture. The production process, known as magnetron sputtering, involves the spraying of materials in a very thin layer onto the surface of cooled float glass.

This process results in a nanofilm layer, rather than one which contains nanoparticles. The materials can be added in multiple layers, with up to 12 or more¹⁹ being used in combination. This allows a range of different materials to be included to provide multiple properties and also to compensate for the low durability of the coatings (95). However, the total layer of coatings remains very small; the Pilkington website suggests that the total coating layer is around 15 nm thick.²⁰

This form of window treatment is known as a 'soft' coating, differentiating it from more traditional 'hard' coatings which are applied during the production of the glass itself. The older treatments were not based on nanomaterials.

The section below will focus on the main properties which result from the use of nanomaterials in the window coating process; it is difficult to establish the exact nanomaterial involved in some cases, particularly for those based on nanofilms.

Low emissivity (low-e) glass

Windows are an important source of heat loss from buildings, accounting for up to 60% of energy loss (96). Insulation of glass is therefore important, and is essential if buildings are to meet the legislative requirements such as those laid down in building regulations e.g. (78). The use of metallic nanofilms on the internal surfaces of double glazing panels reportedly reduces heat loss by almost a quarter²¹ by reflecting long wave heat back into a room. The resulting reflectivity is higher than that for traditional hard coatings, and hence the insulating effect is higher. The nanofilms also have higher transparency than the older coatings (95), being less likely to show a haze or colour distortion. Their disadvantage as mentioned above is their low durability. Interviews conducted for this research indicate that nanofilm coated glass is widely used for thermal insulation in construction, particularly in commercial buildings. However, some window manufacturers still favour the more robust non-nano coatings due to the lower risk of the coating being damaged during production.

¹⁹ www.guardian.com/commercial/AboutGuardianSunGuard/AboutSunGuardGlass/PostTemperableSputterCoatingTechnology/index.htm

²⁰ www.pilkington.com/en-gb/uk/householders/types-of-glass/self-cleaning-glass/faqs/technical-faqs

²¹ <http://oaklandglass.co.uk/product/oaksoft-double-triple-glazing/>

Self-cleaning glass

Self-cleaning glass, as with self-cleaning additives for concrete discussed above, is generally based on titanium dioxide and works through the same photocatalytic mechanisms (97) when applied to the glass surface as a nanofilm. Figure 7, drawn from a manufacturer's website, illustrates the principles. The roof of St Pancras Station in London (Figure 8) is reported to be constructed using self-cleaning glass (40); interviews conducted for this research found self-cleaning glass to be widely used, particularly in the conservatories of domestic properties.

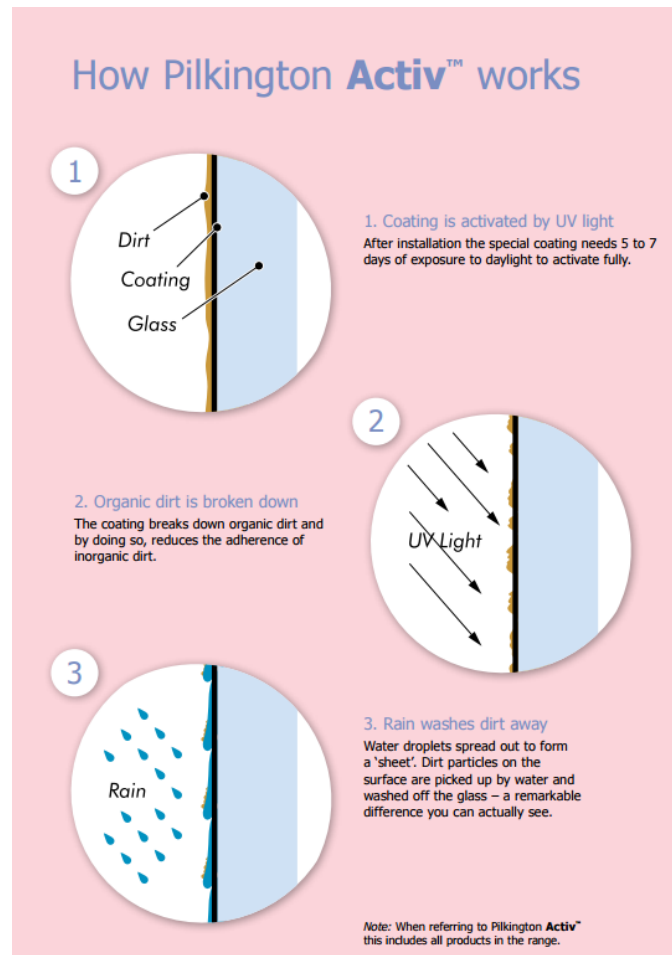


Figure 7 How self-cleaning glass works²²

²² <http://claxtonhomeimprovements.co.uk/conservatories.html>, used with permission of Pilkington UK Ltd



Figure 8 The roof of St Pancras station in London reportedly has self-cleaning glass

Coatings are also sold for use on existing windows, applied as sprays either by professionals or home users. These are more likely to be silica-based than titanium. They result in glass which is easy to clean (because of its smooth surface) rather than being self-cleaning. As these do not rely on a photocatalytic effect they can be used indoors; but as they are coatings rather than an integrated layer they last for only a few years, rather than the lifetime of the window (97).

Solar control glass

Solar control windows can be used in warm climates to reduce solar gain and hence reduce the need for air conditioning. As with low-e windows, versions are available which use traditional hard coatings as well as the ones with nanofilms. Solar control aspects can be combined with low-e coatings to produce windows which reduce both heat gain and heat loss.

Smart windows

Smart windows are those which can switch between high transparency to allow maximum day light; and high solar protection to reduce heat gain when required (95). Although the process of change from one state to another can be triggered by temperature change (thermochromic windows (98)) or light levels (99), the most successful models are those which allow for electrical switching between the states based on manual control by the building user (100). These are based largely on tungsten oxide and have reportedly been used successfully in California, although their use is not widespread and they are still at a relatively early stage of commercialisation.

Fire safety glass

High levels of fire protection can be achieved in architectural glass through the use of an intumescent layer sandwiched between two plates of glass. In case of fire, this expands and turns opaque, providing a high level of integrity and insulation.²³ This type of glass has been available for over 30 years²⁴ but is used only where a high level of thermal insulation is required, for example for escape routes or large expanses of glass; integrity-only glass (which is not nano-enabled) is much more commonly used. Silica fume is reportedly the main material used (71) although fumed silica is also

²³ www.pilkington.com/en-gb/uk/products/product-categories/fire-protection/pilkington-pyrostop

²⁴ Personal communication with glass manufacturer

marketed for this purpose.²⁵ Unlike the window coatings described above, fire safety glass is not made with nanofilms but through the introduction of the particulate silica fume or fumed silica into the space between two sheets of window glass during manufacture.

Examples of nano-enabled windows

Table 6 below gives examples of windows currently available which are based on nanotechnology, and the most likely materials involved where these are known. This is not an exhaustive list, and additional nanomaterials may be involved in some cases.

²⁵ <https://www.aerosil.com/sites/lists/RE/DocumentsSI/TI-1407-AERODISP-Fumed-Silica-Dispersion-for-Fire-Resistant-Glass-EN.pdf>

Table 6 Examples of windows containing nanomaterials

Window Property(ies)	Nanomaterial	Manufacturer and brand names	What the manufacturers' literature says
Self-cleaning	Titanium dioxide	Activ (Pilkington) Bioclean (SGG)	"Pilkington Activ™ is based on a thin film of titanium dioxide rather than particles of titanium dioxide and the film is approximately 15 nanometres thick" ²⁶
Low emissivity (low e glass)	Metal oxide coating (probably silver)	Optitherm (Pilkington) Planitherm (SGG) Clima guard (Guardian)	"Low-E coatings are made up of a series of nearly invisible layers of various materials and rely on one or more silver layers to reflect exterior and interior heat" ²⁷ "Sputter coatings consist of multiple layers of incredibly thin, nearly invisible metal oxides (silver, nickel, tin) and other compounds. Each layer is roughly 1/10 000 the thickness of a human hair" ²⁸
Solar control		Suncool (Pilkington) Cool-lite (SGG) Sunguard (Guardian)	"SGG COOL-LITE is a solar control glass manufactured by depositing a coating of metallic oxides by magnetically enhanced cathodic sputtering under vacuum conditions onto clear or body-tinted glass" ²⁹
Fire safety	Silicon dioxide	Pyrostop, Pyrodur (Pilkington) Pyranova (Schott) Pyroguard (CGI);	"A transparent, fire resistant layer that intumesces up in the event of a fire has been placed between the panes" ³⁰
Smart-switchable	Tungsten dioxide	E-Control glas View glas Sage glass	"SageGlass nanotechnology incorporates layers of coatings on glass, which in total are less than 1/50 th the thickness of a human hair Applying a low voltage of electricity darkens the coating as lithium ions and electrons transfer from one electrochromic layer to another electrochromic layer" ³¹

²⁶ www.pilkington.com/en-gb/uk/householders/types-of-glass/self-cleaning-glass/faqs/technical-faqs

²⁷ www.guardian.com/residential/LearnAboutGlass/FAQs/index.htm

²⁸ www.guardian.com/residential/LearnAboutGlass/AdvancedLearning/index.htm#coatingtypes

²⁹ <http://uk.saint-gobain-glass.com/product/721/sgg-cool-lite>

³⁰ www.schott.com/architecture/english/products/fire-rated-glass/pyranova.html

³¹ <http://sageglass.com/technology/how-it-works/>

4.1.3. Coatings

Coatings are the most numerous and readily available nanoscale products in construction, being marketed for both professional and DIY use as well as being applied to products during manufacture. Many coatings contain silica (either as particles or in polymers) and are marketed for waterproofing or easy clean/dirt repellent properties.

Coatings may also contain titanium dioxide nanoparticles which provide self-cleaning properties through photocatalysis, or antimicrobial silver nanoparticles.

CNTs and graphene are carbon nano-objects which offer strength, corrosion resistance and conductivity for coatings but only a very small number of such products are commercially available. Carbon black is a much more commonly used (and familiar) material used, for example, for shielding against radio waves.

Surface coatings are reported to be the most dominant nano-enabled applications in the building industry (101). As shown in Table 4, they account for around half of the products identified in this study. They are also readily available to consumers and professionals.

- Some products are sold for domestic and DIY use, e.g. as liquids or sprays.
- Some are found in professionally applied coatings and paints.
- Some products are incorporated on the surfaces of items such as ceiling tiles or toilets during manufacture. These may not even be recognised by the purchaser or user as being a coating, being seen simply as a feature of the product.

Identifying the specific nanomaterial contained in surface coatings is extremely difficult, as few manufacturers specify the details, using instead vague terms such as '*nanostructured composite consisting of organic and inorganic phases*'³² and '*a seamless bond that is impenetrable by liquids*'.³³ Also, products which at first glance appear similar to each other might differ greatly in the proportion of nano-enabled product contained; whether this exists as nanoparticles or is bound up in a polymer or film; and the impact this has on the functional properties of the coating as well as on any potential health impact.

Silica coatings

Silicon dioxide is commonly used to make coatings resistant to water and other contaminants. This can make surfaces easier to clean by reducing adhesion between, for example, dirt or graffiti and the surface. Gressler et al (102) describe the lotus leaf effect as being a mechanism which enables this. Minute protrusions on the surface make it superhydrophobic - particles or droplets are unable to adhere and simply run off, with water droplets carrying away any contaminants or dirt which are present.

Not all waterproof coatings work in this way. Gressler et al (102) also describe how very smooth surfaces can prevent adherence of contaminants. Alternatively, nanomaterials can be used to coat surfaces and thus provide protection by waterproofing them. For example, Surfacore describe how the (undefined) nanoscale particles in their product are able to penetrate into the pores of substrates and coat the surface in order to provide protection and water resistance without sealing in moisture (see Figure 9).

³² http://neicorporation.com/tds/NANOMYTE_SR-500EC_TDS.pdf

³³ www.nanotechcoatings.com/residential

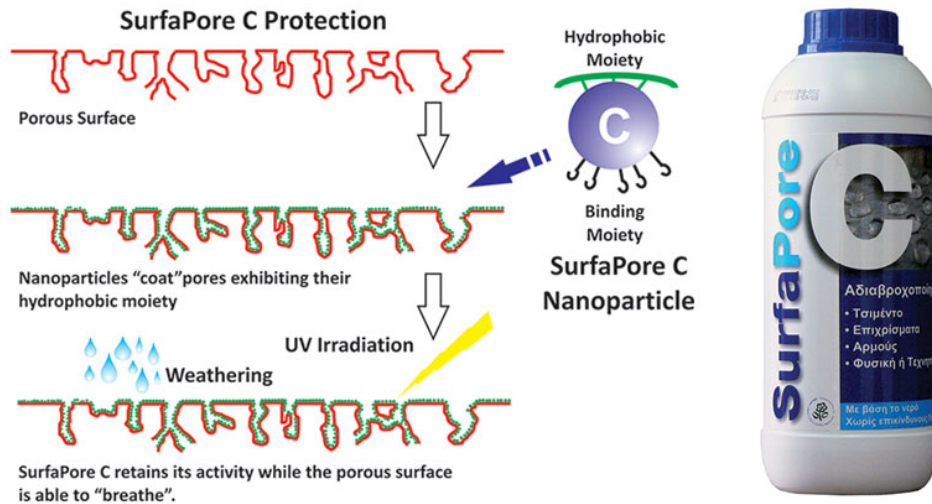


Figure 9 Website extract illustrating how SurfaPore waterproof coating works³⁴

Not all silica-based coatings contain nanoparticles; manufacturers also refer to the use of silanes, siloxanes and polysilazanes. Some waterproof coatings may contain nanomaterials other than silica but these are difficult to identify.

Titanium dioxide coatings

Titanium dioxide is described in the academic literature as providing self-cleaning properties to surfaces through photocatalysis, and has been discussed above in relation to concrete and window glass. Sunlight reacts with organic debris in the presence of titanium dioxide and breaks it down to carbon dioxide and water, which can then be easily washed off. Although titanium dioxide has also been used to create hydrophobic coatings (103), it more usually provides hydrophilic properties, enhancing the self-cleaning process as water spreads into sheets rather than remaining in drop form (102).

The photocatalytic effect of titanium dioxide nanoparticles also reportedly enables these coatings to reduce air pollution, breaking nitrogen dioxide down to nitric acid (104) and then to nitrates, carbon dioxide and water. This is a surface reaction and therefore the use of coatings is a more economical way of achieving this effect than mixing titanium dioxide particles into concrete (as discussed above in section 4.1.1). The photocatalytic reaction requires ultra violet light and is therefore most effective on outdoor surfaces (or used indoors with the addition of UV lighting). Some companies market such products for use indoors, activated by daylight, to improve the internal air quality (e.g. Lotusan), and there is evidence for the reduction of contaminants such as formaldehydes (105). There are, however, also suggestions that the use of titanium dioxide coatings indoors risks an increase in the release of such substances through incomplete breakdown of impurities (106).

Non-nano titanium dioxide is also photocatalytic, and is cheaper than nanotitanium. Therefore it may be used in preference, although the reactivity is lower and the product does not have the transparency which can be achieved with nano-enabled versions (37). This again makes it difficult to identify where nanomaterials are actually being used, in what form and in what quantities.

³⁴ <http://nanophos.com.gt/productos/surfa-pore/surfa-pore-c/> (illustration used with permission of NanoPhos)

Silver coatings

Silver has been known for its anti-microbial properties for hundreds of years with silver ions being used in medical dressings, creams and equipment since the 1960s (107). Products are now available which use silver nanoparticles to achieve this. It is not clear whether silver nanoparticles have a specific antimicrobial effect in addition to the impact of the silver ions they release (108). However, there is some evidence that the use of nanoparticles allows antimicrobial effects at lower silver concentrations, reducing the potential for environmental toxicity compared to the use of ionic forms (109,110).

Identifying products which contain silver nanoparticles is difficult as many manufacturers do not specify clearly the form of silver which they use in their products. The Project for Emerging Nanotechnology's database of consumer products (32) shows silver to be the most frequently declared nanomaterial, accounting for over 400 products, around one quarter of those in the database. However, fewer than 10% of these products actually provide evidence that they are based on silver nanoparticles. Similar uncertainties exist with construction products, where nanosilver is marketed for use in coatings for both indoor and outdoor use. For example, a range of coatings produced by Bioni are marketed particularly for use in healthcare and food preparation environments, with claims that the product can reduce contamination levels by 99.999%³⁵. These coatings are clearly declared to contain nanosilver. However, other silver-based products marketed for use in similar circumstances (e.g. Biocote³⁶) do not claim to be based on nanosilver and may operate through different mechanisms (such as release of silver ions).

Nanosilver is one of the nanomaterials most frequently reported in surveys which ask about the use of nano in construction (40,41). In fact there is some evidence that its use is overestimated: Hincapié et al (41) found that estimates for its use accounted for seven times the quantities which are reported to be manufactured (111).

Coatings with CNTs and other forms of carbon

Overall, the current market for coatings based on CNTs appears to be small, presumably due to the high cost and difficulties of working with these materials. For example, Hanus and Harris (35) summarise a number of journal papers which illustrate the antimicrobial properties of CNTs. However, these seem unlikely to become widespread in buildings in the short to medium term given the availability of cheaper and more straightforward alternatives such as those based on silver. A very small number of CNT coatings are available which take advantage of the material's conductive capability as well as its strength. For example, one coating is sold which offers high corrosion resistance for metal³⁷. Another range of coatings are marketed as containing graphene, and offering similar properties³⁸.

CNTs have the potential to be used for heatable paints and to shield rooms from radio and microwaves. However, these functions can also be achieved through the use of other forms of carbon such as carbon black, and there is limited evidence currently of CNTs being used in this context. CNTs are also marketed as having potential for flame resistance (e.g. as a coating for metal pipes) and for keeping surfaces clean in marine environments (antifouling)³⁹, but products based on these have not been identified during this research.

³⁵ <https://bioniusa.wordpress.com/health-care/>

³⁶ www.biocote.com/home

³⁷ www.teslanano.com/

³⁸ <http://graphenstone.co.uk/Graphenstone-graphene-inside.html>

³⁹ www.nanocyl.com/#

Other coating materials

Other substances are also used in surface coatings. For example, nanolime (calcium hydroxide particles suspended in alcohol) is used in building conservation, where its addition to damaged stone results in the deposition of calcium carbonate to restore surfaces and strengthen the underlying material (112). Aluminium oxide particles 'fused in resin' can be added to floor coatings to provide abrasion resistance.⁴⁰ Hanus and Harris (35) report that several metal or metal oxide particles including copper, magnesium and zinc can be used in antimicrobial coatings, although these are not highly visible in the marketplace in the way that silver coatings are. Finally, many substances used in organic pigments (in paints) contain nanoparticles – these have been reviewed, for example by the Danish government (113) to determine how they should be handled under nano-specific regulation. There are claims from industry that these products have been in use for many years and should not be regulated specifically as nanomaterials given their lack of novelty and their long history of safe use.

Laboratory testing of coatings

Fifteen coating materials were assessed using SEM and EDX to determine their composition. The products tested were either marketed as 'nano' in some form or had characteristics which might suggest nano-enablement (such as super hydrophobia, or antimicrobial properties). They were also freely available in the marketplace, either in liquid form for applications by consumers or professionals; or pre-applied to surfaces such as work tops or shower enclosures.

Three of the products tested contained no nanoparticles or other nano-objects. It was not determined whether they contained nanomaterials in some other form e.g. as a nanoscale film. The remainder contained a relatively small number of nano-objects which were predominately silica-based, and occasionally titanium or carbon (either nanoparticles, or nanoplates). Examples of the findings are shown in Figure 10, Figure 11 and Figure 12.

