Report of

Nanomaterials
Health and Safety Updates

Prepared for

The Refractories Institute

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Introduction

Nanomaterials are materials with at least one dimension smaller than 100 nanometers (1 nanometer is 1 millionth of a millimeter), about the size of a virus particle. They occur naturally, as a by-product of some man-made activities, and can be intentionally engineered. It is the final category that has seen explosive growth, as governments and private companies invest in research and manufacture nanotechnology-based products that impact electronics and communication, textiles, refractories, food and medicine, and more.

While the development and use of nanotechnology has been explosive, very little is known about the safety impacts and potential long-term health effects that may result from workplace exposure. This paper will explore what and where nanomaterials are, potential safety concerns and health effects from exposure, and current regulations / best practices that should be followed to protect workers.

What are nanomaterials?

Scientists generally agree that nanomaterials are tiny particles with at least one dimension measuring less than 100 nanometers.[1] Nanomaterials have unique optical, magnetic, and electrical properties that are commercially useful in electronics, cosmetics, medicine, refractories and textiles.

In general, all particles have different physical and chemical properties at the surface as compared to the bulk material. Nanomaterials are special because they have a large surface area compared to the total volume. Lower chemical bond energy levels and shorter bond lengths at the surface mean that some reactions involving nanomaterials can occur more rapidly and at lower temperatures. Refractory products are benefiting from advances in nanotechnology, as they can be made lighter and stronger by incorporating nanomaterials.[2]

Where are nanomaterials found?

There is no single type of nanomaterial. Nanomaterials exist naturally, such as blood borne proteins and lipids. They also can be created as incidental by-products from thermal decomposition, such as particles from diesel fuel combustion, carbon black generated by the incomplete combustion of heavy petroleum products, or microsilica generated during the production of silicon and ferrosilicon alloys. Engineered nanomaterials can be created from nearly any chemical substance and can differ with respect to their composition; particle size, shape and bonds; and surface coatings. The engineered nanomaterials are intentionally designed to take advantage of features presented by the nanoscale size of the particle.

[1] National Institute of Environmental Scientists: NIH. Nanomaterials

[2] Salomao, R., Souza, A.D.M., Fernandes, L., Arruda, C.C. American Ceramic Society Bulletin (2013) Vol 92 No 7 pp 22-27. www.ceramics.org

Nanoparticles are used in refractories to create denser and stronger structures and products. For example, as additives during mixing-casting, the very small particles fill in the spaces between all the larger particles, resulting in a denser final structure. In another example, as binders, the nanoparticles incorporate even smaller colloidal binders, which have strong chemical bonds and can replace conventional hydraulic binders, resulting in a stronger structure. The physicochemical properties of nanomaterials provide increasing opportunities to create new alloys, compounds and composites with improved structural integrity. Table I lists different types of nanomaterials and their origin.

TABLE I – Examples of Nanomaterials and Origin

Naturally Occurring	Man-Made - Incidental	Man-Made - Engineered
Smoke particles from forest fires	Smoke particles from cooking	Carbon - Nanotubes
Volcanic ash	Diesel exhaust	Semi-conductors - Quantum dots
Viruses	Particles in welding fumes	TiO2 in Sunscreen pigments
Bloodborne proteins	Sandblasting	Colloidal silica / colloidal alumina

Most nanoparticles are free-flowing, but some agglomerate into larger particles due to their high surface energy. The agglomerated nanoparticles may still have at least one dimension < 100 nm.

Do nanomaterials present any health or safety risks?

The properties that make nanomaterials so beneficial in product development, such as their size, shape, high reactivity and other unique characteristics, are the same properties that cause concern about safe handling of the particles and the nature of their interaction with biological systems.[1]

Health

Nanotechnology is still very new, and very few health studies have been performed to determine the possible health risks from exposure. Until more toxicological information is known, scientists and EHS professionals must leverage information and experience from other small particles, such as asbestos, diesel exhaust or welding fumes. [3]

The most likely exposure route for workers is inhalation. A number of forces determine the ultimate deposition of inhaled particles, but a general breakdown can be made depending upon the particle size:

- **Inhalable:** Particles > 10 microns < 100 microns are inhaled, may be heavy enough to be deposited within the mouth and nose, and then ingested when mucous is swallowed.

