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Field Report

Exposures during wet production and use processes of nanomaterials: a summary of 11 worksite evaluations

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Abstract: From 2011–2015, the National Institute for Occupational Safety and Health Nanotechnology Field Studies Team conducted 11 evaluations at worksites that either produced engineered nanomaterials (ENMs) via a wet process or used ENMs in a wetted, suspended, or slurry form. Wet handling or processing of ENMs reduces potential exposure compared to dry handling or processing; however, air sampling data indicated exposures may still occur. Information was gathered about each company, production processes, ENMs of interest, and control measures. Exposure assessments included air sampling using filter media, surface wipe sampling, and real-time particle counting by direct-reading instruments. Electron microscopy analysis of air filters confirmed the presence of ENMs of interest (10 of 11 sites). When a method was available, chemical analysis of filters was also used to detect the presence of ENMs (nine of 11 sites). Wipe samples were collected at four of the 11 sites, and, in each case, confirmed the presence of ENMs on surfaces. Direct-reading data showed potential nanomaterial emissions (nine of 11 sites). Engineering controls included fume hoods, cleanrooms, and enclosed processes. Personal protective equipment was required during all 11 evaluations. Recommendations to address potential exposures were provided to each company following the hierarchy of controls.

Key words: Industrial hygiene, Nanotechnology, Work environments, Exposure assessment, Electron microscopy, Direct-reading instruments

Introduction

Advances in nanoscience and nanoengineering have resulted in numerous commercial applications for engineered nanomaterials (ENMs). Consequently, an increasing number of workers are handling nanomaterials in manufacturing, research and development (R&D), recycling, waste disposal, and other applications[1)]. Nano-objects, including their aggregates and agglomerates greater than 100 nanometers (nm) in size, can exhibit properties that are different from their bulk or non-nanoscale parent material[2)]. The unique physical and chemical properties imparted to nanoparticles make them essential to certain industries and applications, but little is known about what effects these properties may have on human health[3)], presenting a challenge for worker safety and health practitioners.

In 2004, the National Institute for Occupational Safety

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and Health (NIOSH) established the Nanotechnology Research Center (NTRC) to conduct research to better understand the effects of exposure to ENMs on human health, as well as methods to control or eliminate exposures[4]. Additionally, the NIOSH/NTRC is charged with identifying critical issues related to potential worker exposure to ENMs, creating a strategic plan for investigating these issues, coordinating the NIOSH research effort, developing research partnerships, and disseminating information[4]. The NIOSH/NTRC established a Field Studies Team in 2006 to conduct on-site assessments of potential occupational exposure to a variety of nanomaterials and to evaluate methods to mitigate worker exposures[5]. To date, the NIOSH/NTRC Field Studies Team has completed over 100 field survey assessments across a variety of industries, including: nanomaterial producers, government research and development laboratories, university laboratories, and manufacturers incorporating nanomaterials into products[6].

In 2009, the Nanoparticle Emission Assessment Technique (NEAT)[7, 8] was published describing the sampling techniques used by NIOSH field researchers. This document also grouped sampling results from several NTRC on-site studies. With increased understanding of nanomaterial uses, controls, and sampling techniques, NIOSH issued NEAT 2.0[1], an updated version that is currently used as a framework for NIOSH/NTRC Field Studies Team evaluations. The original NEAT made use of direct reading instruments (DRIs) to identify workplace tasks associated with nanoparticle emissions. If emissions are identified, task-based filter samples are used to confirm and quantify these materials, using both laboratory chemical analysis and electron microscopy. The updated NEAT 2.0 places a stronger emphasis on full workday exposures, incorporates background monitoring, and emphasizes using integrated filter sampling in the worker's breathing zone over the use of area air sampling with DRIs.

From May 2010 to September 2012, NIOSH conducted an industry-wide exposure assessment study for carbon nanotubes (CNTs) and carbon nanofibers (CNFs) at 14 sites throughout the United States[9, 10]. A conclusion from these studies was that caution should be taken in workplaces handling large quantities of CNTs and CNFs, particularly in dry powder form[10]. When discussing the hierarchy of controls in this work, it is noted that "substituting a nanomaterial slurry for a dry powder version will reduce aerosolization and reduce potential for exposure for workers handling the material"[11]. With these conclusions in mind, the NIOSH/NTRC Field Studies Team reviewed past fieldwork conducted from 2011–2015 at sites to identify common trends, potential ENM exposures, and control techniques to mitigate ENM exposures. In this paper, we grouped companies that used wet processes for producing or using ENMs. For the purpose of this document, wet processes are those in which the ENM is produced or converted into a liquid slurry form before use. We summarize company descriptions and characteristics, the processes and nanomaterials evaluated, results from filter-based air samples, surface wipe samples, and conclusions made from DRI data, and the control measures and personal protective equipment (PPE).

Methods

Site descriptions

Several different industrial sectors are represented by these companies, including nanomaterial producers, companies that incorporated nanomaterials into their products, companies that both produce nanomaterials and incorporate them into secondary products, and an R&D facility. Detailed results of the site evaluation for the R&D facility have been published[12] and are included here with results from ten additional site evaluations. Processes at four companies were evaluated a second time due to changes in the production or manufacturing process, production volume, or physical relocation; these accounted for eight of the 11 evaluations. Two evaluations were conducted for the same company but at different manufacturing locations. Summaries of the evaluations are presented in Tables 1–3. While the size of the companies represented in this study ranged from a large multinational firm to a university research lab, it should be noted that in all cases, the observed tasks involving ENM handling typically involved only one to four employees.

