ESH590 – Engineered Nanomaterials Orientation

Purpose and Objectives

Nanomaterials are a unique class of materials that are on the forefront of research and development. At Argonne we manufacture, modify, use, ship, and dispose of nanomaterials. When working with nanomaterials, there are some special requirements that apply to unbound engineered nanoscale particles (UNP's).

This course will provide information on how to carry out activities with UNPs in a safe and environmentally responsible way. Upon completion of this course, you will be able to:

- Define nanomaterials.
- Define UNP.
- Identify the potential health, safety, and environmental hazards posed by UNPs.
- Explain how to control personal and environmental exposure to UNPs.
- Describe how we measure UNP levels in the workplace.
- Identify currently available guidance documents that apply to UNPs, in the absence of current regulations.

What Are Nanomaterials?

- Nanoscale materials are very small structures with at least one dimension between 1 and 100 nanometers (nm).
- Nanoscale particles are nanomaterials with one or more dimensions between 1 and 100 nanometers (nm).
- Nanoscale particles are either naturally occurring or man-made.
- Engineered nanomaterials (ENM) are materials created by manipulation of matter at the nanoscale to produce new materials, structures, and devices.
- Unbound engineered nanoparticle (UNP) means those engineered nanoparticles that, under reasonably foreseeable conditions encountered in the work, are not contained within a matrix that would be expected to prevent the nanoparticles from being separately mobile and a potential source of exposure. An engineered nanoparticle dispersed and fixed within a polymer matrix, incapable, as a practical matter, of becoming airborne, would be "bound," while such a particle suspended as an aerosol or in a liquid would be "unbound .

Nanomaterials Are NOT New

We have been exposed to nanomaterials for years. Most exposures to nanoscale particles come from the following natural and man-made sources:

- Diesel exhaust
- Volcanic ash (which can travel thousands of miles in clouds)
- Welding fumes
- Particulates given off when cooking
- Paint pigments
- Photocopier toner
- Cigarette smoke and other combustion products
- Viruses and bacteria fall within the nanoscale (10 nm to 10 µm in size)

Many of these have chronic effects. Our knowledge of these effects has led us to have concern about this class of materials when they are in the particulate form within a size range where they can result in exposure by inhalation or inadvertent skin contact.

Nanomaterial Form is Important

Nanomaterials are only a health hazard when they are present as respirable or dispersible dry or wet particles. The particles exist in any of the following forms:

- Unbound
  - Dispersible – loose, powders
    - They can become airborne easily and stay in the air for a long time.
  - In suspension – colloidal suspensions in liquids, also unbound (by definition).
    - These can get into the air as mists.
    - Dried suspensions leave unbound particles on surfaces where they may, then get into the air.

- Affixed to surfaces or imbedded in a matrix
  - This results in a limited exposure potential.
  - Unless the matrix is dissolved or disturbed in some way, the particles seem to pose little hazard.

Potential UNP Hazards

The physical and chemical properties of nanoscale materials have been shown to differ from those of the individual atoms and molecules, or larger scale materials of the same elements. For this reason, what is known about a common material may not apply to the nanomaterial of the same composition.

- UNPs can be toxic because they are available for uptake by the body.
- Studies on animals show that effects of some UNPs may be different than the effects of larger particles of the same composition.
- UNPs may have a **stronger** effect than an equivalent amount of larger particles of the same composition.

Toxicity – Routes of Entry

You can be exposed to UNPs in the same way as other hazardous particles. The three primary routes of entry are inhalation, ingestion, and dermal.

Inhalation (lungs)

- Respiratory tract is a significant route of entry and requires a great deal of protection.
- UNPs released into the air (unbound) will remain airborne for considerable periods.
- Inhaled UNPs may collect in all regions of the respiratory system.
- Studies on UNPs suggest that particles may cause granulomas (microscopic nodules) and inflammation.
- Granulomas can lead to tissue damage and reduced lung function.
- Limit exposures to airborne UNPs to the extent feasible. Prevention of inhalation by engineering controls (fume hoods, glove boxes, etc.) or use of respirators are primary controls to prevent exposure by this route.

Ingestion (swallowing)

- As with any chemical, UNPs can be ingested from the contamination of hands, food, beverages, and other materials.
- UNPs that have been caught in nasal mucous can also be swallowed and subsequently coughed up from the respiratory tract.
- Studies suggest that ingested UNPs may accumulate in various organ systems.
- Limiting dispersion of UNPs by working within a fume hood or glove box, effective glove removal, combined with good hand hygiene practices are effective mechanisms to limit exposure by ingestion.

