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Nanomaterials Risk Assessment in the Process Industries: Evaluation and Application of Current Control Banding Methods

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Nanotechnology is a rapidly growing field and industrial developments are more and more challenged by potential health and safety risks pertaining to manufactured nanomaterials. This matter is far from being solved due to the current lack of reliable data addressing occupational safety as well as environmental field. In this context, the Control Banding (CB) approach appears particularly interesting to assess ESH risks associated to nanomaterials. Our study focuses more specifically on four CB methods which have been analysed in order to highlight their a priori limits and evaluate their effectiveness for perform risk assessment in the industry. Our study concludes that too conservative frameworks, multiplicity of factors and complex algorithm are critical elements that can limit the effectiveness of the tools for risk assessment in the industry.

1. Introduction

Despite the numerous technological innovations brought by nanomaterials (NMs), the size reduction that is so expected to enhance product performances may also be associated to new hazards that have to be managed to ensure a safe and sustainable development. The usual risk assessment tools fail when applied to NM because toxicological data are lacking, as some relevant physicochemical information (e.g. size, shape, or state of agglomeration) which are rarely available in material safety datasheets (MSDS) (Lee, 2012).

The Control Banding (CB) framework has been widely adopted by decades by the pharmaceutical industry to assess risks associated to new components. Indeed, it has proven to be an effective strategy for controlling worker exposure in the absence of complete relevant information about toxicity and exposure, , i.e. without Occupational Exposure Limit (OEL). CB has been widely adopted as an alternative option for controlling exposure to NMs. It can be considered as a first step in a complex risk assessment process that may involve quantitative exposure measurements and accidental risk assessment.

A conceptual model was notably presented by Maynard using “impact” and “exposure” indexes (Maynard, 2007). He highlighted that a big challenge remains for a relevant and efficient definition and weighting of the risk factors. Recently D.H. Brouwer published a very interesting review which aims at identifying the intrinsic differences and similarities of some CB tools (Brouwer, 2012). Our paper is complementary to the Brouwer’s study as it will focused on advantages and drawbacks which may be practically encountered in using CB tools for the process industries.

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2. Overview of the current CB methods

Our study will focused on four CB methods: Groso's method (Groso, 2010), CB NanoTool (Paik, 2008), ANSES method (ANSES, 2010) and Stoffenmanager Nano (Van Duuren-Stuurman, 2012) here designated by "STM Nano". This part consists in brief descriptions on these four methods.

2.1 Groso's method

Groso"s method does not follow exactly the classical CB framework and is rather a decision trees approach that helps managing the risks in laboratories involving NM thanks to a classification into three hazard classes (from nano 1 to nano 3). This tool, which target researchers (users) with no specific knowledge in nanosafety, provides an easy way to assess and compare the level of risk. The method focuses on the level of containment which can lower the hazard level to its minimal value "nano 1", in case of total enclosure. By using such tree-based approach, notions of hazard and exposure are merged in a unique index, pushing the simplicity of the method to the highest reachable level (no calculation algorithm) but loosing the ability to identify both aspects distinctively. Safety guidelines (technical, organizational and PPE) are provided to put in front of the different classes. It consists essentially of a mix between general good laboratory practices, safety measures and personal protective equipments (PPE).

One particularity of the Groso's method is to differentiate the impact of the quantity factor for handling and production operations. The threshold quantities has been computed from an hypothetical accidental scenario (spillage) which may occur in the surrounding space (arbitrary defined as a 10 cubic-metres volume) and compare to the BSI recommendations (BSI, 2007).

For nano-objects in suspension, a hazard class is attributed as a function of the volume of the solution and the ability to the process to generate droplets and aerosols. For liquids containing NMs, the generation of droplets by the process (Johnson, 2010) is considered as a potential exposure scenario that leads to the hazard class "nano 3". Nanocomposite preparation is a potential way of exposure considered as a process step that can release aerosols in the environment (Fleury, 2011). Here the lower hazard class "Nano 1" is attributed if the process does not involve any mechanical or thermal treatment.

