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THE STUDY OF THE COMPOSITION OF THE NATURAL NANOSTRUCTURED MATERIAL - CHRYSOTILE ASBESTOS

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The article discusses the properties of the natural nanostructured material - chrysotile asbestos. The object of the research is produced at the minefield in Zhitikara, Kostanai region. Some areas for possible application of asbestos as a material consisting of nanotubes are offered. Chrysotile fiber has been tested by means of X-ray techniques, including X-ray diffraction and small-angle scattering measurement. The experiments are based on the use of X-ray multifunctional processor.

Keywords: chrysotile asbestos, nanotubes, X-ray analysis techniques

When considering the entire set of nanostructured materials, natural materials are of particular interest. In some cases their preparation is significantly cheaper than the artificial synthesis of such materials. On the other hand, making use of all possibilities (economic, physical, technical) turns out that the use of natural materials opens up completely new possibilities for the development of nanotechnology.

The aim of the paper is to discuss the properties of the natural nanostructured material - chrysotile asbestos, which until recently has been considered only in terms of its use as a constructional material. This trend led to the development of the mining industry in a number of countries where ore extraction containing chrysotile asbestos increased to the annual production of thousands of tons. In particular in Russia and Kazakhstan quarries for mining and enterprises for processing asbestos containing ore for its enrichment were established, and these companies were the core for the formation of such towns as Asbest (Sverdlovsk region, Russia) and Zhitikara (Kostanay region, Kazakhstan). During the recent years, however, the evident negative ecological consequences of mining of these minerals have become apparent and a number of countries in the world legislated against their extraction as well as use.

At the same time, the discovery of fundamentally new properties of nanomaterials and the rapid development of their application in different areas of the industry made it possible to formulate new possibilities for the use of asbestos, as it turned out, that this material has the properties of nanostructures, i.e. chrysotile asbestos fiber itself is a nanotube (Figure 1).

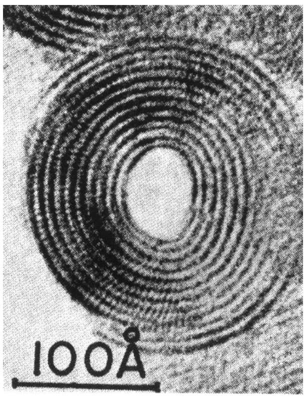


Fig.1. Transmission electron microscopy of chrysotile. The convolution between slightly silicon enriched tetrahedral sheet and magnesium enriched octahedral sheet. [1]

Figure 1 shows that the structure of the fiber chrysotile asbestos itself was identified relatively long ago, but at that time there were no specific ideas about nanomaterials and their characteristics, so this result has long remained virtually untapped.

In this regard, we have tried to highlight and discuss the use of chrysotile asbestos as a material consisting of nanotubes, and propose a way to use it taking into account regional characteristics and the needs for the development of industry and agriculture of the Republic of Kazakhstan.

For the focused study of fundamental and applied properties of asbestos as a nanostructured (nanotubular) material it is necessary: to refine the fiber structure in order to visualize its structure in the form of nanotubes, to define the composition of tubes by means of X-ray microanalysis, to test the possibility to apply additional techniques for the analysis of the physical properties of the fiber and to find possibilities for the use of chrysotile fibers as a material for nanotechnology.

Sufficient experience of using nanotubes [2], mainly synthesized carbon nanotubes, has been gained so far, which can be used for focused study, modification and determination of application areas for chrysotile asbestos.

1. Nanotubular materials are known to have extreme sorption capacity that draws the attention of developers, particularly in the field of production of filters for different use. In this regard, the possibility of creation and extensive use of cheap filters for treatment of liquid and gaseous media is of great importance.

2. In some cases, such filters can meet the challenges of mobile supersensitive monitoring of contamination of liquid and gaseous media, which is important for solving the problems of defense and anti-terror measures.

3. The development of research work on a broad study of the properties and structure of nanotubes, in particular those of natural chrysotile nanotubes opens possibilities for practical application areas, which have only been so far known in the form of laboratory experiments. In particular, it is pointed out that the use of such materials is particularly advantageous for creating nanowires of various materials (metals, semiconductors). In this regard the use of natural nanotubes is particularly attractive, as in case of their extensive use economic factors become dominant.

