Armenian Journal of Physics, 2015, vol. 8, issue 2, pp. 91-101

PHYSICAL PROPERTIES OF MODIFIED HIGH-EFFICIENCY SYSTEMS ON THE BASIS OF SUPER-THIN BASALT NANOSTRUCTURES

V.V. Harutyunyan[1], N.A. Hakobyan[1*], E.M. Aleksanyan[1], E.A. Akhverdyan[1], V.A. Atoyan[2], V.B. Gavalyan[1], V.S. Baghdasaryan[1], M.G. Vardanyan[2], and K.I. Pyuskyulyan[2]

[1] *A.I. Alikhanyan Yerevan Physics Institute, Yerevan, Armenia*
[2] *Armenian Nuclear Power Plant, Metsamor, Armenia*
*e-mail: nick@mail.yerphi.am

Received 2 April 2015

Abstract – A method for mixed two-stage modification of mineral fibers on the basis of natural basalts in various media is developed. Such processing allows achieving a substantial increase in sorption capacity of materials. The nitrogen vapor adsorption method and BET model are used to determine the specific surface area, as well as to assess the pore size distribution. It is shown that chemical leaching creates a developed system of mesopores. High sorption activity of superfine basalt fiber adsorbents against radioactive aerosols makes it possible to recommend them as starting materials for adsorption filters when creating reliable emergency air purification systems used at NPP and other enterprises with nuclear installations.

Keywords: Filtration, fiber, basalt, sorbent, mesopores, aerosol, nuclide, leaching.

1. Introduction

Currently, one of the global environmental problems is the pollution by various kinds of toxins of anthropogenic origin. Of a special hazard are releases of radionuclides entering the environment during the operation of nuclear fuel enterprises, nuclear power plants, thermonuclear facilities, etc.. Therefore, the development of highly efficient power saving and resource-conserving safe technologies for treatment of radioactive emissions (radioactive aerosols) is evidently an actual task. In the field of adsorption techniques, one of the most promising approaches is based on the use of spatial organized units with a regular packing of planar sorbent materials (so-called "active filters"). To create high capacity absorbers with a regular structure, it is necessary to develop new planar adsorbents (felt, wool and so on) with an optimal set of filtration and structural properties [1-6]. Fiber filters are the most effective means of fine gas cleaning from suspended particles. Particle capture efficiency in fibrous filters is significantly higher than in other types of porous media at the same pressure drop. These filters are systems of randomly positioned fibers oriented predominantly perpendicular to the flow direction [3-7].

A similar set of properties reveal the materials on the basis of super-thin basalt fibers (chemically modified, leached). Adsorption properties and dynamic characteristics of such materials are sufficiently studied, however literary data concerning their structure porosity in the literature are contradictory [6 -11].

Basalt by its nature is an effusive rock. The name "basalt" is derived from the Ethiopian "basal", which means "boiled": basalts were born in volcanic orifices. Armenian Highland is one of the classic areas of ancient volcanism.

Source materials in the production of super-thin basalt fibers are basaltic rocks. They have high natural chemical and thermal resistance. Basalt rocks are one-component materials, their enrichment, melting and homogenization were done as a result of ancient volcanic activity. In doing so, the main energy expenditures connected with primary melting of basalts were made by nature. In contrast to the raw material for glass production, basalt is a ready-to-use natural product for the production of super-thin fibers.

Unfortunately, up to the present day basalt rocks were not paid proper attention as a raw material for the production of super-thin basalt fibers (STBF).

Super-thin basalt fiber can be successfully used in the nuclear industry to clean radioactive aerosols (a part of the fission products, decay products and nuclides with induced activity, which can enter the environment with air flows) in high-radiation areas as well as in controlled zones such as the Armenian NPP [6].

The aim of this work is to study the adsorption properties of chemically modified super-thin basalt fibers for the purpose of increasing the aerosol particles capture (which coefficient in general is a function of many parameters: radius, density of trapped nanoparticles; air rate, viscosity, pressure, temperature; as well as dispersion that characterize the internal structure of fibrous materials).