⁴⁰ www.rustoleum.com/product-catalog/consumer-brands/nano-shield/nano-shield-rapid-cure

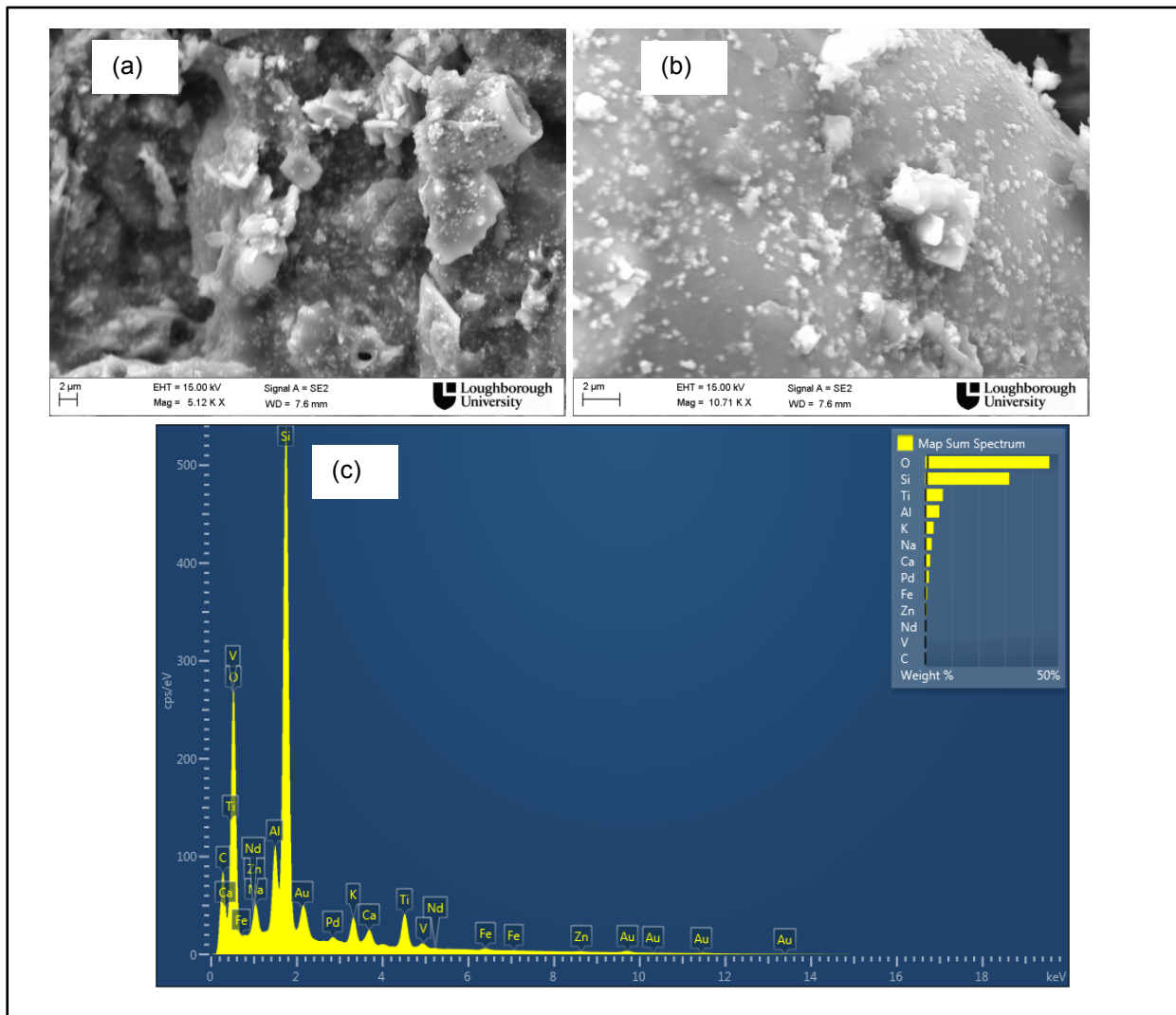


Figure 10 Microscopy images (a and b)⁴¹ (previously published in (83)) and EDX output (c)⁴² of a product marketed as a self-cleaning render which contains nano-quartz.

The product contains a small number of nanoparticles (silicon dioxide and titanium dioxide) but most particles are larger

⁴¹ The scale bar is 2 µm (2000 nm), so that nanoparticles are those one twentieth of that size.

⁴² Energy-dispersive X ray spectroscopy (EDX or EDS) works by firing charged particles into the sample. This results in rearrangements of the electrons in the materials, and the patterns of energy release allow identification of which elements are present. In this case, oxygen, silicon and titanium are the main elements, in the form of silicon dioxide and titanium dioxide.

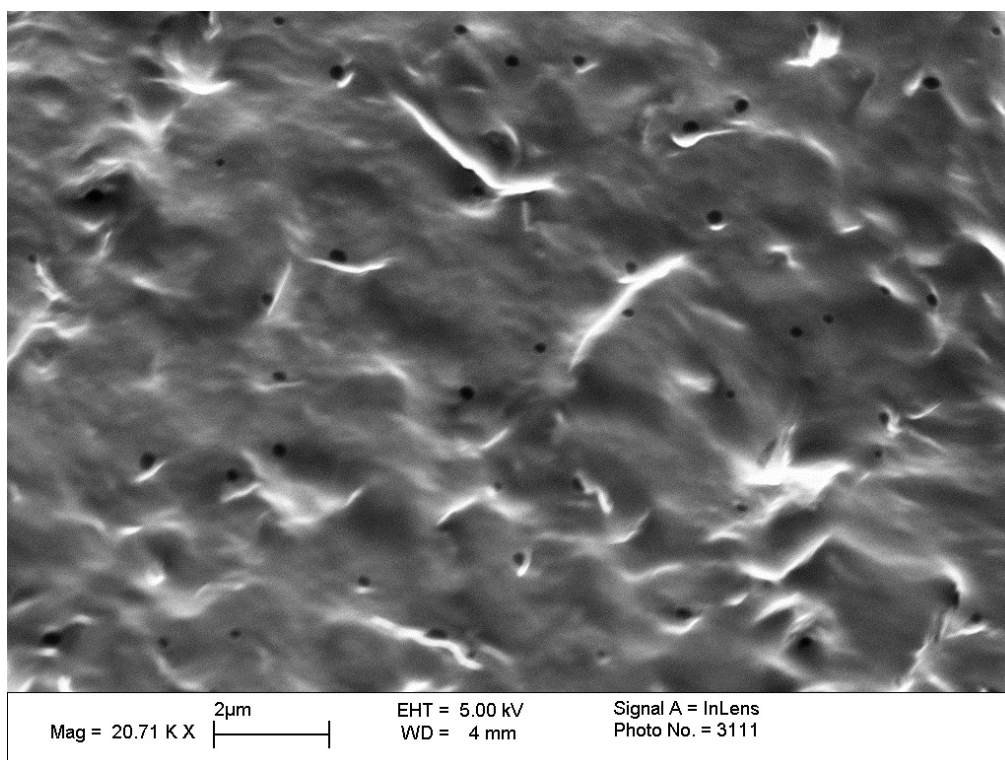


Figure 11 Microscopy of a product marketed as providing electromagnetic shielding: it contains nanoscale graphite (a nanoplate, similar to graphene but with many layers)

(Illustration previously published in (114))

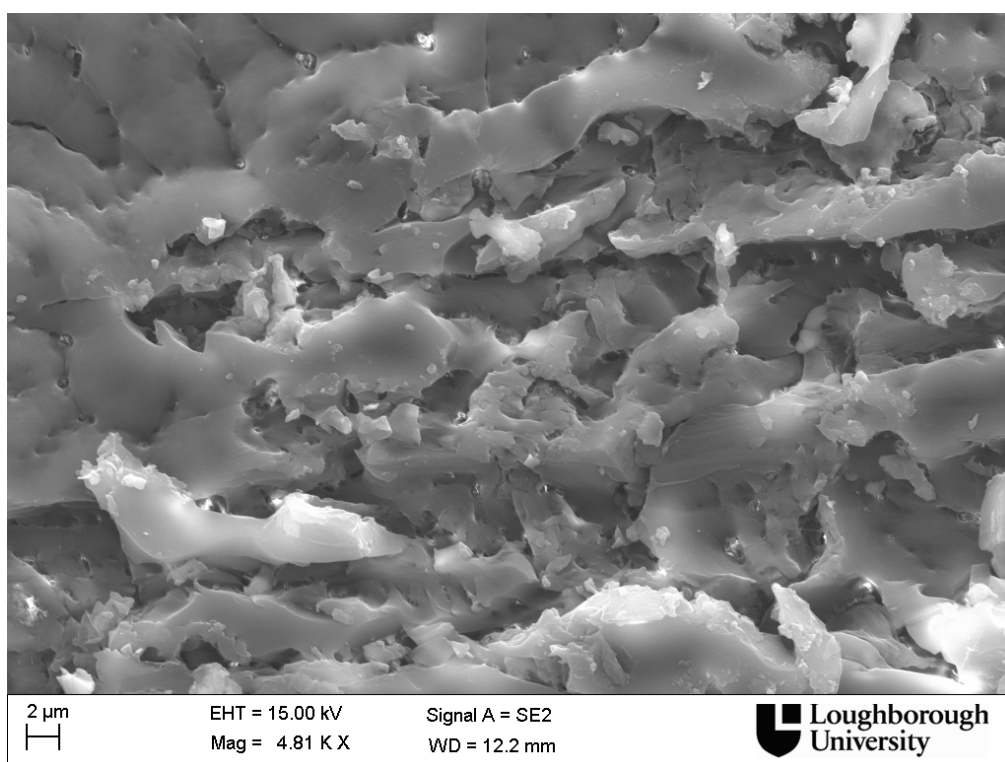


Figure 12 Microscopy of a product marketed as a 'nano' coating; no nanoparticles are visible, so if nanomaterials are present, they are presumed to be in the form of a nanoscale film

(Illustration previously published in (114))

Examples of coatings which contain nanomaterials

Table 7 gives examples of coating products currently available which might be nano-enabled, and the materials which are most likely to be involved in each case. This is not an exhaustive list, and in most cases there is a lack of rigorous evidence regarding the nature of the nanomaterials used. It is also not always possible to distinguish between those which contain nanoparticles and those which are based on films of nanoscale thickness.

Table 7 Examples of coatings which contain nanomaterials

Nanomaterial	Property(ies) attributed to nanomaterial	Brand names (manufacturer or supplier)	What the manufacturers' literature says	Other products with similar properties
Silicon dioxide (silica) (including silane, siloxane and polysilazane)	Water repellency Easy cleaning, stay clean Graffiti resistance Hardening, protection Scratch resistance	Nanoset densifier (newLook) Nanosilica densifier (adseal) Nanoclean cleaner (adseal) Tutoprom (AZ/Merck) ThermoSan (Caparol) Nansulate (industrial nanotech) Nanostone (nanoprotect) Nanowood (nanoprotect) Ecocoat	"NanoClean Cleaner perpetually fortifies polished concrete surfaces by introducing Nano-silica into the substrate as it cleans" ⁴³ "Innovative silicone-resin binder combination with integrated Nano-Quartz Matrix Structure providing clean façades" (ThermoSan website) ⁴⁴ "Surfaces coated with this aqueous, two-component polymer combination are UV-resistant, scratch-proof, scrub and scour-resistant, hydrophobic and water-impermeable, yet open to water vapour diffusion" (emcephob LE website) ⁴⁵	Surfapore (nanophos) Emcephob nanowax, Emcephob LE (MC Bauchemie) Nanoshell (nanoshell) Nanoguard (nanogate) Wondergliss (nanogate) NewGuard Nanopool Lotusan (Sto)
Titanium dioxide	Protective, antibacterial Anti-pollution Self-cleaning	FN coating (FN Nanoinc) KNOxOut (Boysen) P and T 230 (nanoprotect)	"ultrafine titanium dioxide, that absorbs energy from light and transforms ordinary water vapor into hydroxyl and peroxy radicals at the surface of the Titanium dioxide " (Boysen) ⁴⁶ "nanotechnology liquid formulation... acts by absorbing surrounding light and transforming it in chemical power" (Surfashield) ⁴⁷	Surfashield (nanophos) NOxer (Eurovia) Climasan (Sto)

⁴³ www.adsealcolours.co.uk/NANO-Cleaner-and-Maintainer.html

⁴⁴ www.caparol.de/uploads/pics/caparol_import/caparol_de/ti/65605/TI_156_EN.pdf

⁴⁵ www.mc-bauchemie.com/en/en/Emcephob-LE-sets-new-standards.aspx

⁴⁶ www.knoxoutpaints.com/howitworks.do

⁴⁷ <http://nanophos.com/eng/product/surfashield/surfashield-c-detail>

Nanomaterial	Property(ies) attributed to nanomaterial	Brand names (manufacturer or supplier)	What the manufacturers' literature says	Other products with similar properties
Silver	Antimicrobial	NPS 100, 200 (nanoprotect) Bioni roof, Bioni hygienic Bioni nature	"Through the use of a totally new compound of substances based on nano-silver.... Bioni Hygienic not only provides long-lasting preventive protection from the creation of germs and bacteria but also against the formation of mould in damp areas such as showers or kitchens" ⁴⁸ "The nanosilver when in contact with bacteria, virus and fungus will adversely affect cellular metabolism and inhibit cell growth" (NPS website) ⁴⁹	Bacterlon (nanopool)
CNTs	Corrosion resistance Fire resistance, antifouling	Teslan (Tesla nano) Biocyl, Thermacyl (nanocyl) (these are additives for products rather than being construction products in themselves)	"Teslan Carbon Nano coating is a two-coat system featuring low VOC epoxy primer and topcoat with significant advantages not only in corrosion protection... it is formulated with carbon nanotubes that assemble into ropelike structures that make them tough and flexible" ⁵⁰	
Other carbon forms	Electromagnetic shielding Anti-condensation Heating paint	Carbo e-Therm (future carbon) Carboshield (future carbon) Bloc paint (Craig and Rose) Graphenstone (graphenstone)	"Biosphere Premium is a natural exterior paint, it contains graphene and... reduces condensation and delays degradation of buildings" (Graphenstone website) ⁵¹ "Carbo e-Therm is a carbon nanomaterials-based, electrically heated coating" ⁵²	

⁴⁸ www.bioni.de/en/index.php?page=produktprogramm_bioni_hygienic&lang=en

⁴⁹ www.nanoprotect.co.uk/anti-bacterial-fungi.html

⁵⁰ www.teslanano.com/about/

⁵¹ www.graphenstone.co.uk/Graphenstone-Biosphere.html

⁵² www.future-carbon.de/fileadmin/user_upload/Tech_Flyer_Carbo_e-Therm_R2015-01_EN.pdf

4.1.4. Insulation materials

Insulation materials are generally based on silica aerogels, which can be used in insulation blankets, translucent windows or vacuum insulated panels. These materials are highly effective insulators but are expensive and currently not widely used outside of specialist projects.

Aerogels have been described as “the most effective thermal insulation on earth”.⁵³ They are formed by replacing the liquid in an amorphous silica gel with air, leaving a material which is around 97% air (115) in a silica framework. The excellent insulating properties of the materials therefore arise from the poor conductivity of air, plus the improved resistance to heat flow which is associated with decreasing pore size i.e. the very small spaces within the silica structure (35,71). Aerogels are commonly described in manufacturers’ and academic literature as being ‘nanoporous’ (37) or nanostructured and as not generally containing nanoparticles. Figure 13 shows a small block of aerogel (costing over £20!), which is translucent and brittle.



Figure 13 A small sample of aerogel material

Aerogels are used in three main types of insulation material. The first are translucent granules which can be used within walls or ceiling materials designed to allow daylight entry (116). The second are blankets (see Figure 14) where the aerogel is included in a fibre matrix to produce a durable and flexible material which has additional benefits of providing noise insulation and fire retardancy (117). These blankets can be wrapped around pipes and other structures or applied to plasterboard to create thermal panels. The third insulation type are Vacuum Insulated Panels, where a silica aerogel is contained in a vacuum inside a panel constructed of impermeable laminates (118,119).

⁵³ www.aerogel.com/

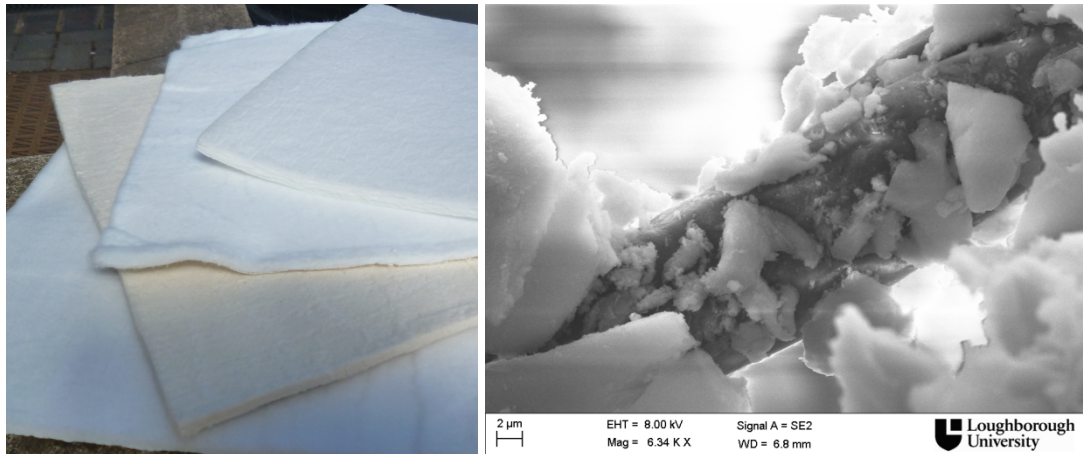


Figure 14 A selection of aerogel blankets, and the internal structure of one, showing aerogel particles around a polymer fibre

(Illustration previously published in (83))

Figure 15 shows the conductivity of a range of insulation materials. From this it is clear that the nano-enabled products (silica aerogels and vacuum insulation panels) are able to provide extremely high levels of insulation compared to the more commonly used materials such as mineral wool. They have the added advantage of being light and thin. The main limiting factor in their use is their cost relative to conventional products, Cuce et al (120) suggest that aerogel blankets currently cost around ten times more, and aerogel windows six times more than the commonly used equivalents. However, costs are expected to fall as production methods evolve, and rising energy prices might also increase the potential for cost savings by using such products (117). No examples of nano-enabled insulation materials have been seen in the construction projects visited for the current research, although two interviewees had used them in a previous project.