4. Further development of research work on the use of the sorption properties of specially prepared natural chrysotile fibers, can be especially promising for Kazakhstan oil industry to refine crude oil from accompanying impurities, particularly sulfur.

The properties of chrysotile asbestos nanotubes. Briefly list the properties of chrysotile asbestos, which are most attractive for practical use.

Chrysotile is a fibrous kind of hydrous magnesium silicate - serpentine, its composition corresponds to the formula $Mg_6[Si_2O_5](OH)_8$ or $3MgO \cdot 2SiO_2 \cdot 2H_2O$. The natural chrysotile asbestos contains impurities of Fe_2O_3, FeO, Al_2O_3, Cr_2O_3, NiO, MnO, CaO, Na_2O and H_2O. It forms streaks in dark green serpentinites and exhibits generally cross-fibrillar structure. In a dense piece, chrysotile asbestos is of green or yellowish-green color and pearly luster, but after splitting (fibrization) into individual fibers it turns into white fuzz-like mass. Chrysotile asbestos has a rather high melting point (1521^{o}C), at about 700^{o}C it loses crystallization water and becomes brittle. It is the most heat-resistant of all kinds of asbestos. Compared to other types of asbestos, such as amphibole asbestos, it is less resistant to acids (it decomposes in hydrochloric acid), but it is alkali-resistant, it has high sorption, thermal, acoustic and electrical insulating properties.

No known material of asbestos substitutes has the whole range of useful properties of chrysotile asbestos: breaking strength of more than 3000 MPa, density from 2.4 to 2.6 g/cm^3, melting point from 1450^{o}C to 1500^{o}C; friction coefficient of 0.8 units; alkali resistance of 9.1 to 10.3 pH; specific surface area of 20 m^2/g.

According to its strength characteristics asbestos is divided into normal or high strength (tensile strength of about 300 kg/mm^2), semibrittle or low strength, and brittle or weak strength (tensile strength of 110-220 kg/mm^2). Chrysotile asbestos of low strength is recorded in the weathering zone, it is of a whitish color, and is characterized by low crushability, less elasticity and some reduction in the amount of MgO. Brittle asbestos is considered as the product of a high temperature transformation of normal chrysotile asbestos, it is distinguished by elasticity, lower tensile strength, a slight decrease in the amount of MgO and water of crystallization, the increase in the amount of FeO.

The industry uses high and low strength fiber of greater than 0.5 mm length. It is widely used in various industries both in pure form and in combination with other materials (cement, textiles, cardboard, etc.).

Asbestos nanotubes are a natural material, the product of formation of rocks and exhibit unique mechanical characteristics (great rupture energy along the fiber of 400 kg/mm^2), which has found application in construction industry, they are distinguished by chemical resistance, low heat conductivity, and their capability to adsorb various substances.

Asbestos nanotubes, unlike carbon ones, are harder and don’t twist when trying to cut them, they are oriented in the natural material in a clear prevailing direction, and formed as a result of the formation of two matrices of MgO and SiO_2. Due to the difference of the their elastic constants the ultra fine layers twist into a tube of a certain diameter and the resulting tube has no defects, there are types of a cone in a cone, a cylinder in a cylinder and a tube with a cavity filled with an amorphous substance (a mixture of MgO and SiO_2).

An important characteristic of asbestos is the elastic modulus. The average value of the modulus of elasticity of chrysotile asbestos range from 16104 to 21104 MPa.

Sorptivity of asbestos.

Tubular nano-objects are of an entirely surface structure that can be considered as the most suitable object for physical sorption. Due to the developed surface (surface area of ~20 m^2/g) and to alignment of tubes with hydrophilic properties, chrysotile exhibits high sorptivity.

