A CASE STUDY OF THE USE OF FUNCTIONAL PROCEDURES FOR MANAGEMENT OF NANOMATERIALS
What is Nanotechnology

**Nanotechnology:** The science of developing and using technology at the atomic, molecular, or macromolecular range of approximately 1-100 nanometers (nm) to create structures, devices, and systems that have novel properties. Scale: 100 nm = 0.1 micrometer (mm) or 0.1 micron

**Nanomaterials:** Materials incorporating engineered nanoparticles or nanoscale features that exhibit unique physical and chemical properties as a result of the nanoparticles or nanoscale features.

**Nanoparticles:** Engineered particles in the range of greater than molecular to 100 nano-meters (nm) in at least one dimension.

**Ultrafine particles:** Used to describe in the context of incidentally produced particles (e.g., combustion products), those particles smaller than 100 nm in diameter as it pertains to aerosol research and occupational and environmental health.
Why Nanotechnology?

• Carbon Nanotube (CNT) Infusion Process
  – Technology to infuse carbon nanotubes in a scalable continuous process on a variety of host fiber materials.
  – Used to recreate the random orientation of CNTs in composite coating while maintaining high absorption (desired outcome).
  – Utilize CNT infused fiber high absorption properties (directional current) and for its light weight vs copper bridge.

CNT Enhanced Properties Relative to Current Composites

- Flexure strength (~200%)
- Improved (~150%) Inner laminar shear strength
- Enhanced buckling load (~100%)
- Mode I fracture toughness (~300%)
- Harmonic damping (~400%)
- Electrical conductivity (7X)
- Thermal expansion reduction (~200%) – through thickness
- Improved thermal conductivity (10X)
- Toughness/Stiffness (2X)
- EMI Shielding – Equal to metals
- Lighting Strike Protection – Like metal
CNT Infusion Process

Fiber Payout → Fiber Spread → Plasma Treatment → Catalyst Application → CNT Growth → Re-spool/Filament Wind

Fiber spreading
Fiber surface preparation
Catalyst particles deposited
Full radial coverage of CNTs on fiber

CNT Enhanced Properties Relative to Current Composites
CNT Base Growth

CNT Infusion At The Fiber Surface
CNT Infused Fiber
CNT Sheets

- 4'
- 25'
- 12"
- 21'
Test Results – Lightning Test

Tested in accordance to SAE ARP5577 for compliance to Direct Lightning Effect requirements of Federal Aviation Regulations 25.581

- Up to 200 kA applied to the surface of panel
- No damage observed in unpainted CNT-infused glass panel

Initial Results Show Promise for Lightening Strike Applications
Application to the Orion Capsule
Orion Capsule
Risk Assessment and Procedures

• Actual health effects from the inhalation of CNTs are not currently known.

• Until proven otherwise, current safety practice is to ensure most stringent safety precautions.

• The work area was segregated from the rest of the production facility and entry was restricted.

• Operations involving CNTs will be evaluated and a risk assessment performed in accordance with site policy.

• Industrial hygiene monitored for airborne particulates using a condensation particle counter (Lesson Learned)

• Waste management practices involved placement of all contaminated waste in a specially marked drum to ensure materials would not be retrieved from the trash and minimize production of airborne particles. (Lesson Learned)

• PPE utilized to ensure maximum protection to workers. Combination HEPA and vapor cartridge due to solvents used.
Panel Lay Up

- CNT sheets were infused with a resin using a proprietary process by an outside source.
- Nanotube sheet material impregnated with very thin film of 977-3 resin on one side only
- Used the thinnest possible resin layer to minimize both weight and resin effects on electrical properties.
- CNT sheet and resin layer appeared to be two distinct layers resulting in difficulty in handling and wrinkling during application.
Panel Cure

• Fabrication with CNT sheets laid on top of fiber placed panel, then flipped over for cure resulted in defects on nano surface of panels

• Fabrication of panel with CNT sheets layed up on top of tool surface resulted in more surface defects