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[3]The Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR): European Commission.2009. ec.europa.eu/health/scientific_committees/opinions_layman/nanomaterials/en/

- **Thoracic:** Particles > 4 microns < 10 microns are inhaled past the nose and mouth and are deposited within the pulmonary airways (trachea and bronchi).
- **Respirable:** Particles < 4 microns are small enough to reach the pulmonary alveolar region where gas exchange occurs. Nanoparticles are included in this class of particles. Additionally, their small size may allow them to leave the lungs and enter the bloodstream and relocate to other organs or organ systems.

Other potential exposure pathways for nanomaterials are dermal and ingestion. Nanoparticles have been used in medicine in wound dressings and ingested to be used as delivery agents for drugs. Early studies confirm that the nanoparticles have been able to translocate to other organ systems.[4]

An additional health concern is the potentially rapid conversion of one chemical ion into another one more hazardous, either before or after worker exposure occurs. For example, can the increased reactivity of nanoparticles allow a more rapid and unwanted conversion of trivalent chromium to a much more toxic hexavalent chromium? More information is needed to clearly explain the potential impacts of nanoparticles on biological systems.

Safety

Smaller particles are known to be more energetic due to their large ratio of surface area to particle volume. Aluminum powder is commonly used in the refractory industry and in the micron scale is known to be explosive. Reaction rates are higher for nanoparticles than micron particles, and sensitivities are much lower. A study that compared friction and impact sensitivities of nano versus micron particle sizes of tungsten (IV) oxide mixed with aluminum showed increased impact sensitivity, and much higher friction sensitivity and rates of combustion at the nanoscale.[5] Results are reported in Table II.

TABLE II – Sensitivities for nano vs micron Al/WO_3 thermite[5]

Al diameter (nm)	WO_3 diameter (nm)	Impact (J)	Friction (N)	Combustion rate (m/s)
1912	724	>49 (insensitive)	>353 (insensitive)	<0.08
51	50	42 (insensitive)	<4.9 (very sensitive)	7.3

[4] OSHA Fact Sheet: Working Safely with Nanomaterials. https://www.osha.gov/Publications/OSHA_FS-3634.pdf

[5] Piercey, D., Klapotke, T., Nanoscale aluminum – metal oxide (thermite) reactions for application in energetic materials. *Central European Journal of Energetic Materials,* 2010, 7(2), 115-129.

What EHS regulations govern nanomaterials?

Nanotechnology is a rapidly emerging field, and while regulatory bodies around the world are studying the health and safety aspects of nanomaterials, few regulations have been promulgated. Also, while occupational exposure limits have been established or recommended for some widely used substances, it is important to understand that these established exposure limits for larger particles don't necessarily apply to nanoparticles of the same substance. OSHA has recommended following the National Institute of Occupational Safety and Health (NIOSH) Recommended Exposure Limits (REL) for carbon nanotubes and carbon nanofibers and nanoparticles of titanium dioxide.[6] Table III illustrates how the exposure limits for larger particles and nanoparticles can vary.

TABLE III – Exposure Limits of Large Particles versus Nanoparticles

Substance	OSHA PEL – large particles	OSHA recommended limit – nanoparticles
Carbon black	3.5 mg/m^3 8-hour TWA	1.0 µg/m^3 8-hour TWA carbon nanotubes and nanofibers
Titanium dioxide	15 mg/m^3 8-hour TWA As total dust	0.3 mg/m^3 8-hour TWA

The United States Environmental Protection Agency (EPA) issued a Nanotechnology Reporting and Record-keeping Requirements Rule, effective August 14, 2017. This rule establishes one time reporting and record-keeping for nanoscale chemical substances that are manufactured or processed. The rule is designed to gather data on nanomaterial use that may inform future employee health and safety programs, regulatory decisions and product development.

