Application of Industrial Hygiene Tools and Tenets to Controlling Nanomaterials in R&D Operations

Anticipation, Recognition, Evaluation and Control

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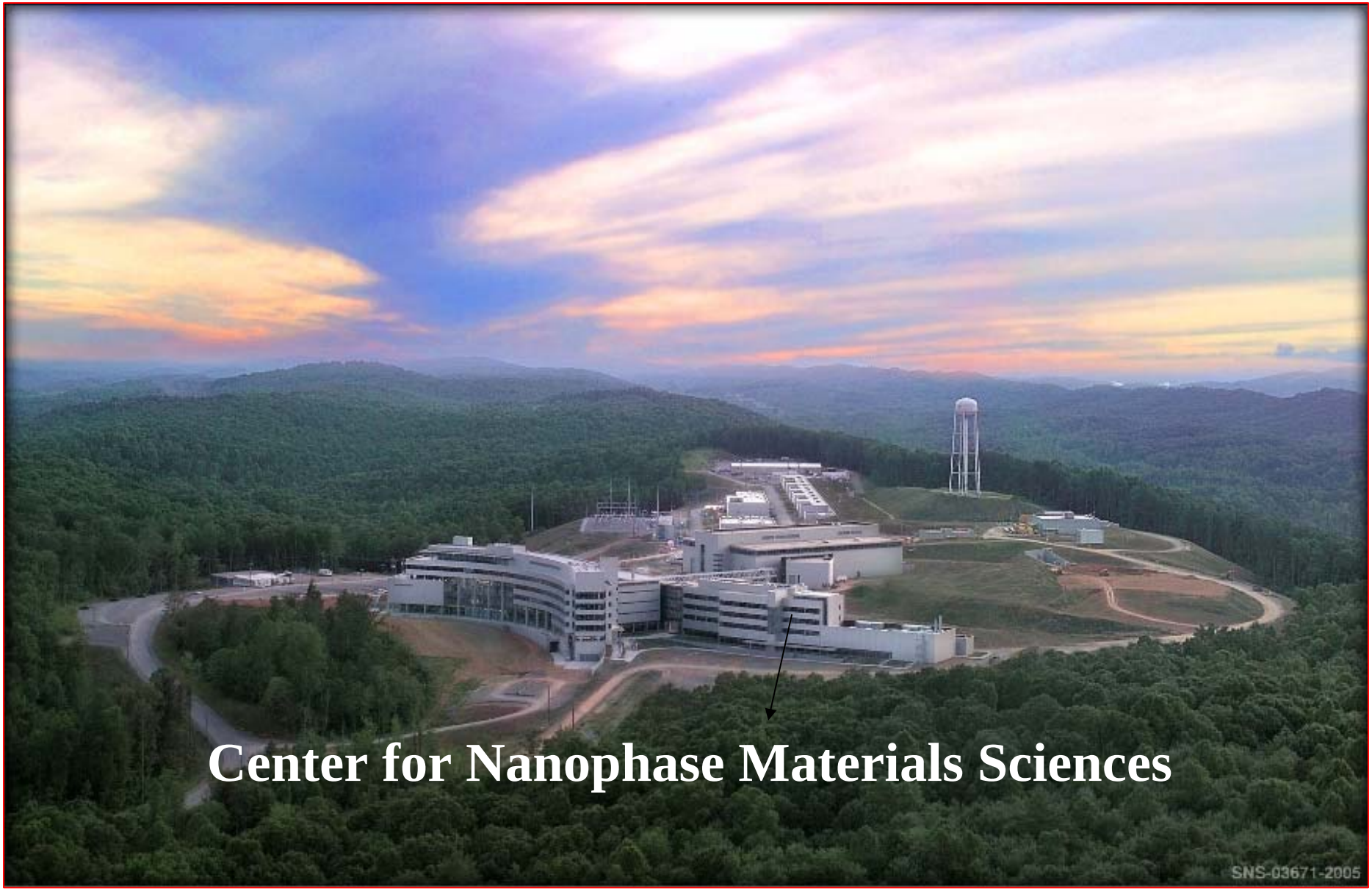
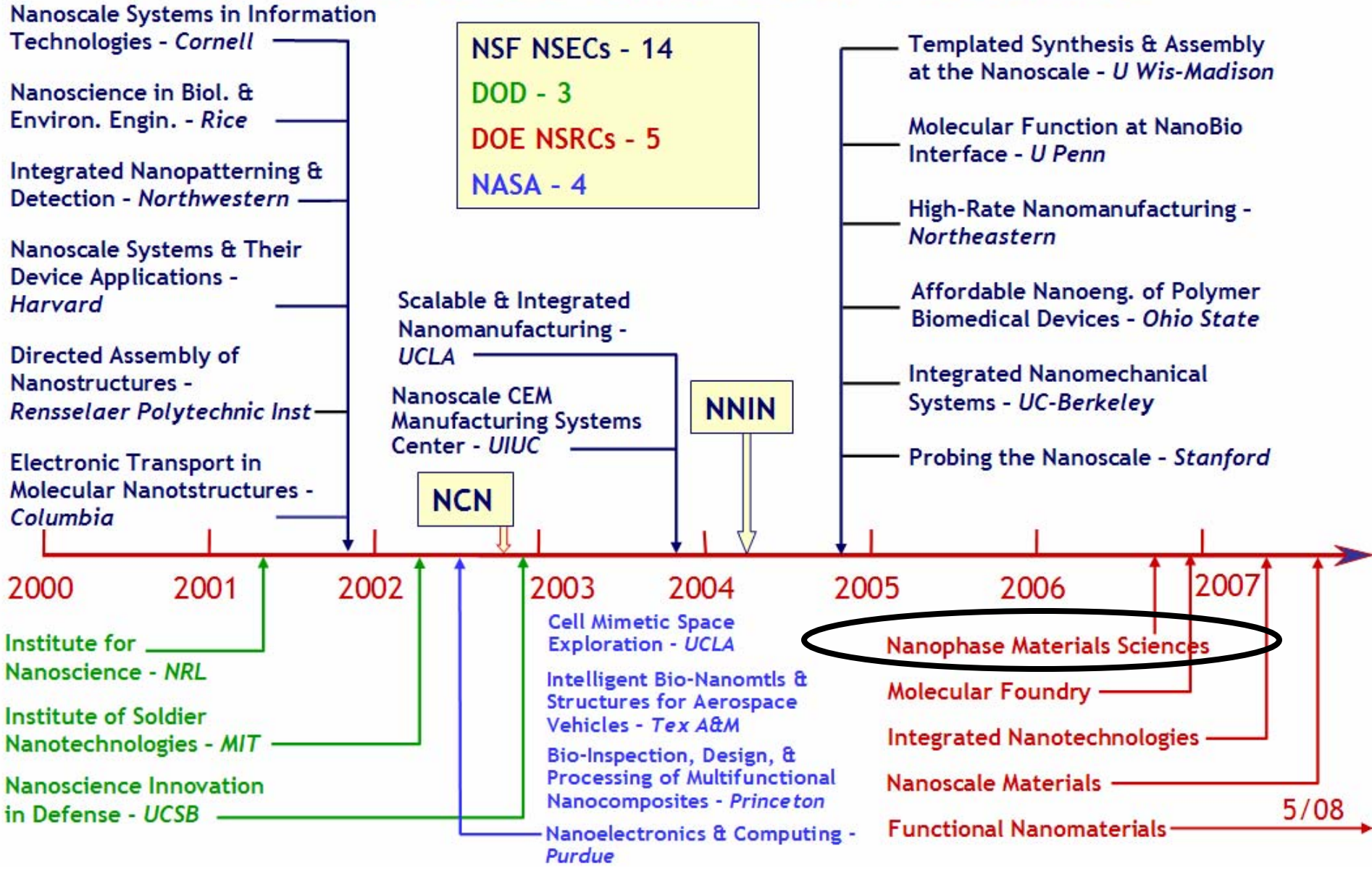
Commercialization of Nanomaterials 2007
November 12, 2007
Pittsburgh, PA