• Excess resin inhibits the performance of the nanomaterials’ electrical properties

• Learned CNT sheet and resin appeared to be 2 distinct layers, little resin infusion

† Bottom side of arrow is resin side of one sided tacky CNT sheet
Lesson Learned

• How to sample.
• Evidence of residual contamination?
• Dumpster diving
• Scanning Electron Microscope:
  – identified that the bundled nature of the nano particles did not show any fraying and did not reveal any residual nano particles on the paper backing.
• Agglomeration
Nanotube Sheet – Electron Microscopy

Nanotube sheet, cross section, 80x

Nanotube sheet, cross section, 1000x
Nanotube Sheet – Electron Microscopy

Nanotube sheet, cross section, indicating filament cluster, 2000x

Nanotube sheet, cross section, indicating filament cluster, 5000x
Backings Material – Electron Microscopy

Entire sheet of backing material as submitted

Nanotubes in resinous material on sample edge.
Routes of Occupational Exposure

- Noteworthy quantities of air-borne particles less than 100 nm in size came only with the industrial revolution in the form of air pollution, an unintentioned but largely unavoidable byproduct of high-temperature industrial processes.
  - The main route of exposure is inhalation (like smoke or vapor)
  - Other possible exposure routes are:
    - Ingestion
    - Direct penetration (absorption) through the skin
Nanoparticle Distribution

How far will nanoparticles go?

<table>
<thead>
<tr>
<th>Particle Category</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse</td>
<td>Particles with an average diameter of $&lt; 10 \mu m$</td>
</tr>
<tr>
<td></td>
<td>($\mu m = \text{micron}$)</td>
</tr>
<tr>
<td>Fine</td>
<td>Particles with an average diameter of $&lt; 2.5 \mu m$</td>
</tr>
<tr>
<td>Ultrafine (Nanoparticles)</td>
<td>Particles with an average diameter of $&lt; 0.1 \mu m$ ($&lt; 100 \text{ nm}$)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ultrafine (Nanoparticles)</th>
<th>UFP – Approx. size*</th>
<th>Potential Entry Point$^{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>70 nm</td>
<td></td>
<td>alveolar surfaces of the lung</td>
</tr>
<tr>
<td>50 nm</td>
<td></td>
<td>cells</td>
</tr>
<tr>
<td>30 nm</td>
<td></td>
<td>central nervous system</td>
</tr>
<tr>
<td>$&lt;$20 nm</td>
<td></td>
<td>no comprehensive scientific data as yet</td>
</tr>
</tbody>
</table>

*The contribution of size vs. the contribution of material composition to a particle’s toxicity has not been clearly established. There are indications that size matters as much as or more than the material of which the particle is composed.
Health Effects – Given Facts

• Nano-sized particles are highly respirable, but agglomerate into larger particles due to chemical and physical characteristics. They may present the potential for chronic lung diseases due to their size and respirability.

• Individual nanoparticles have the potential to embed deeply in the lung.

• Until proven otherwise, accept and act on the general principle that toxicity and reactivity of particles increase as particle size decreases. Cannot predict toxicity based on its physiochemical (e.g. chemistry, density) properties.
Agglomeration of Nanoparticles

- Hazard from airborne particles varies with their physical, chemical or biological properties.
  - Agglomerates are assemblies of aggregates held together by weak bonds which may be due to van der Waals forces or ionic/covalent bonds.
  - When two particles collide those forces will keep them irreversibly together. This "hit and stick" process among particles is called agglomeration. As agglomeration proceeds, particle number is reduced, but the average diameter grows. Eventually an agglomerate grows to such size that it settles to the ground and is thereby removed from the atmosphere.