How can employers manage worker exposures to nanomaterials?

To summarize the discussion in the previous sections:

- Nanomaterials are tiny particles with at least one dimension < 100 nanometers;
- Nanoparticles are desirable in multiple industries because they have a large surface area to total surface volume ratio, providing more of the unique physicochemical properties per particle that exist for larger particles.
- The unique physicochemical properties that make nanoparticles desirable in industry are the same properties that may present health and safety risks to workers.
- Nanotechnology is growing rapidly and very few regulations govern their use or limit employee exposures.

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[6] Introduction to Nanotechnology and Occupational Health.
https://www.osha.gov/dte/grant_materials/fy10/sh-21008-10

Given all of the above, it can be difficult for an employer to know how to protect employees who work with nanomaterials. Because there is insufficient data pertaining to the toxicity of engineered nanomaterials, it is prudent to protect employees from exposure to these particles until there is clear proof that they are not hazardous. OSHA recommends assessing the potential for worker exposures to nanomaterials, and then protecting employees through a combination of engineering and administrative controls plus personal protective equipment. A discussion of each step follows.

1. Assess Potential Exposures (Risk Assessment)

As previously mentioned, nanomaterials can exist naturally, can be man-made as a by-product from other activity, or can be engineered. It is the last category that represents the majority of new nanomaterials. To assess whether nanomaterials are present in the workplace, employers should include consideration of nanomaterials as a component of a workplace assessment; however, special considerations should be used to accurately assess exposure potential to nanomaterials.

First, the assessment should include whether any smokes, fumes or dust clouds are generated as a result of other on-going activities (*Incidental* category of nanomaterials). To assess whether *Engineered Nanomaterials* are present in the workplace, employers can request that their suppliers of raw materials provide notification if their products contain any unbound nanomaterials. Safety Data Sheets may list nanomaterials specifically but there is currently no requirement to list nanomaterials unless there is a specific chemical hazard classification or occupational exposure limit.

The World Health Organization (WHO) recently published guidelines recommending that hazard classes be assigned to engineered nanomaterials under the GHS classification system, but it will take some time for that recommendation to be considered and universally implemented.[7] In the meantime, the WHO Guideline Development Group (GDG) assigned some GHS hazard classes to engineered nanomaterials by evaluating toxicity data collected and reviewed by the Organization for Economic Cooperation and Development (OECD) and reported in specific nanoparticle dossiers. The results of their classifications are included in the WHO Guidelines report; a photograph of their Table is shown in Figure 1.

The Risk Assessment should also consider workflow, number of workers and tasks, quantities and duration of materials handled, effectiveness of controls, and quantitative monitoring results, if available. By understanding the potential GHS hazard classifications for these materials, employers can begin to understand the rigor level of controls that must be employed to control exposures.

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[7] WHO guidelines on protecting workers from potential risks of manufactured nanomaterials. Geneva: World Health Organization; 2017. Licence: CC BY-NC-SA 3.0 IGO.

TABLE 2. CLASSIFICATION OF HAZARDOUS PROPERTIES OF NANOMATERIALS (MNMS) THAT HAVE AN EXISTING OECD DOSSIER

MNM	Acute toxicity	Skin corrosion/ irritation	Serious eye damage/eye irritation	Respiratory or skin sensitization	Germ cell mutagenicity	Carcinogenicity	Reproductive toxicity	Specific target organ toxicity (single exposure)	Specific target organ toxicity (repeated exposure)
Fullerene (C_{60})	No[a]	No	No	No	No	No data[b]	No data	No data	No
SWCNT	No	No	No	No	Cat 2B[c] (L)[d]	No data IARC[e] 3	No data	No data	Cat 1 (L)
MWCNT	No	No	Cat 2A (H)[g]	No	Cat 2 (H)	MWCNT-7: Cat 2 (M)[f], IARC 2B Other MWCNTs: IARC 3	No	No data	Cat 1 (M)
AgNP	No	No	No	Cat 1B (M)	No	No data	No	No data	Cat 1 inhalation (H) Cat 2 oral (H)
AuNP	No data	No data	No data	No data	No data	No data	No data	No data	Cat 1 inhalation (H)
SiO_2	No	No	No	No	No	No data	No	No data	Cat 2 inhalation (H)
TiO_2	No	No	No	No	No	No data; IARC 2B	Cat 2 (L)	No data	Cat 1 inhalation (H)
CeO_2	No	No data	No data	No data	No data	No data	No data	No data	Cat 1 inhalation (M)
Dendrimer	No data	No data	No data	No data	No data	No data	No data	No data	No data
Nanoclay	No data	No data	No data	No data	No data	No data	No data	No data	No data
ZnO	No	No	No	No data	No	No data	No	No data	Cat 1 inhalation (M)

