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Technical and Technological Characteristics of the Cross-Flow Filter with Plasma-Chemical Nanostructured Membranes.

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ABSTRACT

The article presents the testing results for the cross flow filter (CFF, also known as tangential) with a plasma-chemical nanostructured membrane designed to clean radioactive, uranium-containing and other liquids from mechanical impurities. Comparative CFF operation in the modes of dead-end and cross flow filtration has shown that in the dead-end filtration mode it is necessary to regenerate a filtering element with a plasma-chemical membrane in a period not exceeding 10 hours; whereas in the course of CFF operation in the cross flow filtration mode, no regeneration of the Ti – membrane surface was required. During the CFF endurance tests (up to 50 hours), the liquid purification rate was constant and equal to 0.50 $m^3/m^2 \cdot$atm.$\cdot$h. The following possible operations were envisaged in the modes of CFF dead-end and cross flow filtrations:

- Control of the initial and current concentration of mechanical impurities in the liquid under purification;
- Once-through liquid purification with its pumping to a separate tank or into the environment;
- Continuous or periodical removal of the residuals of the liquid under purification;
- Visual control over the liquid purification process;
- Continuous liquid purification in the *"recycle"* mode.

The analysis of the size range and the number of mechanical particles has shown that in the vast majority of cases the filtrate contains particles with a size less than 0.3 µm.

Keywords: tangential filter, uranium environment, the fluid flow, regeneration, mechanical impurities, recycle, performance.

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INTRODUCTION

A great number of R&D and academic institutions over the whole world are involved into development of theoretical fundamentals for membrane process physics and various membrane technologies [1 – 7]. At the same time, their industrial production is concentrated within a limited number of manufacturing companies that are in the meantime leading developers of membranes and technologies of their production. It is explained by the fact that only large-scale, to the maximum extent computer-aided manufacturing can provide a high stable quality of the products with their minimum price. Thus, the leaders in the production of micro-filtration membranes and cartridges have become such companies as "Millipore", "Pall", "Pentek", "Harmsco". The main manufacturers of ultra-filtration membranes are "Norit", "Inge", "Hydranautics", "Membrana GmbH". Membranes for reverse osmosis and nano-filtration and modules made of them are produced by "Dow Chemical", "Toray", "Koch", "GE Water" (Osmonics), "Hydranautics". It should be stated that in the majority of cases the membrane manufacturers are not involved with fabrication of devices and systems based on them. The only exception is the "GE Water" (Osmonics) Company that produces the complete line of the products. The principal manufacturers in the Russian Federation are the following: Research and Production Enterprise (RPE) "Express-Eco", ZAO "Filter", RPE "Technofilter", OOO "Promfilter", ZAO "Tensor-Microfilter", ZAO "Russian Membranes Nanotech".

Membrane technologies of liquid purification that entered the market are very promising but far from being universal. In order to be effective in the use of membrane technology, it is necessary to take into account their strong and weak factors [8 – 13].

The most economical mode of filtration membrane operation is a dead-end one, when the entire volume of the liquid under purification goes through the membrane. In order to remove the accumulated precipitate from the surface and from the volume of the filtering element, the reverse flushing method is used, when the filtrate goes through the filtering element in the direction opposite to that of filtration.

The drawback of the dead-end method of the liquid membrane purification consists in fast membrane clogging with mechanical impurities, which makes the membrane technology of liquid purification much more complicated.

In the course of cross flow (tangential) filtration, the liquid flow goes with a high rate along the membrane surface. Part of the liquid penetrates through pores inside the membrane. The unfiltered part of the liquid goes continuously back to the surface of filtration membrane in the recycling mode. The cross flow filtration process goes on until all the technical requirements to the liquid are fulfilled.

In the cross flow filtration, the liquid under purification runs in parallel with the membrane surface, and part of it bursts through the membrane under pressure. At a low liquid flow rate along the membrane surface, there occurs deposition of precipitates on its surface, and thus, with time, the filtration rate will decrease to the values unacceptable in the specific technological process. When the liquid flow rate along the membrane surface goes up, deposition of precipitates on the membrane surface is suppressed by the tangential component of the velocity. The precipitate layer is cut off the membrane surface and its particles go back to the liquid under purification under the influence of buoyancy forces. There occurs such a cross flow filtration mode when a constant filtration rate is maintained during a sufficiently long period of time.

