In-Depth Survey Report

# Assessment of Engineering Controls for Reducing Contaminant Emissions from Producing Carbon Nanotubes


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**Site Surveyed: Nanomaterial manufacturing facility, eastern United States**

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# Abstract

This report summarizes the survey results from a joint study conducted by the National Institute for Occupational Safety and Health (NIOSH) Engineering and Physical Hazards Branch (EPHB), Purdue University, and the University of Massachusetts Lowell. The study site produced carbon nanotubes (CNTs) using the chemical vapor deposition (CVD) process. Four major processes/tasks were evaluated during the site visit, including: 1) product harvesting; 2) product sieving or sizing; 3) product milling, and; 4) material handling. After the completion of the CVD process inside a furnace, the product is harvested in a custom-built glove box to prevent nanomaterial emissions during product harvest. Following product harvesting, sieving was done by a shaker inside an unventilated, enclosed cabinet to grade the product. If required, the product was also milled using a small ball mill in a separate room. The emission from these processes and the performance of control measures on mitigating exposures during the conduct of these tasks were evaluated using directing-reading instruments and collecting air filter samples for transmission electron microscope (TEM) inspection.

Three fume hoods were available for the handling of precursor and product materials, but only one of them was used to handle and transfer nanomaterials. The survey results showed that the fume hood effectively controlled the release of nanoparticles. The glove box also effectively controlled particle release from the unloading of the production furnace during CNT harvesting. Air samples showed evidence of very low levels of airborne CNTs around the product furnace. No release of nanoparticles was detected during the ball milling process using direct-reading instrumentation, while the TEM analysis of air filters collected in the ball mill room showed the presence of CNTs in the room air at very low levels. During the sieving process, particle emissions were detected by the direct-reading instruments and area air filter samples when the worker opened the cabinet following completion of the process. Increasing the waiting time before opening the cabinet did not help reduce particle emissions. Overall, few airborne CNTs were identified in area air samples at the furnace location, near the sieving operation and in the ball mill room.

Based on the findings in this study, recommendations can be made to control containment of emissions from the sieving process. The addition of local exhaust ventilation (LEV) on the sieving cabinet would help reduce the potential for release of product into the work environment when unloading the sieve. This improvement could also lower the risk of transporting

contaminants to other working areas. Besides, the total exhaust flow for each of the three laboratory fume hoods should be increased to provide a minimum average face velocity of 100 feet per minute (fpm). This may require the upgrading of the exhaust fan and reconfiguration of the exhaust ducting from the hoods.

# Introduction

This in-depth survey was conducted at a CNTs manufacturing facility on September 17-18, 2013 by National Institute for Occupational Safety and Health (NIOSH) in collaboration with researchers from Purdue University and the University of Massachusetts Lowell. The survey results were summarized in this report to identify better engineering controls using to reduce workers' exposure to nanomaterials in the workplace, and to provide recommendations for improving control measures.

## Background

Around the world, the introduction of nanotechnology promises great societal benefits across many economic sectors: energy, healthcare, industry, communications, agriculture, consumer products, and others [Sellers et al. 2009]. Over 1600 consumer products containing engineered nanomaterials were publicly available in 2013 [The Project on Emerging Nanotechnologies 2013]. The financial resources put into the development and production of nanomaterials, however, has far outpaced funding to assess health and safety issues. The lack of a good understanding of hazards of nanomaterials has raised concerns over potential unintended human health and environmental risks during manufacturing use of nanomaterials. The Engineering and Physical Hazards Branch (EPHB) of the Division of Applied Research and Technology (DART) in NIOSH is conducting field surveys to study the effectiveness of engineering controls in reducing occupational exposure to engineered nanomaterials. Each of these studies has been documented to create a more general awareness of the need for or availability of effective control measures for the nanotechnology industry.

## Potential Health Effects

Asbestos fibers have been classified by the International Agency for Research on Cancer as carcinogenic for humans. The similarities between asbestos and high aspect ratio nanoparticles (HARN) were reported by the Institute of Occupational Medicine [Tran et al. 2008]. This suggests that HARN (e.g., CNTs) could have similar characteristics as pathogenic fibers. Single-walled CNTs (SWCNTs) were found to be more toxic than asbestos in a few studies [Inoue et al. 2008; Jia et al. 2005; Murr et al. 2005; Tian et al. 2006]. From animal in vivo exposure studies and cell-culture-based in vitro experiments, CNTs have been shown to contribute to fibrotic lung response, inflammation, and granulomas, and can induce oxidative stress and cellular toxicity. In addition, CNT toxicity may be affected by their purification process [Carrero-Sánchez et al. 2006; Muller et al. 2005; Wick et al. 2007], surface area and surface chemistry [Tian et al. 2006], and structure [Kostarelos 2008; Poland et al. 2008]. Several CNT summary risk assessment reports of risk are available [Kobayashi et al. 2009; Nanoceo 2011; SWA 2009].

## Occupational Exposure Limits (OELs)

OELs are useful in reducing work-related health risks. They provide a quantitative guideline and basis to assess the worker exposure potential and the performance of engineering controls and other risk management approaches. Currently, no regulatory standards for nanomaterials have been established in the United States. However, NIOSH has published a current intelligence bulletin (CIB) regarding occupational exposures to carbon nanotubes and nanofibers. In this document, NIOSH proposes a recommended exposure limit (REL) of 1 μg/$m^3$ elemental carbon as a respirable mass 8-hour time-weighted average (TWA) concentration [NIOSH 2013].

In the absence of governmental or consensus guidance on exposure limits, some manufacturers have developed suggested OELs for their products. For example, Bayer has established an OEL of 0.05 mg/$m^3$ for Baytubes® (multiwalled CNTs) [Bayer MaterialScience 2010]. For Nanocyl CNTs, the no-effect concentration in air was estimated to be 2.5 μg/$m^3$ for an 8-hr/day exposure [Nanocyl 2009].

# Plant and Process Description

Figure 1 shows the schematic diagram of the study site. The facility produced CNTs using a chemical vapor deposition (CVD) furnace and harvested the products inside a glove box that allowed for the collection of products within ventilated containment. Following production, materials could be purified in one of the laboratory fume hoods, size classified using the sieve/shaker, or processed further using a ball mill. Three laboratory fume hoods were available for tasks such as CNT treatment, weighing, transfer, or other laboratory activities. A sieve/shaker system was located inside an unventilated, enclosed cabinet (i.e., a refrigerator without freezing function) to prevent particle emissions. Milling of products using a small ball mill was conducted in a separate room without general or local exhaust ventilation.

