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The Potential Risks of Exposure of Nanodispersed Metal and Non-Metallic Powders on the Environment and People

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Abstract: Modern systems of labor protection in the nanopowders production and research, including the training programs and risk assessment and control, do not exclude the occurrence of adverse effects on human. The data on the degree of danger of various metal nanopowders and their compounds to the health of workers and on potential adverse acute or chronic effects on humans and the development of specific or non-specific pathology have been obtained. According to the experimental data it was found that the technological processes associated with the production of metal and non-metallic nanopowders have an average level of potential danger to the environment and personnel that allowed developing the safety standard for the nanoparticles content in the environment (air) in the working places.

Key words: Potential danger · Toxicity · Health effects and metal and oxide nanopowders · The air of the working area · The environmental aspects

INTRODUCTION

The objective of the article is to solve a specific task: to develop a set of methods and technical means to detect nanoparticles and study their effect on the human body. The objects of the study were powders of different metals, oxides, ceramics of different composition and composite materials.

Production of ultrafine powders faces many challenges conditioned by different degrees of risk of environmental pollution and health effects [1].

According to the current literature, the most active countries participating in the inter-governmental program for identification of potential risks of nanomaterials are the U.S., Japan and UK. There is a kind of specialization between them: U.S. investigates the toxicity of nanomaterials, environmental pollution and terrorism using nanomaterials, Japan studies the toxicity of nanomaterials and UK is developing standards for nanomaterials safety [2].

China has developed a number of National standards related to terminology (GB/T19619-2004); measuring particles (GB/T13221-2004, GB/T19587-2004; GB/T19627-2005) and specification of nanomaterials (GB/T19588-2004 - GB / T19591-2004).

Being supplied from different sources in the environment, the nanoparticles, due to their small size, are able to penetrate in the most different areas of the world. The particles move between habitats (air, hydrosphere and lithosphere) and migrate to diverse biological objects (human and other terrestrial inhabitants, flora and fauna of the aquatic system, soil and sediment and so on).

Coming to the air, nanoparticles can form aerosols, which being stable in time, penetrate into the terrestrial biological objects by the air, though breathing, skin and digestive tract. Through adsorption the nanoparticles from aerosol are absorbed by plants, actively penetrating in the plant world, being a food source for almost all bio-objects. The nanoparticles dispersed in the air can be absorbed by the water of lakes, rivers, etc. and the precipitated ones are supplied into the soil and ground.

In soil, the nanoparticles can break its microbiological composition, providing an indirect effect on fertility [3]. From soil nanoparticles can penetrate into benthos (set of organisms of animal and plant origin), living on the ground and in the soil of water reservoir bottoms, which is saturated with nutritive substances in the processing of soil and further up the food chain to algae and more complex organisms of the animal world.

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The nanoparticles in the air can deposit on leaves and other ground parts of plants and the nanoparticles of the hydrosphere and lithosphere interact with the parts of plants, located respectively in these environments. Accumulation of nanoparticles on the surface of plants can affect photosynthesis and gas exchange and, consequently, their vital functions.

Being supplied in the air from the hydrosphere and with sewage, the nanoparticles form suspensions, which are primarily absorbed by plankton and invertebrates, living in the deposits on the bottom. Invertebrates - arthropoda consist of more than one million species, where a special place is occupied by the class of crustaceans, being a kind of "filters" for the substances that are toxic to larger organisms, as well as a food source for algae and fish. They are one of the primary representatives of the organisms subjected to ecotoxicological effects of nano- and micro-materials [4].

The easiest and the most effective way of nanoparticles occurrence is specific for all organisms, producing food from soil, water and other biological objects (plants and animals). This way was proved using the most sensitive participants of food chains, the invertebrates, the majority of which lives in the aquatic environment.

MATERIALS AND METHODS

The paper used the complex for mixing and activation of powder compositions, the set for determining the particle size for the study of specific surface of nanopowders, the complex for investigation of the surface and chemical composition of the substance, the complex for nanoparticles spectrophotometric analysis, X-ray diffractometry, the set for determining the mechanical properties of powders and materials. Besides, the authors used scientific, methodological and regulatory literature, including foreign legal documents on nanosafety.