AgNP: silver nanoparticles; AuNP: gold nanoparticles; CeO_2: cerium dioxide; MWCNT: multi-walled carbon nanotubes; SiO_2: silicon dioxide; SWCNT: single-walled carbon nanotubes; TiO_2: titanium dioxide; ZnO: zinc oxide.

[a] No: no hazard class assigned based on data.

[b] No data: no studies available in OECD dossier.

[c] GHS categories: Cat 1 usually implies serious and/or irreversible damage; Cat 2 milder or reversible damage. Within a category A implies more serious and B milder damage.

[d] L: low level of evidence.

[e] IARC refers to the International Agency for Research on Cancer categories of confidence in carcinogenicity: IARC Cat 2B = possibly carcinogenic; IARC Cat 3 = not enough evidence to draw conclusion.

[f] M: moderate level of evidence.

[g] H: high level of evidence.

Figure 1 – WHO GHS Classification of Manufactured Nanomaterials (MNMs)[6]

Traditional IH monitoring techniques may not be effective for measuring airborne nanoparticles if there isn't enough mass to be accurately detected. NIOSH has developed a process that uses a combination of techniques to measure airborne nanomaterials. The NIOSH process is called NEAT: Nanoparticle Emission Assessment Technique. The process calls for an initial measurement using particle counters, followed by source and personal samples collected onto filters using very high flow rates (7 L/min). Particle analysis is completed using electron microscopy.[8]

2. Apply Engineering Controls

Best industry practice is to apply the hierarchy of controls to limit worker exposure. The first two steps within the hierarchy of controls are (1) eliminate the hazard; (2) substitute the hazardous agent for a less hazardous one. In the field of engineered nanomaterials, elimination is unlikely; substitution might be used to the extent that material with a lower tendency toward aerosolization could be used. The

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[8]Kreider, M.L., Burns, A.M., DeRose, G.H., Panko, J. M., Protecting Workers from Risks Associated with Nanomaterials: Part 1, Exposure Assessment. *Occupational Health & Safety,* 2013.

next level of controls is engineering controls. Engineering controls are exposure control measures that work independently of worker involvement. Engineered nanoparticles are typically manufactured in very well controlled conditions in order to protect the product. The safeguards that protect the product also serve to protect workers.

Examples of engineering controls include closed cleaning processes and dust suppression techniques, filtered isolation rooms or glove boxes, and filtered local exhaust ventilation at the source of emission. High-Efficiency Particulate Air (HEPA) filters are capable of trapping 99.97% of particles that are 0.3µ Median Mass Aerodynamic Diameter (MMAD). HEPA filters trap particles using a combination of mechanisms: impaction, interception, and diffusion, as shown in Figure 2.[9]

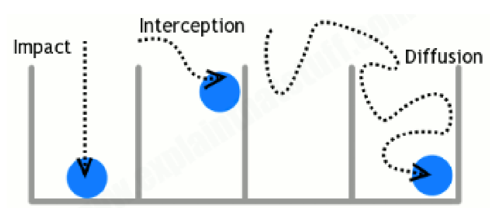

Figure 2. Mechanisms of particle capture. Impaction captures particles that crash into the filter media. Interception is when a particle moving in the airstream is 'snagged' by a filter fiber. Diffusion captures particles moving at slower air speeds when particles collide and are pushed into the filter media.

