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## Nano-metal oxides: Exposure and engineering control assessment

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### ABSTRACT

In January 2007, the National Institute for Occupational Safety and Health (NIOSH) conducted a field study to evaluate process specific emissions during the production of ENMs. This study was performed using the nanoparticle emission assessment technique (NEAT). During this study, it was determined that ENMs were released during production and cleaning of the process reactor. Airborne concentrations of silver, nickel, and iron were found both in the employee's personal breathing zone and area samples during reactor cleaning. At the completion of this initial survey, it was suggested that a flanged attachment be added to the local exhaust ventilation system.

NIOSH re-evaluated the facility in December 2011 to assess worker exposures following an increase in production rates. This study included a fully comprehensive emissions, exposure, and engineering control evaluation of the entire process. This study made use of the nanoparticle exposure assessment technique (NEAT 2.0). Data obtained from filter-based samples and direct reading instruments indicate that reactor cleanout increased the overall particle concentration in the immediate area. However, it does not appear that these concentrations affect areas outside of the production floor. As the distance between the reactor and the sample location increased, the observed particle number concentration decreased, creating a concentration gradient with respect to the reactor. The results of this study confirm that the flanged attachment on the local exhaust ventilation system served to decrease exposure potential.

Given the available toxicological data of the metals evaluated, caution is warranted. One should always keep in mind that occupational exposure levels were not developed specifically for nanoscale particles. With data suggesting that certain nanoparticles may be more toxic than the larger counterparts of the same material; employers should attempt to control emissions of these particles at the source, to limit the potential for exposure.

### KEYWORDS

Engineering control;  
exposure assessment;  
nanomaterials

### Introduction

Nanotechnology refers to the creation, use, and manipulation of particles below 100 nm in size. Current applications range from enhancing metal and plastic fabrication, producing chemical additives for foods or fuels, creating sophisticated drugs to treat disease, and developing smaller and more powerful electronics among others. Researchers specializing in areas of biology, material science, chemistry, and electrical engineering have contributed to the growing knowledge of the nanotechnology industry, its products, and their applications.

Nanoparticles differ in physical and chemical properties from their parent materials.<sup>[1]</sup> This is often attributed

to an increase in surface to mass ratio. Principles of quantum mechanics play a role in the unique properties of nanomaterials when dealing with particles consisting of less than a couple hundred atoms.<sup>[2]</sup> The ability to push the boundaries of nanotechnology is mostly limited by the capability to observe and manipulate ever smaller phenomenon.<sup>[3]</sup> Parent materials do not necessarily present the same level of hazard as nanomaterials.<sup>[4–13]</sup> Similarly, the mode of action for affecting human health can differ. The nano derivative of innocuous parent materials could potentially cause damage at a lower dose simply because of the size and shape of the particles.<sup>[1,4]</sup> This uncertainty has created many challenges in

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identifying best practices while minimizing the risk posed by nanomaterials in the workplace.

This article discusses the evaluation of a facility that produces engineered nanomaterials (ENMs). These ENMs consist of various metals including iron, nickel, silver, manganese, and palladium. Although occupational exposure levels are not available for these metals, studies have indicated that it may be prudent to keep exposures to the nano-scale metal as low as possible. *In vitro* studies performed by Gopinath, Gogoi, Chattopadhyay, and Ghosh<sup>[14]</sup> indicated that in comparison with a material's larger (parent) counterpart, nanomaterials can move easily through cell membranes and can cause severe toxic effects on human health. The *in vitro* studies showed that the toxicological effects specific to exposure to nanoscale nickel oxide and nickel have been found to be more toxic to lung epithelial cells than larger-sized nickel particles.<sup>[15,16]</sup> *In vitro* studies on silver nanoparticles have indicated movement through cell membranes and cell necrosis,<sup>[14]</sup> in addition to decreasing metabolic activity and arresting growth and cell division.<sup>[17]</sup> An *in vitro* study on exposure to iron nanoparticles indicated that the reactive oxygen species produced by exposure may increase cell permeability thereby increasing the potential for vascular movement.<sup>[18]</sup> Much of the data available on palladium focus on dermal or ingestion exposure; the chronic effects are not well understood.<sup>[19,20]</sup>

Given the available limited data on the metals evaluated, caution is warranted. One should always keep in mind that the current OELs were not developed specifically for nanoscale particles. With limited data suggesting that certain nanoparticles may be more toxic than the larger counterparts of the same material; employers should attempt to control emissions of these particles at the source, to limit the potential for exposure. For most processes and job tasks, the control of airborne exposure to nanoparticles can be accomplished using a wide variety of engineering control techniques similar to those used in reducing exposures to general aerosols.<sup>[21-24]</sup>

### Description of the process evaluated

In January 2007, the National Institute for Occupational Safety and Health (NIOSH) conducted a field study to evaluate process specific emissions during the production of ENMs. This study was performed using the nanoparticle emission assessment technique (NEAT).<sup>[25,26]</sup> During this study, it was determined that ENMs were released during production and cleaning of the process reactor. Airborne concentrations of silver, nickel, and iron were found in the PBZ and area samples during reactor cleaning. At the completion of this initial survey, it was suggested that a flanged attachment be added to the local exhaust ventilation (LEV) system.<sup>[27]</sup>

NIOSH re-visited the facility in December 2011 to assess worker exposures following a change in production rates. This study included a fully comprehensive emissions, exposure, and engineering control evaluation of the entire process. This study made use of the nanoparticle exposure assessment technique (NEAT 2.0).<sup>[28]</sup> The results of this study identify potential improvements of the LEV system for reactor cleaning processes. Also, the use of an un-flanged LEV for emission reduction during rolling of manganese infused cathodes was evaluated. Wipe samples were collected and evaluated for all metals currently being used at this facility to assess the migration of materials beyond the process areas.

The nano metals are produced within stainless steel reactors through a process known as gas phase condensation. The products are used in high capacity, energy efficient batteries and fuel cells. The 7,500 square foot facility houses 6 individual reactors, each capable of producing upwards of 1 kg of ENM per day. A single production technician, with assistance from the project manager, performs both production and cleaning tasks. The facility operates on 8-hr shifts, 5 days per week.