<table>
<thead>
<tr>
<th>size</th>
<th>settling velocity</th>
<th>diffusion velocity (drift)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 nm</td>
<td>0.07 um/s</td>
<td>330 um/s</td>
</tr>
<tr>
<td>31 nm</td>
<td>0.23 um/s</td>
<td>110 um/s</td>
</tr>
<tr>
<td>100 nm</td>
<td>0.88 um/s</td>
<td>37 um/s</td>
</tr>
<tr>
<td>312 nm</td>
<td>4.48 um/s</td>
<td>15 um/s</td>
</tr>
</tbody>
</table>
Particle Removal

A: impaction
B: interception
C: diffusion
Particle Removal

![Diagram of Particle Removal Efficiency vs. Particle Diameter](image)
1. Gravitational settling
   • relatively large particles (> 5 µm)
   • occurs in nasopharynx primarily
   • less significant in tracheobronchial and gas exchange compartments

2. Impaction
   • important mechanism of deposition
   • sizes from ~ 1 µm and larger
   • nasopharynx: impaction on nasal hairs and turbinates, naso- and oropharynx
   • tracheobronchial: impaction at bifurcations in bronchi, bronchioles
   • gas exchange: little impaction because of low velocities
3. Interception
   • most significant for fibrous aerosols
   • can occur in all 3 compartments

4. Diffusion
   • for sizes < ~ 0.5 µm or 500 nm
   • most significant in gas exchange region [low velocity, short distances]

5. Electrostatic
   • of little significance because of rapid humidification of inhaled air
Various mechanisms of clearance:

1. physical: sneezing, coughing, swallowing
2. chemical: dissolution
3. biological: muco-ciliary escalator, phagocytosis
Clearance of Deposited Particles

- **Naso-pharyngeal clearance:**
  - $t_{1/2} < 1$ day
  - sneezing, blowing nose
  - muco-ciliary clearance

- **Tracheobronchial clearance:**
  - $t_{1/2} \sim 0.7$ day
  - coughing
  - muco-ciliary escalator

- **Pulmonary clearance:**
  - 2 modes: slow, $t_{1/2} \sim$ months; fast, $t_{1/2} \sim$ weeks
  - solubilization
  - phagocytosis
Health Effects – Point/Counterpoint

• Nano-sized particles will behave like fibers (asbestos) – See Poland (2008)
• Fibers of >5 to 20 um and as aspect ratio (length/width ratio) >3 are of greatest toxicological interest
• Respirable fibers in concentrations >0.1 fibers cm\(^{-3}\) are of concern based on associated carcinogenicity.
• Toxicity of nanoparticles is greater (NIOSH) than that of the same mass of larger particles of similar chemical composition.

YET:
• Fibers <5 um are expected to behave like particles in the lungs
Nanoparticle Behavior

• Behave more like gases
  – Move from areas of highest concentration
  – Tend to “clump”
  – Settle slower than macro particles
  – Will widely spread out
  – Can be re-suspended easily
  – Particles less than ~16 µm can slip between air molecules. Brownian motion (hence diffusion)

• Less drag → higher velocity
  – Increase velocity on an impactor leads to particle bounce and bias in sampling
Functional Procedures

- Use current hazard information related to CNT
- Bulk ("free-form") vs Bound – engineering controls
- Evaluate the performance of engineering controls
- Routinely evaluate airborne exposures to ensure that control measures are working properly
- Hazard assessment to determine proper personal protective equipment
- Educate workers on the sources and job tasks
- Use light-colored PPE and work bench surfaces to facilitate observation of contamination by dark CNT
- Segregate and contain waste
Hazard Assessment

• A plan must be developed and executed that addresses the following requirements per NASA requirements:

• Hazard Analysis
  – Identify potential adverse health effects and environmental impacts posed by unique characteristics of material

• Exposure Assessment
  – Evaluate all tasks involving nanomaterials and identify where exposures could occur, including:
    • Chemical intermediates
    • By-products
    • End-products
    • Waste products
    • Processes and process equipment
    • Amount of material used
    • Material form
    • Degree of containment
    • Duration of use
    • Work space including laboratory and manufacturing space.
Hazard Assessment (cont)