Particles at 0.3µ are the most penetrating (hardest to capture); studies have shown that HEPA filters have greater efficiency capturing larger and smaller particles, including nanoscale particles, as shown in Figure 3. Both High Efficiency Particulate Air (HEPA) and Ultra-Low Penetration Air (ULPA) filters can be specified for engineering controls.[9, 10]

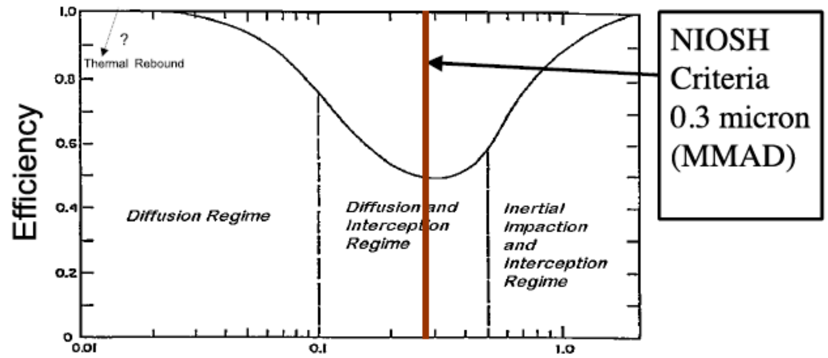

Figure 3. Graph depicting methods of filtration by particle size, and filtration efficiency of a HEPA filter. The NIOSH rating is for the most penetrating (least filtered) particle size of 300 μ MMAD.

[9] Steffens, J. and J. Coury, Collection efficiency of fiber filters operating on the removal of nano-sized aerosol particles: I—Homogeneous fibers. *Separation and Purification Technology*, 2007. 58(1): p. 99-105.
[10] Nanotechnology and Respirator Use. 3M Technical Data Bulletin #171. June 2015

3. Add Administrative Controls

Administrative controls are methods such as worker education and training on proper work techniques, or worker rotation as a means to limit exposure. Proper work techniques may be the same as for larger scale particles: sweeping versus blowing dust; technique of gently brushing residue toward LEV; gently folding an inner bag liner prior to disposal versus shaking; use of wet wiping versus dry wiping during cleanup.

4. Use Personal Protective Equipment

NIOSH has established three levels of filter efficiency for particulate filtering respirators: 95%, 99% and 99.97% (typically rounded up to 100). For each level of efficiency, NIOSH has also assigned three categories of resistance to degradation by oils: ***N:*** ***N***ot resistant to oil; ***R:*** ***R***esistant to oil; and ***P:*** Oil-***P***roof.

The mechanisms of filtration have been studied extensively and have been well explained. Particles at the upper end of the nano-range are captured via diffusion; even smaller particles are captured via electrostatic attraction. N95 respirators have media with a charge, and can capture nanoparticles via an electrostatic attraction. Studies have shown that N-95 and P-100 filtering respirators are efficient at capturing nanoparticles at 93% and 99%, respectively. [10, 11]

Figure 4 shows filtration efficiencies of NIOSH approved N-95 respirators. Note that not all particles in the nanoscale are filtered, and the filtering efficiency is not 100%. But the study does show that the N95 respirators are partially effective at filtering nanoparticles and thereby reducing their exposures.[11]

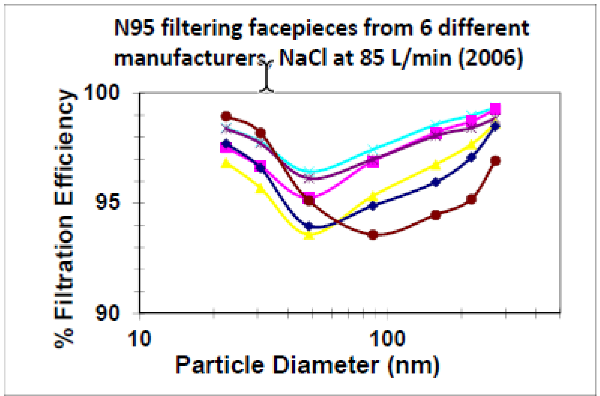

Figure 4. Averaged filtration efficiencies of N95 respirators from 6 different manufacturers.