2. Methods and Techniques

When adjusting the leaching techniques, different acids, their concentration, temperature and treatment time were varied. Two leaching techniques were developed: one-component and two-component (mixed) ones.

To the sorbent materials, depending on their application conditions, quite different requirements are imposed, such as durability, recovery and regeneration with the purpose of repeated application, and so forth.

From the literature it is known that for all silicon-containing materials (zeolites, granites, silicate glasses) including basalt, many of their physical and chemical properties are determined by SiO_2/Al_2O_3 (the ratio of oxides content) and impurity atoms in their unit cell [5].

The content of basic oxides in the investigated rocks was within the following ranges (in mass %): SiO_2 43-58%; TiO_2 1-2%; Al_2O_3 11-20%; $FeO+Fe_2O_3$ 8-16%; MgO 4-12%; CaO 7-13%; $Na_2O + K_2O_3$ 2-4 % [5,12,13]. With increasing alumina content mechanical properties of the fibers were improved. This fact counts in favor of the statement that basalts from not all deposits are suitable for the production of super-thin basalt fibers.

According to the literature [2-4] basalt fibers obtained by extrusion do not usually have porous structure. To use them as sorbents, their chemical treatment (leaching, modification) is necessary. The chemical treatment is carried out taking into account the chemical composition and structure of basaltic rock, especially the acid-base character of its components [2,5].

It is known that exposure of basalt fibers in solutions of strong acids leads to selective dissolution of metal oxides that form their structure when the structure of the silica skeleton remains the same [5]. During the acid treatment of fibers porous structure is developed in them, allowing to use leached basalt fibers as adsorbents [14,15].

When adjusting the leaching techniques, different acids (sulfuric, hydrochloric), their concentration, temperature and treatment time were varied.

Super-thin basalt fiber has the following technical characteristics:

- Average fiber diameter 1-3 microns
- Density 20-23 kg/m^3
- Moisture content 2%
- Operating temperature from -260^{0}C to +750^{0}C.

Increasing the sorption capacity of the sorbent for purification of gases and aerosols (^{60}Co, ^{137}Cs, ^{134}Cs, ^{54}Mn, ^{110m}Ag radionuclides) - as a method for production of sorbents was achieved by chemical treatment (leaching) of super-thin basalt fibers in hydrochloric and sulfuric acid solutions of various concentrations.

The modification of super-thin basalt fibers and determination of their porosity characteristics was performed by Brunauer-Emmett-Teller (BET) method [2]. This method allows calculating the specific surface area of solids, such as superfine basalt fibers, determining pore size and volume from their effective radii as well as pore size distribution. BET method is the most common method for determination of porosity characteristics.

The density of leached basalt fiber is $\rho = 2.0\ g/cm^3$, its porosity makes *85%*. Chemical and neutron activation analysis of the obtained material have shown that it is almost pure silica.

From the adsorption-desorption isotherms of liquid nitrogen vapor, specific surface area and porosity of the samples as well as the pore size distribution were calculated.
The porous characteristics of super-thin basalt fibers, both untreated and treated (chemically modified by hydrochloric acid) were determined using Accusorb2300A (Micromeritics Company, USA).

Chemical processing (modification) was carried out taking into account the chemical composition and structure of raw basaltic materials from various Armenian deposits (Zolakar and Kotayk). The diagnostics of the adsorbents obtained by what was carried out after leaching of basalt fibers. Table 1 shows the chemical composition of basalt raw materials from various Armenian deposits.

