A human risk banding scheme for high aspect-ratio materials

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Background, Motivation and Objective

High aspect ratio materials (HARM) like carbon nanotubes (CNT) show material properties that enable innovative applications but also raise concerns about harmful effects to humans due to their asbestos-like morphology. A banding approach for HARM with hazard- and exposure-related parameters has been developed as a promising way to enable risk assessment and risk mitigation for an important family of advanced materials. It also provides guidance for a safer design of HARM and corresponding products.

Statement of Contribution/Methods

Our scheme attributes HARM to three risk levels: low, moderate and high. The two-dimensional risk matrix builds on a hazard and an exposure banding by band limit values. Parameters for hazard banding are biopersistence, fibre length and fibre rigidity. The latter has been derived from an extension of the classic fibre principle with the intrinsic material property flexural rigidity, hypothesized to play a significant role in limiting the toxicity of inhaled fibres towards pulmonary macrophages that attempt to uptake the fibres. Our current research efforts focus on further investigating the influence of flexural rigidity on fibre toxicity, supported by uptake analysis with macrophages, aiming at threshold values e. g. for the fibre diameters, which can be used as band limits.

For exposure banding, relevant parameters are the material dustiness, the propensity of release of fibres with a critical morphology and the degree of fibre agglomeration. Fibres with a critical morphology are defined according to the WHO-convention for asbestos (thinner than 3 µm, longer than 5 µm, aspect ratio greater than 3:1). To characterize the dustiness of fibrous materials, we have developed and evaluated the 'fluidizer' as an aerosol generator to adequately perform dustiness testing with powders of HARM [1]. In combining aerosol characterization and sampling with subsequent particle-morphological analysis with the help of scanning electron microscopy, we enable the identification and characterisation of HARM with relevant potential for release of fibres with a critical morphology.

We also developed approaches to assess the potential release of HARM from HARM-composite polymers during their lifecycle. We compared the rate of release and form of release during ISO-standardised simulation of lifecycle stresses.

Results/Discussion

We applied our risk banding scheme on 15 different types of multi-walled CNTs (MWCNTs) by determining their parameters for hazard, exposure and risk banding. MWCNTs show high variance resulting in allocations to all three risk levels [2]. The use of our risk banding scheme also enables identification of low risk MWCNTs to support a safe design of nanoproducts.

[1] Broßell, D. Heunisch, E. Meyer-Plath, A., Bäger, D., Bachmann, V., Kämpf, K., Dziurowitz, N. Thim, C. Wenzlaff, D., Schumann, J., Plitzko, S., Assessment of nanofibre dustiness by means of vibro-fluidization, Powder Technol, 342 (2019) 491-508.

[2] Broßell, D., Meyer-Plath, A., Plitzko, S., Wohlleben, W., Stahlmecke, B., Wiemann, M., Haase, A., Synthetic Nano- and Microfibers- Chapter 7: A human risk banding scheme for high aspect-ratio materials, ed. Wagterveld, R.M., Marijnissen, J.C.M., Gradón, L. and Moskall, A.

Exposure potential banding

Release propensity (dustiness)

Descriptor: Average particle number concentration (P) during fluidizer dustiness test

Band	Low	Moderate	High
Band limit	< 100 #/cm³	100 – 1000 #/cm³	> 1000 #/cm³

Dust agglomeration

Descriptor: Grade of agglomeration of dust released during fluidizer dustiness test

Band	Low	Moderate	High
Band limit	< 0.5	0.5-0.99	> 0.99

WHO-fibre concentration

Descriptor: Average number concentration (P_{WHO}) of WHO-fibres extrapolated from fibre counting on aerosol samples collected during fluidizer dustiness test with 95% confidence

Band	Low	Moderate	High
Band limit	< 10^4 WHO-fibres / m³	10^4 – 10^5 WHO-fibres / m³	> 10^5 WHO-fibres / m³

Hazard potential banding

Rigidity (thickness)

Descriptor: Mean fibre flexural rigidity, mean of diameter distribution of primary particles as a surrogate until rigidity can be directly measured adequately.

Band	**Flexible**	**Rigid**
Band limit	<10^{-19} N m², (< 38 nm)	>10^{-19} N m², (> 38 nm)

Water solubility

Descriptor: Complete or incomplete dissolution after 24 hours in sodium bicarbonate buffered water (pH 7).