Nanomaterials of Interest

The NIOSH/NTRC Field Studies Team evaluated seven ENMs that were used and/or handled during the 11 evaluations: silver nanowires (AgNW), aluminum oxide nanoparticles, silicon dioxide nanoparticles, hafnium oxide nanocrystals, titanium dioxide nanoparticles, and nanocellulose (as fibers and crystals). Of these, only titanium dioxide has a nano-specific occupational exposure limit (OEL). The NIOSH recommended exposure limit (REL) is 0.3 micrograms per cubic meter ($\mu g/m^3$) of air for ultrafine ($\leq$100 nm) titanium dioxide particles as a time-weighted average (TWA) concentration for up to 10 h per day during a 40-h workweek. No OELs have been developed for the other ENMs evaluated.

Table 1. Results of filter and surface wipe analysis

Site Code	Industrial sector	Exposure scenario(s)[A]	ENM of interest	Results		
				Mass for chemical analysis	TEM	Surface wipes
A1	Manufacturer/ Producer	manufacturing of ENM; cleaning tasks	Ag nanowire (liquid suspension)	+	+	+
A2		manufacturing of ENM[B]		–	–	+[C]
B	R&D	liquid ENM waste handling	Al_2O_3 nanoparticles; SiO_2 nanoparticles (liquid suspensions)	–	+	not collected
C1	Producer	ENM synthesis; filtration; packaging; cleaning	hafnia nanocrystals (dry powder; liquid suspension); zirconia nanocrystals present	–	+[D]	+
C2		handling of dry ENM powder; ENM synthesis; harvesting of ENM	zirconia nanocrystals (liquid suspension)	+	+	+
D1	Manufacturer	spraying/application of ENM	TiO_2 nanoparticles	+	+	not collected
D2				+	+	not collected
E	Manufacturer	release of fibers from collection tank during production process	cellulose acetate nanofibers	not collected	+	not collected
F1	Government R&D	centrifuge operation; removal of product from freeze dryer; clean up including vacuuming	cellulose nanocrystals; cellulose nanofibrils; cesium present as label on cellulose	+	+	not collected
F2		production, cutting, milling of composites		+[E]	+	not collected
G	University R&D	grinding; spray drying; particles escaping baghouse	nanocellulose	not collected	+	not collected

[A] with the exception of site A2 where no airborne emissions were detected, exposure scenarios listed are those that are associated with positive results and not necessarily inclusive of all potential/sampled scenarios.
[B] no airborne emissions detected.
[C] ENMs present on non-production surfaces.
[D] zirconia nanocrystals present.
[E] collected for cesium.
R&D: research and development; ENM: engineered nanomaterials; TEM: transmission electron microscopy.

Processes of interest

A variety of nanomaterial processes were observed during the 11 evaluations. The most common activities included enclosed synthesis reactions; mixing nanomaterial-containing powders with solvents to form slurries, suspensions, or dispersions; filtering of the aqueous suspensions through centrifuges or other processes; transferring or manual handling of the nanomaterial product; and manually cleaning equipment. Nanomaterial-containing slurries were made from either water (≥98%) or solvents. While this paper primarily focuses on ENMs in aqueous suspensions and in wet processes, some aspects of these activities begin with dry ENMs or end in a drying process. These cross-media considerations are discussed further in the limitations section.

The volumes of ENMs handled during these evaluations ranged from small (two liters or kilograms) to larger production processes involving tens of kilograms or several thousand liters of ENMs.

Sampling approach

The Field Studies Team used a combination of filter-based air sampling and surface wipe sampling, paired with DRIs for particle counting and sizing, to determine potential exposures in the 11 workplaces. The goal was to determine TWA nanomaterial exposures to workers throughout the workday[3]. Exposure assessment followed the methodology in NEAT 1.0[7, 8] and 2.0[1], using a mix of quantitative and qualitative characterization approaches. For example, chemical analysis of air filters is a quantitative approach that can be referenced against relevant OELs. In contrast, visualizing airborne particles using transmission electron microscopy (TEM) to evaluate their size, shape, and agglomeration characteristics is an example of a qualitative approach. The ENMs of interest may have distinct features that distinguish them from other types of particles. Although DRIs provide non-specific information on nanomaterials, they do provide insights into potential emission sources and areas for application of exposure controls.

Filter-based air sampling

Personal and area filter-based air samples were collected to determine the presence and quantity of ENMs. Area samples were typically collected in or near areas where ENM handling occurred. Area samples were also collected away from the ENM handling, such as offices or conference rooms, to account for non-process-based aerosols or migration of nanomaterials. Personal samples (PS) were attached to the workers' lapels.