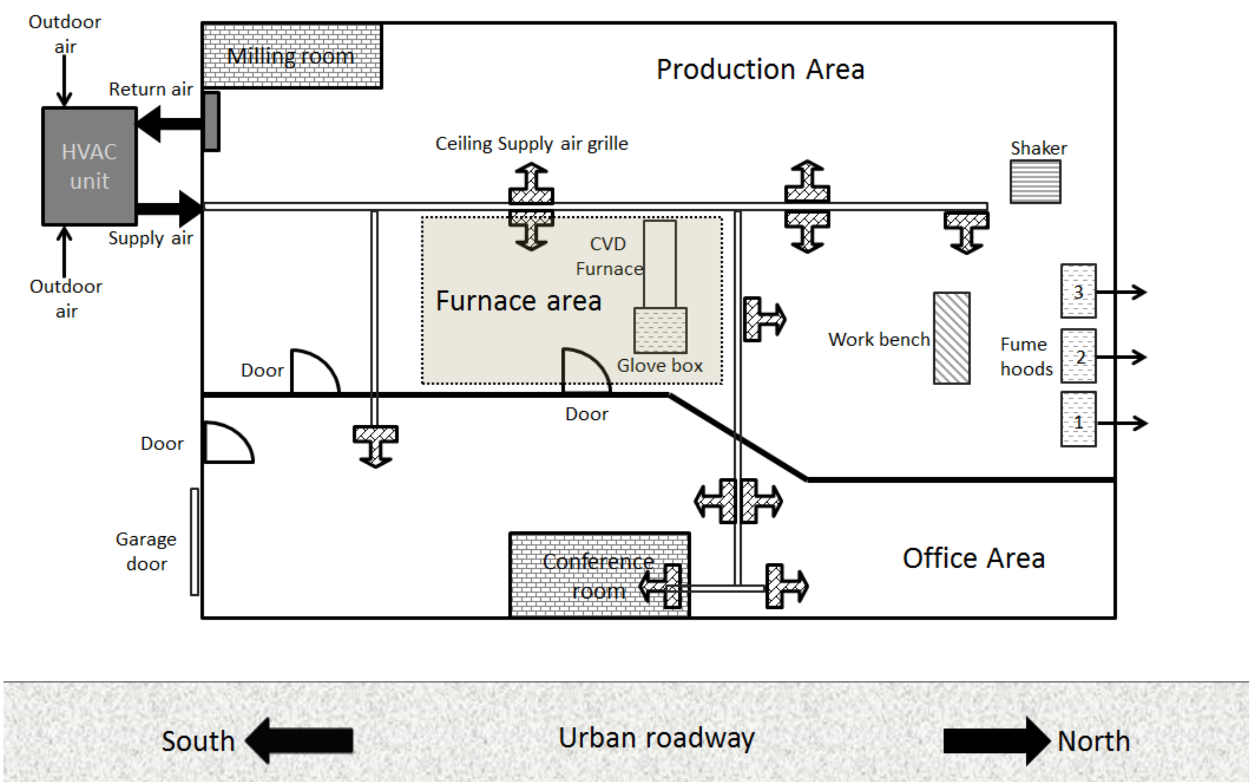



Figure 1. Plant layout showing ventilation distribution details and location of operations and fume hoods.

## Facility General Ventilation System

There was one heating, ventilating, and air-conditioning (HVAC) unit servicing the production and office areas within the facility around 5,000 square feet ($ft^2$) (Figure 1). Outside air was filtered and mixed with recirculated air and tempered to maintain the temperature set point controlled at a thermostat located inside the production area. The outdoor air intake was 35 inches (in, width) x 24 in (height) and was integral with the HVAC unit. A damper valve adjusted the amount of outside air introduced into the facility. All supply registers were located approximately 10 ft above the floor of each room. The main return air grille (29 in wide by 30 in high) was located at the south end of the facility and was ducted directly into the central HVAC unit located just outside the building.

## Manufacturing Processes

The company is a manufacturer of carbon nanotubes and nanomaterials. CVD furnaces were used to produce nanomaterials. The nanomaterials were harvested inside ventilated glove boxes enclosing the unloading ports of the furnaces. To prepare nanomaterials for postprocessing, a laboratory fume hood (i.e., Hood 3 in Figure 1) was used to contain particle emissions during the transfer of nanomaterials to wire mesh sieves or ball milling jars. The sizing or sieving process was performed inside an unventilated sealed cabinet. The milling process was operated in a room without any general or local ventilation.

### CNT Production

The facility produced CNTs in multiple furnaces in an open area marked as furnace area in Figure 1. The company set up their production furnaces on workbenches. As shown in Figure 2, there were no control devices used at the loading port of furnace, because of all required chemicals and catalysts were delivered to the product chamber directly. However, a custom-built glove box was connected to the furnace to allow for the unloading of products materials while preventing nanomaterial emissions during harvesting. A stainless steel rod was used to unload the nanomaterials out of the furnace chamber. The glove box was ventilated by an exhaust fan (Model TA 450S A30390-10, Nidec Co.) with a HEPA filter (8 x 8 x 6 in, Magna 1000 Series, Glasfloss Industries). The filtered air was released into the general working araes.

When the production process was complete and the furnace was turned off for cool down, the product was ready for harvesting. This harvesting process took place in a custom-built glove box attached to the outlet of the furnace. The total time of product harvest only took nearly 11 minutes, starting opening the unloading port to unload the product tray, closing the furnace, transferring the product to a container, cleaning work surface, and removing the product container and trash out of the glove box through the access door in the glove box.

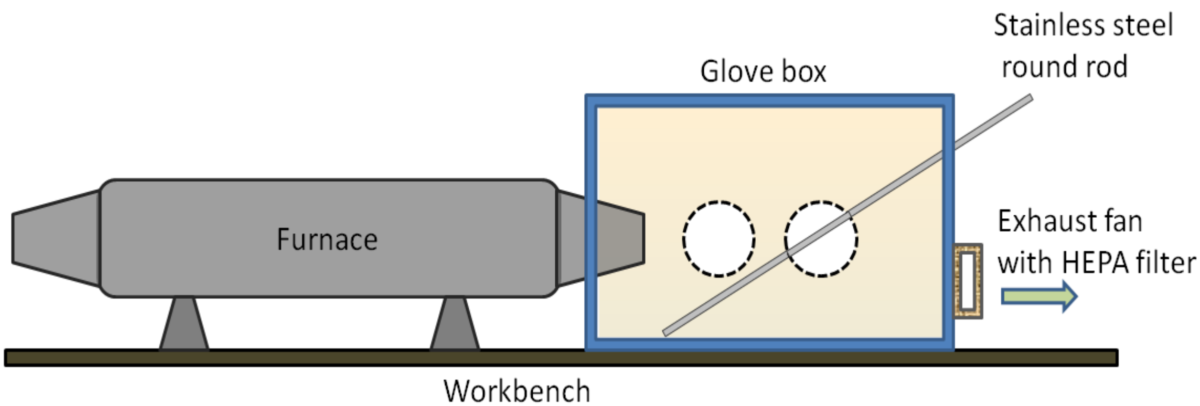



Figure 2. CNT production system. A ventilated glove box was installed at the unloading port of the furnace for product harvest.

### Dry powder Transfer

There were three laboratory fume hoods in place and operating along the North end of the facility (Figure 1). Nanomaterial handling and transfer tasks were only conducted inside Hood 3. Hood 1 was a constant flow, laboratory fume hood (BMC Manufacturing Inc., Muskegon, NJ) with an opening of 39 in (width) by 32 in (height). The sash was opened 19 in at the design height (operating height) and 32 in at the fully open position. Hood 2 was a Supreme Air bypass laboratory fume hood (Kewaunee Scientific Co., Statesville, NC) with an opening measuring 40 in (width) by 30 in (height). The bypass hood differs from a constant flow hood in that it is designed to maintain a constant face velocity independent of sash position while the constant flow hood face velocity increases at decreasing sash height. Hood 3 was also a Kewaunee Supreme Air bypass hood with an opening measuring 64 in (width) by 27 in (height). Hoods 1 and 2 were exhausted through a common main exhaust duct. Inspection of the ductwork indicated that hood 1 was added after the installation of hood 2 and ducted to the existing ductwork feeding into the main duct at a 90 degree entry angle. Hood 3 was exhausted through its own exhaust system. No dedicated makeup air system was utilized to balance the volume of air exhausted through the laboratory fume hoods so the facility operated at negative pressure with respect to the outdoors and adjacent areas.

