LAWRENCE LIVERMORE NATIONAL LABORATORY

LLNL-CONF-412815

Engineered Nanomaterials, Sexy New Technology and Potential Hazards

R. A. Beaulieu

May 6, 2009

2009 Safety Analysis Workshop
Las Vegas, NV
May 8-14, 2009

Engineered Nanomaterials, Sexy New Technology and Potential Hazards

Ronald A. Beaulieu, Lead Safety Analysis Engineer
Lawrence Livermore National Laboratory
Lawrence Livermore National Security, LLC
Nuclear Operations Directorate
Safety Basis Division
P.O. Box 808 (L-372)
Livermore, CA 94551
Phone 925-424-2086, Fax 925-424-4334
beaulieu2@llnl.gov

Abstract

Engineered nanomaterials enhance exciting new applications that can greatly benefit society in areas of cancer treatments, solar energy, energy storage, and water purification. While nanotechnology shows incredible promise in these and other areas by exploiting nanomaterials unique properties, these same properties can potentially cause adverse health effects to workers who may be exposed during work. Dispersed nanoparticles in air can cause adverse health effects to animals not merely due to their chemical properties but due to their size, structure, shape, surface chemistry, solubility, carcinogenicity, reproductive toxicity, mutagenicity, dermal toxicity, and parent material toxicity. Nanoparticles have a greater likelihood of lung deposition and blood absorption than larger particles due to their size. Nanomaterials can also pose physical hazards due to their unusually high reactivity, which makes them useful as catalysts, but has the potential to cause fires and explosions. Characterization of the hazards (and potential for exposures) associated with nanomaterial development and incorporation in other products is an essential step in the development of nanotechnologies. Developing controls for these hazards are equally important. Engineered controls should be integrated into nanomaterial manufacturing process design according to 10CFR851, DOE Policy 456.1, and DOE Notice 456.1 as safety-related hardware or administrative controls for worker safety. Nanomaterial hazards in a nuclear facility must also meet control requirements per DOE standards 3009, 1189, and 1186. Integration of safe designs into manufacturing processes for new applications concurrent with the developing technology is essential for worker safety. This paper presents a discussion of nanotechnology, nanomaterial properties/hazards and controls.

Science Background

"Nanoscience involves research to discover new behaviors and properties of materials with dimensions at the nanoscale which ranges roughly from 1 to 100 nanometers (nm)," states the National Nanotechnology Initiative web site[1]. One nanometer is one billionth of a meter. "Nanotechnology is the way discoveries made at the nanoscale are put to work. Nanotechnology is more than throwing together a batch of nanoscale materials—it requires the ability to manipulate and control those materials in a useful way."

Nanotechnology is the art and science of manipulating and rearranging individual atoms and molecules to create useful materials, devices, and systems. With this manipulation, products can be made with fewer imperfections and more durability, drugs can be more efficient and have fewer side effects, and energy sources can be cleaner and more cost-effective.

Nanotechnology will affect everyone on the planet and may change civilization as it is known. Nanotechnology is a new technology that will find usage in medicine, space exploration, communications, manufacturing, cancer treatments, solar energy, energy storage, water purification, and almost every other aspect of modern society.

DOE P 456.1[2] states “Nanomaterials exhibit unique properties that can affect physical, chemical and biological attributes. Much of the scientific information on the safety, health and environmental hazards of working with these materials is yet to be determined.”

Technology Advances and New Hazards Analogies

When the steam engine was introduced as a new technology, it had the impact to change transportation on a global scale. The advent of the steam engine and its boilers brought with it the peril of high temperatures and pressures and commensurate unexpected explosions and severe consequences. Many workers were severely injured, maimed, or killed outright by boiler explosions. With thousands of boilers in operation throughout the country, there was also widespread ignorance about the properties of steam and the causes of boiler explosions. During the 1850’s, explosions were occurring at the rate of almost one every four days. And, in 1865, the worst boiler disaster in history occurred when the Mississippi River steamer Sultana, took over 1,200 lives[3]. To mitigate this consequence Hartford Steam Boiler Company was created and they developed engineered safety features for boilers of all types, especially locomotive boilers. Thus, steam locomotives became safer and more efficient with time, but at a cost. This engineered safety feature application evolved into the modern American Society of Mechanical Engineers Boiler and Pressure Vessel Code[4]. The significance of the confined temperature and pressure is proportional to the consequences of postulated releases and resulting consequences (an application of hazards and accident analysis). Boilers in fossil-fuel fired steam boilers have less consequences of release compared to nuclear-fueled boilers, which have safety class and safety significant engineered features per regulatory requirements. However, both are operated safely to known regulatory engineering standards and are excellent examples of integrating safety into design.

