ESH590 – Engineered Nanomaterials Orientation

Purpose and Objectives

Engineered nanomaterials (ENM) 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 engineered nanomaterials.

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

- Define engineered nanomaterials (ENM)
- Identify the potential health, safety, and environmental hazards posed by ENMs
- Explain how to control personal and environmental exposure to ENMs
- Describe how we measure ENM levels in the workplace
- Identify currently available guidance documents that apply to ENMs, 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 two or three 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

Nanomaterials are not new

We have been exposed to nanomaterials for years. Most exposures to nanoscale particles come form 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 nanoparticles.

Nanomaterial form is important

Nanoparticles exist in one of the following forms:

- Dispersible – loose, unbound
  - They can be airborne easily and stay in the air for a long time
- In suspension – colloidal suspensions in liquids
  - 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 ENM hazards

The physical and chemical properties of nanoscale materials can differ from those of larger scale materials of the same chemical composition. For this reason, what is known about a common material may not apply to the nanomaterial of the same composition.

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

Toxicity – routes of entry

You can be exposed to nanoparticles in the same way as larger 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
- Nanoparticles released into the air (unbound) will remain airborne for considerable periods
- Inhaled nanoparticles may be collected in all regions of the respiratory system

- Studies on ultrafine particles suggest that particles may cause granulomas (microscopic nodules) and inflammation
- Granulomas can lead to tissue damage and reduced lung function
- Because nanoparticles readily agglomerate (stick together), some suggest this may lower the risk
- Limit exposures to airborne nanoparticles to the extent feasible

Ingestion (swallowing)

- As with any chemical, ENMs can be ingested from the contamination of food, beverages, and other materials
- Particles can also be swallowed that have been caught in mucous and subsequently coughed up form the respiratory tract
- There are not credible studies on the health hazards from swallowing nanoparticles
- Ultrafine particle studies suggest that ingested nanoparticles may accumulate in various organ systems
- **Avoid ingestion!**

Dermal (skin)

- Although there is no conclusive evidence that nanoparticles can enter the body through intact skin, there is some reason to believe that this may be possible
- We must assume that the intact skin is a plausible route of entry
- **We must take precautions to protect the skin, eyes, and mucosa including the use of personal protective equipment**

Material Safety Data Sheets

Material Safety Data Sheets (MSDS) may be misleading or of limited value

- The MSDS for a parent compound cannot be used to present the hazards from a nanomaterial of the same composition. Unfortunately, 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.

While there is limited toxicity data on ENM, we do know a good deal about how nanomaterials behave.

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

Prudent avoidance

- We should be cautious
- With nanomaterials, we recognize the potential for human harm – the materials could 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 exposure control strategies and good practices are important. We have been controlling natural and man-made ultrafine and nanoparticles for decades.

The following rules apply:

- Handle dispersible nanoparticles in ventilated hoods or cabinets
- HEPA filters can remove all but the smallest particles from the air
- 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 nanomaterials are manufactured, stored, and used
- Label containers of engineered nanomaterials in accordance with Chemical Hygiene Plan

Evaluation exposures

Evaluating exposures to ENMs is a challenge

- Allowable exposure standards are typically based on the mass concentration of material (mg/m^3)
    - The higher the mass or dose, the greater the risk of a negative health outcome
- Nanomaterials are so different that we need to look at other aspects of the material
- Some toxic effects seem to be related to the surface area of the material
- Some effects seem to be related to number of particles in the air (like asbestos)
- The surface chemistry and/or particle shape may also be important
- New information suggests new, significant routes of exposure
- Signs and symptoms of excessive exposure have not yet been reliably described
    - To date, there are no reports of ill effects in people, although chronic effects take many years to be seen

Measuring airborne concentrations

EQO-Industrial Hygiene has instrumentation for measuring airborne concentrations of particles.

- Direct read instruments provide real time data on particle counts, size ranges, and surface area results, which are relevant to an applicable region of the lung
- Although interpretation of sampling data remains problematic, it is not a valid reason to choose not to sample
- Simply knowing the relative increase in nanoparticles can be an important indication that additional controls are needed

Nanomaterial waste handling

Virtually all R&D facilities produce waste and some fraction of that waste is considered hazardous. Currently, hazardous waste regulations do not specifically address nanoparticles.

We do know:

- Many nanoparticles are not biodegradable
- Very little is understood about the health and environmental effects of nanoparticle exposures
- If nanomaterials are dispersed into the environment, there is a great likelihood that they could accumulate in the food chain
- It is also likely that nanomaterials could accumulate within some species
- Until we have more and better information on toxicity, we should minimize waste generation, where possible, and carefully track and document nanoparticle wastes

Instructions for nanomaterial waste generators

Do:

- Make sure nanowastes are compatible with the waste storage container
- Label waste containers as containing nanowaste
- Identify the nanomaterials that are in the wastes on the waste disposal requisition
- If nanowastes are in a matrix which itself is a hazardous waste, treat the nanowaste as a hazardous waste, but identify the nanomaterials
- If the nanowaste is a characteristic hazardous waste, treat it as such
- Plan work/research so as 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)

Transportation and shipping

Transportation of engineered nanomaterials

- There is no special Department of Transportation (DOT) regulations about shipping engineered nanomaterials
- Before you ship engineered nanomaterials, you must provide information sufficient to characterize the materials
- If a new ENM is created and subsequently shipped, determine whether or not an MSDS needs to be created
- Contact your ESH Coordinator or the Shipping Department at 2-5779 for assistance
- Please refer to the Argonne Transportation Safety Manual
- You may also consult with the Argonne Transportation Safety Program Manager at 2-5712

Additional Argonne program elements

- Job and Hazard Questionnaire (JHQ) identifies individuals that work with ENMs
- Experiment safety reviews must consider nanoparticles and materials
- Guidance is provided in ESH Manual Section 4.13
- Argonne is staying abreast of nanoscale activities worldwide to identify hazard, monitoring, and control advances
- Argonne participates in DOE and multi-organizational workshops directed toward nanomaterial research

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 ESH Manual Section 21.2
- The process encompasses all ISM and work planning and control actions

Requirements and guidance

- No OSHA standards or ACGIH Threshold Limit Values (TLV) at this time
- DOE P 456.1 Secretarial Policy Statement on Nanoscale Safety
- Office of Science Nanoscale Science Research Centers ESH Working Group
- American Society for Testing and Materials (ASTM) standard
- ESH Manual Section 4.13, Safe Handling of Engineered Nanomaterials
- Division Chemical Hygiene Plan
- Experiment Safety Reviews (ESH Manual Section 21.2)

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/

- Rice University's International Council on Nanotechnology (ICON)
  http://icon.rice.edu/

- Nanoparticle Information Library (NIL)
  http://www2a.cdc.gov/niosh-nil/index.asp

For more information on nanomaterials:

- Contact EQO-Industrial Hygiene at 2-3310

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

http://www.aps.anl.gov/Safety_and_Training/Training/Courses/esh590/