2.2 CB Nanotool

(Paik, 2008) introduces a pilot CB tool named "CB Nanotool" based on existing knowledge of NM toxicology based on the CB framework proposed in earlier publications. CB Nanotool consists of a Risk-Level (RL) matrix, similar to that used in the implementation of CB through the HSE's COSHH Essential program, leading to four categories of "bands", namely control bands, which indicates a level of technical control that must be set up to manage the risk. The risk level (RL) is determined by severity score and the probability score which are both classified into four bands and are analogous to the impact and exposure indexes described in (Maynard, 2007). The three lowest risks level (RL1 to 3) correspond to engineering control measures, whereas the higher risks level (RL4) consists in asking for a specialist advice.

Many efforts have been put in CB Nanotool hazard assessment. It is based on toxicological information available in the current literature in 2008 that seems hardly changed from nowadays. Hazard assessment is performed through a quite long list of factors that are expected to be determinant in the overall NM severity. These factors can be classified into two groups: physicochemicals properties (surface chemistry, shape, size and solubility) and toxicological properties (carcinogenicity, mutagenicity and dermal toxicity). Practically, most of these factors cannot be determined and properties of the parent material (e.g. carcinogenicity, mutagenicity, reproductive toxicity, and dermal hazard) are used to provide a starting point in the NM hazard assessment. The parent factors counts for 30% of the total score in the hazard index calculation (greater consideration is given to the NM characteristics).
The second axe of the CB matrix "probability" focuses on the potential exposure by inhalation. The index gathers process information (amount of NMs, frequency, duration), physicochemical properties (dustiness/mistiness) and organisational information such as number of employees with similar exposure.

In both probability (exposure) and hazard banding cases, the user keeps the possibility to answer "unknown" when the factors remain undetermined. To avoid CB Nanotool to be overconservative, it was decided that the factor "unknown", which can play a major role for assessing NM hazard, will be assigned to 75% of the maximum value. Even if this has not been demonstrated practically yet, CB Nanotool has been design as a dynamic tool in which risk factors can evolve as a function of available scientific data, especially concerning NM toxicology (Paik, 2008). These new data might change the relative importance of one factor compare to the other. The score and range of value can also be modified according to the level of risks one is willing to accept, or for large-scale manufacturing of NMs (particularly for the probability factors ranges).

2.3 Stoffenmanager Nano

Initially, the generic Stoffenmanager is a web-based control banding tool which was design to help small- and medium-sized companies to handle hazardous substances with more care (Marquart, 2008). Recently, TNO has developed a nano-specific module within the generic Stoffenmanager for helping in managing the risks associated to NMs. This module was first presented to the 2010 Nanosafe conference and then published in (Van Duuren-Stuurman, 2012). Similarly to the COSHH approach. STM Nano risk-banding tool has been developed for employers and employees handling NMs and having limited experience in occupational health. Input parameters for the hazard assessment were selected based on their “theoretical” availability in the MSDS and the technical data sheets. Stoffenmanager combines the available hazard information with a qualitative assessment of the potential exposure. The authors of STM Nano highlight the importance of basing the hazard banding system on inputs parameters which are available to the user and for which information is accessible (for instance, water solubility is used as a surrogate for solubility in biological media).

2.4 ANSES method

The Anses method respects a standard CB framework by crossing hazard bands with emission potential bands. The determination of the hazard index starts from the properties of the parent material or an analogous material (CLP R-phrases) which is then passed through an incremental tree composed by 4 factors that enable to determine the final hazard classification. The emission potential is determined as a function of the physical form of the NM (solid, liquid, powder or aerosols) incremented if transformations are likely to occur during the process (e.g. spraying)

Emission potential and hazard assessment lead to determine a control class (CL) for which technical recommendations are furnished (mainly containment and ventilation). Both highest CL recommend a full containment in addition to a review by a specialist (a toxicologist) for CL 5. This specialist request may be particularly annoying because it seems quite discouraging trying to find a toxicologist to bring answer that probably goes beyond the state-of-the-art research or may require long and expensive research study.

3. Discussions

This part aims to discuss on seven properties that have been pointed out as critical elements to ensure the relevance of the NM risk assessment in the industry. These statements are issued from the observation of INERIS in workplaces of various industries involving different type of NMs.

3.1 Quantity

Amount of NM is probably one of the most relevant and available factor to assess exposure to NM as it is usually tightly linked to the potential amount of airborne material released at workplace. Two tendencies have been observed among the studied methods: the one like STM Nano and Anses which discard the amount of NM in the risk band calculation, and the others (CB Nanotool and Groso’s method) which include this factor but fail to comply with industrial activities due to an upper limit not greater than 100 mg. This 100mg threshold is reached in almost all large scale processes, then the range factor being inefficient to distinguish the likely of exposure between two different industrial operations which may involve very different quantities of nanoscale products (e.g. both 10 g and 1 kg will lead to the same score). Surprisingly, although STM Nano does not consider the amount of product, the weight fraction is a parameter which is taken under consideration to compute the exposure index.