The constant-flow hood (BMC hood) constitutes the oldest, simplest chemical hood design. The exhaust fan introduces a constant volumetric airflow moving through the sash opening. For this hood design, the face velocity is lowest when the sash is wide open; when the sash is lowered the face velocity increases. The bypass hood (Kewaunee hoods) maintains a constant hood face velocity and incorporates a bypass grille located above the sash opening. When the sash is wide open it blocks the bypass grille, allowing all of the air to flow through the hood opening. As the sash is lowered, it uncovers increasingly greater amounts of the bypass grille, allowing increasing amounts of air to flow through this alternative path. If it is designed and operated properly, the amount of air flowing through the bypass grille is just sufficient to maintain a constant face velocity. Typically, however, this constant velocity can be maintained only over a certain part of the sash’s total range.

A crucial performance element for any laboratory fume hood is the face velocity, defined as the average air velocity at the face of the hood at the sash opening. Maintaining a constant, minimum face velocity provides confidence that operations (and hazardous agents) within the hood will be contained. The current consensus of the literature is that the average face velocity for a laboratory chemical hood should be in the range of 80–120 fpm [Burgess et al. 2004]. In addition to the face velocity, it is important that the airflow be distributed evenly across the hood face. ACGIH recommends that variations of face velocity should be no more than ±10% from point to point across the hood face [ACGIH 2013]. When variations exceed this value, fume hood baffles should be adjusted to improve distribution.

### Sieving

For sizing of products, CNT product materials were sieved with standard wire meshes by a shaker table located inside an unventilated sealed cabinet (Figure 3). A metal lid was put on top of the sieve tray stack to reduce particle emissions during shaking. The cabinet (a refrigerator without freezing function in this case) uses a magnetic seal to keep the door closed during sieving operation. Following the completion of the cycle, the worker waited for a specified time period (usually 5 minutes) before opening the cabinet door to remove the wire meshes and product.

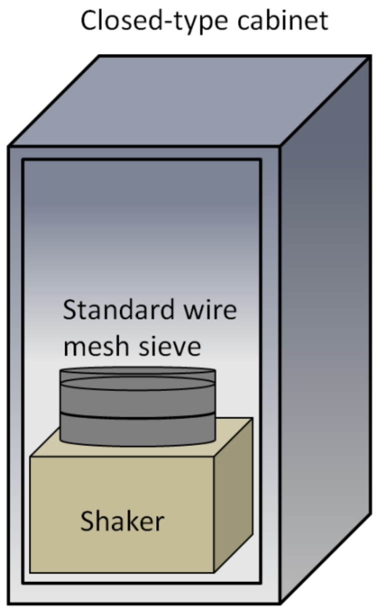



Figure 3. Sieving process. The process was done by shaking standard wire mesh sieves inside a closed cabinet without any local ventilation.

### Milling

Ball mills are common industrial equipment which utilizes balls constructed of grinding media like stainless steel or ceramic to grind products to produce finer, more uniform sized materials. To produce desired CNT particle size, the company used a ball mill to grind nanomaterials in a closed jar (Figure 4). Loading and unloading nanomaterials into and from milling jars were performed inside Hood 3. The milling process was conducted over an extended time (often overnight) as required to produce the uniform size distributions. The milling room (Figure 1) did not have any general ventilation (HVAC) or LEV to capture or dilute nanomaterials that may leak into the facility environment.

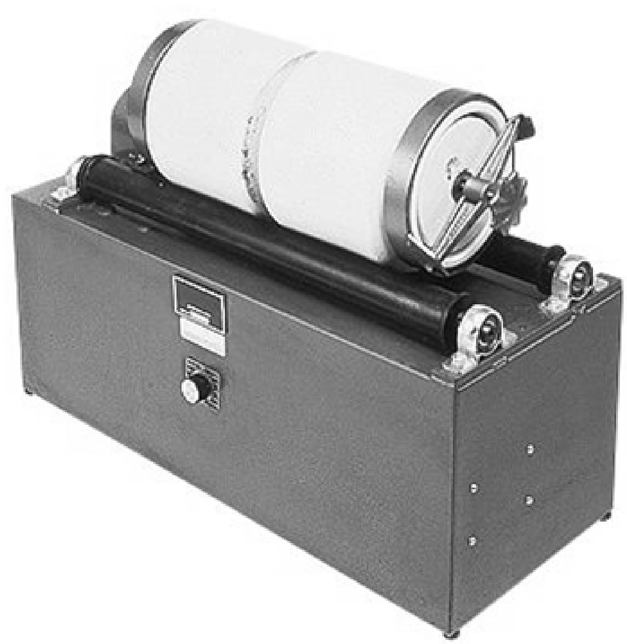


Figure 4. A high-capacity laboratory jar on a roller. The study site used similar equipment to grind nanomaterials (photo source: http://www.coleparmer.com/buy/product/52775-one-tier-jar-high-capacity-laboratory-jar-mill-24-roller-115-vac-60-hz.html).

## Methodology

The manufacturing processes and control measures were evaluated by monitoring activities with direct-reading instruments and through area air filter samples for off-line laboratory analysis. The sampling was collected at worker’s breathing zone, source, and background to characterize airborne nanomaterials released from process tasks/activities.

Besides aerosol monitoring, ventilation measurement was also conducted to evaluate the general ventilation system and engineering controls including the glove box and fume hoods. A Velocicalc™ multi-function ventilation meter (model 964, TSI, Inc., Shoreview, MN) was used to measure face velocities across the return air grille, the outside air intake grille, and the open faces of the laboratory fume hoods. Total HVAC system airflow was approximated by multiplying these average face velocities with the open area of the associated grilles.

## Direct-Reading Aerosol Measurement

Portable direct-reading instruments used in this site study included, Optical Particle Sizer (OPS), SidePak Personal Aerosol Monitor, and DustTrak Aerosol Monitor (all made by TSI Inc., Shoreview, MN). Each instrument provided real time measurements to help identify particle emissions from activities or tasks.

The OPS can detect particles ranging from 0.3 to 10 µm at a sampling flowrate of 1.0 lpm in up to 16 user-adjustable size channels. It also can estimate mass concentration if refractive index and particle density are input by the user. The SidePak aerosol monitor provides total mass concentration covering particle sizes from 0.1 to 10 µm at a sampling flowrate of 1.7 lpm. Due to its compact size and light weight, the SidePak is an ideal tool for measuring personal particulate exposures. The DustTrak measures airborne particles from 0.1 to 15 µm at sample flowrate of 3.0 lpm. It can simultaneously measure size-segregated mass fraction concentrations corresponding to PM1, PM2.5, Respirable, PM10 and Total PM size fractions.

## Filter Sampling

Area air samples were collected on 25- or 37-mm-diameter, open-face mixed cellulose ester (MCE) filters for characterizing airborne particles in the facility and from the evaluated processes. The filter size does not have any effect on analysis results. The filters were sampled at nominal 4 liters per minute (l/min) with personal air sampling pumps (GilAir Plus, Sensidyne LP, St. Petersburg, FL). The sampling pumps were calibrated at the beginning of study days and checked at the end of each day.

