PRELIMINARY RISK EVALUATION OF POTENTIALLY HAZARDOUS CARBON NANOMATERIALS


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WHY THIS WORK?

- The need to evaluate risk for CNTs in Supercapacitor research project.
- Carbon nanotube properties are comparable to those of asbestos from a structural resemblance (Poland et al. 2008, Ali-Boucetta et al., 2012).
- Evidence data for potential adverse health effects of single-walled carbon nanotubes (SWCNT), multi-walled carbon nanotubes (MWCNT) and carbon nanofibres (CNF) from reported animal and in-vitro cellular studies. The Potential adverse health effects: pulmonary inflammation, interstitial fibrosis, fibrotic lesions in lungs and possibly genotoxicity. (NIOSH (2010) and Savolainen et al. (2010a))
- Exposure limits are very low: 7 µg/m³ (USA and Australia), 5 mg/m³ (EU) (8-hr-time-weighted average)
- There was not available a risk assessment tool directed to university conditions.
Risk management guides NIOSH, ECHA, Safework Australia, HSE

Risk assessment in guides: based on job & tasks assessment to determine potential for exposure

Safework Australia presents two options to manage risks: (A) detailed hazard analysis and exposure assessment, (B) Control banding

Instructions in guides:

Detailed risk evaluation procedures from Safework Australia and HSE

Instructions for PPE

Packaging & transport instructions

Emergency and cleaning procedures

Disposal procedures


Safe work Australia. Safe handling and use of carbon nanotubes; 2012.

EU-OSHA. Tools for the management of nanomaterials in the work place and prevention measures, E-FACTS 72; 2013


HSE. Using nanomaterials at work including carbon nanotubes (CNTs) and other biopersistent high aspect ratio nanomaterials (HARNs), Health and safety executive; 2013

OUR APPROACH TO RISK EVALUATION AT LUT

- The information aggregation concerning CNTs and CNFs from the guides by NIOSH, Safework Australia, HSE and DuPont&Environmental Defense Fund (Nano Risk Framework)

- The guides are directed to enterprises which may already have routines in other hazard material handling especially for commercialization purposes.

- Our approach to preliminary risk management is directed to universities and research institutes

- The aim is to quantify the risk and follow a control flowchart for objective decision making in follow-up actions.
<table>
<thead>
<tr>
<th>EVALUATION PARAMETER DESCRIPTION</th>
<th>REASONING</th>
<th>SOURCES WHERE ADAPTED FROM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material risk (very hazardous, less hazardous forms)</td>
<td>Different forms of nanocarbons are available</td>
<td>NIOSH, HSE, Safe work Australia</td>
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<tr>
<td>Quantity risk (over 1 kg : 100 g -1 kg : 10 g-100 g : 1 mg - 10 g)</td>
<td>The amount correlates to potential exposure</td>
<td>Safe work Australia, DuPont&amp;Environmental defense</td>
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<tr>
<td>Handling risk (dry/wet/degrading matrix/ non-degrading matrix)</td>
<td>Nanocarbons in attached media is less potential for exposures</td>
<td>Safework Australia, NIOSH, HSE</td>
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<tr>
<td>Processing risk (weighing dry material/milling/ grinding/scraping/no mechanical treatment)</td>
<td>Processing correlates to potential exposure</td>
<td>NIOSH, HSE, Safe work Australia</td>
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<td>Human exposure risk (organizational competence for engineering controls)</td>
<td>Engineering control facilities and preparedness to engineering controls essentially influences human exposures</td>
<td>Risk management methods do not regard safety baseline of organizations.</td>
</tr>
<tr>
<td>Personnel risk (students / professional persons)</td>
<td>Experienced and trained professionals in research work provide good capabilities for handling nanocarbons</td>
<td>In principle, risk management methods suppose professional personnel involvement</td>
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<tr>
<td>Work environment risk (flammable compounds, reactive compounds or electric systems present, heat, pressure etc. / no flammable or reactive systems, ambient conditions)</td>
<td>Other potential hazards raises the level of risk</td>
<td>HSE, Safe work Australia, DuPont&amp;Environmental defense</td>
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<td>Environmental load risk (possibility to be released in environment / no possibility to be released)</td>
<td>Nanocarbons may be environmental risk</td>
<td>Safe work Australia, DuPont &amp; Environmental defense</td>
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<tr>
<td>Organizational control preparedness (level of safety and work procedures documentation)</td>
<td>Established safety and work procedure documentation system provides capabilities for administrative controls</td>
<td>In principle, risk management methods suppose safety documentation is established during the risk management planning.</td>
</tr>
<tr>
<td>Commercial use risk (home, outdoors, work places, factories)</td>
<td>Evaluation of future potential exposure for users: level of safety procedures in organizations and enterprises may be higher than e.g. at homes.</td>
<td>DuPont &amp; Environmental defense</td>
</tr>
<tr>
<td>Commercial product risk (CNT fraction and quantities in product, CNT production/raw material volumes etc.)</td>
<td>Evaluation of future potential exposure for a product itself.</td>
<td>DuPont &amp; Environmental defense</td>
</tr>
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</table>
RISK EVALUATION PROCESS IN CNT HANDLING PROCESSES