Table 1. Chemical composition of super-thin basalt fibers

Material	Chemical composition							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O+ K_2O	Impurity	Total
Zolakar STBF	51,40	16,83	11,90	7,70	3,48	1,76	2,42	95,80
Kotayk STBF	50,94	17,85	10,71	8,40	3,48	1,76	0,00	93,20

For the first time, a two-stage chemical process was used for mixed treatment (using two acids, HCl and H_2SO_4) of super-thin basalt fibers. According to literature data, sulfuric acid (H_2SO_4) leaching, as compared to hydrochloride acid treatment promotes the formation of STBF samples with more regular pore structure [2-4]. We can assume that combination of sulfuric acid and hydrochloride acid leaching for the same STBF sample has a positive impact on its sorption characteristics (capacity).

The technique of sulfuric acid (H_2SO_4) leaching of STBF.

The method of sequential three-stage sulfuric acid leaching of basalt fibers (with some minor changes) was used. After the sulfuric acid leaching and drying, STBF samples lose 51% of their original weight. The results of chemical analysis of the treated STBF are given below:

SiO_2 - 96.27%,
Al_2O_3 - 1.80%,
Fe_2O_3 - 1.00 %.

(the sum of components is: 96.27% + 1.80% + 1.00% = 99.07%).

The technique of hydrochloric acid (HCL) leaching of STBF.

Hydrochloric acid leaching of STBF results in 57% yield by weight. Silica content in STBF ranges within 48 ÷ 54%. Consequently, taking into account some inevitable losses of the product during the processing, it is possible to assume that the used methodology allows thorough leaching of STBF, i.e. chemical modification using hydrochloric acid.

3. Experimental results and discussion

Experimental studies have shown (Figures 1-4) that the penetration of radioactive aerosol particles in the fiber medium depends on their type, shape, size, velocity and charge state, as well as on adsorption properties, chemical modification of structures.

Figure 1 shows a fragment of the photography of aerosol particle capture by modified STBF after two-stage mixed chemical treatment.

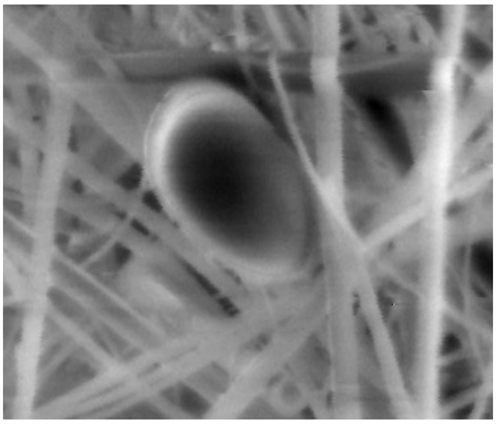

Fig. 1. A fragment of the photography of aerosol particle capture by modified STBF.

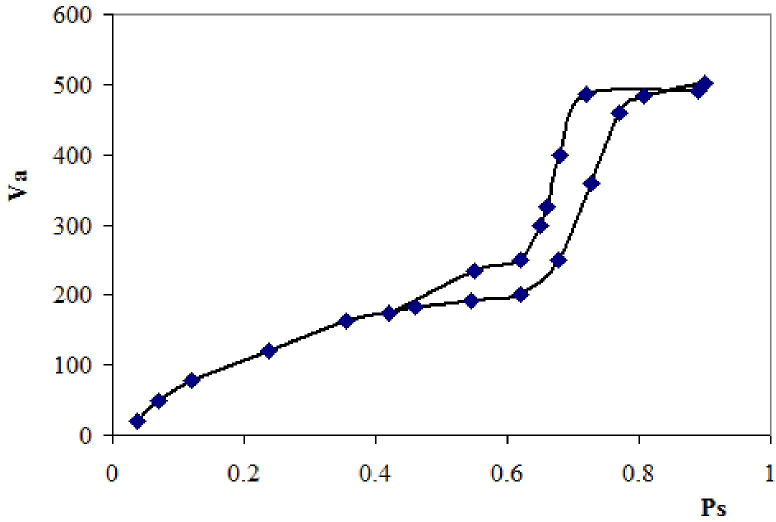

Fig. 2. Adsorption isotherm vs. the gas volume
(nitrogen adsorbed on the surface of untreated STBF).

