Nanoscale Science Research Centers Symposium:
Safe Handling of Engineered Nanoscale Materials
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The NIOSH Nanotechnology Field Research Team – A Brief Summary and Update of Activities

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National Institute for Occupational Safety and Health

CDC Workplace Safety and Health

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NIOSH

Field Research Team Background

- Formally organized in 2006 as a component of the NIOSH Nanotechnology Research Center
- Conducted 18 site visits in a variety of workplaces
- Consists of a Team Leader and other scientists
- Tasked with “seeing what’s out there”….
- Attempting to fill an important knowledge gap regarding nanomaterial creation and use:

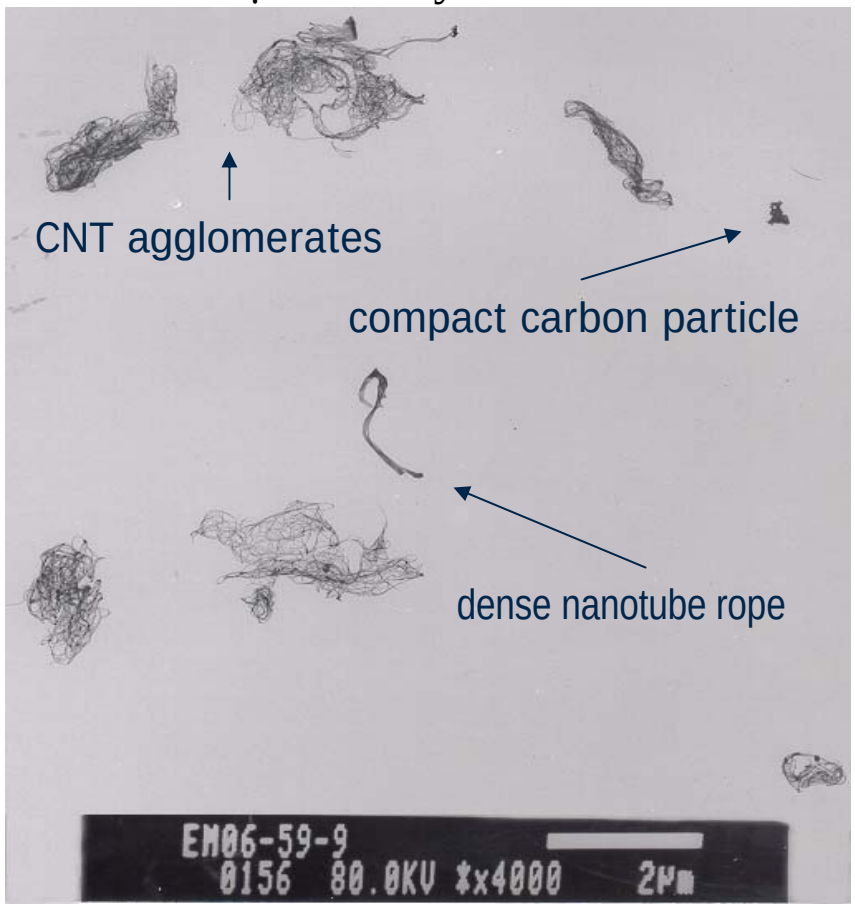
IS THERE A RELEASE???? TO WHAT EXTENT?

Diversity of sites and tasks evaluated by the NIOSH Field Team

Carbon Nanotube Air Sample

Which metric to use?

0.18 – 0.32 μm aerodynamic diameter



Particle Number: A Starting Point

Condensation Particle Counter (CPC)

TSI 3007: particle size range of 10 – 1000 nm with a concentration range of 0 to 100,000 particles/cc.

Optical Particle Counter/Sizer (OPC)

ART Instruments (ARTI) HHPC-6: 300 nm to >10 um in six size ranges simultaneously (particles/L)

Mention of trade names does not imply endorsement.

Nanoparticle Emission Assessment Technique (NEAT): *A Progression*

- Initial assessment: Semi-quantitative technique based on a comparison of particle number concentrations at “suspected” emission sources to “background” particle number concentrations.

