

Clemson University
Nanomaterial Safety

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Introduction

Applicability and Scope

The following interim procedure is intended using engineered nanomaterials at Clemson University.

It sets forth practices for managing environmental, safety and health concerns associated with:

- “Engineered” or naturally occurring nanomaterials, i.e., materials consisting of, or containing structures between 1- and 100-nanometers (nm) at their smallest dimension, that use the properties unique to nanoscale forms of materials.
- Precursors, intermediates, and wastes used during, or resulting from synthesizing such nanomaterials.

Purpose

This document was prepared as an interim policy for managing nanomaterials whose hazards have not been determined.

This document is based on the Brookhaven Lab Nanotech Management document, which is in turn based on DOE Nanotech documentation.

Limitations

- The following guidelines are not intended to discourage responsible efforts to develop or refine alternative approaches to evaluating and managing risks.
- Any guidance contained herein that conflicts with any regulatory requirements or consensus standards, the more conservative approach will be used.
- Information about the safety and health effects caused by nanomaterials is changing rapidly; this document will be updated as necessary.

Background

- Nanoscale materials are of considerable scientific interest because some material properties change at this scale. However, these changes also challenge researcher’s, manager’s, and safety professional’s understanding of hazards, and their ability to anticipate, recognize, evaluate, and control potential health, safety, and environmental risks.
- Exposures to these materials during research and development may occur through inhalation, dermal contact, and ingestion. Animal studies indicate that low-solubility ultrafine particles might be more toxic than larger ones on a mass-for-mass basis. Because of their tiny size, they can get deep into the lungs and may be translocated to other organs following pathways not demonstrated by previous studies with larger particles.
- The nanoparticulate forms of some materials show unusually high reactivity especially for fire, explosion, and in catalytic reactions. Nanometer particles and nanostructured

porous materials have been used effectively for many years as catalysts for increasing the rate of reactions, or decreasing the temperature needed for reactions in liquids and gases. Depending on their composition and structure, some nanomaterials may initiate catalytic reactions that would not otherwise be anticipated from their chemical composition.

- Federal OSHA has made it clear that the agency expects those engaged in the emerging field of nanotechnology to act responsibly in evaluating and controlling the associated environmental, health and safety risks.
- Although there is a lack of specific guidance on evaluating and controlling the risks posed by nanomaterials, preliminary research suggests that some of the controls used in conventional laboratory settings will work effectively for them.
- Lacking other guidance and recognizing the benefits to themselves, their sponsors, and their shared user community, Clemson University will use the following relatively conservative policies and risk-control strategies until more authoritative guidance is available.

Clemson University Policy

- Clemson University, as part of its efforts to develop state-of-the-art capabilities for fabricating and studying nanoscale materials, will endeavor to ensure that adequate Health and Safety controls are applied during this research including the application of this policy.
- The Clemson University Institutional Biosafety Committee (IBC) will act as an advisory body to EHS for the implementation of this policy. The IBC will review and make recommendations where compliance to this policy cannot be reasonably achieved and/or alternative approaches employing equivalent level of safety are proposed.
- In conformance with the general principle in the National Research Council's *Prudent Practices for Handling Hazardous Chemicals in Laboratories*, nanomaterials will be treated as though they are a toxic and otherwise hazardous material until empirical-based evidence shows otherwise.
- Nanomaterials whose hazards have been studied should be managed in a manner consistent with the disclosed risks.
- Nanoparticle contamination of exhaust systems is not permitted; see Ventilation, below.

Routine Laboratory Operations

Work Planning

Review all planned projects involving nanomaterials for Health and Safety concerns. The PI will as a minimum:

- Develop a well-defined description of the work,
- Consult CU EHS,
- Specify hazard controls, including (but not limited to):

- Engineered controls
 - Design reviews
 - Formal procedures
 - Use of personnel protective equipment
 - Training
 - Other administrative controls
 - Defined criteria for protocol-change control
- Review chemical hazard information for bulk/raw materials when developing controls, and any new information specific to the material at the scale being used.
 - Ensure that EHS evaluates the potential for generating nanomaterial bearing waste streams before starting any new work.
 - Have EHS evaluate laboratory equipment and exhaust systems before removing, remodeling, servicing, maintaining, or repairing them to prevent the exposure of maintenance personnel to the nanomaterials, or their escape into the environment.
 - Review the hazards of precursor materials in evaluating process hazards.
 - Consider the high reactivity of some nanopowders as potential fire- and explosion-hazards.

