PROGRAM STATUS
Nanoscale Material Activities Control

May 15, 2008

Background

Jefferson Science Associates (JSA) serves as the contractor for the Thomas Jefferson Accelerator Facility and the FEL Facility

Research on nanomaterial at Jefferson Laboratory started in July 2000. The goal was to create carbon nanotubes using a precursor target of carbon with other metal catalysts. The nanotubes would be ablated from the target using the free electron laser. Originally the research was a collaborative effort with NASA Langley Research Center, University of William and Mary, and Pennsylvania State University. By the time of first lasing, only NASA and William and Mary remained in the collaboraton. The research was conducted at the Jefferson Laboratory the Free Electron Laser (FEL) Facility, Building 18. Two user laboratories in that facility were designated: Lab 1 for laser activities, and Lab 3a for target preparation and sample handling. Carbon nanotubes were produced from 2000 through 2007 during intermittent 3-4 hour runs using the free electron laser, producing milligram quantities of nanomaterial product.

A 5000 Watt carbon dioxide laser was procured by NASA in 2007 and located at the FEL Lab 3a. The free electron laser and Lab 1 were then no longer needed for nanotube production. Carbon nanotube production ended, and Lab 3a is used to produce boron nanotubes beginning in October 2007.

A typical production run yields a few milligrams of nanomaterial product. The nanomaterial product is transported to NASA. The nanomaterial product is considered to be the property of NASA once it leaves Jefferson Laboratory. It undergoes analysis using SEM and TEM . It is also evaluated for electrical and mechanical properties, thermal conductivity TGA analysis (thermographic analysis). The goal is to mix the nanomaterial product into polymers to investigate the added utility of its properties.

Previous microscopy on FEL carbon nanotubes indicates that the nanotubes form into a tangle of mattes of fibers. The clumps of fibers are 3 dimensional and typically tens of microns, which would be easily captured by HEPA filtration. The boron nanotubes are estimated to have an effective diameter in the millimeter range, due to the unique properties of the synthesis; it forms in self assembled long fibrous strands that coil upon each other. Actual microscopy studies are not yet complete.

DOE P 456.1 Secretarial Policy Statement on Nanoscale Safety Contractor and Site Office Implementation	STATUS
1. DOE will adopt and implement, as appropriate, both existing and future environment, safety and health best practices, "National Consensus Standards," and guidance relating to nanotechnology developed by recognized standard-setting organizations. Further, any existing DOE Directives and Standards which contain provisions that are relevant to nanotechnology work must be appropriately applied. 2. DOE and its contractors will identify and manage potential health and safety hazards and potential environmental impacts at sites through the use of existing Integrated Safety Management Systems, including Environmental Management Systems. 3. DOE organizations working with nanomaterials will stay abreast of current research and guidance relating to the potential hazards and impacts of nanomaterials, and will ensure that this best current knowledge is reflected in the identification and control of these potential hazards and impacts at their facilities. 4. DOE will continue to both support research on the environmental and safety and health impacts of nanomaterials, and participate in government-wide activities aimed at identifying and resolving potential environmental, safety, and health issues. 5. RESPONSIBILITIES Everyone involved with nanotechnology research and development activities shares responsibility for protecting the safety and health of workers and the public, and in safeguarding the environment from the hazards presented by the conduct of their activities. Authorized DOE employees (or personnel) are responsible for conveying to contractors and grantees the expectation that appropriate programs must be in place to maintain a level of worker, public, and environmental safety consistent with the intent of this policy.	1. Contractor SOP for the only nanomaterial R&D project complies with and references Department of Energy Nanoscale Science Research Centers (NSRC) Approach to Nanomaterial ES&H guidance document. 2. EMS environmental checklist developed for the nanomaterial related R&D project in the FEL. Environmental aspects are identified and addressed in the contractor SOP. 3. DOE Site Office Environmental Program Manager has used as reference the NSRC guidance, ASTM guidance, and NIOSH guidance. Plans to attend the Symposium on Safe Handling of Engineered Nanoscale Materials is for Site Office and JSA summer of 2008. 4. NA for TJSO site office 5. Full compliance

Department of Energy Nanoscale Research Centers (NSRC) Approach to Nanomaterial ES&H Contractor Requirements	**STATUS**
Conform to the general principle in the National Research Council's *Prudent Practices for Handling Hazardous Chemicals in Laboratories*: Laboratory personnel should treat "all new compounds, or those of unknown toxicity, as though they could be acutely toxic in the short run and chronically toxic in the long run."	Full compliance
3.1 Work Planning Review all work with nanomaterials for ES&H concerns following an established safety- assessment process. Before starting work, a safety assessment consistent with the home Laboratory's process is conducted The assessment should, as needed, 1. Begin with a well-defined description of the work 2. Involve ES&H subject matter experts (SMEs) 3. Specify hazard controls, including, Engineered controls, Design reviews, Formal procedures. 4. Use of personal protective equipment (PPE) 5. Training 6. Other administrative controls 7. Defined criteria for work-change control 8. Consider chemical hazard information for bulk/raw materials when developing controls for nanomaterials, and any new information specific to the material at the scale being used. 9. Before starting any new work, ensure that the Center's subject matter expert (SME) or the home Laboratory's authority over waste management : • evaluates the potential for generating new nanomaterial-bearing waste streams • defines waste management procedures for wastes that contain nanomaterials 10. Evaluate the potential for worker exposure to nanomaterials and their escape into the environment before removing, remodeling, servicing, maintaining, or repairing laboratory equipment and exhaust systems. 11. Consider the recognized and foreseeable hazards of the precursor materials and intermediates as well as those of the resulting nanomaterials. • Consider the higher reactivity of some nanoscale materials as requiring that they be treated as potential sources of ignition,	Fully compliant: The established process for new experiments includes: 1. Experiment design review approval. Followed by with experimental safety analysis form (referred to as safety approval form) which must contain a detailed description of the work. The nanotube experiment at the FEL is controlled by: • laser standard operating procedure • experiment safety approval form • SOP for sample preparation, handling, and transfer of nanomaterial precursors and products. An additional procedure is maintained by a subcontractor for periodic maintenance of local exhaust/filter change outs. 2. Industrial Hygiene group is involved in identifying controls and receives draft work control documents for comments. Any other ES&H SMEs are identified at that time. Joint walkthrough of experiment area prior to implementation of SOP by SMEs, line management to ensure all controls are in place. 3. Establishment of hazard controls: combinations of isolation, filtered local exhaust, housekeeping, and postings are detailed in SOP. 4. Training and medical approval for