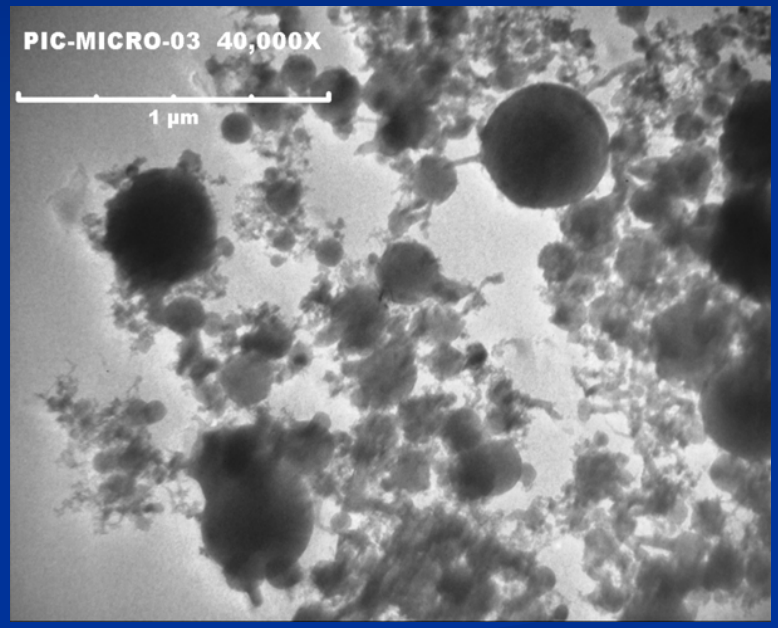
- Expanded investigation: NEAT serves as a guide to a more detailed investigation, using less portable, more expensive particle analyzers.

NEAT- Initial Assessment

- What has been used?
  - Direct-reading, Real-time, instrumentation capable of measuring particle number concentrations
  - Transmission Electron Microscopy (TEM) evaluation of filter-based samples to examine: particle morphology, size, count, elemental analysis
  - Non-Gravimetric, filter-based samples to measure mass: Example - Metals, Carbon (filter selection may vary depending on analytical methodology and material of interest)

Correlate Simple and Complex Measurements

Starting Point



Mass, Size Distribution, Surface Area, Etc.

TEM analysis of aerosol

NEAT - Initial Assessment Procedure

1. Hold preliminary discussions. Review product literature.
2. Observational walkthrough to get familiar with processes, work practices, existing controls, use of Personal Protective Equipment (PPE).
3. System Off - Measure background particle number concentrations with CPC and HHPC-6
4. System On - Measure “suspected” or potential emission points with CPC and HHPC-6

NEAT - Initial Assessment Procedure

5. Are particle number concentrations “higher” with process on? (if no- stop, no further sampling indicated)

6. Collect filter-based air samples for TEM and mass (side-by-side) for duration of task; (nominally 7 Lpm for 30 minutes).

NEAT- Initial Assessment Procedure

7. Collect a pair of background filter-based air samples
8. Repeat background particle number concentrations with CPC and HHPC-6
9. Subtract average background from process-specific measurements

Nanoparticle Emission Assessment Technique

Production System **Off** → Measure background particle number concentrations at 3-5 locations with a CPC and a HHPC-6

Turn Production System **On** → Repeat particle number concentration measurements at suspected emission sources

Are particle number concentrations with the production system on ~25% higher than average background particle number concentrations with the system off?

No

↓

Controls appear to be adequate.
No further testing necessary.