When asbestos or vinyl chloride was first used the hazards were unknown. Many early asbestos or vinyl chloride workers had little or no personnel protective equipment other than rough clothes for hard work, which may have included coveralls, hardhat, gloves and boots for their assignment. Respirators or other engineered barriers between the worker and the hazardous materials they were handling either were not required or not used in many industrial applications. Years have transpired between the first uses of asbestos (in some cases on the very same boilers mentioned earlier) and today’s knowledge of the hazards of friable asbestos and safe handling practices. However, now that safety professionals understand the hazards of friable asbestos or vinyl chloride, commensurate and appropriate protective measures are taken to protect workers from the specific hazards that could affect them and their work. Today, 10 CFR 851, *Worker Safety and Health Program*[5], "establishes the framework for a worker protection program that will reduce or prevent occupational injuries, illnesses, and accidental losses by requiring DOE contractors to provide their employees' with safe healthful workplaces."

For example, single-walled carbon nanotubes (SWCNTs) are promising new materials, whose potential applications range from novel interconnects in electronics, to energy-storage solutions that combat global warming, to solar cells[6], to treating cancer painlessly. The industry is expected to grow at an unprecedented rate and current global production capacity is measured in hundreds of metric tons. To secure the potential wonder chemical, environmental risk assessment and sound toxicology studies must be in place for SWCNT-based materials. Unwanted metal impurities in SWCNT nanomaterials can also change the properties and the toxicological effects. The environmental behavior of SWCNTs is almost completely unexplored, and current toxicological reports give apparently conflicting results.

Work with engineered nanomaterials should be treated as a new frontier to advance their multitude of applications. Unnecessary roadblocks to efficient manufacture of products using engineered nanomaterials should not be created. However, engineered barriers, as necessary, between workers and dispersible, dry (unbound) engineered nanomaterials should be considered if the engineered nanomaterials are hazardous or if the hazards are as yet unknown.

Hazard Identification

Most nanotechnologies pose no new health or safety risks. However concerns and uncertainties arise in one particular area - the potential health and environmental impacts of free or dispersible (rather than fixed) manufactured nanoparticles and nanotubes. The potential for nanomaterials to enter the body is among several factors that scientists examine in determining whether such materials may pose an occupational health hazard. Nanomaterials have the greatest potential to enter the body if they are in the form of nanoparticles, agglomerates of nanoparticles, and particles from nanostructured materials (e.g., engineered nanomaterials) that become airborne or come into contact with the skin. Nanoparticles and nanotubes should be treated as new substances with new material properties and potential hazards.

The following primary hazard categories may be considered when assessing risk associated with nanomaterials. This information is largely based on the National Institute for Occupational Safety and Health (NIOSH) "Approaches to Safe Nanotechnology: An Information Exchange with NIOSH" (Ref. 7).

- *Surface chemistry*. Surface chemistry is a key factor influencing the toxicity of inhaled particles. Particle surface free radical activity is the primary factor that influences the material's overall surface reactivity. This information is not readily available for most nanomaterials, but toxicological studies provide information for some types of nanomaterials.

- *Particle shape.* Studies have shown that exposure to fibrous particles like asbestos have long been associated with increased risk of fibrosis and cancer. More recently, carbon nanotubes have also been shown to cause inflammation and lesions in rat lungs and may have similar toxic properties as those of asbestos. The toxicity of carbon nanotubes is believed to be associated with their tubular structure.

- *Particle diameter.* Based on the particle deposition model developed by the International Commission on Radiological Protection (ICRP), nanoparticles have a greater chance of depositing in the lungs than larger particles, and therefore have the potential to cause damage by acting directly at the site of deposition, by translocating to other organs, or by being absorbed through the blood.

