NANOTECHNOLOGIES AND ENVIRONMENTAL RISKS OF NANOMATERIALS

Nanotechnologies and Environmental Risks

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Abstract- In the paper various aspects of modern nanotechnologies and, as a result, risks of nanomaterials impact on an environment are considered. The very brief review of the First International Conference on Material and Information Sciences in High Technologies (2007, Baku, Azerbaijan) is given. On this conference many reports were devoted to nanotechnology in biology and business for the developing World, formation of charged nanoparticles for creation of functional nanostructures, nanoprocessing of carbon nanotubes, magnetic and optical properties of manganese-phosphorus nanowires, ultra-nanocrystalline diamond films, and nanophotonics communications in Azerbaijan. The mathematical methods of simulation of the group, individual and social risks are considered for the purpose of nanomaterials risk reduction and remediation. At last, we have carried out researches at a plant of polymeric materials (and nanomaterials), located near to Baku. We have made assessment the individual risk of person affection and constructed the map of equal isolines and zones of individual risk for a plant of polymeric materials (and nanomaterials).

Keywords: nanotechnologies, nanomaterials, risk assessment, simulation

1. Introduction

Nanotechnology can be defined as the control and restructuring of matter below 100 nm in size in order to create materials, devices, structures and functional systems. Simply put, nanotechnology is the direct manipulation of matter at the level of atoms and molecules [1]. Restructuring nature at the nanoscale leads to materials with novel and exotic properties. For existing substances and materials remade at the nanoscale, these properties

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are significantly different to their larger equivalents. The novel properties of nanomaterials make them attractive for use in industrial processes.

Let we brief review of the First International Conference on Material and Information Sciences in High Technologies (2007, Baku, Azerbaijan) [2]. On this conference many reports were devoted to nanotechnology in biology and business for the developing World, formation of charged nanoparticles for creation of functional nanostructures, nanoprocessing of carbon nanotubes, magnetic and optical properties of manganese-phosphorus nanowires, ultra-nanocrystalline diamond films, and nanophotonics communications in Azerbaijan. There are some of them.

First of all, N.Mamedov from Institute of Physics National Academy of Sciences of Azerbaijan has made the report “Photonics (nanophotonics) and optical communications in Azerbaijan: horizons for development”. He noted that current optical research is directed towards the advanced design and fabrication of optical fibers, integrated optics, optical amplifiers, optoelectronic devices and nanostructures, which are all photonic devices. Although research, education, and training on photonics and nanophotonics in Azerbaijan can hardly be taken for fully adequate to the word standards, the forecast given by the Ministry of Communications and Information Technologies with regard to optical communications is optimistic with a significant increase in the nearest future.

Y.Nakavama from Osaka University (Japan) has made the report “Preparation and nanoprocessing of carbon nanotubes”. He noted that because of their structural perfection, tiny size, low density, excellent mechanical property and unique electronic property, carbon nanotubes (CN'I's) have been placed in the research and development of various applications such as reinforcement with electric conductance for functionalized composites and building blocks for future nanoscale electronic or electromechanical devices In his report he reviewed recent works on the synthesis toward mm-long blush-like (vertically aligned) CNTs and nanoscale-engineering of CNTs.

At last, S.Habib from Nanotechnology Center King Abdul Aziz University Saudi Arabia has made the report “Nanotechnology for the Developing World”. He noted that the sheer size of global expenditure on R&D on nanotechnology is a sure indicator attesting to the very promising economical viability of nanotechnology worldwide. Presently the private sector spends over 10% billion annually and the figure is projected to reach S 12 Billion in 2008, while global governmental funding on nanotechnology R&D is about 4 $ billion and rising. By no means this expenditure is evenly distributed among the different countries and as a matter of fact the different regions and contents of the world. A fact indicating how is the possible prime winners of exploiting the emerging trillion dollar nanotechnology market. Competing, for market shares on the nanotechnology products projected to reach a trillion dollar size, some countries are spending around 10 Euros per capita annually to develop such products.

In Azerbaijan roughly US$ tens million is spent each year on the research and development of nanotechnology and nanomaterials. Nanomaterials in the form of nanoscale powders and fibres are already being used in sunscreens, cosmetics, food additives, packaging, scratch-proof and self-cleaning paints and glass, clothing, sports equipment, disinfectants, fuel additives, batteries and a range of other products. The table below outlines the applications for nanomaterials that are currently in use in Azerbaijan or close to commercialisation.

Table. Nanomaterials currently in use in Azerbaijan.