Controlling Exposures in R&D



Co-located with the Spallation Neutron Source (SNS)

NNI Centers and User Facilities



U.S. Department of Energy
Washington, D.C.

POLICY

DRAFT
DOE P 456.1

XX-XX-05

SUBJECT: SECRETARIAL POLICY STATEMENT ON NANOSCALE SAFETY

PURPOSE AND SCOPE

The safety of its employees, the public, and the environment is the Department's number one priority. This policy statement is being issued to establish a framework for working safely with nanomaterials. Nanomaterials exhibit unique properties that can affect physical, chemical and biological attributes. Much of the scientific information on the safety, health and environmental hazards of working with these materials is yet to be determined. With the advent of the Department's Nanoscale Science Research Centers and other emerging programs, work in nanoscience will significantly increase over the next year and beyond.

POLICY

The Department of Energy (DOE) expects that all work with nanomaterials will be conducted in a safe, healthful, and environmentally compliant manner that protects workers, the public, and the environment. Thus, the Department will be prudent and follow a cautious approach in the production, use, and disposition of nanomaterials.

It is imperative that the Department's work with nanomaterials be conducted in a manner that encompasses the following attributes:

- DOE will adopt and implement, as appropriate, both existing environment, safety and health "best practices," standards, and guidance relating to nanotechnology, and related new elements as they are developed by recognized standard-setting organizations.
- DOE employees and contractors (including subcontractors) will identify and manage potential health and safety hazards and potential environmental impacts at their sites through the use of existing Integrated Safety Management Systems, including Environmental Management Systems.
- DOE employees and contractors (including subcontractors) that use nanomaterials are responsible for staying abreast of current research and guidance relating to the potential hazards and impacts of nanomaterials, and for reflecting this best current knowledge in the identification and control of these potential hazards and impacts at their respective sites.
- DOE will continue to both support research on the environmental and safety and health impacts of nanomaterials, and to participate in government-wide activities aimed at identifying and resolving potential environmental, safety, and health issues.