accelerants, and fuel that could result in fire or explosion. • Consider the potential for reactions involving nanomaterials already "captured" in exhaust air filters.	PPE Standard Operating Procedure(SOP) signed off by line management and subject matter experts. 5. Training requirement and signoff for SOP (very limited user population: 1 staff member, 1 user). 6. Other administrative controls are detailed in SOP. 7. New procedures required for work-change, effectiveness reviews conducted to ensure this happens (most recent in April 2008) 8. Industrial Hygiene Group assists with hazard analysis of precursor and bulk material hazards and controls in SOP. 9. Industrial Hygiene Group sets up hazardous waste satellite accumulation area for the experiment byproducts and used HEPA filters and cleanup debris (flammable solids for carbon tubes). 10. Control of any emissions from the experimental area has been evaluated and is through local exhaust that is HEPA filtered. Experimental area smoke tested to ensure negative pressure from rest of facility, dedicated HVAC. 11. Hazard information and controls for precursors and byproducts as well as the intended product are identified in SOP. Exhaust filters associated with the laser table are disposed of as flammable solids because they contain laser ablation decomposition byproducts.
Control Preferences 1.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 matrixes. 2. From a laboratory worker health management perspective, the following represents the order of preference (most preferred to least preferred) for handling nanomaterials:	1. and 2. Three stages consist of experimental production , collection, and sample transfers: a. Complete isolation during production of dry nanomaterial in a collector unit. Backup local

a. Solid materials with imbedded nanostructures b. Solid nanomaterials with nanostructures fixed to the material's surface c. Nanoparticles suspended in liquids d. Dry, dispersible (engineered) nanoparticles, nanoparticle agglomerates, or nanoparticle aggregates Avoid handling nanomaterials in the open air in a "free particle" state. Whenever possible, handle and store dispersible nanomaterials, whether suspended in liquids or in a dry particle form in closed (tightly sealed) containers. 3. Consider the hazardous properties of the precursor materials as well as those of the resulting nanomolecular product.	exhaust is also used. b. A HEPA filtered respirator is worn to supplement local exhaust when disconnecting the collector from the experimental laser table and subsequent transfer to HEPA filtered chemical fume hood. c. Samples sent out for analysis are suspended in isopropyl alcohol. d. Samples which must be transported dry are contained in DOT packing group I containers per NRSC guidance. 3. Hazards of precursor as well as resulting product are addressed in the SOP.
3.3 Engineered Controls **3.3.1 Work Area Design** 1. Consider the need to implement additional engineered or procedural controls to ensure workers are protected in areas where engineered nanoparticles will be handled. 2. Additional controls : step off pads, buffer area, decontamination facilities	1 and 2: step off pad is situated at the exit to the room, housekeeping requirements are in SOP.
3.3.2 Ventilation Preferences 1. Conduct any work that could generate engineered nanoparticles in an enclosure that operates at a negative pressure differential compared to the worker's breathing zone. Examples of such enclosures include glove boxes, glove bags, and laboratory bench-top or floor-mounted chemical hoods. If a process (or subset of a process) cannot be enclosed, then use other engineered systems to control fugitive emissions of nanomaterials or hazardous precursors that might be released. For example, use a local exhaust system like a "snorkel hood." 2. Do not exhaust effluent (air) reasonably suspected to contain engineered nanoparticles whose hazards are not well understood. Whenever practical, filter it or otherwise clean (scrub) it before release. 3. Minimize the dispersal and environmental release of nanomaterials. Carry out all manipulations of engineered nanoparticles in a glove box, glove bag, chemical fume hood, or other airborne contaminant control system. Whenever practical, remove (scrub or capture) the contaminant from the effluent from such a control system before the effluent is released into the general environment. If it is not practicable to	1. Full compliance 2. All exhaust HEPA filtered 3. Full compliance 4. All exhaust filtered and then released outside the building 5. HEPA vacuum cleaner available for emergency spills 6. Biological safety cabinets not in use. 7. Fume hoods and local exhaust smoke tested, fume hoods face velocity monitored, and HEPA filter in fume hood is scheduled for in-situ DOP testing June 2008. 8. All local exhaust units are cleaned annually using asbestos type containment and decontamination procedures.

