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EXPOSURE TO CARBON NANOTUBE MATERIAL: AEROSOL RELEASE DURING THE HANDLING OF UNREFINED SINGLE-WALLED CARBON NANOTUBE MATERIAL

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Carbon nanotubes represent a relatively recently discovered allotrope of carbon that exhibits unique properties. While commercial interest in the material is leading to the development of mass production and handling facilities, little is known of the risk associated with exposure. In a two-part study, preliminary investigations have been carried out into the potential exposure routes and toxicity of single-walled carbon nanotube material (SWCNT)—a specific form of the allotrope. The material is characterized by bundles of fibrous carbon molecules that may be a few nanometers in diameter, but micrometers in length. The two production processes investigated use-transition metal catalysts, leading to the inclusion of nanometer-scale metallic particles within unrefined SWCNT material. A laboratory-based study was undertaken to evaluate the physical nature of the aerosol formed from SWCNT during mechanical agitation. This was complemented by a field study in which airborne and dermal exposure to SWCNT was investigated while handling unrefined material. Although laboratory studies indicated that with sufficient agitation, unrefined SWCNT material can release fine particles into the air, concentrations generated while handling material in the field were very low. Estimates of the airborne concentration of nanotube material generated during handling suggest that concentrations were lower than 53 g/m^3 in all cases. Glove deposits of SWCNT during handling were estimated at between 0.2 mg and 6 mg per hand.

Since the discovery of the spherical molecule C_{60} (buckminsterfullerene or buckyballs) in the 1980s (Kroto et al., 1985), there has been extensive research into the properties and applications of new forms of carbon. In recent years

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a specific atomic configuration resulting in long tubelike molecules of carbon (carbon nanotubes) has been intensely investigated. In their purest form, carbon nanotubes are a single layer of carbon atoms in a cylindrical arrangement, resulting in individual carbon structures around 1.5 nm in diameter, and up to a millimeter or more in length. In this form, the structures are generally referred to as single-walled carbon nanotubes (SWCNTs). Carbon nanotubes may also form as multiple concentric tubes, having diameters significantly greater than SWCNTs; each form has unique properties, and generation of specific nanotube types is a key area of current research.

While commercial mass production of carbon nanotubes is still at an early stage, the predicted properties of the new products that will use the material are sufficiently attractive to support an intense research and commercialization agenda. Nanotubes exhibit great tensile strength, high conductivity (in some atomic arrangements), high surface area, unique electronic properties, and potentially high molecular adsorption capacity. The potential for this material to be used in such fields as novel electronic devices, high-strength materials, reinforced rods, quantum wires, and mechanical memory has been widely discussed (Subramoney, 1998; Sinnott & Andrews, 2001). Development of new technologies and devices using nanotubes is currently constrained only by the limited ability of manufacturers to produce large quantities of uniform and well-characterized nanotube material. As a result, there is considerable effort at present to refine and scale up manufacturing processes.

Against this background, very little is known of the potential toxicity of the material, or how likely inhalation and dermal exposure will be during the handling and manufacturing process. The extreme aspect ratio of individual nanotubes together with their potentially low solubility in the lungs may lead to toxic mechanisms analogous to those observed with other fibrous particles. SWCNT production methods usually lead to the generation of convoluted bundles of nanotubes (nanoropes), generally from 20 to 50 nm in diameter, which in turn form complex clumps and agglomerates with other nanoropes and other carbonaceous and catalyst materials that are present. The health hazard posed by these clumps will depend in part on (1) the ease with which they become airborne, (2) the size of the clumps generated, (3) the propensity for smaller collections of nanoropes to dissociate from the clumps following lung deposition, and (4) the likelihood of individual nanotubes detaching from the ropes in the lung lining fluid. The physical nature of the nanotubes and nanoropes may also lead to some degree of dermal penetration, following deposition on exposed skin, and provide a second exposure route of concern. The potential hazard from dermal and inhalation exposure is further compounded by the presence of small particles of transition metal catalyst (typically around 5 nm in diameter) in the unprocessed material from some manufacturing processes. Although these particles are invariably coated by a layer of carbon, little is known of whether this shell is likely to be stripped away during phagocytosis and/or other processes within the body, and how the size of the particles will affect their toxicity.

To begin addressing some of these issues, research has been carried out into the potential for unprocessed SWCNT material to release particles into the air while being handled, and into the cytotoxicity of the material. In this article, results are presented on measurements of SWCNT aerosol concentration and size distribution following generation in the laboratory and during the handling of unrefined material in the field. In a companion article, data are presented on human keratinocyte cell response to unrefined SWCNT material (Shvedova et al., 2003). Together, these studies provide a preliminary indication of the health hazard and health risk associated with unrefined SWCNT material.

METHODS

Production Processes

One of the principal techniques for nanotube production is to use a transition metal particle as a catalyst in the presence of atomic carbon at high temperature and/or pressure. The two techniques investigated here are the laser ablation process and the high-pressure carbon monoxide (HiPCO) process (Bronikowski et al., 2001). The laser ablation process involves formation of a carbon plug, which contains an intimate mixture of catalyst (usually Fe and/or Ni), and its ablation by laser in an inert gas stream. The resulting product is collected downstream on a coldfinger trap. After ablation of the plug is complete, the plug must be replaced. This approach is inherently a batch process. The collected product is usually fairly compact and the fibers are relatively difficult to separate.

The HiPCO process involves introduction of ultrafine iron (Fe) or a combination of Fe and nickel (Ni) metal catalyst particles into a high-pressure/high-temperature CO gas stream. The product is collected onto a filter and, since it is produced in the gas phase, forms a much-expanded mat of fibers. The bulk density of the collected material is on the order of $1000\,g/m^3$. Both the laser ablation material and the HiPCO raw products can contain up to 30% metal catalyst by mass. During secondary processing, the catalyst is removed to the extent possible; however, much of this metal is completely or partially encased in carbon, making complete removal difficult without destroying the nanotubes. Thus, there is a trade-off in catalyst removal versus amount of purified nanotube product.

Both processes lead to the production of a very-low-density material comprised of nanometer-diameter catalyst metal particles, carbon nanotubes, and other forms of elemental carbon. This material is manually handled prior to further processing, and has the potential to release SWCNT particles into the air as an aerosol.

Laboratory Measurements

Laboratory measurements on the SWCNT material had two aims: to qualitatively assess the propensity for aerosol particles to be released during agitation, and to measure the size of particles released into the air. Because SWCNT is a

new and unique material, it was found that new methods of characterizing the aerosol formed from the material were required. Samples of unprocessed SWCNT material were agitated under controlled conditions, and the size distribution and concentration of the resulting aerosol were characterized. Generated aerosol was directly sampled by three sizing instruments operated in parallel, to give the size distribution between 4 nm and 20 μm: Electrical mobility diameter (d_m) of particles smaller than 0.7 μm was sized using two scanning mobility particle sizers (SMPS). The smallest particles (4.22 nm < d_m < 100 nm) were characterized using an SMPS configured with a nano differential mobility analyzer (DMA) (Electrostatic Classifier, model 3080, using a Nano DMA, model 3085) and a condensation particle counter (CPC; model 3022A, TSI, Inc., St. Paul, MN). Larger particles (69.8 nm < d_m < 777 nm) were characterized by using an SMPS configured with a Long DMA (DMA model 3934 and CPC model 3022A, TSI, Inc.,). The largest particles (523 nm < aerodynamic diameter [d_{ae}] < 20.5 μm) were characterized using an aerodynamic particle sizer (APS) (model 3320, TSI, Inc.,).