AVAILABLE ONLINE AT
www.directives.doe.gov

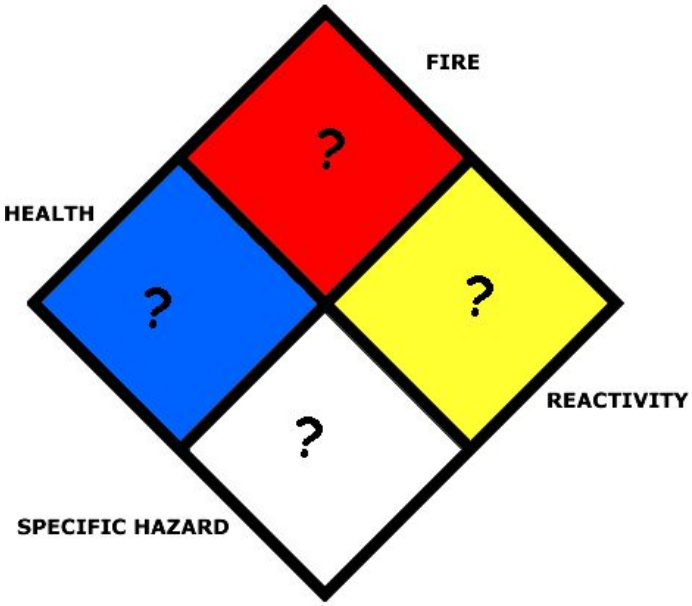
INITIATED BY:
Office of Environment, Safety and Health

Conduct of Work …Attributes

- DOE will **Adopt and Implement** existing and future **best ESH practice** (Consensus Standards). Apply existing related ESH requirements.
- Use ISM to ID and manage potential ESH issues.
- …stay abreast of current research and guidance; ensure **best current knowledge is applied to ID and Control**.
- DOE will support ESH related R&D; **all involved share responsibility for ESH** consistent with Policy

Nanomaterials Safety: Industrial Hygiene Approach

- Anticipation
- Recognition
- Evaluation
- Control



A variety of materials
A variety of hazards

Anticipation
Recognition

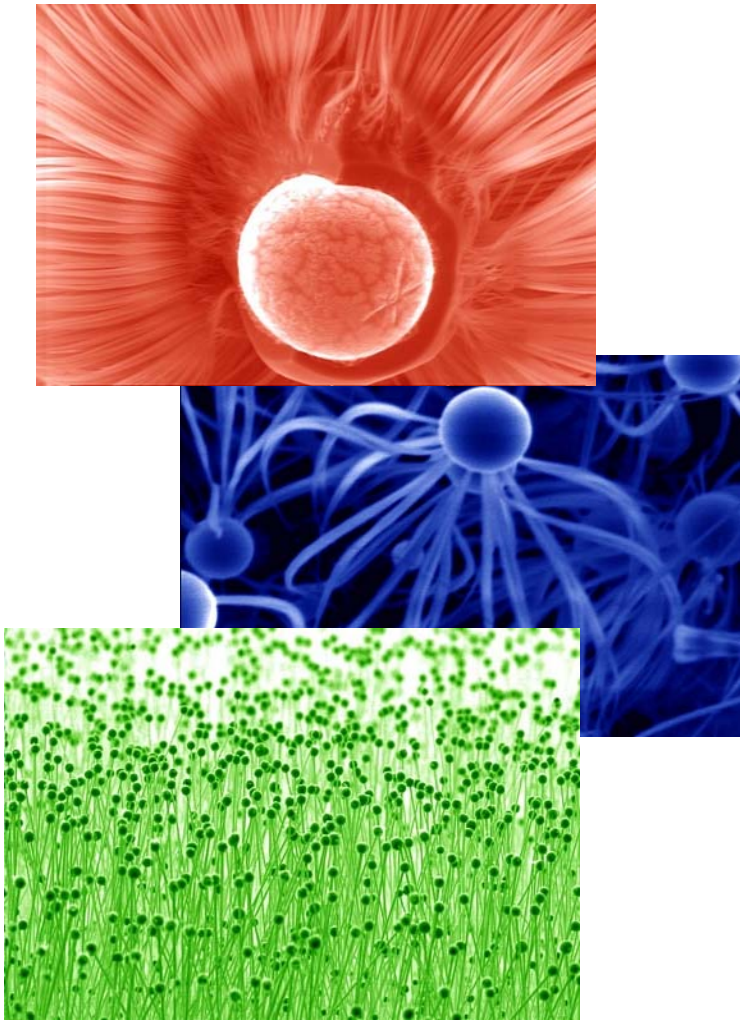
- What do we know from history?
  - Analogies
  - Bass brains
- What material (chem. phys.) properties?
- What does toxicological research tell us?
- Need Dose-Response to set exposure limits.
- Consensus standards, regulatory limits?
- MSDS-NO
- Prudent Practice/Avoidance

Recognition cont.