handle dispersible nanoparticles in such a containment system, conduct and document the results of a hazards analysis before using alternative hazard controls. 4. Duct the exhaust stream outside the building whenever feasible. Filters, scrubbers or bubblers may be appropriate to treat unreacted precursors and may also be effective in reducing emissions. If using portable bench top HEPA filtered units, exhaust them through ventilation systems that will carry the effluent outside the building whenever possible. 5. If it is not feasible to duct HEPA-filtered treated exhaust air outside of the building: • Follow the guidance in ANSI Z9.7, *American National Standard for Recirculation of from Industrial Process Exhaust Systems*. *Current knowledge indicates that a well-designed exhaust ventilation system with a high-efficiency particulate air (HEPA) filter should effectively remove nanoparticles.* • Conduct a hazards assessment and implement appropriate engineering controls. • Do not use horizontal laminar-flow hoods ("clean benches") that direct a flow of HEPA-filtered air into the user's face to control exposure to nanomaterials. 6. Consider exhausting Type II biological safety cabinets, in which free nanomaterials are handled, directly to the exterior (hard ducted) or through a thimble connection over the cabinet's exhaust. Air from inside the cabinet, even if HEPA-filtered, should not be recirculated within the laboratory except as provide for in ANSI Z9.7, *American National Standard for Recirculation of Air from Industrial Process Exhaust Systems*. 7. Maintain and test the effectiveness of exhaust systems and components as specified by the manufacturer. Evaluate equipment previously used to synthesize, handle or capture nanoparticles for contamination and incompatibility before reusing or disposing of it. 8. Evaluate laboratory equipment and exhaust systems for contamination before removing, remodeling, or repairing them.	
3.4 Administrative Controls **3.4.1 Chemical Hygiene Plan** As required in 10 CFR 851.23, develop and implement a chemical hygiene plan satisfying the criteria in 29 CFR 1910.1450. The plan should be specific to the scope of activities.	The JSA nanomaterial work follows the chemical hygiene chapter in the JSA EH&S Manual, Chapter 6610.

3.4.2 Housekeeping Practice good housekeeping in laboratories where nanomaterials are handled. Follow a graded approach paying attention where dispersible nanomaterials are handled. 1. Insofar as practicable, maintain all working surfaces (i.e., benches, glassware, apparatus, exhaust hoods, support equipment etc.) free of engineered nanoparticle contamination and otherwise limit worker exposure engineered nanoparticles and associated hazards. 2. In areas where engineered nanoparticles might settle, perform precautionary cleaning, for example, by wiping horizontal surfaces with a moistened disposable wipe, no less frequently than at the end of each shift. 3. Before selecting a cleaning method, consider the potential for complications due to the physical and chemical properties of the engineered nanoparticles, particularly in the case of larger spills. Complications could include reactions with cleaning materials and other materials in the locations where the waste will be held. Such locations include vacuum cleaner filters and canisters. 4. Clean up dry, engineered nanomaterials using: • A dedicated, approved HEPA vacuum whose filtration effectiveness has been verified • Wet wiping	1. Full compliance 2. Full compliance 3. Full compliance 4. Partial compliance: DOP testing for HEPA filter has been scheduled.
3.4.3 Work Practices 1. Transfer engineered nanomaterials samples between workstations in closed, labeled containers. 2. Take reasonable precautions to minimize the likelihood of skin contact with engineered nanoparticles or nanoparticle-containing materials likely to release nanoparticles. 3. If engineered nanoparticle powders must be handled without the use of exhaust ventilation or enclosures, evaluate hazards and implement alternative work practice controls to control potential contamination and exposure hazards. 4. Handle nanomaterial-bearing waste (see definition above) according to the laboratory's hazardous chemical waste guidelines and Section 6 "Management of Nanomaterial-Bearing Waste Streams." 5. Vacuum dry engineered nanoparticulates only with an approved HEPA vacuum cleaner that has been performance tested and certified according to the laboratories policies and procedures.	1. Full compliance 2. Full compliance: double gloves, long sleeved lab coats 3. Full compliance. 4. Waste handled as hazardous waste according to the JSA EH&S Manual Hazardous Waste Chapter 6761 and appendices. 5. Partial compliance: DOP testing for HEPA filter has been scheduled.