Dermal (skin)

- UNPs can enter the body through intact skin or even more rapidly through any skin where cuts or abrasions are present.
- Precautions to protect the skin, eyes, and mucosa, include the use of personal protective equipment including effective eye protection and use of disposable gloves.

Safety Data Sheets

Due to limited toxicity data on UNPs, Argonne procedures take a precautionary approach to the handling of UNPs.

Safety Data Sheets (SDS) may be misleading or of limited value.

- The SDS for a parent compound cannot be used to predict the hazards from a nanomaterial of the same composition.
- The health effects cannot be readily extrapolated from common (larger) parent material. (For instance, we cannot use the known toxicology of carbon dust to judge the toxicity of single-walled carbon nanotubes.)

Treat nanoscale materials as though they are no less toxic than represented on an SDS.

Prudent Avoidance

- Use caution when working with UNPs.
- With nanomaterials, recognize the potential for human harm as the materials could potentially pose a significant health threat.
- Since we cannot assign a risk to nanotechnology (a high amount of uncertainty exists), we will be cautious and assume that nanomaterials can cause great harm.
- Interim control measures must be developed and used.

Controlling Exposure

Traditional chemical exposure control strategies and good practices are important and been used to control natural and man-made nanoparticles for decades.

The following good practices apply when working directly with UNPs:

- Handle dispersible nanoparticles in ventilated hoods or cabinets.
- PPE and good personal hygiene can reduce exposure to skin and ingestion hazards.
- Limit the spread of contamination by wet-wiping and HEPA vacuuming.
- Clean up spills of liquids.
- Post areas where UNPs are manufactured, stored, and used in accordance with LMS- PROC-83.
- Label containers of engineered nanomaterials in accordance with LMS-PROC-83.

Evaluating Exposures

As there have been no specific diseases in humans attributed to UNPs to date, evaluating exposures to UNPs poses a challenge. Nanomaterials are so unique in their properties that we need to use other aspects of the material to predict potential exposure effects.

- Allowable exposure standards are typically based on the mass concentration of material, (mg/m^3) i.e. the higher the mass or dose, the greater the risk of a negative health outcome.
- Some effects appear to be related to number of particles in the air. (similar to asbestos)
- The shape, size and surface chemistry of the particle can contribute to potential deleterious health effects.
- Chronic health effects from UNP exposure may take many years to be recognized.

Medical Surveillance

Through Directive DOE Order 456.1A, the Department of Energy requires that contractors, such as Argonne National Laboratory, offer a baseline medical evaluation to employees:

- Whose work potentially entails inhalation of or dermal exposure to unbound engineered nanoparticles.
- Who routinely spend time in an area in which engineered unbound nanoparticles have the potential to become dispensed into the air or to accumulate of surfaces.
- Who work on equipment that might contain UNPs or that might release UNPs during servicing or maintenance.

Argonne uses responses on the Job and Hazard Questionnaire to determine to whom the baseline evaluation should be offered.

The requirement for medical surveillance does not apply to non- Argonne employees although Argonne National Laboratory is required to inform “guest workers” of this requirement. Guest workers are considered those performing work here at Argonne, but who are not on the Argonne payroll, such as joint appointees or facility users.

Measuring Airborne Concentrations

Industrial Hygiene has instrumentation for measuring airborne concentrations of particles including UNPs.

- Direct read instruments provide real time data on particle counts, size ranges, and surface area results, which can identify potential exposure to different regions of the lungs.
- Survey of the relative number of airborne UNPs can help determine if additional controls are required to minimize exposure.

Nanomaterial Waste Handling

Currently, hazardous waste regulations do not specifically address UNPs or nanomaterial.

We do know:

- Many nanoparticles are **not** biodegradable.
- If nanomaterials are dispersed into the environment, there is a greater likelihood that they could accumulate in the food chain.
- Until we have more / better information on UNP toxicity, we should minimize waste generation and carefully track and document nanoparticle wastes.

Instructions for Nanomaterial Waste Generators

Do:

- Refer to LMS-PROC-224, Handling of Engineered Nanomaterials for Disposition.
- Make sure nanowastes are compatible with the waste storage container.
- Label waste containers as containing nanowaste.
- Identify all nanomaterials on the waste disposal requisition.
- If nanowastes are within a matrix which itself is a hazardous waste, treat the nanowaste as a hazardous waste, but identify the nanomaterials within.
- If the nanowaste is a characteristic hazardous waste, treat it as such.
- Plan work/research to minimize or eliminate the generation of nanowaste.