The main objectives in the course of designing membrane filters for liquid purification consist in selecting the membrane type, depending on the composition and physical and chemical properties of the original liquid. Reliability of filter operation is provided by the proper choice of the membrane material that could have minimum adhesion to the impurities typical of the given composition of the original liquid, and the module design that should allow the membrane to be hydraulically cleaned with the maximum efficiency [14 – 18]. Moreover, it is necessary to correct the operation modes of the membrane filter, i.e. to arrange and control the flow of the liquid under purification with the aim to extend the cross flow filters lifetime.

This paper presents preliminary technical and technological parameters of a new type of the cross flow filter (CFF) with plasma-chemical nanostructured membranes designed for fine purification of radioactive, uranium-containing, aggressive and other liquids, with removal of mechanical impurities.

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METHOD

The technology of CFF fabrication and testing with the aim to get its technical characteristics is given in the following diagram (Figure 1):

- purchasing of raw and other materials produced in the Russian Federation;
- engineering development and fabrication of the CFF elements;
- development of the technology for manufacturing flat filtering elements with a nanostructured membrane;
- Fabrication of a CFF test model;
- CFF model testing at the test facility;
- Processing and analysis of the CFF test results.

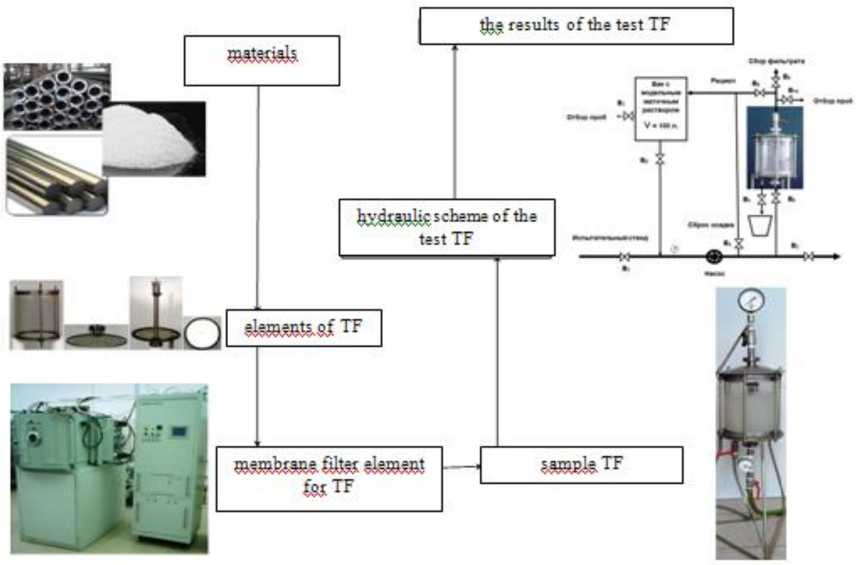

Figure 1 - Technology for manufacturing and testing of the cross flow filter with a nanostructured membrane.
(Raw and other materials-----CFF elements-------CFF membrane filtering element-------CFF test model----------Hydraulic circuit of the CFF testing-----------CFF test results)

Table 1 presents the materials that are used to get a nanostructured membrane.

Table 1 – Characteristics of raw and other materials

Name of raw and other materials	**State-, industry- or enterprise-level standards, technical specifications (TU), regulations or references**	**Standard indices subject to mandatory verification**
Zirconium Э110	[9]	Impurities (%): Nb – 1.1, Fe – 0.015, Ni – 0.007, Ti – 0.003, C – 0.02.
Titanium BT-1-0	GOST 19807-91	Impurities (%): Al-0.7. Fe-0.25. Si-0.10. C-0.07. N-0.04. 0-0.20. H-0.010.
Aluminium 99.99	GOST 11069-2001	Impurities (%): Fe – 0.0015, Cu – 0.001, Zn – 0.003.
Ultra-high-molecular weight polyethylene (UHMWPE) powder	TU № 2211-153-00203335-2004.	–
Pure argon, industrial , %	GOST 10157-79	99.993

The general view of the assembled CFF test model is given in Figure 2. The membrane filtering element is hermetically sealed and fixed in the CFF structure (1). The liquid flow rate and pressure are measured by a flow meter (4) and a pressure gauge (3), respectively.