3.4.5 Marking, Labeling and Signage 1. Post signs indicating hazards, personal protective equipment requirements, and administrative control requirements at entry points into designated areas where dispersible, engineered nanoparticles are handled. 2. Where appropriate, label storage containers to plainly indicate that the contents are in engineered nanoparticulate form, e.g., "nanoscale zinc oxide particles" . 3. When engineered nanoparticles are being moved outside the laboratory, also include label text that indicates that the particulates might be unusually reactive and vary in toxic potential, quantitatively and qualitatively, from normal scale forms of the same material.	1. Full compliance 2. Full compliance 3. Full compliance
3.5 Clothing & Personal Protective Equipment 1. Wear appropriate PPE 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. Alternatively, ensure that engineered controls such as, e.g., laboratory chemical hoods are equipped with performance monitors that will notify users of equipment malfunction. 2. Conduct a hazard evaluation to determine the selection and use personal protective equipment (PPE) appropriate for the level of hazard as per the requirements set forth in 29 CFR 1910. Protective clothing that would typically be required for a wet-chemistry laboratory would be appropriate and could include but not limited to: • 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 • A long-sleeved shirt • Gauntlet-type gloves or nitrile gloves with extended sleeves • Laboratory coats • Wear polymer (e.g., nitrile rubber) gloves when handling engineered nanomaterials and particulates in liquids. 3. Choose gloves only after considering the resistance of the glove to chemical attack by both the nanotube and, if suspended in liquids, the liquid. 4. Because there are no good warning properties, change gloves routinely, alternatively, double glove. 5. Keep contaminated gloves in a plastic bag or other sealed	1. Full compliance 2. Full compliance: not a wet chemistry lab, hazard evaluation and ppe requirements documented in SOP. 3. Full compliance 4. Full compliance, double gloves used. 5. Full compliance. 6. Full compliance 7. Full compliance: hand washing sink located in the lab. 8. Full compliance: safety glasses worn 9. Full compliance: multiple barriers, including local exhaust and isolation worn with P-100 HEPA filter cartridges with a half face respirator under direction of lead scientist and Industrial Hygiene Group. 10. Full compliance 11. Full compliance

container in a hood until disposed. 6. Dispose of contaminated gloves in accordance with Section 6 of this document. 7. Wash hands and forearms after wearing gloves. 8. Wear eye protection, e.g., (spectacle type) safety glasses, face shields, chemical splash goggle, or other safety eyewear appropriate to the type and level of hazard. Do not consider face shields or safety glasses to provide sufficient protection against unbound, dry materials that could become airborne. 9. Use industrial hygiene professionals or paraprofessionals working under the direction of an industrial hygiene professional to evaluate airborne exposures to engineered nanomaterials. If respirators are to be used for protections against engineered nanoparticles, select and use half-mask, P-100 cartridge-type respirators or respirators that provide a higher level of protection. 10. Keep potentially contaminated clothing and PPE in the laboratory or change out area to prevent engineered nanoparticles from being transported into common areas. 11. Clean and dispose of all potentially contaminated clothing and PPE in accordance with laboratory policy.	
3.6 Monitoring and Characterization 1. In consultation with Laboratory's SMEs, use a direct-reading particle-measuring device to screen for suspect emissions. 2. Use more sophisticated techniques, to collect samples to characterize emissions and determine if a control is needed or must be upgraded or serviced. 3. Use the home Laboratory's data management system to link environmental data indicative of exposure to nanoparticulate workers.	1. Particle counters have been purchased: TSI model 3007 particle counter ordered 3/11/08. Has been received. Cost $8K. GRIMM Spectrometer model 1.108 ordered 04/18/08. Cost $18K.Lead time 6 weeks. 2. Sampling protocol has been revised at the direction of the sampling laboratory designated by the NSRC guidance document. 3. Will be in full compliance once particle counters are commissioned sampling results are received.
3.7 Worker Competency 1. Use a worker identification tool to ensure that staff members and support personnel with potential exposure to engineered nanoparticles are given appropriate training. 2. Do not assume that staff members and visiting researchers are aware of the health and safety concerns posed by nanomaterials. At a minimum, provide such personnel conducting hands-on work with an awareness-level orientation that will alert them to concerns (potential hazards) and to the Laboratory's and the NSRC's policies.	1. Smart card access control gives only workers with SOP training access to the room during nanomaterial production.. Workers identified as nanoparticle workers and in Medical Surveillance Program. 2. SOP training is the minimum orientation for visiting researcher and staff- to date, only one visiting researcher and one scientist. General

3. To better ensure understanding and competence, incorporate specific procedural requirements into written procedures or instructions provided to facility users by the laboratory.	hazard awareness class for the FEL staff was developed presented by the principal scientist. A primer on Nanomaterial Safety and Health was developed and was presented by the Associate Director, ES&H for the larger laboratory population. 3. Full compliance.
4 VERIFYING PROGRAM EFFECTIVENESS 1. Identify staff (hereafter "nanoparticle workers") exposed to engineered nanoparticles of unknown health effects. 2. Conduct workplace characterization and worker exposure assessments 3. Provide nanoparticle workers with "baseline" medical evaluations and including them in a nonspecific routine health monitoring program 4. Check wastes for evidence of uncontrolled release of engineered nanomaterials. 5. Effluent monitoring 6. Each of these program elements should be periodically reviewed and refined in a manner reflective of newly available knowledge about human and environmental health effects. They should also be kept as rigorous as current recommendations in professionally-recognized national and international consensus standards.	1. Full compliance 2. Partial compliance: difficulty with IH protocol at the lab specified by the NSRC Guidance. First samples were sent in January 2008, still have not been analyzed by the laboratory. 3. Full compliance 4. Wastes are double contained, stored in central accumulation area, with weekly inspections. Satellite accumulation areas are inspected monthly. 5. Partial compliance: No liquid effluent allowed, all air exhaust is now filtered but not yet DOP testing "in-situ" tested which should satisfy this requirement– estimated June 2008. 6. SOP's are periodically reviewed and updated: 3 revisions in the last 12 months. Industrial Hygiene Procedure is in development for review of program elements.
4.1 Nanoparticle Worker Identification 1. Any staff member meeting one or more of the following criteria be considered an "engineered nanoparticle worker": • Handles engineered nanoscale particulates that have the potential to become dispersed in the air • Routinely spends (significant amounts of) time in an area in which engineered nanoparticles have the potential to become dispersed in the air • Works on equipment that might be contaminated with materials that could release engineered nanoparticles during servicing or maintenance. 2. The Laboratory's nanomaterial hazards awareness training • Use available methods to characterize workplace conditions and exposures of *engineered nanoparticle workers*. 3. Ensure engineered nanoparticle workers are offered	1. Full compliance 2. Training on the SOP serves as the hazard awareness training for the users. General Hazard Awareness Training Class was developed by the lead scientist and given to FEL staff. 3. Full compliance 4. Responsibility assigned to Industrial Hygiene group. Needs formal procedure to ensure requirement is met.