The collected samples were analyzed for CNTs by transmission electron microscopy (TEM, Model JEM-2100F, JEOL Ltd., Peabody, MA) according to a modified NIOSH Method 7402 [NIOSH 1994]. These modifications consist mostly of eliminating all steps related to the identification of asbestos. TEM provides an indication of the relative abundance of nanostructures per air volume, as well as other characteristics such as size, shape, and degree of agglomeration. Three copper TEM grids (3 mm) from each sample were examined at low magnification to determine loading and preparation quality. Multiple grid openings from each TEM grid were examined for identifying nanomaterials.

## Study Design

Two identical instrument sets were used to simultaneously identify particle emissions from the sources and worker's breathing zone (WBZ) during different processes. Sampling probes from instruments were usually located near the worker's head to measure the WBZ concentration, but the locations of monitoring emissions sources needed to be changed based on the tasks. For example, the worker performed the tasks around the furnace and the glove box during product harvest. To evaluate the efficiency of the glove box during product harvest, two other SidePak monitors were also placed inside and outside the glove box.

The sieving process was identified as a high potential contaminant source to release nanomaterials after discussing with the company. Longer waiting time to remove the wire mesh sieves from the cabinet was expected to lower particle emissions. Therefore, regular waiting time (5 minutes) and longer waiting time (10 minutes) were tested twice in two days.

Since it was a long process of the CNT synthesis by CVD furnaces, the sample filter was located near the product furnace collected over 5 hours. For other processes, the sample filters were collected during the tasks performed by the workers. The filter samples for the sieving process were collected on Day 2 only, due to limited MCE filters available on Day 1.

# Results

## Measurements of Room Ventilation and Fume Hood Flows

The air velocity measured at 15 points on an equal area grid across the face of the HVAC return air grille averaged 286 fpm with standard deviation of 22 fpm. This corresponds with an average return air flow of 1725 cubic feet per minute (cfm). The air velocity measured at 6 equal area grids across the face of the outdoor air intake grille averaged 79 fpm with standard deviation of 21 fpm. This corresponds with an average outside air intake flow of 460 cfm. An inspection of the outdoor air damper, which controls the amount of outdoor air introduced into the facility, showed that it was closed and the low amount of outdoor airflow measured was due to leakage around the damper. In this mode, the ventilation system was nearly 100% recirculating indoor air.

Face velocity measurements of lab fume hoods were taken on an equal area grid pattern across the face of the hood made with the hoods operating at their design height sash position and at the fully open. Table 1 summarizes the results of average face velocity and calculated overall hood exhaust flow of each fume hood. A six-point traverse was conducted across the face of the glovebox exhaust filter and averaged across the face area (0.45 $ft^2$) to yield a total exhaust flow of 22 cfm.

Table 1. Ventilation measurement data of fumes hoods at different sash heights.

| | | Hood 1 | Hood 2 | Hood 3 |
|---|---|---|---|---|
| | Hood type | Constant flow hood | Bypass hood | Bypass hood |
| Sash fully open | Open area, in (grid points for measurement) | 39 × 32 (15) | 40 × 30 (15) | 64 × 27 (12) |
| | Average face velocity, fpm (standard deviation) | 30 (11) | 75 (10) | 68 (12) |
| | Calculated exhaust flow rate, cfm | 260 | 625 | 816 |
| Sash at design height | Open area, in (grid points for measurement) | 39 × 19 (10) | 40 × 17.5 (10) | 64 × 19 (8) |
| | Average face velocity, fpm (standard deviation) | 56 (19) | 108 (14) | 85 (8) |
| | Calculated exhaust flow rate, cfm | 288 | 525 | 718 |

The results of the laboratory hood evaluation show that the overall exhaust flow and face velocity of Hood 1 is insufficient to maintain good containment. The average face velocity with the sash at design height (56 fpm) was well below the recommended operating range of 80–120 fpm. This result may be due to the fact that the hood was likely added to the system without upgrading the exhaust blower. It is also not optimal for the exhaust duct to enter the main duct at a 90 degree angle. The ACGIH ventilation design manual recommends that branches should enter a main duct expansion “at the center of the transition at an angle not to exceed 45 degrees with 30 degrees preferred in most cases” [ACGIH 2013]. This reduces energy losses due to turbulence at these junctions (and improves airflow). In addition, point to point variation in face velocities across the hood face was much greater than 10%. Hood 3 was only slightly above the recommended face velocity range at an average velocity of 85 fpm. There was high spatial variability across all hood faces in the fully open sash position.

## Process Evaluation/Exposure Assessment

Overall, no particle releases were detected during handling/transfer of nanomaterials inside the fume hood based on either the real-time monitoring or TEM air filter analyses. Detectable CNT emissions were found based on TEM air filter samples during other tasks conducted outside the hoods, including product harvesting from the furnace, sieving, and ball milling.

### Product Harvest

All data obtained from real-time monitoring during product harvest showed relatively stable concentrations with low variability. As summarized in Table 2, the concentrations both at the source and the worker breathing zone (WBZ) were similar and near the facility background level. In general, the concentrations found at the WBZ were lower than those at the source, except the results shown on SidePak monitors.

During product harvest, two other SidePak monitors were placed inside and outside the glove box to evaluate the efficiency of this control measure (Figure 5). While the average concentration inside the glove box reached 0.0225 mg/m$^3$, the average concentration outside the glove box was 0.0072 mg/m$^3$, similar to the level found at the source (0.0070 mg/m$^3$, Table 2).

Table 2. Average aerosol concentrations from direct reading instruments during product harvest.

| Measuring location | DustTrak [average in mg/m$^3$] | OPS [average in #/cm$^3$] | SidePak [average in mg/m$^3$] |
|---|---|---|---|
| Source | 0.0046 | 5.07 | 0.0070 |
| WBZ | 0.0043 | 4.70 | 0.0085 |

