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The risk assessment of potentially hazardous carbon nanomaterials for small scale operations

T. Koiranen[a,*], T. Nevalainen[a], T. Virkki-Hatakka[a], H. Aalto[a], K. Murashko[a], K. Backfolk[a], A. Kraslawski[a,b], J. Pyrhönen[a]

[a] Lappeenranta University of Technology, P.O. Box 20, FI-53851 Lappeenranta, Finland
[b] Lodz University of Technology, ul. Stefana Żeromskiego 116, 90-924 Łódź, Poland

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ABSTRACT

Carbon nanomaterial applications are expected for consumer use within next decade. Risk management methods are reviewed by National Institute for Occupational Safety and Health, Safe Work Australia, Health and Safety Executive, and additionally Dupont's and Environmental Defense Fund's Nano Risk Framework. A new risk management method for handling carbon nanoparticles is presented, directed especially to universities and to research institutes. Small scale operations are different than those conducted in enterprises. Typically work started from the scratch, and researchers with limited experience of working with hazardous materials are distinctions to enterprise work flows. The promoter in this study has also been the life-cycle perspective for handling hazardous materials already in early stages of the research. Two risk evaluation cases are introduced in the use of multiwalled carbon nanotubes. The method behind inference logics in risk evaluation is demonstrated, and it was successfully implemented in the real carbon nanotube research project. The straight-forward spreadsheet implementation is an additional advantage due to short set-up time, due to easy system maintenance and due to the easy use of different evaluation parameter weights.

1. Introduction

Carbon nanoparticles (CNP) have various applications in semiconductors semiconductors, composites and in the removal of pollutants from water [1–3]. They may be used for fuel cells, batteries, solar panels, super capacitors, memory chips and processor circuits to name a few [4]. Especially strength properties of carbon nanotubes are superior as the tensile strength and elastic modulus are compared to other materials. Also, their electric properties are unique according to the reported electrical current density or electrical conductivity values.

Safety issues have been one obstacle for having carbon nanoparticles or typically composites containing these particles into the market. Carbon nanoparticles can be categorized into carbon nanotubes (CNTs), fullerenes and into carbon nanofibers (CNFs) [5].The material properties of carbon nanotubes are comparable to those of asbestos from a structural resemblance and from potential health risks [6,7]. NIOSH [8] and Savolainen et al. [9] collected evidence data for potential adverse health effects of single-walled carbon nanotubes (SWCNT), multi-walled carbon nanotubes (MWCNT) and carbon nanofibres from reported animal and in vitro cellular studies. The reports indicate that pulmonary inflammation, interstitial fibrosis, fibrotic lesions in lungs and possibly genotoxicity are the potential adverse health effects after exposure to carbon nanotubes. Interestingly, ncRNA and mRNA expression profiles from human blood samples reveal the relation between MWCNT exposure and potential health risks [10]. Especially, the stiff carbon nanotubes (CNT) may be more hazardous than tangled CNTs according to Sund et al. [11]. Typically hazardous CNTs are biopersistent and their aspect ratio is greater than 3 [10]. More long-term research is needed to study possible chronic effects and to classify more specifically CNT/CNF physical properties which can cause adverse effects. As conclusions by NIOSH, all types of CNT and CNF should be considered an occupational respiratory hazard, and the suggested exposure control limit is below 1 $\mu g/m^3$ elemental carbon at 8-hr-time-weighted average [8].

Typical exposures in humans are respiratory and transdermal routes in the case of nanosized materials. At the moment, the occupational exposure is one of the largest concerns. The exposure of consumers in future applications should be of equal concern for the future products which are now in the early stages of R&D. However, internationally accepted quantification methods of carbon

* Corresponding author.
E-mail address: tuomas.koiranen@lut.fi (T. Koiranen).

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nanotubes are not yet available. The International Standardization Committee (ISO) has published their characterization methods [12]. The ISO and the European Chemicals Agency (ECHA) recommendations for exposure assessment and metric measurement can also be found [12,13]. The regulations are diversified and different in EU, Australia, Japan and in the USA [14]. For example, there are no specific requirements for nano-based products in the EU if their manufacturing or importing quantities are less than 1000 kg and therefore e.g. testing requirements are not necessarily needed [4,9]. In the USA and in Australia notifications are needed for SWCNTs and MWCNTs.

The safety hazard evaluation techniques in early phases of chemical process development are typically checklists, what-if analyses, relative ranking methods and preliminary hazard analyses [15]. Process operational methods like Hazard and Operability Analysis (HAZOP), Failure mode and effects analysis (FMEA), and fault or event trees are more commonly used as the scale increases and process descriptions get more detailed. Safety index calculations like DOW index, Mond index, Prototype Index for Inherent Safety (PIIS) and Inherent Safety Index (ISI) indices are also recommended to be applied in Process R&D [16,17]. Nanomaterial risk evaluation tools like Stoffenmanager Nano [18], LICARA NanoScan [19], CB Nanotool [20,21] and SUNDS [22] have been presented in the literature. Typically these tools are designed especially for enterprise use. On contrary to those tools, the ACHiL tool by Marendas et al. [23] can be used to evaluate hazard level in existing laboratories. The hazard levels are mapped into laboratory rooms based on the severity of actions taking place. In this system it is expected that the equality is valid among hazard classification parameters. This definitely does not hold true because e.g. working temperature can not be compared to operating with carbon nanoparticles. Another approach is based on evaluation of activities in nanomaterial uses by Groso et al. [24]. The system is constructed as a decision tree which eventually results to hazard classes. Similarly, it is unclear if importance of questions leading to results can be of equal weight.