- *Particle size.* Particles above a given threshold may be too large to penetrate specific organic media. However, once the particle size is below the threshold, the particle can penetrate organic barriers and cause significant damage. For example, 10 nm or larger silver nanoparticles may be too large to penetrate the nucleus of certain human cells, but 9 nm or smaller silver nanoparticles can penetrate certain human cell nucleus and cause significant damage or mutation[8].

- *Particle charge.* Particles may retain much of the material properties of their parent material such as electrical charge, magnetism, radioactivity, melting and boiling points, etc. However, nanomaterials exhibit unique physical and chemical properties as well.

- *Solubility.* A number of studies have shown that poorly soluble inhaled nanoparticles can cause oxidative stress, leading to inflammation, fibrosis, or cancer.

- *Carcinogenicity, reproductive toxicity, mutagenicity, and dermal toxicity.* This type of information is not available for most nanomaterials. However, some nanomaterials (e.g., titanium dioxide[9]) have been identified as potential carcinogens.

- *Toxicity of parent material.* The bulk materials of some nanoparticles have established occupational exposure limits. While it is known that the toxicity of particles at the nanoscale can differ significantly from their larger counterparts, this provides a good starting point for understanding the toxicity of the nanomaterial.

- *Impurities.* The expectation of specific material properties are significantly altered by the presence of impurities mixed in the feedstock of nanomaterials. Impurities may produce unexpected electrical conductance, pyrophoric, explosive, catalytic, and other properties that are introduced in a violent manner. Impurities (e.g., lead or other metals) have undesirable results due to regulations and increased toxicity.

- *Form or form change*. Nanoparticles may be shipped by the manufacturer as wet particles in an immersion or liquid solution, which is nondispersible. However, if the nanoparticles are allowed to dry to a solid, then the nanoparticles could be readily dispersible.

- *Coating degradation*. Coatings on nanoparticles may inhibit toxicity or other undesirable properties. However, enzymes or process chemicals may cause the coating to break down or disintegrate, which then enables the uncoated nanomaterial to come into contact with organic matter and cause unexpected harm.

Processes generating nanomaterials in the gas phase, or using or producing nanomaterials as powders or slurries/suspensions/solutions pose the greatest risk for releasing nanoparticles. Maintenance on production systems (including cleaning and disposal of materials from dust collection systems) is likely to result in exposure to nanoparticles if it involves disturbing deposited nanomaterial.

Controls

Controls involving handling engineered nanomaterials should minimize exposure of workers and the environment to nanomaterials from the time they are created to the time they are disposed (cradle-to-grave) by identifying operations that utilize nanomaterials, assessing the risk associated with those operations, identifying populations at risk, implementing controls to minimize exposure, and ensuring that the controls are adequately protective of workers and the environment.

As with all work that may expose workers to hazardous substances, the following types of controls, from most to least preferred, shall be considered for minimizing or eliminating worker exposures to nanomaterials. In designing the work area, the potential need to implement additional engineering or administrative controls shall be considered to ensure workers are protected in areas where nanomaterials are handled.

Exposure of humans and the environment to free nanoparticles and nanotubes should be restricted until they are better understood. All relevant regulatory bodies and their respective advisory committees should consider whether existing regulations are appropriate to protect humans and the environment, and should include in their planning, the future applications of nanotechnologies, in order to close the regulatory gaps at an appropriate stage.

Ingredients in the form of nanoparticles in consumer products should undergo a full safety assessment by the relevant scientific body and should be clearly labeled.

Personnel protective equipment (e.g., gloves, respirators) provides a barrier between nanomaterials and the workers.

Engineered Controls

Enclosures used to perform work with nanomaterials shall operate at negative pressure differential compared to the worker’s breathing zone. Flow tests for local exhaust ventilation hoods and fume hoods shall be tested in accordance with an Industrial Hygiene based performance criteria.

When exhausting air that is reasonably expected to contain nanoparticles that are considered hazardous or whose hazards are not well understood, the air shall be filtered (preferably using HEPA filters) or otherwise cleaned (e.g., scrubbed) to remove the nanoparticles prior to exhausting the effluent.