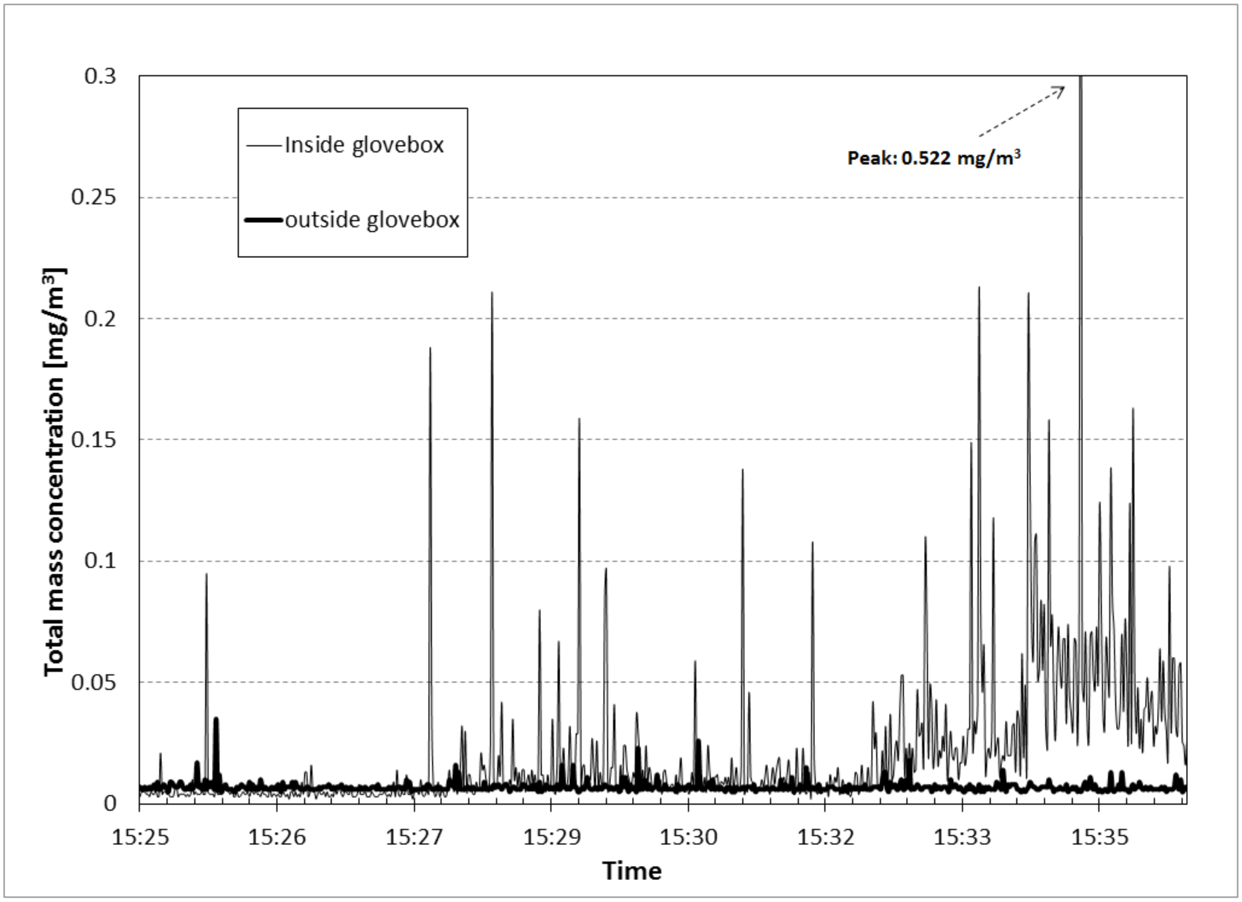



Figure 5. Monitoring data from two SidePaks located inside and outside the glove box during product harvest.

The filter sample collected for area sampling during product harvest (15:25 – 15:36) did not show any CNTs, but CNT structures were identified on the filter located near the product furnace during CNT synthesis (Figure 6). These structures were described by the laboratory as matrix; where CNTs make up a small portion of a structure. The longest dimension and two other dimensions of each structure were measured and averaged to give a rough crosswise dimension or diameter. The TEM results showed that the CNT synthesis process released CNT structures around 5−10 µm, and the CNT counts on the filter were 5 CNTs/$mm^2$ (Table 4).