A number of conventional methods were investigated to form an aerosol from the bulk SWCNT material. Generation using a two-component fluidized bed was found to be the most promising approach, although the aerosol associated with the beads forming the bed dominated the aerosol when using airflow to form the bed. To increase the energy within the fluidized bed, thus potentially increasing the relative aerosol concentration associated with the SWCNTs, a standard laboratory vortex shaker was used to fluidize the beads and nanotubes. SWCNT material was mixed with a small quantity of bronze beads (approximately 70 μm in diameter), placed in a centrifuge tube, and agitated using a vortex shaker (Vortex Genie, Cole Parmer, Vernon Hills, IL). On agitation, the bronze beads formed a fluidized bed, leading to SWCNT aerosol generation through mechanical collisions with the beads. HEPA-filtered air was passed through the tube, and the aerosol was characterized using the parallel instrument array. Background subtraction of the aerosol size distribution associated with the beads alone indicated a measurable component arising from the SWCNT. However, it wasn't clear whether the background aerosol associated with the beads increased following the introduction of SWCNT material. As this generation technique is particularly suited to dense powders, it was used with SWCNT derived from laser ablation. Forty milligrams of laser-ablation SWCNT was placed in the generator at 55% of maximum agitation, and particles between 12 nm and 10 μm measured using a single SMPS and APS in parallel.

To remove the uncertainty associated with the bronze beads, and to more closely simulate handling of the unprocessed SWCNT material, 15.5 mg of SWCNT material was placed in the vortex generator without the beads, and aerosol measurements were made at various levels of agitation. Only HiPCO SWCNT material was used in this generator; the sample of laser-ablation material proved to be too compacted to lead to aerosol release without the addition of the bronze beads. Measurements were made of the aerosol size

distribution between 4 nm and 20 μm, without agitation, and subsequently at increasingly higher levels of agitation. At each level of agitation, three or more replicate measurements of the size distribution were made in series. The mechanical energy within the SWCNT associated with the agitation process was dependent on a large number of parameters and was not quantifiable. The aim was primarily to gain an indication of the propensity of the bulk SWCNT to release particles on agitation, and the size of these particles; agitation level was therefore qualitatively characterized using the stirring intensity settings on the vortex shaker, expressed as a percentage of maximum agitation. This approach allowed a qualitative assessment of the propensity of the SWCNT to release particles into the air on agitation. Measurement of the aerosol size distribution enabled a quantitative assessment of the likelihood of particles within different size ranges being released.

An aerosol of fumed aluminum oxide (aluminium oxide C, Degussa Hüls, Germany) was generated using the two-component vortex generator to provide a reference point for measured generation rates, using a widely available material. Fumed alumina is a low-bulk-density material with a fluffy appearance. It is comprised of large agglomerates of primary particles of the order of nanometers in diameter. While still differing markedly from the SWCNT material, it was considered to be representative of a family of ultrafine powders widely used in industry that would be expected to show similar generation properties to the unprocessed nanotubes. Generation was carried out using a volume of fumed alumina similar to the SWCNT in previous measurements.

Field Measurements

Measurements of unprocessed airborne nanotube exposures were made at four facilities using either the HiPCO or laser ablation production methods, where SWCNT material was removed from production vessels and handled prior to processing. Background aerosol within the environment where the nanotube powder was being handled was reduced using a clean air enclosure. An enclosure (approximately $5 \times 6 \times 7$ ft high) was constructed at each site using 1½-in plastic plumbing pipe as a framework and polyethylene plastic sheet as a covering. This was then sealed, except for a flap, which allowed entrance to the enclosure. Particle-free air was pushed into the enclosure using a high-volume sampling blower with a HEPA filter downstream of the blower. The resulting concentration of airborne particles larger than 10 nm inside the enclosure was reduced from several thousand particles per cubic centimeter to below 50 particles/cm^3 in about 30 min (as measured using a portable condensation particle counter [CPC], model 3007, TSI, Inc., St. Paul, MN). At each facility, the enclosure was sufficiently large to allow workers to remove the SWCNT material without hindrance.

The air inside the enclosure was monitored using the 3007 CPC and a size-discriminating optical particle counter (OPC) (Portable Dust Monitor series 1.100, GRIMM Technologies, Douglasville, GA). The CPC allowed the number concentration of airborne particles between approximately 0.01 μm

and 1 μm to be measured. Both the 3007 CPC and Grimm OPC were placed in a fixed location near the person who handled the nanotube powder (designated *the worker* in the discussion that follows).

Filter samples were also taken within the enclosure. A personal sampler was placed on the worker, on a second person inside the enclosure who was monitoring the operation, and at a fixed site inside and near the wall of the enclosure. The personal samples were collected with 25-mm-diameter open-faced conductive filter cassettes, using methylcellulose ester filters for metals (primarily iron) analysis (NIOSH, 1994). Some of the fixed location cassettes were loaded with 25-mm polycarbonate filters for analysis, using a scanning electron microscope (SEM).

Potential dermal loading was estimated by placing cotton gloves over the rubber gloves normally used by the worker. These were removed immediately after handling the nanotubes and placed in separate sealed plastic bags.

Sampling Locations *Laser ablation facility at NASA* Sampling was carried out during the removal of nanotube material from an experimental laser ablation facility at the National Aeronautics and Space Administration (NASA), Johnson Space Center (JSC), Houston, Texas. A clean-air enclosure was constructed around the entrance to the production vessel and sampling carried out during material removal and cleanup. A vacuum cleaner, fitted with a HEPA filter, was used for cleanup in the enclosure. The filter was later discovered to have been incorrectly fitted, which led to resuspension of dust when the vacuum cleaner was used.

HiPCO process removal simulation at Rice University The production schedule at Rice University, Houston, Texas, did not allow for direct monitoring of material removal from the production facility. Removal was therefore simulated by pouring previously generated material between two buckets normally used for collecting the nanotubes. Sampling occurred while one bucket was filled with material; while the material was poured between the buckets several times; and afterward, during cleanup with a shop vacuum cleaner (low-efficiency filter).

Laser ablation process removal simulation at CNI Sampling was carried out using material produced by laser ablation and the HiPCO process at Carbon Nanotechnologies, Inc. (CNI), Houston, Texas. Due to space constraints, the collection chamber for the laser process was removed from the production system and placed into the clean-air enclosure for powder removal. Sampling was then carried out while the chamber was opened, the material removed, and the area cleaned. A vacuum cleaner was used during cleanup, but was positioned outside the enclosure with the hose extending into the enclosure.