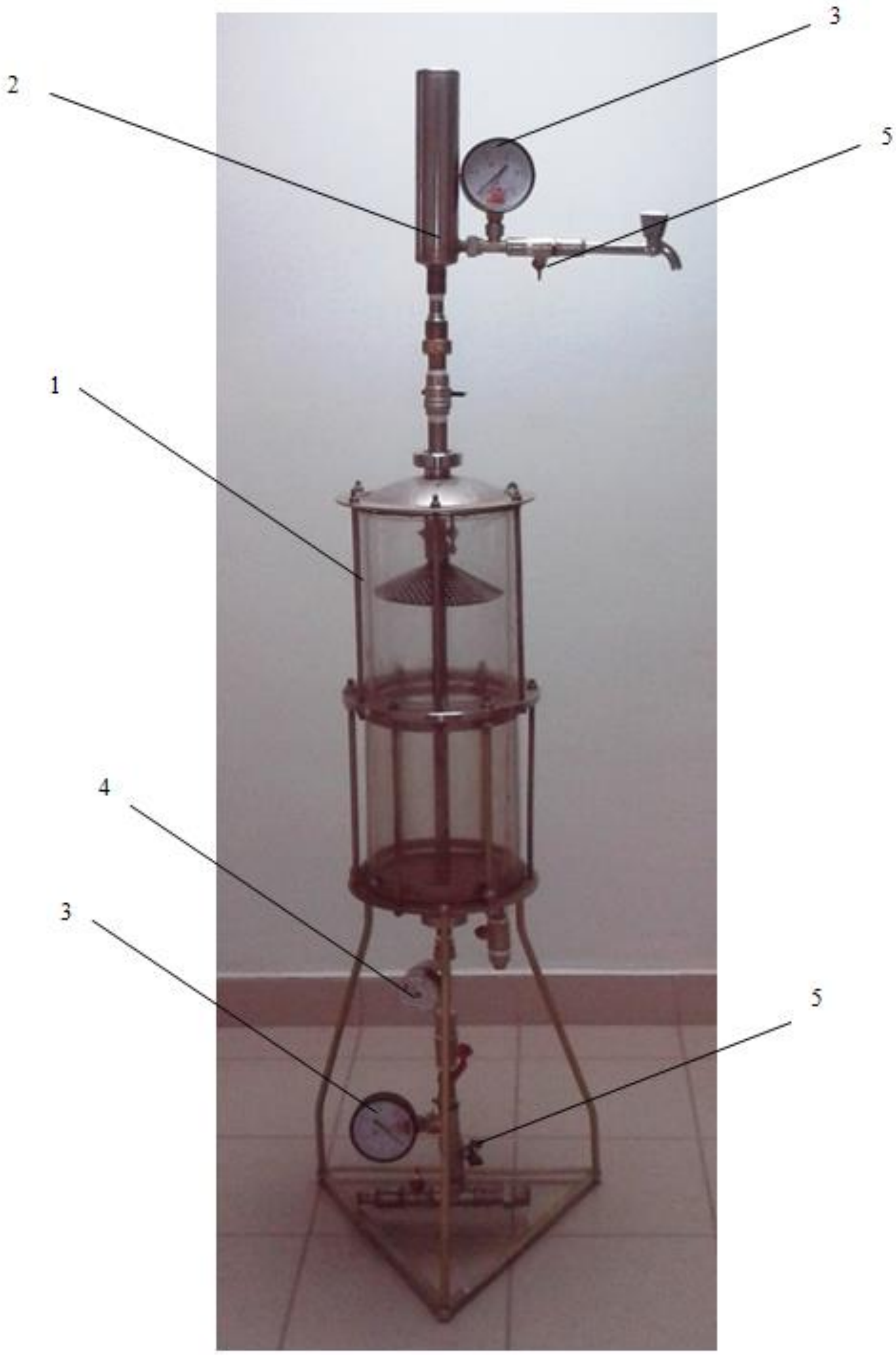

Figure 2 – CFF test model (1- CFF, 2- hydraulic accumulator, 3- pressure gauge "DM-02-100-1-G, 4 – flow meter METER VK-20G, 5-valve).

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Table 2 shows the CFF characteristics.