Control Preferences

1. Follow a graded approach in specifying controls. Operations involving easily dispersed dry nanomaterials deserve more attention and more stringent controls than those where the nanomaterials are imbedded in solid or liquid matrices.
2. Avoid manipulating nanomaterials in the open air in a “free particle” state. Preferably (1) keep them bound in a matrix, (2) suspended in a liquid, or (3) sealed in a container. Preferably, nanomaterials should be kept in the following states (in order of preference) whenever practicable:
 1. Fixed in a matrix
 2. Bound in a solution
 3. Free Particulate
3. Follow the standard hierarchy of hazard controls for nanomaterials:
 1. Engineered controls
 2. Administrative controls
 3. Personal protective equipment
4. Consider the hazardous properties of the precursor materials as well as those (possibly unknown) of the resulting nanomolecular product.

5. Perform all manipulations of free nanoparticulates in a HEPA-filtered bag in/out powered-exhaust chemical hood or glove box. If nanoparticles must be handled outside such a hood, institute other appropriate engineering controls or wear appropriate respiratory protection and other personal protective equipment (PPE) as approved by EHS.

Engineered Controls

Work Area Design

- Consider the necessity for implementing additional procedures to ensure that workers are protected in areas where dispersible nanomaterials are handled. Consider additional controls to better ensure that nanomaterials are not brought out of the work area on clothing or other surfaces, e.g., install step-off pads, create a buffer area, and ensure the availability of decontamination facilities for workers.

Ventilation

- Conduct any work that could generate dispersible nanoparticles in an enclosure that operates at a negative pressure differential compared to the worker's breathing zone. Examples of such enclosures include laboratory bench-top or floor-mounted chemical hoods and glove boxes; these must be HEPA-filtered bag in/out powered-exhaust chemical hoods or glove boxes. If the process cannot be enclosed, then any location at which nanomaterial or a hazardous precursor can enter the atmosphere should be controlled using other appropriate engineering controls.
- Do not directly exhaust effluent (air) into the building ducting that is reasonably suspected to contain nanoparticles. Filter it or otherwise clean it before release. HEPA filtration appears to be adequate. Contamination of the exhaust system must be prevented in order to protect maintenance personnel. A bag in/out HEPA filter must be in place between the work enclosure and the building's ductwork.
- Do not recirculate within the laboratory air from which nanoparticles have been removed. All air exhausted from an enclosure, partial enclosure, or process equipment (reactors, pumps, and furnaces) that might reasonably be expected to contain nanoparticles should be cleaned and then exhausted outside the building. Equipment can be placed in a HEPA-filtered hood, or a HEPA filter can be placed in the equipment's exhaust stream. Alternatively, other strategies, such as scrubbing or using a bubbler, may be utilized to treat unreacted precursors and may also be effective in reducing nanomaterial emissions.
- Do not use horizontal laminar-flow hoods ("clean bench") that direct a flow of HEPA-filtered air into the user's face to control exposure to nanomaterials.
- Type I or Type II biological safety cabinets in which free nanomaterials are handled, must be exhausted directly to the exterior (hard ducted) or through a thimble connection over the cabinet's exhaust. Air from inside the cabinet, even if filtered, may not be recirculated within the laboratory.

- Maintain and test the effectiveness of exhaust systems and components as specified by the manufacturer. Evaluate equipment previously used to synthesize or handle nanoparticles for contamination before reusing or disposing of it.

Administrative Controls

Chemical Hygiene Plan

- Implement the Clemson University chemical hygiene plan (as required under 29 CFR 1910.1450).

Housekeeping

- Practice good housekeeping in laboratories where nanomaterials are handled. Clean all working surfaces potentially contaminated with nanoparticles (i.e., benches, glassware, apparatus, exhaust hoods, support equipment) at the end of each shift using a HEPA vacuum pickup and/or wet wiping methods. Do not dry sweep or use compressed air. Dispose of used cleaning materials in accordance with Clemson University's Hazardous Waste Manual (See "Management of Waste Containing Nanomaterials" later in this document).