HiPCO process at CNI As in the case of the laser-ablation material at CNI, the collection chamber from the HiPCO process was removed from the production system and placed into the clean-air enclosure for powder removal. Sampling was carried out during the following tasks: opening the chamber, removing the material, cleaning the area, and dismantling the enclosure.

A vacuum cleaner was used for this cleanup, but the vacuum unit was placed outside the enclosure to prevent resuspension of the dust, and the hose extended into the enclosure.

RESULTS

Laboratory Measurements

Aerosol generation using the two-component vortex shaker fluidized bed led to a measurable aerosol associated with the SWCNT. Figure 1 shows the resulting aerosol distributions from agitating a small quantity of laser ablation SWCNT material over time, after subtracting the background distribution associated with the bronze beads. Particles below 777 nm are characterized by their electrical mobility diameter (using the SMPS), defined as the diameter of a spherical, singly charged particle having the same velocity as the particle in question in an electrostatic field. Above 777 nm, particles are characterized by their aerodynamic diameter using the APS (assuming a nominal particle density of 1000 kg/m^3), defined as the diameter of a spherical particle with a density of 1000 kg/m^3 (unit density) having the same settling velocity as the particle in question. Without detailed information on the shape and density of the SWCNT particles, measured diameter in neither of these regimes can be directly associated with physical particle diameter. During the generation process, nanotube clumps of the order of millimeters in diameter visibly became

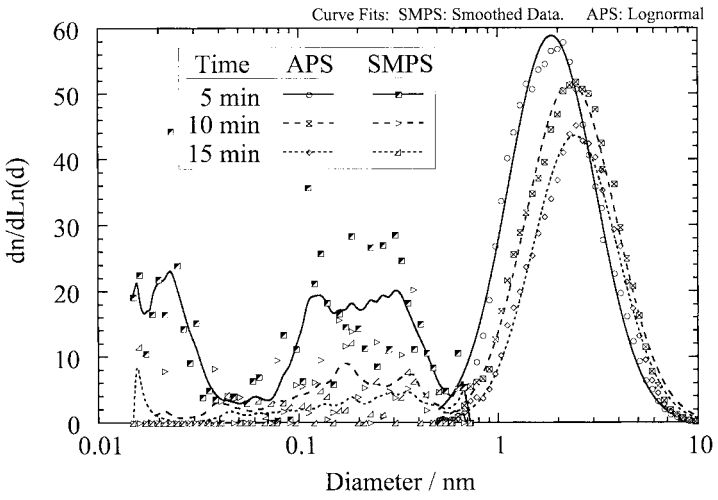

FIGURE 1. Single-walled carbon nanotube aerosol generated using a two-component vortex shaker fluidized bed, plotted as particle concentration as a function of diameter (arbitrary units). SWCNT source: laser-ablation process. Background aerosol associated with the beads alone has been subtracted from the distributions. Times refer to the end of each sampling period. Sampling was started 10 s after agitation was initiated.

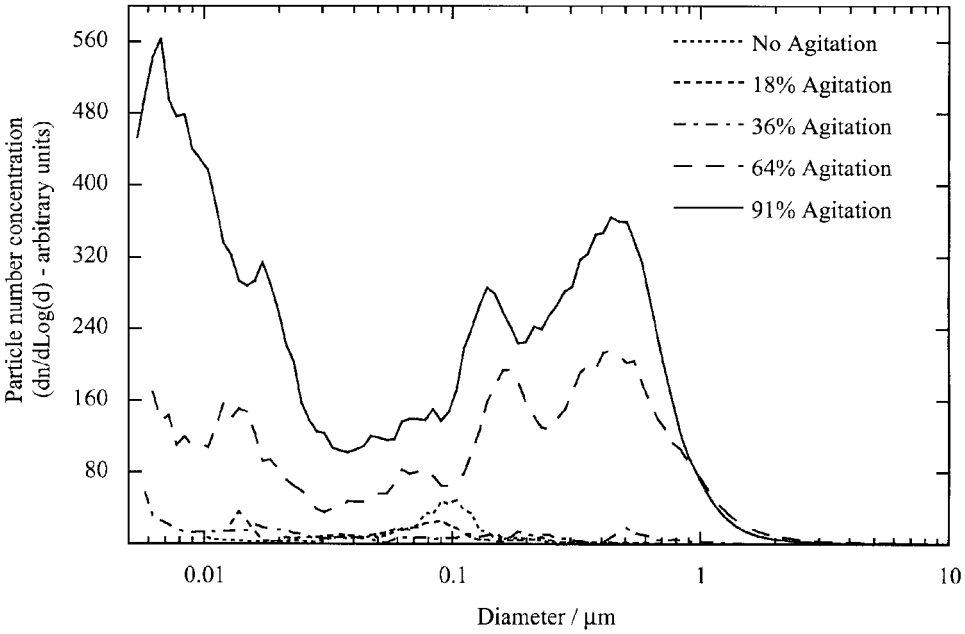

FIGURE 2. Aerosol generated from HiPCO SWCNT using a single-component vortex shaker fluidized-bed generation, plotted as particle number concentration as a function of diameter (arbitrary units). Each plot represents the average of three or more size distribution measurements. Data have been smoothed for clarity.

airborne. These particles will not have been counted by the instruments used to measure the aerosol size distribution. However, qualitatively, the number concentration of these macro-scale particles was over an order of magnitude lower than those associated with detected micrometer-scale particles and below. The concentration of SWCNT aerosol below 0.5 μm was seen to decrease rapidly over time, indicating a small component of the nanotube material was readily aerosolized initially. A second experiment using less nanotube material resulted in no detectable particles generated below 100 nm after the initial agitation period. For comparison purposes, a fumed alumina aerosol was generated using the same vortex generator to provide a reference against which the nanotube aerosol concentration could be qualitatively evaluated. Measurements indicated generation rates of particles from the nanotube material to be approximately two orders of magnitude below that for fumed alumina for similar volumes of material at the same level of agitation.

Generation of HiPCO material in the single component vortex shaker fluidized bed led to measurable aerosol concentrations (Figure 2). With no agitation, particles around 0.1 μm in diameter appear to be released from the SWCNT material, probably as a result of the airflow across the powder. Increasing the agitation led to a reduction in generation rate for particles around 0.1 μm in diameter and an increase in the number of nanometer-sized

particles released. At the highest level of agitation, the measured generation rate was substantially higher than at previous agitation levels, and a clear bimodal distribution emerged (Figure 2).

Field Measurements

Direct-Reading Instruments Measurements using the direct-reading instruments provided information on particle number concentration between 10 nm and 1 μm (3007 CPC), particle size distribution above 0.3 μm (Grimm OPC), and an estimate of aerosol mass concentration (Grimm OPC). In the case of the last, a nominal particle density of 1000 kg/m^3 was assumed. Until a clear measurement of the relationship between optical diameter and mass is derived for nanotube material, these mass data should be treated with caution.