periodic medical evaluations that may include routine tests such as pulmonary, renal, liver, and hematopoietic function and pulmonary function testing. 4. Revisit and refine the definition of *engineered nanoparticle workers* and make recommendations to the Site Occupational Medical Director for changes to any applicable medical examination program.	
4.2 Workplace Characterization and Exposure Assessments 1. Conduct "baseline" monitoring by measuring conditions prior to start up. Measure again at the conclusion of system commissioning and periodically thereafter. Investigate significantly atypical and unexpected measurements. 2. In consultation with Laboratory's SMEs, use direct-reading particle-measuring devices to screen for suspect emissions and atypical conditions that deserve further investigation. 3. Use more sophisticated techniques, to collect and analyze samples that will be used to characterize emissions and potential exposures.	1. In progress 2. In progress 3. In progress
4.3 Worker Health Surveillance Site Occupational Medical Director to determine the advisability of having: 1. Laboratory employees with jobs involving the potential for respiratory or skin exposure to engineered nanomaterials are offered a baseline medical evaluation and periodic medical monitoring consisting of routine non-specific medical monitoring including, for example, urinalysis, blood chemistry, and pulmonary function. 2. Have employees involved in any incident that results in an unexpected and/or unusually high exposure to nanomaterials, through any route of entry, examined by the home Laboratory's occupational medical clinic for a post-incident evaluation as per OSHA 1910.1450(g)(1)(i). 3. Exempting non-resident (e.g., user facility) personnel from medical surveillance.	1. Full compliance 2. Full compliance: requirement is in SOP. 3. Full compliance: modification to SOP requires that user personnel provide proof of equivalent medical surveillance program from home institution to the Laboratory Occupational Health Physician for approval.
4.4 Domestic Waste Surveys 1. Each Center's staff members be instructed to visually inspect domestic wastes periodically and instructed to report to the FEL Safety Officer instances involving the appearance of suspect nanomaterials, including contaminated wipes, in domestic trash containers.	1. Partial: ES&H staff inspect domestic waste streams in the room. Other lab staff have been instructed in General Hazard Awareness by the lead scientist.

4.5 Effluent Monitoring [Reserved – Techniques for monitoring have not yet been established. However, this should not be interpreted as discouraging interested Centers from collaborating on the development of methods.]	
5 TRANSPORTATION OF NANOMATERIALS The guidance under this heading applies to the movement of material from the laboratory to and from off-site locations. Personnel who package and prepare nanomaterials for shipment off-site have and are current on HazMat Employee training required by 49 CFR Subpart H.	Full compliance
5.1 Categories of Materials **5.1.1 Recognized HazMat** **1.** 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 and applicable DOE Orders. 2. Any nanomaterial being shipped by air that meets the definition of dangerous goods according to the International Civil Aviation Organization (ICAO) must be packaged, marked, labeled, and shipped, with an accompanying properly prepared dangerous goods declaration, in accordance with the ICAO technical instructions. **5.1.2 Suspected DOT HazMat** **3.** 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 Section 5.1.1 These materials should be classified and 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). These suspect materials should be packaged in accordance with section 5.2.1. **5.1.3 Other Nanomaterials** 4**.** Nanomaterials that do not meet the DOT's criteria listed above still may pose health and safety issues to personnel handling the material if they are released during its transport. Therefore, all shipments of nanomaterials, regardless of whether they meet the definition for hazardous	1. through 4 : Full compliance

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.	
5.2 Off-site Shipments The information under this heading applies to materials sent to and from the laboratory to off-site locations that do not otherwise meet DOT's definition of "hazardous material". **5.2.1 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.	Full compliance, detailed in SOP
5.2 Off-site Shipments The information under this heading applies to materials sent to and from the laboratory to off-site locations that do not otherwise meet DOT's definition of "hazardous material". **5.2.1 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.	Full Compliance
5.2.2 Labeling 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." 2. If the nanomaterial is in the form of dry dispersible particles, add the following line of text: Nanoparticulates can exhibit unusual reactivity and toxicity. Avoid breathing dust, ingestion, and skin contact. Documentation and notifications for off-site transfer of nanomaterials should include the following:	1. Full compliance 2. Full compliance 3. Full compliance 4.- 5. Partial compliance: Verbal and email notification has been used.

