In-Depth Survey Report

CASE STUDY: Modifying Processes to Control Exposure to Engineered Nanographene Particles

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Abstract

This report summarizes the results of reducing exposure by adopting process changes at a nanomanufacturing site producing graphene platelets. Although the length and width of these platelets are on the order of micrometers, the platelet thickness is under 100 nanometers (nm). Aerosol instruments—including an aerosol photometer, a fast mobility particle sizer, and an aerodynamic particle sizer—were used to measure concentrations during routine product refining and post-processing operations. In some cases, worker activities were recorded on video concurrently with the concentration measurements. The purpose of these measurements was to understand the relationship between concentration and worker activity. Surface temperature measurements were made for two reasons: (1) temperature affects ventilation system performance and (2) surface temperatures in excess of 44°C pose a risk of a contact burn.

During product refining, dust exposures occurred during removal of collection containers from the processing equipment for product harvesting and during transfer of powder from the collection containers to storage containers in a ventilated booth. The emissions from product harvesting can be avoided by allowing the process to rest longer (at least 15−30 minutes in this case). This process change can effectively mitigate dust emissions up to 97.5% (reducing dust concentrations from 2.4 to 0.06 mg/m^3 after a 30−minute delay). During routine operations, the collection equipment surface temperatures can exceed 70°C. A 20−minute cooling time would allow surface temperatures on the sidewall of the collection containers to fall below 44°C and thus reduce the risk of a contact burn during product harvesting.

The ventilated booth, operated at a face velocity of 120 feet per minute (fpm), generally contained the aerosol generated during the transfer process, but dust exposures were elevated from about 0.03 to as much as 0.13 milligrams per cubic meter (mg/m^3) when the worker poured the remaining powder into the storage container. This slight exposure peak could be caused by the fall of the powder or by the obstruction of the booth's inlet. Air from this booth is discharged back into the workplace, and this was probably a source of dust emissions. The efficiency rating of the booth's filters was Minimum Efficiency Reporting Value (MERV) 11, too low to efficiently collect the dust generated by handling the product.

Manual cleaning of process equipment and material handling inevitably cause dust exposures. High particle concentrations generated from process tank maintenance can be largely reduced with process ventilation. The case

study has shown that ventilation exhaust can result in 83% reduction of dust. In the post-processing treatments, cleaning the fiberglass plugs caused concentration spikes of nearly 2 mg/m^3, as compared to a background concentration of 0.05 mg/m^3. At times, the workers would break up clumps of powder in the product collection containers, causing concentration spikes of 1–7 mg/m^3. Good work practices are required to prevent dust emissions, but a down-flow ventilated booth is recommended to minimize exposure and contain particulate emission during the post-treatment process.

Introduction

The Control Technology Team, Engineering and Physical Hazards Branch (EPHB), Division of Applied Research and Technology (DART), conducted an in-depth site survey at this facility in September 2010. A survey report [NIOSH 2011] was prepared by the team to summarize the survey results and provide recommendations for engineering controls to prevent contaminant emissions from the manufacturing processes of nanographene platelets (NGPs). In addition to engineering controls, some process changes were also proposed to the company to mitigate particle release in the workplace.

During prior studies at this facility, noticeable particle emissions occurred during product harvesting from refining and post-treatment processes. On the basis of the test results, a process change or substitution (in this case, product harvesting at lower temperatures) seemed more feasible than adding engineering controls for lowering particle emissions. This assessment parallels the Hierarchy of Controls in process/product design (Figure 1).

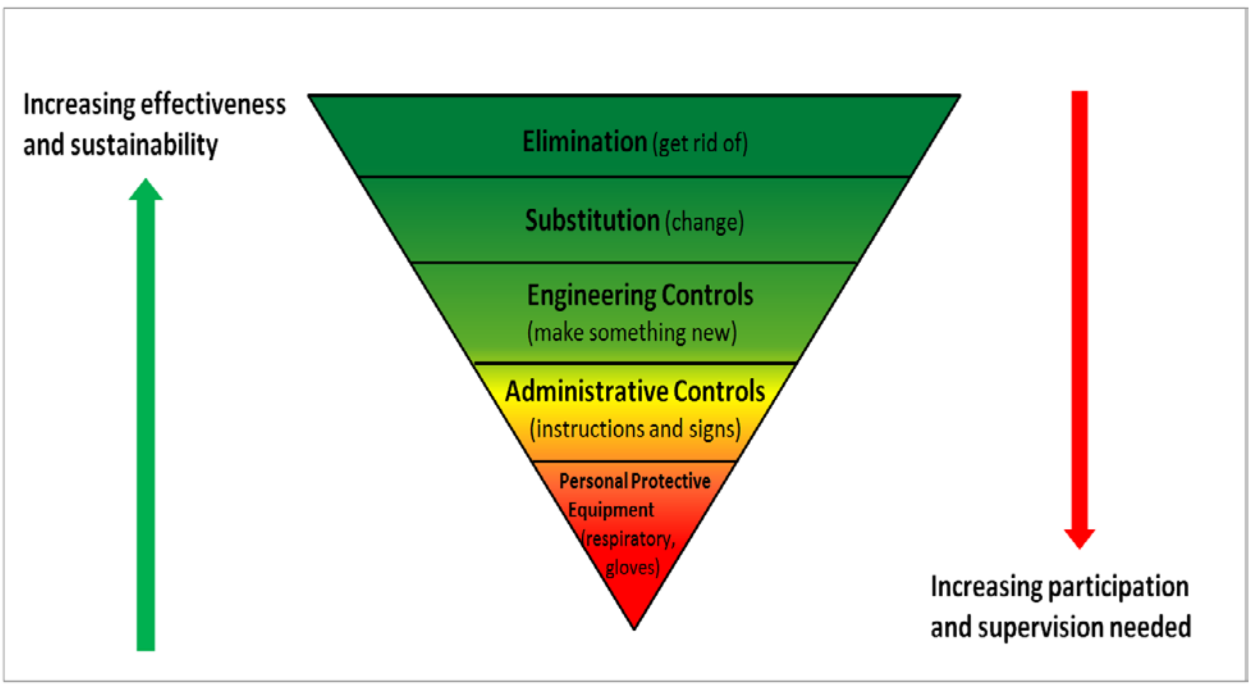

Figure 1. Hierarchy of Controls.

In September 2011, a case study was proposed by the team to evaluate the effects of process changes on particle emissions. In September and November 2011 and February 2012, multiple visits were made to collect test data. This report summarizes the test results to discuss the effects of process changes and engineering controls on contaminant reduction in the nanomanufacturing workplace.

Review of Previous Survey Results

The layout of the two main production areas at this facility is depicted in Figure 2. The refining area is separated from other areas with flexible curtains, but the post-treatment area is an open space.

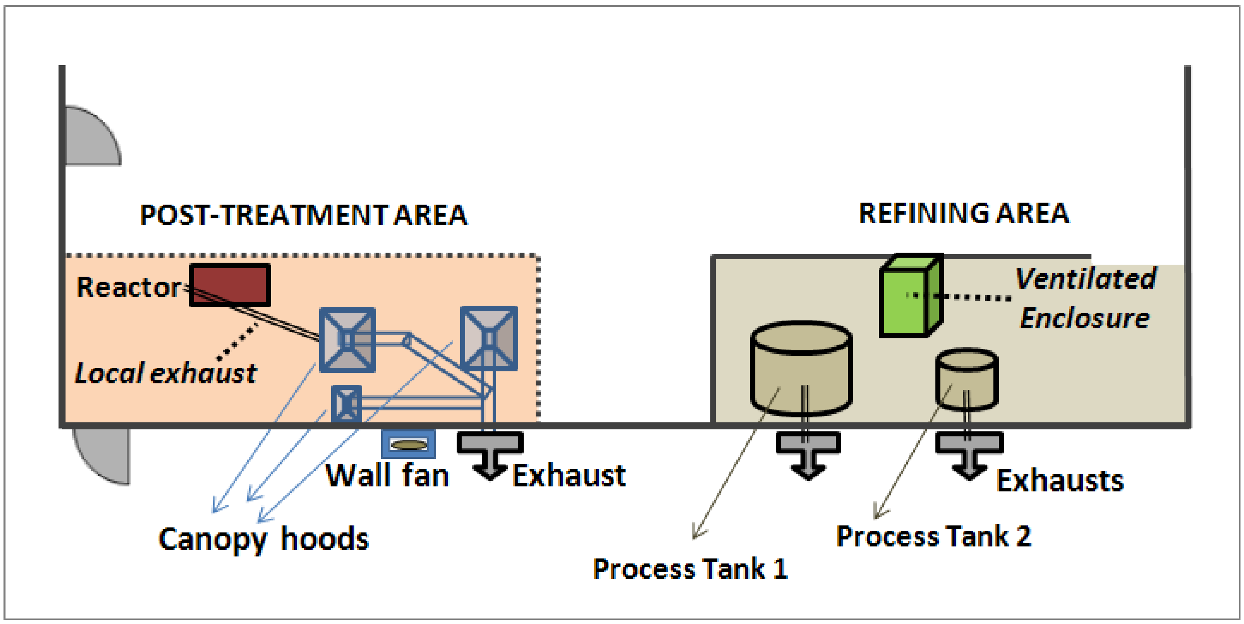

Figure 2. Layout of the production areas at the study site.

The refining system consists of a main process tank and two discharging devices for collecting products. For Process Tank 1 (Figure 3), a blower located between dischargers was used to transport products from the process tank to the dischargers. The final products were deposited in the containers. Product harvesting was performed by a worker manually unlocking the containers and transporting them to the ventilated enclosure (Figure 2) for weighing and packaging. Figure 4 describes Process Tank 2, a smaller refining system that is used for some products.