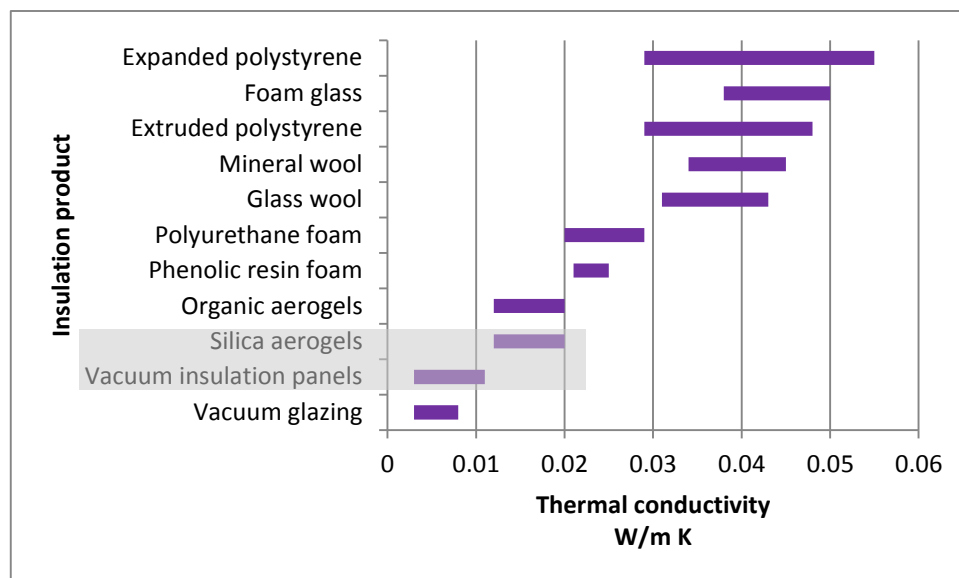


Figure 15 Thermal conductivity of a range of insulation materials, with the nano-enabled materials highlighted, based on data taken from Cuce et al (120)

Table 8 gives examples of the main nano-enabled insulation products which are commercially available

Table 8 Examples of nano-enabled insulation products

Nanomaterial	Manufacturer and brand names	Property(ies) attributable to nanomaterial	What the manufacturers' literature says	Comments
Silica aerogel in translucent particles	Lumira particles (Cabot) (used in wall/ceiling products such as Ecosky, Kalwall, Solera)	High thermal insulation with translucency	"Aerogel is a highly porous open structure with an average pore size of ~20 nanometers. This pore size is smaller than the mean free path of air which greatly restricts gas conduction and convection inside the particles" ⁵⁴	These materials are constructed using aerogels which are ostensibly nanostructured (i.e. they have nano-sized spaces) rather than containing nanoparticles
Silica gel in blanket form	Pyrogel, cryogel, space loft (Aspen aerogels) Thermal wrap (Cabot) Thermablok	High thermal insulation	"The silica solids... comprise only 3% of the volume. The remaining 97% of the volume is composed of air in extremely small nanopores" ⁵⁵ "Thermablok Aerogel is a flexible, nanoporous aerogel blanket insulation that reduces energy loss whilst conserving interior space" ⁵⁶ (Thermablok)	
Silica particles in vacuum insulated panels	Optim -R (Kingspan) Kevothermal	High thermal insulation	"Our ultra thermal insulation is a nanoporous solid with both low density and small pores" ⁵⁷ (Kevothermal)	

⁵⁴ www.cabotcorp.com/solutions/products-plus/aerogel/frequently-asked-questions

⁵⁵ www.aerogel.com/resources/about-aerogel/

⁵⁶ www.thermablok.co.uk/products/thermabloksp-aerogel-blanket

⁵⁷ www.kevothermal.com/the_technology.html

4.1.5. Steel

Steel can be improved through the use of nanotechnology which modifies the grain structure to improve strength, wear resistance and corrosion resistance. There is some limited use of nano-enabled steels e.g. in reinforcement for road building although most applications are targeted at the automotive and airline industries.

Steel can be improved through the use of nanotechnology either as a modification of the bulk material or through the use of protective coatings. Modifications of the bulk material can involve a range of processes which impact on the structure of the grains of which the steel is composed. By refining these down to the nanoscale and driving out impurities such as carbides, by either physical or chemical processes, the steel becomes stronger (15), and more resistant to the corrosion which commonly begins at the point of defects between grains (121). Steel which is enhanced through nanotechnology is therefore an example of a material which is largely nanostructured rather than containing nanoparticles. Manufacturers claim it is cheaper than stainless steel but as effective. It is also reported to be much more effective (and therefore has lower life cycle costs) than more traditional methods of protecting steel against corrosion such as epoxy coatings.⁵⁸ Examples have been given of its use in steel reinforcement for construction, for example by the Virginia Department of Transport which uses it in road bridge construction in preference to epoxy coated rebar (122).

Protective coatings for steel can be constructed using similar principles. Different materials or different methods such as physical vapour deposition or sputtering might be involved but again the outcome is to reduce the presence of defects and the potential for corrosion by reducing the size of the metal grains to nanoscale (121). Steel and other metals may also be combined with non-metals to produce materials such as ceramic metal composites, which can be used as either structural materials or coatings, offering high wear resistance and strength (123). Other coatings used to protect steel are based on the use of nanoparticles, and can be considered as a subset of coatings more generally as discussed previously under section 4.1.3.

Table 9 below shows some examples of nano-enabled steels and metal coatings which are currently on the market. Much of their use is targeted at sectors such as automotive and airline which can benefit greatly from the use of lightweight, strong materials. However there is also potential for use in construction, particularly in high demand/high cost industries such as oil and gas.

⁵⁸ www.mmfx.com/advantages/

Table 9 Examples of nano-enabled steels

Nanomaterial	Manufacturer and brand names	Property(ies) attributable to nanomaterial	What the manufacturers' literature says	Comments
Nanostructured steel or steel alloys	ChromX (Mmfx) AHSS (nanosteel) NSB (nanosteel) Nanoflex (Sandvik) (presumed nano)	High strength, corrosion resistance	“ChrōmX 9100®, steel products have a completely different structure at the nano or atomic scale (a lath structure resembling “plywood”). This “plywood” effect lends amazing strength, ductility, toughness and corrosion resistance” ⁵⁹ “NanoSteel’s nano-structured sheet steel breakthrough design delivers a combination of high strength and high ductility in cold formable steel” ⁶⁰	ChromX is reportedly used in reinforcement for road construction and in other civil projects NanoSteel’s products are marketed more for the automotive industry and for high demand environments such as mining and oil and gas
Ceramic metal composite	Cermet PCompP (Mesocoat)	Hardness, repair of damaged metal surfaces, high wear resistance, corrosion resistance	“CERMET’s revitalization process is based on unique nano-particle technology....CERMET hardens the metal's crystal lattice at the surface up to 30 microns....” ⁶¹ “Particulate Composite Powders. These materials are nano-structured ceramic-metal composites formed with a nanocomposite core and binder coating” ⁶²	May be used in engines or motors used in construction; or in high risk industries such as oil and gas etc.
Metallic coatings	SHS (nanosteel) Santronic (Sandvik)	High strength and toughness in welding, high wear resistance	“nano-structured, high-strength steel materials.... combining the hardness of carbides with the toughness of steel to increase the wear life of critical industrial components” ⁶³ “By combining an advanced vacuum process with nanotechnology, we can produce strip steel with consistent coating layers ranging down to 20 nanometers” ⁶⁴	These have been recommended for the coating of concrete chutes to prolong their life

⁵⁹ www.mmfx.com/technology/

⁶⁰ <https://nanosteelco.com/products/sheet-steel>

⁶¹ www.cermetlab.com/nanotechnology/nano-particle.html

⁶² www.mesocoat.com/coating.html

⁶³ <https://nanosteelco.com/products/metallic-coatings>

⁶⁴ <http://smt.sandvik.com/en/products/strip-steel/strip-products/coated-strip-steel/sandvik-santronic/>

4.1.6. Solar cells

Nanotechnology is an important contributor to electricity generation from solar power. Thin films containing amorphous silicon and other materials (such as copper, indium, gallium, selenium in CIGS solar cells; and cadmium and telluride in CdTe models) are already in use as an alternative to traditional crystalline silicon wafers (95,124,125). These use smaller quantities of materials than traditional solar cells and thus are potentially cheaper to produce, as well as more versatile. Other materials which might be used in solar cells, include perovskite (126), nanotitanium (127), quantum dots (128) and graphene (129). These are at various stages of development with some still involving only laboratory-based work and others closer to commercial development. They open up the possibility of, for example, Building Integrated Photovoltaics, which will allow electricity generation from windows and semi-transparent walls, rather than through the use of externally mounted structures (130).

4.1.7. Other products

A number of other applications for nanomaterials can be found in the literature, some of which are already available and others which are at an earlier stage of development.

Hydromx is a product marketed for use as a radiator fluid, reporting improved heat transfer and therefore energy savings by the use of thermofluids which carry nanoparticles in suspension. The product literature does not identify the nanomaterials involved, but they are likely to be copper or aluminium particles. The academic literature discusses a range of options including metals or oxides (such as copper, silver or iron) and carbon nanotubes (131).

Phase change materials (PCM) are those which can change state (e.g. between liquid and solid) and either store or emit heat in the process. They have many applications including use in building design as a means of absorbing heat during the day for release at night (132). They can be constructed using nanomaterials (133), but it is not clear which nanomaterials might be used or when/whether nano-enabled versions are likely to become available commercially.

Nanoclays are nanomaterials which are either naturally occurring or synthetically created, and are nanoparticles formed of layers of silicate-based materials (134). They can be used in polymers to improve functionality in various ways, but there are no obvious commercial products available currently for use in construction.

There are uses for nanoparticles in electronic devices such as batteries, organic light emitting diodes (Oleds), computer screens and interfaces. These are not construction materials per se, but are likely to be installed by constructors. They will also need to be removed at the end of life and recycled. This is generally a WEEE (Waste Electrical and Electronic Equipment Directive) issue rather than a construction/demolition one (41), although it could have consequences for those involved in recycling, particularly where electronic devices or control panels are built into the fabric of a building.

4.2. Health risks from nanomaterials

This section addresses the research objective:

to summarise the literature regarding the health risks of the nanomaterials most likely to be used in the built environment

It is based on review of the academic literature.

Key points

Potential health risks from nanomaterials are generally associated with the presence of nanoparticles and other nano-objects: the smaller particle size results in increased surface area and therefore increased reactivity. However, the size of objects is not the only factor which influences risk and there are wide variations between different materials in terms of their toxicity. This can be influenced by many factors including size, aggregation and agglomeration (how particles stick together), solubility and electrical charge. Particle shape is of key importance: there are particular concerns about fibre-shaped materials such as long, thin and rigid carbon nanotubes (CNTs) and other fibre or wire-shaped nano-objects. In some cases, these can behave in the same way as asbestos fibres which are able to travel down to the deepest parts of the lungs but are then too long for the normal clearance mechanisms to remove successfully.

Information currently available about the health risks from nanomaterials is based on laboratory research rather than on cases of ill-health in workers. The results of studies are often inconsistent or inconclusive due to variations in the methods and exact materials used.

The potential health risks arising from the use of nanomaterials have been the subject of much research and substantial debate. Krug (75) observes that over 10 000 papers have been written on the matter worldwide over the last fifteen years. There are two broad issues which need to be considered: hazard and exposure. The toxicity of the materials themselves will be addressed in this section; and the potential for exposure, will be considered in section 4.3.

4.2.1. Why might some nanomaterials be hazardous?

The title of this section uses the umbrella term nanomaterials, to maintain consistency with the rest of the report. However, the published literature on health risks focuses specifically on those nanomaterials which contain nano-objects such as nanoparticles and fibres. Therefore the term nano-objects will be used where more appropriate in this section.

Two key factors which contribute to the toxicity of nano-objects are their size and their shape. As particles get smaller, their surface area to mass ratio increases, with an associated increase in their reactivity (47,135). Table 10 below shows how surface area increases exponentially as particle size falls (136). As a general principle toxicity is likely to increase as particle size falls. However particle size and also whether particles aggregate and agglomerate (i.e. how strongly they stick together) also influences in quite a variable way the extent to which objects penetrate deeper into the lungs.

Table 10 How surface area increases as particle size falls (data from (136))

Particle diameter (nm)	Number of particles (per cm ³)	Particle surface area (µm ² /cm ³)
5000	0.15	12
250	1,200	240
20	2 400 000	3 016
5	153 000 000	12 000

Toxicity may arise when insoluble nanoparticles or fibres penetrate deep into the lungs and are difficult for the lungs to clear; they may persist for many years, triggering inflammation and local lung damage (137). They can also trigger inflammation in other parts of the body (such as the cardiovascular system) or can be carried through the circulatory system and onward into other organs (translocation) (14). Nano-objects which are soluble, on the other hand, will dissolve to become molecules or ions – in this respect they lose their ‘nanomaterial’ properties (138) and can be assessed using traditional chemical toxicology principles. In fact, there is no particular evidence for a step change in the toxicity of particles at 100nm for any materials (i.e. that 99 nm is toxic, and 101 nm is ‘safe’). Some authors have suggested that risk for almost all can be assessed and managed using existing models of toxicity, starting with whether the ‘parent’ material (i.e. the non-nanoform) is known to be hazardous (27,75,135).

A second factor influencing the toxicity of nano-objects is their shape. For example, fibres are known to be problematic if they have:

- an aerodynamic diameter which allows them to penetrate deep into the lungs (i.e. they are narrower than 1 µm; (27,47,139); and
- a length which makes it difficult for normal clearance mechanisms to operate, generally above 5 µm (43).

This ‘High Aspect Ratio’, combined with bio persistence (i.e. the body cannot dissolve or break down the particles) underpins asbestos toxicity, a familiar concern to those working in construction and demolition. Asbestos fibres which are longer than 5 µm in length are able to pass through small holes into the pleural space of the lungs but become lodged, causing an inflammatory response (139) (this is the mechanism associated with mesothelioma). Fibres which are longer than 15 µm in length will be deposited within the lungs but the macrophage cells which would normally remove foreign particles are ineffective because of their size, so called ineffective or incomplete phagocytosis (27,140). In nanotoxicology, the impact of shape is most commonly discussed with regard to carbon nanotubes, but it applies to other fibre shaped nano-objects (27). For example research using titanium fibres (141) and silver nanowires (140) confirms the key principle that fibres which are too long for macrophages to break down are likely to persist and become problematic, as illustrated in Figure 16. Nanoplates (such as graphene), which have two large dimensions but are very flat, may be similarly problematic (142).

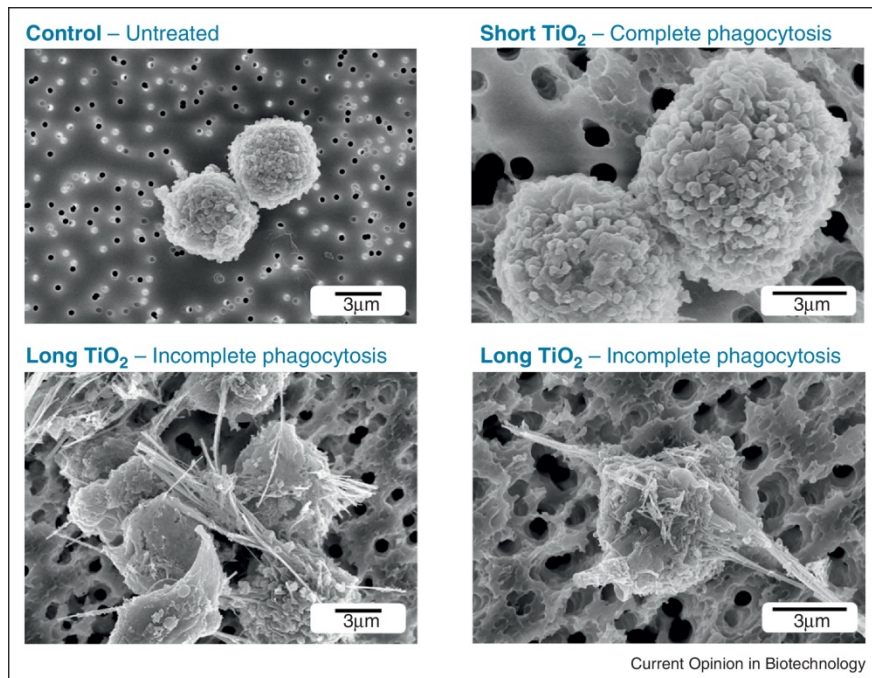


Figure 16 Effect of particle shape/length on macrophage uptake, illustration taken from (27)⁶⁵

The two round bodies visible in each of the top two pictures are the cells which would normally enclose and then remove foreign bodies. In the bottom two pictures the fibres are too long for the cells to effectively enclose, they are therefore unable to expel them from the body.

4.2.2. Evidence that nanomaterials might be hazardous

Evidence of possible harm from nanomaterials comes from epidemiological pollution studies. These have shown the risk of heart disease and stroke to be increased by exposure to airborne particulate matter, particularly fine particles (those smaller than 2.5 µm) (13). Ultrafine particles (i.e. pollutants in the nanoscale range) are likely to be a substantial contributor to this effect (14).

There is potential therefore that engineered nano-objects might have similar toxic effects. However, there is very limited, if any, epidemiological data showing this due to the relatively small number of people exposed to them through their work (45) and the short time for which they have been in extensive use. Hopefully the absence of diagnosed nanomaterial-related illness also indicates that exposures, to date at least, have been well controlled through precautionary measures, although it may also be influenced by long latency periods (143) such as those associated with asbestos-related ill-health.

In the absence of epidemiological evidence, we need to assess nanomaterial, specifically nano-object, hazard using laboratory methods. This is, suggest Donaldson et al (144), preferable to 'counting bodies' (as has been the case with asbestos-related illness). However, much of the nanotoxicology research has been inconsistent or inconclusive as a consequence of methodological limitations, and the variability of the materials.

Limitations of research methods

One reason for uncertainties about health risks arising from nano-objects relates to the research methods used. For example, *in vivo* research into the effects of nano-objects on the lungs may use inhalation, where test animals breathe air which contains them; or instillation, where particles or fibres

⁶⁵ Reprinted with permission from Elsevier and Ray Hamilton

are introduced directly into the airways. The two methods can produce different findings and instillation in particular can result in false positive results - unrealistically high doses can overload the usual protective mechanisms of the lungs and have a suffocating effect (145). Other studies may use different models, for example instillation of particles into the peritoneum as a model for the pleura of the lung (43) so again there may be conflicting findings.

In addition, these models are commonly based on tests with small animals and are not necessarily predictive of health problems in humans. For example, mice may be less sensitive to nanomaterials than humans, resulting in false negative results (146); and the literature also reports that rats are far more likely than humans to develop lung tumours in response to inert inhaled particles, presenting a risk of false positive results (147). Difficulties also arise when *in vitro* methods are used, such as the potential for excessive doses of nanoparticles to overwhelm test materials in a non-specific manner (75).

Variability of nanomaterials

A further challenge when addressing the question 'how safe are nanomaterials?' is the variability of substances. Boverhof et al (46) recommend that all health related research should define nano-objects in at least twelve different ways including size, shape, surface charge, whether particles are aggregated or agglomerated, the rate at which they dissolve and the nature of solvent they are carried in. It has been suggested that between 70 and 90% of existing research fails to meet adequate standards in this respect (75,148). This makes it difficult to compare studies, and differences in specific characteristics of the particles used may explain the contradictory findings of much experimental research (149,150).

4.2.3. Toxicity of specific nanomaterials

It has been discussed above that there is a potential for adverse health effects from nano-objects but that the details are often unclear, and there is variation between substances as well as difficulties with the test methods used. The next section will consider the evidence for adverse health effects in relation to specific substances, focussing on those which are most likely to be used in the built environment.

Carbon nanotube toxicity

Carbon nanotubes which are long, thin and rigid are considered to be potentially toxic due to their high aspect ratio and their bio-persistency – they are similar to asbestos fibres, which can penetrate deep into the lungs and be difficult for the body to remove. However some types of CNTs appear to cause no problems; for example CNTs which are short or tangled and non-biopersistent are less likely to be toxic than those which are long, stiff and biopersistent.

Carbon nanotubes (CNTs) are hollow structures constructed from layers of rolled graphene (carbon layers which are one atom thick). They may be single walled (SWCNTs, diameter 1-3 nm); or may consist of several tubes inside each other, multi-walled carbon nanotubes (MWCNTs), with diameters up to 100 nm (3). Their length can extend to several microns or longer, and it is this combination of small diameter and long length (high aspect ratio) which makes them potentially toxic.