Results of the Study: When developing new technological processes of nanopowders production the researchers usually use such metals as Fe, Au, Ti, C, Mo, Al, Co, Cr and their oxides (TiO2, Al2O3, V2O3, Fe2O3, SiO2, ZnO and CeO2). Currently, the impact of metal powders and their oxides on the human body has been studied insufficiently.

Depending on the extent of damage to various organs and pathological processes, metals can be conventionally divided into three groups.

The first group includes metal aerosols, causing pathological changes in the respiratory system (iron, tungsten, niobium, tin, etc.).

The second group includes aerosols of metals and their compounds that affect the respiratory system and cause dysfunction of the internal organs (chromium, molybdenum, vanadium, nickel, cobalt, copper, silver, etc.).

The third group includes metals having toxic effects that can cause acute and chronic poisoning (e.g. mercury, lead and manganese) [5].

Under adverse working conditions and non-compliance of safety rules, metals and their compounds act on the human body, causing a variety of professional pathology.

We use an approach based on the construction of attributive general table (AGT), listing of characteristics and analysis of potential adverse effects by systematizing functional blocks of the available data on the physical, physical and chemical, molecular-biology, cytology, toxicology and environmental characteristics of nanopowders of metals and metal oxides in order of importance. A quantitative measure of each of the evaluated characteristics within the functional block is the scoring with their eventual graduation (states) and the degree of importance (weight). If the characteristic is alternative, we use two estimates: yes or no. At the maximum expression of a characteristic it is scored 5. If the feature eliminates the risk of nanopowders, it is scored 0. If the data of the considered characteristic is not available, it is recognized uncertain [6]. Calculation of the "private" danger D for each functional block of properties is performed on the formula:

$$D_k = \frac{\sum_{i-1}^{N} R_i \varphi_i}{\sum_{i-1}^{n} R_i^{\max} \varphi_i}$$

where k – is the serial number of the functional block; i - serial number of the characteristic; N - the total number of characteristics in the functional block; R - rating the characteristic severity; ö - the value of the weighing function for the i-feature in accordance with its rank, given in AGT.

Physical characteristics that influence the risk of nanomaterials and nanoparticles to human health, are the size and form. We have studied the structure and properties of nanopowders of copper, nickel, iron,