The direct-reading information from the 3007 CPC and the Grimm OPC were combined to estimate the particle concentration as a function of time throughout the sampling period. Figure 3 presents a simplified representation of the data, showing summed mass and number concentration as a function of

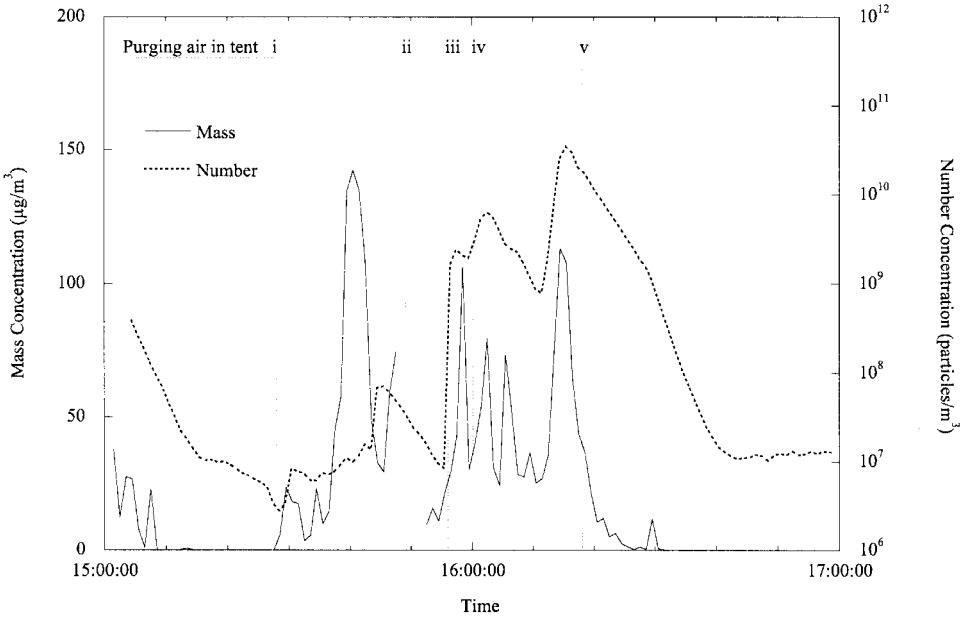

FIGURE 3. Aerosol mass and number concentration with time for each facility where sampling took place. (a) NASA Johnson Space Center (laser ablation). Events: i. Entering tent. ii. Removing SWCNT. iii. Using vacuum cleaner to remove SWCNT. iv. Cleaning inside tent, using vacuum. v. Leaving tent. (b) Rice University (HiPCO material). Events: i. Entering tent. ii. Emptying SWCNT into bucket. iii. Tipping SWCNT from bucket to bucket. iv. Scooping spilt SWCNT off table. v. Cleaning tent with vacuum cleaner (vacuum inside tent). vi. Further cleanup and PPE removal. vii. Leaving tent. (c) CNI (laser ablation). Events: i. Entering tent. ii. Removing SWCNT. iii. Using vacuum cleaner in short bursts (main unit outside tent). iv. Cleaning inside tent, and dismantling tent. (d) CNI (HiPCO). Events: i. Entering tent. ii. Removing SWCNT. iii. Lot of airborne SWCNT clumps visible in tent. iv. Cleaning inside tent, using vacuum (main unit outside tent).

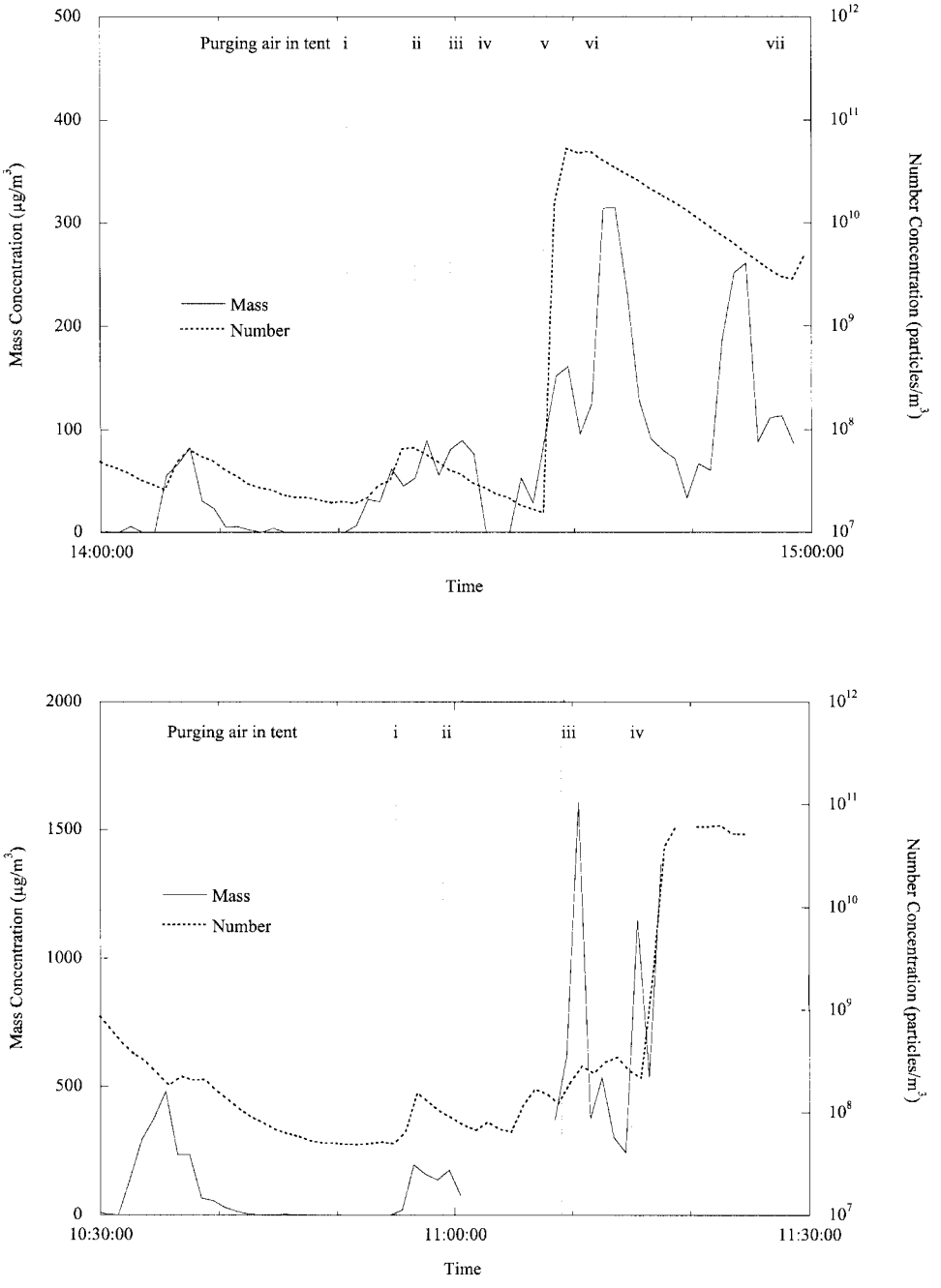

FIGURE 3. (*Continued*)