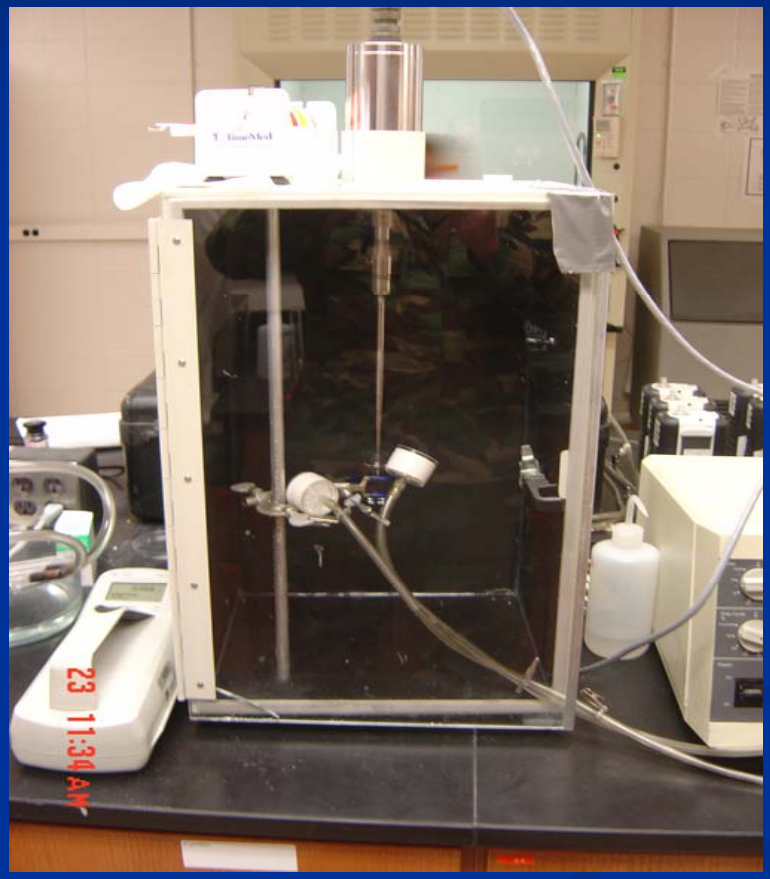
Yes

↓

Collect co-located open-face air filter samples for TEM and analytical analysis at locations of possible emissions identified by the CPC and HHPC. Collect an additional set of co-located open face air filter samples for background, away from the process.

- Side-by-side sampling with the HHPC-6, open face filter cassettes and the CPC

Examples of Sampling



Considerations

- Are particle number concentrations with the production system on ~25% higher than average background particle number concentrations with the system off.

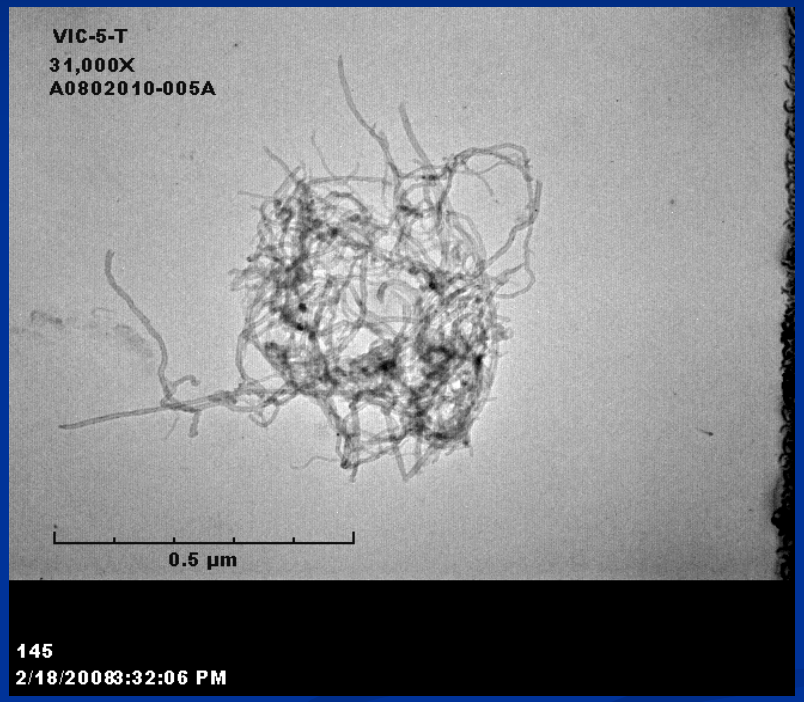
The “~ 25%” is very subjective.