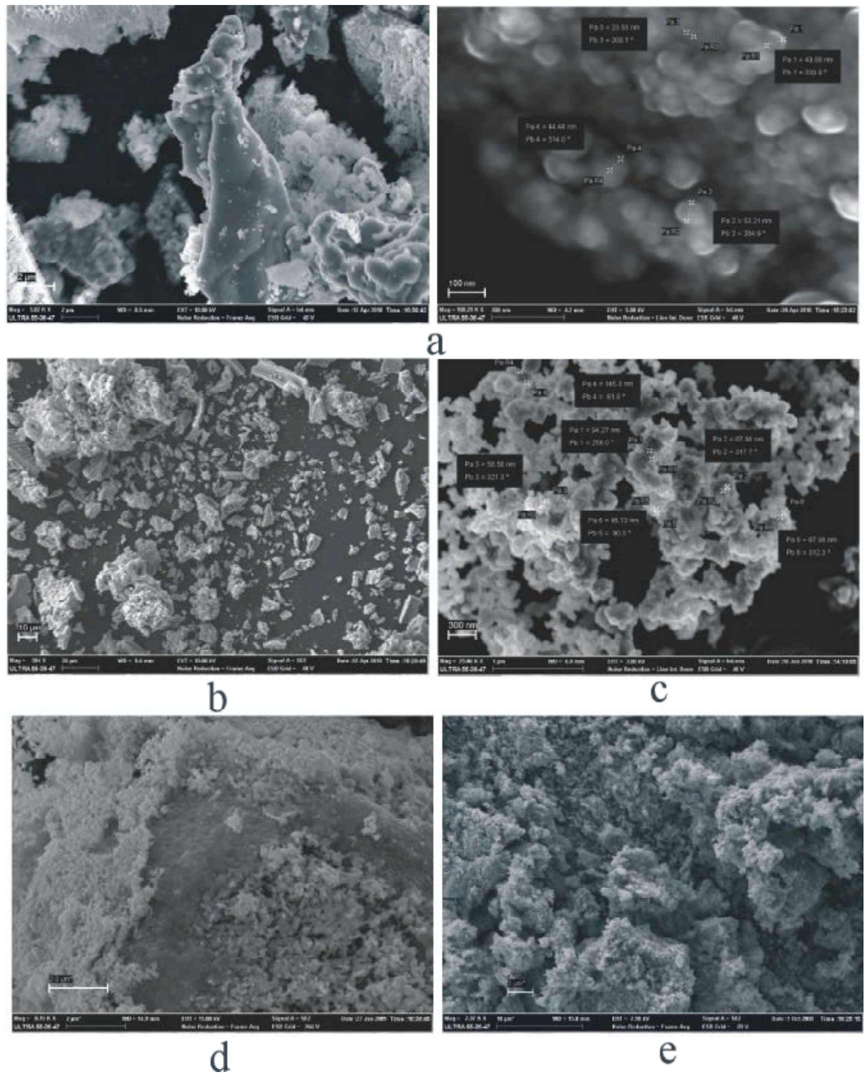

Fig. 1: Morphology of nanopowder based on: *a - zirconium oxide, b – carboxyl, c – aerosyl, d - nickel powder and e – iron.*

aluminum, zirconium and titanium, namely: the form, size and nature of the size distribution of nanoparticles. It was found that the nanopowder particles based on zirconium oxide according to sedimentation analysis showed that the specific surface area of zirconium oxide ranges from 50 to 90 m^2/g, depending on the milling time. Nanopowder of nickel has a specific surface from 0.59 to 14 m^2/g, a particle size of about 50 nm and iron nanopowder has a specific surface from 5 to 50 m^2/g and a particle size of 30-50 nm; powders of carbosilicide and aerosilicide (organosilicon powders) have a particle size of about 70-100 nm. For the metal nanopowders and their oxides the size corresponds to the diameter. Along with the decrease in the particle size the risk of exposure increases, as the basic mechanisms of the nanoparticles damaging effect on living systems are associated with the processes occurring at the interfaces, the form factor (the ratio of minimum to maximum) <10. This form factor is important because the spherical particles are more eliminated by the cells of immune system.

Morphology of nanopowders was studied with the scanning electron microscope “Ultra-55” made by “Cari zeiss” company. The morphology of some nanopowders shown in Fig 1.

Powders, regardless of size, are crystal structures characterized by an oval shape.

Nanoparticles of nickel, iron and cobalt, have the ability to form conglomerates. This is due to autohesive and adhesive interactions. It was found that the cause of harmful factors affecting the environment, can be not only the composition of raw materials, but such properties of nanopowders as flammability, explosiveness and fire and explosion hazard. Nanopowders of metal compounds and their oxides are explosive even at a particle size of 200 nm and a concentration of 10 g/m and the maximum explosion pressure is observed at the concentrations of 50-200 g/m3 and a particle size of 50 nm. Based on the data in the table, obtain the following values for the block 1: D = 0.630.

The study of physical and chemical characteristics that influence the potential danger, showed that our nanopowders are insoluble in water and the insoluble nanoparticles dissociate in biological environments. The charge is an important factor, as the positive particles have the potential genotoxic and mutagenic effects. Our particles are negatively charged and do not have such properties. However, they can damage the skin. Resistance to aggregation is a factor of toxicity of nanoparticles. Nanopowders of metals and metal oxides have a low resistance to aggregation. Hydrophobicity is a factor that facilitates their entry into cells. Based on the above: D = 0.787594.

Molecular-biological characteristics have not been studied. This functional block combines the properties of nanoparticles, consisting in their ability to interact with biological macromolecules and supramolecular structures.

Nanoparticles are able to generate free radicals and to determine the toxic properties of nanopowders. The form of the particle significantly affects the toxicity. The increasing complexity of nanoparticles geometry in most cases leads to increased toxicity. The main mechanism of nanoparticles toxicity is the induction of active oxygen and the reactivity depends not only on the size of the nanoparticles, but also on what is the structure of the nanopowder: crystalline or amorphous D = 0.625.