1. Determine weights for risk evaluation parameters. Commit safety personnel and research group in your organization

2. Determine the risk values for each parameter

3. Calculate Preliminary assessment value for risk management and control according to Eq. (1)

- No (value low)
  - Is value moderate?
    - Yes: Establish a detailed hazard analysis and exposure assessment according to e.g. Safework Australia (Method 1) or HSE's guidance on nanomaterials. Check country specific regulations (e.g. protective equipment)
    - No: Is value high?
      - Yes: Avoid using potentially hazardous CNT or try to find a reliable contract service provider. If not possible, establish a detailed hazard analysis and exposure assessment according to e.g. Safework Australia (Method 1) or HSE's guidance on nanomaterials. Check country specific regulations (e.g. protective equipment). Consider no-go as early as possible for the research.
      - No: Conduct risk management by control banding of e.g. Safe work Australia (Method 2), and assure that procedures are correct and in use at least to disposal, transport, signages, emergency situations and work descriptions. Check country specific regulations (e.g. protective equipment)
The evaluation is a combination of parameter importance and risk parameter values, scale from 1 to 4 (low/moderately low/moderately high/high). The preliminary risk assessment value \( Y \) is normed between 1.0 and 4.0:

\[
Y = \frac{\sum_{i=1}^{N} X_i W_i}{NW_{av}}
\]

where

- \( N \) number of evaluation parameters
- \( X_i \) Importance weight of parameter \( X_i \) value, 1-4
- \( W_{av} \) Average of important weights of parameters \( X_i \)
- \( X_i \) risk parameter evaluation value, 4-1

The weight parameters can be selected by pairwise comparison analysis (Saaty, 1990) in order to determine the importance weights.

Risk assessment values are indicatively: High = 2.6 – 4.0, Moderate = 2.1 – 2.8, Low = 1.0 – 2.3. The overlapping of the values was selected to allow the evaluator judgment in borderline cases.
CASES FOR EVALUATION PROCESS

• The cases presented here are related to Nationally funded Supercapacitor-project at LUT

• **Case 1.** Max. 12 g dry fibrous MWCNT (diameter 90 nm, length 5 µm, aspect ratio 56) is mixed with biodegradable polymer forming a matrix. Several sheets of polymer matrix are made to form raw material for a supercapacitor. Dry weighing and ultrasonic mixing are performed in processing.

• Personal protection equipment available but no facilities for glove boxes or isolated work areas other than fume hoods. The CNT concentration is 15 w-%-30 % in polymer matrix and 10-30 sheets could be done during one day.
• The risk assessment value was 2.7 (moderate/high), and the follow-up actions were:
  1. A glove box was acquired (HEPA-filters outlet/inlet, different glove materials available, underpressure system with alarm for leaks)
  2. Detailed work instructions were done
  3. Hazard analysis (LUT Chem.eng.) was performed
  4. Instructions for PPE
  5. Emergency procedures
  6. Cleaning procedures
  7. Disposal procedure

• **Case 2** Supercapacitor was assembled and tested using the manufactured polymer matrix sheets. The risk assessment value was 2.1 (low/moderate), and the same follow-up actions were used as in Case 1
SUMMARY

• The presented risk evaluation method was developed for the needs in university

• The method takes into account commercialization viewpoints (Commercial use risk and commercial product risk) in the evaluation.

• Method was easily implemented in spreadsheet program (MS-Excel)

• The risk evaluation method can be used aside with Safework Australia and HSE Guides

• The decisions can be documented during the risk evaluation.

• Method can be adapted also for other hazardous particles