When feasible, air that is reasonably expected to contain nanoparticles, hazardous or not, should be ducted to building exhaust. When it is not feasible to duct effluent to building exhaust, the guidance in ANSI Z9.7 "American National Standard for Recirculation of Industrial Process Exhaust Systems[10]," shall be followed, an additional hazard assessment shall be conducted, and controls shall be implemented to minimize the re-entrainment of nanoparticles into work areas.

Horizontal laminar-flow hoods that direct air into the user's face shall not be used to control nanoparticle exposures.

Administrative Controls

Work Practices

- All working surfaces shall be maintained free of nanomaterial contamination by performing precautionary cleaning using a moistened disposable wipe and/or dedicated HEPA vacuum whose filtration effectiveness has been verified in accordance with an IH DAP. This cleaning shall be done minimally at the end of every work shift on surfaces where nanomaterials may have deposited. The working surfaces shall be maintained free of clutter to enable cleaning and to prevent unnecessary contamination of items.

- In selecting a cleaning method, consider the potential for complications due to the physical and chemical properties (e.g., pyrophoric potential) of the nanomaterial.

- Dry sweeping shall not be used to clean nanomaterials.

- Compressed air shall not be used to clean nanomaterials, unless performed within a ventilated enclosure. Care shall be taken to ensure that nanomaterials do not escape the enclosure and potentially expose workers.

- Nanomaterial samples shall be transferred between workstations in closed, labeled containers. (Example of a Specific Administrative Control per DOE STD-1186[11]).

- Precautions shall be taken to minimize skin contact with nanomaterials.

Labeling and Signage

Signs shall be posted at all entry points to areas where engineered nanomaterials may be handled and could potentially result in worker exposure (e.g., Hazard Notice Door Sign, with the words "Engineered Nanomaterials are Present. Nanomaterials can exhibit unusual reactivity and toxicity. Avoid breathing dust, ingestion, and skin contact."). The signs shall indicate hazards, PPE requirements, and administrative control requirements. Equipment or ventilation systems that may be contaminated with nanomaterials shall be labeled with a sign indicating potential contamination.

All storage containers of nanomaterials shall plainly indicate that the contents are in nanoscale form and that the nanomaterial may be unusually reactive and may vary in toxic potential from normal scale forms of the same material.

Training

Worker and Supervisor qualifications should be commensurate with the hazards associated with the specific application. A job hazards analysis may be sufficient to determine the assignment specific training requirements.

Medical Surveillance

Pre-assignment and periodic (e.g., annual) physical exams seem appropriate for personnel with potential exposure to hazardous dispersible or carcinogenic nanomaterials. Details of medical assessments are left to medical professionals. However, components of a comprehensive program could be augmented with worker health surveillance commensurate with the hazards of their assignments. Ongoing/continuous research into available scientific literature could yield discovery of published notification of new-found hazards or consequences correlated to specific nanomaterials. The medical professionals examining the workers should become knowledgeable in the facility's specific nanomaterials and their associated hazards and effects.

When exposure is studied as a risk factor for occupational disease, it can be thought of a process of human interaction with a source of a potential hazard such as dry dispersal nanomaterials at various stages in the product development. Harvard School of Public Health considers that this way of thinking leads to the development of exposure assessment methods which capture the characteristics of exposure having physiologic significance for the health effect being studied. Exposure to the nanomaterials used in products in various stages of reaction would reveal the possible cause of the health effects seen in epidemiologic studies of workers. This research is developing a task-centered approach to characterizing exposure by identifying specific work tasks, and the associated exposures with each to evaluate the variability between individual workers, as well as changes in the composition and intensity of exposure over time. In addition to providing better exposure information for classifying workers in epidemiologic studies, the task based approach also helps identify specific operations and activities which make the greatest contribution to exposure for a work task, allowing the development of effective, targeted intervention methods (controls) to minimize exposure.

The NIOSH issued guidance for medical screening and hazard surveillance for workers potentially exposed to engineered nanoparticles[12].

Workplace Monitoring

The workplace should be monitored for surface and airborne contamination from nanomaterials. Contamination of workstations and worker clothing, especially personnel protective equipment could be cause for concern if hazardous materials are involved. Decontamination procedures should be developed and practiced, as appropriate, commensurate with the hazards.