In nine of the 11 evaluations, 112 filter-based air samples were collected for quantitative chemical analysis (for a list of methods, Table 1). Filter types used varied depending on the ENM of interest and included: mixed cellulose ester (MCE) (25 mm and 37 mm diameter, 0.8µm pore size); polyvinyl chloride (PVC) (25 mm diameter, 5μm pore size); polycarbonate (PC) (25 mm diameter, 0.8μm pore size); and quartz fiber filters (QFF) (37 mm diameter, 0.8μm pore size). In 11 evaluations 132 air samples (132 filters total including 46 PS, 61 area or source, and 25 non-process-associated filters) were qualitatively analyzed by electron microscopy. In some cases, scanning electron microscopy (SEM) was used to quickly scan samples to identify those for further analysis by TEM. In addition to counting and sizing the collected particles, electron microscopy methods can be used to determine if the elemental mass was likely from the nanomaterial of interest or from some other non-process source. Filters were analyzed by TEM (Philips CM-12 TEM with Gresham light element detector and IXRF digital imaging system) following a modified version of NIOSH Manual of Analytical Methods (NMAM) 7402[13]. The analytical modifications eliminated the steps for asbestos identification. TEM grids were prepared from each sample filter using a Jaffee wick washer technique. In general, to be acceptable for analysis, the grid should have at least 75% intact grid openings and a particle loading less than about 25% area coverage. Energy dispersive x-ray spectroscopy (EDS) was used to identify the ENM of interest for nine of the 11 sites. Bulk samples of the ENMs used at the companies were also analyzed to help identify the nanomaterial of interest on the filter-based air samples. All air sampling pumps were calibrated pre- and post-shift as prescribed for the intended method.

Air sampling via direct-reading instruments

Real-time, field-portable, DRIs were used to characterize process emissions by determining the number or mass concentration and approximate size ranges of airborne particles. These instruments are helpful in evaluating airborne particle counts during a work task or across a full-shift[14]. Different DRIs were used in tandem because each can measure particles in different size ranges. A TSI model 3007 condensation particle counter (CPC; TSI, Inc., Shoreview, MN, USA) with a size range of 10–1,000 nm was used during all 11 evaluations. The TSI model 8533 DustTrak DRX Aerosol Monitor (TSI, Inc.) was used during all 11 evaluations to simultaneously measure mass and size fraction of airborne particulate using laser light scattering. The DRX has a size range of 100–15,000 nm and aerosol mass concentration range of 1–150,000 μg/m^3. A TSI model 3330 optical particle sizer (OPS; TSI, Inc.) was used at seven of the 11 sites to measure the concentration and mass of particles. The OPS has 16 size bins with a size range of 300–1,000 nm and a concentration range of up to 3,000 particles per cubic centimeter (pt/cc). An HHPC-6 optical particle counter (OPC; ART Instruments) was used at two of the 11 sites to measure particle concentration and the size distribution at six particle size cutpoints (300 nm; 500 nm; 1,000 nm; 3,000 nm; 5,000 nm; 10,000 nm). A wide-range particle spectrometer (WPS; MSP Corporation, Inc.) was used for one of the 11 evaluations to measure the number of particles per liter of air for particle sizes from 5–10,000 nm. The variety of DRIs that were used was due to the changing availability and capability of these instruments over the 5 yr period that these evaluations occurred.

Surface wipe sampling

Surface wipe samples were collected during four of the 11 site evaluations to determine if ENMs were present in non-production areas, therefore increasing the chance of dermal and/or ingestion exposure. Disposable 10 centimeter by 10 centimeter templates were used to outline a 100 cm^2 sample area[15], and Ghost Wipe towelettes (individually wrapped and pre-moistened with deionized water as purchased from SKC, Inc.) or Whatman filters were used to collect a surface sample in accordance with NIOSH Method 9102 − Elements on Wipes[16] or OSHA Method ID-121 − Metal & Metalloid Particulates in Workplace Atmospheres (Atomic Absorption) (method used at site C2, which allows for the use of Whatman filters)[17]. A total of 92 wipe samples were collected from production and non-production areas. Wipes samples were digested with nitric acid and analyzed for elements via inductively coupled argon plasma atomic emission spectroscopy (ICP-AES).

Exposure controls

Engineering controls

Engineering controls protect workers by removing hazardous conditions or placing a barrier between the worker and the hazard. Coupled with safe handling techniques, they are an effective control strategy for protecting workers from exposure to ENMs[11]. In addition, they are often more feasible than elimination or substitution of the ENM, and are more effective than administrative or PPE control options[11]. The Field Studies Team also observed if any engineering controls were used during each of the 11 evaluations.

Personal protective equipment

PPE is traditionally considered the least desirable method in the hierarchy of controls for protecting worker health and safety. It is often used when engineering controls are not feasible or are not effective in reducing exposures to acceptable levels, or as an interim control until engineering controls are implemented[18]. PPE recommendations for ENM handling are the same as for exposures to powders, fine dusts, and aerosols, and include long sleeves, lab coats, and safety glasses. NIOSH-certified respirators have been shown to be protective for nanomaterials when properly selected and fit tested as part of a complete respiratory protection program[3, 19]. The Field Studies Team observed work practices used during the production or use of ENMs and the use of PPE, including respiratory protection (if any), during each of the 11 evaluations[1, 16]. It is also important to consider the non-nanomaterial chemicals that may be used to prepare or process ENM-containing slurries[1].