- Unlimited number of sizes, shapes, chemistries, physics.
- Nano-hazards we have already lived with.
  - Fumes (50-200+nm) Zn and Mn fumes versus particulate
  - Asbestos
  - Diesel Exhaust
  - Ceramic Whiskers (early ‘90s)
- The ambient air environmental soup we live in:
  - Natural sources of nanomaterials fires, volcano, natural smog
  - Nano in homes offices (1000-100K P/cc)
- Nano-exposures from Consumer products

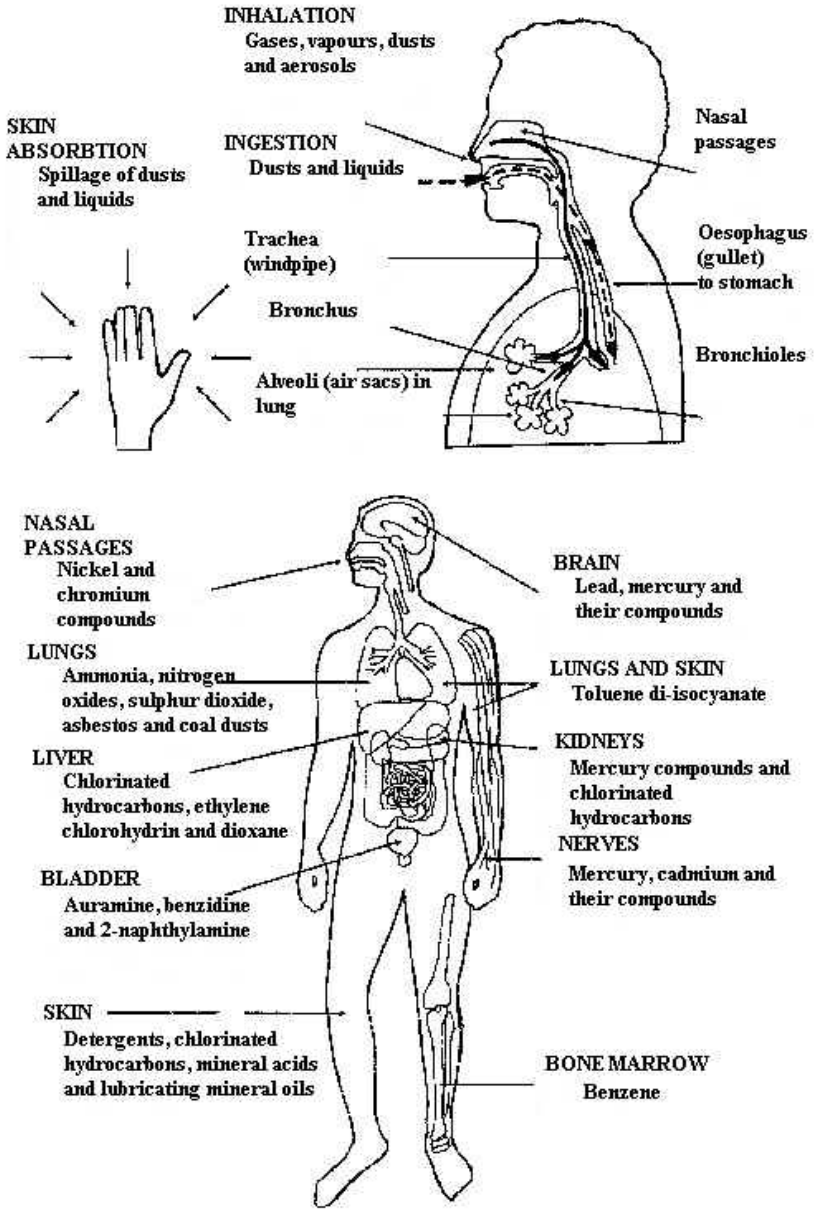
Toxicity – Emerging Information

- Depends on chemistry, morphology, surface charges, etc.
- Probably relates to particle surface area especially for insoluble/low soluble
- Free radicals (in vitro)
- Increased inflammatory response (in vivo)
- Translocation to target organs (rodents)
- Allergic asthma like symptoms
- Aggravate symptoms of pneumonia
- Cardiac effect-2 days later
- Toxicity in aquatic environment



ENN File

Natural and man-made sources can be significant >100K/cc air



Classic concepts of route of entry, target organ, dose-response remain applicable, but may need to use surface area to plot the D-R graph. Watch for silver bullets and nano-radios!