• Exposure Control
  – Implement controls to mitigate worker exposure and environmental emissions
  – Implement Control Bands as indicated on the Control Band Matrix
  – Establish designated areas for Control Banding
    • Examples: entire laboratory or manufacturing area, or portion of the larger area, such as a laboratory hood or glove box
    • The designated will have warning signs informing employees that they are entering a nanomaterial work area as well as signs specifying administrative controls and personal protective equipment (PPE) required for entry
    • Identify appropriate administrative controls
    • Develop practices that do not re-suspend particles
    • Develop Procedures for managing nanomaterial-associated waste
Hazard Assessment (cont)

• Update of Affected Plans, Programs and Training
  – Hazard Communication Plans
  – Job Hazard Assessments
  – Laboratory Chemical Hygiene Plans
  – Update existing training programs and training materials to include nanotechnology hazard information
  • Communicate that exposure leading to adverse health effects may occur via inhalation, ingestion and dermal absorption

• Record Keeping and Surveillance
  – Develop and execute a means of identifying personnel who work with nanomaterials in designated areas
  – Update the facility medical surveillance program to include personnel who work in designated areas

*Characterize, Sample, Assess, Repeat*
# Control Banding for Nanotechnology

<table>
<thead>
<tr>
<th>Exposure Duration</th>
<th>Bound Materials</th>
<th>Potential Release</th>
<th>Free / Unbound</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hazard Group A (Known to be inert)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Short</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Medium</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Long</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td><strong>Hazard Group B (Understand reactivity/function)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Short</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Medium</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Long</td>
<td>1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td><strong>Hazard Group C (Unknown Properties)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Short</td>
<td>2</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Medium</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Long</td>
<td>2</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

**Duration Key:**
- Short: < 4 hrs/day; 2 days/wk
- Med: 4 to 6 hrs/day; 3 to 5 days/wk
- Long: 6 to >8 hrs/day; 3 to 5 days /wk

**Release Key:**
- Bound: Particles in solid matrix
- Potential Release: Particles in friable or sol gel matrix
- Free/Unbound: Unbound, not aggregated

**Control Band Key:**
- Band 1: General ventilation & PPE
- Band 2: Engineering controls and/or Respirators; additional PPE
- Band 3: Containment e.g. glovebox
- Band 4: Specialist Advise
Control techniques such as source enclosure and local exhaust ventilation systems are considered to be effective for capturing airborne nano-particles (Confirmed by independent studies by NIOSH in Baltimore CNT Lab)

Primary Control is always Engineering Controls
Sampling

- **Strategy**
  - No PEL, determine if any airborne releases of nanoparticles
  - Multifaceted approach (No single sampling method)
    - NIOSH Nanoparticle emission Assessment Technique (NEAT)
  - First determine background before particle count
  - Condensation and Optical particle counter used in parallel
    - Above background?
  - Personal and area filter monitoring, TEM for mass concentration
    - Cyclone vs. Open face conductive cowl

- **Traditional size differentiation by using Andersson Impactor (N/A)**
  - most significant mechanisms are impaction and diffusion
  - impaction $\uparrow$ as $V \uparrow$; diffusion $\downarrow$ as $V \uparrow$; Given small size, particles bounce
  - impaction important for large particles; diffusion for small particles

- **Surface Sampling**
  - Ghost wipe with NIOSH Method 9102
**Sampling**

**Count/Sizing Equipment**

**Condensation Particle Counter**
- Alcohol aerosol as condensing medium
- Range 10 nm to 1.0 micron diameter

**Fast Mobility Sizer**
- Lower limit – 5 nm diameter
- Improved resolution below 300 nm

**Light Scattering Counter**
- Limits of 0.3 to 5.0 micron diameter
- Useful to do complete profile

**Nanoaerosol Monitor**
- Measures Fuchs surface area of nanoparticles
- Intended to mimic the tracheobronchial and alveolar regions of the lung
• Detects different carbon types
  • Organic carbon (OC)
  • Carbonates (CC)
  • Elemental carbon (EC)
  • Pyrolytic carbon (PC)

• The upper estimate of the LOQ is 7μg/m3, as an 8-hr TWA concentration

• NIOSH is recommending a REL of 7 μg/m3 as an 8-hr TWA airborne respirable

• Leverages existing accepted test for diesel particulates
Work Area Signs and Labels

• Example signs that are located at entry points of the areas designated for work with nano-materials.