It is also necessary to consider the group of factors associated with nanopowders cytotoxicity. The smaller nanoparticles have a qualitatively new property, namely cytotoxicity.

In a series of different forms of particles: spherical, flake, dendritic, spindle-shaped, the cytotoxicity increases [7, 8]. Since these changes, detected at the cell level, at the level of the body may be regarded as having an adaptive nature, the importance of this feature in the overall assessment of the risk is relatively low, D = 0.826087.

The functional block "environmental characteristics" includes the parameters that determine the probability of human exposure by nanopowders and how they are spread in the environment. The probability of human exposure as a consequence of direct contact with the product and resulting from migration of nanoparticles of metals and metal oxides in the biosphere is large enough D = 0.793478.

Table 1:

No.	Value of D	Degree of potential danger
1	0.441–1.110	Low
2	1.111–1.779	Average
3	1.780–2.449	High

Final evaluation of the risk is considered as the length of the vector in 6-dimensional space of "private" dangers and calculated by the formula.

$$D = \sqrt{\sum_{k-1}^{6} D_k^2}$$

The results of identification ofpotential risks of nanomaterials were evaluated based on the following table: [6]

The value of D from the experimental data shows that the technological processes associated with nanopowders have an average level of potential danger, so some special research was performed.

Inhalation uptake of nanoparticles through the lungs is considered as the most important way.

Anatomy of the lungs with a very large surface area is a good target for nanoparticles. When inhaled, they can get from the lungs into the bloodstream and then proceed through the body.

Nanoparticles being inhaled, in most cases effectively propagate to all parts of respiratory tract [9].

By diffusion the particles penetrate into the skin and then - in the circulatory system.

As an indication of the effect of the harmful factor in these studies, the researchers selected the sickness rate over time or risk of disease, which can be interpreted as the risk of injury when using the product, which forms the hazard. Characteristics of dose exposure are identified from the length and (or) concentration (intensity) of effects [10].

To study the effect of nanopowders on the functional systems of the human body the researchers have established the characteristics of the occupational exposures [11].

Depending on the nature of industrial hazards the employees were divided into 2 groups (Table 2). The first subgroup was exposed to the effect of dispersed metal nanopowders, the second - the metal nanopowders and their oxides. Contact with these hazards was monitored for one year.

Table 2: Distribution of employees depending on the nature of industrial hazards

Industrial hazard	Number of employees	Male	Female
Subgroup No.1	12	10	14
Subgroup No. 2	24	17	7

Table 3. Incidence for personnel in constant contact with the occupational hazard, depending on the influencing factors (%)

Disease	1- subgroup	2- subgroup
Dystonia:		
- In hypertensive type	26.6	25.8
- In hypotonic type	25	31.6
Chronic pharyngitis and bronchitis	30	33.3
Chronic cholecystitis	31.6	33
Chronic gastritis	–	10.5
Dermatitis	41.6	57

Other employees had occasional contact with pathogenic factors. They made up the third group. The group consisted of 60 people: 28 women and 32 men aged 23 to 55 years.

During the study the researchers conducted: the survey on organ systems with a specially prepared questionnaire. Study on organ systems. Consultations with specialists: ophthalmologist, neurologist, otolaryngologist and radiologist. Laboratory tests: blood count, antibody titers to noradrenaline on the membranes of lymphocytes. Overall incidence of employees depending on the nature of occupational exposures is shown in the table below:

Overall incidence of employees depending on the nature of occupational exposures is shown in Table. 3.

CONCLUSION

Thus, the analysis of the data on the effects of nanoparticles of individual metals and their oxides used in technology on the human indicates the primary influence on respiratory tract. The episodic contact with powdered metals causes only a slight increase in the cases of dystonia, whereas the bronchial lesions are not observed. A rising incidence of chronic pharyngitis and bronchitis, a tendency to acute respiratory viral infections in these individuals may be explained by the damaging effects of aerosols of metal powders and especially by their vapors to mucous membranes of the respiratory tract. Signs of heavy metal coniosis in the employees were note detected.

The analysis of hazard exposures has shown a smooth monotonic linear dependence. The risk of disease is about 20%.

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