2nd Annual MA Nanotechnology Workshop
January 29, 2009

Demonstration of the Nanoparticle Emission Assessment Technique (NEAT) used by NIOSH for Identifying Sources and Releases of Engineered Nanoparticles

Laura Hodson, MSPH, CIH

Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health

CDC Workplace Safety and Health

NIOSH

Risk Management of Engineered Nanoparticles:

The Simple Questions

Are they hazardous?

Can they be measured?

Can they be controlled?

Hazard Identification
"Is there reason to believe this could be harmful?"

Exposure Assessment
"Will there be exposure in real-world conditions?"

Risk Characterization
"Is substance hazardous *and* will there be exposure?"

Risk Management
"Develop procedures to minimize exposures"

Adapted from Gibbs, 2006

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

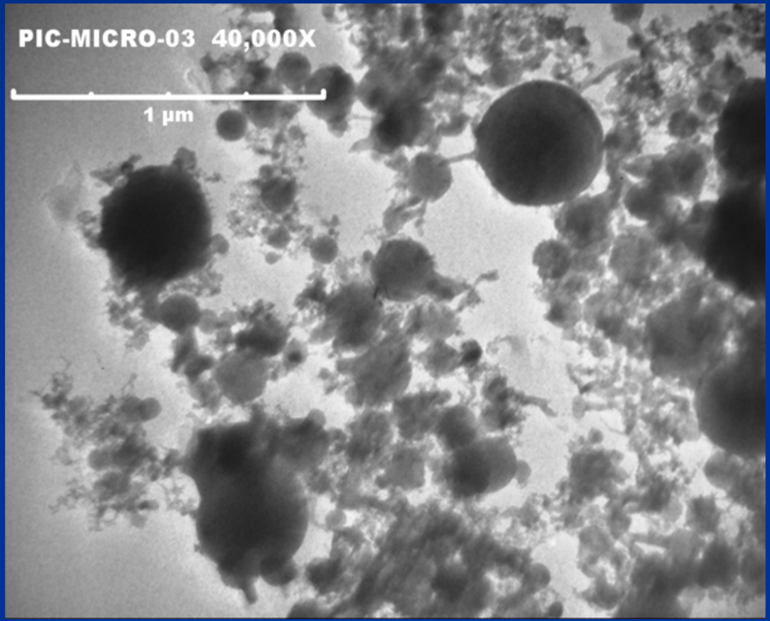
- Initial assessment: Semi-quantitative technique based on a comparison of particle number concentrations at “suspected” emission sources to “background” particle number concentrations.

- 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
  - Electron Microscopy (TEM/SEM) evaluation of filter-based air samples to examine: particle morphology, size, count, compositional analysis
  - Non-Gravimetric, filter-based air samples to measure elemental mass: Example - Metals, Carbon (filter selection may vary depending on analytical methodology and material of interest)

Correlate Simple and Complex Measurements



Starting Point

TEM analysis of aerosol

Mass, Size Distribution,
Surface Area, Etc.

Particle Number: A Starting Point

Condensation Particle Counter (CPC)

TSI 3007 (or P-Trak): particle size range of 10 (or 20) – 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)

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. <u>System/Process Off</u> - Measure background particle number concentrations with CPC and OPC
4. <u>System/Process On</u> - Measure “suspected” or potential emission points with CPC and OPC

NEAT - Initial Assessment Procedure

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

6. Collect “At Source” filter-based air samples for TEM/SEM and mass (side-by-side) for duration of task; (nominally 7 Lpm for 30 minutes, will discuss additional considerations later).

NEAT- Initial Assessment Procedure

7. Collect a pair of background filter-based air samples away from the process

8. Once process stops, repeat background particle number concentration measurements with CPC and OPC

9. Subtract average of before/after 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 an OPC

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

Are particle number concentrations with the production system on 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 OPC. Collect an additional set of co-located open face air filter samples for background, away from the process.

Example of Initial Sampling

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

Considerations

- Are particle number concentrations associated with a given process higher than average background particle number concentrations with the system off.

“Higher than background” is very subjective.