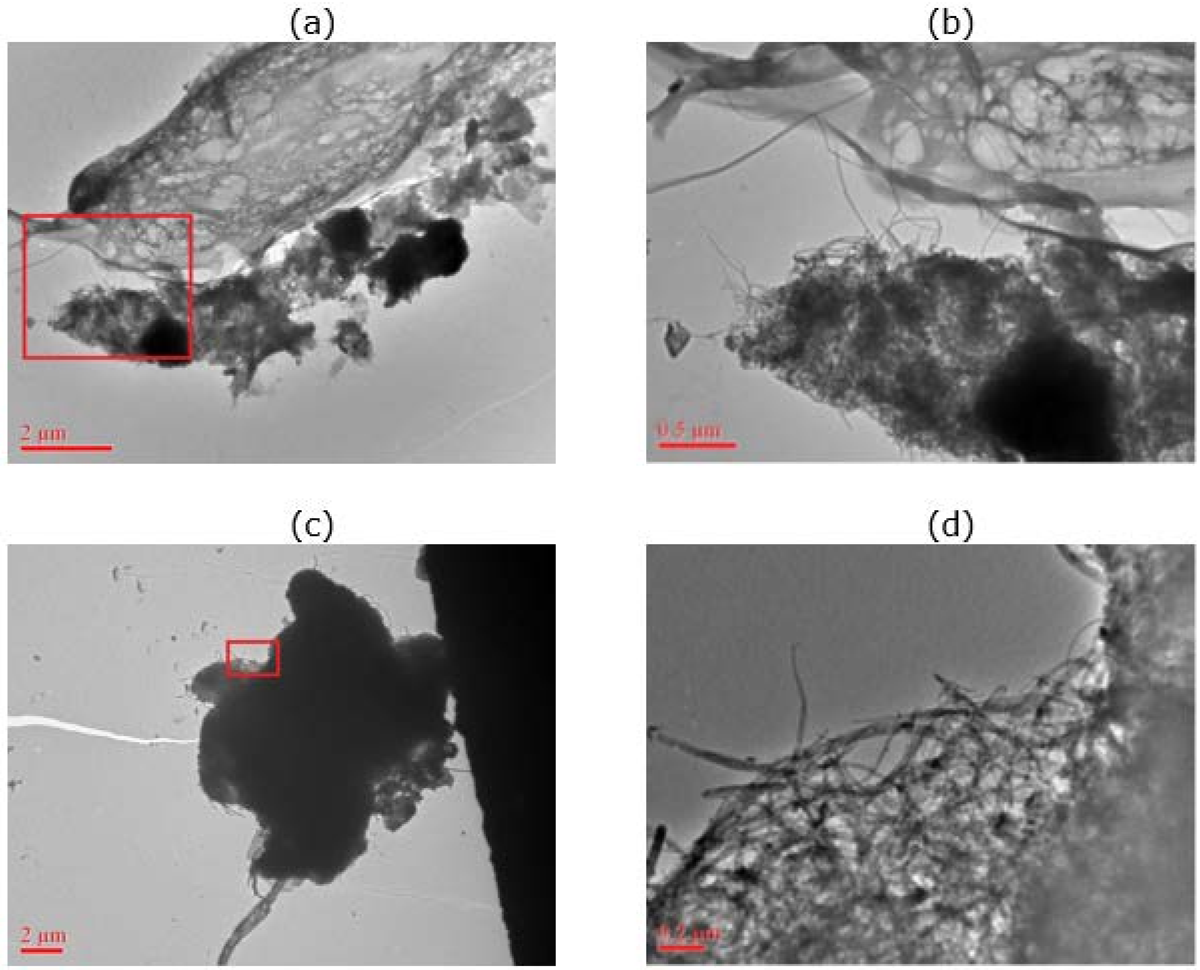


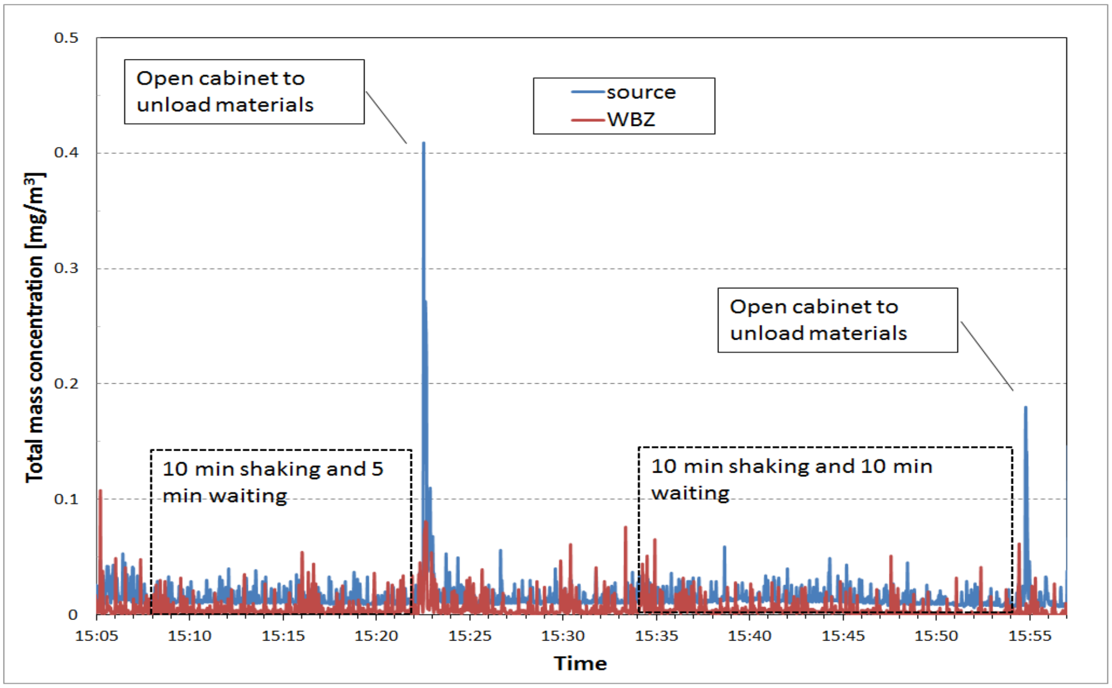

Figure 6. TEM images from the filter sample collected near the production furnace: (a) CNT matrix, (b) closer view of Figure 6-a, (c) another CNT matrix, and (d) closer view of Figure 6-c.

## Sieving

Following the completion of sieving, the operator waited for 5 and 10 minutes to evaluate the effect of allowing the process to settle prior to opening the sealed cabinet. For these trials, the sieving operation was conducted for 10 minutes. For the real-time monitors, the sampling inlets were located on top of the cabinet to capture any particles released from the cabinet. The DustTrak and OPS clearly identified particle emissions when the worker opened the cabinet door to retrieve mesh sieves after 5 and 10 minute waiting times (Figure 7 and Figure 8).

The highest instantaneous particle emissions measured during the opening of the cabinet were approximately 0.4 $mg/m^3$ by DustTrak (Figure 7a) and 260 $\#/cm^3$ by OPS (Figure 7b); the corresponding worker exposures were also increased during this task. Table 3 summarizes the average mass and number concentrations measured by DustTrak and OPS. The data show that particle releases were found at the source as well as in the WBZ. It was also found that increasing the wait time from 5 to 10 minutes had no strong effect on reducing particle emissions. The failure of increased wait time to reduce particle emissions could be due to the lack of LEV installed within the cabinet to remove airborne particles.

(a)




(b)

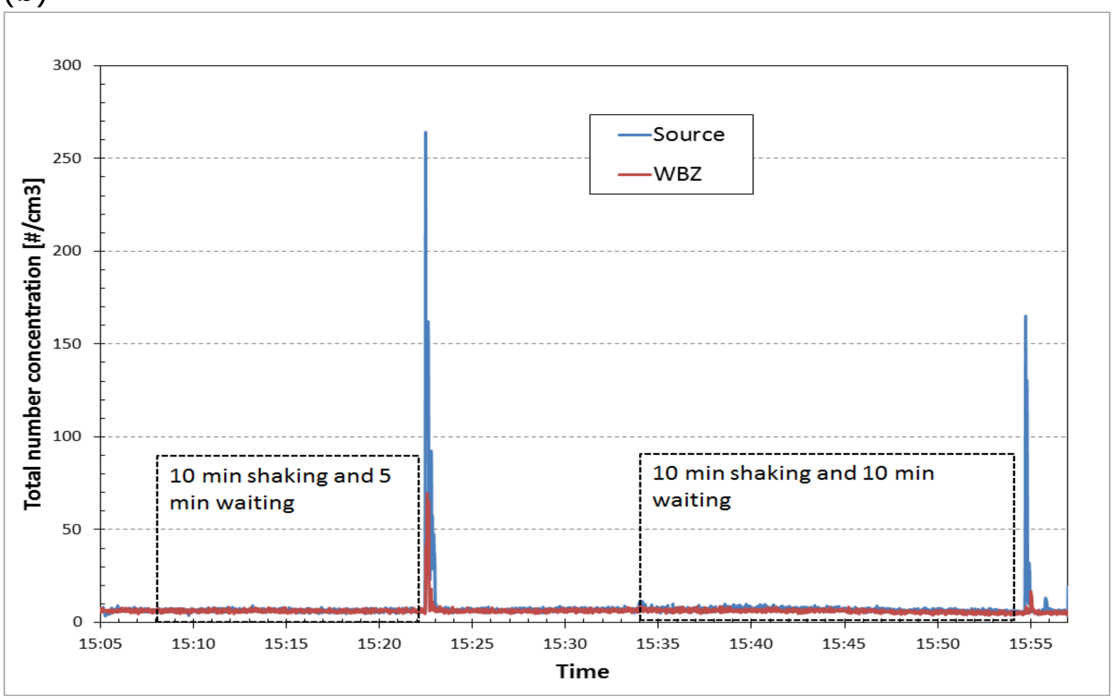
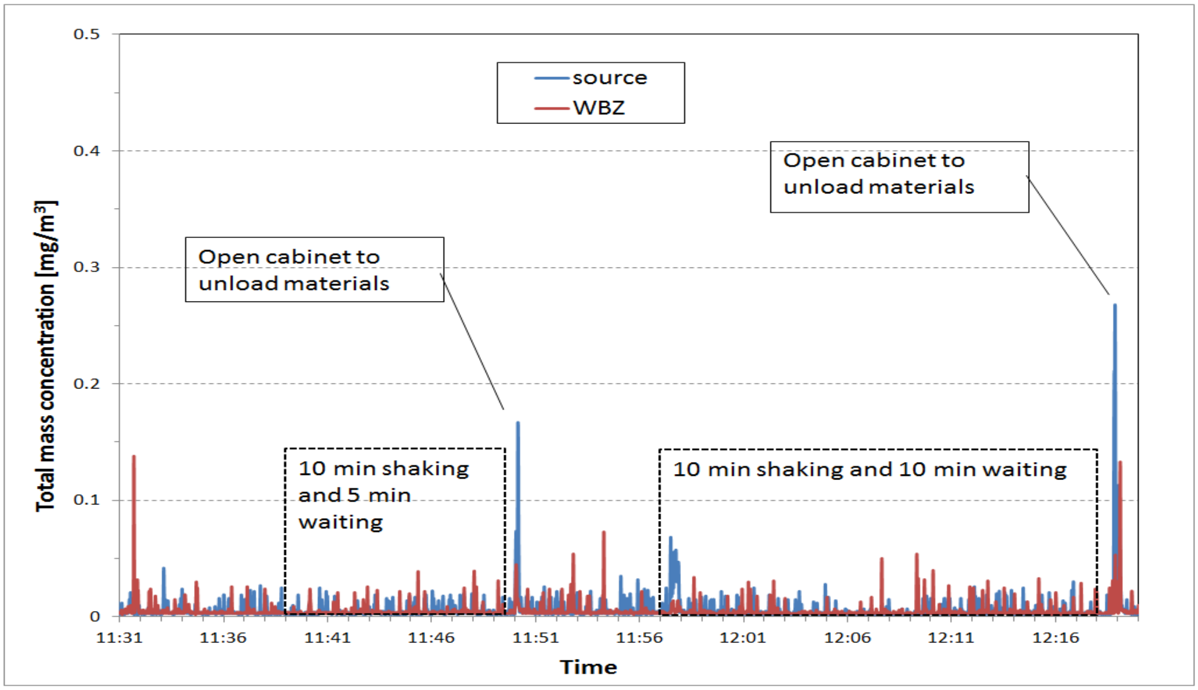



Figure 7. Monitoring data for the sieve shaking process on Day 1: (a) DustTrak data and (b) OPS data.