Results

Filter-based air sampling

Out of the nine evaluations where mass-based samples were collected, six had mass-based samples above both the limit of detection (LOD) and the limit of quantitation (LOQ) based on the analytical method. At site A1, the highest mass concentration of silver was 0.15 $\mu g/m^3$ (LOQ=0.11 μg/sample) from a PS during manufacturing. At site C2, the highest mass concentration of zirconia was 0.1027 mg/m^3 (LOQ=1.0 μg/sample) collected inside a fume hood during dry transfer of the material. At site D1, the highest mass concentration of elemental TiO_2 was 0.0924 mg/m^3 (LOQ=69 μg/sample) collected in the area of product application. At site D2, the highest mass concentration of TiO_2 was 0.24 mg/m^3 (LOQ=0.43 μg/sample) collected at the source. At site F1, the highest mass concentration of cesium was 11.6 $\mu g/m^3$ (LOQ=0.00056 μg/sample) collected while the centrifuge was running. Finally, at site F2, the highest mass concentration of cesium was 0.99 $\mu g/m^3$ (LOQ=0.00023 μg/sample) from a PS during production. Three sites had samples that were between the LOD and LOQ, meaning there was uncertainty in the quantitative result reported. In those cases of uncertainty, the samples were analyzed using TEM methods to determine if the ENM of interest was aerosolized.

TEM analysis positively identified structures consistent with the ENM of interest in PS samples from 10 of the 11 sites (Fig. 1). Interestingly, TEM identified zirconia nanocrystals in filters collected during the evaluation of site C1, while the ENM of interest at that site was hafnia nanocrystals, which were not identified by TEM. ENMs were identified more often in the area/source air samples (34 out of 76 total samples with ENMs of interest present; see Fig. 2), when compared to worker PS (28 out of 76 total samples with ENMs of interest present) and non-process related samples (12 out of 76 total samples with ENMs of interest present). It is important to note that at site B, ENMs of interest were identified by TEM in two filter blanks.

Direct-reading data

DRI data indicated potential releases of nanomaterials into the work environment at nine of the 11 evaluations. This was determined when particle counts and mass concentrations were elevated above the particle counts and concentrations prior to ENM activity, in process areas during activities involving nanomaterials. Of those nine sites, five concluded that the increases in particle counts were likely due to emissions of the nanomaterial. At the remaining four sites, the DRI data indicated that there was a potential for concentrations to be linked to nanoparticle emissions, but other sources could have been contributing to particle counts during the time of the activities (Fig. 3). This included incidental nanoparticles generated by the processing equipment itself (such as electrical motors). It is important to remember that the DRIs used during the evaluations are non-specific and can be subject to interference[1]. Worker activity was documented in part to help determine when these interferences may affect the interpretation of the DRI data.

The DRI data for two of 11 sites suggested that ENM activities did not contribute to particle counts and mass concentrations. Interestingly, at one of these two sites,

