Natural Mineral Sorbents for Chemical and Microbiological Purification of Potable Water

G. A. Skorobogatov and A. I. Kalinin

St. Petersburg State University, Chemical Department, St. Petersburg, 198504 Russia

Abstract—The role of a number of rocks (shungite, glauconite fossil rock, flint) in a chemical and microbiological purification of water was estimated. On the basis of a shungite–dolomite module a simple method for a widescale manufacture of chemically and microbiologically pure potable water with conditionated content of mineral matters was developed.

DOI: 10.1134/S1070363211130032

Technogenic pollution of nature has reached such proportions that there is no place (except, perhaps, Antarctica and Greenland), where natural water can be used for drinking without health detriment. If drinkable water is need for a small group of people, a potable water purifier can be used. To provide communities with safe drinking water special facilities for household water supply are necessary. In the existing technological process for water disinfection one uses chlorination or other oxidants that help to avoid an epidemic of acute intestinal diseases. In this case water is not cleared by the chemical impurities presented in water intake but is also polluted by a number of chemicals (chlorine derivatives, salts of aluminum and iron) [1]. As a result, drinking water causes mass chronic intoxication of population.

The present paper proposes a method for not only disinfection but also obtaining chemically pure drinking water that simulates the natural processes of chemical and biological self-purification of water taking place in

---

German Alexandrovitch Skorobogatov, Dr. Sci. (Phys.-Math.), Prof., Head of Laboratory of Photochemistry and Chemical Kinetics, Chemical Department, S.-Petersburg State University (SPbGU). Scientific areas of focus: foundations of quantum mechanics, kinetic equations, chemical kinetics and photochemistry, radiochemistry, gerontology, environmental chemical pollutions, modeling of global economics.

Alexander Ivanovitch Kalinin, Cand. Sci. (Chem.), consultant of Joint-stock company NPO "RVS Technology". Scientific areas of focus: environmental chemical pollutions, modeling of natural water self-purification, industrial water processing.

the deep land aquifers. The authors took St. Petersburg city area with suburbs (north-west region of Russia) for consideration.

DESCRIPTION OF EXISTING DRINKING WATER SUPPLY SYSTEM

Information on the contamination of water supplies in St. Petersburg city contains in the report [2]: "In 2005, in connection with chemical indicators there are 22.95% samples that do not pass hygienic standards [3 4], 86.88% samples do not pass bacteriological indicators". According to official data [5], "over the past 10 years nothing has changed in the water supply network of St. Petersburg." It is further shown that the situation has not improved to 2010.

Thus, according to the Federal Service for Supervision of Consumer Protection and Human Welfare [6], during the last decade the first place in Russia on the incidence of hepatitis belongs to St. Petersburg. The structure of hepatitis incidence is as follows: 10% of hepatitis A, 30% of hepatitis B, and 50% of hepatitis C. Infection of hepatitis B occurs at sex intercourse and injection among drug addicts. The route of hepatitis C is nearly the same, but 20% of all patients are infected during medical procedures. Finally, the hepatitis A infections which number in hundreds, is transmitted only by water. To control the infection water and wastewater treatment plant increases the dose of chlorination of town water. However, this is insufficient because tap water and sewage often exchange their flows at water supply network of the city, where 65% are worn out, and 24% are in "poor condition" [5].

Table 1. The maximum allowable concentration (MAC) and the measured [1] content ($[X_i]$) of pollutants X_i in tap water in Kronshtadt area and St. Petersburg city in spring and summer 2001

i	X_i	MAC_i, μg l⁻¹		$[X_i]$, μg l⁻¹		
		SanPIN [3]	WHO [7]	South station	New Peterhof	Kronshtadt
1	$CHCl_3$	200	30	6	35	4
2	$CHBrCl_2$	60	30	3	8	15±5
3	CCl_4	2	2	0.6	0.5	0.4
4	Cr	50	50	10	59	45
5	Ni	100	20	10	2	17
6	Mn	100	500	60	55	60
7	Ti	100		1	36	30
8	Fe	300	300	250	380	290
9	Al	500	200	110	180	120
10	Cu	1000	2000	50	42	65
11	Zn	5000	5000	200	70	60
12	Sr	7000		100	50	55
$S_{GOST} = \sum ([X_i]/MAC_i) \le 1$				>2.8	>4.4	>3.8

The data on chemical contamination of tap water of St. Petersburg in 2001 and 2005 is given in [1] and [7] (Tables 1 and 2). According to SanPIN [3, 4] and international standards [8], water is considered harmless if the sum of the same pollution hazard class normalized by maximum allowable content (MAC) class does not exceed unit:

$$S_{GOST} = \sum ([X_i]/MAC_i) \le 1,$$

where S is sum, GOST is the State standard.