Additional Considerations

- The TEM sample can be overloaded by too many particles. What is the optimum air sample size? How long do I run my air sample pumps?
  - We use nominally 7 Lpm for the duration of a task ~ 15-30 minutes.
  - We will be publishing approximate sampling times for TEM grid based on particle number concentrations.

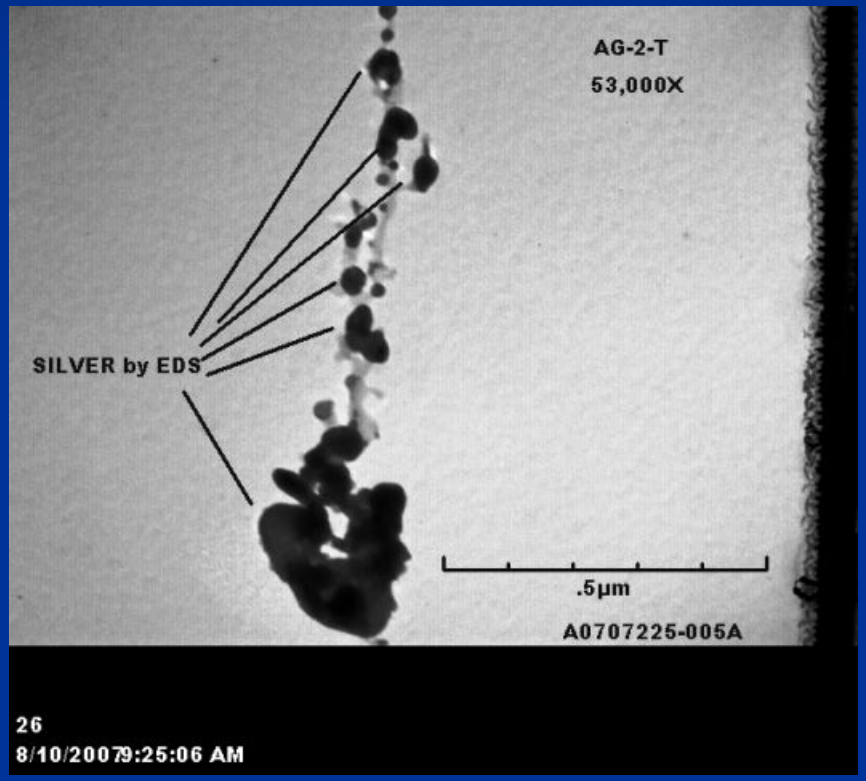
Example of TEM Images from Filters...