Depending on the material being produced, different metals (Fe, Ag, Ni, Pa, Mn), most in powder form, are fed through a hopper into the vacuum reactor vessel. The raw material rests on a ceramic plate (boat) that is superheated. The metal becomes molten, then gaseous, and oxidizes to produce metal oxide spheres in the nano-scale. The spheres then condense on the water cooled exterior of the reactor vessel and are collected via gravity in a glass jar at the bottom of the reactor. The jar is then backfilled with inert Argon gas to prevent further reaction.

### Reactor vessel cleanout

During the initial assessment, it was determined that the reactor cleanout process emitted a substantial amount of ENM's. To control such emissions, the company purchased a portable fume extractor Model Sentry Air SS-300-PFS (Sentry Air Systems, Inc. Houston, TX) with a high-efficiency particulate air (HEPA) filter commonly used during welding processes to capture fumes. The unit selected for use consisted of a 6-in flexible duct attached to a HEPA filtered air handler equipped with a carbon pre-filter. This unit has a stated maximum exhaust flow rate of 350 cfm. The fan was connected to a flange that measured 18 in x 32 in constructed in sheet metal by the shop foreman and used for the duration of the cleanout process. A photo of the LEV attachment on the reactor is shown in [Figure 1](#).

Following production, the reactor is allowed to cool and the casing/jacket is removed by hoist. Then the LEV system is put in place and materials are removed by sweeping with a brush. The swept materials are passed



**Figure 1.** LEV and reactor bottom plate.

through a sieve to collect recyclable/reusable materials. Remaining materials are scraped with a spatula. All materials are collected for recycling. Personal protective equipment (PPE) for this task included a lab coat, gloves, and a full face, powered air purifying respirator (PAPR) with an assigned protection factor of 1000 with P100/OV cartridge.

## Methods

The exposure assessment included task-based and full-shift integrated filter sampling and the use of direct reading instrumentation. Direct reading measurements were taken throughout the entire shift to indicate changes in particle concentration during tasks. Samples were collected on and around the reactors, within the worker's breathing zone, and throughout the facility to monitor migration of the ENMs. A thorough engineering control evaluation was performed which included: Pitot traverse, hood face velocity measurements, and airflow visualization and room pressurization observations using a smoke tracer. The exposure assessment method used for the 2011 field study followed the NEAT 2.0 method.<sup>[28]</sup>

### Filter-based samples

Personal breathing zone (PBZ), area, and task-based samples were collected during the cleaning process to determine the presence and mass concentration of specific metals (Fe, Ni, Ag, Pd) in accordance with NIOSH Manual of Analytical Methods (NMAM) Method 7303 and elements by inductively coupled plasma (Hot Block/Hydrochloric acid/Nitric acid Digestion).<sup>[29]</sup> Sampling included both task-based and full-shift samples. Non-production areas were also evaluated to determine background concentrations of these metals. PBZ samples were collected as close as possible to the subjects' breathing zone while the area samples were collected

outside but adjacent to the reactor vessel to provide an indication of fugitive emissions and subsequent potential occupational exposures. A task-based sample, including filters for both elemental mass and transmission electron microscopy (TEM) analysis, was collected during each reactor cleanout procedure.

Mass-based filter samples were collected with Leland Legacy pumps (SKC Inc., Eighty Four, PA) operating at a flow rate between 3.9 and 4.0 L/min using open face 25-mm mixed cellulose ester (MCE) filters with 0.45  $\mu\text{m}$  pore size. Flow rate was matched to the pressure differential, filter resistance, and cassette size. The flow was set as high as possible in an attempt to collect a detectable concentration over the short duration of the samples. All pumps were calibrated before and after each day of sampling. Samples to assess the physical properties of the production materials were collected simultaneously with the mass based samples. These samples were collected with the same type of pumps and filters. Flow rates ranged from 3.3–4.7 L/min. The samples were analyzed by TEM with energy dispersive spectroscopy (EDS) using a modification of the NMAM Method 7402 (without the counting convention used for asbestos fibers) by transmission electron microscopy.<sup>[30]</sup> TEM with EDS provides an indication of the relative abundance of nanostructures per mm of filter surface, as well as other characteristics such as size, shape, chemical composition, and degree of agglomeration. Counts were provided on a per sample basis and then converted to particles per volume of sampled air.

### Wipe samples

Wipe samples were collected throughout the facility in order to characterize the potential migration of material through the facility. These samples were collected according to NIOSH NMAM Method 9102, Elements on Wipes.<sup>[31]</sup> Samples were collected using pre moistened GhostWipes<sup>TM</sup> (SKC Inc., Eighty Four, PA). Wipe samples were taken in 10 cm  $\times$  10 cm square templates throughout production, laboratory, and office spaces, on horizontal surfaces likely to be used by employees.

### Direct-reading, real-time instruments

Three direct-reading, real-time field-portable instruments were used to characterize process emissions by determining the number or mass concentration and approximate size range of airborne particles. A TSI model 3007 (TSI, Inc., Shoreview, MN) handheld condensation particle counter (CPC) was used to count particles in the size range of 10 to greater than 1000 nm. The data output is expressed as total number of particles per cubic centimeter (cc) of sampled air with an upper dynamic

range limit of approximately 100,000 particles per cc of air (pt/cc).

A DustTrak DRX™ Aerosol Monitor Model 8533 (TSI, Inc., Shoreview, MN) was used to simultaneously measure mass and size fraction of airborne particulate using laser light scattering technology. According to the manufacturer, this instrument responds to particles in the size range of 100 nm to approximately 15,000 nm and aerosol mass concentrations ranging from one to 150,000 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ).

Both a CPC and DusTrak were used for source, area, and background sampling locations. A third direct reading instrument was used solely for source sampling. The TSI Optical Particle Sizer (OPS) Model 3330 (TSI, Inc., Shoreview, MN) is capable of measuring particles in the size range of 0.3–10 micrometers in as many as 16 different size channels. This instrument is capable of measuring particle number concentrations up to 3,000 particles per cubic centimeter.