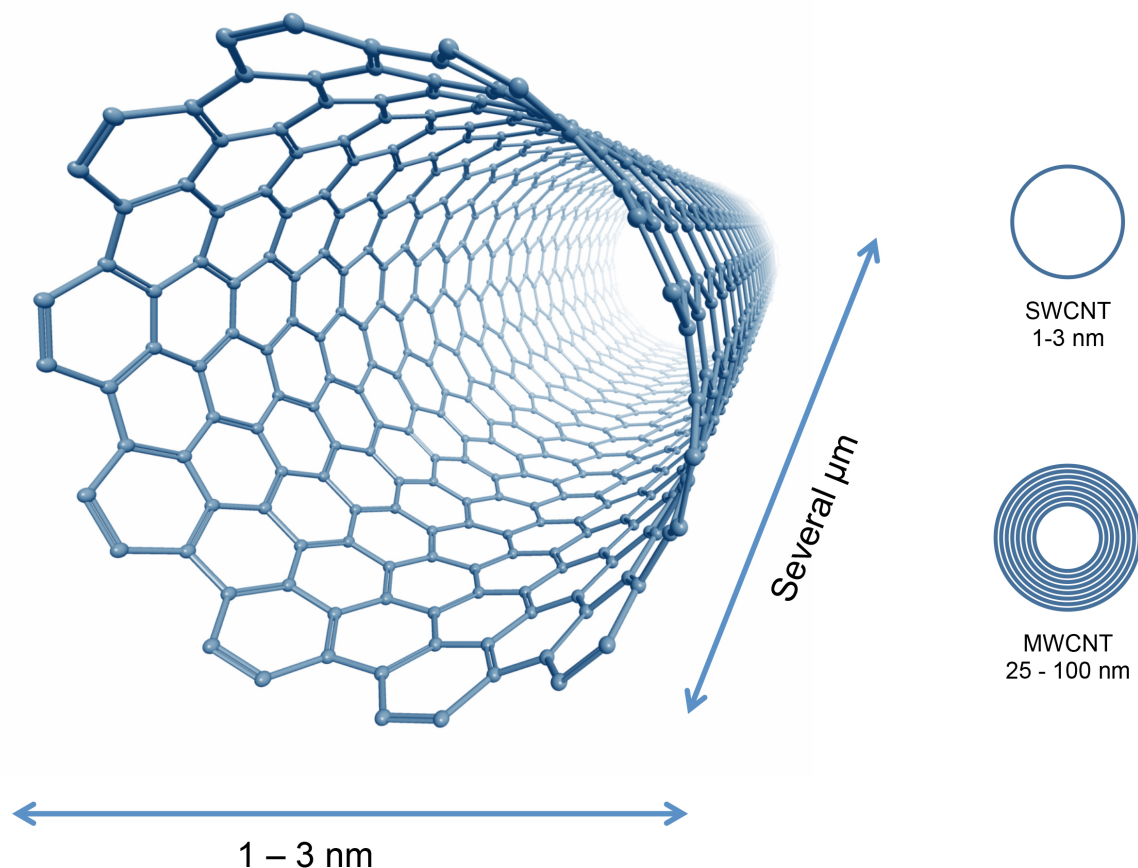


Figure 17 Dimensions of carbon nanotubes (CNT illustration courtesy of Dreamtime)

CNTs have high strength and stiffness, are chemically stable and electrically conductive (93) which makes them hypothetically useful in construction as well as in many other applications. They are, however, expensive to produce and difficult to work with, and hence are not yet widely used in the industry.

- The main concerns regarding the health risks of CNTs arise when they have similarities in structure to asbestos - needle shape, high aspect ratio (i.e. being long and thin) and bio persistence.
- The effects involve inflammation, oxidative stress, fibrosis, and genotoxicity (151,152). CNTs might also result in cardiovascular effects such as clotting or vascular damage (48,153), and influence response to infections and asthma (154).
- As with asbestos, the most toxic CNTs are those which are longer than $5\ \mu\text{m}$, and stiff. Shorter or tangled CNTs are considered less harmful as they are more easily expelled by the lungs' usual protective mechanisms (43). However, some studies have identified that shorter fibres (for example, less than $2\ \mu\text{m}$) can still have adverse effects, and there is also a lack of agreement on the diameter of CNTs which are the most problematic (155).
- Additional factors such as the presence of heavy metals, (which may arise from manufacturing processes) may increase toxicity (48,142,156); but the presence of such contaminants or other defects may also make CNTs more soluble and less bio persistent, thus potentially reducing their risk (43,157,157).
- The extent to which CNTs are aggregated together also affects the health risks (48). Typically, SWCNTs do not exist singly; they agglomerate into ropes including 20-50 tubes. MWCNTs are more generally separate, with only small numbers stuck together as ropes (158). Shorter

Graphene toxicity

There is relatively little published literature regarding the health effects of graphene. In principle it could behave like CNTs as plates of some dimensions can penetrate deep into the lungs; smaller plates are likely to present a lower risk as they are easier for the body to clear.

Graphene has been described as the 'youngest' in the family of carbon nanomaterials (163). Its form is that of a two dimension nanoplatelet – a flat sheet which can be several microns wide in two planes but less than 1 nm in the third, with a surface area potentially as high as 2600m²/g. It can exist as a sheet one atom thick but can also be formed from multiple layers stacked together (164). It is reportedly used in coatings by one manufacturer; otherwise its use in construction is likely to be limited to electronic applications such as electrodes and transistors (165). It has been reported that in principle it can make concrete stronger and denser (166) but there is no evidence that it is close to market in this respect. Despite the growth of graphene research at a 'spectacular pace' (167) in recent years, research into the health effects is at a very early stage, although there are suggestions that smaller particles are less likely to be problematic than larger ones (163). As with CNTs, graphene has proportions which might allow it to penetrate deep into the lung and to resist breakdown due to its large size in two dimensions (163,168) and therefore it should be treated with caution at this stage. The HSE advocates that it be treated with the same level of caution as other HARNs such as CNTs (160).

Carbon black toxicity

Carbon black is classed as a possible carcinogen based on animal-based studies although there is no clear epidemiological evidence of this effect. There is some evidence that carbon black causes irreversible respiratory ill-health, and may be the causative agent behind smoking related ill-health.

Carbon black (CB) is a manufactured substance used predominantly in rubber manufacture and produced in large quantities for the last 100 years (169). In construction it can be used in coatings for example to shield against radio waves or to provide electrical conductivity. It consists largely of elemental carbon. It is important to distinguish it from Black Carbon which is a by-product of incomplete combustion and is a key component of air pollution. Black Carbon is mostly made up of organic carbon as well inorganic compounds, sulphates nitrates etc. (170).

The primary particle size of carbon black can be as small as 15 nm although it exists almost entirely as an aggregate of 80 - 500 nm (171) and release of free carbon black from consumer products such as rubber products is considered to be highly unlikely as the particles are generally attached to the underlying matrix (169). Studies of smokers have suggested that carbon black may be the causative agent behind emphysema (172,173), with toxicity increasing as particle size falls. Epidemiological studies of those working in a manufacturing environment with carbon black have similarly shown evidence of reduced lung function and respiratory symptoms (174), although exposures have fallen markedly with improved occupational hygiene measures.

Carbon black is classified as a 'possible carcinogen' (category 2B) by the IARC based on animal studies (29). Longitudinal studies in the US (175,176) and the UK (177) have failed to find any conclusive evidence which links carbon black to increased mortality in workers or to an increase in lung cancer. However, there are difficulties in drawing firm conclusions due to the impact of smoking as well as limited availability of exposure data.

Silver toxicity

Silver is effective as an antimicrobial in both its nano and non-nano forms. The evidence on the health effects of nanosilver particles is inconclusive. There is relatively little evidence to show it is toxic but neither is there sufficient evidence to identify it as safe.

Silver in its non-nano form is used for its antimicrobial effect: it is toxic to bacterial cells at levels which are not harmful to more complex mammalian cells (178). Few health effects have been identified other than discoloration of the skin or eyes from high exposure to soluble forms (particularly if ingested) (179).

Nanosilver is very effective against microbes (109), although it is unclear whether the nanoparticles themselves are active, or rather the silver ions which they release (180). There is also uncertainty regarding the potential health effects of the nanoform, as some studies have demonstrated adverse effects and potential toxicity (180,181). For example, some *in vitro* studies have suggested it can cause inflammation in the lungs which seems to relate to particle size and concentration, and there is also evidence that silver relocates to other parts of the body such as the liver (48).

Detailed reviews of the literature by Stone et al (48) and Wijnhoven et al (178) have both found insufficient evidence on which to judge the toxicity of nanosilver, particularly as there are so few *in vivo* studies. A review on behalf of the EC (182) reached a similar conclusion but also observed that '*Silver and nanosilver are clearly shown to have toxic potential although toxicity in general in humans seems to be low.*' There is also some limited evidence that the use of nanosilver as an antimicrobial might lead to bacterial resistance to silver (183) but again there is insufficient evidence to draw definitive conclusions. Nevertheless, a review by the French body ANSES recommends that silver be restricted in its use to '*applications whose advantages have been clearly demonstrated*' (184).

Titanium dioxide toxicity

There is evidence to suggest that nanotitanium dioxide particles may be toxic when inhaled. NIOSH in the United States has recommended a maximum workplace exposure level which is one eighth of the exposure level for non-nano titanium dioxide. There is insufficient evidence to exclude it being carcinogenic.

Titanium dioxide is generally considered to be safe for dermal application (e.g. in sunscreen) although there is limited evidence regarding the impact of pre-existing skin damage on this.

The bulk form of titanium dioxide, used as a white pigment because of its brightness and high refractive index, is generally considered to be safe with low solubility and low toxicity (185). It has been identified as a 'possible carcinogen' (category 2B) by the IARC (29); however, this judgement is based on high dose instillation studies in rats, and may reflect lung overload rather than indicating a specific toxicity of titanium (186). Bulk titanium is used in paints, coating, toothpaste, cosmetics and food, as well as artificial joints (185) and sunscreen (30).

Nanoscale titanium dioxide is highly stable, anticorrosive and photocatalytic (185). It appears transparent because it absorbs and scatters light (21), and it is used in construction projects in coatings which take advantage of these properties.

The main concerns around the health risks of nanotitanium dioxide particles relate to inhalation. Long term toxicity studies suggest that high doses can cause moderate inflammation of the lungs. Overall, the data are conflicting, but more studies suggest harm than do not (including those which are based on realistic doses) (185). The toxicity of nanotitanium is higher for some forms (e.g. anatase) than others (such as rutile). It generally increases as particle size falls (48) and may be higher for particles in the size range 10 – 40 nm (187). Some studies also suggest that titanium dioxide nanoparticles can move around the body and can contribute to reproductive, cardiologic and neurological consequences. This evidence is used by Hansen et al (181) as further confirmation of toxicity; although these studies are generally conflicting or based on excessively high doses of titanium and their translation to human harm is unclear (185).

NIOSH recommends airborne exposure limits of 2.4 mg/m³ for fine titanium dioxide and 0.3 mg/m³ for ultrafine (including engineered nanoscale) titanium dioxide, as time-weighted average (TWA) concentrations for up to 10 hr/day during a 40-hour work week (45,188). This limit has also been recommended for use in Australia (45,45).

Becker et al (152) consider that the data on titanium are not adequate to '*make a robust evaluation of its carcinogenicity*' so it must be considered as a suspected carcinogen (152,116,109). Insufficient studies exist to be able to compare the carcinogenicity of nanotitanium to the bulk form.

Nanotitanium may also enter the body through routes other than inhalation. It is extensively used in sunscreen for example, and this may be important for construction workers who are likely to use these to reduce their risk of skin damage from UV light when working outdoors. Reviews on dermal penetration have found little or no evidence that it can penetrate the stratum corneum, and there have been no problems reported in 20 years of use; therefore it is generally considered safe in this respect (30,185). However, eczematous skin can be more permeable to topical substances (189) which may increase the risk of harm to those with skin conditions or damage. Little, if any, research has been conducted on damaged skin, making it difficult to draw definite conclusions on the risk in this situation (48).

Zinc oxide toxicity

There is some evidence for the toxicity of inhaled zinc oxide nanoparticles but overall there is relatively little research and much of it is based on unrealistic exposures. Zinc oxide is also used in sunscreen and is considered safe for this use although as with titanium dioxide there is limited evidence regarding its effect on damaged skin.

Zinc oxide appears to be used in a small number of construction coatings and also in some window coatings (190). Few studies have been conducted to assess the toxicity of zinc nanoparticles (48). Vandebriel and de Jong (191) have reviewed the existing literature and found some evidence for inflammation and cytotoxicity, generally based on the release of zinc ions rather than the nanoparticles themselves due to the solubility of the substance. However, it is difficult to draw firm conclusions in view of the unrealistically high doses used in many of the studies (45). Although the main area of concern is inhalation of zinc oxide nanoparticles, there are also studies into dermal absorption. Zinc oxide is used in sun protection creams and, as with titanium dioxide, studies show that it does not pass beyond healthy skin but there is a lack of evidence regarding the permeability of damaged skin (191).

Silicon dioxide (silica) toxicity

Nanosilica is usually amorphous. This is a different form of silica from the crystalline silica which is recognised as a major hazard in the construction industry, particularly as a dust.

Amorphous silica nanoparticles are considered to be relatively low risk, with any ill effects being largely reversible. However, there is insufficient evidence to declare nanosilica as 'safe' particularly as there are so many different forms of it in use.

Silica exists in many forms, with crystalline silica (quartz) being the form commonly used in construction. This carries health risks including silicosis, lung cancer, airways disease and possibly autoimmune diseases (192,193). The HSE in the UK has a work exposure level (WEL) for Respirable Crystalline Silica of 0.1 mg/m^3 (averaged over 8 hours). Amorphous silica (literally, silica without a clear shape or form, see Figure 18), is a much less hazardous form of the material, illustrated by its WEL of 2.4 mg/m^3 (11). It is used in foodstuffs as a filler, in toothpaste, in rubber tyres, and as a desiccant.

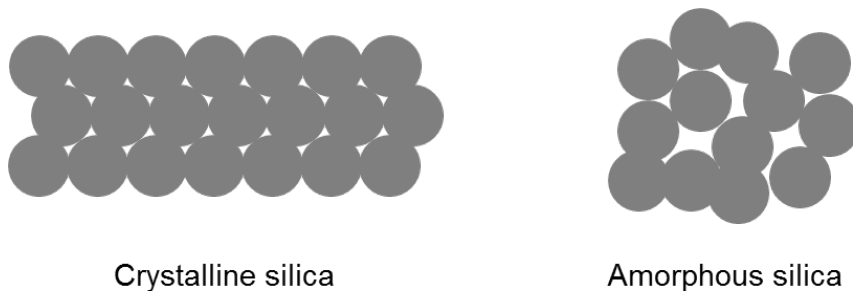


Figure 18 The different molecular structures of crystalline and amorphous silica

Nanosilica exists in many forms across a wide range of particle sizes with many uses in construction products, including silica fume and fumed silica. Almost all of these are amorphous in nature, and nanosilica is generally identified as being at the safer end of the nano spectrum (152,194). Specific studies have found, for example, inflammatory or cytotoxic effects from small nano particles at $10 \mu\text{g/ml}$ (195) and $50 \mu\text{g/ml}$ (196) but these are relatively high exposures, unlikely to occur in practice and therefore not of major concern pragmatically (197). A detailed review by Napierska et al (149) identifies that any effects on the lungs appear to be reversible (i.e. temporary).

Nevertheless, Napierska et al (149) also conclude that there is insufficient evidence to declare nanosilica to be 'safe'. A review by the European Chemicals Agency (ECHA) (198) has reached a similar conclusion, declining to categorise the material as non-hazardous, despite the claims of manufacturers that it has been used for many years without incident. ECHA have based their decision on the variability of the substance, as forms with higher surface area or higher hydroxylation are more toxic than others, and a very small number of studies have shown adverse health effects (although the majority have not). Manufacturers have, according to the decision, failed to provide detailed data indicating exactly which forms of the materials are commonly used. Data regarding likely exposures in practice are also lacking, hence there is insufficient certainty to identify the material unequivocally as being safe in all its forms.

Quantum dots toxicity

Quantum dots vary widely in their composition and their toxicity; some are made from hazardous materials such as cadmium and selenium. Their use in the built environment is likely to be largely limited to electronic devices such as those with LED screens.

Quantum dots are manufactured particles a few nanometres in diameter. They consist of a core, which is generally a semiconductor or a noble metal, with a coating to protect the core and to influence the way the substance interacts with systems (199). Because such a wide range of materials can be used to manufacture quantum dots, it is not possible to draw generic conclusions regarding their toxicity. However, there are certainly many forms of them which contain hazardous substances such as cadmium (200) and selenium (201), and toxicity is also influenced by size, shape, charge and the presence of additional materials (199,202). There are expected to be many uses for them in biomedical imaging and other healthcare applications (203); and they are already being used in LED TVs and phone screens. They are likely to be used in the built environment largely in this context, for example for built-in interfaces. In terms of disposal, they will therefore fall under WEEE legislation rather than normal construction and demolition processes. However, there are potential risks from their recycling, particularly if this takes place in enclosed or poorly managed workplaces and involves large quantities of the materials.

4.2.4. Conclusions and future developments in nanotoxicology

Definitive conclusions on the toxicity of nanomaterials, specifically nano-objects, are difficult due to their variability and also due to limitations in the health research, which lags many years behind the development of new materials. Improvements may come through identification of the key principles which make some materials more hazardous than others, rather than through detailed study of every new material. There is also potential for manufacturers to consider the risk potential of the materials they develop and to design any toxicity out at an early stage. Until the picture is clearer, a precautionary approach is recommended.

The above summary illustrates that nanomaterials, specifically nano-objects, may have adverse health impacts. However, there is variation between different materials and there remains a lack of agreement about various aspects of nanomaterial toxicology. There is substantial ongoing investment to address this uncertainty, by individual organisations and by national and international bodies. For example, the European Union is currently formally evaluating silver and titanium dioxide as part of the review by ECHA (60,198), to add to its recent decision regarding silica (198). The OECD (Organisation for Economic Co-operation and Development) is also gathering data on these materials plus a further eight nanomaterials – they are seeking to draw conclusions about current testing methods as well as the risks arising from the materials (204).

Despite this ongoing work, comprehensive risk assessment of the nanomaterials already in use will take many years and new materials are being developed faster than testing can be performed (205). A particular challenge is the number of variations of each material – for example, there are over 50 000 types of CNTs, each with a potentially different hazard profile (47). Consequently, it has been suggested that rather than focussing on individual testing which Donaldson and Poland (27) describe as a ‘counsel of despair’, work should highlight the similarities and differences between particular materials and groups of materials. ‘Read across’ methods can then be developed, where the conclusions from one material can be used to predict the risk from another, and this can be used as a basis for setting health standards (206).

Another approach to managing nanomaterial risk is to actively design materials which are known to be less hazardous. For example, Bussy et al (163) suggest that graphene is at its safest when particles are relatively small and used in single layers; when they are hydrophilic and well dispersed; and when they have surface modifications which make them easier to degrade in the body. They therefore recommend that developments of new applications should focus on forms of graphene with these characteristics. Donaldson et al (43) have similarly recommended that carbon nanotube development should focus on those which are short and tangled. Studies have been performed which demonstrate that small modifications to CNTs can make them much easier for the body to excrete (207), and other techniques such as the use of surface coatings or breaking fibres down to shorter lengths have also been proposed and explored as ways of reducing toxicity (208).

However, this requires that technological advances proceed with the health risks of new products in mind. This model of Responsible Research and Innovation is one favoured by the EU, and expects business to work with researchers and the public to ensure that the needs of all parties are aligned (209). There is evidence that some companies recognise this responsibility. For example Bayer (who developed 'Baytubes', one of the early CNT products) states on its website, *'we assess the possible health and environmental risks of a product along the entire value chain. This starts with research and development and continues through production, marketing and use by the customer through to disposal'...*⁶⁶ However, taking health risks into consideration will be challenging as long as the evidence regarding what is and isn't safe lags so far behind the technical developments. In addition, there is potential for innovation and commercial considerations to take precedence over potential health risks. For example an article on the development of carbon nanotubes for use in electronic devices celebrates the techniques which have allowed them to separate individual nanotubes and ensure they remain long (210); precisely the characteristics which potentially increase their hazard potential. Close monitoring of the balance between benefit and risk is therefore likely to be an ongoing challenge in this fast developing field.