Work Practices

- Transfer nanomaterials samples between workstations (such as exhaust hoods, glove boxes, furnaces) in closed, labeled containers.
- Do not allow nanoparticles or nanoparticle containing materials to contact the skin.
- If nanoparticle powders must be handled outside a fume- or exhausted laminar flow-hood, use appropriate respiratory protection.
- Handle nanomaterial bearing waste according to Clemson's Hazardous Waste Manual and the "Management of Waste Containing Nanomaterials" section of this document.
- Vacuum dry nanoparticulates only if the vacuum cleaner has a tested and certified HEPA filter. Where possible material should be wetted prior to vacuuming.

Inventory Requirements

- All Clemson Laboratories are required to have a complete and up-to-date inventory of all hazardous materials (chemical, biological, and radiological), and to submit this to EHS both annually and upon request.

Marking, Labeling and Signage

- Post all doors to laboratories with signage indicating the hazards and required Personal Protective Equipment within the laboratory.
- Indicate on container labels that the contents are in nanoparticulate form, e.g., "nanoscale zinc oxide" or other identifier instead of just "zinc oxide."

Clothing & Personal Protective Equipment

- Wear appropriate personal-protective equipment on a precautionary basis whenever the failure of a single control, including an engineered control, could entail a significant risk of exposure to researchers or support personnel.
- Wear clothing appropriate for a wet-chemistry laboratory as per the Clemson Chemical Hygiene Plan including :
 - Closed-toed shoes made of a low permeability material. (Disposable over-the-shoe booties may be necessary to prevent tracking nanomaterials from the laboratory)
 - Long pants without cuffs/pockets
 - A long sleeved shirt
 - Disposable laboratory coats. These coats should be handled in accordance with the “Management of Waste Containing Materials” section of this document.

If non-disposable laboratory coats are preferred, they will remain in the laboratory/change out area when not worn to prevent nanoparticles from being transported into common areas. The coats should be placed in closed bags before being taken out of the laboratory for cleaning in a central approved location. Contact EHS for approved laundry facility locations on the main campus and research parks.

- Wear nitrile gloves when handling nanopowders and nanoparticles in liquids.
- Exposure to nanomaterials is not known to have “good warning properties” so gloves should be changed frequently.
- The contaminated gloves should be kept in a closed plastic bag in the work area until disposal. Manage the resulting waste in accordance with Section 6 of this procedure.
- Outer gloves made of other material, such as cotton, may be used for protection when handling articles wherein the nanomaterials are in bound form.
- Safety glasses, and/or face shields, should be worn as appropriate for the level of hazard. A face shield alone is not sufficient protection against unbound dry materials.
- The appropriate respirator and cartridge combination, based on an Industrial Hygiene assessment, should be worn when deemed necessary by the safety assessment. Personnel should receive medical clearance before being fitted with a respirator; contact EHS to arrange medical clearance and admission to the Respiratory Protection Program. If a respirator is indicated, it should be a minimum half-mask, P-100 cartridge-type respirator that has been properly fitted to the worker by the Clemson Industrial Hygienist.

Monitoring and Characterization

- In consultation with Laboratory’s SMEs, use a direct-reading particle measuring device to screen for suspect emissions.

- Use more sophisticated techniques, to collect samples to characterize emissions and determine if a control is needed or must be upgraded or serviced.
- Link environmental data to potentially exposed personnel using the Laboratory's data-management system.

Worker Competency

- Do not assume that staff members and visiting researchers are aware of the health and safety concerns posed by nanomaterials. Alert all personnel in each group to concerns and to the Laboratory policies about nanomaterials via an awareness-level orientation.
- Incorporate specific procedural requirements into the ESR to better assure understanding and competence.

Medical Surveillance

EHS recommends the PI contact the Occupational Medicine Nurse (OHN) to determine the advisability of:

- Employees with jobs involving the potential for [or “reasonably anticipated”] respiratory or skin exposure to nanomaterials undergoing medical surveillance, as defined by Clemson EHS.
- The employees involved in any incident that results in an unexpected and/or unusually high exposure to nanomaterials, through any route of entry, should be examined by the OHN.
- Non-resident personnel should be exempted from medical surveillance unless requested by the individual.

Transportation of Nanomaterials

The guidance under this heading applies to the movement of material from the Laboratory to off-site locations, and vice versa. Personnel who prepare and package nanomaterials for shipment off-site must have current HazMat Employee training in compliance with 49 CFR Subpart H.