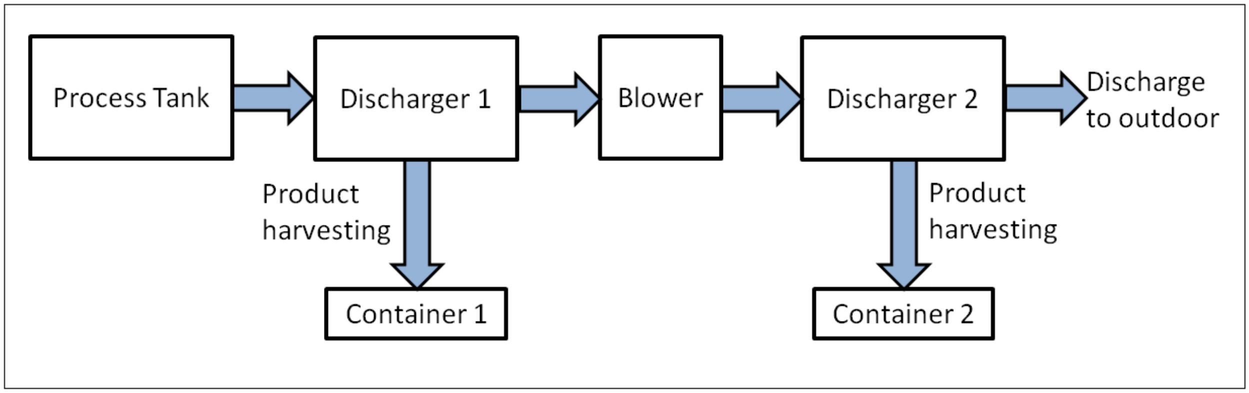

Figure 3. Process Tank 1 used for the refining process. Products are harvested by manually unlocking containers.

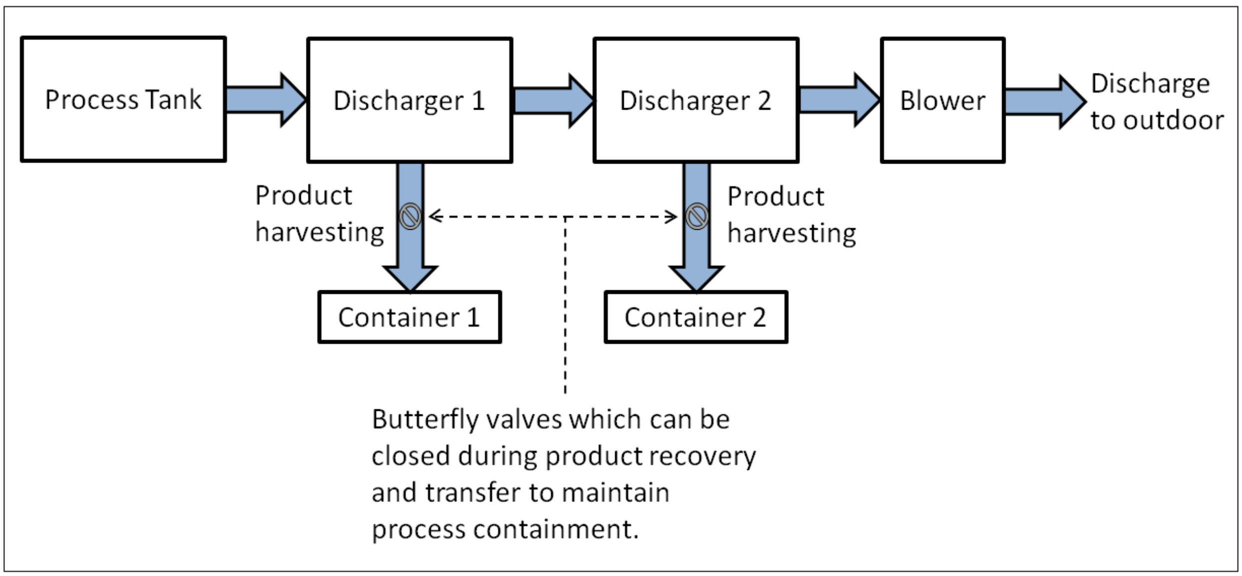

Figure 4. Process Tank 2 used for the refining process. This equipment is smaller than Process Tank 1. It has design features that should minimize dust emissions.

Two process tanks used in the refining process were monitored in real-time by direct-reading instruments, including the Fast Mobility Particle Sizer (FMPS) spectrometer, Aerodynamic Particle Sizer (APS) spectrometer, and DustTrak aerosol monitor. The DustTrak data are shown in Figure 5 for discussion, but all instruments actually provided similar results. The DustTrak detected very minor changes in particle concentration during harvesting from Process Tank 2, but Process Tank 1 released particles (concentrated at <10 nm, 100 nm, and 2 µm) during product harvesting. Both process tanks have similar functions, but they were used to produce different products. Process Tank 1 has a higher product capacity (i.e., larger dimensions).

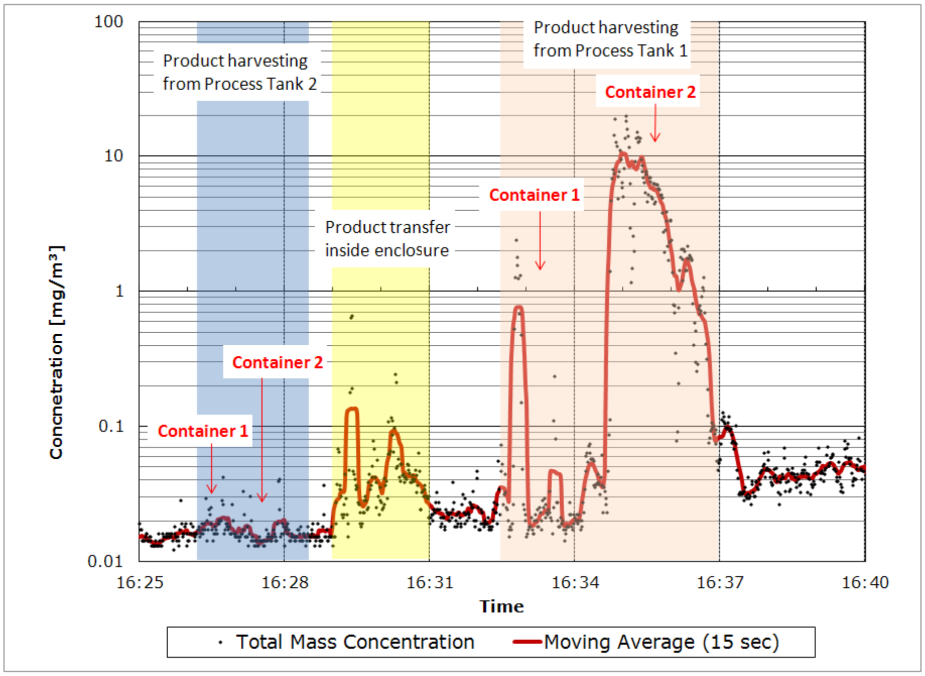

Figure 5. Previous monitoring data of product harvesting from two refining process tanks, as measured by the DustTrak aerosol monitor on September 29, 2010.

The recovery of product from Process Tank 2 involved lower dust emissions (see Figure 5). Features that may have contributed to these lower emissions could include the following:

1. The material being handled had a lower mass.
2. The butterfly valves on the bottom of the product recovery vessels can be closed so that containment is not lost when collection containers are removed.
3. The blower is located downstream of the process equipment. As a result, the static pressure for the process vessels and product recovery devices is less than atmospheric (under negative pressure). This eliminates the possibility of leakage from the process tanks and collection containers during manufacturing and harvesting.

As control measures, features 2 and 3 are examples of “prevention through design.” These are process changes that minimize or eliminate dust emissions.

As shown in Figure 5, the DustTrak also identified particle release from the ventilated enclosure (Figure 2) during product weighing and transfer. Particle-size analysis from the FMPS and APS data showed that fugitive particles were concentrated at 30 nm and 3 µm.

Product temperature appears to affect emission concentrations observed during product harvesting in the post-treatment process (Figure 6). The test clearly demonstrated that the hot and warm tubes resulted in higher particle concentrations (2–3 orders of magnitude greater than background) for a longer time (3–4 minutes), whereas a long cooling time produced lower nanoparticle emissions (less than 2 orders of magnitude) for a short period (~1 min). The high-concentration contaminants detected by the direct-reading instruments may not be the engineered nanomaterials.