Currently, the lack of definitive evidence on the harm from nanomaterials, particularly nano-objects, and the methodological flaws in much of the research is making it difficult for regulatory bodies to draw absolute conclusions or make clear recommendations. Although exposure levels for ultrafine (nanoscale) titanium dioxide particles and carbon nanotubes have been recommended in the United States, there are no recommended exposure levels published by the EU or UK. In the Netherlands, recommendations have been made on 'nanoreference values' (26), to be used as an integral part of a risk management tool, but these are grounded more in the detection limits of monitoring methods than the literature on health effects (211). Until 'safe' levels have been identified, a precautionary approach is advocated by the HSE in the UK, in common with many other national and international bodies' (160,212): in the absence of evidence that nanomaterials are safe, action should be taken to avoid harm which could plausibly occur.

⁶⁶ www.bayer.com/en/product-stewardship.aspx

4.3. Exposure and risk assessment

This section addresses the research objective:

to explore the potential for exposure to nanomaterials during construction and demolition

This section is based on review of the academic literature and on interviews with demolition and recycling managers and workers and visits to their sites.

A second part of this study considers construction and demolition exposures, testing the impact of common processes on the release of nanoparticles from various materials. The results from this will be reported separately (77).

Key points

Assessment of nanomaterial risk is difficult due to the uncertainties over the toxicity of particular nanomaterials and the lack of information on which nanomaterials are contained in which products.

There is some evidence that exposure to nanoparticles from engineered nanomaterials is likely to be low during demolition and construction processes as nanoparticles remain attached to fragments of the underlying matrix. However the evidence base is small and material ageing might also influence this, particularly in the demolition context. Additional exposures may occur as nano-enabled products are recycled and incorporated into new materials.

Measurement of exposure to nanomaterials is complex and data are currently limited. Qualitative assessment methods can be useful as they allow assessments to be made without such measurements, for example categorising activities as low, medium or high risk based on general principles. Such methods tend to reach relatively cautious conclusions, specifying higher levels of protection than expert assessment. Nanomaterial risk may not add substantially to existing construction health hazards (for example silica dust), and commonly used protective methods are likely to be appropriate in many cases.

Assessing risks involves considering both the hazards which arise from a particular material or process (for example, toxicity) and also considering the potential for exposure to the hazard. The current evidence available regarding exposure to nanomaterials is reported to be even more incomplete than that relating to their toxicity (47,48,50,206).

This section will consider nano-risk management in construction and the factors which make exposure and risk assessment particularly challenging.

4.3.1. Identifying the materials used in construction

There are uncertainties around which products might be nano-enabled. Many nanomaterials discussed in the academic literature are at an early stage of development and are not yet used in commercial products. Where commercial products exist, they rarely indicate clearly what their nano content is or provide sufficient details to support proper risk assessment. The complexity of the construction supply chain contributes to the difficulties in getting clear information regarding the nanomaterials contained in products.

Identifying which nanomaterials are used in the construction industry, where, and in what quantities is extremely difficult. The challenges begin with a lack of clarity in the academic literature which leads to confusion; are intensified by limited labelling of products and an absence of relevant details in safety data sheets; and further compounded by the presence of multiple players in the construction supply chain.

Mismatch between literature and reality

The development of nanomaterials is a major topic for publication and discussion in the academic literature. For example, a search on Web of Science using the term 'carbon nanotubes' finds almost 15 000 references for 2015, and almost 350 papers in the last five years which are specifically about carbon nanotubes in concrete or cement. Most of these papers describe research which is still at a laboratory stage, not all of which will progress to market. There is, for example, a substantial practical difference between working with small quantities of cement paste in a laboratory environment and scaling up the process to produce industrial quantities to use in the built environment. However, where summary papers about the extent of nanomaterial use are written, based on the literature, this distinction is not always made, making it difficult to assess the true state of development. For example, one textbook goes so far as to state that, '*carbon-based MNMs, such as carbon nanotubes...are often used in concrete and ceramics to improve strength and durability*' (213) which does not correspond with our research findings. As discussed in section 4.1, the real-world use of CNTs is far less widespread than this suggests, and similar confusions exist for other products.

Uncertainty regarding materials involved

Identification of which construction products contain nanomaterials (and more specifically whether they contain nano-objects) is extremely difficult, as there is no legal requirement in the UK and most other countries for them to be identified nor any constraints on the use of the term 'nano'. Consequently:

- products containing nanomaterials, including those which contain nano-objects, may not state that they do. Interviews conducted for the current research suggest that this may be a conscious decision by some manufacturers to avoid creating anxiety amongst consumers
- materials and products which are labelled as 'nano' may be constructed using nanotechnology (e.g. equipment which can operate at the nanoscale) or be based on nanomaterials which do not contain nano-objects, as this extract from a manufacturers' product literature illustrates: '*[the] name derives from its nanotechnology, ... [the company] does not use Nano particles in any of its products*' (214); and
- products may use the term 'nano' as a marketing device - in the current study, a supplier was contacted after microscopy of a purchased sample did not identify any nano-objects; the response given was that '*Nano coating is purely a name given to the treatment we offer for [the product], rather than a description of the material itself.*' It was not possible to determine whether the product did contain some nanomaterial e.g. a nanoscale film coating.

Neither is there a specific requirement to include details about nanomaterials or nano-objects in a safety data sheet. This means that, even where a product is clearly labelled by a manufacturer as containing a nanomaterial, it is rare that information is provided regarding the nature, size and shape of any particles or fibres present, even though these characteristics may affect its toxicity. In the current study, 70 coating products were identified as being nano-enabled (based on advertising literature, other published reports, or material properties), and the safety data sheets obtained for two thirds of these. Of these 70 products, 25 provided some information on the nanomaterial involved, generally on their website or in advertising literature including eight which suggested that the product did not contain nano-objects. However, only one product mentioned the nanomaterial in the safety

data sheet, and only one provided details regarding the exact nature, quantity or particle size of the nano-objects it contained.

This lack of information was reported as a major concern in the Scaffold study (39), a multinational EU-funded research project looking at the use of nanomaterials in the construction industry. First, without correct and detailed information it is impossible to classify the hazard from a substance (205). Lee et al (55) report examples of safety data sheets for nanomaterials which give occupational exposure limits or Chemical Abstracts Service (CAS) reference numbers which relate instead to the bulk materials – failing to distinguish for example, between graphite and CNTs. Secondly, if there is insufficient information about where nanomaterials and nano-objects are used, it is difficult to assess the potential for exposure, or to plan research which might explore this.

The supply chain

There are usually multiple players involved in the construction supply chain – the manufacturer of the nanomaterial, the company which converts this into an additive for a paint or coating, the company which produces the coating and the company which imports or distributes the final product. This impacts on traceability, as the details of which nanomaterials a product might contain and in what form are progressively lost down the supply chain (215). A scoping study for the forthcoming Belgian registration of nanomaterials found the supply chain to be ‘fragmented and non-linear’ (216). An example of this comes from the use of a bathroom sealant product called ‘Nanomagic’ which was withdrawn from sale in Germany in 2006 following acute ill-health amongst customers who had used it (47,217). The manufacturer was not able to provide clear information on what the marketed product contained due to the fragmented supply chain (although it was ultimately found that nanomaterials were not the cause of the ill-health and, in fact, the product did not contain nanoparticles).

The introduction of nanomaterial registration in France has started to address this situation as downstream users are now more aware of what they are handling and have been able to revise their risk assessment procedures accordingly (57,218). However, there remains a lack of clarity more widely. For example, additives such as Aerosil, Bindzil and Nanobyk are reported in the literature (35,37) as being nanomaterials used in construction products. However, it is very difficult to identify which end-use products contain them. Similarly, websites for companies such as Nanocyl highlight that their CNTs can be used in construction coatings but again, we have not been able, largely due to commercial confidentiality constraints, to identify a marketed product which contains them (or confirm whether one exists).

4.3.2. Exposure routes

Inhalation contributes the greatest risk for nanoparticle exposure. Nanoparticles may also enter the body through the gastrointestinal tract or through the skin although these are generally considered to be less likely or problematic.

Inhalation is generally considered to be highest source of risk for nanoparticle exposure (39). However, nanomaterials may also enter the body through the gastrointestinal tract and potentially through the skin. These mechanisms have been evaluated by Oberdorster et al (136). With regard to gastrointestinal exposure (which can arise from accidental hand to mouth contact; direct ingestion; or following inhalation of nanoparticles which are then cleared into the mucus) there are few studies reported but these mostly show that nanoparticles are rapidly excreted. Exposure through the skin is generally considered to be relatively low risk. Extensive study of nanomaterials which are intentionally applied (for example in sunscreen) has found that there is no penetration through healthy skin

(30,219). However, a review by Filon et al (220) shows that small nanoparticles (<45nm) can pass through skin particularly if it is flexed (221) or damaged. This is of relevance to construction given the relatively high potential for skin damage in the industry.

4.3.3. Exposure potential in construction and demolition

The mechanically destructive processes used in construction and demolition are associated with dust release - for example, cutting, drilling and sanding during construction and explosive methods and aggregate crushing at demolition. There may be a potential for nano-objects to be released if products containing these have been used.

Current evidence suggests that nanoparticles or fibres released in this way are often still attached to fragments of the underlying matrix (and are therefore unlikely to be any more toxic than the base material), but the number of studies in this area is small. Nano-object release may also be influenced by the breakdown of a material over time, induced by weathering. Again, the literature suggests that free nanoparticles are not commonly released by this process but the number of studies is too small to draw firm conclusions.

There is also evidence that nanoparticles are produced by ordinary construction and demolition methods even if they were not intentionally added, e.g. ordinary (non-nano) concrete produces nanoscale particles when broken down.

An additional unknown relates to the use of secondary materials: where nano-enabled products are recycled, this will result in the likely transfer of the nano-component to the newly created materials, possibly without the recycler or user of the products being aware. There is little research into the possible impacts of this.

There are also uncertainties around the developments of new materials. For example polymer composites are being used increasingly in construction and are recognised as being difficult to reuse and recycle; the consequences of nanomaterials being included here are unclear.

The potential for particle or fibre release is influenced by a range of factors. The first is the physical state of a nanomaterial – for example, the release of nanoparticles is considered to be negligible if they are suspended in a stable solid material (181). Where nano-objects are in a liquid form, there is a potential for release if they are used in a way which could produce aerosols, for example by spraying (138) as well as potential for exposure through the skin. Nano-objects which are airborne e.g. dusts create particularly high exposure potential. The nature of construction work may increase the risk due to the processes involved. In addition, release at demolition may be influenced by the processes of weathering and ageing which break materials down over the years a building or facility has existed.

Nanomaterials which do not contain nano-objects, for example nanoscale films or nanostructured materials are not generally discussed in the literature on health risks from nanomaterials. Although there is an argument that 'nanoparticles may not be the only relevant nanomaterials in relation to potential risks to human health' (22), the literature focuses on those which do contain nanoparticles and other nano-objects, presumably on the assumption that these are the ones which give cause for concern.

Processes leading to potential release of nanomaterials

Construction is a high risk industry for the release of dusts. Figure 19 shows dust release from common activities such as cutting or breaking concrete blocks or road surfaces. These and other mechanically destructive processes such as sanding, drilling and machining therefore also have the potential to release nanoparticles or other nano-objects if these are present (222).



Figure 19 Typical construction and demolition activities, releasing concrete dust

These activities can occur throughout the lifecycle of nano-enabled products. Additional exposures can occur at demolition. This may involve step by step dismantling using crushers and excavators to break buildings apart or may use explosive methods (Figure 20). Different materials will then be separated into waste streams for reuse, recycling or landfill with the potential for the release of any nanoparticles contained at each stage.

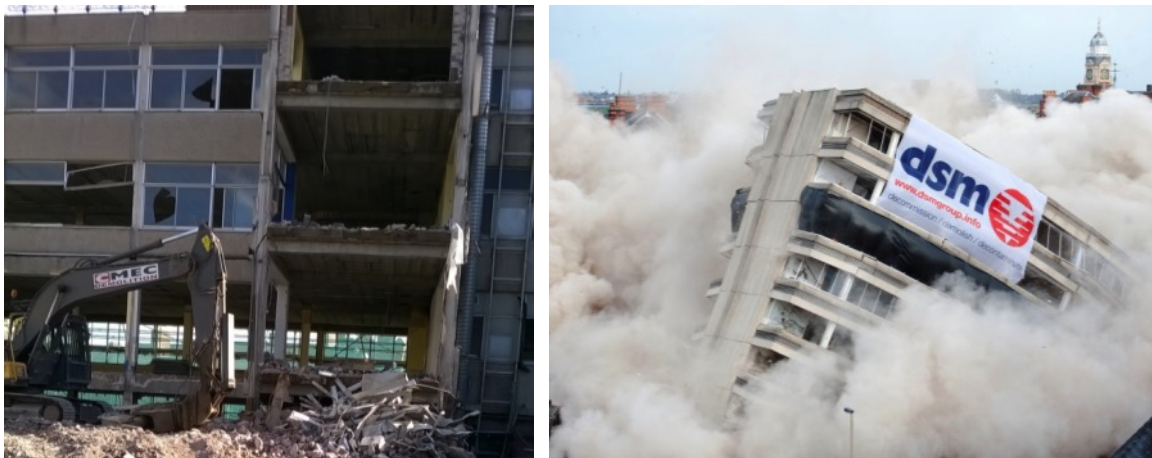


Figure 20 Building demolition
(photo © DSM)

Concrete will contribute a large proportion of the dust generated during demolition itself. Subsequently, most concrete is broken up to create recycled concrete aggregate of various sizes (Figure 21 and Figure 22) to be used in new building projects, accounting for most of the 95% or more of demolition waste which is recycled and reused (223). This process generates dust for those who work on demolition or recycling sites, although the use of water suppression systems can help to minimise this. Any paints or coatings (including those which contain nanomaterials) on the surface of concrete and bricks will be broken down into the overall aggregate mix during this process.



Figure 21 A concrete crusher which will break down waste concrete, bricks etc.

There is evidence that nanoparticles are released by these processes even if they have not been added to the materials. For example, demolition and refurbishment of ordinary concrete has been shown to release a very high number of nanoscale particles (224-226) (although these account for a tiny proportion of the total dust released in terms of mass or volume). There is little information available to show if or how this might be changed by the addition of nanomaterials to the concrete at construction.



Figure 22 Once concrete has been crushed it will be sieved and sorted into different sizes and qualities

Wood, which again may have coatings or paints on the surface, is usually removed either manually or with machinery during demolition. A small amount may be reclaimed, but most is either shredded for fuel or sent to landfill (Figure 23). Historically, wood used for biomass was exported but there is increasing capacity for processing in the UK and Europe as incineration of municipal solid waste is seen as an alternative to landfill (227,228) and suitable plants are being constructed.⁶⁷ The impact of incineration on nanoparticles is not entirely clear, with research suggesting that they may either be released in flue gases (229) or be sent to landfill (230).

⁶⁷ www.woodrecyclers.org



Figure 23 Waste wood, which will be either crushed for fuel or sent to landfill

Glass which breaks during demolition will usually be broken down with aggregates. Larger pieces might be gathered and recycled, being added in to the ingredients for new float glass (Figure 24). Any coatings on the surface (such as nanomaterials added to provide thermal insulation or self-cleaning properties) will be melted down with them.



Figure 24 Small fragments of glass will be mixed in with waste aggregate. Larger pieces may be recycled into new float glass

Metal will be usually be removed from buildings using oxyacetylene cutters or other equipment (Figure 25). It will then be sorted and taken for recycling which involves melting it down for reuse. Coatings on the surface of metals will not alter the way it is handled (although additional personal protective equipment may be used if a coating is believed to contain lead). There is little published specifically on whether the presence of nanomaterials (e.g. as coatings) leads to any particular health risks when recycling metals: but Caballero-Guzman et al (230) note that nanosilver will be destroyed by the temperatures involved in smelting. CNTs in coatings are also likely to be destroyed as they oxidise at temperatures between 600° C and 800° C (231).

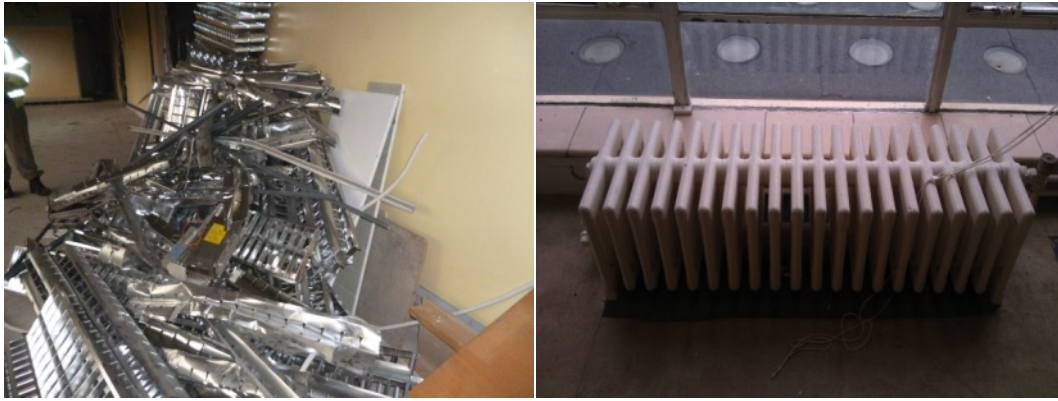


Figure 25 Metals will be sorted into 'ferrous' and 'non-ferrous' and sent for recycling

Insulation materials and ceiling tiles will usually be removed manually during 'soft strip' of a building and sent to landfill, while plasterboard will be sent for specialist disposal (Figure 26).



Figure 26 Insulation materials and plasterboard removal during demolition

Potential for nanoparticle release during demolition

Many of the processes described here will create dust, and if products containing nano-objects have been used during construction these may also be released. Research suggests that the volume of particle release is generally no higher overall for products containing nano-objects than for those which do not (215,222,232).

Where release of added nano-objects does occur, current evidence suggests that the particles are often embedded in matrix particles and therefore no longer nanoscale (233-235). However, the number of studies conducted on the release of nanoparticles from construction and demolition type processes is relatively small and they are typically based on laboratory testing rather than real world exposures (236). Much of the research done on exposure potential during recycling focuses on the environmental risks rather than the potential for worker exposure e.g. (28,41,237).

The studies which have looked at potential for worker exposure often use products which are specially prepared or modified rather than those available in the marketplace. One exception to this is a study by West et al (38) which assessed release of nanoscale titanium dioxide when cutting 'smog eating' roof tiles, in a real world scenario. This study found that most of the titanium dioxide released was bound up with debris, and those particles which were dissociated were 200 nm or larger. Only four free particles smaller than this were found. Total worker exposure was found to be within the recommended NIOSH limits for respirable titanium dust.

These results are encouraging but substantial further research is required before firm conclusions can be drawn. Of particular interest will be findings from research planned in the United States to assess life cycle potential for particle release of CNTs from Teslan, a CNT-based coating which protects metal structures from corrosion.

Potential impact of weathering and ageing

Products such as coatings are expected to deteriorate over time as a consequence of exposure to ultraviolet radiation, temperature cycling, moisture levels and salt air (238). This may affect the release of engineered or manufactured nanoparticles from buildings, particularly those which have been standing for many years prior to refurbishment or demolition. As with machining, the number of studies which assess nanoparticle release due to weathering is relatively small. Many of these have found that where such nanoparticles are released, they are embedded in composite debris or matrix (236), and hence form particles which are larger than nanoscale. In fact, the presence of nanomaterials may actually provide some protection from the impact of weathering (239,240). Nevertheless there are some indications that weathering might result in the release of disassociated nanoparticles (241,242), particularly when used in combination with machining (243). The number of published studies in this area is small (236) which makes it difficult to draw definitive conclusions.

The potential impact of the sustainability agenda

The section above has considered the possible impact of demolition and recycling methods on release of engineered or manufactured nanoparticles and worker exposure. However, there are many unknowns in this area, and also ongoing changes. One influencing factor is the ongoing sustainability agenda – seeking measures to further improve reuse and recycling of materials at the same time as conserving energy and designing buildings which are efficient to heat and run. The next section will consider how the circular economy and the increased use of composite materials might affect nanoparticle exposures.