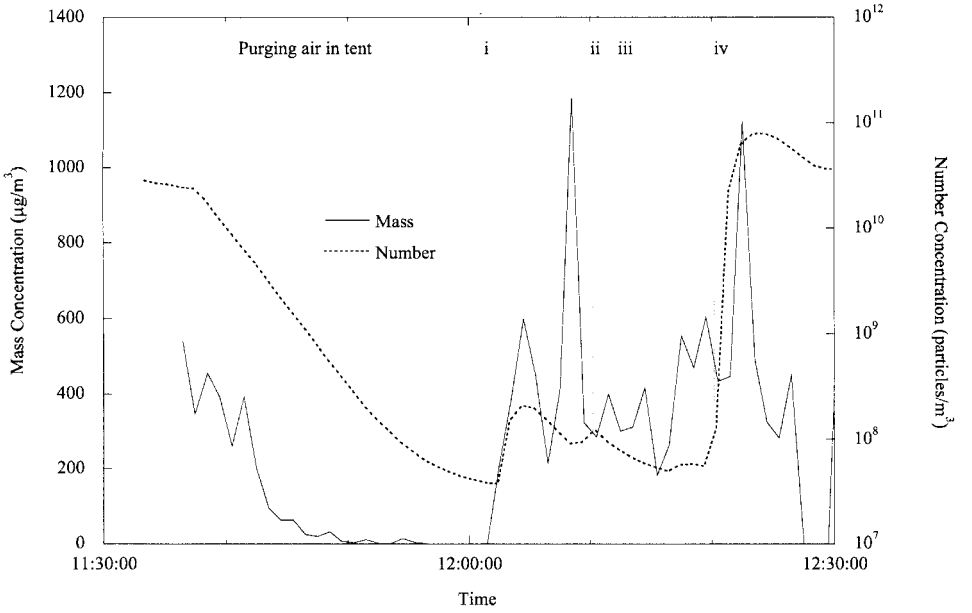

FIGURE 3. (*Continued*)

time. The times when key events occurred during each sampling period are given in Table 1.

Filter and Glove Samples Personal sampler filters and gloves were analyzed for iron and nickel as surrogates for total nanotube product mass, thus providing a low limit of detection (Tables 2 and 3), while discriminating between SWCNT and other airborne material. All samples were wet-ashed with concentrated nitric and perchloric acids. The filter sample residues were dissolved in 10 ml of 4% nitric/1% perchloric acid, while the glove residues were dissolved in 25 ml of 4% nitric/1% perchloric acid. The sample solutions were analyzed by inductively coupled plasma–atomic emission spectrometry (ICP-AES) for trace metal content. Bulk material from a previous HiPCO run was analyzed and shown to consist of 30% catalyst material by mass (Fe in this case). Unfortunately, bulk samples of SWCNT associated with the exposure measurements weren't available for analysis. However, discussions with the producers of these materials indicated that the mass percentage of catalyst metal to SWCNT is only likely to vary within about 5% between production batches and processes. SWCNT mass was therefore estimated for each sample assuming that a combination of Ni and Fe catalyst particles constituted 30% of the mass of the material. The ratio of Fe to Ni was derived from the glove samples. Table 2 shows the results of the analysis on personal air samples. Estimates of nanotube concentrations spanned 0.7 $\mu g/m^3$ to 53 $\mu g/m^3$. Estimates

TABLE 1. Key Events During Each Nanotube Handling Operation

Location	Time (approx.)	Reference	Event
NASA laser	15:28	a	Two workers entering tent
	15:48	b	Starting SWCNT removal
	15:56	c	Intermittent vacuum cleaner use to remove SWCNT
	16:00	d	Cleaning inside the tent, using vacuum
	16:18	e	Workers leaving tent
Rice HiPCO	14:22	a	Workers entering tent
	14:27	b	Opening SWCNT container, and emptying into the first bucket
	14:30	c	Tipping SWCNT from bucket to bucket
	14:33	d	Scooping spilt material off table
	14:38	e	Cleaning inside tent with vacuum cleaner
	14:41	f	Further cleanup inside tent, and personal protective equipment removal
	14:56	g	Workers leaving tent
CNI laser	10:55	a	Two workers entering tent
	10:59	b	Start removing SWCNT from container
	11:09	c	Using vacuum cleaner in short bursts
	11:15	d	Cleaning inside tent, and dismantling tent
CNI HiPCO	12:02	a	Workers entering tent
	12:11	b	SWCNT removal from container
	12:13	c	A lot of large airborne SWCNT clumps visible to the eye in the tent
	12:19		Large cloud of airborne SWCNT clumps in the tent
	12:21	d	Cleaning inside the tent, using vacuum cleaner

Note. Each event is referenced to markers in Figure 3.

TABLE 2. Analysis Results of Personal Air Samples from Each of the Four Field Sites

Sampling site	Mass Fe (μg)	Mass Ni (μg)	Sampled volume (m^3)	Estimated nanotube concentration ($\mu g/m^3$)
Field blank average	1.89	[0.03]	0	—
NASA JSC (laser)	(–0.49)	[0.029]	0.139	[0.70] (Ni)
Rice (HiPCO)	0.86	(–0.01)	0.079	36.29 (Fe)
CNI (laser)	(–0.34)	0.284	0.096	9.86 (Ni)
CNI (HiPCO)	1.91	0.178	0.132	51.73 (Ni) 52.73 (Fe)

Note. Fe and Ni results are reported following blank subtraction. Nanotube concentrations have been estimated assuming the combined mass of Ni and Fe constitute 30% of the SWCNT material. Measured amounts below the limit of quantification are shown in square brackets. Fe: Limit of detection: 0.0643 μg; limit of quantification: 0.212 μg. Ni: Limit of detection: 0.0182 μg; limit of quantification: 0.0601 μg.

of the SWCNT material on individual gloves ranged from 217 μg to 6020 μg (Table 3).

The filter samples were taken over the time period the worker spent in the enclosure, typically about half an hour. In some cases (most noticeably when

TABLE 3. Analysis Results of Glove Samples from Each of the Four Field Sites

Sampling site	Mass Fe (μg)	Mass Ni (μg)	Fe/Ni	Estimated nanotube (μg)
Blank	388	0.629	—	
NASA JSC (laser)	(–267)	65.221	0	217
Rice (HiPCO)	1107	4.361	253.84	3705
CNI (laser)	(–88.5)	258.871	0	863
CNI (HiPCO)	1647	158.871	10.37	6020

Note. Fe and Ni results are reported following blank subtraction. Results for each site are the average of left- and right-hand gloves. The mass of Fe and Ni nanotube mass has been calculated assuming the combined mass of Ni and Fe constitute 30% of the SWCNT material by mass. Fe: Limit of detection: 0.161 μg; limit of quantification: 0.530 μg. Ni: Limit of detection: 0.0455 μg; limit of quantification: 0.150 μg.

handling the HiPCO material), large clumps of nanotube material were visible on the filter samples and may have accounted for a significant fraction of the detected material. In most cases, SWCNT contamination of gloves was visible at the end of the sampling period.