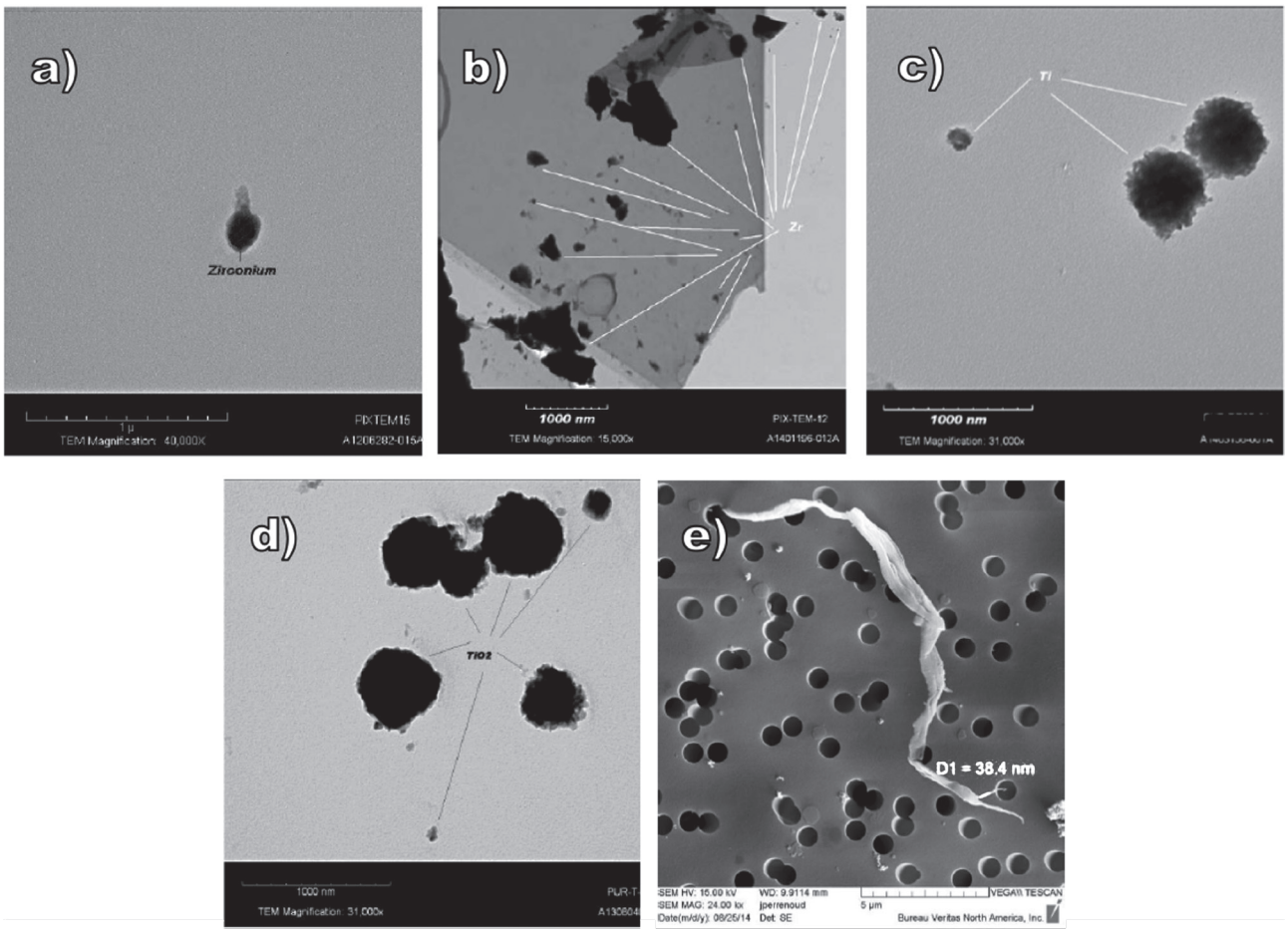

Fig. 1. Representative electron microscopy images of engineered nanomaterials (ENMs) found in worker personal samples (PS) filter samples. a–d) transmission electron microscopy (TEM) images of particles found in worker PS filters; e) scanning electron microscopy (SEM) image of fiber found in worker PS filter. a) Zirconium particle from site C1; scale bar=1 μm. b) Zirconium particles from site C2; scale bar=1,000 nm. c) Titanium particles from site D1; scale bar=1,000 nm. d) Titanium dioxide particles from site D2; scale bar=1,000 nm. e) Nanocellulose fiber from site G; scale bar=5 μm.

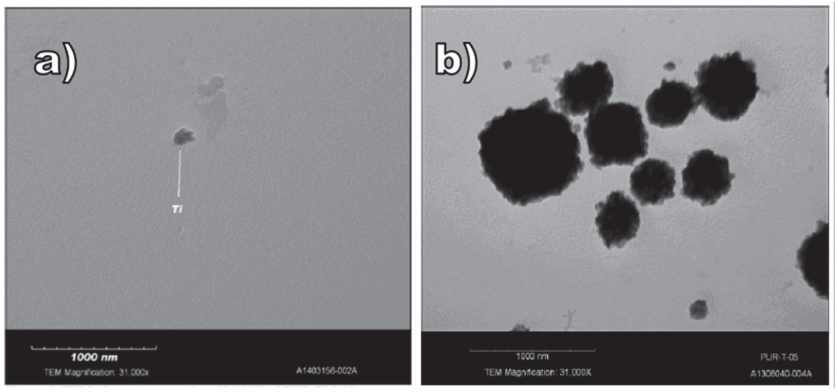

Fig. 2. Representative electron microscopy images of engineered nanomaterials (ENMs) found in area/source filter samples. a) transmission electron microscopy (TEM) image of titanium particle found in source filter sample during product application from site D1; scale bar=1,000 nm. b) TEM image of titanium dioxide particles found in area filter sample during product application from site D2; scale bar=1,000 nm.