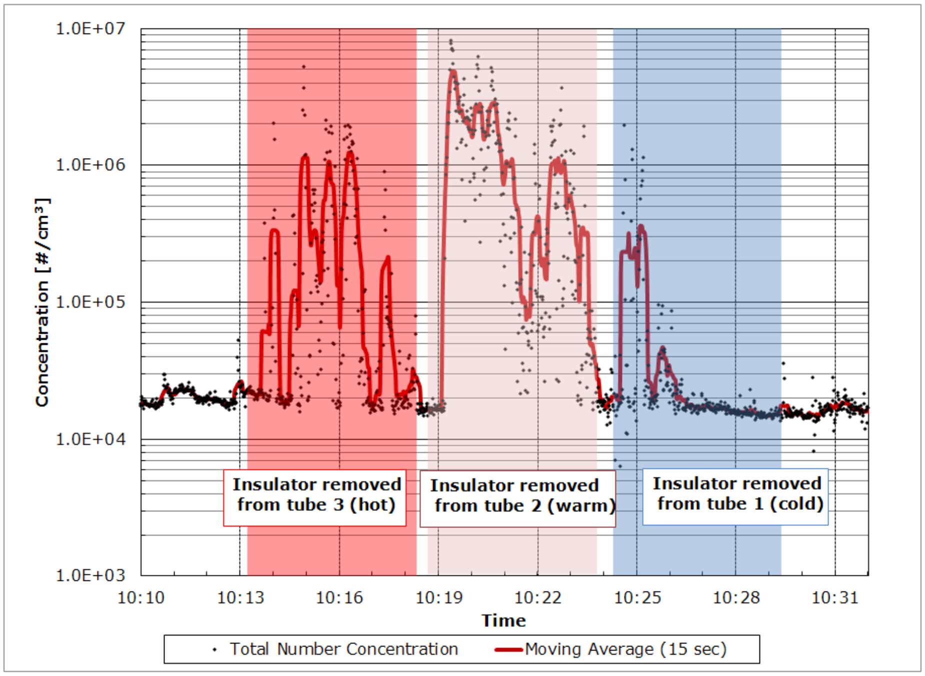

Figure 6. Previous sampling results from the tubes with different cooling times during the post-treatment process, as monitored by the FMPS on September 30, 2010.

Methodology

For this case study, process changes for product harvesting from both areas were evaluated. The effect of applying an engineering control on the equipment maintenance for Process Tank 1 was assessed.

Sampling Plan

Direct-reading Instruments

In this study, the direct-reading instruments (FMPS, APS, and DustTrak) used in the previous survey [NIOSH 2011] and a handheld Condensation Particle Counter (CPC) were used to monitor in real time the variations in particle concentrations in the studied activities. As shown in Table 1, the FMPS and APS provide number size distributions of particles ranging from 5.6 nm to 20 µm. The CPC gives total particle counts. The DustTrak monitors mass concentrations up to 150 mg/m^3.

Although aerosol photometer mass concentrations are highly correlated with gravimetrically determined mass concentrations, response factors relating concentrations measured by these ways can vary by an order of magnitude [Benton-Vitz and Volckens 2008]. Aerosol photometer response is known to be affected by particle size and optical properties, including index of refraction and particle light absorption [Rader and O'Hern 2001]. Thus, aerosol photometer measurements are a good measure of relative concentration. Because aerosol photometers have a 1-second time constant, their use is a trade-off of accuracy for time resolution. Good time resolution is needed to conduct video exposure monitoring so that sources of exposure are identified.

Table 1. Direct-reading instruments used in this case study.

Instrument (TSI Inc.)	Metrics	Specifications
FMPS (Model 3091)	Number	(1) Determining number size distributions with an array of electrometers (2) Size range from 5.6 to 560 nm
APS (Model 3022)	Number	(1) Measuring number size distributions with light-scattering technique (2) Size range from 0.5 to 20 µm
CPC (Model 3007)	Number	(1) Measuring particle number with an optical detector to count alcohol droplets formed by condensing particles (2) Size range from 10 nm to 1 µm
DustTrak (Model 8533)	Mass	(1) Single-channel basic photometric instrument (2) Size range from 0.1 to ~15 µm (size-segregated mass fractions for PM1, PM2.5, respirable, PM10, and total) for concentration range from 0.001 to 150 mg/m^3 (3) Response varies linearly with concentration. However, the response does vary with particle size and optical properties.

Video Exposure Monitoring

Video exposure monitoring (VEM) is a technique in which real-time monitoring devices are synchronized with video of the work activity [Beurskens-Comuth et al. 2011]. The VEM method was initially developed by NIOSH engineers in the late 1980s to bring together work activity data (video recordings) with direct-reading exposure data. VEM aids in the identification of work practices and emissions that cause air-contaminant exposure. In this study, the VEM technique was used to monitor worker activities, including product harvesting from the production processes and nanomaterial handling inside the enclosure. Specifically, exposures were monitored by holding sampling ports in the workers' breathing zone. The sampling ports were connected to the instruments (Table 1) on a cart used for moving equipment to sampling locations. In the post-treatment area, however, this approach was awkward and somewhat impractical because of obstacles and workers' unexpected motions. Data were analyzed in annotated plots, as shown in Figure 6.

Temperature Measurements

A type k thermocouple configured as a surface temperature probe (Infrared Thermometer, model 568, Fluke Corporation, Everett, Washington) was used to measure surface temperatures on production equipment. The thermocouple voltage was converted to a temperature by an infrared thermometer with thermocouple input.

Ventilation Measurements

A hot wire anemometer (VelociCalc Air Velocity Meter 9545, TSI, Shoreview, Minnesota) was used to measure the hood face velocities for the product transfer enclosure. In addition, smoke tubes were used to qualitatively evaluate the airflow into this booth.

Air Filter Sampling

In parallel with real-time monitoring, air filter samples were collected for transmission electron microscopy (TEM) with energy-dispersive X-ray (EDX) analysis. This off-line analysis, combined with real-time instruments, can help identify engineered nanomaterials released from processes and in the workplace [Brouwer et al. 2012]. The sampling media—25-mm mixed cellulose ester (MCE) membrane filters (SKC Inc., Eighty Four, PA)—were prepared according to Method 7402 of the NIOSH Manual of Analytical Methods (NMAM) [NIOSH 1994]. Leland Legacy sampling pumps (SKC Inc.) were used to collect filter samples at the sampling flow rate of 5 liters per minute. In this study, daily filter samples were also collected for area monitoring in the office (nonproduction area), refining area, and post-treatment area.

To prepare sample filters for TEM analysis, portions of each were affixed to glass slides and treated with filter-clearing solution (35% dimethyl formamide, 15% glacial acetic acid, 50% deionized water). Then filters were carbon-coated and placed onto three 200-mesh copper grids for TEM analysis. Particle sizing and elemental identification were performed with a Philips CM-12 TEM, a Gresham light element detector, and an IXRF digital imaging system. At least 40 grid openings or 100 particles, whichever came first, were analyzed. Length and width of the particles were measured. A magnification of 15,000× or higher was used.

As reference material, representative 10-mg portions of the bulk sample were placed in a suspension of 5 mL of acetone. The mixture was ultrasonicated for 3 minutes and centrifuged for 3 minutes. The supernatant was decanted to a level of 0.5 mL. The remaining material was re-suspended and a drop of the suspension was then placed on each of two carbon-coated (3-mm-diameter and 200-mesh) copper grids. The sample grids were dried and then examined with the same instruments used for analyzing sample filters.

Case Studies

Case 1: Effect of Waiting Time for Product Harvesting on Particle Emissions

The particle concentrations during product harvesting from Process Tank 1 were examined at four different waiting times after shutoff of the refining system: 0 minute (i.e., right after completion of the refining process), 10 minutes, 30 minutes, and 1 hour. The sampling ports including filter samples were located as close as possible to the discharger openings once the containers were removed.

Case 2: Equipment Maintenance

Care needs to be taken during equipment maintenance, because nanomaterials can be aerosolized and released to the workplace. Use of proper personal protective equipment to prevent exposure to nanomaterials in the occupational environment was discussed elsewhere [Golanski et al. 2008; Kosk-Bienko 2009; SWA 2009]. In this case study, a control measure (i.e., the blower shown in Figure 3) was operated to evaluate its effectiveness to contain the particle emissions. The control effectiveness was determined by comparing particle concentrations before and after the blower was used to exhaust the generated dust during the maintenance task.

Case 3: Performance Evaluation of Ventilated Enclosure and Local Exhaust Ventilation

The previous field study identified particle release during product weighing and transfer in a ventilated enclosure (Figure 5). Figure 7 is a photograph of this enclosure, and its dimensions are summarized in Figure 8. The air flows in through the front of the booth and out through a MERV 11 filter in its ceiling. A fan is located behind the MERV 11 filter.

As summarized in a NIOSH guidance document [NIOSH 2003], MERV 11 filters have greater than 85% efficiency for particles in the range of 3–10 µm and 65% to 80% efficiency for those in the range of 1–3 µm. The efficiency of a MERV 11 filter decreases from 65% to 35% as particle size decreases from 1 to 0.3 µm [Ward and Siegel 2005]. The performance of the ventilated enclosure was re-evaluated in this study by means of direct-reading instruments and filter sampling. The sample probes were located at the enclosure opening to monitor particle emissions during regular weighing and transfer of nanomaterial.

Figure 7. The ventilated enclosure used for product transfer.