The circular economy

The circular economy reflects the need to improve resource use and reduce waste, thus minimising landfill at the same time as reducing demands for new materials. The construction industry is a very high user of resources and hence an important contributor to this (244,245). For example, it was mentioned above that up to 95% of concrete is recycled or reused in some form when buildings are demolished.

Any nano-objects which are either contained within concrete (such as nanosilica or carbon nanomaterials) or included in paints or coatings on the surface will be transferred into any new concrete made with these recycled materials. This could, in principle, have an influence on the function of those materials (246); on the environment, if waste materials go to landfill or other areas where leaching can occur (230); and on the health of those working with any new materials created from the recycled waste (247). An additional source of nano-objects may be from the use of bottom ash from incinerators. This is an increasingly desirable route for the disposal of municipal solid waste (228), and the ash generated can be added to construction materials (227).

The OECD have identified a need for more research into the issue of secondary materials (i.e. those containing recycled products) being ‘contaminated in an uncontrolled manner’ by the nanomaterials which were added to the source material or product (248). Others have called for improved traceability of nanomaterials before allowing them to enter the recycling/waste streams (e.g. (247,249,250). Certainly, the reuse and recycling of nano-enabled products introduces a further

element of uncertainty, compounding the limited information available about these materials when they are first used.

The use of polymer composite materials

Polymer composite materials in construction are not used solely for sustainability reasons, but the fact that they are strong, light (251) and can be produced from recycled materials can make them desirable in this arena. The use of fibre reinforced polymers is a growing trend in construction, following initial adoption in the aerospace and automotive industries (251,252): it is therefore possible that the use of nano-enabled composites will follow a similar path, so that CNT enhanced materials are used in buildings in the coming years.

Demolition and recycling practitioners interviewed for this research raised concerns about the difficulties of recycling composite materials. They do not fit easily into the traditional disposal routes used in the industry, as multiple layered materials are difficult to separate out; at the extreme are 3D printing methods, producing waste which one interviewee described as 'one big blob'! This perspective is mirrored in the literature, which confirms that there are limited commercial recycling opportunities other than breaking composites down by mechanical means to use as feedstock in new composites (253). This may carry risk of engineered or manufactured nanoparticle release (248) and again raises the issue that the secondary materials will contain any nanomaterials added to the first. Other methods such as chemical and thermal processes are being developed for the recycling of composites but there are substantial unknowns here regarding their impact on nanomaterials and the potential for particle release.

4.3.4. Measuring nanomaterial exposure

Accurate measurement of nanoparticle release is difficult and there are no agreed standards for doing it. Workplace risk assessment may be carried out using qualitative risk assessment tools. However, these tend to result in overcautious assessment, defaulting to a level of 'high risk' when there is a lack of information on the exact materials being used.

It has been identified in this report that the exact nano-content of many products is often poorly defined. In addition, the size and nature of nanoparticles may change as a consequence of incorporation into a product and as a result of changes which occur over time due to wear and tear (254). It is therefore important to measure the release of particles from real nano-enabled products under real life working conditions.

The measurement of nanoparticle release can be particularly challenging (6,27,50). Traditional occupational hygiene methods use mass-based methods, and recommended exposure limits for toxic materials are generally given in mass (e.g. the WEL for crystalline silica in the UK is 0.1 mg/m³). These levels may not be appropriate if a material contains nano-objects, given the potentially increased health risk associated with reduced particle size (42); it may also be necessary to assess whether engineered or manufactured nanoparticles are present in the material released (for example using microscopy, either SEM (scanning electron microscopy) or TEM (transmission electron microscopy) and to consider the impact of this. Detailed study of collected dust samples can be undertaken to distinguish between particles of different sizes, but a relatively large volume of air might need to be sampled; and even if large numbers of nanoparticles are present, these will contribute little to the mass profile and hence may appear to be of low significance.

An alternative method is to measure the number of particles released rather than their mass. This can be done in real time using tools such as an Optical Particle Counter, a Condensation Particle counter

(211) or a Differential Mass Spectrometer (224,225). There are no harmonised methods available for such measurements, which makes comparison of results across studies difficult, although the OECD is seeking to address this (211). There are other challenges to such measurements:

- It can be difficult to distinguish between particles released by a process and those which are present in the background. Van Broekhuizen et al (101) measured particle release from a task involving the drilling of nano-enabled concrete but found that cigarette smoking in the vicinity had a far higher impact on particle counts.
- Distinguishing between nanoparticles produced by a particular process such as crushing of concrete and the exhaust fumes from the equipment being used in the process is also problematic (224).
- It is not always possible to distinguish between individual particles and those which are made up of multiple smaller particles aggregated together; or to identify nanoscale particles which are attached to a piece of the matrix which a nanomaterial was contained in.
- It may be difficult to distinguish between nano-objects which are engineered or manufactured, and those which are generated by the matrix itself (e.g. concrete).

Microscopy-based methods can be used to provide additional information, although these are difficult to perform unless there are high nanoparticle counts in a sample. Microscopy is essential to assess the presence of fibres as these cannot be easily measured by other means (211). Quantitative chemical analysis (e.g. XRF, ICPMS) of the airborne dust collected onto a filter for specific substances could also be useful when assessing nano-objects, providing they are metal-based and no other confounders are present.

Vaquero et al (211) recommend that a combination of mass concentration, particle number concentration and off-line analysis (including microscopy) are required to accurately assess exposure risk. The same paper suggests that where fibres are identified, control measures should be implemented to avoid exposure, regardless of the number of fibres found.

4.3.5. Qualitative risk assessment of nanomaterials

The measurement of nanoparticle release, as discussed above, is complex, and therefore is currently of limited use outside of research environments. Alternative, qualitative methods are therefore needed to support practical risk assessment and control in the workplace, in the absence of detailed data on toxicity and exposure. For example, control banding techniques enable tasks or processes to be identified as low, medium or high risk based on general principles and on the limited information available (255). This allows initial selection of control measures as well as prioritisation of risks which should be addressed first. Stoffenmanager Nano (205) is one such tool and is intended for use by non-professionals (256). It calculates risk using weightings according to parameters including particle size, material structure, frequency of task and room size. Generally, the tool recommends higher levels of control than those reached by expert evaluation (256,257). The tool is skewed to give priority to the hazard related factors, and therefore generally defaults to a high risk outcome in the absence of detailed knowledge about the nanomaterial involved (the common situation in construction).

NanoRisk Cat is a tool which classifies products according to the hazardousness of the materials they contain (in general terms) and the potential for exposure of consumers, professional users and those working in production (27, 31,181). This has been applied to around 1400 products in the Danish Nanodatabase (31). The tool is underpinned by a conservative and cautious approach, identifying almost all nanomaterials as high risk, including those which are typically contained in construction materials. For exposure it allocates a low score for nano-objects which are contained within a solid material (such as sports equipment made from carbon nanotubes in a composite). Medium exposure is predicted for products which have nano-objects bonded to the surface, and high exposure is anticipated where materials are in a liquid or powder form or where there is a potential for release e.g. if surfaces are sanded down or abraded. The majority of construction and demolition tasks (with the

exception of, for example, fitting of nano-enabled windows) are therefore likely to be classed as high exposure under this system.

A control banding system specific to the construction industry has been constructed as part of the Scaffold project, and will be available on line shortly (257). This is based on a development of the Stoffenmanager tool, and is being incorporated into a user-friendly spreadsheet format. Hazard data is built in, and will assign lower risk for materials such as amorphous silica and titanium dioxide than for fibres such as carbon nanotubes. However, the same limitations apply as for Stoffenmanager in that the risk level will inevitably default to a higher category in the many situations where there is incomplete data available. In addition, a nano-specific risk assessment process is only useful if the material user is aware that the product is a nanomaterial.

4.3.6. The precautionary principle

Application of the precautionary principle is recommended by some (such as the HSE in the UK) as being appropriate to risk management of nanomaterials and other novel substances. Unesco (258) has proposed a working definition for the precautionary principle as being that:

“When human activities may lead to morally unacceptable harm that is scientifically plausible but uncertain, actions shall be taken to avoid or diminish that harm.”

A UK government working group (Interdepartmental liaison group on risk assessment, (ILGRA)) identified that the principle should apply when there is good reason to believe that harmful effects might occur (even if the likelihood is remote) and if it is not possible to evaluate the risk based on scientific evaluation (259).

The EU has discussed the precautionary principle in terms of its importance at a regulatory level, considering that it underpins regulations such as REACH and the regulations on cosmetic products. The emphasis is on the need for proportionality when dealing with risk. Inevitably, a precautionary approach involves an element of judgment, and the ILGRA and others observe that a ‘weak’ or ‘strong’ approach might be taken, depending on the extent of risk avoidance that is favoured by those making the decision (who, depending on the context, might be individuals or regulators).

The HSE particularly advocates a precautionary approach to the use of CNTs or other materials with a high aspect ratio (such as nanoplates) (160). This is based on the evidence that harm might occur from (some) such materials. Protective measures are advised which include the use of LEV with HEPA filtration, keeping materials wet or damp where possible and using appropriate PPE. The guidance recommends respiratory protection to an APF (assigned protection factor) of 20 (equivalent to an FFP3 mask) if used in addition to other control measures. If there are no other control measures in place an APF of 40 or more is recommended, although this should happen only in exceptional circumstances.

The HSE guidance, which is generally concerned with laboratory environments rather than the more variable situations present in construction work, also recommends a precautionary approach in relation to other nanomaterials: but emphasises that:

- if small amounts of material are present, and there is a low likelihood of release, the risk is low; and
- the focus should be on the ‘real’ risks, those which are most likely to cause harm. Again, the emphasis is on proportionality.

These are important considerations for construction work, where many of the products used will contain relatively low proportions of nanomaterials, often in a stable form. It also highlights again the

importance of nanomaterial risk not detracting from the need to manage known high risk substances such as silica, diesel, and solvents.

4.3.7. Managing exposure in construction and demolition

Risk management in construction is already difficult because of the nature of the work, and in demolition there are added challenges due to the unknown provenance of the materials involved.

Additional risks from nanomaterials may be insignificant compared to the existing risks for example from silica dust and organic solvents. Where there are risks which cannot be eliminated by collective control measures, standard PPE including face fitted respiratory protection and appropriate gloves are likely to be adequate in most circumstances.

Construction presents particular risk management challenges, including tight deadlines and a high focus on cost control; the industry is historically seen as 'macho' (260) and typically has an itinerant workforce and a low standard of welfare and hygiene facilities (261). Work takes place in highly variable environments, which may be indoors or outdoors, which may change daily, and where there are already substantial health and safety risks to address. The ongoing high incidence of morbidity and mortality due to exposure to silica dust (which kills around 500 workers per year (262)) illustrates the scale of the difficulties.

There are further challenges in demolition, due to the difficulties of identifying the materials which are present in a structure. For example, from interviews in this research it was apparent that construction and demolition workers are confident of identifying materials which are likely to contain asbestos so that the necessary tests can be done and control measures put in place. However, there is no obvious way for them to identify whether nanomaterials are present in a structure. The health and safety file on buildings constructed under the UK's CDM regulations are required to list all hazardous materials in a structure but this is unlikely to include nanomaterials by default as little is currently known about them to classify them categorically as hazardous.

In many cases, the additional risks arising from the use of nanomaterials may be minimal compared to the existing risks of construction work. For example, the organic solvents used in many coatings are likely to be more toxic than any added nanomaterials (211). Similarly, the dust arising from work with concrete is already problematic, and may not be substantially worsened by the addition of some nanomaterials. In addition, existing control measures in place to protect against traditional hazards will often provide protection against nanomaterials.

Protective clothing and equipment

Collective control measures such as ventilation systems are rarely practical on temporary or outdoor sites. Control of airborne dust is usually through a combination of water suppression, maintaining distance (for example, during concrete crushing most workers will be fairly remote to the site of activity, or will be inside a cab) and the use of personal protective equipment (PPE). The wearing of PPE should be the last line of defence but is clearly very important in construction and demolition, and it is important that measures chosen are suitable for protection against nanoparticles and other nano-objects.

Overall, suitable respiratory protective equipment which is properly face fitted will protect against realistic levels of nano-objects in construction (215). If liquid nanomaterials are being used (for example, spraying coatings onto a surface) then a full face mask with a P3 filter should be used.

Otherwise, an FFP3 filtering half mask will provide a suitable level of protection. This is the same standard of mask which is recommended for protection against quartz silica and other hazardous materials in construction (262). The pores in such a mask are larger than the nanoscale particles and therefore do not act as a filter or sieve as might seem logical. However, they remain effective as the small particles are attracted to fibres by electrostatic and other forces (263-265). In fact, the smaller particles are more strongly attracted than larger ones, making many masks particularly good at filtering out the smallest particles. The particles most likely to pass through are those in the mid-range, typically between 40 and 100 nm (264). Even here, however, the penetration is relatively small, usually in the region of 5% provided masks are well fitted.

A higher level of protection should be considered if there is a risk of exposure to CNTs or other HARNs. For example, it was discussed in section 4.3.6 the HSE considers an FFP3 mask to be sufficient if used in addition to other control measures; but advises that a mask with an AOF of 40 should be used if uncontrolled airborne CNTs are present. Currently there is very limited availability of CNT-enhanced concrete. However, there is also very little research regarding the likelihood of fibre release if such products are broken down e.g. through the use of sanding or drilling. Hence, based on the precautionary principle, there must be an assumption that exposures could occur until there is sufficient evidence to the contrary. The safety data sheet supplied with the CNT-enhanced concrete which is currently being commercialised in the United States (and more recently in parts of Europe) states that there is no risk if the product is used as instructed (e.g. during the pouring of concrete). It also states that a mask with an APF of 50⁶⁸ should be used if airborne exposure is anticipated. There is no guidance on the level of protection required if the product is being broken-down e.g. during demolition.

There is also potential for dermal exposures to nano-objects in construction, particularly if incorrect gloves are used, or if they become damaged (39). The high incidence of skin damage and dermatitis in the industry further increases the risk as nanomaterials may be able to penetrate non-intact skin (220). It is therefore essential that suitable gloves are worn, replaced as appropriate and that they are the right size (222). Latex and nitrile coated gloves have been identified as providing good protection against nanoparticles in construction work (266). Nitrile coated gloves will additionally protect against abrasion. Non-woven clothing such as fleece is recommended for use if substances contain nano-objects, providing higher protection than woven fabrics for nanoparticles in aerosol form (267). Where a substance is being used in a liquid form (such as when using spray coatings) materials such as Tyvek are an effective barrier against nanoparticles (222,266).

⁶⁸ An APF 50 respirator in the US would equate to certain types of APF 40 respirator in the UK

5. Building on these findings

This section addresses the research objective:

to produce guidance for IOSH practitioners and industry stakeholders on nanotechnologies in the built environment

Key points

The question 'are nanomaterials hazardous?' is difficult to answer given the wide variability between different substances. The rapid development of materials and new uses for these, and the limited availability of published information from manufacturers further complicates the situation.

It is unlikely that legislative change will have a major impact on this in the short term. Improved clarity will only occur if manufacturers take action to share information more readily, and follow voluntary guidance to include more detail in safety data sheets regarding nanoparticles and other nano-objects. Action by nanomaterial manufacturers to design products and materials which are intrinsically safer is the best route to minimise any risks to workers in the long term.

The use of currently available nanomaterials is unlikely to significantly add to the risks already present for those working in construction. However, in the absence of detailed information, the following steps should be considered:

- robust management of existing health risks, which continue to be significant, notwithstanding any novel risks from nanomaterials;
- the use of a precautionary approach, extending the control measures already taken to protect against known risks to reduce exposures to those where less is known about toxicity;
- asking questions of suppliers and manufacturers regarding the exact content of new products. This is particularly important where fibres or plates may be present as the size and shape of these can influence risk profiles substantially; and
- recording the materials/products used (for example in the CDM file or through BIM) to facilitate decision making during subsequent refurbishment or demolition.

5.1. Overview of findings

This report has illustrated that there is no straightforward answer to the question 'are nanomaterials hazardous?' Although some may be problematic, others are likely to be considerably less so. There is wide variation between different substances and even between different forms of the same substance. Most of the products used within construction are based either on nanoscale films, or on nano-objects which are considered to be at the safer end of the spectrum (such as amorphous nanosilica particles). However, those which are of more concern (such as carbon nanotubes) are starting to be used more widely. This is a rapidly advancing area of technological development and the current, relatively benign situation with regard to health impacts should not lead to complacency.

Currently usage of nanomaterials in construction appears to be relatively low, with nano-enabled coatings and concretes accounting for 5% or less of their respective markets. Window glass (which is typically based on nanoscale films and does not contain nano-objects) appears to be the only nano-enabled construction product which has a substantial market share. Construction is reported to be a conservative industry and cost considerations certainly influence the adoption of new materials,

particularly at the lower end of the market. The need to ensure that buildings are safe and reliable and that products will last as predicted also encourages caution.

However, the costs of nanomaterials have fallen substantially in recent years and production is increasing. Intensive research increases the likelihood that barriers to widespread use can be overcome, such as the difficulties of dispersing carbon nanotubes within a medium. It is therefore likely that growth will continue and potentially accelerate, particularly in relation to the newer materials such as CNTs and graphene. These have historically been used only in specialist applications but are anticipated to be much more widely used in the future in many areas, including construction products.

Much of the information on where nanomaterials (particularly those which contain nano-objects) are used in construction is currently limited and opaque. The research for this report has found that nano-enabled construction products are often labelled incompletely; and safety data sheets lack details regarding the chemical and physical characteristics of nano-objects. This makes it difficult for those using them to carry out suitable and sufficient risk assessment; it also limits the scope for research to assess exposure to nanomaterials.

5.2. Learning from the past – the lessons of asbestos

Comparisons are often drawn in the literature between asbestos and some nanomaterials. There are physical similarities between asbestos and certain types of CNTs – long and needle shaped with the potential to cause fatal lung diseases. The comparisons also reflect anxieties about the potential consequences of introducing new ‘wonder’ materials without careful consideration of the long term impacts.

These concerns are clearly important, but the similarities between the materials do at least provide opportunities to learn from mistakes made in the past. The toxicity of asbestos was recognised by some in the late 19th century (268); and by the early 20th century those working with it were being refused health insurance (269). Epidemiological evidence of problems continued to be published through the middle part of the twentieth century (270,271), yet bans on the use of asbestos were not widely implemented until the 1980s, with a complete ban in the UK in 1999. The lateness of this action has been attributed to a range of factors including confounders such as the overlap in carcinogenicity between smoking and asbestos; the long latency of the diseases involved; and a failure to gather sufficient long term data to influence policy making (268,272). A key lesson to take away, therefore, is the importance of gathering robust evidence regarding health risks at an early stage and to ensure that such information is used to underpin decision making.

The delay in managing asbestos was not just a failure to appreciate the risks but also a disproportionate focus on the benefits: a Lancet article from 1967 argued that ‘it would be ludicrous to outlaw this valuable and often irreplaceable material in all circumstances (as) asbestos can save more lives than it can possibly endanger’ (Lancet, 1967). This highlights the need to strike a balance. CNTs are, like asbestos, a material with great potential which many are keen to take advantage of, but this perspective must not cloud judgements regarding safety aspects.

Hopefully, risk management can be achieved without banning or restricting the development and use of CNTs or other nanomaterials - there are other ways to address potential hazards including distinguishing between toxic and less problematic forms, and specifying how materials might be used, in what form and with what safeguards. ‘Safe by Design’ has been recognised as an important principle in safe construction and is increasingly being acknowledged as important for health. Designing nanomaterials for minimal risk is an excellent example of this. Toxicity can be reduced for example by making CNTs or graphene particles smaller. Other modifications such as the addition of particular chemical elements or molecules, attachment of particles to larger structures or improvements in the stability of nanoparticles within matrices can also reduce the potential for harm

(39). In principle, therefore, it should be possible to take advantage of the benefits of nanotechnology without suffering adverse consequences.