MWCNT's Collected During Weighing and Transfer from balance

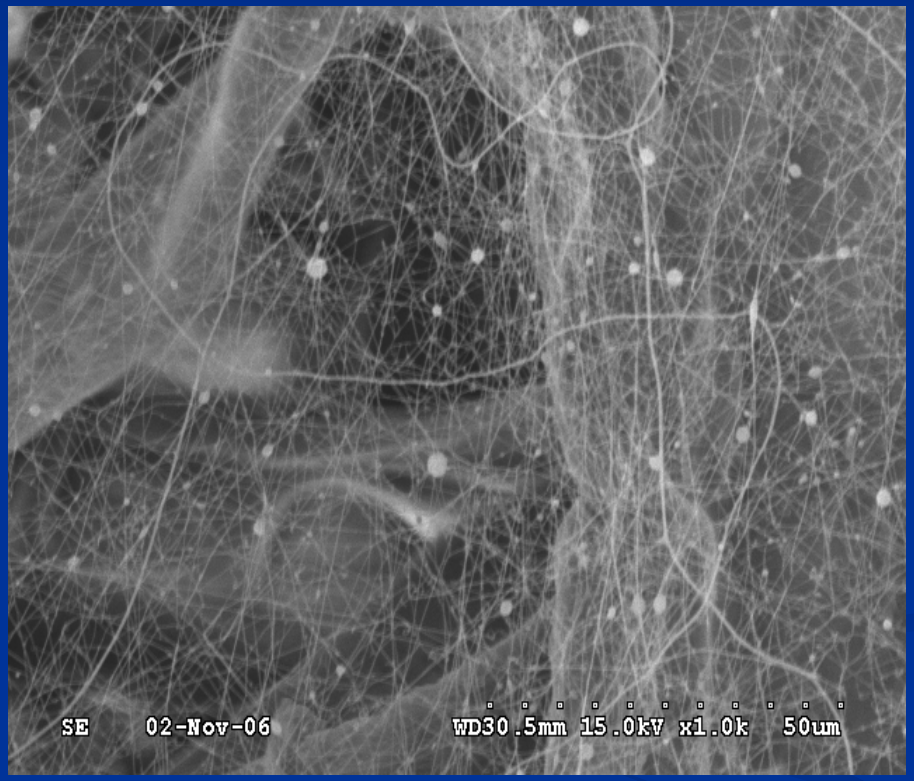


MWCNT's Collected During Sonication

Example TEM/SEM Results



Silver oxide



Electrospun nylon 6

NEAT - Initial Assessment

- Limitations
  - Background fluctuations and other “incidental” sources of nanoparticles
  - CPC maximum concentration is 100,000 particles/cc
  - TEM sensitive to filter loading
  - Area versus personal breathing zone monitoring

Near future modifications to the NEAT

- Collection of Personal Breathing Zone air samples
- Addition of surface area analyzers (e.g. TSI AeroTrak™ 9000, EcoChem DC 2000CE or equivalent)

Mention of trade names does not imply endorsement.