Band	Water soluble	Water insoluble
Band limit	Dissolved after 24 h	Not dissolved after 24 h

Bio-Dissolution

Descriptor: Dissolution rate k in physiological simulant medium

Band	Low	Moderate	High
Band limit	> 100 ng/cm²/h	100 > k > 1 ng/cm²/h	< 1 ng/cm²/h

Risk matrix

Scoring

Dustiness		
low	medium	high
0	**1**	**2**
Grade of agglomeration		
high	medium	low
0	**1**	**2**
WHO-fraction		
low	medium	high
0	**1**	**2**

Limit values

Dustiness [#/cm³]		
low	medium	high
<500	**500 - 1000**	**>1000**
Dust agglomeration		
low	medium	high
<0.5	**0.5-0.99**	**>0.99**
WHO-concentration [#/m³]		
low	medium	high
<10^4	**10^4-10^5**	**> 10^5**

Properties of dust release

Material properties	0	1	3	4	5
3					
2					
1					
0					

Acceptable risk potential

Increased risk potential

Inacceptable risk potential

Scoring

Biopersistence		
soluble	degradable	biopers.
0	1	2
Rigidity		
flexible	rigid	
0	1	

Limit values

Biopersistence		
H_2O-sol.	pH4.5-sol.	biopers.
dissolved	dissolved	biopers.
Rigidity [10^{-19}N m²]		
flexible	rigid	
< 1	>1	

Results

Evaluation parameters of 15 MWCNT materials relevant for hazard and exposure banding.

Material	Mean rigidity	Dustiness	Dust agglomeration	WHO-fibre concentration
Metric	[10^{-19} N m²]	[#/cm³]	Dimensionless	[10^4/m³]
ARIGM001	0.26 ± 0.06	3656 ± 10	0.26 ± 0.03	1125.1 ± 375.3
ARIGM002	1.02 ± 0.01	1222 ± 8	0.29 ± 0.01	0
ARM006	0.51 ± 0.01	1186 ± 12	0.96 ± 0.03	1210.8 ± 2.1
Baytubes C150P	0.08 ± 0.01	173 ± 1	0.99 ± 0.17	0
C2148	0.04 ± 0.01	454 ± 4	0.98 ± 0.08	0
C2154	1.26 ± 0.01	7539 ± 44	0.91 ± 0.01	4149.1 ± 150.9
C2158	1.84 ± 0.29	3947 ± 17	0.52 ± 0.01	6520.7 ± 799.7
CNT-MW	0.19 ± 0.01	422 ± 6	0.51 ± 0.01	94.4 ± 8.3
MRCSD	321.70 ± 103.81	478 ± 5	0.61 ± 0.06	5835.3 ± 54.8
MWCNT-7	20.11 ± 1.06	134 ± 7	0.41 ± 0.03	1554.6 ± 2355.8
NC 7000	0.03 ± 0.01	204 ± 2	0.99 ± 0.03	0
NM 400	0.05 ± 0.09	179 ± 1	0.83 ± 0.01	132.8 ± 64.5
NM 401	28.12 ± 0.1	44 ± 3	0.58 ± 0.03	206.6 ± 281.2
NTX3	0.91 ± 0.19	8779 ± 54	0.99 ± 0.01	1306.1 ± 1349.2
SMW 100	0.03	204 ± 1	0.99 ± 0.01	0

Scores and risk banding for the studied MWCNT-materials.

Material	Exposure	Toxicity	Risk
ARIGM001	6	3	
ARIGM002	4	3	
ARM006	5	3	
Baytubes C150P	1	3	
C2148	2	3	
C2154	5	3	
C2158	5	5	
CNT-MW	2	3	
MRCSD	4	5	

Material	Exposure	Toxicity	Risk
MWCNT-7	5	5	
NC 7000	2	3	
NM 400	4	3	
NM 401	3	5	
NTX3	4	3	
SMW 100	1	3	

"InnoMat.Life" is funded by the German Ministry for Education and Research, grant no. 03XP0216B

GEFÖRDERT VOM Bundesministerium für Bildung und Forschung

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