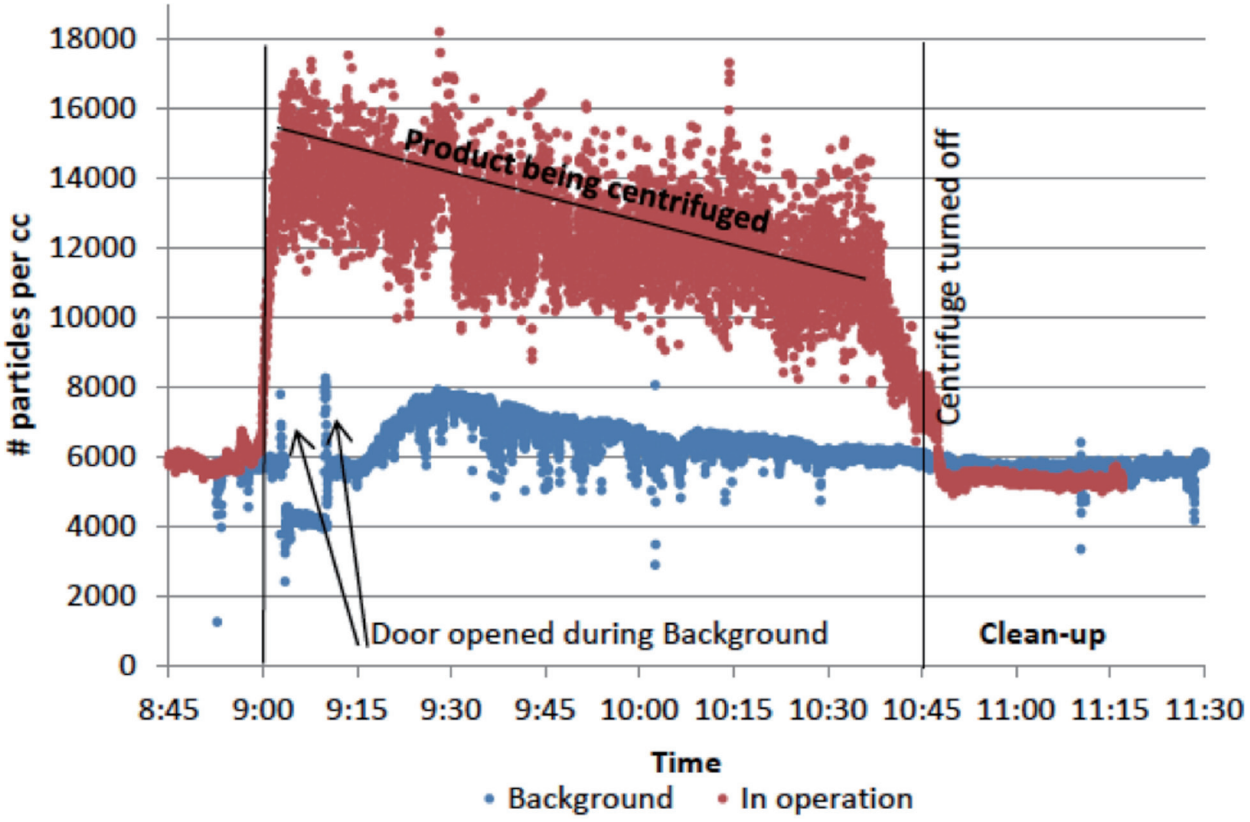

Fig. 3. Direct reading instrument (DRI) particle concentration data before, during, and after product centrifugation.
Background samples were collected at site F1 with the condensation particle counter (CPC) inside the centrifuge cabinet while the centrifuge was not in operation. Sampling also was performed during centrifugation of product on day two. As indicated in the figure, the particle count while the centrifuge was in operation was higher than the background. The average background inside the closed cabinet was 6,192 particles per cubic centimeter (p/cc) averaged over 7 h and 13 min. The average concentration within the cabinet during operation was 10,169 p/cc over 1 h and 48 min, indicating the operating sample was more variable than the background sample collected. The peak particle count average started at 13,000 p/cc and decreased to 11,000 p/cc over 1 h and 34 min. It is important to note that the upper concentration limit for the CPC is 100,000 p/cc, after which counting errors are more likely to occur. The particle counts monitored during the site visit did not exceed the instrument limits.

the ENM of interest was positively identified in the air samples analyzed under TEM, and, at the other site, the ENM of interest was positively identified in wipe samples via ICP-AES. This indicates that DRIs may be the least sensitive instrument for detecting ENM emissions, and may underestimate particle counts.

Surface wipe sampling

A total of 92 wipe samples were collected from process and non-process areas at four sites. Results from surface wipe sampling are included in Table 1. Surface wipe sampling results indicated ENMs were present on surfaces in both processing and non-processing areas at all four sites sampled (ENMs identified in 57 out of 92 total samples).

Engineering controls

For nine out of the 11 evaluations, some form of process-associated engineering control, such as a closed system design, vented cabinet, or a cleanroom, was used to control ENM emissions (Table 2). The most commonly identified control measures in the evaluations were the use of a closed system or process (seven of 11 evaluations), laboratory fume hood (four of 11 evaluations), or a cleanroom (three of 11 evaluations). Some of the sites used a closed production system, such as a synthesis reaction chamber or a sealed vessel during batch mixing. However, these still required the handling of ENMs in a fume hood either prior to or after completion of the production process. The remaining engineering controls observed included local exhaust ventilation systems at two of 11 sites, and the use of an anteroom (one of 11 evaluations)

Table 2. Engineering controls used

Site code	Industrial sector	Exposure scenario(s)[A]	ENM of interest	Engineering controls utilized					
				Fume hood	Local exhaust ventilation	Clean-room	Ante-room	Sticky mat	Other
A1	Manufacturer/ Producer	manufacturing of ENM; cleaning tasks	Ag nanowire (liquid suspension)	√	√	√	–	–	–
A2		manufacturing of ENM[B]		–	–	√	√	√	top-down laminar flow hood
B	R&D	liquid ENM waste handling	Al_2O_3 nanoparticles; SiO_2 nanoparticles (liquid suspensions)	–	–	√	–	√	enclosed process; vented cabinet
C1	Producer	ENM synthesis; filtration; packaging; cleaning	hafnia nanocrystals (dry powder; liquid suspension); zirconia nanocrystals present	√	–	–	–	–	closed system
C2		handling of dry ENM powder; ENM synthesis; harvesting of ENM	zirconia nanocrystals (liquid suspension)	√	√	–	–	–	closed system
D1 D2[C]	Manufacturer	spraying/application of ENM	TiO_2 nanoparticles	–	–	–	–	–	–
E	Manufacturer	release of fibers from collection tank during production process	cellulose acetate nanofibers	√	√	–	–	–	closed system
F1	Government R&D	centrifuge operation; removal of product from freeze dryer; clean up including vacuuming	cellulose nanocrystals; cellulose nanofibrils; cesium present as label on cellulose	–	–	–	–	–	closed system; large fan to move airborne particulate away from worker
F2		production, cutting, milling of composites		–	–	–	–	–	closed system
G	University R&D	grinding; spray drying; particles escaping baghouse	nanocellulose	–	–	–	–	–	closed system; baghouse

[A] with the exception of site A2 where no airborne emissions were detected, exposure scenarios listed are those that are associated with positive results and not necessarily inclusive of all potential/sampled scenarios.
[B] note that no airborne emissions detected.
[C] D2 used an outdoor process (no engineering controls utilized).
ENM: engineered nanomaterials; R&D: research and development.

and sticky mats (two of 11 evaluations) to provide a buffer from the processing area to the non-processing area and to prevent migration of ENMs on surfaces.