Table 2 – Principal CFF characteristics.

CFF Characteristics	Units of Meas.	Value
Mass	kg	20.5
Temperature of the liquid under purification	^0C	under 60
Efficiency of removing the particles of over 0.3 µm	%	No less than 99.0
Maximum allowable pressure, not more than	MPa	0.4
Capacity (at the input pressure of 0.1 MPa)	l/h	50.0

The hydraulic circuit for CFF testing is given in Figure 3.

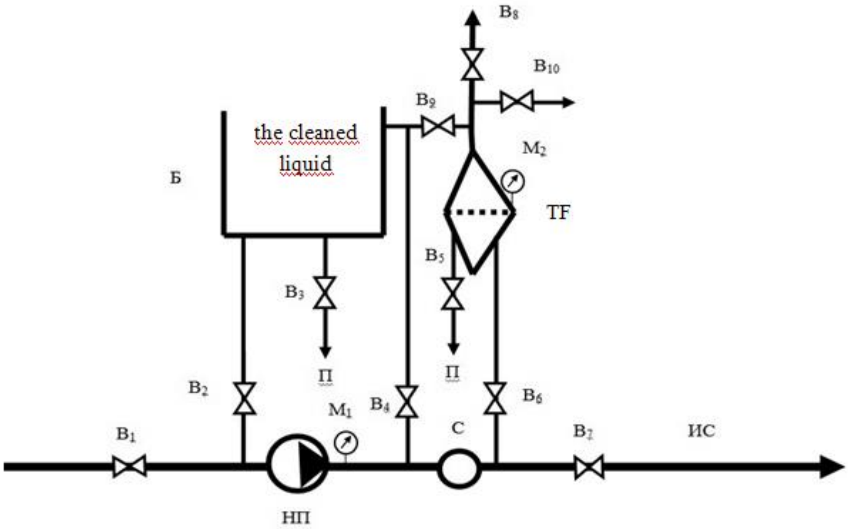

Figure 3 – Hydraulic circuit for CFF testing. (liquid under treatment)

In the course of CFF testing, the following operations are performed:

- once-through liquid purification;
- liquid purification in the recycling mode;
- determination of the CFF capacity;
- taking samples at the CFF inlet and outlet to determine the amount of mechanical impurities.

Samples are taken via the valves B_5 (original liquid), B_3 (precipitate), B_{10} (purified liquid).

During the initial period it is necessary to provide liquid stirring, which is done with the valves B_2 and B_4 open and the rest valves closed.

The once-through liquid purification is performed with the valves B_2, B_6 and B_8, open, and the rest one closed.

Liquid purification in the recycling mode is performed with the valves B_2, B_6 and B_9 open, and the rest one closed.

The CFF capacity is determined by means of the counter (C). The purified liquid is transported to a special tank or into the environment according to the once-through purification circuit.

At the stage of CFF test preparation, determination is made of the hydraulic characteristic $Q = f(\Delta P)$, (Figure 4), where $\Delta P = P1 - P2$, P_1 is the CFF input pressure, P_2 is the CFF output pressure, and Q is the liquid flow rate through the filter.