Inspection of area samples, analyzed with the scanning electron microscope, showed relatively few particles on the samples. Samples from HiPCO SWCNT contained a small number of particles, on the order of 100 μm to 1 mm in diameter, having relatively open nanorope structures (Figure 4a). However, most micrometer-sized particles in the analyzed HiPCO sample appeared to have a compact structure, with very few nanotubes apparent (Figure 4b). In contrast, micrometer-sized particles from the laser ablation process were more clearly comprised of nanoropes (Figure 5). No evidence of millimeter-sized nanotube material clumps was found in aerosol samples from laser-ablated material. From looking at samples of bulk material in the SEM, these compact particles consisting of nanoropes and other forms of carbon are generally present in unrefined material associated with the two production processes investigated.

DISCUSSION

The laboratory study indicates that respirable nanotube aerosol generation from production powders is an inefficient process. Relatively gentle agitation in the presence of large bronze beads did not lead to significant aerosol generation. More energetic agitation initially led to the generation of particles smaller than 100 nm in diameter from laser-ablated material, which may have corresponded to small clumps of nanoropes, although the generation within this size range rapidly decreased with time (Figure 1). Vigorous agitation of the HiPCO material generated particles below 10 nm (Figure 2). At this stage, it is not clear whether these particles were associated with the nanotubes, compact carbonaceous material in the sample, or catalyst particles. Generation within this size range was stable over 15 min, which indicated a steady release of material. Both

materials led to particles that had aerodynamic diameters between 1 and 10 μm, which were generated by vigorous agitation. It is interesting to note that reasonably good agreement is seen between the SMPS and APS data, suggesting the SWCNT particles were behaving similar to compact particles with unit density in the measurement instruments. There was some evidence that the laser-ablation material led to particles around 200 nm in diameter being released initially. However, in each case, generation rates were around two orders of magnitude lower than those from a similar volume of fumed alumina—another low-density material comprised of nanometer-sized primary particles. Low generation rates from both SWCNT sources were confirmed in the field studies.

The laser ablation material was compact and difficult to break down into smaller particles on a macro scale (mm), so it was anticipated that generation rates of airborne particles would be low. This assumption was confirmed in the laboratory. The HiPCO powder was a much expanded material and loosely bound together. Although the powder could readily be broken down into smaller particles in the laboratory, generation of this material was still relatively inefficient. It is quite likely that the expanded nature of the powder prevented transmission of sufficient force locally, within the powder, to overcome the van der Waals forces and release small particles.

The mechanics of aerosol release from powders are complex, and it should not be assumed that the laboratory-based method of aerosol generation provides a definitive characterization of workplace-related processes. However, examination of variations in aerosol number and mass concentration when nanotube material was handled (Figure 3) appears to support the conclusion that it is difficult to form an appreciable respirable aerosol from the material. In each instance of handling the material in the field, there is no evidence of an increase in particle number or mass concentration during that task. On the contrary, increases in concentration are associated with workers entering the enclosure before the material was handled and aerosol generation during cleanup. In each case, the aerosol number concentration decreased during the nanotube material handling, which indicates no detectable release of very fine material. Mass concentrations between 100 and 500 $\mu g/m^3$ (nominal values) were seen as workers entered the enclosure, resulting from the release of non-nanotube particles from clothing and other surfaces within the enclosure. Similar mass concentrations were seen during cleanup and were possibly attributable to the same aerosol sources. More significantly, three of the sites showed a large increase in particle number concentration during cleanup, which does not correlate well with changes in mass concentration and indicates the release of very fine particles into the enclosure. In two of these cases, a vacuum cleaner was used in the enclosure, and the changes in number concentration correlate closely with its use. This device was clearly a source of submicrometer particles both times, although whether these arose from nanotube material being aerosolized during cleanup or from particle generation from the unit's carbon brush motor is unclear. When the vacuum cleaner motor was located outside the enclosure in one instance (Figure 3c), there was no change in number

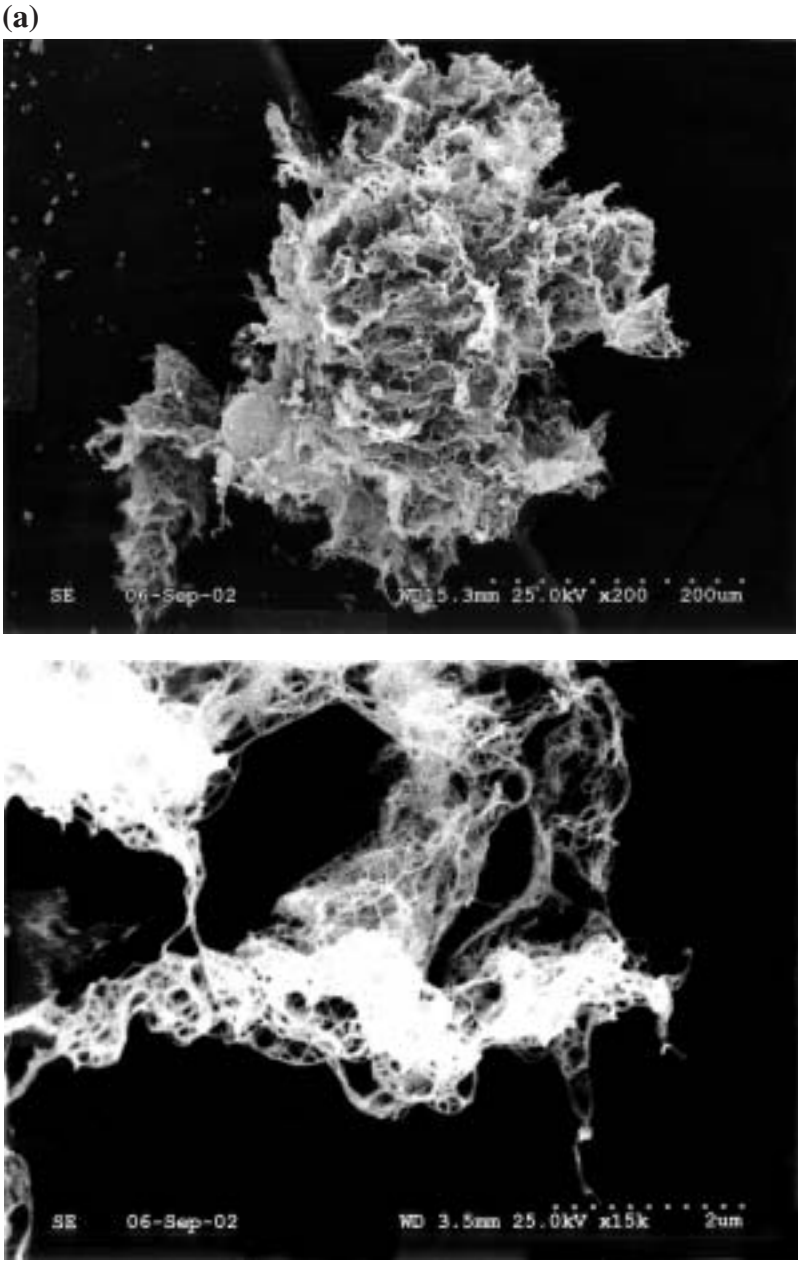

FIGURE 4. SEM images of aerosol particles generated from handling HiPCO SWCNT. (a) Particles lager than ~100 μm in diameter. (b) Particles of the order of μm in diameter.