### Airflow measurements

Air velocity measurements were made across the face of the reactor using a TSI VelociCalc Plus Model 8388 thermal anemometer (TSI Incorporated, St. Paul, MN). For this study, the open face of the reactor was divided into three measurement planes, A', B', and C' (see Figure 2). Readings were collected in the exhaust opening (A'), the face of the hood (B'), and the end of the work area of the reactor (C'). Air velocity measurements were taken along a grid at each plane. The exhaust air temperature in each duct was also measured using the thermal anemometer after the air temperature had stabilized.

A Pitot tube traverse was used to measure velocity in the duct to estimate total exhaust airflow rate. Two 8-point orthogonal traverses were performed to determine average duct air velocity.<sup>[32,33]</sup> The traverses were performed in a rigid duct extension that was connected to the flexible duct to allow for the flow to stabilize and collect the

readings. The measurements were collected 7 duct diameters downstream of the plain opening and 3 duct diameters upstream of the bend of the flexible duct in accordance with standard practice. Air velocity in the duct was calculated from the velocity pressures, and volumetric flow rate through the duct was determined by multiplying the average velocity by the cross-sectional area of the duct. The fume extractor fan unit was used with the flange for reactor cleanout at full flow and then moved into the lab area where it was used as a collection system (without flange) at a reduced flow rate. Exhaust duct velocity measurements were collected at both full and reduced flow.

### Smoke observations

A Wizard Stick (Zero Toys, Inc., Concord, MA) smoke generator was used to visualize air movement around the face of the reactor. Smoke was released in areas near where the contaminants are released and at the edge of the reactor to qualitatively evaluate the capture efficiency and determine areas of potential concern. If the smoke was captured quickly and directly by the hood, it was a good indication of acceptable control design and performance. If the smoke was slow to be captured when released at various emission points, the hood design was considered marginal. Also, the adverse effect of cross drafts on the hood was evaluated by releasing smoke near the edge of the reactor. Smoke was also used to evaluate room pressurization schemes by releasing a small amount of smoke around doors and hallways to determine the pressurization status of the production area compared to the adjacent rooms (laboratory and office space).

## Results

### Filter-based air sampling

Filters collected during reactor cleanout were analyzed for iron, nickel, palladium, and silver. Palladium was detected on a single filter (Mass-12) at a concentration of  $2.38 \mu\text{g}/\text{m}^3$  (see Table 1). The most abundant metal was nickel, which was detected on all filters except the laboratory background (Mass-2). Of the positive samples, three were under the limit of quantitation (LOQ) but above the limit of detection (LOD). Of the quantifiable results, the concentrations ranged from  $0.32$ – $6.21 \mu\text{g}/\text{m}^3$ . The lowest concentration was found in the conference room (Mass-3), while the highest concentration was found in the production area (Mass-8). Only two of the samples (Mass-4, Mass-12) yielded iron concentrations above the LOQ. The results from these two samples were similar;  $11.87 \mu\text{g}/\text{m}^3$  and  $11.90 \mu\text{g}/\text{m}^3$ , respectively. Quantifiable silver concentrations were found on 5 filters; Mass-4, Mass-5,

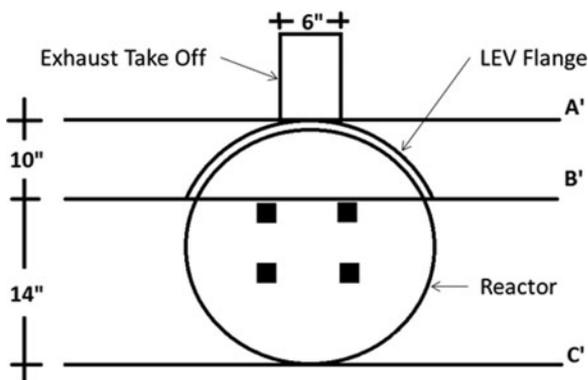


Figure 2. Top view of reactor. Place selection for face velocities.

**Table 1.** Filter-based air samples: Reactor cleanout mass concentration of metals.

| Location                                       | Name                    | Sample Number | Sample Duration (minutes) | Iron Concentration ( $\mu\text{g}/\text{m}^3$ ) | Nickel Concentration ( $\mu\text{g}/\text{m}^3$ ) | Palladium Concentration ( $\mu\text{g}/\text{m}^3$ ) | Silver Concentration ( $\mu\text{g}/\text{m}^3$ ) |
|--|-------------------------|---------------|---------------------------|---|---|--|---|
| Tool Storage Area                              | Area                    | Mass-1        | 311                       | ND  | (0.13)  | ND   | (0.06)  |
| Background - Lab                               | Background              | Mass-2        | 303                       | ND  | ND  | ND   | (0.06)  |
| Background - Conference room                   | Background              | Mass-3        | 337                       | (0.90)  | 0.32  | ND   | (0.07)  |
| Personal sample of employee handling materials | Personal Breathing Zone | Mass-4        | 160                       | 11.87   | 2.37  | ND   | 2.37  |
| Area behind Reactor                            | Area                    | Mass-5        | 312                       | (1.22)  | 0.49  | ND   | 0.18  |
| Employee Activity Area                         | Area                    | Mass-6        | 316                       | (1.04)  | 0.50  | ND   | (0.07)  |
| Employee Activity Area                         | Area                    | Mass-7        | 314                       | (1.37)  | 0.52  | ND   | 0.11  |
| Employee Activity Area                         | Area                    | Mass-8        | 11                        | ND  | 6.21  | ND   | ND  |
| Reactor (Fe)                                   | Source                  | Mass-9        | 31                        | ND  | 2.78  | ND   | ND  |
| Reactor (Ni)                                   | Source                  | Mass-10       | 21                        | ND  | 3.25  | ND   | ND  |
| Reactor (Ni)                                   | Source                  | Mass-11       | 21                        | ND  | (2.53)  | ND   | ND  |
| Reactor (Fe)                                   | Source                  | Mass-12       | 21                        | 11.90   | 3.45  | 2.38   | 0.48  |
| Area behind Reactor (AgPa)                     | Area                    | Mass-13       | 18                        | ND  | (1.81)  | ND   | 5.14  |