Categories of Materials

Recognized HazMat

Any nanomaterial that meets the definition of a hazardous material according to 49 Code of Federal Regulations (CFR) Part 171.8 and can be classified as a hazardous material in accordance with 49 CFR 173.115 through 141 and 173.403 through 173.436 must be packaged, marked, labeled, shipping papers prepared, and shipped in accordance with 49 CFR 100 to 185.

Any nanomaterial being shipped by air that meets the definition of dangerous goods according to the International Civil Aviation Organization (ICAO) must be packaged, marled, labeled, dangerous goods declaration prepared, and shipped in accordance with the ICAO technical instructions.

Suspected DOT HazMat

Nanomaterials that are suspected to be hazardous (e.g., toxic, reactive, flammable) should be classified, labeled, marked, and manifested as though that hazard exists in accordance with the “Recognized HazMat” section above. These materials should be shipped as samples per 49 CFR 172.101c(11) unless the material is specifically prohibited by 173.21, 173.54, 173.56(d), 173.56(e), 173.224c or 173.225(b).

Other Nanomaterials

Nanomaterials that do not meet the DOT’s criteria listed in above still may pose health and safety issues to personnel handling the material during its transport. Therefore, all shipments of nanomaterials, regardless of whether they meet the definition for hazardous materials or not, should be consistently packaged using the equivalent of a DOT-certified Packing Group I (PG I) container and labeled as described below.

Off-site Shipments

The information under this heading applies to materials sent to Clemson University, and materials sent from Clemson University to off-site locations.

Packaging

The outer and inner package should meet the definition of a Package Group I (PG I) type package. The innermost container should be tightly sealed to prevent leakage of nanomaterials. It should have a secondary seal, such as tape seal, or a wire tie to prevent a removable closure from inadvertently opening during transport.

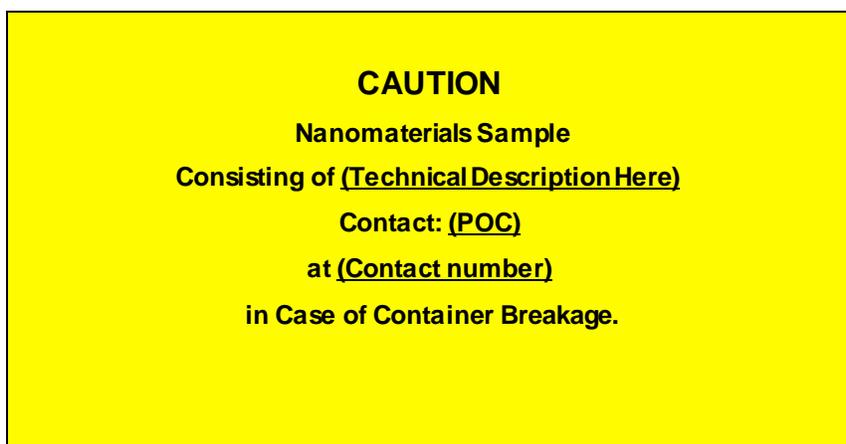
The outer package should be filled with shock absorbing material that can

- Protect the inner sample container(s) from damage
- Absorb liquids that might leak from the inner container(s) during normal events in transport.

Labeling

As depicted in Figure 1, the inner package should be labeled (not to be confused with DOT hazard labeling) “Caution: Nanomaterials Sample Consisting of (technical description here). Contact (name of point of contact) at (contact number) in Case of Container Breakage.” (see figure 1)

Figure 1 - Recommended Inner Packaging Label



Documentation & Notifications

Documentation and notifications for Off-Site transfer of nanomaterials should include the following:

- A signed and complete dangerous goods declaration and shipping papers prepared in accordance with the ICAO and DOT regulations by certified/qualified hazmat employees that have authority to ship materials from the lab (NOT students).
- Notification to receiving facility of the incoming shipment.

Modes of Transport

All transportation should be performed using a low cost, qualified carrier. Recommended modes for off-site shipment of nanomaterials include:

- FedEx, or other certified hazardous-materials carrier
- Roadway, UPS Ground, or other commercial LTL-certified hazardous-materials carrier
- Dedicated highway hazardous-materials carriers for exclusive-use shipments.