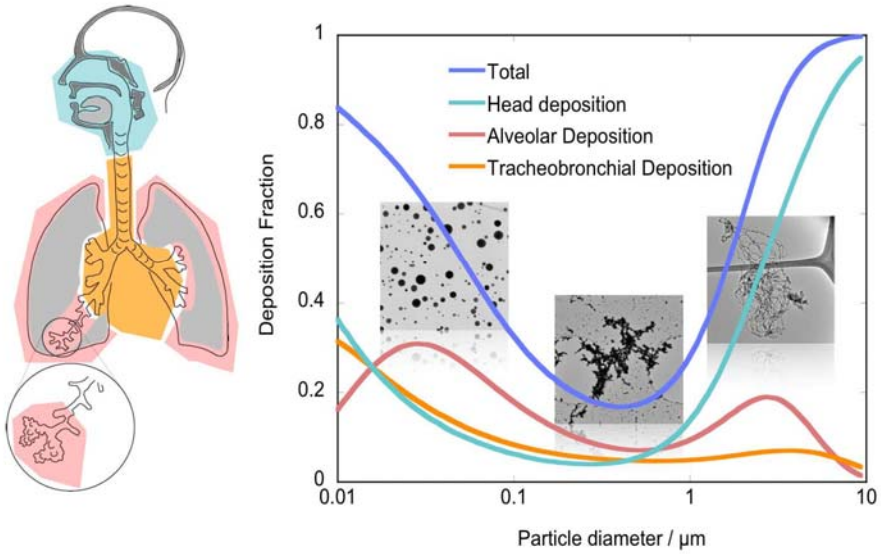
The small size plays a role in all aspects, enhances movement in the body and in the environment and may add skin absorption as a route of entry. Increase solubility!

Toxicity mechanisms may change for particles less than 10 nm?

Nanoparticles in Respiratory System

- Benign residence
- Solubility and chemical relocation
- Translocation (intra and extra cellular)
  - Lymph, CNS, Mitochondria, DNA
- Residence with inflammation (proinflammatory chemokine)
- Free radicals (nano-carbon black induce more hemeoxygenase)
- Removal by muco-ciliary-escalator (not in alveoli)
- Longer time for clearance of insoluble nanoparticles?
- Surface area (contact) for insoluble more important than mass

If we inhale them, where do they go?



Where do the nanoparticles go? *Modeled deposition probability of inhaled particles in the deep lungs (alveolar region), upper respiratory tract (tracheobronchial region) and the upper headways [14]. Silver and single walled carbon nanotubes are shown to give a feel for where these particular agglomerates might deposit. However, deposition probability will depend on their shape and structure as well as physical size, meaning that they could penetrate far deeper into the lungs than indicated (or indeed deposit higher up the respiratory system).*

from Andrew Maynard's *People breathing in nanoparticles?* www.SafeNano.org

Tools for Evaluating Nanomaterial Exposures

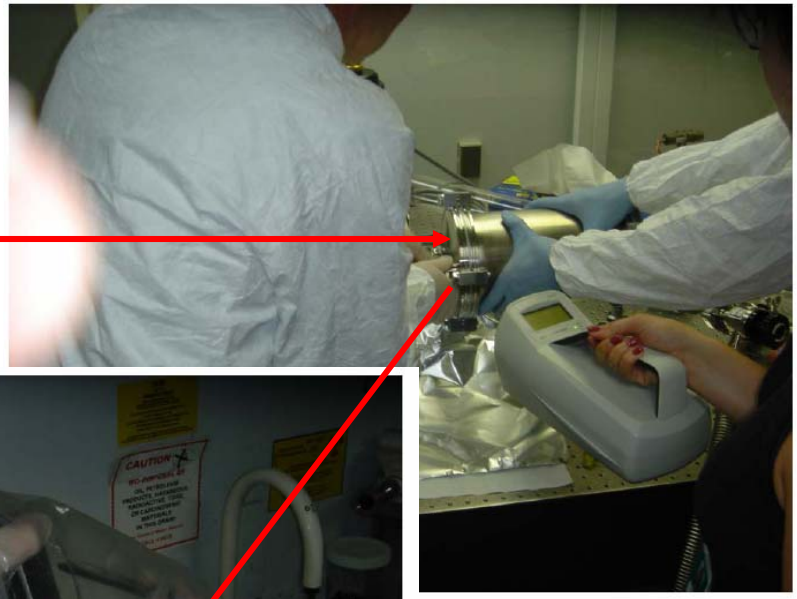
- Surface area – diffusion charger
- Scanning Mobility Particle Sizer (SMPS)
- Count – CPC (TSI)
- Composition/Chemistry - GC-MS
- Filter/Impinger/Impactor-TEM/SEM

Sampling Approach for CNMS Activities

- TSI 3007 CPC, particle counts to 10nm
- Nucleopore filter + SEM/TEM
  - size,
  - shape,
  - metallic composition
- Baseline index of “clean” watch for other sources (air pollution, combustion)
- Direct count, estimated mass, and surface area for each process
- Passive monitoring (TEM/SEM Stub or grid) weeks

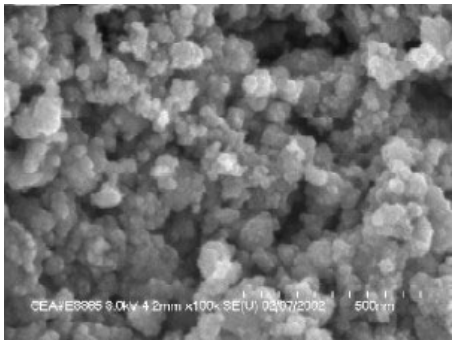
IH Monitoring of Laser Ablation

Laser ablation set up. Quartz tube holds laser t
nanomaterials.