Level of detection (LOD) – Iron 1  $\mu\text{g}/\text{sample}$ ; Nickel 0.07  $\mu\text{g}/\text{sample}$ ; Palladium 0.2  $\mu\text{g}/\text{sample}$ ; Silver 0.04  $\mu\text{g}/\text{sample}$

Level of quantitation (LOQ) – Iron 4.2  $\mu\text{g}/\text{sample}$ ; Nickel 0.25  $\mu\text{g}/\text{sample}$ ; Palladium 0.54  $\mu\text{g}/\text{sample}$ ; 0.13  $\mu\text{g}/\text{sample}$

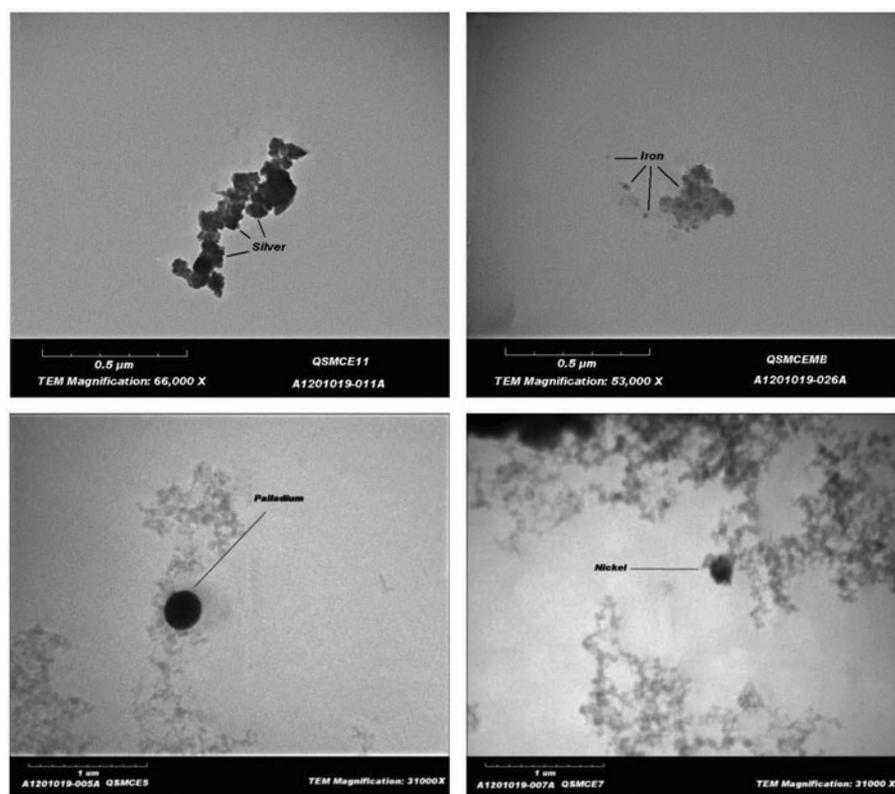
ND – Not detected

Results within parentheses are an estimated value between the LOD and LOQ.

Mass-7, Mass-12, and Mass-13. The silver concentrations ranged from 0.11–2.37  $\mu\text{g}/\text{m}^3$ . The highest concentration was obtained in the PBZ sample. Figure 3 shows a layout of the facility with sample locations.

Samples collected for TEM analysis during reactor cleanout were analyzed for structure size and count for the same metals. The results of this analysis are provided in Table 2. All samples were found to contain quantifiable traces of iron. The iron structure concentration ranged

from  $4.32 \times 10^5$  –  $8.45 \times 10^6$  structures per cubic meter ( $\text{s}/\text{m}^3$ ). Three of the samples (TEM-4, TEM-2, TEM-1) did not contain nickel. Among the nickel containing samples, concentrations ranged from  $1.44 \times 10^4$  –  $9.89 \times 10^5$   $\text{s}/\text{m}^3$ . Only four samples (TEM-5, TEM-3, TEM-9, TEM-13) were identified with palladium structures. The concentrations of these four samples ranged from  $1.36 \times 10^4$  –  $1.57 \times 10^5$   $\text{s}/\text{m}^3$ . Two samples (TEM-5, TEM-10) did not contain silver. The concentrations among samples



**Figure 3.** Electron micrographs of silver, iron, palladium, and nickel nanoparticles.

**Table 2.** Filter-based air samples: reactor cleanout structure concentration of metals.

| Location                                       | Sample Type             | Sample Number | Sample Duration (minutes) | Iron Concentration (s/m <sup>3</sup> ) | Nickel Concentration (s/m <sup>3</sup> ) | Palladium Concentration (s/m <sup>3</sup> ) | Silver Concentration (s/m <sup>3</sup> ) |
|--|-------------------------|---------------|---------------------------|--|--|---|--|
| Tool Storage Area                              | Area                    | TEM-5         | 311                       | $7.28 \times 10^5$                     | $1.44 \times 10^4$                       | $2.16 \times 10^4$                          | ND                                       |
| Background - Lab                               | Background              | TEM-7         | 303                       | $5.28 \times 10^5$                     | $2.16 \times 10^4$                       | ND  | $4.32 \times 10^4$                       |
| Background - Conference Room                   | Background              | TEM-4         | 337                       | $4.32 \times 10^5$                     | ND                                       | ND  | $6.17 \times 10^4$                       |
| Personal sample of employee handling materials | Personal Breathing Zone | TEM-6         | 137                       | $9.72 \times 10^5$                     | $4.01 \times 10^5$                       | ND  | $2.62 \times 10^5$                       |
| Area behind Reactor                            | Area                    | TEM-2         | 312                       | $5.09 \times 10^5$                     | ND                                       | ND  | $3.25 \times 10^4$                       |
| Employee Activity Area                         | Area                    | TEM-1         | 316                       | $4.5 \times 10^5$                      | ND                                       | ND  | $1.69 \times 10^5$                       |
| Employee Activity Area                         | Area                    | TEM-3         | 314                       | $9.8 \times 10^5$                      | $2.72 \times 10^4$                       | $1.36 \times 10^4$                          | $5.17 \times 10^5$                       |
| Employee Activity Area                         | Area                    | TEM-8         | 11                        | $1.49 \times 10^7$                     | $6.08 \times 10^5$                       | ND  | $1.22 \times 10^6$                       |
| Reactor (Fe)                                   | Source                  | TEM-9         | 31                        | $1.32 \times 10^6$                     | $2.84 \times 10^4$                       | $1.42 \times 10^4$                          | $2.12 \times 10^5$                       |
| Reactor (Ni)                                   | Source                  | TEM-10        | 31                        | $8.45 \times 10^6$                     | $9.89 \times 10^5$                       | ND  | ND                                       |
| Reactor (Ni)                                   | Source                  | TEM-11        | 21                        | $1.13 \times 10^6$                     | $1.26 \times 10^5$                       | ND  | $1.07 \times 10^5$                       |
| Reactor (Fe)                                   | Source                  | TEM-12        | 21                        | $1.31 \times 10^6$                     | $7.70 \times 10^4$                       | ND  | $1.03 \times 10^5$                       |
| Area behind Reactor (AgPa)                     | Area                    | TEM-13        | 19                        | $1.48 \times 10^6$                     | $1.57 \times 10^5$                       | $1.57 \times 10^5$                          | $1.92 \times 10^6$                       |