Management of Nanomaterial Spills
Dry Nanomaterials

- If a potential exists for dry nanomaterials to be tracked outside the immediate spill clean-up area, a walk-off mat shall be positioned where clean-up personnel will exit the access-controlled area to reduce the spread of dry nanomaterials.

- Spills shall be cleaned using wet wiping methods, HEPA vacuum, and/or other facility-approved methods. Spill clean-up materials, including the HEPA filters from the HEPA vacuum, shall be considered nanomaterial-bearing waste.

- Dry sweeping or compressed air shall not be used to clean spills.

- HEPA vacuums, dedicated for nanomaterial spill cleanup (if feasible), shall be certified annually, and labeled according to their purpose. A log shall be kept to record the type of materials collected. Avoid mixing potentially incompatible materials in the vacuum.

- Some normally stable nanomaterial powders may become pyrophoric if deposited on a filter and subject to high airflow due to possible air reactivity of nanoparticles. This potential reactivity shall be considered prior to using a HEPA vacuum.

Liquids

- If a potential exists for liquid-suspended nanomaterials to be tracked outside the immediate spill clean-up area, an absorbent walk-off mat shall be positioned where clean-up personnel will exit the access-controlled area to reduce the spread of liquids containing nanomaterials.

- Barriers, such as plastic sheeting, shall be placed across the surface of liquid spills to minimize air currents that may spread contamination from the spill.

- The spill shall be cleaned in a similar manner as that used to clean dry nanomaterial spills (e.g., wet wiping, HEPA vacuum to clean up residual nanomaterials after the spill has dried, and the like). Spill clean-up materials shall be considered nanomaterial-bearing waste.

Engineered Nanomaterial Critical Topic Areas

NIOSH has identified 10 critical topic areas to guide in addressing knowledge gaps, developing strategies, and providing recommendations. Each topic provides a brief description of the research that NIOSH is conducting in the area of nanotechnology and the applications and implications of nanomaterials in the workplace.

Toxicity and Internal Dose

- Investigating and determining the physical and chemical properties (e.g., size, shape, solubility) that influence the potential toxicity of nanoparticles

- Evaluating short and long-term effects that nanomaterials may have in organ systems and tissues (e.g., lungs, kidneys, liver)
- Determining biological mechanisms for potential toxic effects
- Creating and integrating models to assist in assessing possible hazards
- Determining if a measure other than mass is more appropriate for determining toxicity

Risk Assessment

- Determining the likelihood that current exposure-response data (human or animal) could be used in identifying and assessing potential occupational hazards
- Developing a framework for evaluating potential hazards and predicting potential occupational risk of exposure to nanomaterials.

Epidemiology & Surveillance

- Evaluating existing epidemiological workplace studies where nanomaterials are used
- Identifying knowledge gaps where epidemiological studies could advance understanding of nanomaterials and evaluating the likelihood of conducting new studies
- Integrating nanotechnology health and safety issues into existing hazard surveillance methods and determining whether additional screening methods are needed
- Using existing systems to share data and information about nanotechnology

Engineering Controls and PPE

- Evaluating the effectiveness of engineering controls in reducing occupational exposures to nanoaerosols and developing new controls where needed
- Evaluating and improving current personal protective equipment
- Developing recommendations to prevent or limit occupational exposures (e.g., respirator fit testing)
- Evaluating suitability of control banding techniques where additional information is needed; and evaluating the effectiveness of alternative materials

Measurement Methods

- Evaluating methods of measuring mass of respirable particles in the air and determining if this measurement can be used to measure nanomaterials
- Developing and field-testing practical methods to accurately measure airborne nanomaterials in the workplace
- Developing testing and evaluation systems to compare and validate sampling instruments

Exposure Assessment

- Determining key factors that influence the production, dispersion, accumulation, and re-entry of nanomaterials into the workplace
- Assessing possible exposure when nanomaterials are inhaled or settle on the skin
- Determining how possible exposures differ by work process

- Determining what happens to nanomaterials once they enter the body

Fire and Explosion Safety

- Identifying physical and chemical properties that contribute to dustiness, combustibility, flammability, and conductivity of nanomaterials.
- Recommending alternative work practices to eliminate or reduce workplace exposures to nanoparticles.