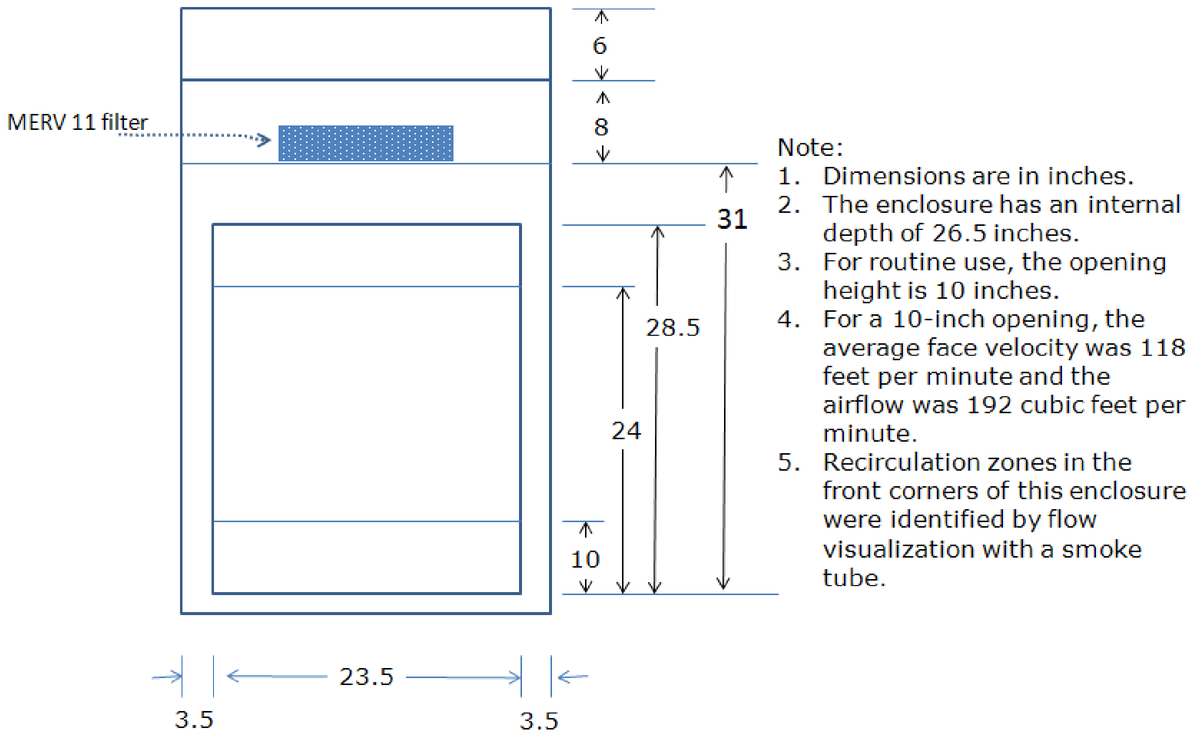

Figure 8. Dimensions of the ventilated enclosure used for product transfer.

Case 4: Safety Issue—High Surface Temperature on Production Equipment

Elevated surface temperatures increase the potential risk for contact burns. The surface temperatures on the refining process equipment and on the tubes used in the post-treatment process appeared to be high enough to cause contact burns. Also, temperatures can affect emissions and how ventilation is applied to control air-contaminant exposures. Thus, surface temperatures were measured as a function of time for the refining process and for postprocessing (on glass tubes). Surface temperatures were measured with a type K thermocouple incorporated into a surface temperature probe (IR thermometer, Fluke model 568).

Case 5: Effect of Waiting Time on Emissions from Harvesting Product During Post-treatment Process

For the post-treatment process, product harvesting from glass tubes was performed only at room temperature, because harvesting at different temperatures had been tested in the previous study [NIOSH 2011]. Filter samples were collected in the worker's breathing zone to determine whether the released particles were engineered nanomaterials. The results were compared with the background data to quantitatively evaluate the local exhaust ventilation on top of the reactor.

Results and Findings

Case Study 1: Effect of Waiting Time for Product Harvesting on Particle Emissions

The results of FMPS and APS sampling in the worker's breathing zone right after processing was stopped (0-minute waiting time) are shown in Figure 9 and Figure 10, respectively. Removing the collection containers immediately increased the number concentration in the size range of 0.1 to 10 µm. For particles smaller than 0.1 µm, the aerosol does not differ noticeably from background air pollution. On the other hand, TEM showed that the particle size distributions at 0 minute were 60% in the range of 0.1 to 1 µm; 29%, 1 to 5 µm; 4%, 5 to 10 µm; and 6%, >10 µm. The data indicate that there is a noticeable dust concentration in the size range of 0.5 to 10 µm. Because these particles are detectable by the DustTrak, it can be used to explore how process changes affect aerosol concentration.

At a 30-minute or 1-hour waiting time, aerosol concentrations near where the collection containers were mounted on the processing equipment were generally indistinguishable from background air pollution when the production system was completely stopped (Table 2). On September 27, Container 1 was removed after the process had been stopped for 30 minutes. However, Discharger 2 was still being pulsed with compressed air, and this may have transported dust out of the opening for Container 1. Consequently, a concentration spike of about 5 mg/m^3 occurred, as shown in Figure 11. Once the concentration spike was identified by direct-reading instruments, the pressure pulsing was turned off, and the aerosol concentration during the removal of Container 2 was indistinguishable from background air pollution. On the following day, September 28, testing with a 30-minute waiting period was repeated; this time, the pressure pulsing was off when the production system was stopped. As shown in Table 2 and Figure 12, the aerosol concentration during container removal was not distinguishable from background aerosol concentration.

Comparison of the results in Figure 5, Figure 11, and Figure 12 shows that removal of the collection containers can be an emission source during product harvesting. Pressure pulses for Process Tank 1 can force dusty air out of the opening caused by removing the collection containers. During normal operation, a quiet time of 30 minutes apparently allowed the dust within the process equipment to settle. The installation of butterfly valves, as shown in Figure 4, may also reduce these emissions. These valves would simply be closed to contain the process while the collection containers are removed.

Table 2. Summary of data on particle emissions sampled during product harvesting from the refining system after different waiting times.*

Variable	Waiting time							
	0 min		30 min†		30 min		1 hr	
Sampling date	09/26		09/27		09/28		09/27	
Sampling time	15:10–15:25		15:18–15:29		11:02–11:12		10:56–11:05	
Container	1	2	1	2	1	2	1	2
DustTrak concentration (mg/m^3)	2.40	0.36	0.24	0.05	0.06	0.05	0.05	0.05

*A 10-minute waiting time was tested but not reported on here because it yielded few nanomaterials.

†Discharger 2 was still being pulsed with compressed air when the worker was harvesting products from Container 1.

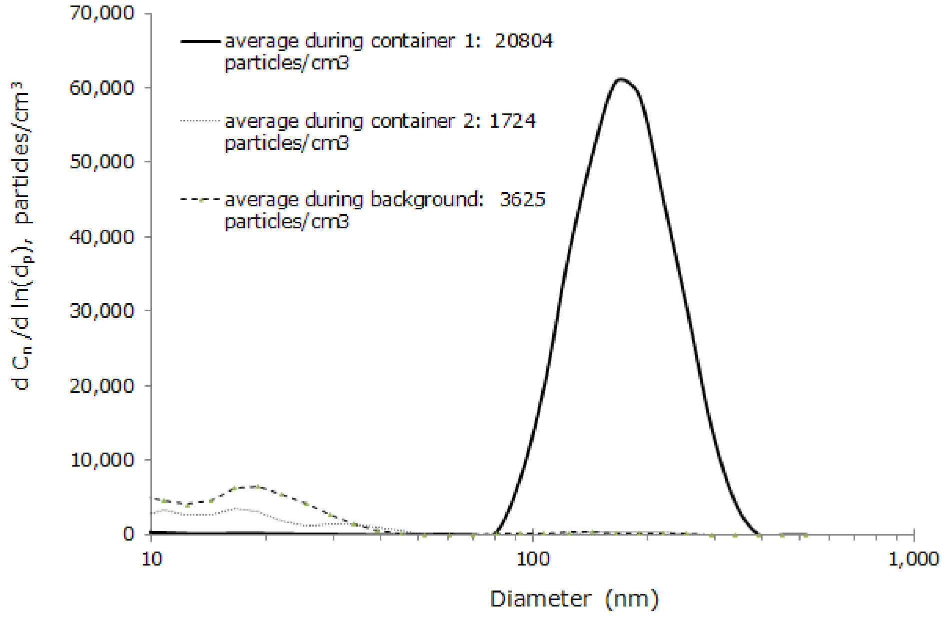

Figure 9. Size-dependent concentrations measured with the FMPS during container removal on 9/26.

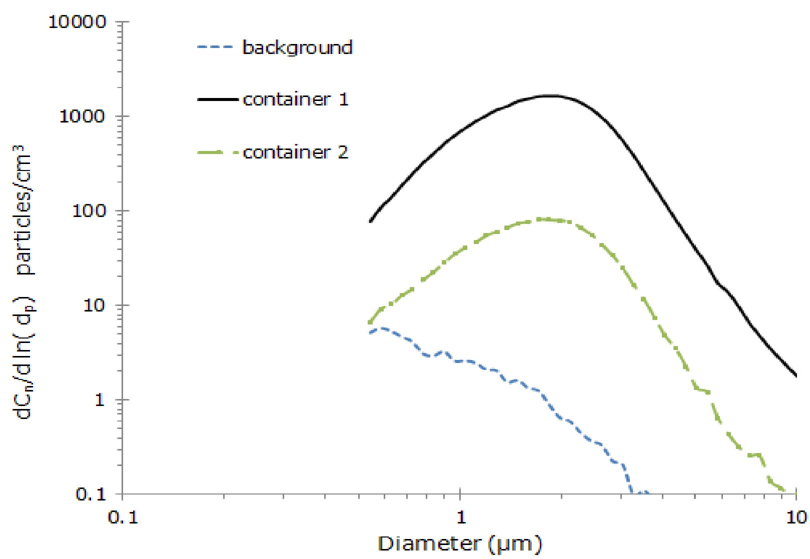

Figure 10. The graphene platelets recovered from the process had aerodynamic diameters larger than 0.5 µm. During disconnection of Containers 1 and 2, the mass concentrations estimated from the APS number concentrations were 9 and 0.4 mg/m^3 on 9/26.