Nanotubes differ from other sorbents in sorption mechanism [3]. In papers on carbon nanotubes it is particularly stressed that capturing a sorbate in the tube cavity, the tube transforms and draws the absorbed substance into the channel, while preserving the capability to sorption in the intertubular space of the bundle. It is noted that getting into the channel or intertubular space is energetically favorable for the absorbed substance, that is, after the sorption the substance is in a stable condition. Thus, it is necessary to distinguish between two types of sorption for nanotubes: a capture in the channel of a tube and sorption in intertubular space. For ultimate estimate of gas sorption capacity by nanotubes a formula is given:

$$\eta_g = \frac{\rho_g}{\rho_g + \rho_c}$$

where ρ_g is mass density of the gas, ρ_c is mass density of nanotubes, η_g is % content in the mass.

Since chrysotile asbestos has different electrostatic properties for the surface outside and inside (saturated Mg and Si layers at different sides), some selectivity in the sorption may be expected. Selectivity can also be achieved by surface modification using polymer compounds in such a way as to change hydrophilic and hydrophobic properties.

Based on the above, we can assert that one of the fundamental properties of the nanotubes, regardless of their composition, is their sorption property. Consequently, there is a wide range of potentialities to use the sorption properties of chrysotile nanotubes to manufacture filters used for treatment of liquid and gaseous media.

In the course of investigations, a system of experimental methods for study of chrysotile asbestos has been developed and tested. Among them particularly important are X-ray techniques, such as X-ray diffraction analysis, X-ray fluorescence and small-angle scattering. The techniques are based on the use of X-ray multifunctional processor. [4] The results of applying some of the techniques are listed below.

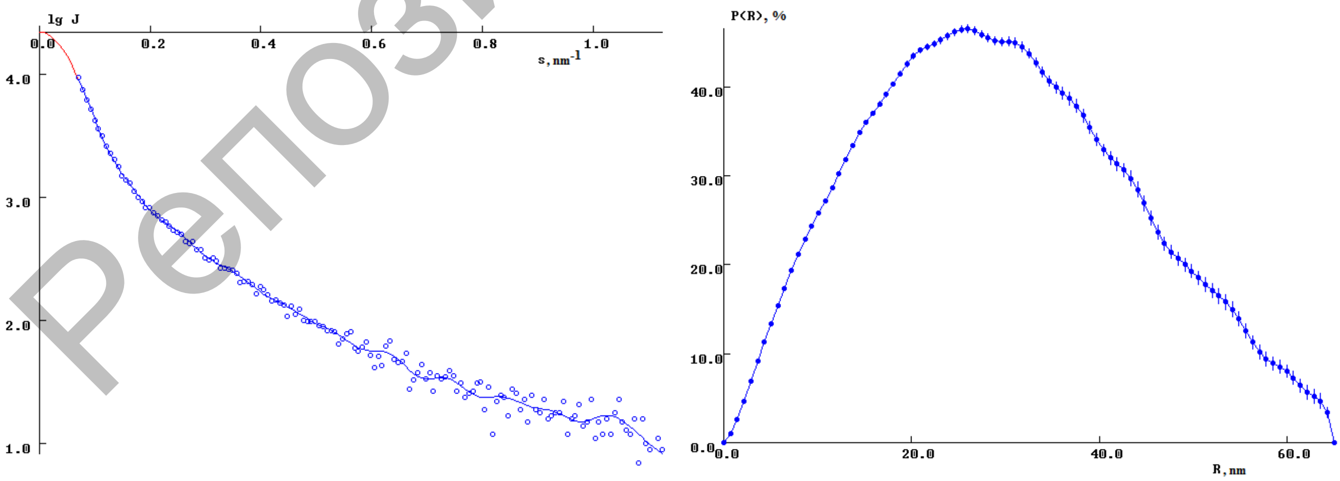
Measurements of small-angle scattering. Small angle measurements of the scattered sample by X-rays with a wavelength of ≈0.1 nm make it possible to define the characteristic size and concentration of particles and pores generally in the range from 1 to 100 nm.

To make small angle measurements using X-ray "transmission" technique, a sample holder is installed on the displacement device for moving absorbing screen. The device provides the orientation of the sample surface perpendicular to the direct beam. To record data the scheme shown in Figure 2 is used.

Fig.2. Scheme for measuring small-angle scattering: F is a focus, D is a primary diaphragm, S is a screen, M is a mirror, O is a sample.