However, another lesson which asbestos has taught us is the need to remain vigilant and to continue to make smart decisions and to encourage others to do so. Despite the wealth of evidence on the toxicity of asbestos it is still actively mined and used in many countries such as India, China and Russia (273). In countries such as the UK where it is banned and robustly managed, exposures still occur – through ignorance, when tradespeople are working in domestic properties; and through the activities of rogue practitioners who fail to comply with regulations.

It is therefore important that appropriate measures are taken to manage the potential risks from nanomaterials on an ongoing basis. The next section will consider what these measures might be and where the responsibilities for them lie.

5.3. Government and manufacturer actions to manage nanomaterial risk

5.3.1. Legislation

A key theme in this research has been the lack of information available regarding nanomaterial use in construction products, largely because there is no legal requirement to make such information available. Such legislation is unlikely to be forthcoming at a European level; the European commission is continuing its ongoing discussion about extending REACH to improve the level of information available regarding nanomaterials (particularly nano-objects), but is expected to produce only a voluntary 'observatory' rather than a compulsory register.⁶⁹

Legislation may develop further in individual countries, such as that introduced by European member states France, Denmark and Belgium. The introduction of product registration in France and Belgium has reportedly improved the flow of knowledge, so that companies are becoming more aware that they are dealing with nano-objects and can manage the risks accordingly.⁷⁰ It is unclear whether this will increase the availability of information about nanomaterials more widely, especially in countries such as the UK which do not have specific legislation.

5.3.2. Manufacturing

Manufacturers do not need to wait for legislation to drive improved practice in terms of labelling and design of nanomaterials. For example, guidance exists on how to complete safety data sheets in respect of nano-enabled substances (52) although no examples of this being followed were found during the current research. If companies voluntarily followed such guidance and operated 'best practice', this would provide useful information for industry to support their risk assessments and would also facilitate research on the real world impact of the materials being used. Additional research on exposures to nano-objects as a consequence of real world use is particularly important, but is difficult to plan without a clear understanding of where the materials are being used.

Manufacturers need to ensure that they consider health risk at an early stage of product development and recognise it as a key factor alongside functionality and cost. For example, outputs from the European funded Nanoreg study have recommended that preliminary assessment of solubility, genotoxicity and immunotoxicity should take place at the earliest stages of nanomaterial development (274). This information can then be used to support decisions to either redesign problematic substances or to discontinue their development.

⁶⁹ <http://www.anec.eu/attachments/ANEC-PR-2016-PRL-001.pdf>

⁷⁰ https://chemicalwatch.com/48058/nano-registers-improving-information-along-supply-chain#utm_campaign=47992&utm_medium=email&utm_source=alert

5.3.3. Research

There are many areas where further research is needed to inform decision making with regard to the development and use of nanomaterials, particularly those which contain nano-objects.

Toxicity

Research is ongoing across Europe and the US to assess the toxicity of nanomaterials. The variability of nanomaterials and the speed with which new ones are being developed makes it difficult for such research to 'keep up', so efforts are also being focussed on improving understanding at a higher level – for example, developing 'read across' methods which enable informed decisions on the toxicity of new materials, based on their similarity to previous substances.

Safer by design

The development of 'safer by design' nano-objects is important to managing health risk, as discussed under Section 5.2 , and research to support this is ongoing (275).

Exposure and lifecycle research

Exposure research is urgently required which assesses the impact of real products in real scenarios. Such research would be made easier if products were better labelled and described by manufacturers.

Research studies which assess worker exposures to nanoparticles and other nano-objects during construction and demolition are currently few in number. Additional work is needed, and needs to be extended to consider the impacts of secondary materials (i.e. those based on recycled nanomaterials and recycled nano-enabled products) in terms of possible worker exposures. Research also needs to consider the lifecycle of newer products such as composites which may not be recycled through traditional routes.

5.4. Construction industry actions to manage nanomaterial risk

Given that detailed guidance and information is lagging behind the development of nanomaterials, constructors need to make pragmatic decisions to help manage any associated risks in the interim. Nanomaterials are already being used in construction products and are likely to become more prevalent. In the next few years they may also begin to be found in buildings which are being refurbished or redeveloped, so are of concern to those working in demolition as well.

5.4.1. Manage existing risk

Construction is, and always has been, a hazardous industry, and the use of most nano-enabled products is not likely to increase this substantially. For example, the presence of amorphous nanosilica and silica fume particles in concrete may not add significantly to the risk already present from respirable crystalline silica dust; and the organic solvents used in coatings are likely to be a more significant risk at application than the presence of nanosilica particles. The priority therefore must be to ensure that good practice is evident on all construction sites, managing risks from both existing and new materials.

5.4.2. Ask questions

Where new materials are being used with novel properties, construction professionals and those who supply them should become more inquisitive. They should be asking the questions of their suppliers and of the manufacturers: not just 'what substance is in this product?' but 'what size and shape is this

substance?’ In particular, users should be asking suppliers of novel products whether these contain nanofibres or nanoplates, particularly those which are longer than 5 µm in length.

5.4.3. Take a precautionary approach

Where new materials are being used, constructors should err on the side of caution. In the absence of evidence that nanomaterials are safe, action should be taken to avoid harm which could plausibly occur. In most cases this will be best achieved through managing existing risks such as dust and fumes through collective measures where possible (such as extraction or dust suppression) and the use of PPE where no alternative exists, or to provide secondary protection. Control measures which are effective against known hazards are likely to provide protection against many less familiar or unrecognised hazards (as discussed in section 4.3.7). In some cases, it might be appropriate to avoid using a particular material if sufficient evidence cannot be obtained to confirm its acceptability – this may be particularly relevant where products are believed to contain fibres (remembering that the fibres of concern are not visible with the naked eye).

5.4.4. Document what is used

The Construction, Design and Management Regulations (2015) require that all hazardous materials are recorded in the health and safety file, so that those working on buildings subsequently can manage any risks accordingly. Building products which contain nanomaterials will not automatically fall under this as they are rarely designated as hazardous. However, where nano-objects are being used (or unfamiliar products with novel properties which might indicate nano-enablement) this should be documented, for example as part of BIM processes or in the health and safety file. This is particularly important for products which may contain fibres. This will enable any necessary precautions to be taken in the future as better information about the potential toxicity of the materials used becomes available.

5.4.5. Develop and use shared resources

Although it can be difficult to identify nano-enabled products with certainty, there is a growing evidence base. Those responsible for risk assessment should ensure they are using the most up-to-date resources available to inform their decision making.

Two published resources are of relevance to construction. The first is the eLCOSH Nano website.⁷¹ This is an inventory of construction-enabled products which are believed to be nano-enabled, and highlights in each case any details which have been provided by the manufacturer. The site is focussed on the American market but many of the products are also available in the UK. The site is maintained by the CPWR (The Center for Construction Research and Training), who are also carrying out ongoing research into particle release from nano-enabled products during construction.

A second resource is expected as an output from Scaffold⁷², a European project into occupational risk management of nanomaterials in construction, which ended in December 2015. There are multiple research reports generated by the project, many of which have been referenced in this report. The project website reports that it will be publishing specific guidance for the construction industry in the form of a handbook and an electronic tool for risk assessment in late 2017.

⁷¹ <http://nano.elcosh.org/>

⁷² <http://scaffold.eu-vri.eu/filehandler.ashx?file=13742>

5.5. Strengths and limitations of this research

A key challenge in this research has been to gather accurate information regarding the use of nanomaterials: an early finding of the study was that such information is difficult to access, and that nano-enabled products are rarely labelled in a useful manner. Additional difficulties have stemmed from issues around commercial confidentiality. This has made it difficult to get information on the content of some products and also limited access to product samples where these are not available through traditional purchasing channels.

The main impact of this is a potentially incomplete view of the use of nanomaterials in construction: there may be nano-enabled products in use which the work has been unable to identify or recognise. It has also been difficult to distinguish between materials which are nanostructured or film-based; and those which contain nano-objects such as fibres or particles.

To overcome these difficulties, the research has combined data from multiple sources to determine what nano-enabled products are currently available and used within the construction industry. This multi-method approach, which has triangulated the academic literature with the information made available by manufacturers, and added to it by talking directly to manufacturers and to professionals working in the construction and demolition sectors, is a strength of the research. It has allowed the research questions to be addressed despite the limited and often contradictory nature of the available information. In addition, close liaison with researchers on other projects has allowed ongoing validation of the findings and overall conclusions.

A limitation of the research is the speed with which this field is developing - there is a risk that the current findings will be quickly out of date. It is therefore important that those working in construction are alert to new developments and that the subject is kept under ongoing review.

5.6. Concluding thoughts

Nanomaterials have much to offer the construction industry, and their use is expected to grow substantially in the future. If good practice and the right controls are in place and used correctly, for all existing hazardous substances in the construction industry, then the use of most currently available nanomaterials is unlikely to significantly increase the risk or require any additional control measures. Nevertheless, it is important that we balance the benefits and the opportunities for improved functionality with a degree of caution, particularly in light of the increased development and usage of CNTs. This includes an ongoing research agenda to improve knowledge and understanding, challenge to manufacturers and suppliers to provide more detailed information, and a questioning approach by the industry. This will enable us to continue making well informed judgements to protect the workforce in the longer term.

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Appendix – results of materials testing

1. Introduction

This appendix summarises the findings of laboratory testing of construction products, carried out as a separate strand of this research project.

Product types chosen for testing were concretes, coatings and insulation materials – these are common construction materials which are produced in nano-enabled forms. Specific product choice was influenced by:

- the experience of the laboratory team involved, to take full advantage of their expertise and to focus on areas of most concern; and
- availability - products were purchased through normal commercial routes or were obtained as samples from manufacturers or suppliers. Where suitable product samples were not available, test materials were created in the laboratory to allow testing to proceed. This enabled the research to consider risks from products which are not yet widely available on the open market.

Further details regarding this laboratory research can be found in the report: "Identification of nanomaterials and assessment of nanoparticle release", available from Loughborough University (contact a.g.gibb@lboro.ac.uk or m.song@lboro.ac.uk)

2. Testing methods

This research was conducted from a materials perspective, focusing on the structure and content of particles present and released. The laboratory procedures available and included in the research proposal were not able to measure the specific quantities of particles released. The following were the main techniques involved:

- Microscopy was used to generate images of materials and released particles at a high resolution. Techniques used included optical microscopy, transmission microscopy, and scanning electronic microscopy.
- Energy-dispersive X-ray spectroscopy (EDX, also known as EDS) was used to provide information about the elemental composition of the samples i.e. what substances they contained.
- A Malvern Mastersizer was used to assess the size of released particles i.e. to establish if they were at the nano-scale. Released debris was added to a liquid medium and light diffraction was used to assess the distribution of particle sizes.

3. Main findings

3.1. Aerogel insulation products

Testing was aimed at:

- identifying the nanomaterials contained in a selection of aerogel materials; and
- assessing likely particle release from these.

3.1.1. Nanoparticle content of aerogel

Four samples of proprietary aerogel blankets were purchased and examined using electron microscopy and spectroscopy. The majority of particles found in the materials were of a micron-scale and only a small number of nanoparticles were found. The main material was silicon dioxide. This supports the manufacturers' literature for these materials which typically reports them to be silica aerogels; and to be based on nanostructured materials rather than nanoparticles (see Figure 2 in the main report for an explanation of these terms).

3.1.2. Particle release from aerogels

The samples were cut into pieces, as they might be during installation, and were placed in a chamber with variable air flow to assess particle release (by measuring weight loss from the samples). Figure 1 shows that there was a variation between the different products in the amount of particle release over time, with one of the products releasing a much higher amount of “dust” than the others. Microscopy of released particles from all products showed these to be generally micron rather than nano-sized (Figure 2).

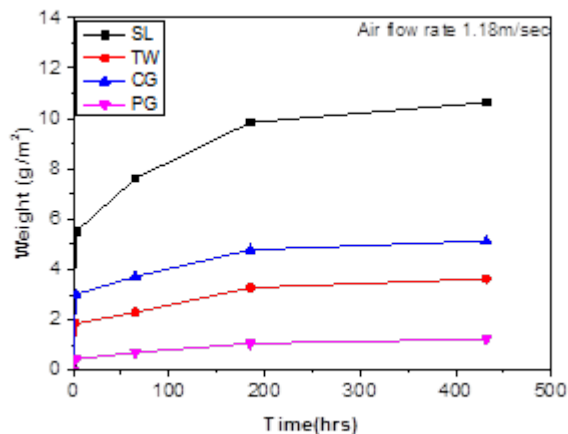


Figure 1 Weight lost per square metre vs time for aerogel-based insulating materials (air flow rate 1.18m/sec)

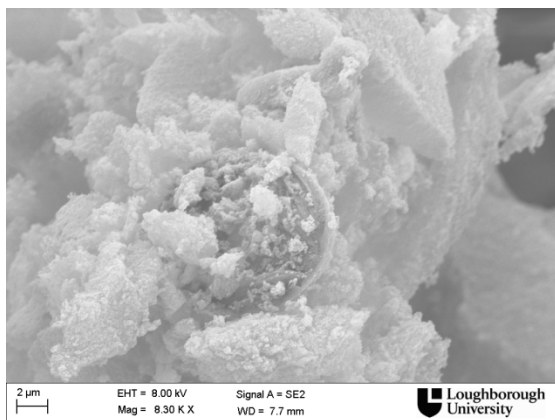


Figure 2 SEM image of particle (probably silica) released from aerogel

3.2. Concrete

Testing was aimed at:

- identifying the presence of nanoparticles in a selection of concrete samples; and
- assessing likely particle release.

Materials were provided by four manufacturers. Most were samples of silica fume concrete, supplied as blocks of cured concrete. One sample of nanotitanium-enhanced concrete was produced in our own laboratory using a proprietary mix.

In addition, a concrete composite containing Carbon Nanotubes (CNTs) was produced in the laboratory.

3.2.1. Nanoparticle content of concrete

The majority of particles observed were micron sized silicon dioxide (silica); a very small number of silica nanoparticles were seen (see Figure 3). In addition, a small number of titanium nanoparticles were seen in the titanium-enhanced concrete.

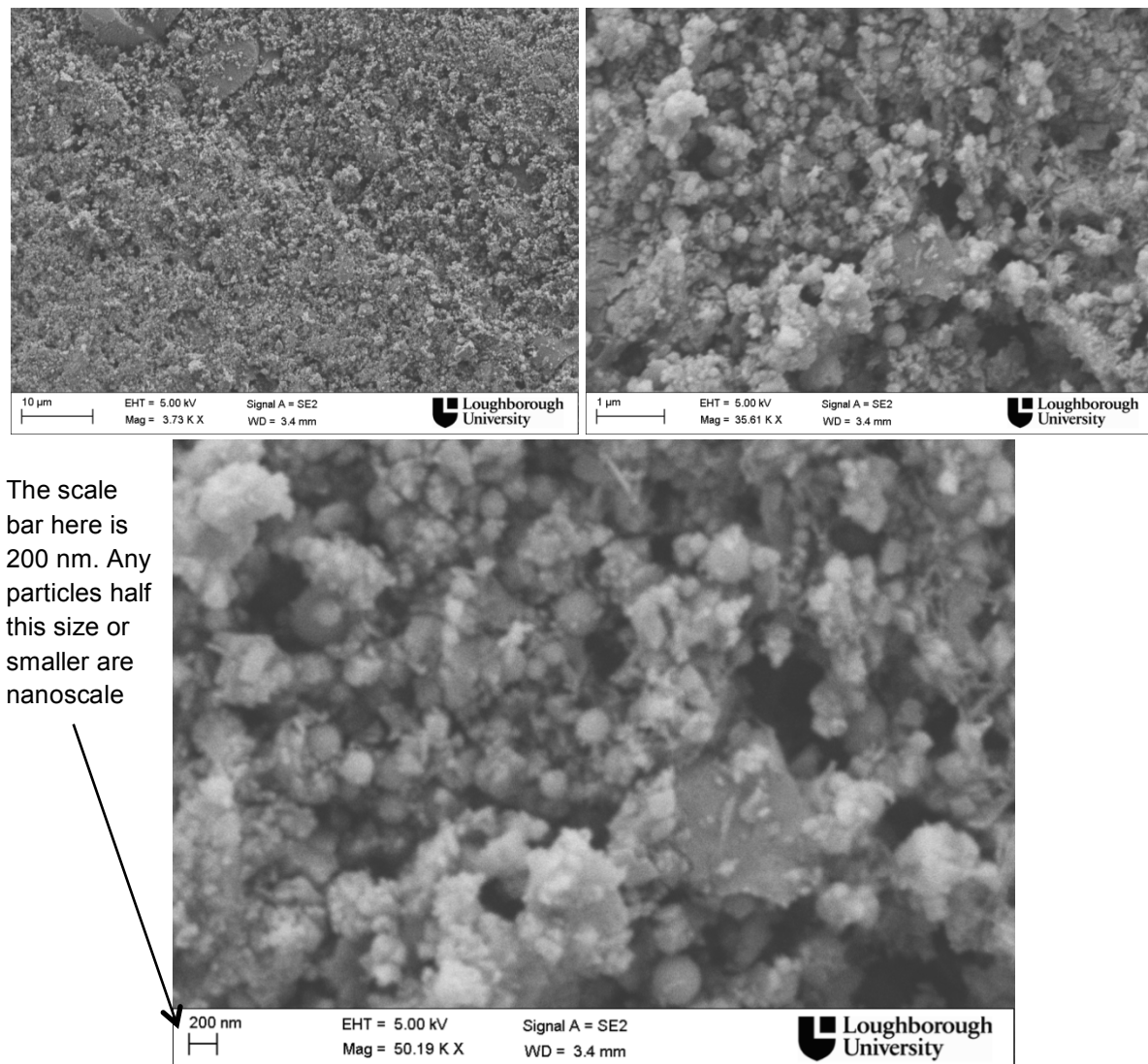


Figure 3 SEM images for silica fume concrete with different amplified scales

3.2.2. Particle release from concrete into water

Concrete samples were submerged in water, which was then agitated (to simulate the impact of rain on concrete). The particles released were collected and analysed. None of these were found to be nanoscale (see Figure 4). SEM analysis showed that any nanoparticles present remained embedded in the matrix even after breakdown and particle release.

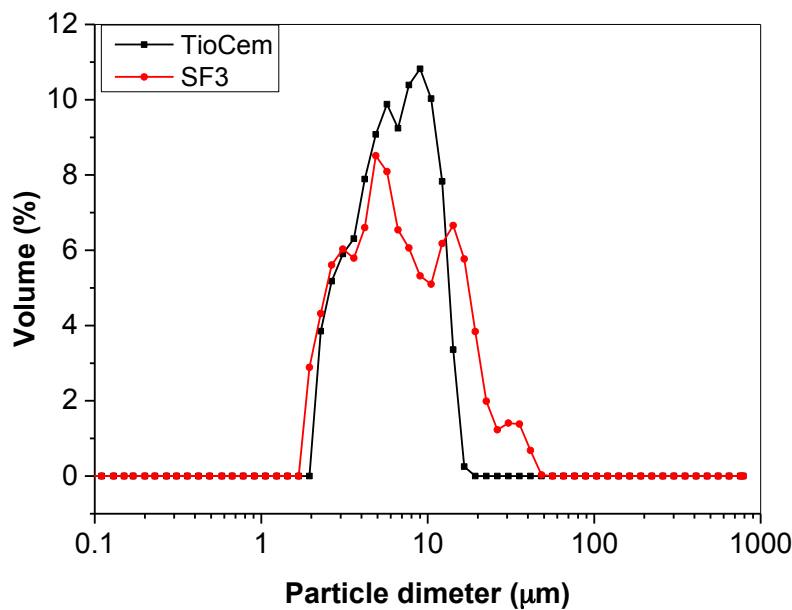


Figure 4 Particle size and distribution of silica fume (G627-SN) and nanotitanium (TioCem) concrete powder, released by agitation in water

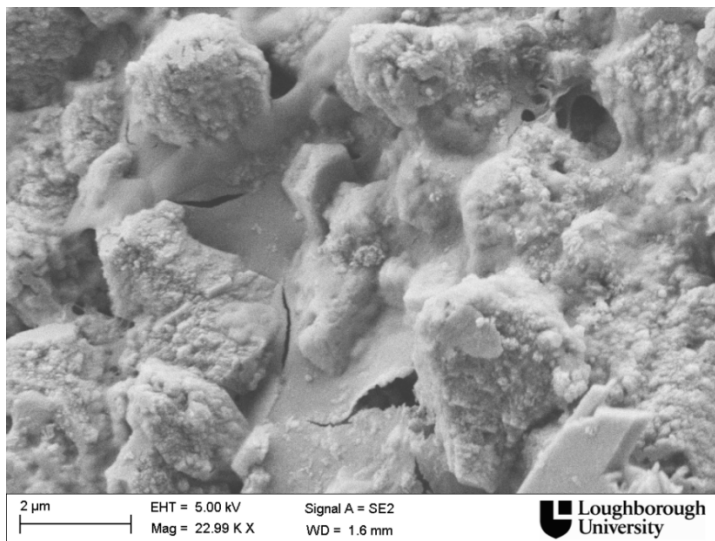


Figure 5 SEM images of silica fume concrete powder, showing embedded nanoparticles

3.2.3. 'Demolition' techniques applied to concrete

To mimic the demolition of concrete, two samples were drilled using a diamond tipped corer, with water running over the surface. The run-off water was collected, dried out and the particle size of the dust assessed. One sample was a standard concrete, the second was a silica fume concrete. As Figure 6 shows, the particle size of the released dust was similar for the ordinary concrete and the silica fume concrete. A small proportion of the dust released by the breakdown of both the normal and the silica fume-enhanced concrete is nanoscale.