Additional Considerations: Other sources of nanoparticles exist in the workplace and can affect measurements

Additional Considerations

- The sample submitted for analysis via Microscopy can be overloaded by too many particles. What is the optimum air sample size? How long do I run my air sample pumps?

  - We routinely use 7 Lpm for the duration of a task ~ 15-30 minutes.

  - We will be publishing approximate sampling times for TEM/SEM based on particle number concentrations.

Additional Considerations

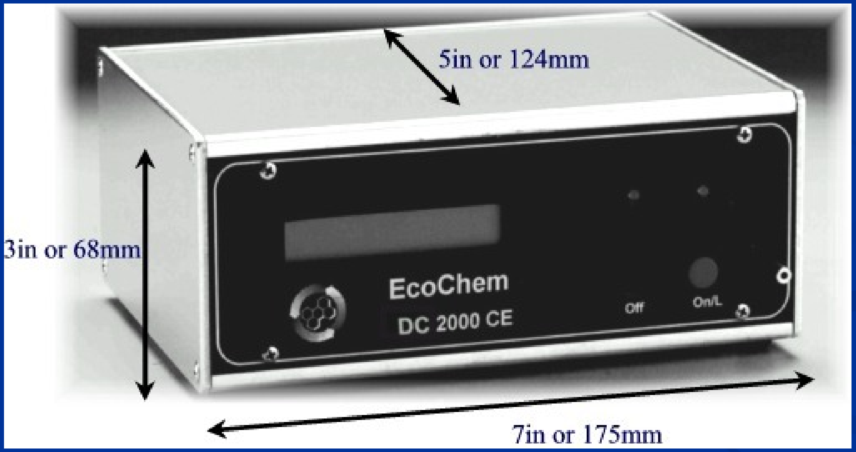
- Collection of Personal Breathing Zone samples (with and without a cyclone)

Additional Considerations

- Does the OPC indicate the majority of particles in the 1.0 µm or larger size? Are you sampling titanium dioxide?
  - Use a personal cascade impactor or respirable cyclone attached to the filter cassettes used for TEM/SEM and mass. Consider a second set without the impactor/cyclone (open-faced) to determine the contribution of particles >1 µm.

Modification to the NEAT for Research Purposes

- Use of particle surface area analyzers (e.g. TSI AeroTrak™ 9000, EcoChem DC 2000CE or equivalent)



Demonstration of NEAT – Initial Assessment –

"Nanotubes R Us" produces kilogram quantities of Multi-Walled Carbon Nanotubes (MWCNT) in a single reactor. Processes planned for today include:

1. Checking a reactor vent for emissions/leaks.
2. Packaging dried MWCNTs into 500 mg quantities to send to customers.

Collect initial background samples

Data Gathering

Size (nm)	Initial Background	
10-1000	8,311	P/cc
20-1000	6,750	P/cc
300	25,491	P/L
500	1,134	P/L
1,000	185	P/L
3,000	36	P/L
5,000	5	P/L
10,000	1	P/L

Collect sample at “reactor”

Data Gathering & Interpretation

Size (nm)	Backgrnd	Reactor	Reactor Backgrd Corrected	
10-1000	8,311	24,000	15,689	P/cc
20-1000	6,750	16,604	9,854	P/cc
300	25,491	97,296	71,805	P/L
500	1,134	85,139	84,005	P/L
1,000	185	12,651	12,466	P/L
3,000	36	258	222	P/L
5,000	5	1	0	P/L
10,000	1	**1**	0	P/L

Collect filter samples at reactor

- For total and elemental carbon using quartz fiber filters (QFF) 37 mm open face filter cassettes,
- For TEM analysis using 0.8 µm pore size mixed cellulose ester (MCE) 37 mm open face filter cassettes.
- 7 Lpm for the duration of the reactor cleaning process.