This Paper concentrates on potentially hazardous carbon nanotube handling in which even small quantities (less than 10–100 g) processing give rise for risk assessment. The risk management guidance by NIOSH [8], HSE [25,26], Safe work Australia [27,28] and Nano Risk Framework [29] are reviewed. A new model for the assessment of risk management in non-commercial research like in universities and in research institutes is presented as a fusion of those risk management guides. The motivation for the development of this model is to guide user to concentrate on essential safety aspects, and also to take into consideration a product life-cycle if commercialization would result from the research. The evaluation parameters are considered to have different weights along with the straight-forward spreadsheet implementation for improving system flexibility. The aim is also to quantify the risk and follow a control flowchart for objective decision making in follow-up actions. The proposed safety evaluation method was implemented in the carbon nanotube project concerning the development of supercapacitors, and the case examples are presented.

2. Risk management methods for carbon nanotubes

European Agency for Safety and Health at Work (EU-OSHA) has published "Tools for the management of nanomaterials in the workplace and prevention measures" [30]. It introduces risk management tools to aid in the selection of workplace prevention measures and to support performing risk assessment. Prevention measures are introduced based on control hierarchy: substitution, isolation, engineering controls, administrative controls (safe working procedures) and personal protection. Risk management is needed with biopersistent fibrous and non-fibrous nanomaterials and also when nanomaterials become airborne. Nanomaterial-containing R&D work, cleaning and maintenance of installations are also in the scope of risk management. Control banding tools have some limitations according to the comparison in the report: detailed information about nanomaterials is needed as input data; exposure band covers only a few determinants; and some computer programs as yet are unfinished.

In 2012 ECHA has launched "Appendix R14-4: Recommendations for nanomaterials", which is intended for preparing registration dossiers for nanomaterials based on REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) Implementation Project on Nanomaterials 3 (RIP-oN 3) [13]. The document consists of nanomaterial measurement techniques, advice for data analysis, sampling and data quality classification. It should be noted however, that most of the measurement instruments are massive and analyses require trained personnel.

Organization for Economic Cooperation and Development (OECD) countries are actively participating in the OECD Working Party on Manufactured Nanomaterials (WPMN) including SWCNTs and MWCNTs. OECD's Environment directorate Joint meeting [31] has addressed the specific research needs in the determination of appropriate metrics for expressing exposure and dose, and in development of adequate sample preparation and dosimetry approaches. This key challenge has been also addressed by Schulte et al. [32] and by Savolainen et al. [33]. According to the Joint meeting opinion there are no fundamental differences in general risk assessment paradigms for chemicals and nanomaterials but management with risk assessments with limited critical data is a subject of the research. ISO has published guidance document for risk management [34] which has a similar lifecycle framework concept like Nano Risk Frame Work has [29].

In the US the SWCNTs and MWCNTs have been subject to strict notification requirements within the context of the Toxic Substances Control Act from 2010 [14]. The NIOSH report includes guidance for preparing risk management adaptable into registration material [8].

British authorities [35] have presented guides "Risk Management of carbon nanotubes" and "Using nanomaterials at work" which contain instructions for handling CNTs at workplace. The material can be applied also for other biopersistent high aspect ratio (length/diameter > 3) nanomaterials (HARNs).

A summary of the contents of risk management guides by NIOSH, HSE and Safe work Australia (Table 1) gives an indication of commonly accepted issues concerning the CNTs. The aim of the guides is to protect primarily the employees from potentially hazard nanocarbons. So, instructions in using personal protective equipment (PPE), packaging, transport, training and exposure controls are well-documented.

It should be noted that occupational exposure limits (OEL) and monitoring are not commonly accepted issues because currently it is very problematic to separate background nanoparticles by straightforward concentration measurements or by size distribution measurements [33]. Short descriptions of HSE's risk management are given in Table 2, and Safe work Australia's risk management is given in Tables 3 and 4.

The basic principles of risk management are different by comparing NIOSH to HSE and Safe work Australia. NIOSH has made a medical review of animal toxicological studies in order to get estimation of exposure limits, exposure times and effect of metal contents in CNTs/CNFs. NIOSH tiered strategy is shortly described as constant sampling, analyzing and exposure control. HSE and especially Safe work Australia strategies are to develop safe work environments by risk management instructions. They also attempt to give more detailed instructions/recommendations, and NIOSH strategy is to guide stakeholders to make their own instructions.