Reporting limit – 0 structures/mm<sup>2</sup>  
 ND – Not detected.

that did contain silver ranged from  $3.25 \times 10^4$  –  $1.92 \times 10^6$  s/m<sup>3</sup>. Only three samples (TEM-3, TEM-9, TEM-13) yielded quantifiable structure counts for all of the metal analytes. Electron micrographs are provided in Figure 3 to illustrate the size and shape of the particulates sampled.

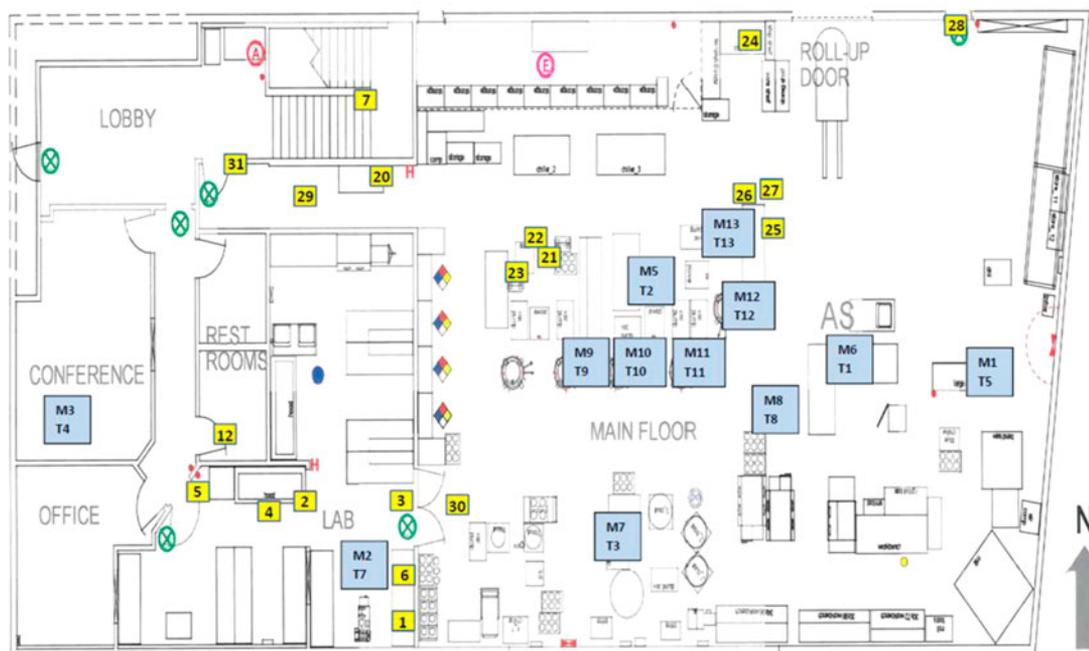
### Surface wipe sampling

A total of 27 wipe samples were collected from various surfaces throughout the facility. Some wipe samples yielded results for nickel and silver that exceeded the recommended surface level, as suggested by BNL

(Table 3). Two thirds all of the samples yielded results that exceed the suggested surface level for silver of 1 µg/100 cm<sup>2</sup>. Only one sample (Wipe-26) yielded nickel concentrations in excess of the suggested surface level of 100 µg/100 cm<sup>2</sup>. BNL does not provide suggested acceptable surface levels for iron and palladium. Figure 4 shows the plant layout with all the sampling locations.

### Real-time sampling

Data collected from each of the direct reading instruments were separated and categorized by date



- \*Samples in yellow boxes are wipe samples
- \*Samples indicated with 'M' were collected for elemental mass analysis
- \*Samples indicated with 'T' were collected for TEM analysis