Figure 2 shows adsorption (1) and desorption (2) isotherms of liquid nitrogen vapor at its boiling temperature for **untreated** super-thin basalt fibers from Kotayk deposit.

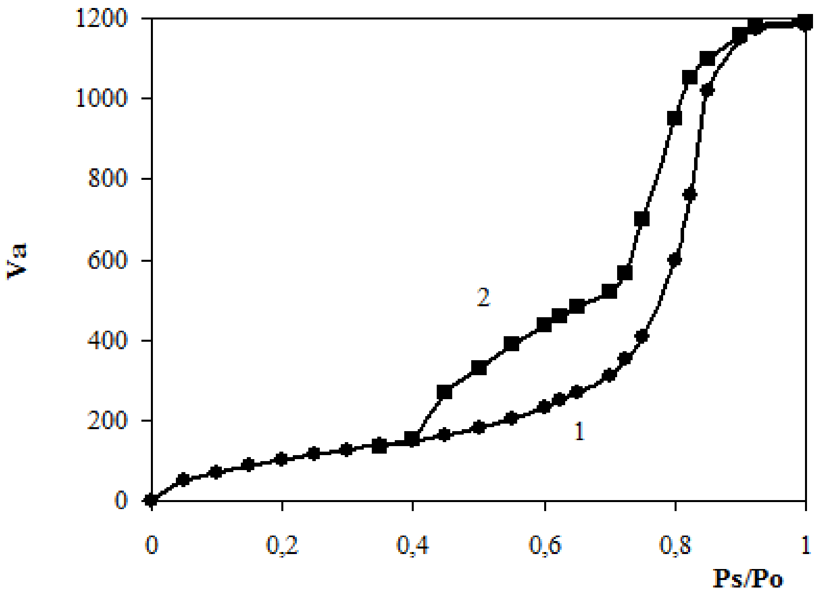

Fig. 3. Adsorption (1) and desorption (2) isotherms of liquid nitrogen vapor at its boiling temperature for chemically treated super-thin basalt fibers (two-stage processing: H_2SO_4+ HCl).

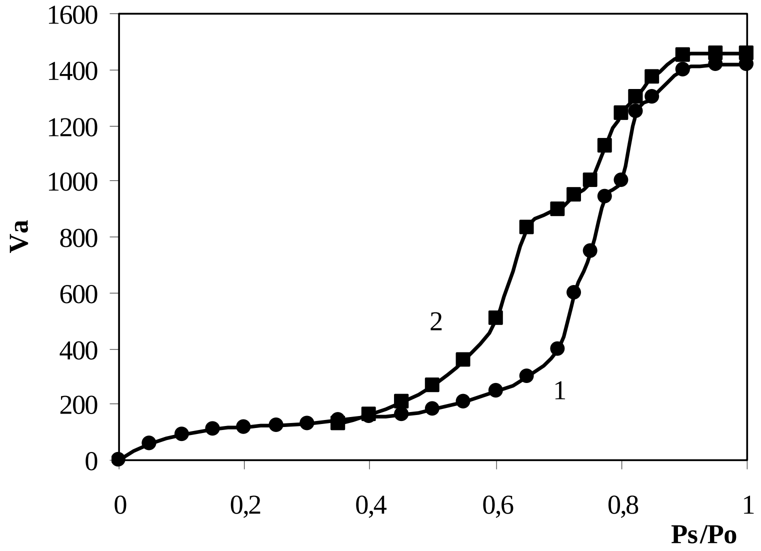

Fig. 4. Adsorption (1) and desorption (2) isotherms of liquid nitrogen vapor at its boiling temperature for chemically treated super-thin basalt fibers (two-stage processing: $HCl+H_2SO_4$).