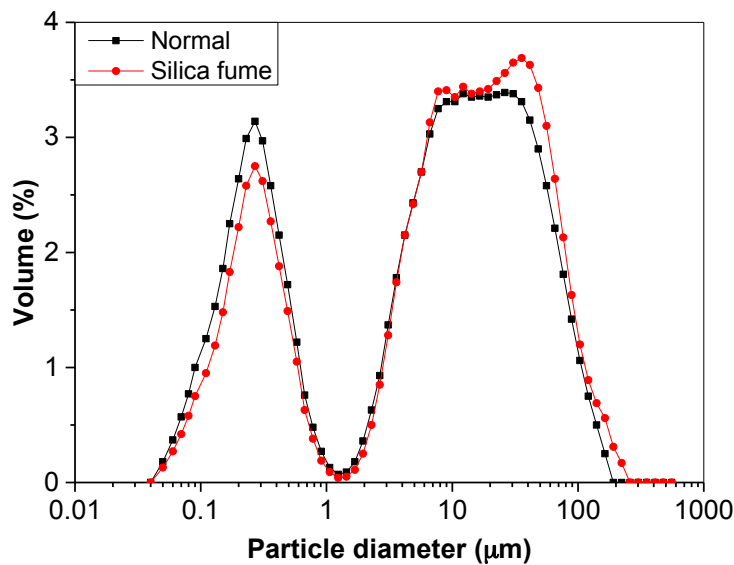


Figure 6 Size and distribution of dust released on the breakdown of standard concrete and silica fume concrete

This test was 'proof of concept' only; more in-depth testing would be required to confirm these findings with a wider range of concrete samples.

3.2.4. Breakdown of CNT-enhanced concrete

A concrete composite sample containing MWCNTs was prepared (a proprietary CNT-enhanced concrete mix was not available, although such a product is in the early stages of commercial use). The sample was broken down by grinding it with steel balls in a ceramic container at 60 cycles per minute. As Figure 7 shows, the CNTs were no longer visible after grinding for 48 hours.

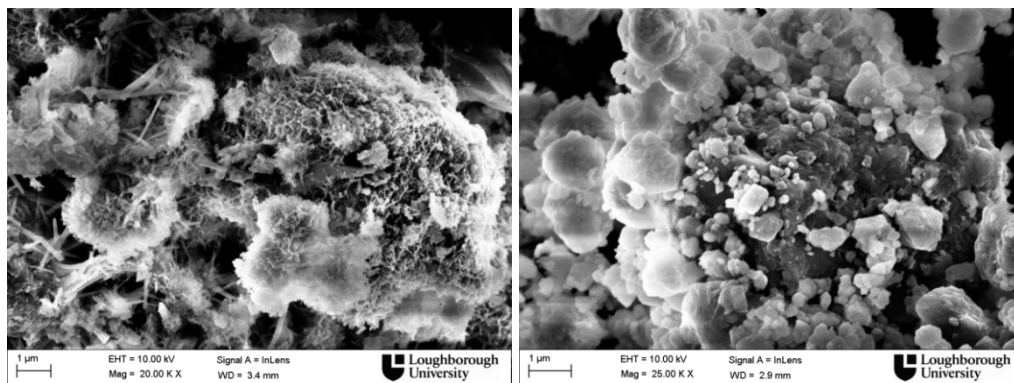


Figure 7 SEM images of the concrete/MWCNTs composite with 1wt% MWCNTs treated by ball milling as prepared and after 48 hours

In addition, CNTs (without concrete) were ground using the same milling process. It was found that the CNTs were broken down into shorter lengths, so that average CNT length fell from 50 μm to about 10 μm. Hence the likely explanation for the 'disappearance' of the CNTs in the concrete sample (as shown in Figure 7) is that they had been broken down.

A sample of concrete-CNT composite was added to water and agitated. The particles released were examined by electron microscopy. Released particles had visible MWCNTs in the matrix, although no free MWCNTs were seen, as shown in Figure 8.

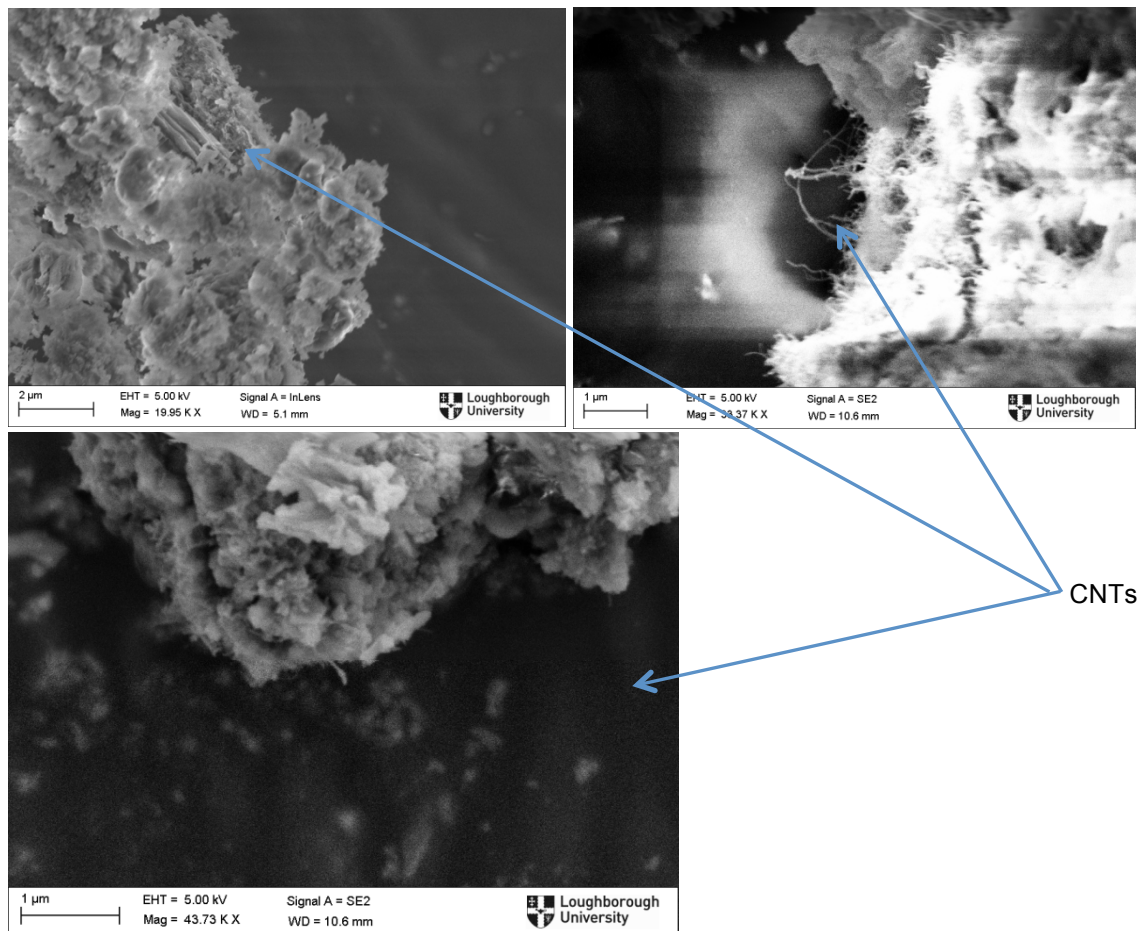


Figure 8 SEM images of particles released from the surface/subsurface of the concrete/MWCNT nanocomposite

3.3. Coatings

Testing was aimed at:

- identifying the presence of nanoparticles in a selection of coating samples; and
- assessing likely particle release from these.

Three samples were obtained. In each case the coatings had been applied to the substrate (glass or metal) during manufacture.

3.3.1. Nanoparticle content of coatings

The three manufacturer coatings were silica-based, with or without nickel. Very few nanoparticles were visible.

3.3.2. Nanoparticle release from coatings

Scratch testing was carried out on the three manufacturer-coated samples. In all three cases, the materials scratched off in the form of a film (see Figure 9); there was no evidence of particles being released. The total materials content of the film was 14-30g/m², indicating that the materials were a very thin film.

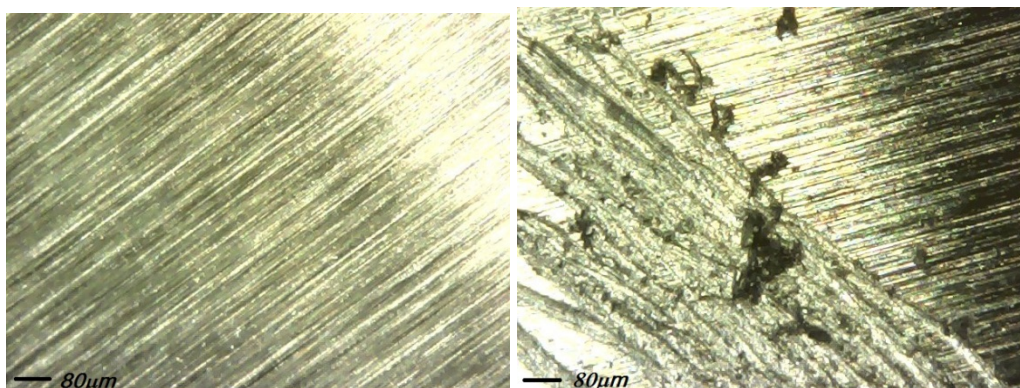


Figure 9 Images of optical microscopy of the scratched surface of a manufacturer applied coating

These findings relate only to sol-gel coatings applied by the manufacturer. The outcomes of testing for coatings applied by the user may be different depending on whether such coatings actually contain nanoparticles.

3.4. Polyurethane Coatings

This testing was aimed at assessing the potential for release of CNTs from a polyurethane composite, during simulated ageing. A sample was prepared which contained polyurethane with and without the addition of 3% MWCNTs (as a proprietary product was not available for testing, although a small number of such products are available commercially for specialist use).

3.4.1. Nanoparticle release with ageing

The sample was aged for 30 days at 120°C, which equated to 20-30 years of environmental ageing. Fragments were taken from the surface of the coating at various stages using scotch tape. As the material was aged, these fragments were increasingly seen to contain CNTs, as shown in Figure 10.

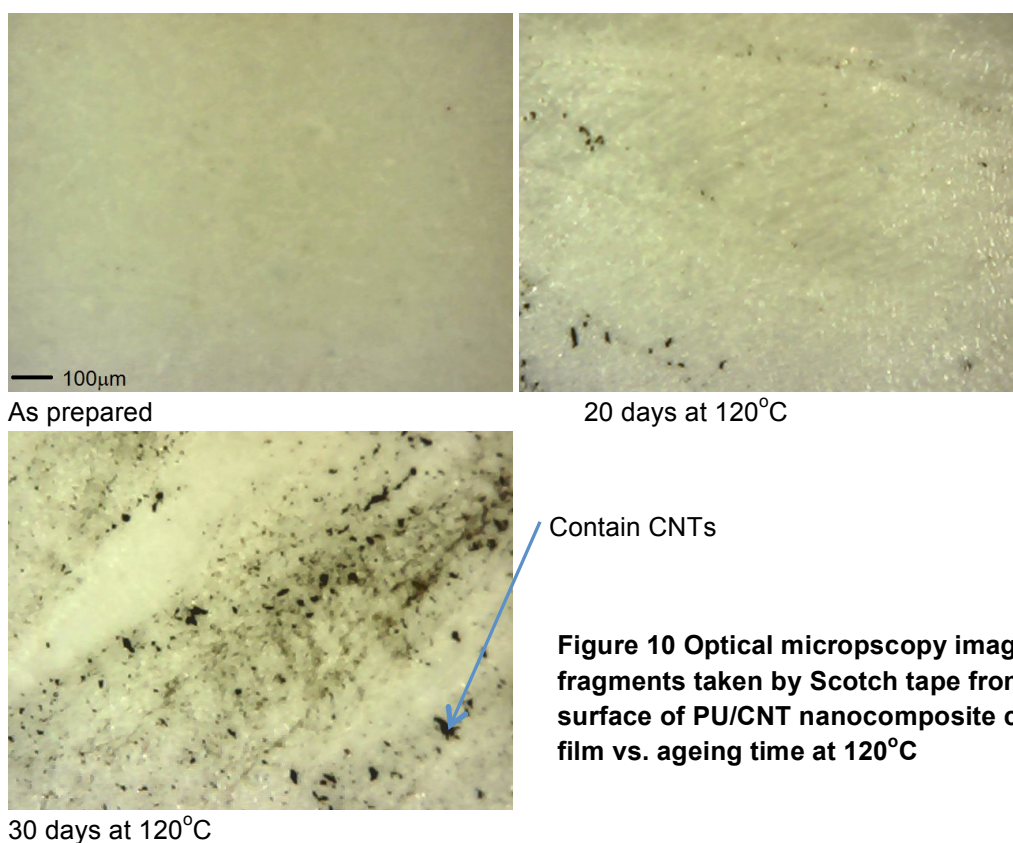


Figure 10 Optical microscopy images of fragments taken by Scotch tape from the surface of PU/CNT nanocomposite coating film vs. ageing time at 120°C

This indicates that weathering of materials increases the likelihood of CNTs being released. The CNTs were still attached to elements of the PU matrix, as shown in Figure 11, rather than being found as free fibres.

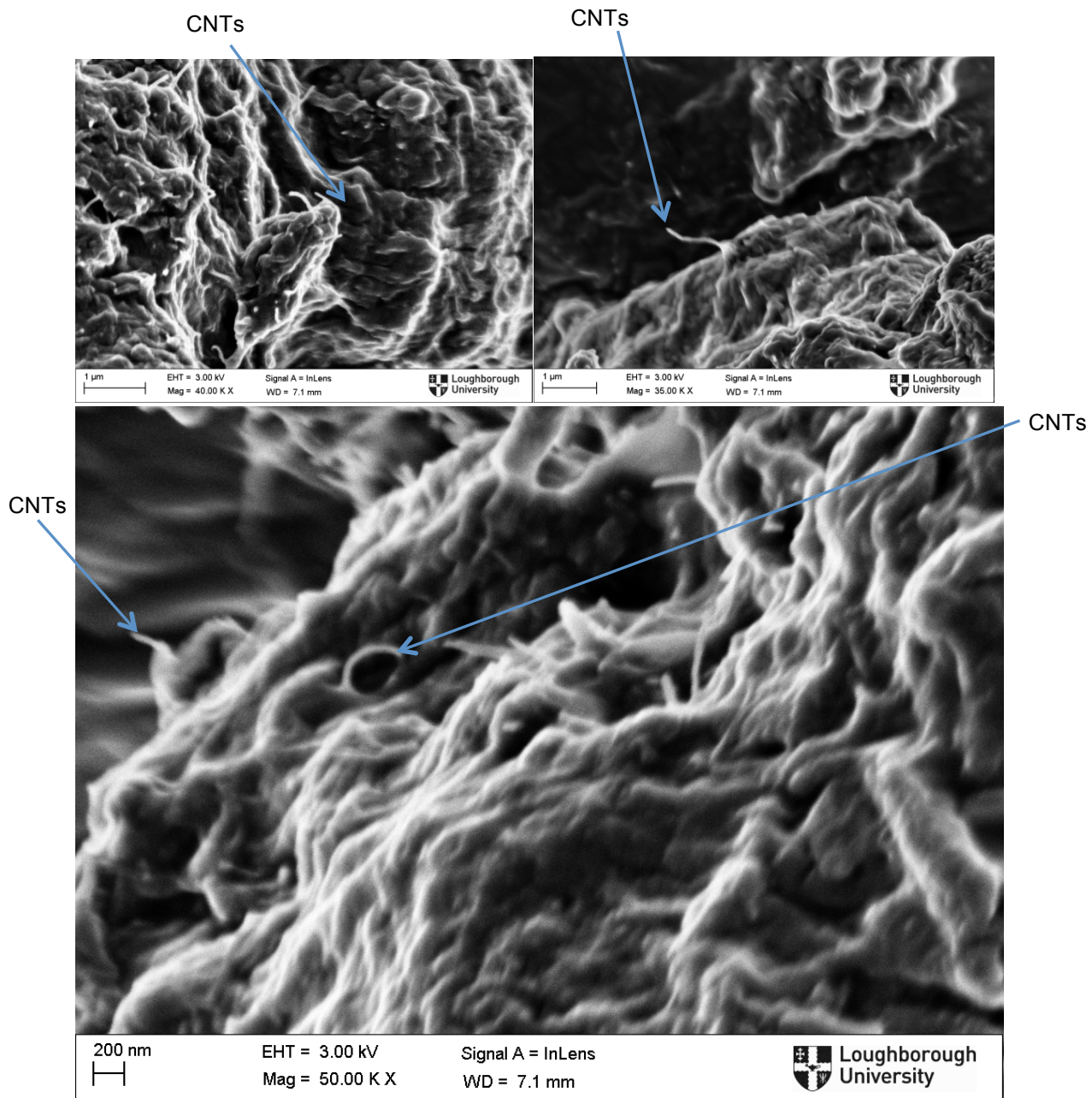


Figure 11 SEM images of fragments taken with Scotch tape from the surface of PU/CNT nanocomposite coating film, aged for 30 days at 120°C

4. Summary

Overall, very few nanoparticles were seen in the samples of silica fume concrete, aerogel insulation and manufacturer-applied coatings which were studied in this research. Samples were tested with methods similar to those which might be used in construction or demolition: for aerogels the particles released were mostly micron sized and for coatings, release was in the form of a nanoscale film rather than particles.

Laboratory produced samples of concrete with CNTs and polyurethane coatings with CNTs were prepared as manufacturers' samples were not available, although similar products for construction are known to exist. CNTs were found in dust which was washed off from the surface of the concrete when

the sample was immersed in water. When the CNT-enabled concrete sample was ground down, as it might be during demolition, the CNTs were broken down by these processes into shorter lengths, with the potential for release.

When CNT-enabled polyurethane coating was aged using heat, CNTs were visible in fragments gathered from the surface of the sample.

The testing undertaken with CNTs in concrete and polyurethane found the CNTs released to be embedded in particles of concrete and PU matrix, rather than being free fibres. However it was not possible to rule out the likelihood of free fibre release with a combination of machining or other construction/demolition processes together with ageing and weathering. Further research in this area is recommended.

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