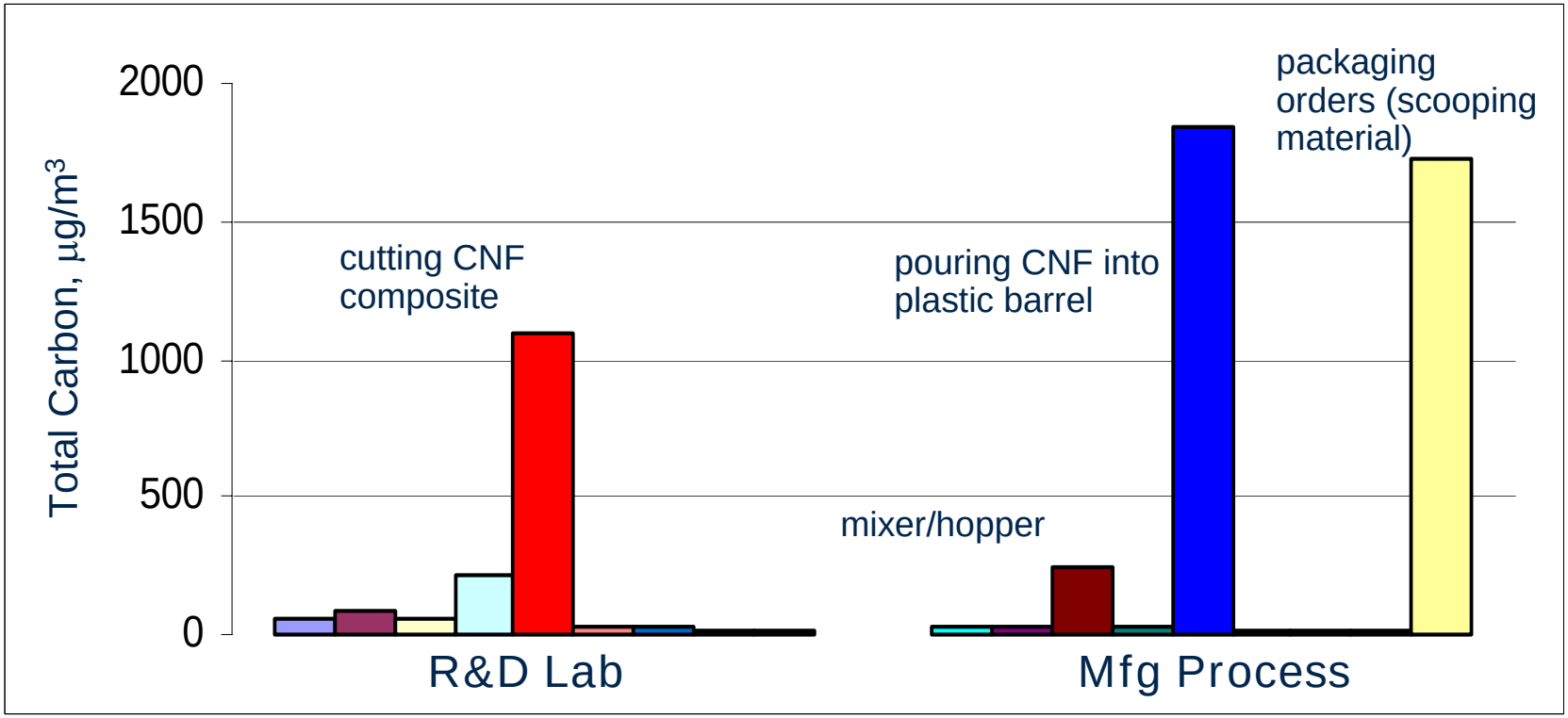
Field Studies: NIOSH Findings

- Nanoparticle emissions in the workplace can be measured
- NEAT requires careful data interpretation
- Has it been successful?
  - Good for a “yes/no” approach on “suspected” emissions and control effectiveness
- Traditional exposure control methods (*i.e.* ventilation) are effective for many processes

Examples of NIOSH Field Investigations

Type of Facility	Type of Particle, Morphology	Size of Particle	Range of "Potential" Exposure Concentrations
University Research lab	Carbon Nanofibers	Approx. 100 nm diameter, 1-10 microns long	60-90 µg/m^3
Metal Oxide Manufacturer	TiO_2, Lithium Titanate, powder	100-200 nm	<100 nm: 1.4 µg/m^3 (TiO_2) Total dust: 4-149 µg/m^3 (TiO_2) <100 nm: ND (Li) Total dust: ND -3 µg/m^3 (Li)
Manufacturer	Carbon Nanofibers	Approx. 100 nm diameter, 1-10 microns long	15 - 1800 µg/m^3
Research and Development lab	Quantum Dots, spheres	2 -8 nm	ND
Metal Oxide Manufacturer	Manganese, Silver, Nickel, Cobalt, Iron oxides, spheres	8 -50 nm	67 - 3619 µg/m^3
Research and Development lab (Pilot-Scale)	Aluminum, spheres	50 – 100 nm	40 - 276 µg/m^3
Research and Development lab	Elemental Metals - Silver, Copper, TiO_2	15 – 40 nm	ND
Filter Media Manufacturer	Nylon 6 Nanofiber	70 - 300 nm diameter, continuous length	ND

CNF Air Sampling Results as Total Carbon (µg/m3)



Can they be controlled?

A Case Study on the Effectiveness of Local Exhaust Ventilation (LEV) on Nanoscale Metal Oxides

Thanks to my coworker

Mark Methner, PhD, CIH

Nanotechnology Field Research Team Leader

Background of Facility

- Producing nanoscale metal oxides such as manganese, iron, silver, nickel and cobalt
- 15-50 nm diameter spherical particles
- Using gas phase condensation reactors
- Produce approx 1 kg/day per reactor

Actual Field Use of NEAT

- Use of the Condensation Particle Counter (CPC) to measure particle number concentration (particles/cc) in the 10 nm - 1000 nm size range