Thus, the calculations using BET method have shown that leaching significantly increases the adsorption capacity: for the initial basalt fiber the maximum amount of nitrogen absorbed is 25 cm^3/g, whereas for the laboratory leached basalt at different stages of chemical treatment 1200 cm^3/g (Fig. 3) and 1500 cm^3/g (Fig. 4). Chemical treatment has increased the fiber porosity by a factor of 50-60.

Pore size distribution (pore size spectrum) was determined by nitrogen vapor desorption method. Entertaining conventional pore classification on the basis of their diameter (macropores have diameter greater than 50 nm, mesopores - within the range of 2 -50 nm, micropores - less than 2 nm) [2], all the studied samples should be recognized as mesoporous. Calculations have shown that the pore diameter in the initial material varies from 45 to 140 nm (2% of mesopores, 1% of micropores, 97% of macropores), in the laboratory leached basalt - from 2.5 to 140 nm (2% of macropores, 0.5% of micropores, 97.5% of mesopores). Detailed features of pore size distribution of various basalt fibers vary significantly depending on the chemical treatment procedure.

Surface area and porosity of basalt fibers

Pore distribution: for the initial sample total pore volume was 0,0308 cm^3/g, for the leached ones 1,7314 cm^3/g (one-stage hydrochloric acid treatment) and 1,2193 cm^3/g (sulfuric acid treatment).

Specific surface areas calculated by the BET method have revealed the following values: initial - 11.5 m^2/g, after one-stage leaching - 348,2 m^2/g (one-stage hydrochloric acid treatment) and 265,3 m^2/g (sulfuric acid treatment).

The experimental installation for study of the filtering material efficiency

The main equipment in the schemes of air purification from nuclides is filters which differ in their form, operating mode, design, filtering materials, etc.

It is known that the service life of any filter is subjected to several factors: 1) increase in filter air flow resistance as a result of dust deposition in filtering materials; 2) increase in filter radiation intensity as a result of accumulation of nuclides in filters; 3) destruction of filter material under the impact of aggressive substances in the air[16-19].

The practice of using filtering materials shows that the main reason that determines service life of filters is the increase of their air flow resistance. As consequence they have to be thrown away, not fully utilized for their intended purpose. To extend service life of nuclide filters the air should be subjected to coarse cleaning and then fine cleaning.

Filter operation is characterized by the following indicators: cleaning efficiency, filter porosity, filtration rate, dust holding capacity, flow resistance, as well as technical and economic data.

For preliminary study of filtering properties of the filter materials of various modifications, an experimental installation was designed and constructed. It included rotameters for determination of air consumption, special valves for variation of air consumption, filter holders, devices for the determination of aerosol activity upstream and downstream of filters.

Figure 5 shows a part of the experimental stand for determination of the effectiveness of air purification from radioactive aerosol by basalt fiber filters.

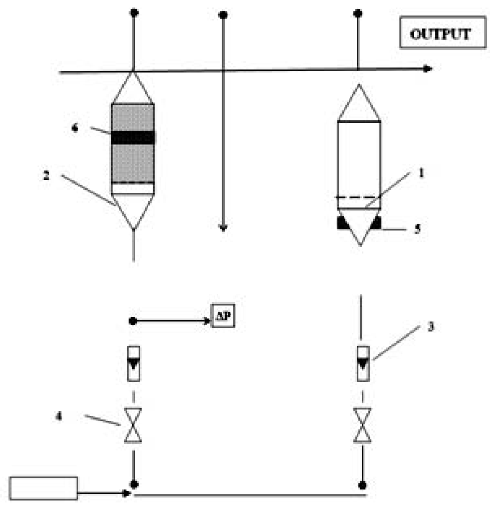

Fig. 5.   1 and 6 - Basalt filters; 2 -   tested filter, 3 - rotameter; 4 - valve; 5 - grid; ΔP - manometer.

The filters located in their holders are single-layer round gauze frames, to which various modifications of basalt fibers are applied (similar filters with Petryanov fabric are used to determine aerosol activity in indoor air and various ventilation systems of NPP in normal mode. Fig. 6 shows schematically such filters.