Energy and Environment	Industrial catalysts Fuel additives Membrane separation Water/air purification, fuel cells technologies
Electronic	Semiconductors Memory applications Flexible displays
Manufacturing	Coatings; catalysts Coatings for food protection Zinc oxide (ZnO) in paints, sunscreens
Mining and Agribusiness	Alumina platelets Mineral Separation Bioextraction; applications for particles, oxide powders
Health and Medical	Diagnostic markers Particle engineering Biosilicates for tissue engineering

Let we consider some common nanomaterials and their uses.

2. Some common nanomaterials and their uses.

Zinc oxide and titanium dioxide powder have been used in sunscreens extensively since their inception, lending them their distinctive thick white appearance [3]. While these conventional powders are opaque, nanoscale zinc oxide and titanium dioxide particles in the order of (40÷50) nm are transparent while still retaining the ability to block UV rays. By substituting conventional powders of zinc oxide and titanium dioxide with nanoparticles, manufacturers are able to produce a sunscreen that is transparent when applied. In Azerbaijan, nanoscale titanium dioxide and zinc oxide began to be used in 2003.

Carbon nanotubes consist of carbon atoms arranged in a lattice and rolled into a tube of variable length, but only a few nm in diameter. They are needle-like in shape and have a structure similar to that of asbestos [2]. Carbon nanotubes are extremely strong, up to 10 times that of steel, while remaining very light. Their high strength to weight ratio makes them especially suitable for reinforcing materials ranging from tennis rackets and car tyres, to military tanks. Carbon nanotubes also exhibit novel electrical conductivity, and they are being developed for use in high performance circuits and displays.

Catalytic nanomaterials are used in many different industrial processes ranging from mineral refinement, chemicals production and the manufacture of polymers, for example, in Chemical Plant of Polymer in Baku. Researchers at Rutgers University in the US having been developing nanoscale iron and cobalt particles for use in the chemical conversion of coal to diesel [4]. With these new catalysts, researchers hope to continue transport fuel production through the conversion of coal.

During the manufacture, transport, use and disposal of nanomaterials and those products containing nanomaterials, the release of these materials into the environment is inevitable. As the use of nanomaterials increases, so too will their presence in the environment. While pathways such as the waste stream from industrial processes or product disposal are similar to those for other substances, the use of nanomaterials in sunscreens and cosmetics can also lead to the environmental presence of nanomaterials. In Europe, ecologists are detecting the active ingredients of sunscreens and skin care products in inland lakes at levels that are starting to have an impact on wildlife [5]. This suggests that even the use of these consumer products, which aren’t traditionally seen as entering the environment after use, will likely lead to the environmental release of nanomaterials. Since nanomaterials are, can and will enter into the environment it is crucial to assess the potential risk these materials may have for human health and environmental harm.

3. The risk assessment of nanomaterials

The unique properties and extremely small size of nanomaterials are such that even determining the full extent of the risks to human health and environment is currently beyond the means of existing risk assessment frameworks [3].

Given that nanomaterials can be more toxic than their conventional equivalents, it is clear that the risks associated with nanomaterials cannot be inferred from the relative risk or safety of their bulk equivalents. That is, although some nanomaterials are made of substances that have long been used in other forms, their very different physical and chemical properties mean they may pose different risks than conventional materials. The toxicity of a nanomaterial cannot be assumed by comparison with another nanomaterial since toxicological properties arise from a variety of features, such as their surface characteristics, size, shape, overall composition and chemical reactivity. There are in essence several independent and interdependent variables that dictate toxicity.

The dedicated testing of each individual nanomaterial will be particularly pertinent when next-generation nanotechnology develops complex nanostructures and devices those themselves actively interact and manipulate molecules and organic compounds. The level of interactions possible with living organisms and the wider environment will be so broad and complex that the data derived from testing one next-generation nanomaterial cannot be used to determine the safety or risk of any other next-generation nanomaterial due to the inordinate number of variables in play.

While there is an established methodology for assessing the toxicity of conventional substances, the report into the risks associated with Nanomaterials by Britain’s Royal Society notes that current testing regimes are not entirely suitable for nanomaterials [6]. For example, the European Commission’s *Scientific Committee on Emerging and Newly Identified Health Risks* has suggested that any determination of the critical dose of nanomaterials must also take into account the number of particles and total surface area, rather than just the exposure mass of a substance, which is the current practice [3]. In addition, the effects of surface characteristics and coatings, their size and shape, physical composition and chemical reactivity, and the potential for aggregation (clumping) all need to also be specifically tested to develop a comprehensive assessment of the risks of nanomaterials. The Royal Society flags as a priority the need to establish a standardized set of methodologies to effectively assess the contribution of all these factors to nanotoxicity in both the environment and in humans [6].