- Use of the Optical Particle Counter (HHPC-6) to measure particle number concentration (particles/L) in the 300 nm - 10,000 nm size range

- Air sample filter cassettes for mass (metals) and TEM analysis (open face, 37 mm, 0.8 m pore size MCE, 7 Lpm for duration of task 10-30 minutes)

Initial Assessment

- Initial walkthrough and air sampling assessment determined that nanoparticles were released to the general plant atmosphere during reactor cleanout
- Suggested the use of a commercially available, portable, local exhaust ventilation (LEV) system equipped with HEPA filtered exhaust. (Commonly used as a welding fume extractor.)
- Company purchased the LEV, then asked field team to return to determine the effectiveness of the control.

Reactor cleanout process (before LEV control)

Photo of LEV used during reactor cleanout procedure
(Exhaust flow rate of 1,000 cfm)

Effectiveness of LEV in Reducing Release of Aerosol During Reactor Cleanout Operations:

Mass Air Concentrations of Metal Oxides With/Without LEV
Micrograms/cubic meter (g/m^3)

Operation	**Air Concentration "Without" LEV**	**Air Concentration "With" LEV**	**Percent Reduction in air concentration due to use of LEV (%)***
Manganese (Mn) Reactor cleanout	3,619	150	96
Silver (Ag) Reactor cleanout	6,667	1,714	74
Iron (Fe) Reactor cleanout	714	41	94
Background (Reactor area Prior to cleanout)	ND	ND	N/A
Mean (+/- S.D.)			**88 (+/- 12)**

* Percent reduction calculated as follows: [(Without LEV - With LEV)/ Without LEV] x 100

Typical location of LEV and production operator during reactor cleanout activities

Filter-based air sampling devices located in upper left corner of photo

Effectiveness of LEV in Reducing Release of Aerosol During Reactor Cleanout Operations:

Particle Number Concentrations and Percent Reduction due to LEV

Silver (particles/L)

Particle size (nm)	Measured Concentration (**Without LEV**)	Measured Concentration (**With LEV**)	Average Background Concentration	Adjusted Concentration ** (**Without LEV**) (subtraction of background)	Adjusted Concentration (**With LEV**) (subtraction of background)	Percent Reduction (%)
300	150,684	90,909	104,708	45,976	0	100
500	88,872	13,721	14,813	74,059	0	100
1,000	58,561	6,113	4,009	54,553	2,105	96
3,000	45,108	4,253	2,097	43,012	2,157	95
5,000	28,699	2,431	851	27,849	1,581	94
10,000	4,597	388	64	4,534	325	93
(10 - 1000)*	18,196	10,556	12,146	6,050	0	100

* Particles/cc

** Adjusted concentration = measured concentration – average background concentration. If the background concentration exceeds the measured concentration, the adjusted concentration is considered to be zero.

Effectiveness of LEV in Reducing Release of Aerosol During Reactor Cleanout Operations:

Particle Number Concentrations and Percent Reduction due to LEV

Manganese (particles/L)

Particle size (nm)	Measured Concentration (**Without LEV**)	Measured Concentration (**With LEV**)	Average Background Concentration	Adjusted Concentration ** (**Without LEV**) (subtraction of background)	Adjusted Concentration (**With LEV**) (subtraction of background)	Percent Reduction (%)
300	152,058	107,766	104,708	47,350	3,058	94
500	77,068	13,637	14,813	62,225	0	100
1,000	62,866	3,738	4,009	58,858	0	100
3,000	9,153	2,045	2,097	7,057	0	100
5,000	9,481	869	851	8,611	19	100
10,000	88,328	73	64	88,265	10	100
(10 - 1000)*	29,063	13,144	12,146	16,917	998	94

* Particles/cc

** Adjusted concentration = measured concentration – average background concentration. If the background concentration exceeds the measured concentration, the adjusted concentration is considered to be zero.