Tables 1 and 2 show that S_{GOST} amount exceeds 3–6 times the unit at any location in St. Petersburg and at any time of observations of town water. The data in Tables 1 and 2 were obtained with the chemical routine equipment without detecting the most dangerous pollutants in water in the concentration of below 1 mg l⁻¹. Therefore, the values of S_{GOST} in these Tables are not accurate and seem to be increased by 2–3 times [1].

Water-testing laboratories of water services company Vodokanal should regularly analyse the town water according to [3, 4] but data of these tests have not been published. There is an independent organization Environmental Safety Center (ESC) of Academy of Sciences in St. Petersburg whose duty includes "the solution of practical problems of regional and impact monitoring" [9]. But over the past 20 years ESC has not published any report with the results of "impact monitoring" of the town water in the city region. Therefore, the integral data on contamination of the town water by inorganic toxicants due to the content of these pollutants in wastewater have been extracted from the data published in [10] (Table 3).

Wastewater of the housing and communal sector of St. Petersburg make 85–87% of the whole wastewater and unlike industrial or rain-storm runoff, contain only those inorganic matter (except iron), which originally were contained in tap water, as there is no chemical production in residential areas. Therefore, the data in Table 3 characterize the integrated pollution of tap water in the city in 2007, which is 3–5 times higher than the allowable limit [4]. The town water is particularly highly polluted with aluminum, as aluminum hydroxide

Table 2. The results of the quantitative determination of inorganic impurities in tap water of the Old Peterhof, supplied by "Vodokanal St. Petersburg" from underground sources in the period from 09.01.2004 to 31.08.2005 [7]

i	X_i	MAC_i, mg l^{-1} [4]	Element concentration $(X_i)_j$ in the sample №j, mg l^{-1a}						
			j=1	j=2	j=3	j=4	j=5	j=6	j=7
1	Ca	280−x	76	69	71	60	90	90	28
2	Mg	0.6·x	11	10	>3	>3	7	13	>1
3	SiO$_2$	10	0.57	0.34	0.53	0.75	0.22	0.3	0.29
4	Sr	7	0.12	0.10	0.12	0.10	0.13	0.08	0.05
5	Zn	5	0.07	0.06	0.08	0.07	0.04	0.04	0.05
6	Cu	1	0.002	0.004	0.004	0.005	0.003	0.002	0.001
7	Al	0.5	0.69	0.35	0.64	0.48	0.69	0.67	0.12
8	Fe	0.3	0.63	0.48	0.37	0.35	0.31	0.34	0.38
9	Ni	0.1	0.002	0.003	0.002	0.003	0.003	0.005	0.001
10	Mn	0.1	0.01	0.01	0.01	0.01	0.01	0.01	0.01
11	Ti	0.1	0.11	0.07	0.19	0.27	0.12	0.04	0.04
12	Ba	0.1	0.043	0.056	0.040	0.050	0.040	0.051	0.026
13	Pb	0.03	0.001	0.002	0.001	0.009	0.004	0.001	0.001
$S_{GOST} = \sum([X_i]/MAC_i) \leq 1$			5.59	4.13	5.33	6.10	4.59	4.02	2.46

[a] Sample j = 1 was collected in September–October 2004. Sample j = 2 was collected in November–December 2004. j = 3 was collected in Januar–February 2005. j = 4 was collected in March–April 2005. j = 5 was collected in May–June 2005. j =6 was collected in July–August 2005. j =7 was collected in September 2005.

is used for water clarification, and iron, as the distribution networks are made of this metal.

NATURAL MINERAL SORBENTS (NMSs) AS WORKING BODIES IN DEVICES PRODUCING DRINKING WATER

NMSs are represented by rocks and minerals with high ion exchange, adsorption, catalytical and filtration properties. Some types of NMSs are surface-active, others are ion exchangers (zeolites, glauconite, bentonite, palygorskite). Amorphous NMSs are opal-cristobalites.

Some NMSs have catalytic properties that can be intensified by heating to 150–400°C, when the adsorbed water is removed.