The surface of the flat mirror M is installed parallel to the axis of the X-ray beam. The beam is collimated by three circuit elements: a rectangular edge of the screen S, which can be moved perpendicular to the beam, the bottom edge of the diaphragm D and the mirror M. The diaphragm D is used for the primary limiting the angular divergence and to reduce the impact of extra-focal radiation. The optimum conditions are maximum approaching of the diaphragm to the focus of the tube and the approximate equality of its width to the size of the projection of the tube focus. In this case, the diaphragm can be regarded as a fictitious focus scheme free from the halo effect of extra-focal radiation. As well as in the focus scheme of Kratki, there is no exit slit in front of the sample. It minimizes the background of the scattered radiation. Measurements of the scattering diagram are carried out in the shadow zone behind the mirror in the direction of the arrow.

X-ray small-angle scattering of A-4-30 sample of asbestos. The study found out nanoscale objects in the sample. Below are the small-angle scattering curve (Figure 3a), and a graph of the distance distribution function, characterizing the average maximum size of scattering objects (Figure 3b). According to the obtained data the characteristic size of the scattering objects is of 20-30 nm (up to 60 nm).



a b

Fig.3. a - a general view of the curve of small-angle scattering; b - the graph of the distance distribution function, calculated on the basis of the curve of small-angle scattering.

Diffractometry. Many powder objects are known to have the characteristic size of grains or crystallites of D order and are less than 100 nm. Diffractometric measurements make it possible to define D by diffraction broadening, and to determine preferred orientation on the basis of the ratio of the intensity of the diffraction peaks. For diffractometric measurements of powders the standard scheme of focusing according to Bragg-Brentano is used

X-ray diffractometry of A-4-30 sample of asbestos. The study showed that the given sample is a pure chrysotile asbestos $Mg_3\ [Si_{2-x}O_5](OH)_{4-4x}$. Other phases in the sample have not been found (Figure 4).

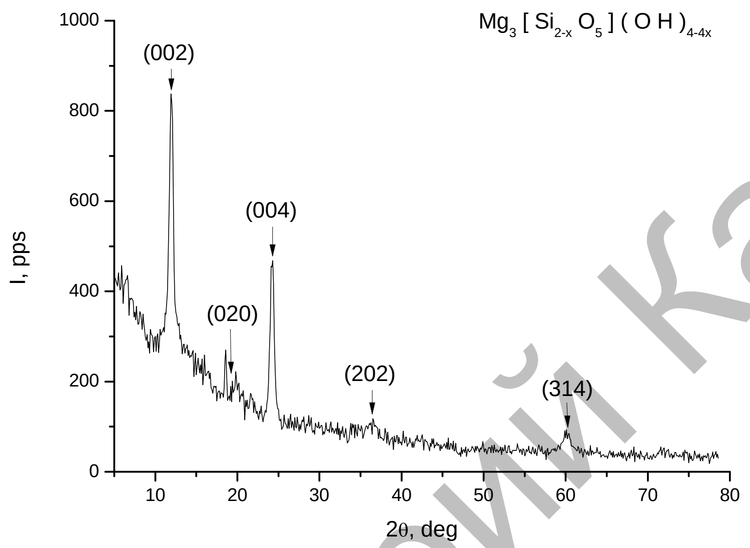


Fig.4. The study of chrysotile asbestos composition by means of X-ray diffractometer.

Conclusion

Thus, the sorption properties are one of the fundamental properties of nanotubes, regardless of their composition. In this regard, possibility to use asbestos nanotubes for total treatment of liquid and gaseous media is currently important. In the latter case, it is a huge range of industrial emissions, exhaust gases from internal combustion engines and other sources polluting the atmosphere. Treatment of liquid media, such as the treatment of domestic, agricultural and industrial effluents should be particularly mentioned. And a global task is the problem of treatment the water of unused lands because of the strong salinity of groundwater in Russia and Kazakhstan. Another important task of the state, particularly of Kazakhstan, is the problem of refining crude oil, having a great amount of sulfur impurities. Results of the study opened new opportunities for efficient use of asbestos as a material with properties of nanostructures, as the very fiber of asbestos chrysotile is a nanotube in itself.

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