Recommendations & Guidance

- Using the best available science to make interim recommendations for workplace safety and health practices during the production and use of nanomaterials
- Evaluating and updating occupational exposure limits for mass-based airborne particles to ensure good continuing precautionary practices

Communication & Information

- Establishing partnerships to allow for identification and sharing of research needs, approaches, and results
- Developing and disseminating training and educational materials to workers and health and safety professionals

Applications

- Identifying uses of nanotechnology for application in occupational safety and health
- Evaluating and disseminating effective applications to workers and occupational safety and health professionals

Nuclear applications of engineered nanomaterial hazards in a nuclear facility must also meet control requirements per DOE standards 1027, 3009, 1189, and 1186.

Conclusions

All work with dispersible (unbound) engineered nanomaterials must be conducted in a safe and responsible manner that protects workers, the public, and the environment. Work must follow a cautious approach in the production, use, and disposition of nanomaterials.

A comprehensive approach to hazardous engineered nanomaterials should include appropriate barriers (e.g., confinement) between workers and hazardous engineered nanomaterials during all stages of work involving hazardous engineered nanomaterials. A cradle-to-grave approach should include transportation of engineered nanomaterials including off-site shipments (e.g., receipt of raw materials) and on-site transfers of engineered nanomaterials evaluation of engineered and administrative controls at workstations and management of nanomaterial-bearing waste streams.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

April 2009

References

1 National Nanotechnology Initiative web site. http://www.nano.gov/

2 DOE P 456.1, "Secretarial Policy Statement on Nanoscale Safety," U. S. Department of Energy, September 15, 2005.

3 Hartford Steam Boiler web site History. http://www.hsb.com/about.asp?id=50

4 American Society of Mechanical Engineers, Boiler and Pressure Vessel Code, New York, NY. http://www.asme.org/Codes/International_Boiler_Pressure.cfm

5 10 CFR 851 *Worker Safety and Health Program*, U.S. Department of Energy, February 9, 2006.

6 Stelzner, Th, et al, *Silicon Nanowire-Based Solar Cells*, June 10, 2008 stacks.iop.org/Nano/19/295203.

7 National Institute for Occupational Safety and Health (2006) *Approaches to Safe Nanotechnology: An Information Exchange with NIOSH*. Version 1.1, U. S. Department of Health and Human Services, Centers for Disease Control and Prevention National Institute for Occupational Safety and Health, July 2006. http://www.cdc.gov/niosh/topics/nanotech/safenano/pdfs/approaches_to_safe_nanotechnology_28november2006_updated.pdf

8 Schrand, Amanda M, et al, *Can Silver Nanoparticles be Useful as Potential Biological Lables?* May 6, 2008 stacks.iop.org/Nano/19/235104.

9 International Agency for Research on Cancer (IARC). (2006) Titanium dioxide (IARC Group 2B), February 2006. Lyon: IARC Press.

10 ANSI Z9.7, "American National Standard for Recirculation of Industrial Process Exhaust Systems," American Industrial Hygiene Association, Fairfax, VA, 2007 Edition.

11 DOE-STD-1186-2004, Specific Administrative Controls, U.S. Department of Energy, August 2004.

12 "Current Intelligence Bulletin 60: Interim Guidance for the Medical Screening and Hazard Surveillance for Workers Potentially Exposed to Engineered Nanoparticles," National Institute for Occupational Safety and Health www.cdc.gov/niosh/docs/2009-116/.

Additional Information Not Cited as References

ASTM International (2007) Terminology for Nanotechnology. West Conshohocken, PA: ASTM International, E2456-06.

Maynard, A. (2007) *Nanotechnology: The next big thing, or much ado about nothing?* Annals of Occupational Hygiene; 51(1): 1-12.

Maynard, A and Kuempel, E. (2005) *Airborne Nanostructured Particles and Occupational Health*. Journal of Nanoparticle Research; 7: 587-614.

Nanoscale Science Research Centers' "Approach to Nanomaterial ES&H," Revision 2 (June 2007).

Nanoscale Science Research Centers' "Approach to Nanomaterial ES&H," Revision 3a (May 2008).