(b)

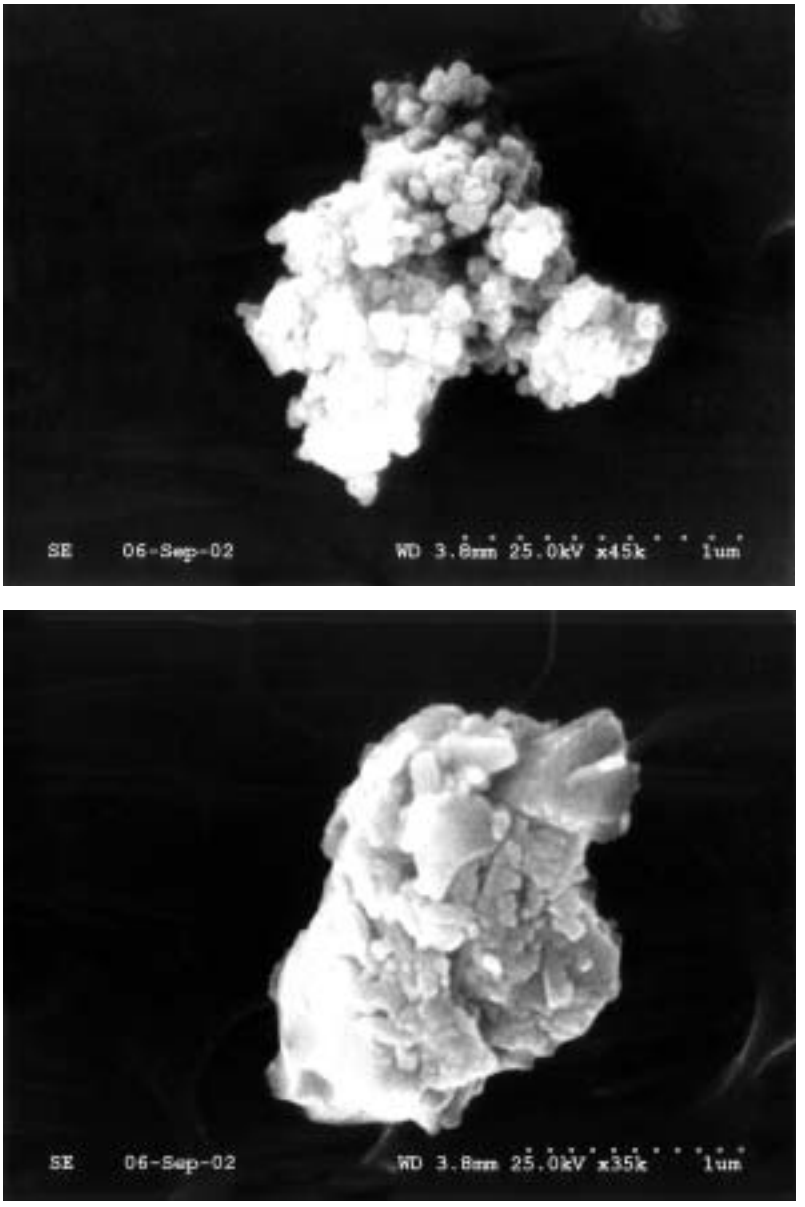

FIGURE 4. (*Continued*)

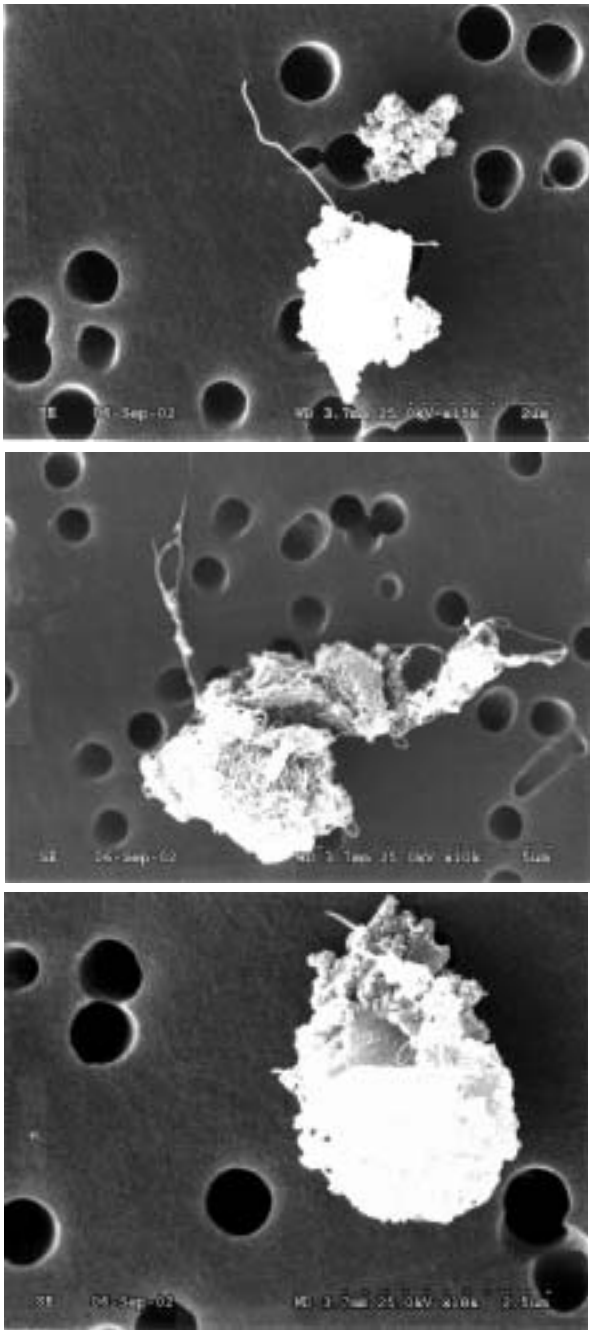

FIGURE 5. SEM images of typical micrometer-sized aerosol particles collected during handling laser ablation nanotube material.