The two evaluations that did not have process-associated engineering controls were aerosol spraying applications, with one of these occurring outdoors. TEM analysis positively identified ENMs of interest on filter samples collected from worker PS, process and non-process areas during both of these evaluations.

Personal Protective Equipment (PPE)

Every site required PPE to be worn during certain tasks of the observed processes (Table 3). Required PPE observed at the sites included respirators, safety glasses, nitrile gloves, and laboratory coats. Nine sites required the use of laboratory coats or long sleeves, and/or cleanroom garments. Regarding eye protection, eight sites required the use of safety glasses and five required a face shield. In four of the 11 evaluations more than one type of eye protection was required (for example, both safety glasses and a face shield). Two sites did not require some form of

Table 3. Personal protective equipment (PPE) used

Site code	Industrial sector	Exposure scenario(s)[A]	ENM of interest	PPE utilized					
				Respiratory protection	Gloves	Safety glasses	Lab coats[B]	Face shield	Other
A1	Manufacturer/ Producer	manufacturing of ENM; cleaning tasks	Ag nanowire (liquid suspension)	√[C]	√	√	√	–	–
A2		manufacturing of ENM[D]		√	√	√	√	√	–
B	R&D	liquid ENM waste handling	Al_2O_3 nanoparticles; SiO_2 nanoparticles (liquid suspensions)	–	√	√	√	√	hard hat
C1	Producer	ENM synthesis; filtration; packaging; cleaning	hafnia nanocrystals (dry powder; liquid suspension); zirconia nanocrystals present	√	√	–	√	√	–
C2		handling of dry ENM powder; ENM synthesis; harvesting of ENM	zirconia nanocrystals (liquid suspension)	√	√	–	√	–	–
D1	Manufacturer	spraying/application of ENM	TiO_2 nanoparticles	√	–	–	√	–	–
D2				√	√	√	√	–	–
E	Manufacturer	release of fibers from collection tank during production process	cellulose acetate nanofibers	√	√	√	–	–	–
F1	Government R&D	centrifuge operation; removal of product from freeze dryer; clean up including vacuuming	cellulose nanocrystals; cellulose nanofibrils; cesium present as label on cellulose	√	√	√	√	√	hearing protection; splash apron
F2		production, cutting, milling of composites		√	√	√	√	√	hearing protection; splash apron; hard hat
G	University R&D	grinding; spray drying; particles escaping baghouse	nanocellulose	√	√	√	–	–	hearing protection; steel-toe boots

[A] with the exception of site A2 where no airborne emissions were detected, exposure scenarios listed are those that are associated with positive results and not necessarily inclusive of all potential/sampled scenarios.

[B] also includes long sleeves and cleanroom garments.

[C] voluntary use of N95 respirators.

[D] note that no airborne emissions detected.

ENM: engineered nanomaterials; R&D: research and development.

eye protection. Nitrile gloves were worn during nine of 11 evaluations to prevent dermal contact. An aerosol spraying activity was observed during the two evaluations where glove protection was not required.

Along with the commonly required safety glasses, nitrile gloves, and laboratory coats, respiratory protection was used at 10 out of 11 sites, including one where wearing a respirator was voluntary (site A1). Respirators were mostly worn during production-related tasks when the potential for generating particles or aerosols was likely to occur. The types of respirators used included N95 and P100 filtering facepiece respirators, and half-mask and full facepiece respirators. Other PPE used at the sites, but not specifically for ENM protection, included hearing protection (three of 11 sites), splash aprons (two of 11 sites), steel-toe boots (one of 11 sites), and hard hats (two of 11 sites).

Discussion

The number of filter samples collected at each site depended on a few factors. First, for all 11 evaluations, only a subset of employees were observed handling ENMs. ENMs were identified most often in the area/source air samples, but were also identified in PS and non-process area samples (Figs. 1 and 2). For all four

evaluations where surface wipe samples were collected, ENMs of interest were identified, including in non-process areas. Identifying ENMs in the non-process area samples indicates that there is migration of the nanomaterial out of processing areas and into the non-processing areas.

While DRIs are useful in measuring nanoscale particulate near nanomaterial processes, determining if materials are migrating from process to non-processing areas[11] and evaluating the effectiveness of engineering controls, they have limitations. DRIs provide time-resolved information on nanoparticle concentrations not available from filter-based samples. This type of data, along with observations, helps the researcher better determine if the particle concentrations measured are likely to be process-derived. However, because of the background of ultrafine particles in the ambient environment, an increase in particle concentration over the background, as well as an elemental analysis of filter-based samples, is necessary to more definitively indicate the potential for exposure[20]. DRIs are most informative when concentrations of ENMs are high enough that you can distinguish between background particles and potential process emissions.

Despite the use of engineering controls, air filter samples showed the presence of the nanomaterial of interest at all sites (Table 1). However, many of the task-based samples were collected during exposure scenarios expected to result in release of nanomaterials, including collection of dry materials, harvesting, and equipment cleaning, spraying of nanomaterial suspensions, and cutting/grinding of nanocomposites.