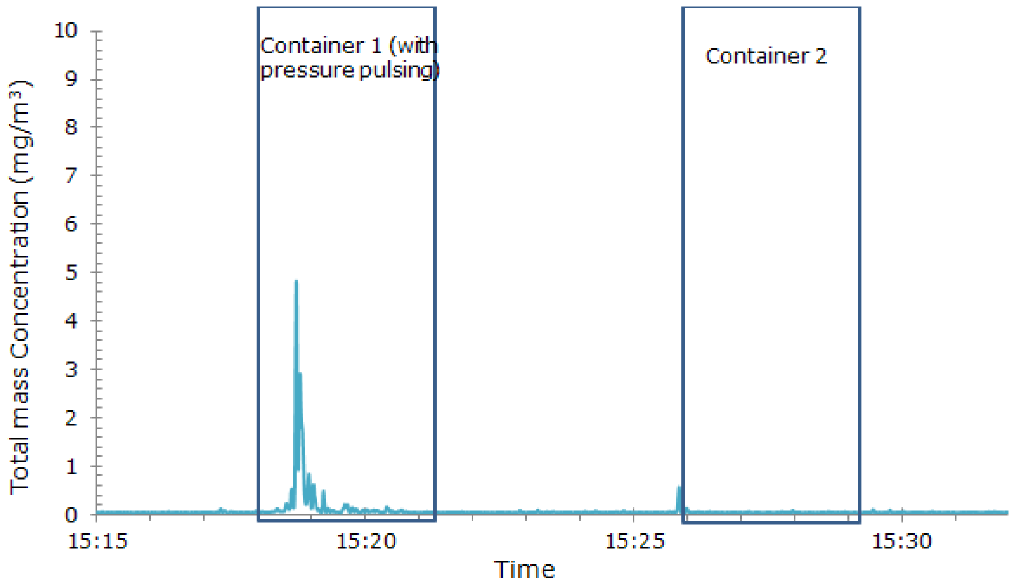

Figure 11. Results from DustTrak with a 30-minute delay in product harvesting. Pressure pulsing was on until Container 1 was removed.

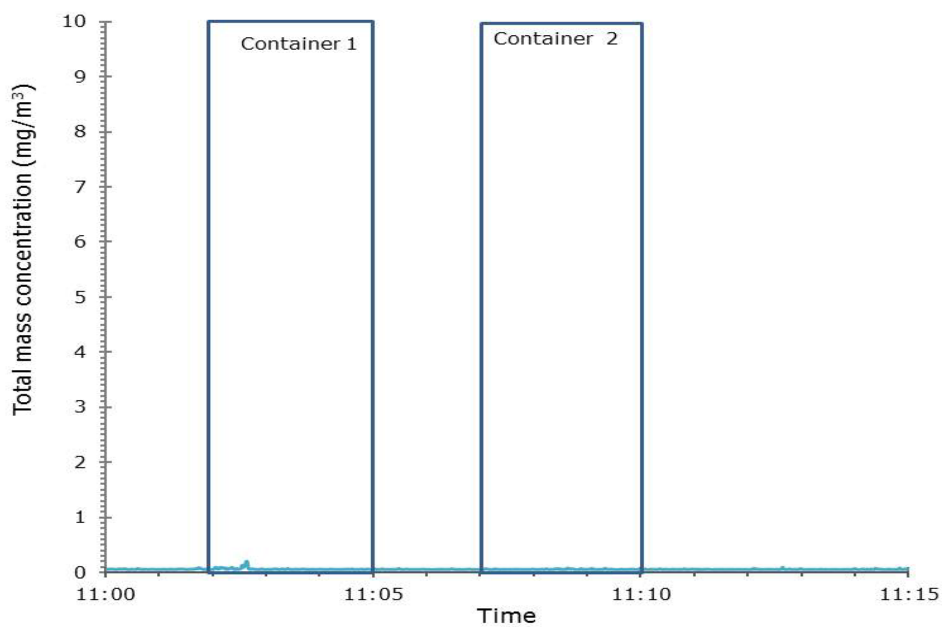

Figure 12. Results from DustTrak with repetition of a 30-minute delay in product harvesting. The process, including pressure pulsing, was completely shut down before removal of Container 1.

Case Study 2: Equipment Maintenance

The DustTrak was the only instrument used to monitor fugitive nanomaterials generated during maintenance cleaning of the process tank. The task usually lasts less than 10 minutes. For the test done on September 15, the sampling probe was first located slightly inside the tank and then in the worker's breathing zone. The test results showed that the average mass concentration can reach 6.87 mg/m^3 inside the tank due to maintenance (Figure 13). The average aerosol concentration around the worker's breathing zone increased to 0.71 mg/m^3 during the task, more than 50 times higher than the background aerosol concentration (0.013 mg/m^3) before the task.

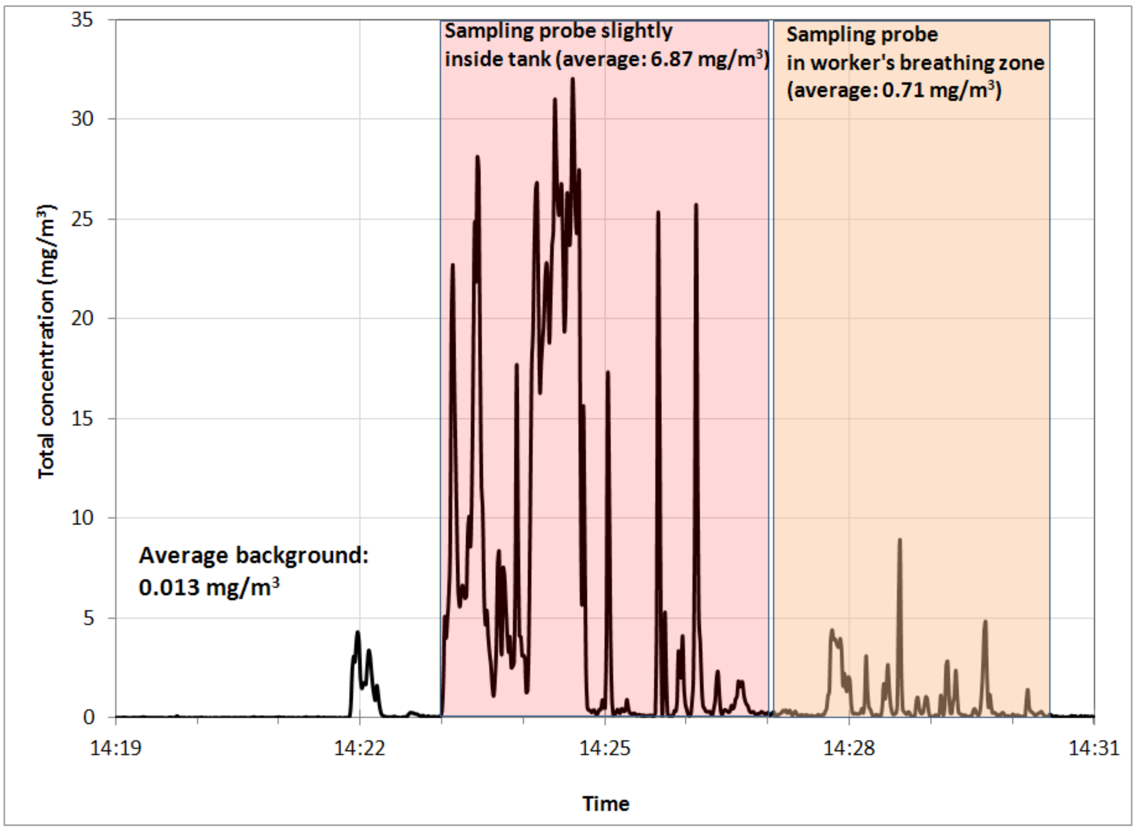

Figure 13. Real-time monitoring of nanomaterials released during maintenance cleaning of Process Tank 1 on 09/15. The regular task procedures were followed, with no engineering controls.

On September 28, the same maintenance task was performed but the fan (Figure 3) was turned on to collect the airborne dust through the equipment's product recovery devices. The airflow measurement showed that the average face velocity at the view window is 130 feet per minute (fpm). This is equal to an exhaust of 223 cubic feet of air per minute. Also, a smoke test showed that good capture can be maintained up to the distance the worker stands from the tank to perform the maintenance task. With the fan on, the average mass concentration around the worker's breathing zone was as low as 0.18 mg/m^3, only 3 times higher than the background concentration of 0.059 mg/m^3 before the maintenance (Figure 14). Compared with the net emissions, this is a nearly 83% reduction with use of the exhaust blower during tank maintenance. Clearly, this engineering control reduced the magnitude of the worker's dust exposure during tank cleaning.