Effectiveness of LEV in Reducing Release of Aerosol During Reactor Cleanout Operations:

Particle Number Concentrations and Percent Reduction due to LEV

Cobalt (particles/L)

Particle size (nm)	Measured Concentration (**Without LEV**)	Measured Concentration (**With LEV**)	Average Background Concentration	Adjusted Concentration ** (**Without LEV**) (subtraction of background)	Adjusted Concentration (**With LEV**) (subtraction of background)	Percent Reduction (%)
300	189,525	93,040	104,708	84,817	0	100
500	80,892	13,520	14,813	66,079	0	100
1,000	45,114	5,709	4,009	41,106	1,701	96
3,000	32,032	3,914	2,097	29,936	1,818	94
5,000	17,646	2,287	851	16,796	1,437	91
10,000	1,827	449	64	1,764	386	78
(10 - 1000)*	25,097	14,071	12,146	12,951	1,925	85

* Particles/cc

** Adjusted concentration = measured concentration – average background concentration. If the background concentration exceeds the measured concentration, the adjusted concentration is considered to be zero.

Effectiveness of LEV in Reducing Release of Aerosol During Reactor Cleanout Operations:

Mass Air Concentrations of Metal Oxides With/Without LEV
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Background (Reactor area Prior to cleanout)	ND	ND	N/A
Mean (+/- S.D.)			**88 (+/- 12)**

* Percent reduction calculated as follows: [(Without LEV - With LEV)/ Without LEV] x 100

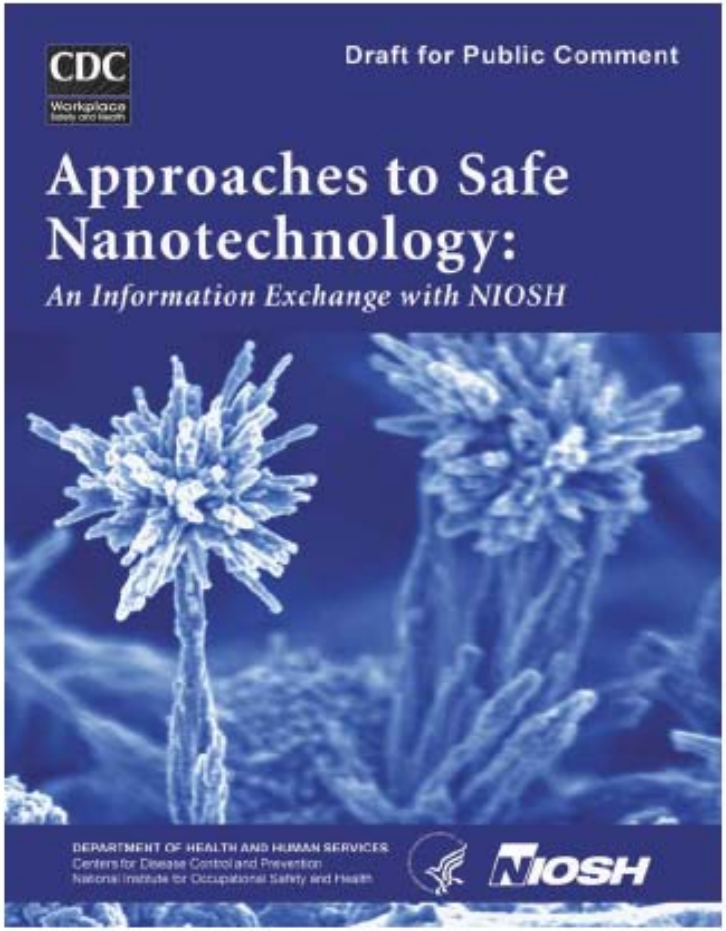
Conclusions of LEV Effectiveness Study

Average percent reduction from the use of a local exhaust ventilation unit

96 +/- 6% based on particle number concentration data

88 +/- 12% based on air sampling mass concentration data

NIOSH Guidance



- Summary of issues
- Approaches to consider
- NIOSH recommendations
- Updated as new information is available
- *Review and input are requested*

www.cdc.gov/niosh/topics/nanotech

Thank you!

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