Collect sample at “packaging station”

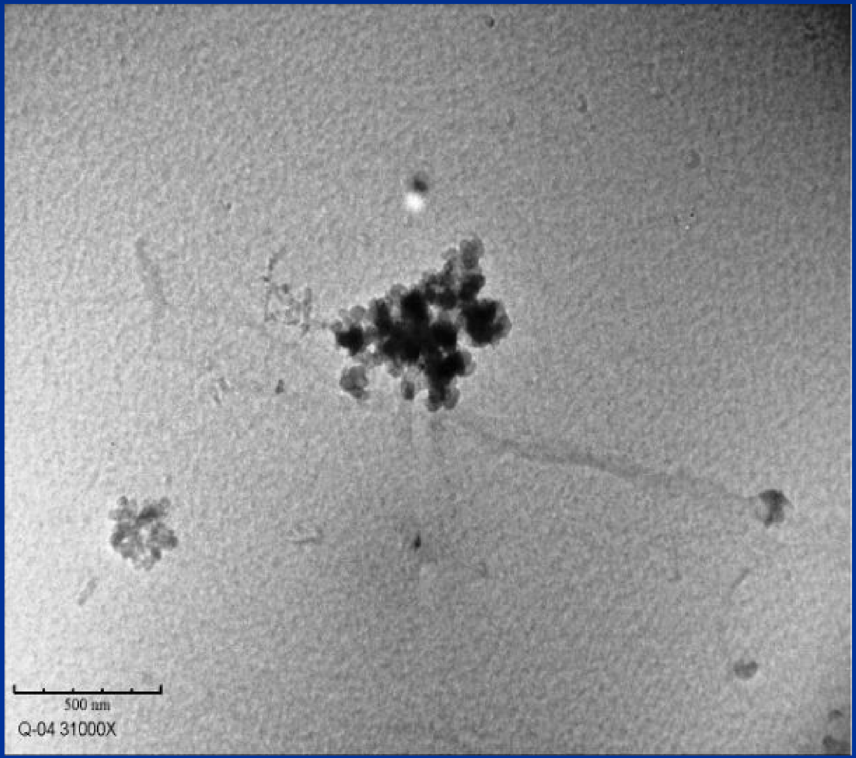
Data Gathering & Interpretation

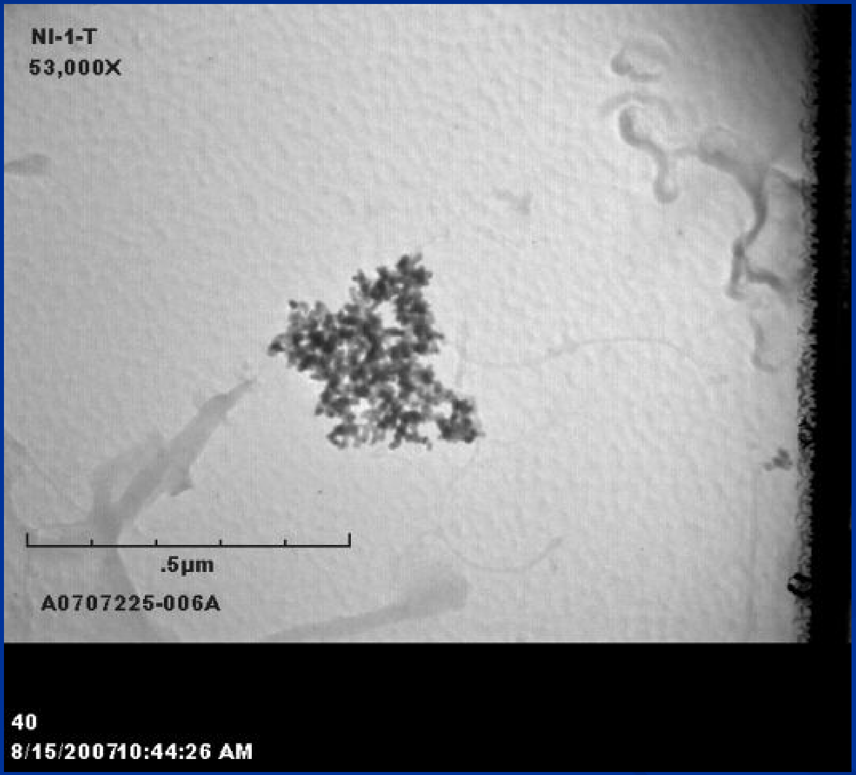
Size (nm)	Backgrnd	Packaging	Packaging Backgrnd Corrected	
10-1000	8,311	9,658	1,347	P/cc
20-1000	6,750	10,112	3,362	P/cc
300	25,491	26,760	1,269	P/L
500	1,134	2,459	1,325	P/L
1,000	185	8,456	8,271	P/L
3,000	36	15,671	15,635	P/L
5,000	5	10,760	10,755	P/L
10,000	1	6,422	6,421	P/L