Harvesting nanomaterials inside glove bag, inside down draft hood.

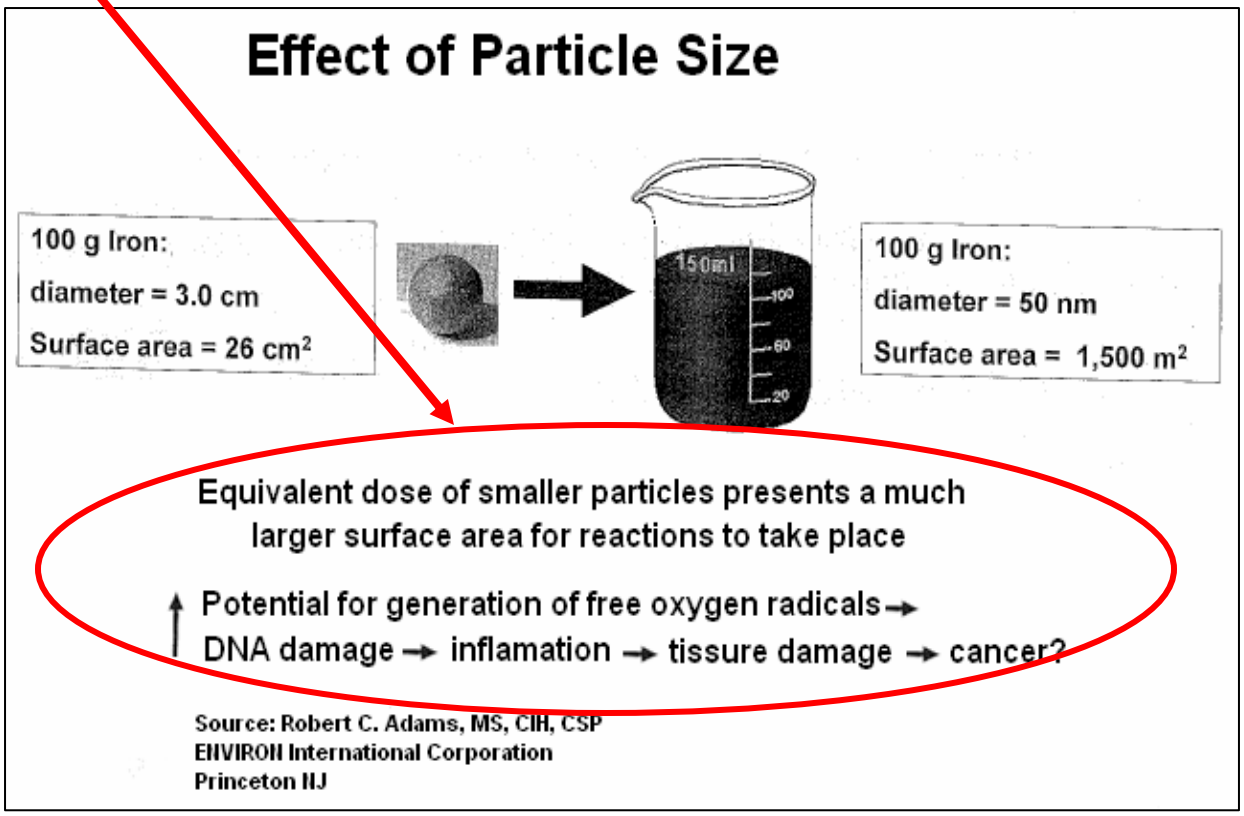
NIOSH on Titanium Dioxide



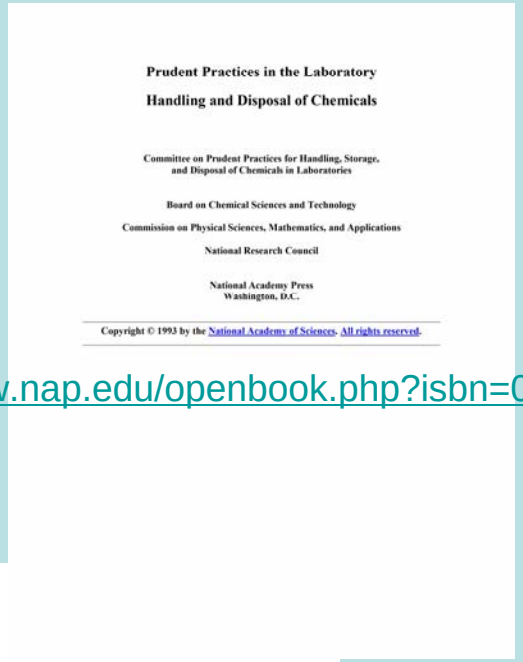
- Exposure limit of 1.5 milligrams per cubic meter for fine TiO2 (particles greater than 0.1 micrometers in diameter)
- 0.1 mg/m3 for ultrafine particles as time-weighted averages for up to 10 hours per day during a 40-hour work week
- Suggests that ultrafine TiO2 particles may be more potent than fine TiO2 particles at the same mass. This may be due to the fact that the ultrafine particles have a greater surface area than the fine particles at the same mass

We may have sufficient information to set Control Limits for some other materials

Surface area as dominant characteristic contributing to toxicity is plausible



Nanotechnology Controls


Prudent Practices in the Laboratory

Handling and Disposal of Chemicals

Committee on Prudent Practices for Handling, Storage, and Disposal of Chemicals in Laboratories

Board on Chemical Sciences and Technology

Commission on Physical Sciences, Mathematics, and Applications

National Research Council

National Academy Press
Washington, D.C.