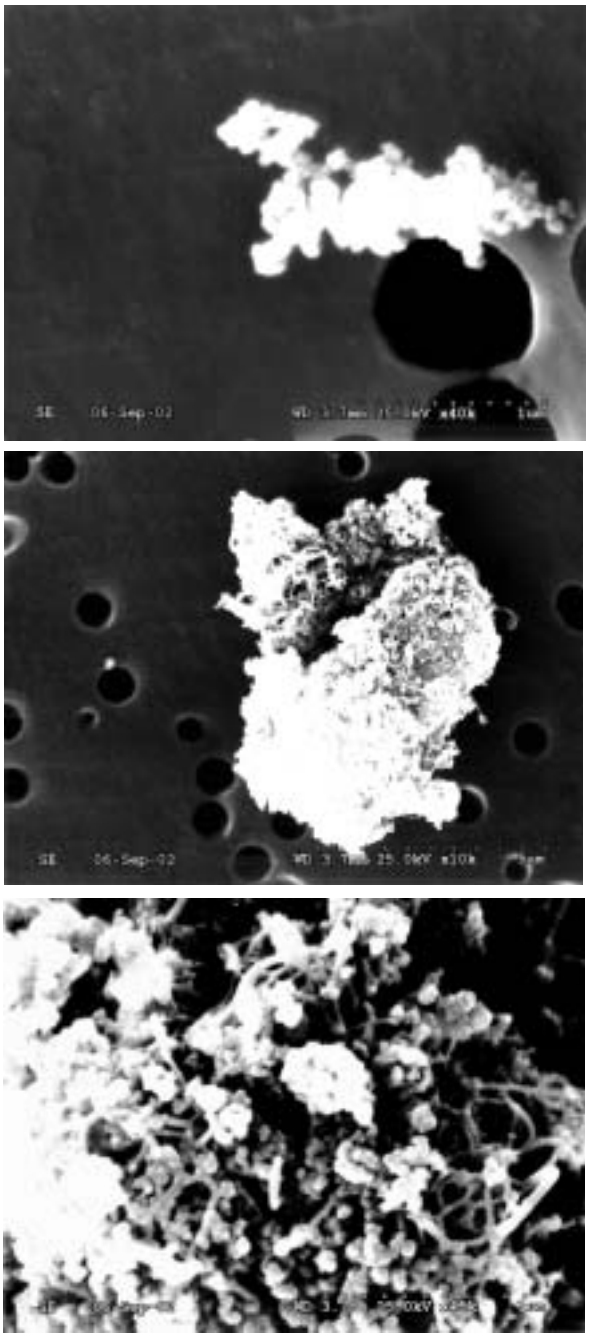

FIGURE 5. (*Continued*)

concentration associated with its use, indicating the source of fine particles to be from air passing through the cleaner.

Interpretation of aerosol mass concentration measurements is confounded by uncertainty over instrument response to nanotube particles. Estimated SWCNT mass concentrations for the HiPCO material appear to agree to within a factor of two with the real-time data during material handling (Figure 3, b and d). However, the data in Figure 3 have been derived using a nominal particle density of 1000 kg/m^3 in the absence of further information on the density of individual particles. If the aerosol had been completely comprised of nanotubes, it would be reasonable to use an effective density three orders of magnitude below this, leading to estimated nanotube mass concentrations well below 1 $\mu g/m^3$. However, SEM images of micrometer-sized particles show relatively compact particles, indicating that an effective density between 100 and 1000 kg/m^3 (estimate) may be more appropriate.

Estimates of the nanotube aerosol concentration need to be qualified by visual recognition of large clumps of material released during material handling. Since our filter samples did not differentiate between inhalable and noninhalable particles, they will have included some of the clumps. Based on the effective bulk density estimated earlier for HiPCO product, a 3-mm-diameter clump would have a mass of 14 μg and an aerodynamic diameter of about 95 μm. Only two or three such particles in a sample would account for the Fe and Ni masses measured. Such a particle would not penetrate to the gas exchange region of the lungs if inhaled, and thus it is highly likely that the respirable fraction of the nanotube aerosol was smaller than the estimated mass concentrations. However, such particles could be readily inhaled and deposited in the mouth or nasopharyngeal region, producing a potential health risk, since a number of materials, including Ni, have been associated with increased risk of nasal cancer (Feron et al., 2001). Large airborne clumps of SWCNT also posed a potential dermal exposure hazard as they deposited on surfaces, skin, and clothing.

In none of the field studies is there any indication that handling the nanotube material leads to an increase in the number concentration of fine particles, suggesting that released particles tend to be larger than 1 μm or so in diameter. These findings concur with the laboratory data indicating that submicrometer particles are not readily released at low levels of agitation. The worker at each location was careful to move slowly and attempted to minimize disturbance of the nanotube material during removal from the reaction tube.

More energetic processes would be expected to release higher concentrations of nanotube aerosol. There is some question over whether the use of a vacuum cleaner during cleanup led to large releases of small nanotube clusters, or whether the observed particles originated from the device itself. This is clearly an area requiring further investigation, but at this stage it would seem prudent to use HEPA-filtered cleaners with correctly fitted filter units to prevent the potential release of large nanotube number concentrations.

The gloves worn by the workers were visually contaminated with nanotube material, with a maximum average of 6 mg per glove estimated for the CNI HiPCO material (Table 3). Most of the material appeared to end up on the parts of the fingers in direct contact with surfaces, that is, the inner surfaces of the fingers and palms. While it is likely that the cotton gloves used to collect the hand samples will have retained more material than latex gloves (or similar) or bare skin, these results do underline the significance of dermal contact as a potential exposure route if the relevant protective measures are not followed. SWCNT produced using the HiPCO process appeared to lead to higher airborne concentrations and higher glove contamination levels. The higher levels may have been associated with the lower density, "fluffier" HiPCO material becoming more easily airborne as large clumps of material. It is possible that the distinction seen in concentrations between the two processes is associated with our assumption on the percentage of catalyst material in the laser-ablation SWCNT. However the catalyst mass fraction of the laser-ablation material would have to be between 1 and 5% for estimated laser ablation SWCNT concentrations to be comparable to those from HiPCO SWCNT, and this appears technically unlikely.

SUMMARY

While laboratory studies have indicated that with sufficient agitation SWCNT material can release fine particles into the air, the aerosol concentrations generated while handling unrefined material in the field at the work loads and rates observed were very low. Estimates of the airborne concentration of nanotube material generated during handling suggest that concentrations were less than 53 $\mu g/m^3$, and probably significantly below this. Filter samples indicated that many of these particles may have been compact, rather than having an open, low-density structure more generally associated with unprocessed SWCNT. Air measurements will have included large airborne clumps of material that were not respirable. However, these large particles, together with surface deposits, would have posed a dermal exposure risk. Glove deposits of SWCNT during handling were estimated at between 0.2 mg and 6 mg per hand. Measurements indicated higher air and glove SWCNT concentrations for the HiPCO material. Although the use of gloves and other personal protective equipment (PPE) will minimize dermal exposure while handling this material, the propensity for large clumps to become airborne and remain so for long periods may lead to dermal exposures in less well protected regions. This research has provided an initial indication of the propensity with which unprocessed SWCNT forms an aerool during handling. Further research into the mechanisms by which aerosol particles are released from the bulk SWCNT material, and the physical nature of the particles with respect to their size, will lead to a greater understanding of the importance of particle size, structure, morphology, and composition when considering the health risks associated with handling the material.

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