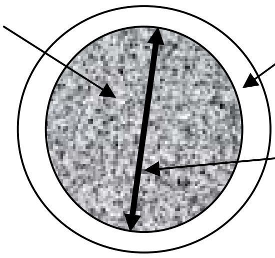

Fig. 6 STBF based filters

The experimental installation was used to study filtering characteristics of basalt fiber filters as a function of various physical and chemical parameters of tested samples. The efficiency of the investigated filters was measured at different flow rates through the filters: from 1.6×10^4 l/hr (design flow rate) to 3.2×10^4 l/hr. At the output, aerosol activity downstream of filters was measured by two independent measuring devices DBG2 and AERM. The activity of aerosols deposited on the investigated filter was measured using a low background gamma spectrometer with germanium detector and GENIE software. The measurements of filtering materials with different parameters at different air flows will be continued. Filters were exposed for 1 week.

Efficiency of Basalt Fibers

Table 2 shows the results of evaluation of the efficiency of unmodified and modified basalt fiber filters. Data presented are averaged over a series of eight measurements.

The efficiency is defined by the following formula:

$$\text{Efficiency} = \frac{\text{N(before filter)} - \text{N(after filter)}}{\text{N(before filter)}} \times 100\%$$

Table 2. The results of evaluation of the effectiveness of unmodified and modified basalt fiber filters.

Filter type	Isotope	Activity upstream of filter, 10^{-4} Bk/m^3	Activity downstream of filter, 10^{-4} Bk/m^3	Cleaning efficiency (%)
Non-modified basalt fiber	^{137}Cs	119,2	10,7	91.02
	^{134}Cs	61,6	5,54	91.0
	^{60}Co	275,6	22,05	92.0
	^{110m}Ag	97,9	7,80	92.0
Average over isotopes				**91.5**
($STBF_{H2SO4}$)	^{137}Cs	119,2	0.60	99.50

	^{134}Cs	61,6	0.36	99.41
	^{60}Co	275,6	1.1	99.60
	^{110m}Ag	97,9	0.29	99.70
Average over isotopes				**99.50**
($STBF_{HCL}$)	^{137}Cs	119,2	1.31	98.90
	^{134}Cs	61,6	0.7	98.86
	^{60}Co	275,6	2.48	99.1
	^{110m}Ag	97,9	0.98	99.0
($STBF_{H2SO4+HCL}$)				99.63
($STBF_{HCL+H2SO4}$)				99.78
Average over isotopes				**99.72**

When assessing treatment effectiveness of radioactive aerosols even tenths of percent play significant role as increased requirements are imposed upon air cleaning systems at NPPs. The analysis of data from Table 2 shows that the efficiency of filters based on modified basalt fiber is significantly higher than that of based on unmodified basalt fibers and completely meets the requirements of NPP cleaning systems.

4. Conclusion

The developed two-stage procedure of leaching basalt fibers allows obtaining the adsorbents that satisfy the basic requirements imposed upon porous adsorbing substances. Porous basalt fibers can be effectively used in installations of regular structure for cleaning any gases from nano-diameter aerosols as well as sulfur-containing acid gases and water vapors. Reason for high economic feasibility of these installations is low aerodynamic resistance of the working layer. As mentioned above installations with adsorption-active filters based on leached super-thin basalt fibers can be more economical than units with traditional sorbents taking into account their simple producing technology.

We believe that active filters based on porous basalt fibers with high adsorption capacity, fair aerodynamic properties, radiation, chemical and thermal resistance can be recommended for use in nuclear industry.

References

1. **P. Rayst,** *AEROSOLS Introduction to Theory*. Moscow "Mir", (1987).

2. **I. N. Beckman,** *Diagnostics of basalt fiber adsorbents*, Vestn. Mosk. Univ. Ser. 2. Chemistry, 2 V.44. N.5, pp. 342-351(2003).