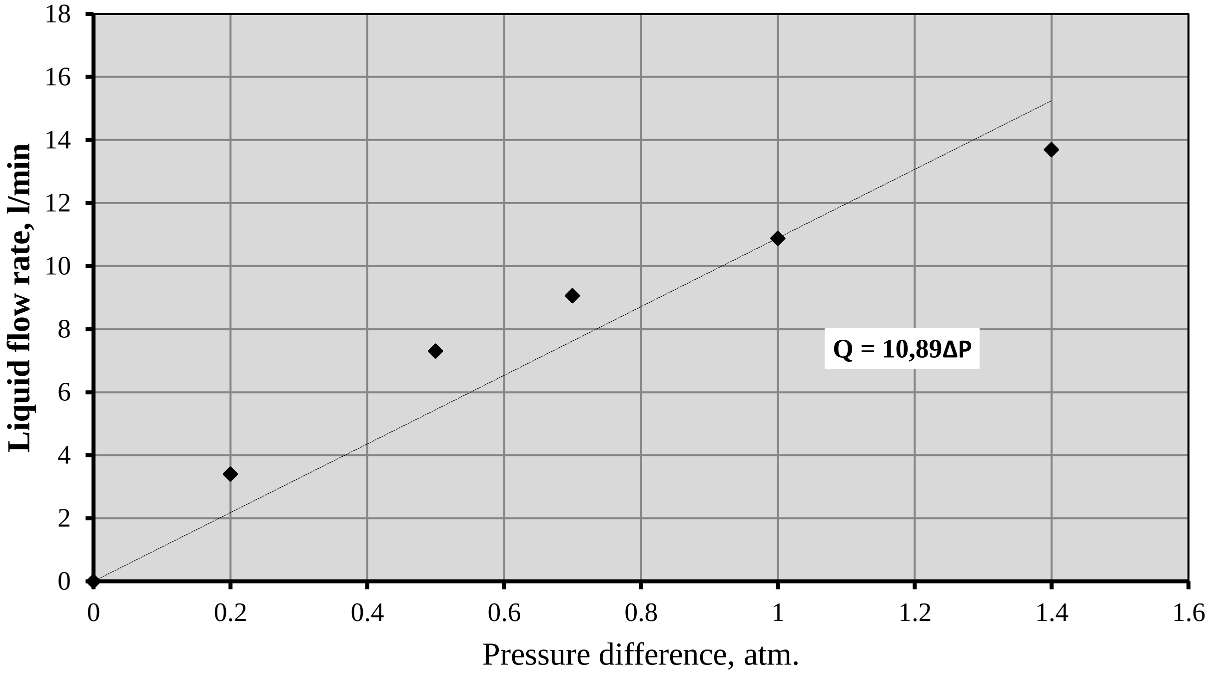

Figure 4 – Distilled water flow rate Q as a function of CFF pressure difference ΔP.

In order to eliminate the influence of the contamination layer formed in the course of filtration on the hydraulic characteristic that is determined, $Q = f(\Delta P)$, the liquid without any impurities (distillate) is usually used.

The dependence $Q = 0{,}89\Delta P$ is required to design specific structural features of the CFF under development and to preliminary select membrane filtering elements.

Figure 5 shows polymer substrates required to produce flat filtering elements. The structure of thermally sintered polymer powder UHMWPE is given in Figure 6.

Figure 5 – Porous polymer substrates.