(a)




(b)

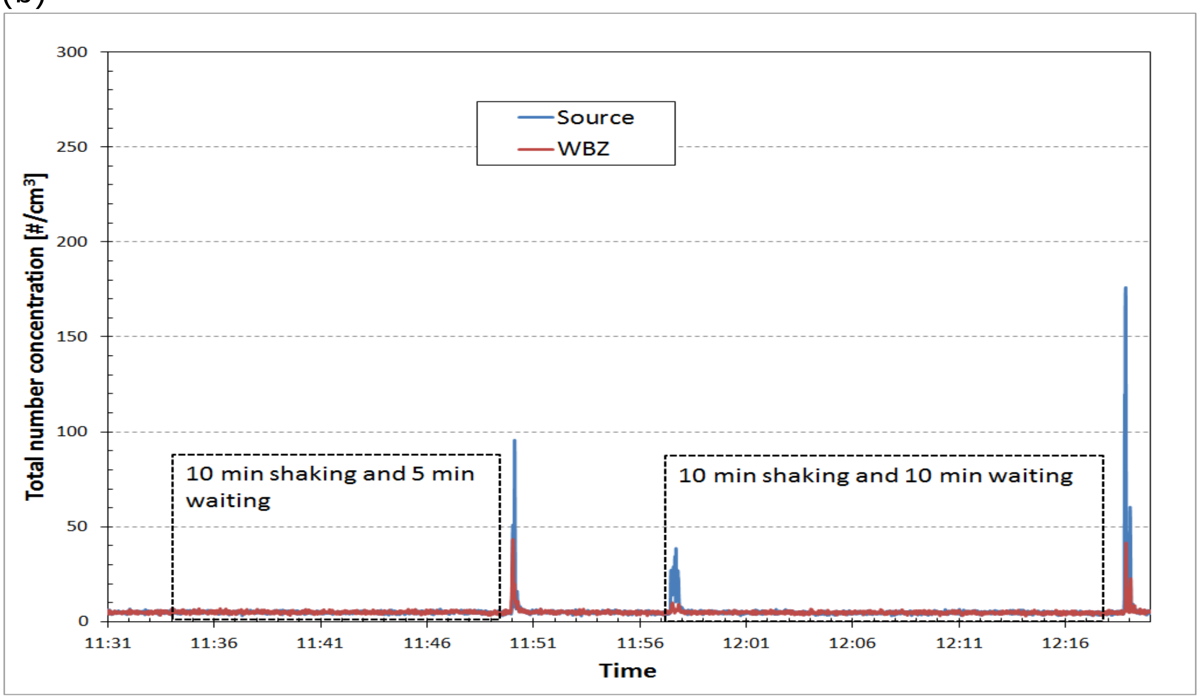



Figure 8. Monitoring data for the sieve shaking process on Day 2: (a) DustTrak data and (b) OPS data.

Table 3. Summary data of evaluating the closed-type cabinet and waiting times for reducing particle emissions from the sieve shaking process.

| Waiting time | Tool | Location | Testing on Day 1 | | Testing on Day 2 | |
|---|---|---|---|---|---|---|
| | | | During process | Opening Cabinet after process | During process | Opening Cabinet after process |
| 5 min | DustTrak [mg/m$^3$] | Source | 0.013 | 0.089 | 0.005 | 0.030 |
| | | WBZ | 0.005 | 0.028 | 0.005 | 0.011 |
| | OPS [#/cm$^3$] | Source | 6.5 | 55.8 | 5.0 | 16.9 |
| | | WBZ | 6.3 | 17.3 | 5.1 | 13.0 |
| 10 min | DustTrak [mg/m$^3$] | Source | 0.013 | 0.069 | 0.005 | 0.067 |
| | | WBZ | 0.004 | 0.007 | 0.005 | 0.021 |
| | OPS [#/cm$^3$] | Source | 6.9 | 55.0 | 5.1 | 35.4 |
| | | WBZ | 6.1 | 7.7 | 4.9 | 10.2 |

The TEM analysis results showed that both CNT matrix (Figure 9a) and CNT cluster (Figure 9b) were on the filter sampled on top of the cabinet on Day 2. The CNT cluster is the structure comprised primarily or exclusively of CNTs. In this case, the diameters of the CNT structures ranged from 2 µm to greater than 10 µm. The CNT counts on the 25-mm filter were 35 CNT/mm$^2$ (Table 4).

(a) (b)

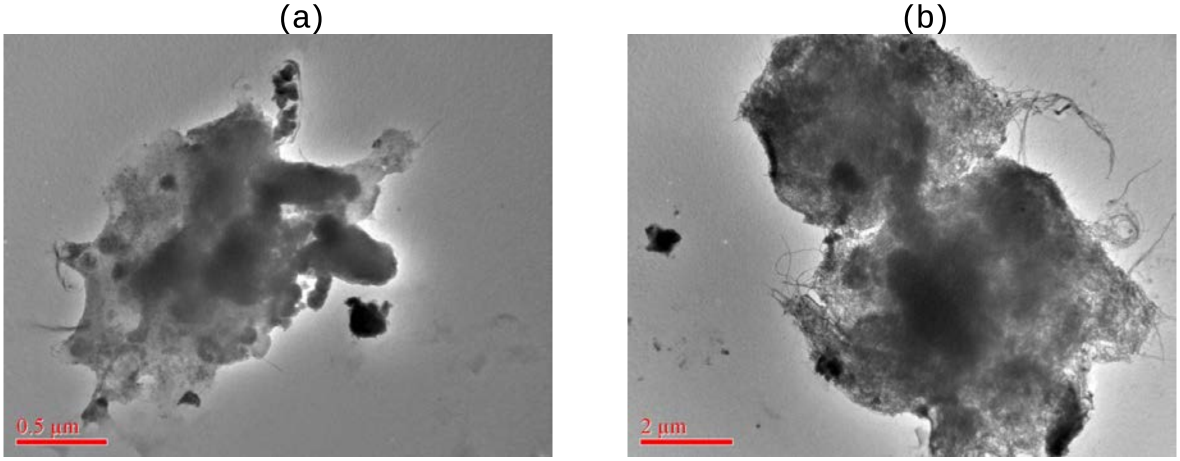



Figure 9. TEM images from the filter sample collected at top of the cabinet for the sieve shaking process: (a) CNT matrix, and (b) CNT cluster.

### Ball Milling

For the ball milling process, airborne particle concentrations monitored by direct reading instruments were stable and kept at low concentration level. However, CNT matrices were found on the filter sample by TEM analysis (Figure 10), and the CNT counts on the 37-mm filter were 8 CNT/mm$^2$. The estimated CNT concentrations in this study site were summarized in Table 4 for comparison.