3.2 Size and agglomeration state:

Size is also a relevant factor to assess the risks associated to NMs since it plays a relevant role in hazard assessment as size predicts how far the NMs will penetrate into the respiratory tract and the possible translocation into the body. But considering exposure, size and density parameter will also be relevant to predict the behaviour of airborne release (air capture, filtration efficiency, sedimentation). Then it is quite surprising this parameter is not part neither from exposure nor hazard index calculation in both Anses and Groso’s methods (STM Nano only considers it in the hazard band calculation). Furthermore, agglomeration and aggregation state is a critical parameter that is relevant for both exposure and hazard assessment although this factor is hardly considered in the risk banding calculation. In Groso's method, the agglomeration factor is incremental and used to differentiate class "nano 2" from class "nano 3", when the amount of powder is greater than 100 mg. In Stoffenmanager Nano, aggregate and agglomerates of size exceeding 100 nm are considered as cluster of NMs and considered as such, as they could possibly retain nano-specific properties and are identified through the specific surface area and the primary particle size criterion. Practically such data are scarce in MSDS or technical data sheet and the knowledge of the state of agglomeration would require additional tests that have to be performed by an expert.

3.3 Aspect ratio and fiber paradigm

Fiber-shaped nano-objects are considered to have a high potential hazard due to the fiber paradigm (asbestos-like carcinogen effect). Anses, Groso's and STM Nano methods are quite conservative on this point since a length-to-diameter aspect ratio greater than 3 will lift up the hazard band to its highest level (unless the fibers are embedded in a solid matrix). Insoluble nanofibers exceeding a length of 5 µm are considered as persistent, in accordance with the fiber paradigm (Donaldson, 2009). Unlikely, CB Nanotool considers the fiber shape of NM as factor which increase hazard but does not require automatically the highest hazard band. Moreover, the fiber shape often comes together with the notion of bio-persistent particle which require in-depth toxicological study and is generally not known neither through the generic documentation of the product (i.e. MSDS and technical datasheet) nor through the up-to-date scientific literature. Therefore, the conservative approach on the fiber-shaped NMs causes some difficulties for practical applications.

3.4 Factor availability

CB method has to deal with the strong uncertainties which affect NMs and then an efficient hazard banding will have to rely on relevant factors that will be available for the person intended to perform the risk assessment (in general a non-expert). To ensure accessibility to the numerous factors, STM Nano relies on MSDS which are supposed to contain enough information about the involve NM to give ability to the user to answer. A recent study has shown that MSDS are not so as perfect as they should be and it is often hard to access to basic parameters that are addressed in the risk banding (e.g. size, solubility, moisture content, dustiness) (Lee, 2012). (Maidment, 1998) stressed the importance of limiting the number of factors in the CB model to reduce its complexity and increase its applicability for non-experts. Paik hazard assessment goes deeper in details than the other methods and allows "unknown" answers. This is particularly useful for handling toxicological parameters (e.g. carcinogenicity or mutagenicity) which are generally highly uncertain. If the unknown-answer trick offers more convenience for practical application, the lack of information causes the final hazard banding to be uncertain and mostly guided by the properties of the parent materials. Even if the number of factors is reduced in Anses method, the availability is not improved since the incremental factors like "solubility" or "evidence of higher activity" can hardly be found in MSDS too.

3.5 Role of parent materials in hazard banding

In many cases poor level of information is available to assess NM risks. Therefore the "trick" is to call for parent material properties so as to provide a first estimation of the potential hazard of the NM. This is done in CB Nanotool, which gives a 30% score to the parent in any case but also in the Anses and the STM Nano methods which propose a classification of NM based on the parent material. (Zalk, 2010) mentioned ones would have required the weight of the parent material to be higher than 30% (cumulative scores related to the parent material in the severity score calculation on the maximum severity score) but one has to be careful by the fact that nanoscale product does not necessarily exhibit the same toxicological properties than their larger counterparts (the parent material). Some NMs, like carbon nanotubes, may seriously affect human health whereas the closest parent (graphite) which does not exhibit similar hazardous properties at all. For this kind of material, increasing the weight of the parent material in the hazard scoring will tend to lower the severity level, in contradiction with the precautionary principle.