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[11] Kulinowski, K. and Lippy, B., Introduction to Nanotechnology and Occupational Health. Produced under OSHA grant number SH-21008-10-60-F-48

Figure 5 shows that the most penetrating size nanoparticle in both the N-95 and P-100 respirator is 40 nm, but particles larger and smaller are captured with greater efficiency.[11]

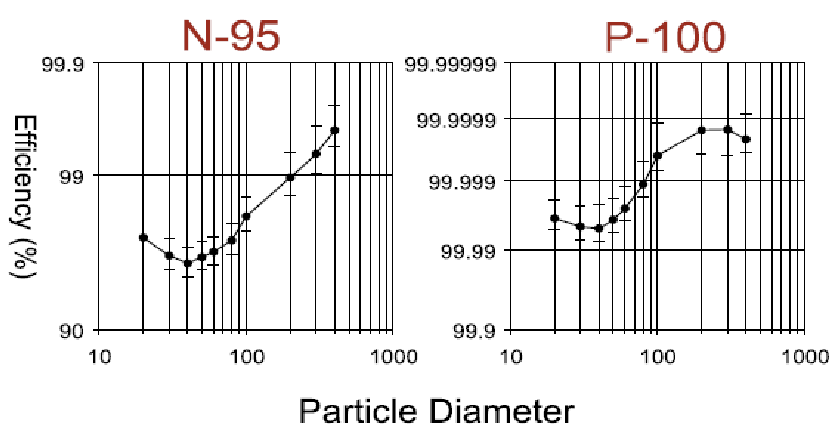

Figure 5. Particle diameter (nm) filtration efficiencies for N-95 and P-100 respirators.

It is imperative that Personal Protective Equipment (PPE) is used either as a last resort or as redundant protection in addition to engineering controls and administrative controls. Typically, respirators are selected based on an Action Level for estimated or measured exposures and a known respirator Assigned Protection Factor (APF). N-95 and P-100 filtering respirators have demonstrated 93 and 99% efficiencies for filtering nanoparticles, and are assigned an APF of 10. Choosing the best respirator will rely upon professional judgment after assessing the task. Any respirator use must be part of a comprehensive respirator protection program, including training and proper fit testing. For dermal exposure protection, often Tyvek suits and nitrile gloves are worn; if available, manufacturer's recommendations should always be followed.

OSHA regulations governing the use of PPE include 29CFR1910.132 (Personal Protective Equipment), 29CFR1910.133 (Eye and Face Protection), 29CFR1910.134 (Respiratory Protection Standard), and 29CFR1910.138 (Hand Protection).

Conclusion

The creation and use of engineered nanomaterials has and will continue to increase due to the vast possibilities offered by their unique physicochemical properties. The same unique properties that make these particles so attractive for commercial applications may also present unique hazards for safe handling and for biological systems. Little data is available regarding occupational exposure effects; therefore, no widespread regulations have been established to govern the safe use of nanomaterials. Employers are encouraged to leverage information known about other ultrafine particles when assessing potential exposures and selecting control measures. It is advised to consider nanomaterials as toxic (and handle accordingly) until data becomes available clearly proving they are not.

Additional Reading

Additional resources have been published by the American Industrial Hygiene Association:

1. Nanoparticle Sampling and Analysis: https://www.aiha.org/government-affairs/PositionStatements/Nanoparticle%20Sampling%20and%20Analysis_FINAL.pdf
2. Personal Protective Equipment for Engineered Nanoparticles: https://www.aiha.org/government-affairs/Documents/Personal%20Protective%20Equipment%20for%20Engineered%20Nanoparticles_Final.pdf

The Environmental Protection Agency has issued the following Technical Fact Sheet: https://www.epa.gov/sites/production/files/2014-03/documents/ffrrofactsheet_emergingcontaminant_nanomaterials_jan2014_final.pdf