(a) (b)

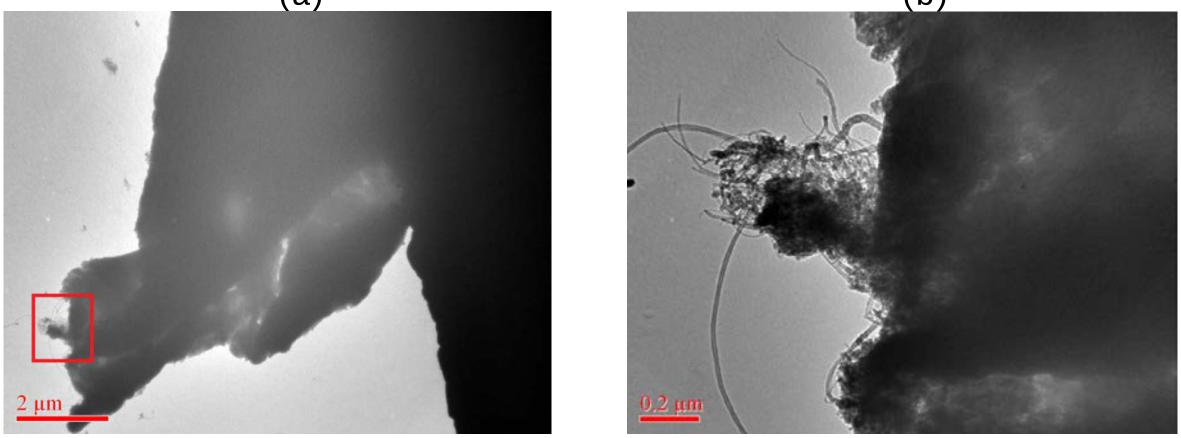



Figure 10. TEM images from the filter sample collected in the ball milling room: (a) CNT matrix, and (b) closer view of Figure 10-a.

Table 4. Summary of estimated CNT concentrations from TEM analysis.

| Sampling location | Sampling time | Identified CNT |
|---|---|---|
| | min | #/mm$^2$ |
| Production Furnace | 348 | 5 |
| Closed-type cabinet for sieve shaking | 48 | 35 |
| Ball milling room | 149 | 8 |

# Conclusions and Recommendations

## Laboratory Fume Hood

Research performed at the University of Massachusetts Lowell has demonstrated that nanomaterial powders may be released back into the work area from chemical fume hoods during tasks such as weighing or transferring from container to container [Tsai et al. 2009]. Releases that are not detectable on a mass basis were found to have a very high particle number concentration. Experiments performed on constant flow and bypass hoods demonstrated that working with the sash either too low or too high could cause nanoparticles to escape from the hood. When the sash is too high, the face velocity can fall below the recommended minimum of 80 fpm. This low face velocity and the large opening created by the high sash allow random room air currents to enter the hood, entrain airborne nanomaterials, and can carry them out of the hood. When the sash is too low, the face velocity can exceed the recommended maximum of 120 fpm. This causes a strong turbulent wake in the space between the worker and the hood face, which can pull airborne nanomaterials from the hood. Because of the possibility of loss of the nanomaterial at high face velocities, the correct sash height should be determined for the specific process being carried out, based on the ability of the chemical hood to capture the nanomaterial. Because of the potential to create turbulence, the hood should be as uncluttered as possible, and the researcher should remove his arms or other objects from the hood very slowly [Tsai et al. 2009].

Fume hood operating and work practice recommendations are detailed in the NIOSH document, General Safe Practices for Working with Engineered Nanomaterials in Research Laboratories [NIOSH 2012]. The following factors relative to the hood location are very important for proper hood performance:

- Air currents outside a hood may disrupt the airflow at the face and therefore impact the ability of a hood to contain the contaminant.
- The hood should not be located next to any laboratory entry door or any other high-traffic location.
- The hood should be at least 5 feet from any HVAC air supply grille; a distance of 10 feet is preferred.

The following practices are important for working in laboratory chemical hoods:

- The hood sash should be kept wide open during equipment set-up only; during actual use, the sash should be lowered to the position that gives proper hood face velocity (design height).
- Equipment should be at least 6 inches behind the sash opening (many hoods have a recessed floor starting at this distance, to encourage proper use).
- When working in the hood, the user should avoid working at the edge of the hood and should minimize arm movements; all such movements should be slow and smooth.
- Traffic past the hood should be minimized when nanomaterial powders are being manipulated. Research has shown that the passage of a person past the hood face at walking speeds creates a turbulent wake sufficient to pull contaminants from the hood [Johnson and Fletcher 1996].
- During experiments, when no access is required, the sash should be kept in the same position as when work is performed (for constant flow and bypass hoods).
- When using a local exhaust system, do not directly exhaust into the work environment any effluent (air) that is reasonably suspected to contain nanomaterials. The exhaust air should be passed through a HEPA filter and, when feasible, released outside the facility [NIOSH 2007]. If the exhausted air is recirculated, then steps should be taken to ensure that recirculated air doesn't contain the engineered nanoparticle.
- Handle exhaust filters from the chemical hoods in a manner that minimizes exposure. Put a plastic-lined bag around the filter at the source when removing it so that particulates are not potentially released to the work environment. Wear appropriate personal protection equipment (including respirators, gloves, and coverall work clothing) during all maintenance and cleaning activities.
- Storage of materials in the chemical hood should be minimized or eliminated. Materials stored in the hood can adversely affect the containment by disrupting airflow. If items must be placed inside the hood, make sure they are placed near the back and do not block the air slots.

## Process Evaluation / Exposure Assessment

The real-time monitoring and off-line TEM analysis have shown that the sieving process released nanomaterials into the workplace when the worker opened the cabinet door to retrieve wire mesh sieves. However, the cabinet contained nanomaterials well during the process. An exhaust fan could be installed to keep the cabinet under negative pressure and remove generated airborne contaminants.

For the production furnaces, the design and use of the ventilated glove box were shown to prevent particle emissions from product harvest. No significant emissions of airborne particles were detected by direct-reading instruments in the milling process and around the fume hood for nanomaterial handling. The sieving process performed in the cabinet was the emission source identified by direct-reading instrument and filter samples. However, the presence of CNTs was found on the filter sample collected near the production furnace and in the ball milling room that had neither LEV nor general ventilation. It indicated that the contaminants released from the sieving process could be transported by workers or production equipment to other working areas.

## Specific Exposure Control Recommendations

To lower the potential of contaminant transportation, the control measures and the facility general ventilation can be improved by:

1. Increasing exhaust flows for laboratory fume hoods 1 and 3. Both hoods should be adjusted to an average face velocity of approximately 100 fpm.
2. Re-configuring the exhaust ductwork for hoods 1 and 2 to improve the duct entry between hood 1 and the main exhaust duct and investigate increasing exhaust fan flows.
3. Installing exhaust ventilation on the sieving cabinet to reduce the potential for release of airborne nanomaterials into the facility environment.
4. Using a ventilated enclosure around the ball mill during standard operations. This unit could also be placed in a laboratory fume hood during these tasks to effectively contain emissions.
5. Increasing outside airflow on existing HVAC system or add makeup air system to account for exhaust from laboratory fume hoods and reduce uncontrolled infiltration. Indoor air quality problems could occur when the outside air dampers are close or not open enough to provide adequate amounts of outside air. The American Society of Heating, Refrigerating, and Air Conditioning Engineers (ASHRAE) recommends that a ventilation system should deliver at least 15 cfm of outside air per occupant [ASHRAE 2001]. More detailed outdoor air requirements for ventilation in industrial facilities can be found in Table 2 of this standard.

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