3. A signed and complete dangerous goods declaration or shipping papers prepared in accordance with the ICAO and DOT regulations by certified/qualified HazMat employees who are authorized to release materials from the site. 4. Available descriptions of the material (e.g., MSDSs). [With respect to samples researchers should prepare a document that describes known properties and other properties that deem reasonably likely to be exhibited by samples] 5. A notification to receiving facility of the incoming shipment.	
5.2.3 Modes of Transport 1. All materials are transported by a qualified carrier, for which the DOE or the GSA has a tender on file. All transportation services must comply with the Federal Acquisition Regulations (FAR). 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 using a carrier approved by the DOE's Motor Carrier Safety Program (MCEP). 2 Shipments of nanomaterials classified as "other materials" (neither recognized HazMat or suspected DOT HazMat) may be transported using the most expeditious method provided they are packaged as per the requirements in section 5.2.1 and: • The driver must have a valid state driver's license appropriate for the vehicle being operated • The vehicle must be in good mechanical condition and have a valid state safety inspection • The vehicle must be insured with at least the required minimum liability insurance required by the state where the vehicle is registered • The driver must obey all state and local traffic rules and regulations • The driver must possess basic hazard information on the commodity being transported, i.e., material name, quantity, form and material safety data sheet if available.	1. Shipment carrier is Yellow Freight Ground. 2. Shipments of boron nitride nanotubes is considered "other materials", are generally transported by private vehicle to NASA Langley Research Center and SOP states the requirements listed in this section.
On-Site Transfers of Nanomaterials 1. The on-site transfer of nanomaterials should follow the DOE-approved, site-specific, transportation safety document	1. On site transfers are limited to the central accumulation area and comply with DOT requirements. Exception: air

or other institutional document (i.e., chemical hygiene plan); in lieu of such a document, the transfer should fully comply with the DOTs' requirements. The site's transportation authority (e.g., Transportation Safety Officer or equivalent) should be the authority having jurisdiction on the requirements for packaging, marking, and documentation necessary for on-site transfers. 2. For nanomaterials, the following is suggested: Assess and record the hazards posed by the material(s) following a graded approach that takes into account the form of the material(s) (e.g., free particle vs. fixed on substrate). 3. Use packaging consistent with the recommendations for off-site shipment or packaging that affords an equivalent level of safety. 4. Mark the transfer containers in accordance with the (above) recommendations for off-site shipments. 5. 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.	cassette samples taken for industrial hygiene characterization. 2. Full compliance 3. Full compliance 4. Full compliance 5. Non compliant: information has been sent via email. Emergency response guides for the precursor material are sent with the shipment. Industrial Hygiene procedure needs development to comply.
6 MANAGEMENT OF NANOMATERIAL-BEARING WASTE STREAMS **6.1 Applicability** The following waste management guidance applies to nanomaterial-bearing waste streams consisting of: Pure nanomaterials (e.g., carbon nanotubes) • Items contaminated with nanomaterials (e.g., wipes/PPE) • Liquid suspensions containing nanomaterials • Solid matrixes with nanomaterials that are friable or have a nanostructure loosely 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.	Applicable to this experiment: waste streams consist of wipes and PPE, spent HEPA filters.
6.2 Nanomaterials in Waste Streams 1. Consider any material that has come into contact with dispersible engineered nanoparticles (that has not been decontaminated) as belonging to a nanomaterial -bearing waste stream. This includes PPE, wipes, blotters and other disposable laboratory materials used during research activities. 2 In order to reduce waste generated, 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.	1. Full compliance. 2. The liquid of choice is mineral oil would allow a waste product to be incinerated. So far, waste has been sent out dry, but this is under evaluation for future waste shipments. 3. Daily wipes used to wet wipe surfaces are collected for disposal as nanomaterial- bearing waste.

3. Evaluate surface contamination or decontaminate equipment used to manufacture or handle nanoparticles before disposing of or reusing it. Treat wastes (cleaning solutions, rinse waters, rags, PPE) resulting from decontamination as nanomaterial - bearing waste.	
6.3 Classification and Disposal of Nanomaterial-bearing Waste Streams 1. Do not put material from nanomaterial - bearing waste streams into to the regular trash or down the drain. Seek evaluation and approval for sink discharge from your home institution's environmental subject matter expert. 2. Do not permit nanomaterial-bearing wastes to be shipped to off-site researchers' home institutions for disposal. 3 Characterize and manage nonmaterial-bearing waste streams as either hazardous or nonhazardous waste based on the requirements in 40 CFR 261.10 to 38, or equivalent state regulations, considering their known characteristics and/or listing of the waste. 4. 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. 5. Label the waste container with a description of the waste and the words "*contains nanomaterials*". Include available information characterizing known and suspected properties. 6. Collect paper, wipes, PPE and other items with loose contamination in a plastic bag or other sealing container stored in the laboratory hood. When the bag is full, close it, take it out of the hood and place it into a second plastic bag or other sealing container. Label the outer bag with the laboratory's proper waste label. 7. Send otherwise non-hazardous nanomaterial-bearing waste to a RCRA-permitted treatment, storage and disposal facility (TSD). Direct the TSD as to the selected treatment method best suited to controlling hazards associated with the waste.	1. SOP specifically prohibits this disposal to trash and drains. 2. All hazardous wastes generated in this experiment are disposed of under the TJNAF EPA ID number in accordance with the laboratory hazardous waste program. 3. Full compliance with Virginia DEQ hazardous waste regulations. 4. Full compliance 5. Full compliance 6. Full compliance 7. Full compliance
7 MANAGEMENT OF NANOMATERIAL SPILLS **7.1 Access Control** 1. Determine the extent of the area reasonably expected to have been affected, and demarcate it with barricade tape or use another reliable means to restrict entry into the area. 2. Consider using a HazMat crew from the Laboratory's waste management organization for clean up of significant spills and restrict entry into the area to personnel from that organization. 3. Allow trained personnel from the Laboratory to clean up smaller spills, following the home institution's cleanup	1. Full compliane: in SOP 2. SOP indicates that Industrial Hygiene group, who manages the Hazardous Waste Program, is to be notified for spill mitigation. 3. In SOP 4. In SOP