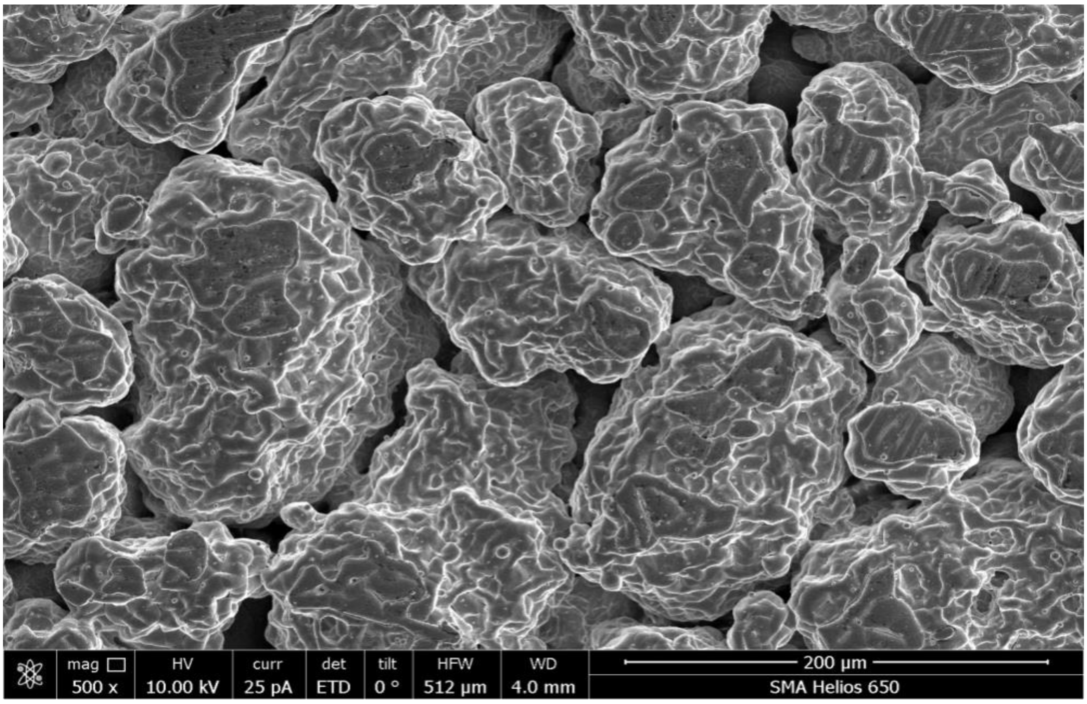

Figure 6 – Polymer substrate surface structure

Filtering plasma-chemical membranes are applied onto the surface of the porous substrate in the vacuum working chamber of the membrane application machine (MAM) (Figure 7).

a b

Figure 7 – The vacuum machine (MAM) for plasma-chemical membrane application (a –control cabinet, b – working chamber)

Figure 8 shows a mimic panel to control the vacuum MAM parameters.

Figure 8 – The mimic panel **to control the process of plasma-chemical membrane formation on the porous substrate surface.**

The main parameters of plasma-chemical membrane formation by the MAM are: gas flow rate (Ar, N_2, O_2 etc.), arc parameters of four cathodes (cathode current I_c, Zener current I_1, I_2 and membrane application time) and those of an ion source (voltage $U_к$ and ion cleaning time). At the MAM the technique was developed and the optimum mode was selected to apply plasma-chemical Ti – membrane on the surface of the basic filtering element for the CFF.

For the purpose of comparison, let us perform CFF testing in the modes of dead-end and cross-flow filtration of the liquid under treatment. Figure 9 demonstrates kinetics of plasma-chemical membrane surface clogging in the course of CFF operation in the dead-end filtration mode. With time the liquid membrane purification rate goes down and reaches the preset minimum level of 10 – 20 % of the initial rate value. As a result, the need arises to regenerate the CFF, i.e. to recover the performance efficiency to the value close to the initial one.

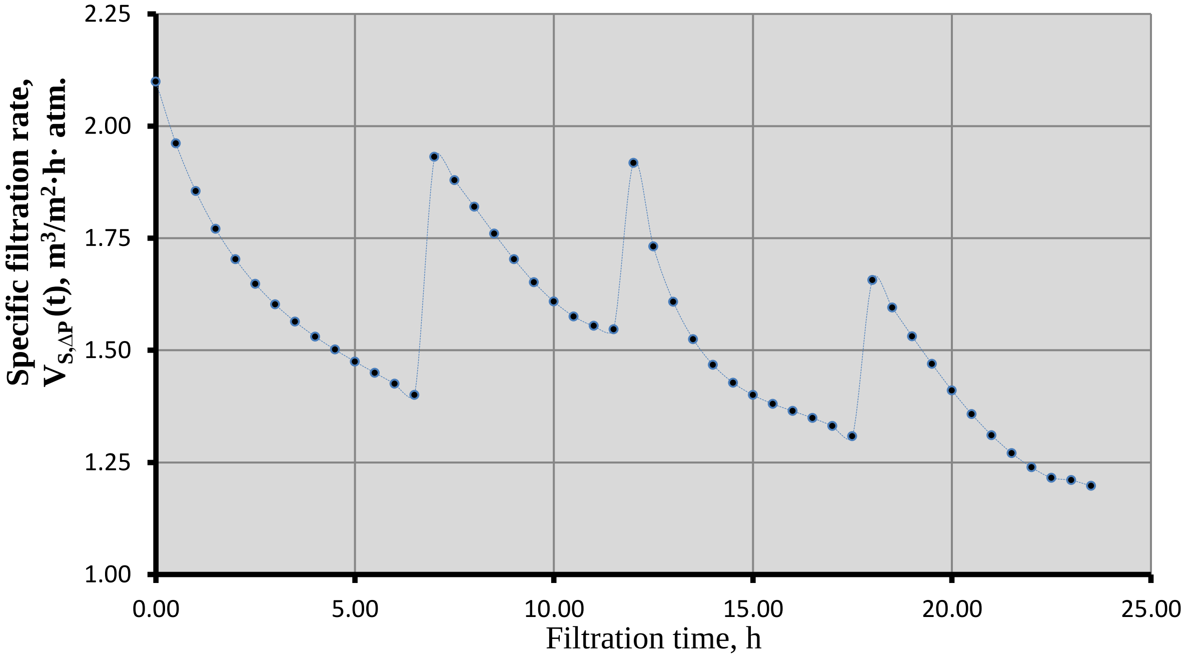

Figure 9 – Kinetics of plasma-chemical membrane surface clogging in the course of CFF operation in the dead-end mode of filtration.

