

Research Paper

OCCUPATIONAL EXPOSURE ASSESSMENT OF MULTIWALLED CARBON NANOTUBES

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ABSTRACT

Pulmonary toxicity of CNTs is well established by many laboratory investigations. The toxicity studies were challenging due to lack of occupational exposure assessments. In the present study exposure assessment of MWCNTs was carried out by measuring the mass concentrations in personal breathing zone of a manufacturing facility using filter sampling procedure. The measured concentrations were used to calculate the amount of MWCNTs that can be deposited on the alveoli of human lung. The obtained results indicate that the amount of CNTs that will be deposited on the pulmonary alveoli / day / body weight is 0.179 $\mu\text{g}/\text{kg}/\text{day}$.

KEY WORDS: carbon nanotubes; production methods; properties; health effects; toxicity.

INTRODUCTION

CNT's have diameters of 100 nm or less with high structural integrity. Though these CNTs comprises of only carbon atoms, they have excellent mechanical properties and semiconducting characteristics. The quantum of production will increase to greater magnitude in near future. Potential human health hazards are caused by inhalation, dermal and oral exposure to CNTs. Among all the exposures, pulmonary toxicity of carbon nanotubes is well established. Many laboratory studies were conducted for understanding the cytotoxicity of Multiwalled carbon nanotubes. All these studies lack correlation to occupational exposure in workers mainly due to the lack of human exposure assessment data. At present the scale of the industries manufacturing and handling is small, but in future it is expected to develop extensively. This scenario is due to the fact that small size of workforce is prevailing in carbon nanotube manufacturing industry. Exposure assessment methods and exposure metrics such as particle number, surface area and mass which are correlating with adverse health effects are not in consensus with each other. This study was conducted to assess exposure concentrations of MWCNTs at different locations in a MWCNT manufacturing facility, located at Noida.

MATERIALS AND METHODS

Filter based sampling was employed to assess exposure concentrations in the industrial air environments. An aerosol monitor was used to monitor particle mass concentration. An impact or with a cutoff of 1 μm was used to allow sampling from 0.1 to 1 μm as the mass measurement is dominated by larger sized particles. A filter testing chamber was designed to determine mask filter particle retention in the workplace during

realtime operating conditions and exposure situations. Particle laden air during regular production was drawn in with a vacuum pump and controlled by a rotameter. Pressure drop between two compartments was measured with a manometer. The data set included measurements under background and production conditions. These are the two diverse environments with respect to concentration levels. Five sampling locations were chosen to capture the spatial and temporal variation in particle levels. The sampling inlets were positioned at 1.2m above the ground. This level will quantify the breathing concentration between standing and sitting working position. Worker's activity includes reactor maintenance and cleaning, mechanical adjustments to the reactor system and its operation, powder handling and packaging and work place cleaning. Background levels were determined each day prior to the production start. Temporal measurements were also made with the same sampling system by collecting samples during the months of May and June. The filters were analysed gravimetrically for the mass concentration of MWCNTs using Pyris 1 TGA.

RESULTS AND DISCUSSION

The MWCNTs concentrations were estimated at five different activities in the industry. The results obtained are presented in the table 1. The major emission source in the production facility is production unit i.e., near the reactor. Only a small difference was observed between samples collected during May and July months. But the concentrations of samples collected at various sampling points in the industry are varying. There is significant variation in particle distribution spatially. This distribution could be because of improper mixing of air in the production area. Low concentration in inhalable dust fraction is observed at the site of packaging.