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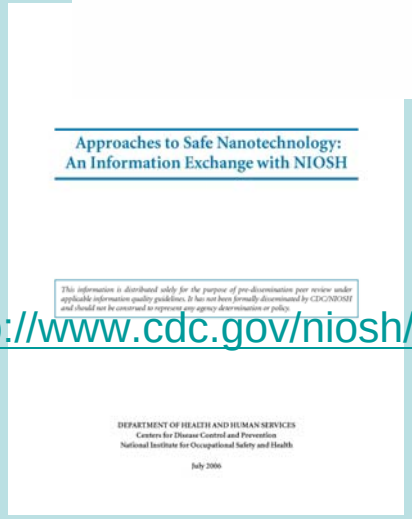
http://www.nap.edu/openbook.php?isbn=0309052297


Approaches to Safe Nanotechnology:
An Information Exchange with NIOSH

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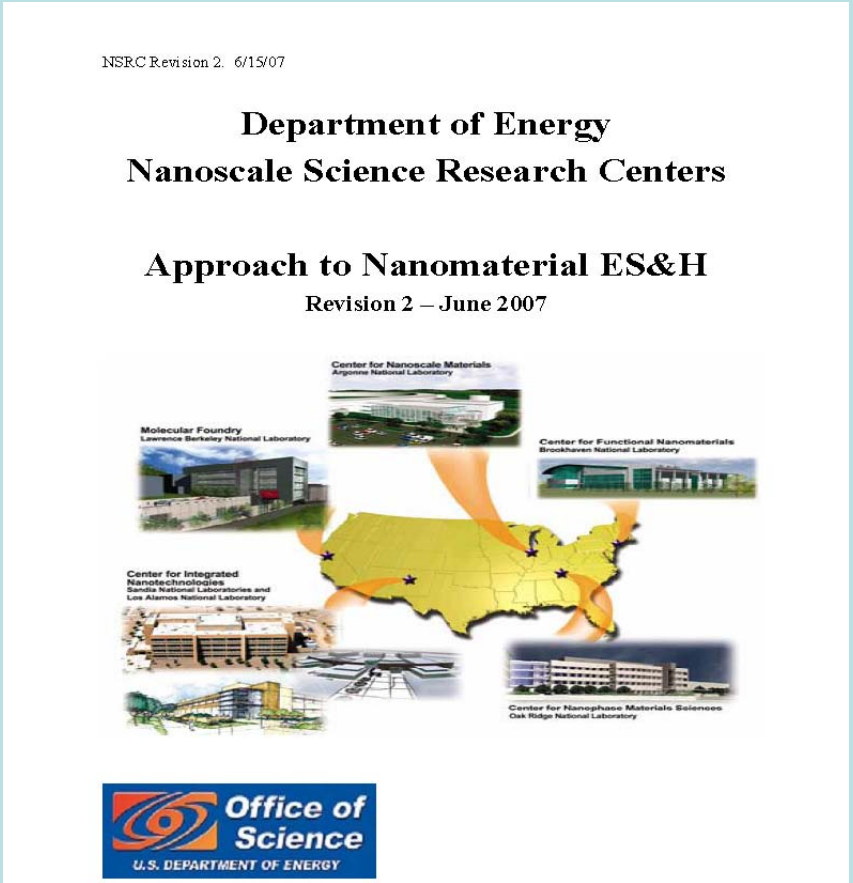
DEPARTMENT OF HEALTH AND HUMAN SERVICES
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health

July 2006

http://www.cdc.gov/niosh/topics/nanotech/


NSRC Revision 2. 6/15/07

Department of Energy
Nanoscale Science Research Centers

Approach to Nanomaterial ES&H
Revision 2 – June 2007

Center for Nanoscale Materials
Argonne National Laboratory

Molecular Foundry
Lawrence Berkeley National Laboratory

Center for Functional Nanomaterials
Brookhaven National Laboratory

Center for Integrated Nanotechnologies
Sandia National Laboratories and Los Alamos National Laboratory

Center for Nanophase Materials Sciences
Oak Ridge National Laboratory

Office of Science
U.S. DEPARTMENT OF ENERGY

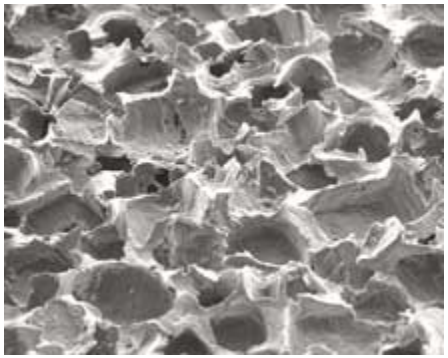
http://orise.orau.gov/ihos/nanotechnology/nanotech_doe_nanoscale_sc.html