Current toxicological methodologies express toxicity with respect to a critical mass concentration beyond which harm occurs. Yet hazardous dosages expressed in mass concentrations do not give an accurate indication of the exposure amount for nanomaterials above which harm is induced. This is because the minimum toxic dose for nanomaterials is also affected by the total surface area available for biological reaction and the number of particles present.

The risk assessment of nanomaterials is further complicated by a lack of established standardised indicators for nanotoxicity. While factors such as surface characteristics and coatings, shape, physical composition and chemical reactivity, and the potential for aggregation may all play a role in nanotoxicity, their exact contribution is not known.

Researchers are still clarifying the way nanomaterials are transported within living organisms and the regions and organs in which they concentrate. This information is essential in establishing the risk of nanomaterials as it gives an indication of which organs and processes are most vulnerable to toxic effects.

The extremely small size of nanomaterials puts them completely beyond the ability of optical microscopes to detect and analyse. The instruments required to track and observe nanomaterials, such as scanning tunneling microscopes and atomic force microscopes, are extremely expensive machines that are confined to the laboratory. Even for toxicological studies conducted within the lab using cell cultures or test animals, these instruments are unsuitable for tracking and analyzing nanomaterials within individual organisms or single cells. This makes it difficult to study the behaviour of nanomaterials in living organisms and is one of the reasons why this area of knowledge is so limited.

And so, without a coherent testing regime within which the risks of nanomaterials can be appropriately assessed, it is currently impossible to make informed decisions regarding their handling and use. Not only is there not enough information about the actual hazards of nanomaterials currently in use to effectively manage these risks, but there are no established risk assessment regimes capable of considering the unique characteristics and properties of these new materials.

4. Simulation of risk assessment of nanomaterials

The analysis of nanomaterials manufacture shows, what even at normal functioning, the influence of such objects on an environment is connected both to social - psychological influence on people, and with the potential danger of pollution of an atmosphere and territory dangerous substances [8÷12]. Therefore, the model of risk should reflect all essential factors on which functioning system to the greatest degree depends should be taken into account.

Output parameters of mathematical model of risk determine a mathematical expectation of amount of the affected people living in area of industrial object [13]. We shall consider possible analytical approaches to the decision of a problem. The mathematical expectation (risk R) of amounts of affected people can be determined dependence

$$R = \int_{\varphi=0}^{2\pi} \int_{l=0}^{\infty} r(\varphi,l) \cdot P(\varphi,l) d\varphi \cdot dl ,$$

Where: $r(\varphi,l)$ is a distance from a plant up to the person in polar coordinates (the beginning of coordinates is superposed with plant); $P(\varphi,l)$ is a probability of affection of the person in a point with (φ,l) coordinates.

The probability of affection $P(\varphi,l)$ is defined as follows:

$$P(\varphi,l) = P_0(\varphi) \cdot P_l(l,\varphi_0),$$

Where: $P_0(\varphi)$ is a probability of that at the moment of emission the direction of wind $\varphi = \varphi_0$ will be realized; $P_l(l,\varphi_0)$ is a probability of affection on distance l from a place of emission in direction φ_0.

As a pollution is equiprobable at any moment then $P_0(\varphi)$ should be defined on the basis of a wind rose in the given zone or region. If to neglect differences in characteristics of an underlying surface on each of directions of possible distribution of harmful emission and to enter concept of the average characteristic it is possible to simplify essentially a problem, having divided variables:

$$R = \int_{l=0}^{l=\infty} P(l) \int_{\varphi=0}^{\varphi=2\pi} r(\varphi,l) \cdot P(\varphi) d\varphi \cdot dl$$

This approach to calculation of risk criterion is one of possible variants of an analytical method of assessment. In practice of risk assessment the following approaches to mathematical modelling risk are considered by us.

Modelling of individual risk. Individual risk is probability of the person affection in the course of year from the certain reasons in the certain point of space. Results of the analysis of individual risk are displayed on a map of the plant as the closed lines of equal values (isolines).

The construction of isolines of individual risk is carried out under the formula (1)

$$R_i(x,y) = \sum_{m \in M} \sum_{l \in L} P_{Q(x,y)} F(A_m) \qquad (1)$$

Where: $P_{Q(x,y)}$ is a probability of influence on the person in a point with coordinates (x, y) of the damaging factor Q with the intensity corresponding to affection of the person (healthy man of 40 years) under condition of realization of A_m event (pollution); $F_{(Am)}$ is frequency of occurrence of A_m event per year; M is a set of indexes which corresponds to considered events; L is a set of indexes which correspond to the list of all damaging factors arising at considered events.

We have carried out researches at a plant of polymeric materials (and nanomaterials), located near to Baku. Isolines of equal risk and zones of individual risk are resulted on fig. 1 for this factory.