Table 1: Exposure concentrations in the selected facility

S. No	Sampling location	MWCNTs Concentration		Background corrected concentration of MWCNTs	
		During the month of May	During the month of July	During the month of May	During the month of July
1	Near the reactor	2.1 $\mu\text{g}/\text{m}^3$	1.9 $\mu\text{g}/\text{m}^3$	2.0 $\mu\text{g}/\text{m}^3$	1.8 $\mu\text{g}/\text{m}^3$
2	During reactor cleaning	2.2 $\mu\text{g}/\text{m}^3$	2.0 $\mu\text{g}/\text{m}^3$	2.1 $\mu\text{g}/\text{m}^3$	1.9 $\mu\text{g}/\text{m}^3$
3	At the site of powder handling	1.5 $\mu\text{g}/\text{m}^3$	1.4 $\mu\text{g}/\text{m}^3$	1.4 $\mu\text{g}/\text{m}^3$	1.3 $\mu\text{g}/\text{m}^3$
4	At the site of packaging	1.2 $\mu\text{g}/\text{m}^3$	1.4 $\mu\text{g}/\text{m}^3$	1.1 $\mu\text{g}/\text{m}^3$	1.3 $\mu\text{g}/\text{m}^3$
5	During workplace cleaning	1.8 $\mu\text{g}/\text{m}^3$	1.7 $\mu\text{g}/\text{m}^3$	1.7 $\mu\text{g}/\text{m}^3$	1.6 $\mu\text{g}/\text{m}^3$
Background concentration		0.1 $\mu\text{g}/\text{m}^3$			

The measured concentrations near the MWCNT emission sources are utilized for the estimation of exposure. MWCNT inhalation exposure of workers who directly handles MWCNT powder can be estimated using the exposure scenario. The table 2 shows the classification of exposure potential according to material forms, exposure control, working scales and exposure frequencies. The estimated ambient air concentrations and assumed exposure scenario was used to estimate the amount of MWCNT powder that a worker will be exposed to by inhalation without exposure control. Assuming the exposure frequency to

be high (8 hrs per day \times 5 days per week) the amount of exposure concentration was roughly estimated. In the working environment particle emission and exposure occur simultaneously. The environmental fate has to be considered in alleviating the exposure. The results of the onsite investigation are close to exposure concentrations. And the decrease in concentrations due to environmental fate was ignored and the exposure control absence was assumed. Keeping these things in mind the same concentrations were used for exposure assessment studies.

Table 2: Classification of exposure potential of nanomaterials based on material forms, exposure control and working scale

Class	Material Form	Exposure control	Working scale ⁴ (or exposure Frequency)	Exposure potential (low-high, 1-5)
A	Fixed state (e.g., mixed in resins)	-	-	1
B	Nanomaterials in liquids ^a	-	-	2
C	Dry nanomaterial powder	Closed system/unattended operation/automatization ^b	-	1
D1		Local ventilation equipment ^c	Small (low)	2
D2			Large (high)	3
E1		Only personal protective equipment ^c	Small (low)	3
E2			Large (high)	4
F1		No exposure control ^c	Small (low)	4
F2			Large (high)	5

(Source: NEDO project on Research and development of nanoparticle characterisation methods)

a: Exposure can occur when the liquid itself is splashed (e.g., during agitation, ultrasonication, processes involving foaming and spraying).

b: If an operation involves the opening of a closed system (sample collection, maintenance, cleaning, etc.), it will be regarded as Class D-F

c: Class D-F operations in which workers directly handle the nanomaterial powder include the following: unpacking, weighing, subdividing, scooping, blending, charging into manufacturing/processing equipment's, collection from manufacturing/processing equipment's, transferring to other containers, packing/bagging, cleaning/maintenance, treatment of wastes, etc.

d: Examples of the working scale: laboratories (small); industrial production (large).

EXPOSURE ASSESSMENT

In estimating the exposure, the amount of MWCNTs deposited on the pulmonary alveoli has to be calculated. MWCNTs with an aerodynamic diameter of 20 nm will have high deposition rate, approximately 40%, while those with an aerodynamic diameter of more than 10 µm had a deposition rate of 0%. In estimating the exposure potential, the alveolar deposition fraction was assumed to be 10%. The workers would be exposed to MWCNT particles at a high exposure frequency i.e., 8 h/day and six days per week. Breathing rate of 20 m³/hr and a body weight of 70 kg was assumed. Then, the amount of MWCNTs deposited on the pulmonary alveoli per day per body weight is expressed as follows

Amount of exposure =

Exposure concentration × Alveolar deposition fraction × Exposure frequency × Breathing rate.