“Approach to Nanomaterial ES&H”(Scope)

1. Introduction
2. Conceptual Foundations
3. Controls for R&D Laboratory Operations
4. Verifying Program Effectiveness
5. Transportation of Nanomaterials
6. Management of Nanomaterials-Bearing Waste Streams
7. Management of Nanomaterial Spills
8. Example Industrial Hygiene Sampling Protocol

Engineering Controls for *Nano-hazards*:

- Agglomeration during synthesis (will agglomerates de-agglomerate??)
- Enclosed reactors
- Ventilation
- Encapsulated in processes
- HEPAs work
- Polymer gloves work
- Tyvek works
- Do HEPA Respirators work? (avoid N95), provide reluctantly
- In R&D the devil often lives in researchers' work practices!

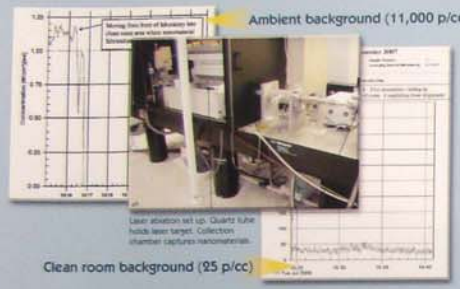


Measurement and Hazard Analysis of the Carbon Laser Ablation Process

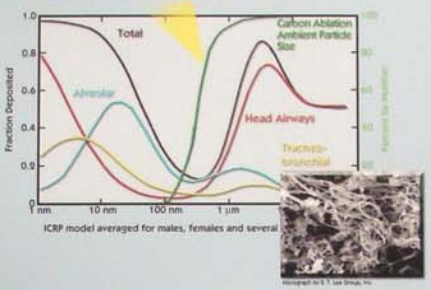
(applying an operational exposure control limit)

T. L. Zontek, Ph.D., Western Carolina University and J. T. Jankovic / R. B. Ogle, Oak Ridge National Laboratory Center for Nanophase Material Sciences

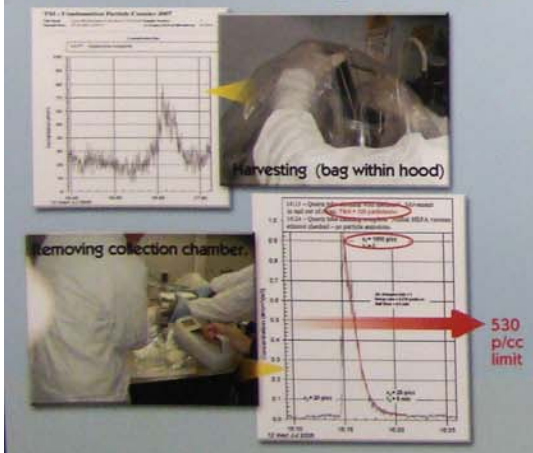
Carbon Laser Ablation Process



Particulate is larger than 100 nm



Job concentration average = 310 p/cc



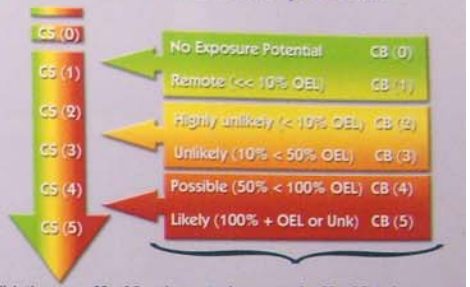
Traditional industrial hygiene controls (ventilation, process enclosure, HEPA vacuuming) effectively control inhalation exposure.

Exposure Control for a New Process

- Initial hazard assessment initiated in research safety summary
- A preliminary control band based on similar task group is assigned
- Control bands incorporate requisite controls based on beliefs re: toxicity, exposure potential, monitoring capability, process stability
- Control band designation is validated/modified by process monitoring
- Validated control band incorporates requisite resample frequency

A Control Band (CB) designation reflects a belief about the level of control for a particular process.

Validation of the process's CB designation determines the actual control status (CS).



Validation as a CS of 3 or less permits continued operation of a process.

Assignment of a CB of 3 or less permits start-up and interim operation of a process under surveillance.

Control Band 2

Laser ablation nano particle generation and harvesting

Conclusions

- Process is controlled using existing methods.
- Inhalation hazard is low for agglomerated particulate
- Operational exposure limit is protective and achievable
- Monitoring results combined with professional judgment using Bayesian techniques confirm control band 2 is justified for operations whenever controls as specified are implemented.
- Resample in 12 – 24 months by performing a spot check (three BZ measurements). If median is less than or equal to 265 p/cc process is considered to continue as well controlled.

While we discuss the future of nanotechnologies,
Many will continue to doubt the safety!

THE END?