**Figure 4.** Plant layout with sampling locations.

**Table 3.** Wipe samples mass concentration of metals ( $\mu\text{g}/100\text{ cm}^2$ ).

| Location Number | Date      | Sample Number | Iron    | Nickel | Palladium | Silver |
|-----------------|-----------|---------------|---------|--------|-----------|--------|
| 1               | 12/9/2011 | Wipe-1        | 110.00  | 7.60   | ND        | 2.40   |
| 2               | 12/9/2011 | Wipe-2        | 12.00   | 1.80   | (0.29)    | 3.10   |
| 3               | 12/9/2011 | Wipe-3        | 43.00   | 23.00  | 0.84      | 3.10   |
| 4               | 12/9/2011 | Wipe-4        | 90.00   | 6.00   | ND        | 1.90   |
| 5               | 12/9/2011 | Wipe-5        | 8.80    | 4.80   | ND        | 0.36   |
| 6               | 12/9/2011 | Wipe-6        | 13.00   | 3.10   | ND        | 0.26   |
| 7               | 12/9/2011 | Wipe-7        | 48.00   | 3.30   | (0.15)    | 1.30   |
| 8               | 12/9/2011 | Wipe-8        | 62.00   | 4.30   | ND        | 0.98   |
| 9               | 12/9/2011 | Wipe-9        | 12.00   | 1.20   | 0.45      | 2.00   |
| 10              | 12/9/2011 | Wipe-10       | 13.00   | 0.87   | ND        | 0.33   |
| 11              | 12/9/2011 | Wipe-11       | 22.00   | 0.88   | (0.16)    | 1.20   |
| 12              | 12/9/2011 | Wipe-12       | 9.30    | 7.10   | ND        | 0.27   |
| 14              | 12/9/2011 | Wipe-14       | ND      | ND     | ND        | ND     |
| 15              | 12/9/2011 | Wipe-15       | (1.20)  | ND     | ND        | ND     |
| 16              | 12/9/2011 | Wipe-16       | ND      | ND     | ND        | ND     |
| 20              | 12/9/2011 | Wipe-20       | 110.00  | 6.90   | 1.20      | 4.00   |
| 21              | 12/9/2011 | Wipe-21       | 320.00  | 28.00  | 2.10      | 21.00  |
| 22              | 12/9/2011 | Wipe-22       | 610.00  | 72.00  | 12.00     | 97.00  |
| 23              | 12/9/2011 | Wipe-23       | 120.00  | 8.10   | 2.80      | 5.50   |
| 24              | 12/9/2011 | Wipe-24       | 140.00  | 8.00   | 0.75      | 5.80   |
| 25              | 12/9/2011 | Wipe-25       | 370.00  | 46.00  | 1.40      | 31.00  |
| 26              | 12/9/2011 | Wipe-26       | 4500.00 | 400.00 | 5.80      | 190.00 |
| 27              | 12/9/2011 | Wipe-27       | 610.00  | 46.00  | (0.30)    | 23.00  |
| 28              | 12/9/2011 | Wipe-28       | 48.00   | 5.10   | ND        | 0.68   |
| 29              | 12/9/2011 | Wipe-29       | 450.00  | 55.00  | 0.93      | 17.00  |
| 30              | 12/9/2011 | Wipe-30       | 390.00  | 31.00  | ND        | 4.70   |
| 31              | 12/9/2011 | Wipe-31       | 82.00   | 16.00  | ND        | 1.50   |

Level of detection (LOD) – Iron 1.0  $\mu\text{g}/\text{sample}$ ; Nickel 0.2  $\mu\text{g}/\text{sample}$ ; Palladium 0.1  $\mu\text{g}/\text{sample}$ ; Silver 0.06  $\mu\text{g}/\text{sample}$

Level of quantitation (LOQ) – Iron 4.2  $\mu\text{g}/\text{sample}$ ; Nickel 0.73  $\mu\text{g}/\text{sample}$ ; 0.33  $\mu\text{g}/\text{sample}$ ; 0.18  $\mu\text{g}/\text{sample}$

ND – Not detected

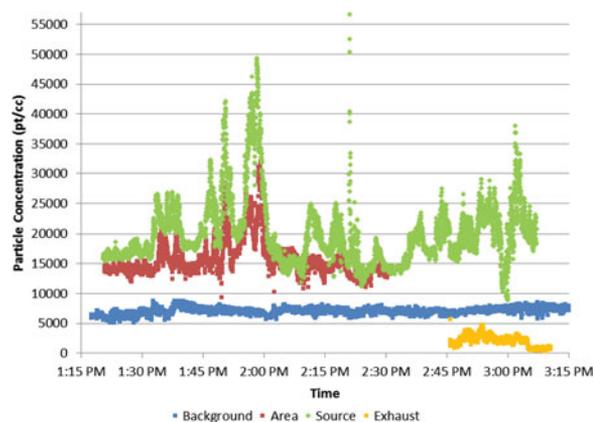
Results within parentheses are an estimated value between the LOD and LOQ.

and collection instrument. Data collected simultaneously during the same process were then plotted on a single chart, to allow for visual comparison of the average and peak emissions. The concentrations reported do not necessarily suggest the presence of a specific nanomaterial; instead simply reflect the overall number or mass concentration of particles within the dynamic size range of the instruments.

Particle number concentration data logged by the CPC in the size range of 10 nm – 1  $\mu\text{m}$  during reactor cleanout are provided in Figure 5. It should be noted that increases in the source sample are not accompanied by a similar increase in the background. However, the area sample, which was collected in the production room, did show a similar increase. The increase in the area sample was not as significant as the increase in the source sample, suggesting this increase was due to reactor cleanout. In fact, it appears that a concentration gradient is formed with respect to the reactor. As the distance from the reactor increased, particle number concentrations decreased.

**Airflow measurements**

Air velocity measurements were collected in three planes, A, B, and C’ to map airflow velocities in and around the



**Figure 5.** Airborne particle number concentrations for sizes ranging from 10 nm – 1  $\mu\text{m}$  during reactor cleanout using the CPC.

ventilated area (Figure 2). Air velocity was measured in feet per minute (fpm); area is shown in square feet ( $\text{ft}^2$ ), and flow is calculated in cubic feet per minute (cfm). The average air velocity across planes A, B, and C’ was 1440 fpm, 120 fpm, and 41 fpm, respectively. Two 8-point orthogonal Pitot traverses were collected to estimate airflow from the system. Measurements were collected at full flow which was used during reactor cleanout and at a reduced flow rate which was used during laboratory rolling operations. At full flow, the LEV unit flow was 255 cfm while at reduced flow, it was 131 cfm.

**Airflow visualization results—Hood capture and room pressurization**

Smoke was pulled into the hood fairly quickly as long as it was released within the perimeter of the reactor when the fume extractor LEV system was on. Smoke seemed to escape the control area when released at or outside of a 5-in perimeter around the reactor. However, the general trend of flow was into the hood. No changes were observed when conducting smoke observations with the ceiling fans “On” with respect to same releases with the ceiling fans “Off.” Smoke observations were also conducted with the ceiling fans “On” and the garage door opened. In this case, airflow into the hood seemed to be disrupted from drafts created by outside air entering the building through the garage door.

Room pressurization was evaluated by releasing smoke near doors and entryways between different sections of the facility. The production area was under negative pressure with respect to the office space. The laboratory area was under negative pressure when compared to the production area and the office space as the smoke was pulled into the laboratory space when released outside of the double-door that provides access from the production area.