On-Site Transfers of Nanomaterials

The on-site transfer of nanomaterials should follow the Chemical Hygiene Plan. The Clemson University Chemical Hygienist is the authority having jurisdiction on the requirements for packaging, marking, and documentation necessary for on-site transfers. For nanomaterials, the following is suggested:

- Following a graded approach that takes into account the form of the material(s) (e.g., free particle vs. fixed on substrate), assess and record the hazards posed by the material(s).
- Use packaging consistent with the recommendations for off-site shipment or packaging that affords an equivalent level of safety.
- Mark the transfer containers in accordance with (above) recommendations for off-site shipments.

- Include the following documents in the package:
 - The results of the safety assessment
 - An MSDS if available (or a similar form) detailing possible hazards associated with the material; otherwise, if an MSDS is unavailable, the Principal Investigator should supply material-specific knowledge.
- Notify the receiving facility of the incoming shipment.
- Management of Nanomaterial bearing waste streams

Management of Waste Containing Materials

Applicability

This applies only to nanomaterial bearing waste streams consisting of:

- Pure nanomaterials (e.g. carbon nanotubes)
- Items contaminated with nanomaterials (e.g. wipes/PPE)
- Liquid matrixes containing nanomaterials (e.g. hydrochloric acid containing carbon nanotubes)
- Solid matrixes with nanomaterials loosely embedded or attached to the 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.

This does not apply to nanomaterials embedded in a solid matrix that can not reasonably be expected to break free or leach out when they contact air or water.

Control Waste generation

- Consider reducing the risk of loss of nanomaterials into the air and surrounding environment by suspending powders in a small volume of a non-hazardous liquid. Balance the added safety, if any, against the risks and costs of the increased volume of waste.
- Do not dispose of nanomaterial bearing waste streams directly into the sanitary system.
- Evaluate surface contamination or decontaminate equipment used to manufacture or handle nanoparticles before disposing or reusing it.

Classification and Disposal of Nanomaterial bearing Waste Streams

- Characterize nanomaterial bearing waste streams as either hazardous or non-hazardous waste based on the requirements in 40 CFR 261.10-38, considering their known characteristics and/or listing of the waste.
- Dispose of nanomaterial bearing waste streams that meet the definition of RCRA hazardous waste following the Clemson Hazardous Waste Management Manual.

- Dispose of nanomaterial bearing waste streams that are NOT classified as RCRA hazardous waste through EHS as a non-hazardous waste. Include available information characterizing known and suspect properties.
- Dispose of all nanomaterial wastes generated through EHS. Do not permit nanomaterial wastes to be shipped off-site for disposal by anyone other than CU EHS.
- Package nanomaterial bearing wastes in containers that are compatible with the contents, in good condition, and that afford adequate containment to prevent the escape of the nanomaterials.
- Do not place nanomaterials in the regular trash.

Management of Nanomaterial Spills

This applies to the response, control and clean up specific to nanomaterial spills.

Access Control

- Determine the extent of the area reasonably expected to have been affected, and demarcate it with barricade tape or use another reliable means of restricting entry into the area.
- To clean up significant spills, contact EHS to evaluate whether or not CU Fire and EMS need to be contacted, and restrict entry into the area.
- To clean up of smaller spills, lab personnel must be trained in the appropriate cleanup procedures.

Dry Materials

- Position a walk-off mat (e.g., Tacki-Mat→) where clean-up personnel will exit the access-controlled area.
- Do not dry sweep spilled accumulations of dry nanomaterials. Use only HEPA-filtered vacuum cleaners to clean up nanoparticles.
- Ensure that the functioning of the HEPA filters was properly tested as frequently as the manufacturer's recommends. HEPA vacuums for nanomaterials should be dedicated and labeled "For Use with Nanomaterials Only". Used HEPA filters must be appropriately characterized, collected, and disposed of as hazardous or potentially hazardous waste based on the material involved.

Liquids

Employ normal hazmat response based on the spilled material's known hazards. The following are additional considerations to mitigate nanomaterials left behind once the liquids have been removed:

- Position an absorbent walk-off mat where the clean-up personnel will exit the access controlled area.
- Place barriers that will minimize air currents across the surface affected by the spill.

- Use a HEPA-filtered vacuum dedicated to the clean-up of nanomaterials.
- Treat all materials used to clean up the spill (absorbent mats, absorbent material, wipes etc) as hazardous waste based on the material involved.

Wastes

- Manage all debris resulting from the clean up of a spill as though it contains sufficient nanomaterials to be managed as Hazardous Waste.