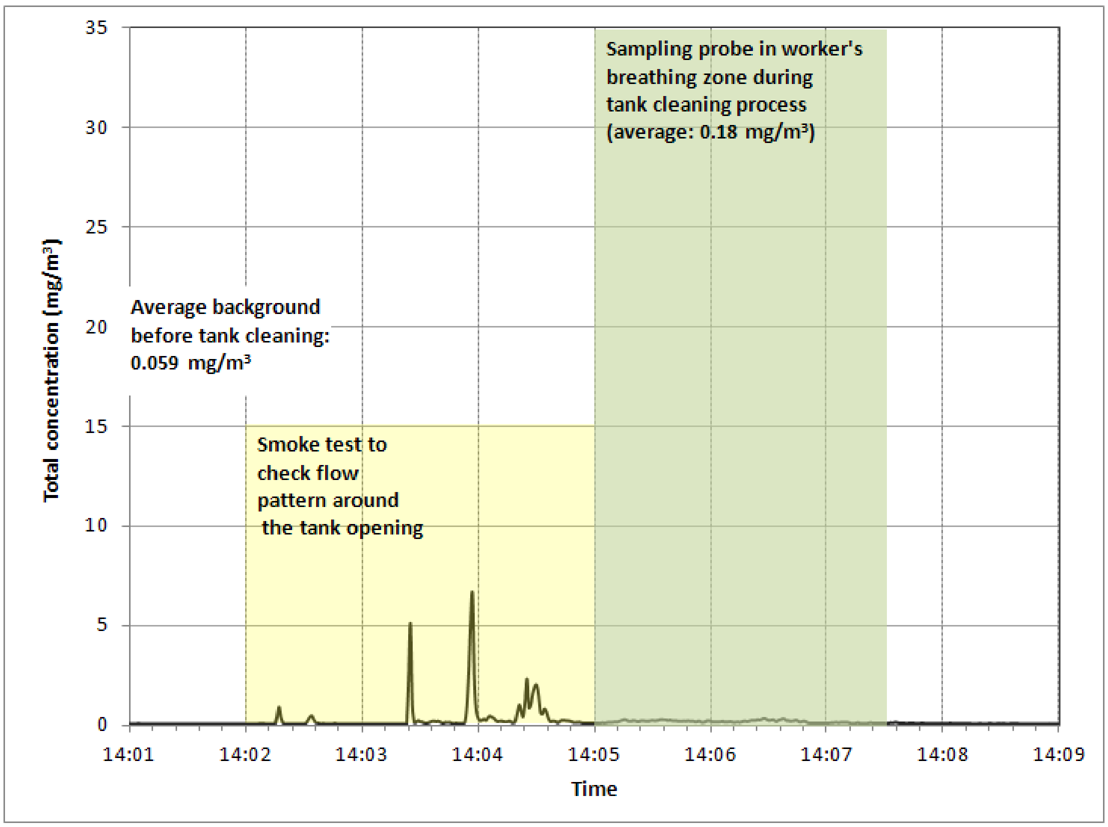

Figure 14. Real-time monitoring of nanomaterials released during the maintenance task for Process Tank 1 on 09/28. The task was performed with the fan on to exhaust fugitive nanomaterials.

Case Study 3: Performance of Ventilated Enclosure for Product Transfer

The airflow into the ventilated enclosure is summarized in Figure 8. The air flowed upward, toward the filters in the ceiling of the enclosure. The average face velocity was 118 fpm during routine use (the opening height was 10 inches). Smoke tubes were used to visualize the airflow. There was no evidence of a recirculation zone caused by the investigator's torso as the air flowed into the enclosure during routine use. Recirculation zones were observed in the enclosure, behind the front corners. When objects were placed near the opening, the airflow appeared to be deflected outside of the hood, and then the air flowed back into the hood and toward the ceiling of the booth.

The flow visualization results suggest that the enclosure will contain the dust as long as the worker positions the powdered material in the enclosure to avoid the recirculation zones identified by the smoke tests. Generally, the worker's dust exposure was indistinguishable from background aerosol concentrations, as measured by the DustTrak. This is clearly the case shown in Figure 15, where exposures were generally below the background readings plus three standard deviations, which were computed on the basis of the previous 10 minutes. For the task of product packing, however, the worker's dust exposure increased noticeably above the background concentration (Figure 16). As shown in Figure 17, the worker was pouring the last bit of material from the collection container into a large jar for storage. This activity probably generated more dust. The positions of the collection container and the jar may have obstructed airflow into the enclosure, causing air to flow outside of the booth.

In the self-contained enclosure, contaminants are removed from recirculated air as it passes through MERV 11 filters. As discussed earlier, the collection efficiency of MERV 11 filters decreases from about 65% to 35% as particle size decreases from 3 to 0.3 µm. If the airborne dust generated from handling the powder is similar to the dust generated by removing the containers from the process equipment, then much of the aerosol generated within the enclosure will be discharged into the workplace air. A review of the results in Figure 9 and Figure 10 shows that most of the aerosol particles are smaller than 3 µm. Therefore, because most of this aerosol will likely penetrate MERV 11 filters, the enclosure may be a source of exposure to graphene.

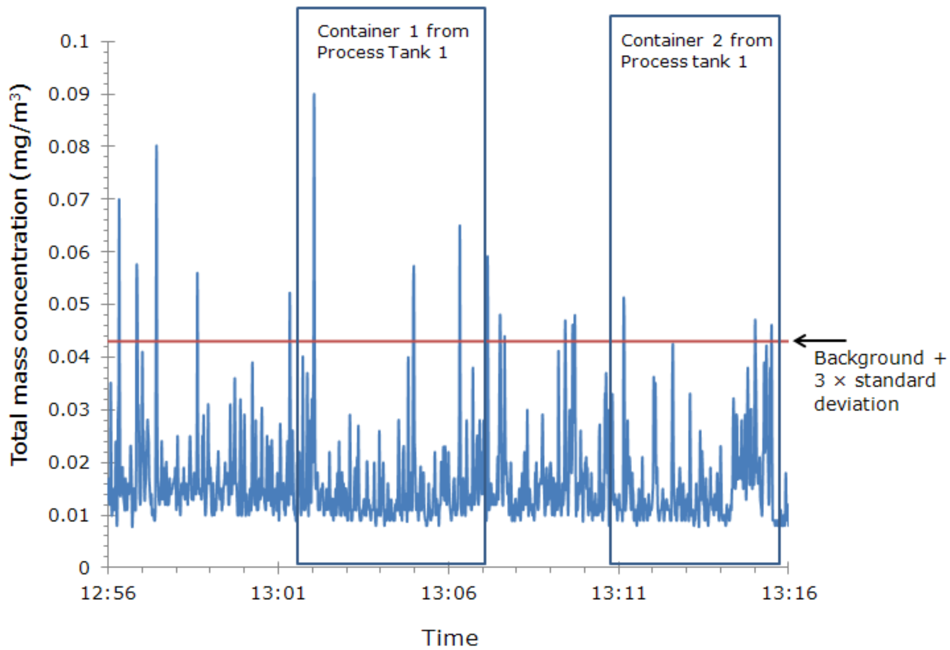

Figure 15. Dust exposures during the first weigh-out session.

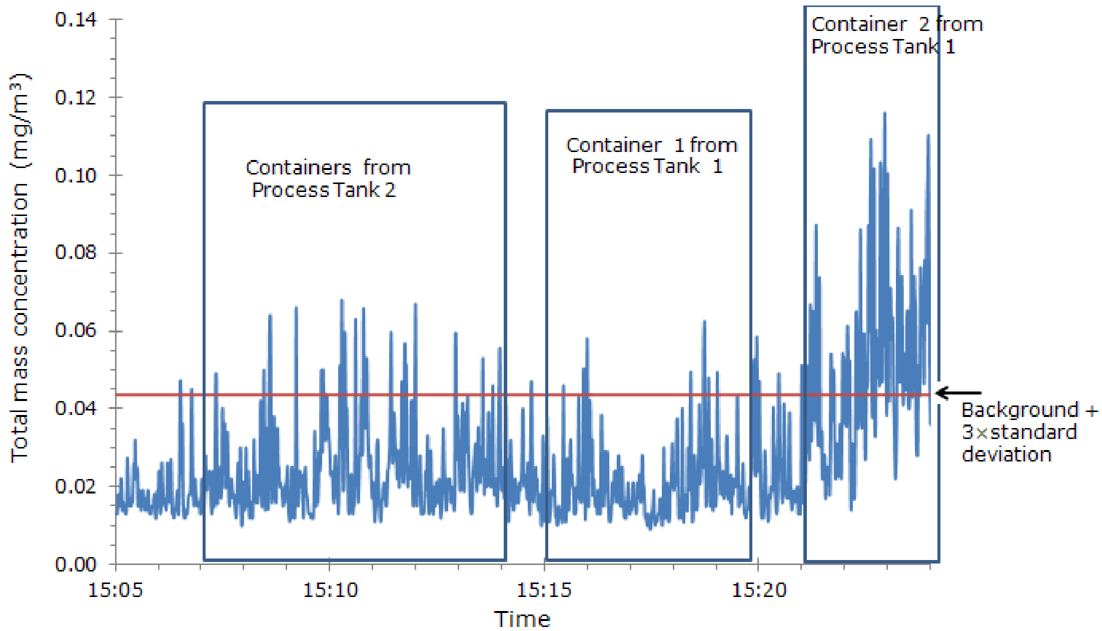

Figure 16. Worker's dust exposure during product packaging. At 15:23, the worker's exposure increases noticeably above the background exposure. The background concentration plus three standard deviations is the horizontal line. The statistics for the background concentration were computed from the concentrations between 14:55 and 15:05.

Figure 17. Worker activity at 15:23:01. The worker is pouring material from the collection container into a storage container.

Case Study 4: Surface Temperature Safety Issues

During the refining process described in Figure 3, the surface temperature of the pipes/ducts and the product recovery equipment downstream of the process tank is elevated. Surface temperatures are plotted as a function of time after the termination of process operations, and the initial temperatures are the steady-state temperatures during the process (Figure 18). Some steady-state surface temperatures were nearly 100°C, posing a risk to the worker of second- or third-degree contact burns. Some surface temperatures are excessive according to American Society for Testing Materials Standard C1055-3 [ASTM 2009] . This consensus standard addresses the prevention of contact burns from hot surfaces. For industrial operations, this standard specifies that surface temperatures be kept below 70°C for a contact time of 5 seconds or less. The standard also specifies maximum contact times, which decrease from 6 hours to 5 seconds as surface temperature increases from 44°C to 70°C. In the literature summarized by this standard, 44°C was thought to be the threshold temperature for pain and reversible injury.