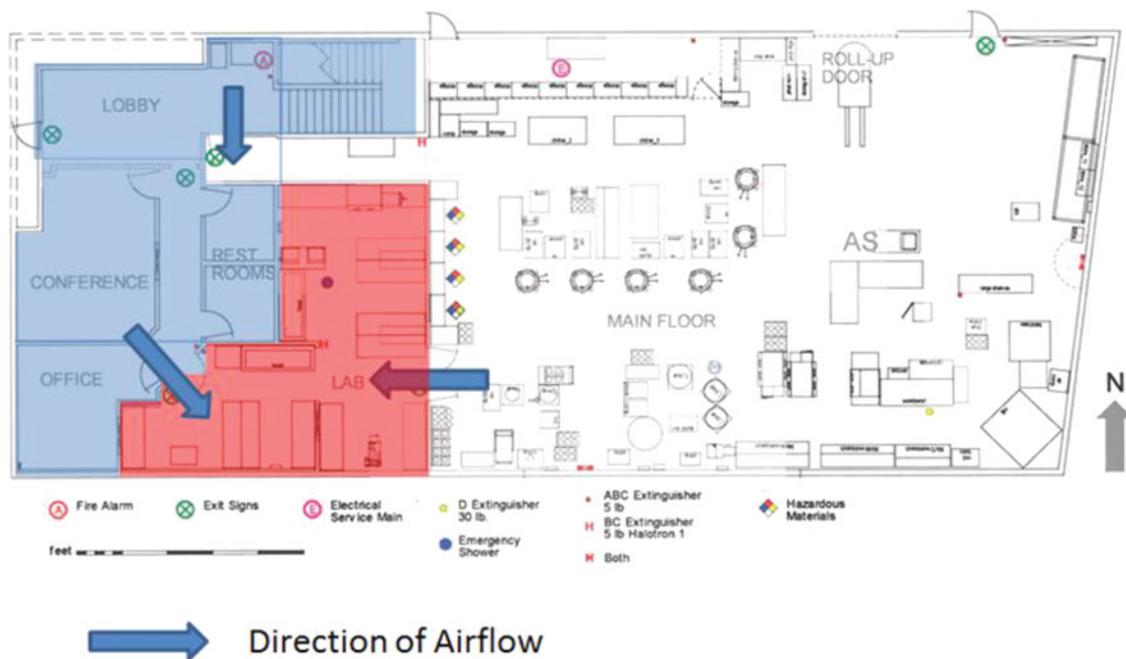


Figure 6. Airflow visualization of pressure schemes.

## Discussion

### Exposure assessment

Data collected during the 2009 investigation to evaluate the effectiveness of the flanged LEV suggested reductions in metal concentrations of approximately 92% during reactor cleanout. Concentrations measured during the December 2011 site investigation support the findings of previous visits and are much less than those measured in July 2009. Concentrations from the July 2009 investigation range from  $3 \mu\text{g}/\text{m}^3$  to greater than  $200 \mu\text{g}/\text{m}^3$ . The highest mass concentration measured during the December 2011 investigation for any metal was approximately  $12 \mu\text{g}/\text{m}^3$ .

Some of the highest concentrations of iron and silver were found on the PBZ sample. Only one location (Mobile 5) yielded a higher iron concentration and Mobile 6 location yielded a higher silver concentration than the field study conducted in 2009.<sup>[27]</sup> The employees' working area during cleanout contains some of the highest concentrations measured during this survey. The highest structure concentration of iron, as determined by TEM analysis, was found on the PBZ sample, again suggesting the presence of the ENM of interest in the breathing zone of the employee responsible for reactor cleanout. Very few sample locations yielded silver structure concentrations higher than that observed in the PBZ sample. Even when samples analyzed for mass concentrations of metals were non-detect (ND), the paired TEM samples tended to identify structures of the ENM of interest. Given the very low mass contribution of nanoparticles,

this finding reinforces the idea that assessment of mass concentrations alone is not an accurate indicator of the presence of ENM. Instead, TEM structure counts are able to identify the ENM of interest at concentrations that may not result in a detectable mass concentration.

The airborne mass concentrations for all metals were well below any reported (non-nanomaterial specific) occupational exposure limit (OEL). The limits provided are not specific to the oxides being produced, but rather to the metal of interest and these limits are not specific to nano-sized particles. Evidence suggests that in general some nanomaterials can be more toxic than their macro-scale counterparts, and therefore caution is warranted. It appears that the personal protective equipment utilized by the employee was appropriate for this type of operation. It should be noted that the use of respiratory protection should not be used as sole protection for any worker, but providing a fit-tested respirator will serve to further decrease the potential for exposure. Instead, it is recommended to control the dispersion of product at the source using local exhaust ventilation, ventilated containment, or fume hoods.

Data obtained from the direct reading instruments, most notably the CPC 3007, suggest that reactor cleanout increased the overall particle concentration in the immediate area. However, it does not appear that these concentrations affect areas outside of the production floor. As the distance between the reactor and the sample location increased, the observed particle number concentrations decreased, creating a concentration gradient with respect to the reactor.

## Surface contamination

Brookhaven National Laboratory (BNL) released a “Surface Wipe Sampling Procedure” to provide a standard methodology to collect representative surface samples.<sup>[34]</sup> This document outlines proper sample selection, collection, and analysis of wipe samples. The BNL document also provides suggested recommended levels of surface contamination, both for equipment release and housekeeping guidelines that are specific per element. As is implied, the equipment release level suggests an accepted level of surface contamination on equipment or surfaces being removed from the production area and housekeeping levels suggest surface contaminant concentrations accepted after cleaning. These BNL levels of contamination are only recommendations, except for beryllium, for which is a mandatory requirement by OSHA.<sup>[34]</sup>

Eighteen wipe samples resulted in silver concentrations greater than the recommended surface contamination level of  $1 \mu\text{g}/100\text{cm}^2$ , as prescribed by BNL. Only one wipe sample resulted in nickel concentrations in excess of the recommended surface contamination level ( $100 \mu\text{g}/100\text{cm}^2$ ). This surface contamination is most likely due to cleaning, as the reactor vessels are closed and sealed during production. There is also a possibility of dermal exposure to these nanomaterials, as they were present in nearly every work area. Work stations within the production area, as well as those far removed from the production area were found to have quantifiable levels of surface contamination. Materials present on the skin provide the potential for exposure via ingestion. In addition, employees may transport contaminants outside of the facility on skin or clothing, potentially contaminating vehicles and homes and providing the potential for secondary exposures.