Exposure concentration	= 2.2 µg/m ³
Alveolar deposition fraction	= 0.1
Exposure frequency	= (8h/24h) × (6days/7days) = 0.286
Breathing rate	= 20 m ³ /day/70 Kg
Amount of Exposure	= 2.2 × 0.1 × 0.286 × 20 / 7 = 0.179 µg/kg/day

The Amount of CNTs that will be deposited on the pulmonary alveoli/day/body weight is 0.179µg/kg/day.

CONCLUSION

The concentrations of MWCNTs were measured at an industrial site and the measured concentrations were utilized for calculating the exposure amounts by workers, who are working in that industry. The highest concentration was observed at the reactor site as 2.2 µg/m³. Hence, this concentration was used for calculating the exposure potential of the MWCNTs. The amount of CNTs that will be deposited on the pulmonary alveoli / day / body weight is 0.179µg/kg/day. This might lead to potential hazards if there are no safety precautions. In the industry in which we have measured the concentrations, they are following highest safety standards. Safety is given priority in that premises.

REFERENCES

- Approaches for assessing and Controlling workplace releases and exposures to new and existing Nanomaterials. EPA/OPPT/CEB Internal CEB Interim Draft. May 2012.
- Cui L. 2013. Exposure assessment and Inflammatory response among Workers Producing Calcium Carbonate Nanomaterials. Dissertation. University of Washington.
- Dahm M., and Schubauer- Berigan M. 2013. Carbon Nanotube and nanofiber Exposure Assessments: An Overview. Greater St. Louis Safety & Health Conference, October 22.
- DahmMM., Evans DE., Schubauer-Berigan MK., Birch ME., Deddens JA. 2013. Occupational Exposure Assessment in Carbon Nanotube and Nanofiber Primary and Secondary Manufacturers: Mobile Direct-Reading Sampling. Ann Occup. Hyg.,Vol 57, No.3, 328-344.
- Demessie ES., Zhao A., Salamon AW. A Study of Aged Carbon Nanotubes by Thermogravimetric Analysis. Application Note.

- Deddens JA., Birch ME., Evans DE., Erdely A. 2013. Industry wide Exposure Assessments and Cross-Sectional Epidemiologic Studies of Workers at Facilities Manufacturing , Distributing, or Using Carbon Nanotubes or Carbon Nanofibers in the United States.
- Demou E., Peter P., Hellweg S. 2008. Exposure to Manufactured Nanostructured Particles in an Industrial Pilot Plant. Ann. Occup. Hyg., Vol. 52, No. 8, 695-706.
- Erdely A., Dahm M., Chen BT., Zeidler-Erdely PC., Fernback JE., Birch ME., Evans DE., Kashon ML., Deddens JA., Hulderman T., Bilgesu SA., Battelli L., Schwegler-Berry D., Leonard HD., McKinney W., Frazer DG., Antonini JM., Porter DW., Castranova V., Schubauer-Berigan MK. 2013. Carbon nanotube dosimetry: from workplace exposure assessment to inhalation toxicity. Erdely et al. Particle and Fiber Toxicology, 10:53.
- Kobayishi N., Ogura I., Gamo M., Kishimoto A., Nakanishi J. 2009. Risk assessment of manufactured nano materials- Carbon Nanotubes (CNTs). Interim Report issued on October 16.
- Mald AK., Unice K., Kreider M., Kovochich M., Bebenek IG., Abramson MM., ChemRisk LLC., Viejo ACA., Pittsburgh PA. Risk Ranking Framework to Assess the Health Hazard of Nanomaterial Containing products in an Industrial and Consumer Application Setting.
- Metrology and Exposure Assessment of Carbon Nanotubes. Inno.CNT Workshop. Schloss Burg, Germany. 29-30 November 2011.
- Schneider T., Brouwer DH., Kponen IK., Jensen KA., Fransman W., Duuren-Stuurman BV., Tongeren MV., Tielemans E. 2011. Conceptual Model for Assessment of Inhalation Exposure to Manufactured Nanoparticles. Journal of Exposure Science and Environmental Epidemiology, 1-14.