We can see from fig.1, that near of plant (zone 1) the individual risk of person affection is high, R=10^{-4}. In zone 2 R=10^{-5} (the individual risk of person affection is acceptable). At last, in zone 3 R=10^{-6}, i.e. the individual risk of person affection is low.

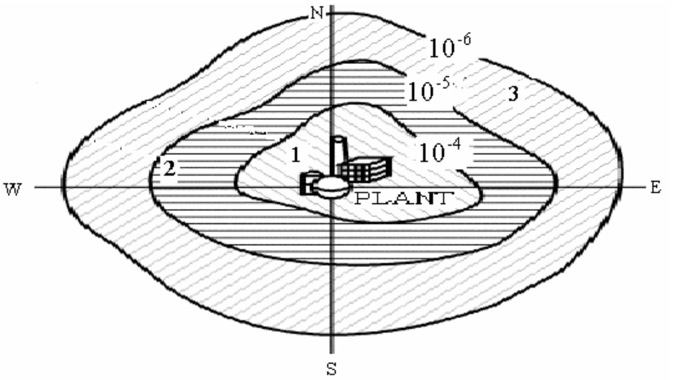

Fig.1 Construction isolines of equal risk and zones of individual risk for a plant of polymeric materials (and nanomaterials): 1, 2, 3 are zones of accordingly high, acceptable and low risk.

Modelling of social risk. The social risk is a dependence of occurrence frequency of the events causing affection of people, on this number of people. Social risk R - F (N) characterizes scale of possible extreme situations. The social risk can be designed under the formula (2)

$$R_s(N) = \sum_{m \in M} \sum_{l \in L} P\left(\frac{N}{Q_m}\right) P\left(\frac{Q_m}{A_l}\right) F(A_l), \qquad (2)$$

Here: $P\left(\frac{N}{Q_m}\right)$ is a probability of N people affection from the damaging factor Q_m; $P\left(\frac{Q_m}{A_l}\right)$ is a probability of occurrence the damaging factor Q_m at realization events A_l.

Modelling of risk at accidents on chemically dangerous plants manufacturing of nanomaterials. On known toxic doze D in a point with coordinates (x, y) a mathematical expectation of losses among population $M(N)$ is determined under the formula

$$M(N)=\int_{S_r}\int P[D(x,y)]\cdot\psi(x,y)dxdy \qquad (3)$$

Where: S_r is an integration domain, i.e. the area of a part of city within the limits of which people affection is possible at accidents on the set plant; $\psi(x,y)$ is a density of people location in vicinities of a point with coordinates (x, y); $P[D(x,y)]$ is a probability of people affection depending on amount of a toxic doze in a point of city with coordinates (x, y), determined from the parametrical law of people affection harmful substances; $D(x, y)$ is the toxic doze chemically dangerous substance for a point with coordinates (x, y) under the formula

$$D(x,y)=\int_{t_n}^{t_k}\Omega(x,y,t)dt$$

Where: t_n.........t_k are intervals of time; $\Omega(x,y,t)$ is a concentration of chemically dangerous substance in an atmosphere for a point with coordinates (x, y) during the set moment of time t.

Under the formula (3) mathematical expectation of losses is determined for a case when the initial data are known. At preliminary definition of a mathematical expectation of losses it is necessary to take into account variability of a direction (θ) and speeds of a wind (v) within one year. Then losses can be determined under the formula

$$M(N)=\int_{S_r}\int\int_{0}^{2\pi}\int_{V_{\min}}^{V_{\max}} f(\theta,V)P[D(x,y)]\psi(x,y)dVd\theta dxdy \qquad (4)$$

Where: $f(\theta v)$ is a function of density of distribution of a direction 0 and speed v a wind; v_{min} and v_{max} are minimal and maximal possible values of speed of a wind; S_r is an integration domain. Other designations are same, as in the formula (3).

Taking into account expression (4), the assessment of individual risk at a plant can be carry out under the formula

$$R_e=\frac{H}{N}\int_{S_r}\int\int_{0}^{2\pi}\int_{V_{\min}}^{V_{\max}} f(\theta,V)P[D(x,y)]\psi(x,y)dVd\theta dxdy$$

Where: H is a probability of pollution in the course of year; N is population size.

5. Conclusion

In the paper various aspects of modern nanotechnologies and, as a result, risks of nanomaterials impact on an environment are considered. The mathematical methods of simulation of the group, individual and social risks are considered for the purpose of nanomaterials risk reduction and remediation. At last, we have carried out researches at a plant of polymeric materials (and nanomaterials), located near to Baku. We have made assessment the individual risk of person affection and constructed the map of equal isolines and zones of individual risk for a plant of polymeric materials (and nanomaterials).

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