The greatest surface concentrations for all metals were found in areas near the six reactor vessels (samples 21, 22, 23, 25, 26, and 27). Concentrations appear to taper off consistently as the distance from the reactors increases, creating a concentration gradient of surface metal contamination. It also appears that some surfaces are not included in the general housekeeping of the facility. For instance, a flat table surface (sample 23) yielded  $120 \mu\text{g}/100\text{cm}^2$  of iron. Within just a couple feet from where this sample was taken, samples were taken from the reactor control station and yielded iron concentrations on the mouse (sample 21) of  $320 \mu\text{g}/100 \text{cm}^2$  and keyboard (sample 27) of  $610 \mu\text{g}/100 \text{cm}^2$ . If this control station is included in the routine housekeeping of the facility, the increased concentrations may be due to material transport by the employees. The same concentration gradient is observed for nickel and silver. Due to lower overall palladium concentrations and limited use within

the facility, a concentration gradient was not as obvious. However, the highest concentration was observed on the step ladder near reactor 6 (samples 25, 26, and 27), which was the case for all of the metals.

To reduce surface contamination and, in turn, reduce the likelihood of undesired material flow outside of the facility, a comprehensive housekeeping program should be implemented. Such a program may include wet wiping methods or vacuuming using a HEPA filter. A quality housekeeping program should not include any means by which the material may become re-aerosolized such as pressurized air or some dry sweeping methods.

## Ventilation assessment

### Airflow measurements

Air sampling provided an indication of the effectiveness of the LEV system. Despite the good performance of the fume extraction LEV unit during reactor cleanout tasks, ENM's were detected on some area samples and wipe samples. The positive samples can be considered as an indication that the emissions are not completely controlled.

Ventilation measurements (exhaust air volume and face velocities) were taken at various locations of the LEV. Average face and capture velocities in planes A' and B' were adequate to provide control of any potential release. The ACGIH Industrial Ventilation manual Table 6-2 recommends 75-100 fpm for processes with little air motion.<sup>[33]</sup> Given the activity and thermal drafts in the production areas, higher capture velocities across the reactor face are warranted to provide good containment.

The capture velocity at the edge of the reactor (opposite from the location of the LEV) averaged 41 fpm across the measurement plane. Background air drafts in workplaces average approximately 60 fpm requiring exhaust airflows above this level for reasonable containment effectiveness.<sup>[35]</sup> In addition, the buoyant updraft from the hot air produced from a furnace or hot process can easily exceed the exhaust flow rate. This can cause air to leak out of gaps along the top of the containment vessel or out of the top part of a front or side opening. Exhaust airflow rates should be increased to address the buoyancy effects from the hot air and to maintain good capture velocities at the face of the enclosure. Cleanout activities that occurred well inside of the reactor perimeter (closer to the LEV) seemed to be well controlled by the fume extraction LEV unit. Some emissions on the edge of the reactor may not have been captured due to the low capture velocities measured on this area (plane C'). Performing cleanout operations with the garage door opened and ceiling fans “On” could also be a contributor

to fugitive emissions finding their way out of the LEV controlled area due to increased potential for cross drafts.

### Room pressurization schemes

Room pressurization was evaluated by releasing smoke near doors and entryways between different sections of the facility. The office space was under positive pressure when compared to the rest of the facility. The laboratory area was under negative pressure when compared to the production area and the office space. The laboratory area was equipped with two fume hoods that exhaust air through the rooftop. There was a fan designated to provide make-up air to the laboratory space, but facility representatives mentioned that it was not working at the time of the survey.

### Conclusions and recommendations

The portable fume extraction LEV system used at this facility contained emissions well and resulted in relatively low worker exposures. However, area and wipe samples indicate that some reactor emissions may be capable of escaping the fume extraction LEV unit. Capture velocities in the outer perimeter of the reactor opposite from the fume extraction LEV unit were low and may not be sufficient to capture all process emissions.

The following recommendations are provided to prevent worker exposure to ENM's and to provide a safer and healthier work environment.

- Work areas should be cleaned at the end of each work shift (at a minimum) using either a HEPA-filtered vacuum cleaner or wet wiping methods. Dry sweeping or air hoses should not be used to clean work areas. Cleanup should be conducted in a manner that prevents worker contact with waste material; the disposal of all waste should comply with all applicable federal, state, and local regulations.
- Hand-washing facilities should be provided and workers should be encouraged to use them before eating, smoking, or leaving the worksite.
- Exhaust flow rates on the LEV should be increased to maintain adequate capture across the reactor face (normally between 80–150 fpm). This may require a redesign of the LEV flange to ensure adequate capture velocities at each location on the perimeter of the reactor. In addition, exhaust airflow rates should be increased to overcome background air drafts on plane C' and strong thermal updrafts from the heated reactor.
- Use makeup air in the laboratory space to reduce drafts, maintain exhaust system performance, and develop and implement a pressurization scheme. The lack of replacement air may cause uncontrolled

drafts, degradation of exhaust system performance, and problems with the opening/closing of doors in the facility.

- Ensure that ventilation systems maintain the ENM production area under negative pressure relative to the rest of the plant. This will prevent air contaminants in the production area from spreading to the rest of the plant. Ensure that air from this room is not recirculated to other areas of the facility and is exhausted directly to the outdoors in accordance with any environmental regulations. Production areas should not share ventilation systems with office areas.
- Ensure that exhaust air discharge stacks are located away from air intakes, doors and windows. According to ASHRAE, outdoor air intakes shall be located at least 25 ft from potential sources of air contaminants such as exhaust outlets of ventilating systems.<sup>[36]</sup> A properly designed exhaust stack can help prevent re-entry of contaminated air into the building.
- Install and use tacky mats to reduce dust in areas and prevent tracking of materials from production areas to non-production areas.

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