An online calculator provided by the National Institute of Building Sciences can estimate the thickness of insulation needed to keep surface temperatures below 44°C [National Institute of Building Science 2011]. According to the online calculator, 2.5 cm of fiberglass insulation can be used to keep surface temperatures below 44°C. The risk of contact burns should be managed as part of a comprehensive occupational safety and health program, as described by the American National Standards Institute [ANSI 2005]. The removal of the collection containers from the process equipment described in Figure 3 should be delayed until temperatures are below 44°C; this should require about 15 minutes.

For the post-treatment process, the surface temperatures in the middle of the tubes will initially exceed 70°C (Figure 19). The risk of burns is apparently mitigated by allowing these process tubes to cool down to room temperature for product harvesting. This practice avoids the dispersal of aerosol generated by the handling of hot fiberglass used as end plugs.

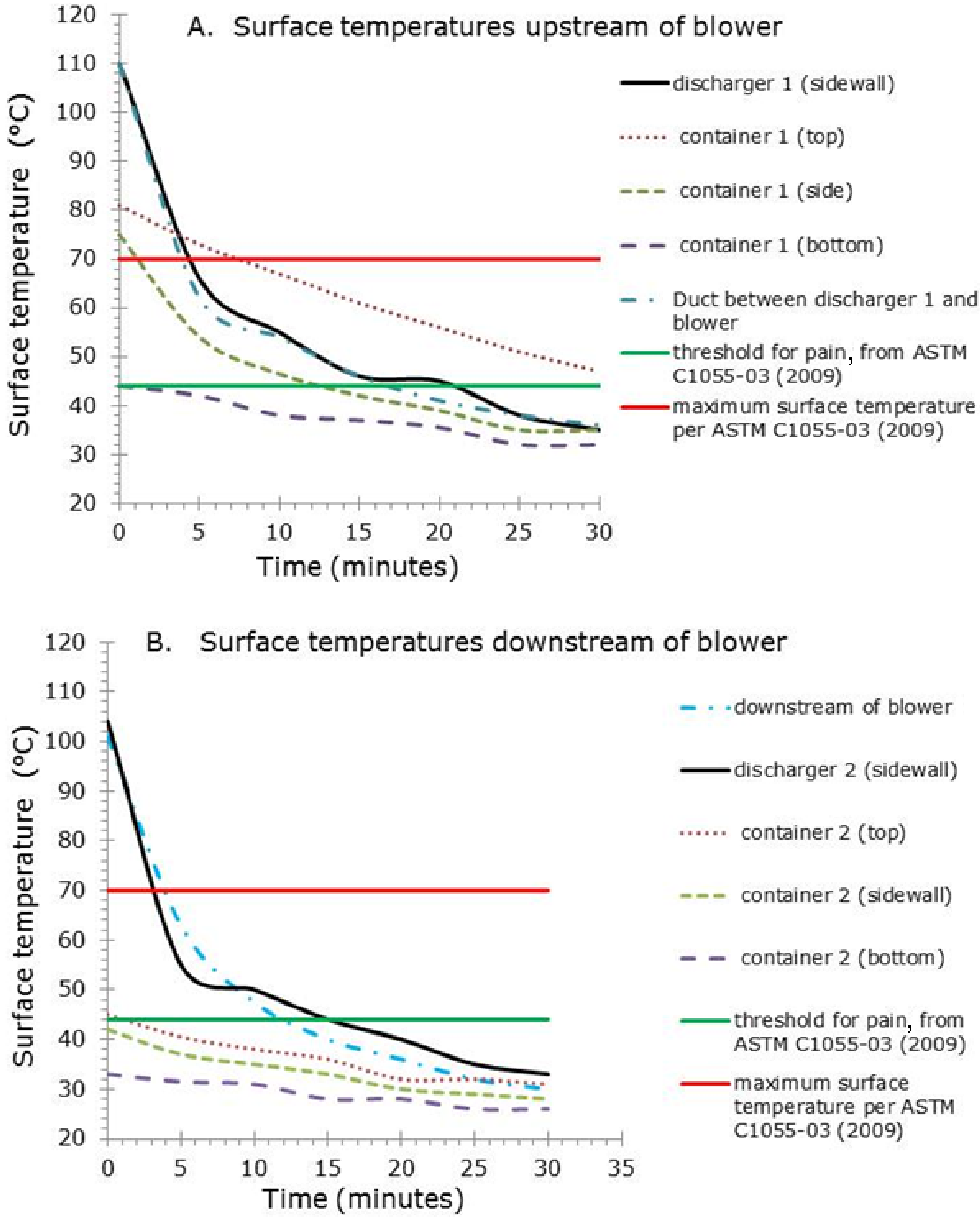

Figure 18. Surface temperature changes on the refining equipment. The temperatures at time = 0 minutes are steady temperatures at the end of the process.

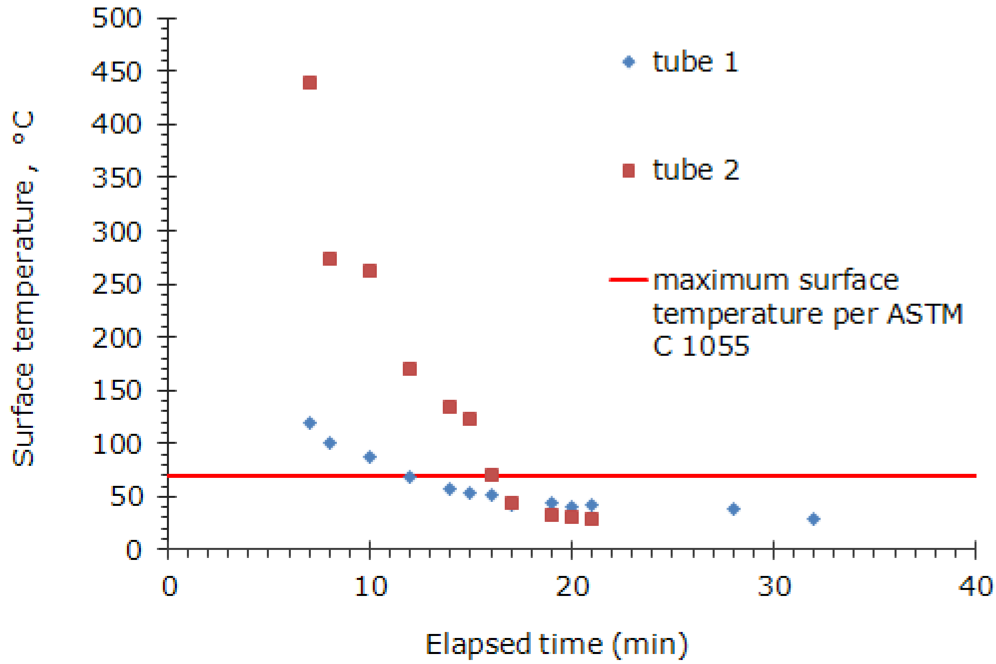

Figure 19. Surface temperature change over time on the glass tubes for the post-treatment process. Cooling time can be used to mitigate the risk of a contact burn. This suggests that about 20 minutes is needed to minimize the risk of a burn.

Case Study 5: Monitoring the Post-treatment Process

During this task, it was difficult to keep the sampling ports in the worker's breathing zone. Although the FMPS concentration measurements were unaffected, the DustTrak measurements appeared to be affected by the worker's activities and tasks. On the basis of the videotape, an annotated plot of concentration versus time (Figure 20) was prepared for product harvesting from the process. Because of the videotape was insufficient, however, the plot in Figure 21 was annotated with use of notes. We inconsistently observed exposure peaks for the following:

a. Handling the fiberglass plugs. In some cases, the fiberglass plug was cleaned of product and recycled. This seemed to create dust exposures that approached 8 mg/m^3 (Figure 20 and Figure 21).

b. Checking the storage jar and breaking up clumps. This task caused peak exposures that approached 7 mg/m^3 (Figure 20).

c. Emptying the process tubes. Gently emptying the tube so that fall distances are minimized resulted in exposures that were just barely noticeable (Figure 20). However, when the worker bumped into the collection container, an exposure peak of 2 mg/m^3 (Figure 21) was observed. Forceful handling of powders and increased drop distances are likely to increase the amount of dust generated.

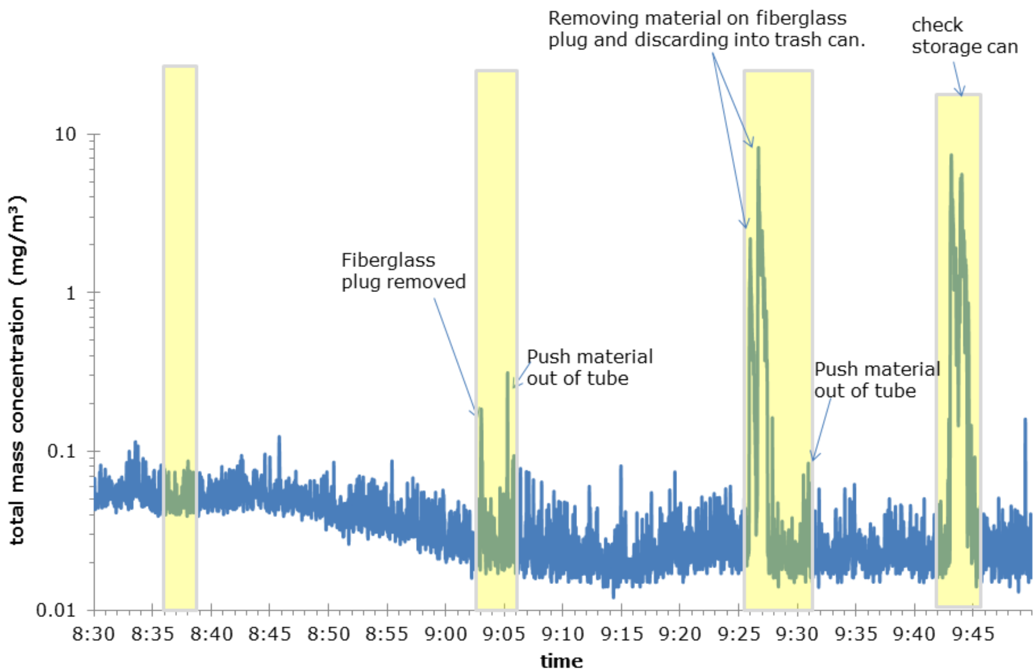

Figure 20. Monitoring data for the post-treatment process (annotations were based upon videotape).