Collect filter samples at packaging station

- For total and elemental carbon using quartz fiber filters (QFF) 37 mm open face filter cassettes,
- For TEM analysis using 0.8 µm pore size mixed cellulose ester (MCE) 37 mm open face filter cassettes.
- 7 Lpm for the duration of the reactor cleaning process.
- Did you remember that we also need a background filter set away from the process?

Example TEM Results

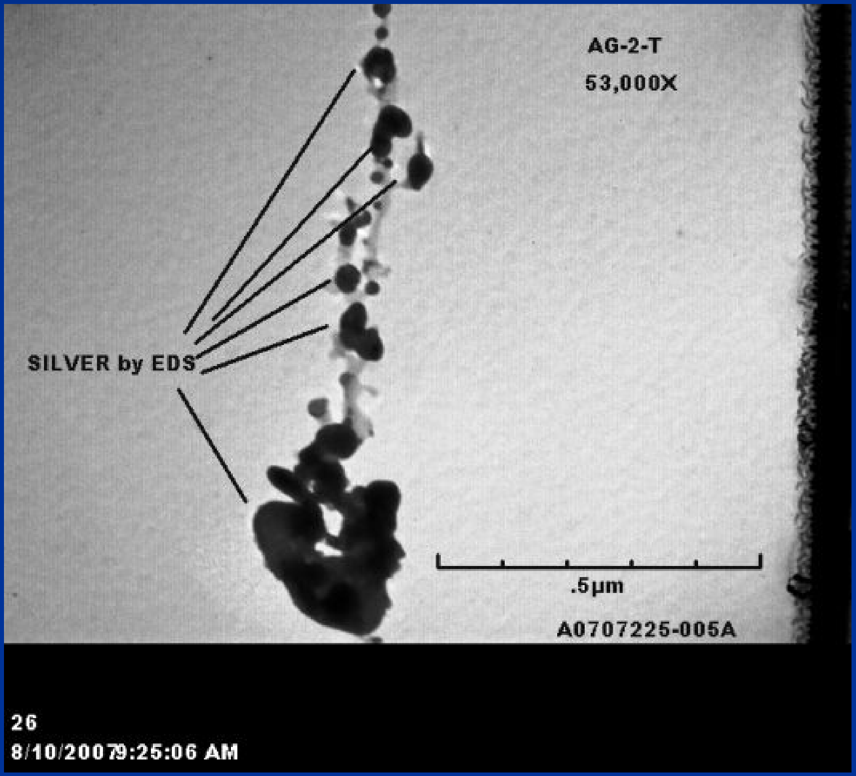


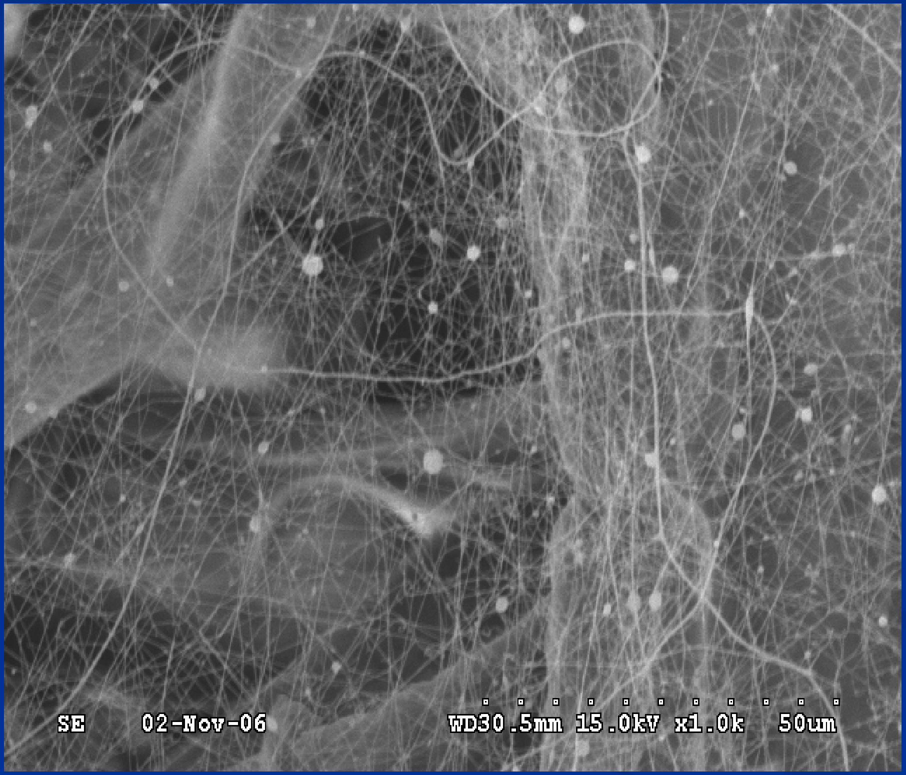


Manganese oxide

Nickel oxide

Example TEM/SEM Results

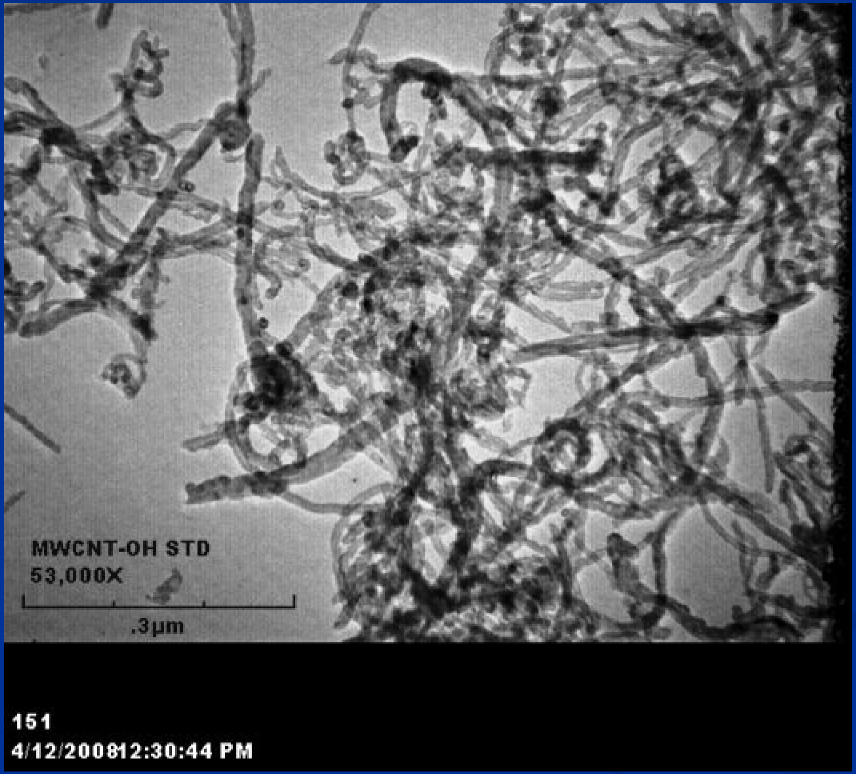




Silver oxide

Electrospun nylon 6

Example TEM Results



MWCNT-functionalized

MWCNT-functionalized

Example TEM Results

Carbon nanofiber

Carbon nanotube

Challenge: The diversity of "Nanomaterial Production and Use"

Can they be controlled?

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

Thanks to:

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 µm 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 ($\mu g/m^3$)

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.

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

Thanks for listening

www.cdc.gov/niosh/topics/nanotech

LHodson@cdc.gov
MMethner@cdc.gov