• Signage will also be affixed to all ventilation and process equipment, indicating the presence of/exposure to nano-materials and nano-particles.

• Communication of potential hazards is a requirement of OSHA’s HazComm (49CFR1910.120) as well as contractor (Lockheed Martin Corporation ESH-12) standards.
NANOMATERIAL AREA
ENTRY RESTRICTED TO LISTED NANOTECHNOLOGY PERSONNEL
PERSONAL PROTECTIVE EQUIPMENT REQUIRED

FOR ACCESS PLEASE CONTACT
A. Rovira (Safety) 7-0881
Regulations: PPE Use

• NIOSH has demonstrated that HEPA respirators are effective in reducing worker exposure.

• EPA 40 CFR 721.10155 Significant New Use Rules requiring NIOSH-approved air-purifying, tight-fitting full-face respirator equipped with N100 filters.

• Specific requirements for “releases into water” 40 CFR 721.90

• NIOSH study (2006) titled “Penetration of Nanoparticles through Respirator Filter Media” indicated a 99.99% efficiency
  – Nanoparticle penetration decreases continuously with decreasing particle size down to 3 nm.

• Site requires double glove protection

• Site requires disposable tyvex type suits
Regulations

Who Regulates?
• EPA Toxic Substances Control Act (TSCA)
  – TSCA gives EPA broad authority to regulate chemical substances
  – Evaluate “new” or “existing” chemicals under Section 3 and possibly a Premanufacture Notice (PMN) under Section 5 required.
  – EPA take is that chemical substance with molecular identity not identical to any substance on TSCA Inventory is considered to be a new chemical.

• Responsibility lies with the Company
  – EPA require certain data on nanoscale substance to determine if chemical covered by existing list.
    • Companies arrange a pre-notice consultation with EPA; or
    • Submit a request for an Inventory search.
Waste Management

• Wastes from engineered nanomaterial-bearing need to be controlled and these waste streams consist of:
  – Pure engineered nanomaterials (e.g., carbon nanotubes),
  – Items contaminated with, or containing engineered nanomaterials (e.g., wipes/personal protective equipment),
  – Liquid suspensions contaminated with, or containing engineered nanomaterials and waste waters from wet-processing of nanomaterials,
  – Solid matrixes with engineered nanomaterials that are friable or have a nanostructure loosely attached to surface such that they can reasonably be expected to break free or leach out when in contact with air or water, or when subjected to reasonably foreseeable mechanical forces, and/or solid matrixes with engineered nanomaterials.

• Generators of waste containing nanomaterials, including waste waters, may need to be evaluated to determine whether it is a hazardous waste or special waste per the state. These requirements apply to all wastes containing nanomaterials.
Engineered Nanomaterials in Waste Streams

In terms of disposal, no promulgated environmental protection (except water) or waste management regulations specific to nanomaterials by either EPA or any other State:

• NASA Current Practices
  - Decontaminate equipment used to manufacture or handle nanomaterials before disposing of or reusing it. Treat wastes (e.g., cleaning solutions, rinse waters, rags, etc) resulting from decontamination as engineered nanomaterial-bearing waste.
  - Do not put material from engineered nanomaterial-bearing waste streams into the regular trash, segregate waste and label as non-haz.
  - Do not put nanomaterial-bearing waste down any drain without authorization.
  - Do not permit engineered nanomaterial-bearing wastes to be shipped to off-site locations
Questions