A need to regenerate the filtering element with a plasma-chemical membrane arises in less than 10 hours (Figure 10). The CFF operation in this mode is not practical or reasonable.

1 2

Figure 10 – Plasma-chemical membrane surface (1 – initial (basic), 2 – before regeneration)

RESULTS AND DISCUSSION

In order to purify the liquid in the cross-flow mode, it was necessary to introduce additional structural elements in the CFF design that could provide cleaning of the membrane surface and washing the particles away to the settler.

The results of CFF endurance tests in the cross-flow filtration mode are given in Table 3 and in the graph (Figure 11). The testing conditions were the following:

- the plasma-chemical filtering membrane was made of titanium;
- the filtering element of Ø 22 mm in diameter and with a thickness of δ = 0.5 cm has a filtering surface S = 379 cm^2;
- input pressure of the liquid under purification was ΔP_{input} = 0.1 MPa;
- output liquid pressure ΔP_{output} = 0 MPa during 50 h;

Table 3 – Endurance testing of the CFF test samples

No.	Time t, h	Amount of liquid passed through Q, m^3	No.	Time t, h	Amount of liquid passed through Q, m^3	No.	Time t, h	Amount of liquid passed through Q, m^3
1	0	0	16	6,5	3,018	30	17,67	8,745
3	1.13	0.31	17	7.25	3.406	31	18.75	9.22
4	1.25	0.39	18	8.08	3.826	32	21.25	10.363
5	1.5	0.43	19	8.58	4.119	33	22.16	10.8
6	1.75	0.618	20	9.08	4.359	34	24.78	11.991
7	2.17	0.844	21	9.58	4.622	35	26.17	12.76
8	2.42	0.991	22	10.58	5.195	36	30.03	14.78
9	2.75	1.184	23	11.3	5.546	37	34.21	16.87
10	3.08	1.38	24	11.8	5.774	38	37.11	18.32
11	3.58	1.659	25	12.58	6.086	39	41.01	20.75
12	4.25	2.005	26	13.42	6.371	40	43.31	21.42
13	4.75	2.201	27	13.86	6.925	41	47.29	23.41
14	5.25	2.481	28	14.3	7.078			
15	5.5	2.529	29	16.42	8.309			