procedures. 4. Refer personnel exposed to nanomaterials in the course of a spill to the Laboratory's Medical Services.	
2 Dry Materials 1. Position a walk-off mat (e.g., Tacki-Mat®) where clean-up personnel will exit the access-controlled area to reduce the likelihood of spreading nanoparticles. 2. Clean using wet wiping methods. Characterize, collect and dispose of spill clean-up materials as nanomaterial -bearing waste. 3. A tested and certified HEPA vacuum or other facility-approved methods that don't involve dry sweeping of the use of compressed air can also be used. 4. Ensure that the effectiveness of HEPA filters is verified at a frequency consistent with manufacturer recommendations. 5. When feasible, use only "dedicated" HEPA vacuums used for nanomaterial clean up. Label the units accordingly, e.g., "Use only for nanomaterial spill clean up." 6. Use a "log" to record the type of material collected and avoid mixing potentially incompatible materials in the vacuum or filters. 7. Characterize, collect and dispose of used HEPA filters as nanomaterial bearing waste.	1. In SOP 2. In SOP 3. In SOP 4. Industrial Hygiene procedure is in place for control of the HEPA vacuums. 5. Dedicated HEPA vacuum is supplied to the lab from Industrial Hygiene and is labeled for nanomaterial. Wet Wipe machine is also labeled. 6. Log is not maintained. Amount of nanomaterial generated (less than mg quantities per production run) does not indicate the need, since the HEPA filters are changed out annually according to Industrial Hygiene Procedure. 7. Full compliance
3 Liquids 1. 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: 2. Position an absorbent walk-off mat where the clean-up personnel will exit the access-controlled area to prevent the spread of liquids containing suspended nanoparticles. Place barriers (e.g., plastic sheeting) that will minimize air currents across the surface affected by the spill. 3. Use a wet-wiping method to clean the spill. A HEPA-filtered vacuum dedicated to the clean up of nanomaterials may also be used to clean up residual nanomaterials left behind after the spill area has dried. 4. Treat all materials used to clean up the spill (absorbent mats, absorbent material, wipes etc.) as hazardous or potentially hazardous waste based on the material involved.	1 – 4: Full compliance
4 Wastes 1. Manage all debris resulting from the clean up of a spill as though it contains sufficient nanomaterials to be managed in accordance with Section 6 of this procedure.	1. Full compliance

ADDITIONAL RESOURCES

- ASTM *Standard Guide for Handling Unbound Engineered Nanoscale Particles in Occupational Settings*. E2535- 2007

KEY DOCUMENTS

- *ESAF 00-044 FEL Synthesis of Carbon Nanotubes* 7-26-2000
- Experiment Safety Approval Form(ESAF) 05-006 6-3-2005: *Synthesis of Carbon and Boron Nanotubes/Nanoparticles* (superseded by ESAF 07-003)
- Experiment Safety Approval Form(ESAF) 07-003 revision 1-10-2007, revised 2-21-2007 *Synthesis of Carbon and Boron Nanotubes/Nanoparticles* (superseded by ESAF 07-013)
- Experiment Safety Approval Form (ESAF) 07-013 11-1-07. *Boron Nitride Molecule Synthesis via CO2 Laser Vaporization.*
- Standard Operating Procedure FEL- 06-005 SOP 12-18-2006 *Nanoparticle/Nanotube Target Preparation and Sample Handling* – (superseded by OSP FEL-08-002-OSP)
- Laser Standard Operating Procedure –FEL-07-009-L 9-28-2007: *Nanotube Production Using High Power Lasers*
- Operational Safety Procedure FEL-08-002-OSP 2-15-2008: *Nanoparticle/Nanotube Target Preparation and Nanomaterial Sample Handling*
- Department of Energy Nanoscale Science Research Centers *Approach to Nanomaterial ES&H* Revision 2- June 2007.
- JSA ESH Manual Chapter 3130 *The FEL Experiment Review Process and Appendices*
- JSA ESH Manual Chapter 6610 *Chemical Hygiene and Appendices*
- JSA ESH Manual Chapter 6761 *Hazardous Waste and appendices*.

TJSO ASSESSMENTS

1. TJSO Occupational Safety Manager and Environmental Programs Manager reviewed the Nanotube Experimental Setup with the NASA user as a followup to the 2005 ORO assisted Laser Safety Assessment. No issues resulted.
2. TJSO Occupational Safety Manager reviewed the Nanotube Standard Operating Procedure(2005)and the Operational Safety Procedure (2007).
3. Walkthrough ORION WALK-A2H-3/10/2008-36571
   3/7/2008: Inspection of satellite accumulation area in FEL User Lab 3a for nanotube associated hazardous waste storage. There is one small flammables cabinet that is labeled for use as the SAA. The waste is contained in small gallon size containers that were properly labeled and tightly sealed. Other material that was in the cabinet was not properly labeled. This was immediately corrected. Recommended to the Hazardous Waste Coordinator that bags should be made available for the waste HEPA filters that are routinely changed in this laboratory, and that all HEPA filters should be checked to ensure that they are DOP certified prior to use.
4. Walkthrough ORION WALK-A2H-3/21/2008-9376
   3/13/2008: Conducted a work observation in FEL User Lab 3a in the FEL. This laser lab produces milligram quantities of boron nanotubes. Local exhaust for the process consists of one HEPA filtration unit and one chemical fume hood. The JSA Mechanical Engineer and Industrial Hygienist were assessing the chemical fume hood for a planned