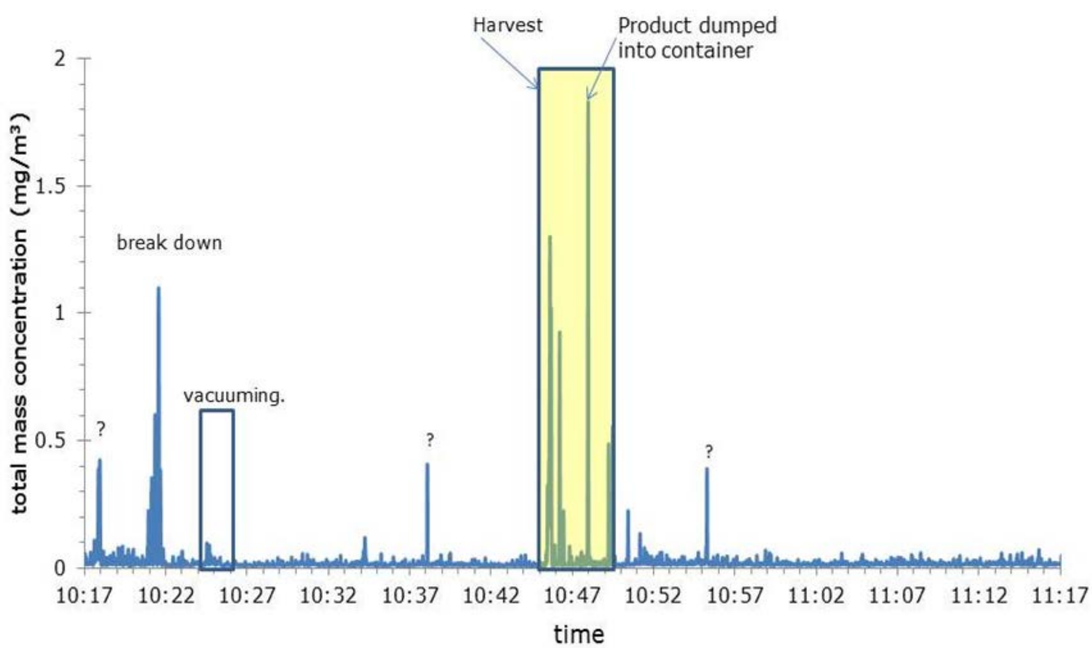

Figure 21. Monitoring data for the post-treatment process (annotations were based upon notes).

Conclusions and Recommendations

Refining Process Area

For the refining process, several specific conclusions and recommendations can be made:

1. For product harvesting from the refining process, allow the product system to rest for at least 15–30 minutes. This will allow dust to settle in the product dischargers and will minimize dust exposure during removal of the collection containers. Resting times of 30 minutes were observed to largely eliminate dust exposures during such removals. Furthermore, this will reduce the risk of burns from touching hot processing equipment. If this delay is unacceptable, then installing valves between the collection containers and the bottom of the dischargers might prevent exposures. In addition, the collection containers need to be replaced or modified so that surface temperatures remain below 44°C, therefore minimizing the risk of contact burns.

2. Generally, the ventilated enclosure for nanomaterial handling appears to contain the dust generated during product transfer. However, when the worker's activities block the airflow into the enclosure, a recirculation zone may cause air to flow out of the hood. Perhaps this can be avoided by moving the operations toward the back of the enclosure. As a practical matter, manual powder handling will cause dust exposures. To a limited extent, work practices can be refined to minimize these exposures.

   A self-contained enclosure may discharge dusty air into the workplace. In addition, as shown by the size distributions of dust generated by product handling, the MERV 11 filter allows most of the dust from product transfer to be dispersed into the workplace air. Simply upgrading the filter in such an enclosure may not be helpful. More efficient filters generally have a higher pressure loss that may drastically reduce airflow. Nanomaterials should therefore be handled in an exhausted enclosure from which a duct moves air outside or through high-efficiency particulate air (HEPA) filters before it flows back into the workplace. HEPA filters are 99.97% efficient at 0.3 µm.

3. During maintenance, manual cleaning of the tank inevitably creates dust exposure. Using the process ventilation to collect this dust appears to reduce exposures by about 83%.

Post-treatment Process Area

In the post-processing area, the process equipment did not appear to be a source of ultrafine aerosol emissions into the workplace. The process tubes were allowed to cool to room temperature before recovering product. This prevented the emission of ultrafine aerosols that may be caused by removing fiberglass plugs under high temperature. However, several sources of dust emissions were noted:

1. After the tubes were cooled to nearly room temperature, the fiberglass plugs and the product were removed from them. Handling the fiberglass plugs can create a noticeable dust exposure. This source of dust exposure could be avoided by discarding the fiberglass plugs after each use.

2. Generally, the dust concentration increased slightly above the background concentration during product harvesting, when the product was pushed into a collection container. However, if the fall distance was too large or the container was bumped, then noticeable dust emissions occurred.

3. The worker sometimes broke up clumps of product stored in containers, which caused dust generation.

The tasks in the preceding list all involve manual material-handling. Good work practices can be used to minimize dust emissions, but inevitably certain tasks will create exposures. To further reduce these dust exposures, these tasks could be performed in an enclosure or a room that uses vertical plug flow, or downflow ventilation. Downflow booths or rooms deliver clean airflow uniformly through the ceiling to protect workers and remove contaminated air from lower exhaust to minimize dispersion of contaminants. A general design rule of downflow booths can be found on Page 6-14 in the Industrial Ventilation Manual [ACGIH 2010]. The downflow booth shown in Figure 22 is a control measure specifically designed for manually handling materials.

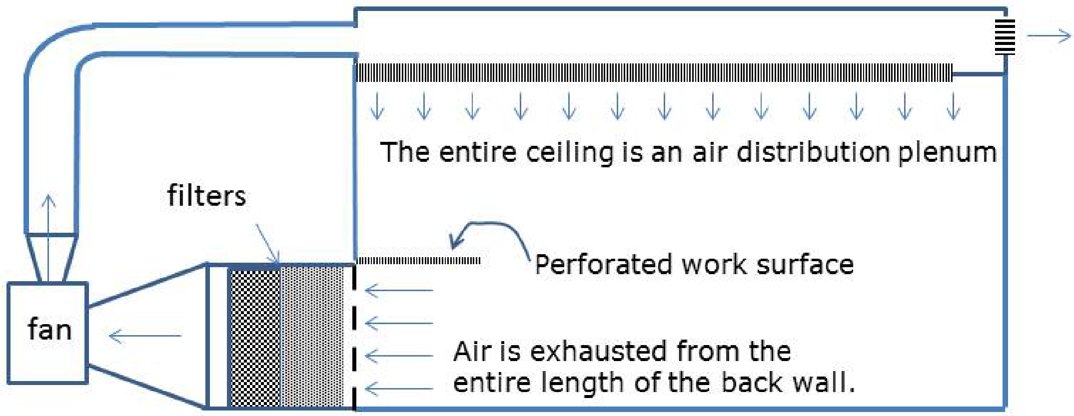

Figure 22. Conceptual sketch of downflow-ventilated booth or room. The airflow from the ceiling should be 35–100 fpm [Heinonen et al. 1996; Floura and Kremer 2008].

General / Strategic Considerations

Most dust emission sources can be identified by a safety review during the facility design phase. Safety system engineering methods aid in the identification of emission sources and other hazards. Also, plans should include process or equipment design features that eliminate hazards. For example, consider the placement of valves for Process Tank 1 (Figure 3) to eliminate emission sources during product harvesting. Process Tank 2 (Figure 4) has valves that can be shut to separate the collection containers from the dischargers so that emissions cannot escape from the opening caused by removing the container. This is an example of preventing a hazard by means of equipment design. For information on the NIOSH Prevention through Design (PtD) initiative, see www.cdc.gov/niosh/topics/ptd/. During project or process design, Several safety system techniques can be to identify hazards so that the designer can make choices that eliminate hazards [Manuele 2008]. A simple example is a Preliminary Hazard Analysis or Initial Hazard Analysis, in which one lists the hazards and subjective ratings of risk and severity. Then one lists control measures along with risk and severity after control measure implementation. This organized, systematic approach is imbedded into formal safety programs [ANSI 2005].

When respiratory protection is mandatory, the Occupational Safety and Health Administration requires a formal respiratory protection program per 29CFR1910.134, in the Code of Federal Regulations, which can be found on the OSHA Web site [OSHA]. The program specifies the procedures for selecting respirator for use in the workplace, the medical evaluations for using respirators, the fit testing procedures, the training of employees in the proper use of respirators, and the respiratory maintenance.

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