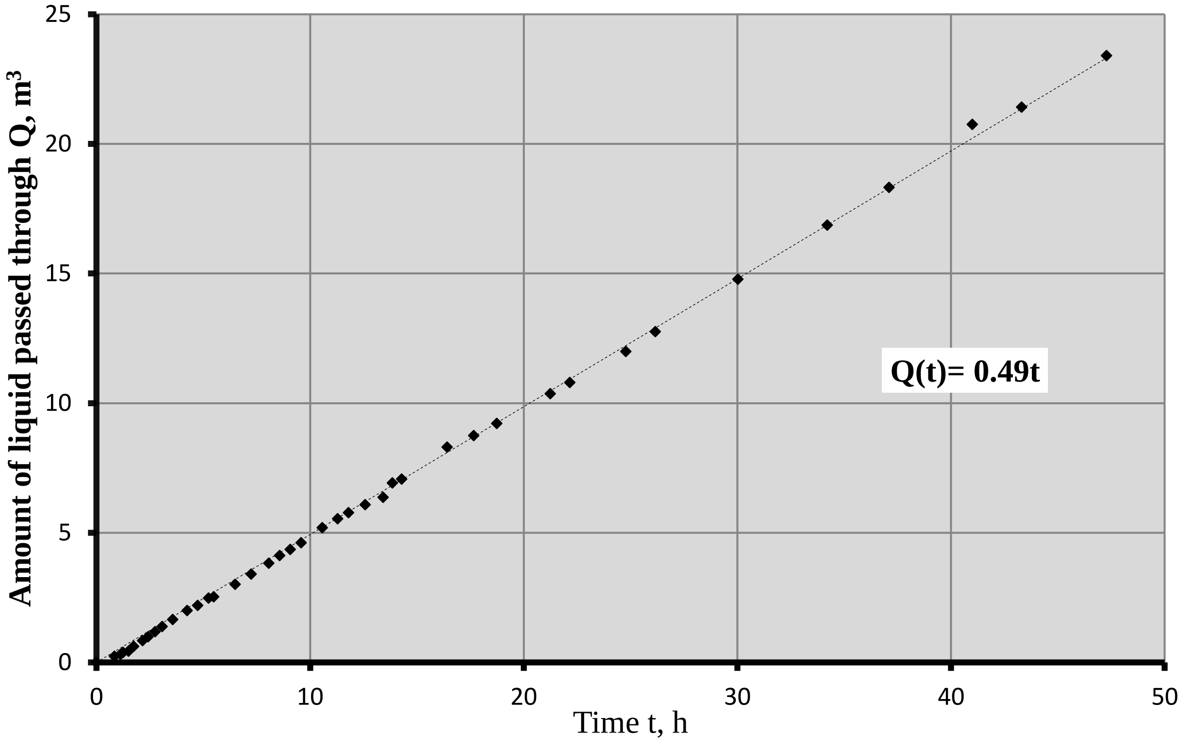

Figure 11 – The amount of passed-through liquid as a function of time.

During the entire CFF endurance testing, there was no need in regeneration of the Ti – membrane surface. The liquid purification capacity was constant and equal to $\frac{\partial Q(t)}{\partial t} = 0.49 m^3/h$.

The quality of the CFF with a nanostructured membrane was determined by means of the method of aerosol particles permeability in porous materials, developed at the SCC RF - IPPE [14]. The efficiency of removing the particles with the size over 0.3 µm was shown to be at least 99.5%. In addition, the bubble point method was used to determine the CFF quality.

By means of the bubble point method the maximum and mean values of CFF pore diameters were calculated according to the following formula:

$$D = 4\gamma(\cos\theta) \,/\, \mathrm{P} \qquad (1)$$

where γ is a surface tension force for the liquid (dyn/cm), P stands for displaced liquid pressure before air bubble formation (atm), θ is a contact angle of capillary wetting in the porous membrane. For alcohol γ = 1.7 dyn/cm, θ = 0.

In the research under consideration, a special cell was designed (Figure 12), in which a filtering element preliminary saturated with isobutyl alcohol (γ = 1.7 dyn/cm) was fixed to the structure by means of a screw joint with a sealing gasket. The structure was hermetically sealed inside a transparent glass cylinder to visually observe the formation of gas bubbles on the membrane surface in the course of testing. Alcohol was poured inside the cell in such a way that the liquid layer could completely cover the top adapter of the filtering element.

Figure 12 – The device to determine the bubble point in filtering membrane elements (1 –cell, 2 – air pressure control unit, 3 – valve, 4 – pressure gauge)

Membrane filtering element testing has demonstrated that its maximum and mean equivalent diameters of pores correspond to the values not exceeding 0.3 µm. and 0.15 µm. (respectively).

CONCLUSIONS

The following strategy was followed in the course of development of the cross-flow (tangential) filter:

- the product should be robust, with a long lifetime;
- regeneration of the plasma-chemical membrane surface clogged with mechanical impurities should be fully automatic, without the structure dismantling and without any stop in the cross-flow filter operation;
- the efficiency of removal of impurities with the size not exceeding 0.3 µm should be no less than 0.99%.

The following structural materials were used in the cross-flow filter: stainless steel 1X18H10T, Zr, Ti, etc.

The proper selection of plasma-chemical membrane material, the mode of supply of the liquid under purification to the filter and introduction of additional structural elements provided a continuous regeneration of the filtering membrane surface.

The comparative CFF operation in the dead-end and cross-flow filtration modes has demonstrated that in the dead-end filtration mode it is necessary to regenerate the filtering element with a plasma-chemical membrane in a time period not exceeding 10 hours; whereas in the course of CFF operation in the cross flow mode there is no need to regenerate the Ti – membrane surface. During the CFF endurance testing (up to 50 hours) the liquid purification capacity was constant and equal to $dQ(t)/dt = 0.50\ m^3/h$.

GRATITUDE

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