3. **I.S. Akhatov, J.M. Hoey, O.F. Swenson and D.L. Schulz**, *Aerosol focusing in micro-capillaries: Theory and experiment*, Journal of Aerosol Science, V. 39, Issue 8, pp. 691-709(2008).

4. **M.E. Borisova, S.N. Koikov**, *Physics of Dielectrics*, Publisher: Leningrad University, Leningrad pp.240,(1979).

5. **S. I. Gutnikov,** *Effect of aluminum oxide on properties of continuous basalt fibers* (CBF), http://www.lomonosov-msu.ru/2008/24.pdf

6. **R.M. Avagyan, G.H. Haroutyunyan, V.V. Harutyunyan, V.S. Bagdasaryan, E.M. Boyakhchyan, V.A. Atoyan, K.I. Pyuskyulyan, M. Gerchikov,** *Study of Physical Regularities of Behavior of a Wide Spectrum of Aerosols When Filtering Using Various Filter Materials* PROCEEDING of the Yerevan State University, Physical and Mathematical Sciences, N.3, pp.51-56,(2010).

7. **I.B.Stechkina and V.A. Kirsh,** *Optimization of parameters of filters in a multistage system of fine gas filtration,* Theoretical Foundations of Chemical Engineering, V. 37, N. 3, pp. 218-227(2003).

8. **V.A.Kirsch**, *Calculation of the van der Waals force between a spherical particle and an infinite cylinder,* Advances in Colloid and Interface Science, Vol. 104, N. 1. p.p. 311–324(2003).

9. **A.L.Chernyakov, A.A. Kirsh, and V.A. Kirsh,** *Efficiency of inertial deposition of aerosol particles in fibrous filters with regard to particle rebounds from fibers*, Colloid Journal, V. 73. N. 3 pp. 389-393(2011).

10. **A.L.Chernyakov, A.A. Kirsch., and V.A. Kirsch**. *Elastic vibrations of a fiber due to impact of an aerosol particle and their influence on the efficiency of fibrous filters*, Physical Review E, V. 83, N. 5, pp. 056303-056322(2011).

11. **V.A.Kirsch, A.A. Kirsch,** *Deposition of aerosol nanoparticles in model fibrous filters,* Aerosols - Science and Technology, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, pp. 283-314(2010).

12. **Jing Wang, Seong Chan Kim, David Y.H. Pui**, *Investigation of the figure of merit for filters with a single nanofiber layer on a substrate*, V. 39, Issue 4, pp. 323-334(2008).

13. **L. Boskovic, IE Agranovski, IS Altman and D. Braddock,** *Filter efficiency as a function of nanoparticle velocity and shape,* Journal of Aerosol Science, V. 39, Issue 7, pp. 635-644(2008).

14. **S.K. Nikoghosyan, A. A.Sahakyan, V. B. Gavalyan, V. V. Harutyunyan, A. S. Hovanisyan, V. A. Atoyan, K. I. Puskulyan, M. Gerchikov,N. Hakobyan**, *The influence of hydrochloric acid treatment and temperature on the electro-physical properties of super-thin basalt fiber*s, Central European Journal of Physics,V.9,N.6,pp.1482-1487,(2011).

15. **S. K. Nikoghosyan, A. A.Sahakyan, V. B.Gavalyan, V.V.Harutyunyan, A. S.Hovanisyan, H.N.Yeritsyan*, V. A. Atoyan, K.I. Puskulyan, M. Gerchikov, N. V. Hakobyan, A. V. Hovannisyan**, *Electro-physical properties of super-thin basalt fiber chemically modified by sulfuric acid*, Journal of Modern Physics, N.12, pp.1450-1454(2011).

16. http://www.junantai.com/en/products/basalt/basalt_fiber.htm.
17. http://www.bvolokno.ru/index.php.
18. http://naftaros.ru/kompozitsionnye/bazaltovyetehno/.
19. http://www.izhstroy.ru/catalog/articles/9/.