As mentioned in the PPE section, all sites required employees to wear PPE during nanomaterial handling. However, it was frequently observed that sites lacked either a formal administrative program or standard operating procedures for informing employees of the required PPE to be worn during nanomaterial handling activities. Wipe samples showing the presence of ENMs on surfaces both in and outside of the process areas also indicate the need for improvement in glove use, hand hygiene practices, and housekeeping (Table 1).

Conclusion

While handling wetted ENMs versus dry likely reduced the potential for worker exposure at these facilities, potential exposures to ENMs were still found. Mass-based air samples collected at nearly every site visited provided evidence of ENMs of interest, and electron microscopy confirmed their identification. However, in some instances, detection by mass-based analysis, electron microscopy, or by DRIs was not consistent, even within the sampling sites. This emphasizes the importance of using multiple sampling strategies whenever possible to identify potential exposures. Airborne exposures to ENMs identified during these evaluations were associated with the absence or poor design of engineering controls, and a lack of established and enforced administrative controls. The recommendations provided by the NIOSH/NTRC Field Studies Team could reduce or eliminate the potential for exposures to engineered or incidental nanomaterials. NIOSH recommends following the hierarchy of controls when working with nanomaterials, and when possible, using a wetted or slurry form of the materials as opposed to dry powders[11].

Recommendations

The recommendations below are based on the findings from our evaluations. The list order is based on a well-accepted approach called the "hierarchy of controls". The hierarchy of controls groups actions by their likely effectiveness in reducing or removing hazards. In most cases, the preferred approach is to eliminate hazardous materials or processes and install engineering controls to reduce exposure or shield employees. Until such controls are in place, or if they are not effective or feasible, administrative measures and PPE might be needed.

1. Use ventilation to capture or contain nanomaterials. For example, installing or redesigning local exhaust ventilation systems to capture nanomaterial emissions at their point of generation will reduce worker exposures. Another example is maintaining nanomaterial processing areas under negative air pressure to reduce potential migration of nanomaterials to non-process areas, such as employee breakrooms and offices.

2. Develop (or update) a written PPE program. Although all the sites visited required employees to wear PPE during nanomaterial handling, some sites did not have a written program, and there was inconsistency between sites on the required PPE. For example, at two sites, employees that handled nanomaterials were not required to use nitrile gloves. The NIOSH/NTRC Field Studies Team recommends wearing gloves, gauntlets, and/or laboratory clothing or coats to protect the skin from dermal exposure to ENMs. The resistance of the PPE to the nanomaterial and any other chemicals or liquids that may come in contact with the PPE should be taken into consideration[21].

3. Develop a written housekeeping program. Some sites did not have written programs or a scheduled frequency for housekeeping in the nanomaterial processing areas. Periodic surface sampling in non-process areas may also

be useful to evaluate the efficacy of the housekeeping.

4. Develop employee work practices that reduce the unnecessary exposure to nanomaterials. For example, sticky floor mats can reduce migration of nanomaterial from process to non-process areas. Establishing and/or enforcing hand washing, PPE donning and doffing procedures, and not wearing potentially contaminated PPE outside of process areas can reduce unnecessary exposure to nanomaterials.

Limitations

While these sites did handle wet engineered nanomaterials or use a wet process with engineered nanomaterials, there were several sites that also either handled or processed dry nanomaterials, or dried the wetted nanomaterial. This sometimes occurred during site evaluation. In most of these cases, air sampling and direct-reading instrumentation could not distinguish whether wetted or dry nanomaterials processes were the major contributor to airborne concentrations. For instance, most of the filter-based sampling done in accordance with the NEAT 2.0[1)] methodology were integrated samples taken over the full-shift, and were not tasked based. As a result, any positively identified ENMs of interest in full-shift filter samples analyzed via TEM could not be tied to a specific work activity. For example, if a company utilized both wet and dry nanomaterials, or had a closed wet nanomaterial activity and later processed nanomaterial in a dry form, the specific activity that likely contributed to a release of the nanomaterial could not be distinguished.

Additionally, often only one day of sampling was performed, depending on the nanomaterial process (i.e., all work completed in one day), thereby reducing the number of filter samples that could be collected at those sites versus sites with sampling performed over the course of two or more days.

A limitation unique to site B was the presence of ENMs of interest (silica and alumina nanoparticles) on MCE filter blanks that were analyzed by TEM[12)]. Because of this blank contamination, the Field Studies Team recommended that different filter media—e.g., polycarbonate (PC)—be used for future evaluations, as they are typically contaminant free. Alternatively, airborne silica and/or alumina nanoparticles could be collected directly onto TEM grids using an electrostatic precipitator (ESP) or thermophoretic sampler (TPS), thus eliminating the need for a sample filter.

Lastly, for many ENMs, quantitative methods via chemical analysis are not available. Due to this limitation, we report here areas where ENMs are found and therefore do not quantify or qualify high or low ENM contamination. Additionally, it is important to note that this report encompasses 11 site evaluations conducted by different NIOSH researchers over the course of five years and so this accounts for some discrepancies in the methods and instruments used for data collection and analysis.

Disclaimer

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Conflict of Interest

The authors declare no conflicts of interest.

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