3.6 Monitor safety barriers improvements

One great advantage of STM Nano is to include the measures of exposure reduction (control measures and PPE) into the exposure score calculation, then it is possible to score any progress that will be done in term of prevention and protection (new or improved barrier). This is not the case in the other methods which do not take into account the level of prevention and protection when determining the exposure band.

However, risk assessment should be performed without considering PPEs that should not be include as a factor of reduction in the exposure score of the workplace itself and should only be considered in the last case , e.g. in accidental case, when control measures might be deactivated.

3.7 Coactivity

It is quite frequent to observe that several processes take place in the same area and then it is important to take into account the exposure caused by coactivity. Stoffenmanager takes into consideration the different sources of exposure at workplace: background, near field and far field. This is particularly useful regarding the risks of exposure due to co-activities in the same area which may be discarded with other methods focusing only on the near field sources. This point out some indirect exposure scenario in case of handling of very dusty NM or mistiness provoked by high energetic processes (e.g. mixing, spraying), (Johnson, 2010).

Table 1: Comparison of seven properties that have been pointed out as critical elements to ensure the relevance of the NM risk assessment in the industry over the four studied CB tools.

	Groso	CB Nanotool	STM Nano	Anses
Quantity	Not adapted to industrial activities (100 mg)	Not adapted to industrial activities (100 mg)	Not considered	Not considered
Size	Not considered	Included in the hazard factors	50 nm limit hazard factor	Not considered
Aspect ratio / shape	Fibre (L/D > 3)	Included in the hazard factors	Highest class if bio-persistent fibre	Highest class if bio-persistent fibre
Factor availability	Mostly available	Mostly unavailable for NM	Based on MSDS but often unavailable	Often unavailable
Parent material	Not considered	Count for 30% of the hazard score	Use in case of NM uncertainties	Starting point for the hazard banding
Monitor safety barrier improvements	Not possible	Not possible	Yes, through exposure reduction factors	Not possible
Coacticity	Not considered	Not considered	Near filed and far filed concepts	Not considered

4. Conclusion

This study has described and compared 4 different methods which aim to manage the risk associated to NM trough a CB framework.

Anses method may be one of the most conservative because some incremental factors can lead straight to the highest hazard band (HB5), for instance if there is no parent material of if it is not possible to statue about the biopersistence in case of fiber. This over-conservative approach tends to put a large amount of workplace to the same level of hazard and may pose some difficulties in the prioritizing task that should follow the risk assessment.

If STM Nano seems to be one of most complete tool to manage the nano risks, this coverage is paid by an increased complexity (large number of parameters and complex calculation algorithm) that may limit the applicability of the method by non hygienist persons. Particularly, the on-line web application may appear like a black-box in which the computation leading to the exposure and hazard banding may not be fully understood.

The tree approach of Groso's method offers a very convenient form which may easily be exploitable by non-specialists. Unfortunately the mix between hazard and exposure factors caused by the tree-approach and the low level of recommendation which come in face of the risk levels limit the scope of the method.
Finally CB Nanotool benefits from the “unknown” answer that enables the user to discard some uncertain properties (often the case in industrial production) that are partially replaced by properties of the parent

material (own for 30% of the final score). However, this low-conservative approach leads to lower the hazard of NM exhibiting more hazardous properties than their larger counterparts.

From that study, it should be underlined as well that current control banding approaches are intrinsically limited and cannot cover all types of hazards: if they are mainly focused on health risks and do not address safety (fire/explosion) or environmental risks, these aspects should not be neglected for an efficient-in-practice risk assessment (Vignes, 2012). Similarly, degraded working conditions (maintenance, cleaning) are not covered although these scenarios often increase the risk due to safety barriers deactivation (hood stopped, glovebox opened…).

As mentioned in the 3rd RIP-oN final report (European Commission 2011), it is challenging to see how CB tools could be used without a critical review of the input parameters and collection if much more information about them in relation to each case of its use. This comment, which was initially dedicated to CB Nanotool and Anses tool, indeed can be extended to all CB tools for which this kind of review is still scarce. As (Brouwer, 2012) did in his paper, this work provides first elements to fill the lack raised by the RIP-oN report and aims to be complemented by the results of on-going studies at INERIS.

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