modification which will add a HEPA filter to its exhaust. The fume hood is a sample prep area for laser processing and also a nanotube sample packaging area. The Industrial Hygienist conducted small and large volume smoke test on the chemical fume hood and local exhaust unit using a theatrical smoke generator. After installation of the HEPA filter the chemical fume hood will be retested to ensure adequate capture and face velocity, and an in-situ DOP test will also be conducted. Also verified that the laboratory is under negative pressure with respect to the rest of the facility. Lines of Inquiry:
a. JSA mechanical engineer was not certain if the HEPA filter was DOP tested- it was.
b. The JSA mechanical engineer selected an optimal location (for future maintenance) for installation of the filter.

5. Walkthrough ORION WALK-RVD-4/25/2008-78506
4/23/2008: Effectiveness review of JSA SOP for FEL User Lab 3a: Walked through the entire SOP with lead scientist to ensure that all controls were in place, and that all procedural steps were consistent with the work control document

AREAS OF CONCERN

- Responsibility assigned to Industrial Hygiene group to revisit medical surveillance requirements with the Occupational Health Physician as new information emerges. Needs formal procedure to ensure requirement.
- Modification to SOP is needed to require that user personnel provide proof of equivalent medical surveillance program from home institution to the Laboratory Occupational Health Physician
- Verbal and email notification has been used for hazard communication information prior to shipping nanomaterials, emergency response guides are sent with the shipment. Formal Industrial Hygiene procedure should detail additional hazard communication information to be sent in accordance with NSRC guidance.
- Industrial Hygiene group needs to validate appropriate glove selection by testing efficacy according to ASTM F739 Method.
- Workplace Characterization and Exposure Assessments: difficulty in having the analytical laboratory analyze the sampling needs to be pursued.

CONTRACTOR ASSESSMENTS/OVERSIGHT

- JSA Industrial Hygiene Group conducted joint walkthroughs with FEL Line Management of the nanotube laboratory and sample prep areas for each Experimental Safety Approval Form. Three have been issued since 2000, each representing initial and then modifications to the experiment materials or controls.
- JSA Industrial Hygiene observes all cleaning of local exhaust units associated with nanotube material.
- JSA Corrective Actions Tracking System INSP-2006-008 1-13-06: Issue resulted in requirement for HEPA filter to be placed in front of local exhaust pipe for nanotube experiment. Issue was resolved.
- JSA Corrective Actions Tracking System INSP-2006-083 6-26-06: Issues concerned electrical safety with pump associated with nanomaterial experiment. Issue was resolved.

- JSA Corrective Actions Tracking System INSP-2006-102-03 11-2-06: Issues concerned evidence of breakthrough for HEPA filter located before local exhaust, respirator for nanotube experiment left out on table, and cart used for nanotube experiment had 4 flat tires. Issues were resolved.
- Joint JSA/NASA/DOE Site Office Meeting 12-12-06: Convened at FEL Facility with FEL nanotube workers, Industrial Hygiene Group, FEL Line Managers and NASA Branch Head for Advanced Sensing and Optical Measurements to review NASA and JSA respirator safety, medical surveillance, and training requirements. Result was NASA user compliance with JSA and NASA respiratory protection program requirements.
- JSA Corrective Actions Tracking System INSP-2007-066 8-10-07: Issue concerned housekeeping for laser table used for nanotube experiments. Issue was resolved.
- JSA Corrective Actions Tracking System INSP-2007-090 10-31-07: Issues concerned the laser that generates the nanomaterial. All issues were resolved.

PATH FORWARD

- Ensure that JSA Industrial Hygiene Group formalize procedures for their handling of nanomaterial, to at least address air sample and waste handling safety concerns, and transportation hazard communication requirements.
- Ensure that user personnel provide proof of equivalent medical surveillance program from home institution to the Laboratory Occupational Health Physician.
- Industrial Hygiene group validate appropriate glove selection by testing efficacy according to ASTM F739 or equivalent method.
- Ensure that JSA Industrial Hygiene Group resolves difficulty in having the analytical laboratory analyze passive air samples per the NSRC Industrial Hygiene Sampling Protocol.
- Ensure that the nanomaterial workers continue to use multiple engineering controls and back up respiratory protection when handling nanotubes.
- Ensure that JSA Industrial Hygiene group commission and use particle counters to aid in characterization of the air quality in the nanotube user laboratory.
- Consider alternate procedures for hazard assessment and controls for use in the nanotube user laboratory, such as ASTM Standard Guide Handling Unbound Engineered Nanoscale Particles in Occupational Settings.
- Continue research on emerging findings relating to effective use of industrial hygiene principles in evaluation of nanomaterial use by JSA.
- JSA Environmental Engineer has developed a draft environmental checklist for nanomaterial research and development for a categorical exclusion for the nanomaterial research and development. This should be finalized.

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