Do NOT:

- Dispose of solid nanowastes in regular trash.
- Pour liquid nanowastes down drains.
- Comingle nanowastes with non-nanowastes. (minimize nanowaste volume)

Packaging, Transfer and Shipping of Nanomaterials

Shipping Precautions for Nanomaterials

There is no special Department of Transportation (DOT) regulation dealing with the shipment of engineered nanomaterials (either bound or unbound). Before you ship nanomaterials, you must provide information sufficient to characterize the materials as with any new chemical. If a new nanomaterial is created and needs to be shipped, determine whether an SDS needs to be created as per LMS-PROC-288.

- Contact your ESH Coordinator or the Shipping Department at 2-5779 for assistance.
- Refer to the Argonne Transportation Safety Manual.
- Consult with the Argonne Transportation Safety Program Manager at 2-5712 as needed.

Shipping UNPs

Argonne's procedures for packaging, transfer and shipment of UNPs are contained in LMS-PROC-84. All onsite transfers and offsite shipments of UNPs must comply with this PROC.

Packaging of ENMs

Package UNP's as follows:

- Place UNP into the chemically compatible inner receptacle and hermetically seal the container.
- Mark the outside of the inner receptacle with the word "NANOMATERIAL" or with the label, as shown **below:**

Sealed, labeled compatible inner container

Sealed Intermediate Container

Liquids

Intermediate container must be completely wrapped by absorbent.

Rigid External Container

- Seal the inner receptacle to prevent opening during transport and handling.
- Place the inner receptacle into a chemically compatible intermediate packaging with:
    - Sufficient cushioning to prevent damage to the inner receptacle.
    - Sufficient absorbent to absorb the total liquid contents.
- Seal intermediate packaging to prevent opening.
- Place a "UNP" label on the outside of the intermediate packaging.
- Place the intermediate packaging into a rigid outer package.

Paperwork

For off-site shipment, complete an ANL-126C "Shipping Order" in the PARIS system, which will print a "Transfer Order".

For on-site transfer, complete an ANL-8 for the material to be transferred.

Attach the "Transfer Order" (from the ANL-126) or the ANL-8 to the outside of the rigid packaging:

- If the contents are nonhazardous, place it where the T-Run will pick it up.
- If the contents are hazardous, contact 2-4939 and request a pick-up by the HAZMAT T-Run.

To move it yourself, attach the "Transfer Order" or the ANL-8 to the outside of the rigid packaging. Use a government vehicle to transport the material directly to the on-site destination. The driver of the government vehicle must be informed of the presence of the material in the vehicle, hazards of the material, and their controls. During transportation, the package must be secured and must not be opened or altered.

Note: Bicycles (personal or Argonne Bike Share) **MUST NOT BE USED** for transportation.

Additional Argonne Program Elements

Argonne participates in DOE and multi-organizational workshops directed toward nanomaterial research. Argonne is staying abreast of nanoscale activities worldwide to identify hazard, monitoring, and control advances.

- Job and Hazard Questionnaire (JHQ) must identify individuals that work with UNPs.
- Experiment safety reviews must indicate the use of UNP's and the proposed controls for dispersion. (See guidance in LMS-PROC-84.)

Integrated Safety Management

Work with engineered nanomaterials must be done in accordance with the Integrated Safety Management process.

- Experimental work must be authorized using the experiment safety review process contained in LMS-PROC-200, Local Work Planning and Control Implementing Procedure.
- The process must encompass all ISM and work planning and control actions.

Requirements and Guidance

- There are no OSHA Standards or ACGIH Threshold Limit Values (TLV) at this time.
- DOE P 456.1 Secretarial Policy Statement on Nanoscale Safety.
- DOE N 456.1 The Safe Handling of Unbound Engineered Nanoparticles.
- Office of Science Nanoscale Science Research Centers ESH Working Group.
- American Society for Testing and Materials (ASTM) Standard.
- LMS-PROC-83, Safe Handling of Engineered Nanomaterials.
- LMS-PROC-84 Packaging, Transfer and Shipment of Unbound Engineered Nanomaterials.

- Division Chemical Hygiene Plan.
- LMS-PROC-200, Local Work Planning and Control Implementing Procedure.

Nanomaterial Resources

There is much to learn about the hazards of nanoscale particles. Various organizations continually collect and assess studies on the toxicity of nanoscale particles.

Please visit the websites listed below for more information.

- National Institute for Occupational Safety and Health (NIOSH) http://www.cdc.gov/niosh/topics/nanotech/
- National Nanotechnology Initiative (NNI) http://www.nano.gov/
- Nanoparticle Information Library (NIL) http://nanoparticlelibrary.net/

For more information on nanomaterials:

- Contact Industrial Hygiene at 2-1213.

To take the exam and receive credit for this course, please use the link below.

TAKE EXAM