Shungites are carbon-containing rocks [11], where the carbon component is firmly connected with alumosilicates and other minerals. Shungite differs from graphite with the lack of crystal lattice, from coal and bitumen differs with a two-dimensional structure and low content of volatile components. High-carbon rocks (mass fraction $R_C \geq 98$, or 35–75%) are just called shungites (type I and II, respectively); intermediate-carbon

Table 3. Average concentration of inorganic toxicants in wastewaters of St. Petersburg (X_i) in 1990–2007 [10]

I	X_i	MAC_i, µg l^{-1} [4]	$[X_i]$, µg l^{-1}		
			1990	2006	2007
1	Cd	1	1.75	0.052	0.013
2	Pb	30	51	1.05	0.56
3	Cr^{6+}	50	48	–	–
4	Ni	100	32	3.8	3.7
5	Mn	100	116	67	70
6	Fe	300	1400	365	500
7	Al	500	1740	550	1140
8	Cu	1000	58	3.0	2.5
9	Zn	5000	180	104	107
$S_{gost} = \sum([X_i]/MAC_i)$			>14.2	>3.2	>4.8
$S_{gost} = \sum([X_i]/MAC_i)$ without iron			>9.5	>2.1	>3.1

(R_C 20–35%) are named shungite-like rocks (type III); rocks with R_C 10–20% or less are called low-carbon or shungite-containing rocks (type IV and V). Subjected to the access of oxygen of the air and water containing organic pollutants (propanol, butanol, toluene, benzene, chloroform, chlorophenols, etc.) for sufficient contact time (hours) shungite catalyzes the oxidation of the latter [12, 13].

Silica rocks are quartzite, quartz sandstone and vein quartz considered integrated as high-silica rocks. They contain SiO_2 (46.7 wt.% Si and 53.3 wt.% O). Crystalline silica can have one of the following modifications: quartz (modifications α and β), tridymite (modifications α, β and γ) and cristobalite (modifications α and β). Phase transitions within each type pass rapidly, and the transformation of one type into another is slow. Polymorphic modifications of silica are chalcedony (cryptocrystalline variety of β-quartz) and opal. In siliceous rocks represented by amorphous silica ion exchange capacity is related to the ability of the reaction of silanol groups Si-OH and their number on the surface. Glauconite (monoclinic dioctahedral iron-magnesian mica with up to 28% Fe_2O_3, to 9.5% K_2O, 9% FeO, 4.5% Mg0) belongs to siliceous minerals. Sorption activity of glauconite is associated with ion exchange properties and extended specific surface. Flint is a silicic acid anhydride (fine crystals of chalcedony or quartz and amorphous opal forming a perfect cubic packing of very fine grains of silica). Flints occur in sedimentary strati-

fied rocks, especially chalk and carbon. Flint surface contacting water changes its pH from 7.0 to 10.0–13.5 with observed pH dependence on the number of water contact cycles. In contrast, water in contact with the opal, which gives a predominance of amorphous silica and contains β-tridymite and β-cristobalite, has pH 5.0.

Carbonate rocks are also used for water treatment. Rock-forming mineral for limestone is calcite $CaCO_3$ (56.0 wt.% CaO and 44.0 wt.% CO_2). Dolomite consists from 10 to 50% of limestone $CaMg(CO_3)_2$ with CaO content 30.41 wt.%, MgO content 21.86%, CO_2 content 47.73%). Dolomite crystallizes in the trigonal crystal system, hardness 3.5–4 units, density 2.75–2.85 g cm^{-3}, porosity of 0.4–12.6 units. Dolomite is divided into two groups: the sedimentative (chemical rocks with biogenic differences) and metasomatic (redistribution product of sediments during late diagenesis and catagenesis). Moderately burned dolomite is used in the water treatment for magnomass suitable for the stabilization of water treatment and neutralization of sulfate wastewater.

SIMULATION OF THE NATURAL SOURCE "TSAREVIN KLUCH"

In nature, NMSs sometimes occur in the order making precipitated water self-cleaning while percolating through them. This is the spring "Tsarevin Kluch" 2.5 km near Zazhoginsky deposit of schungite rocks in Republic of Karelia. The structure of this spring

Table 4. Organoleptic properties and pH data on tap water (the numerator) and water from agricultural irrigation canal (the denominator) before and after filtration through the columns with the NMSs

Values, units	Pristine water	Standard [4]	Material			
			Shungite	Silica	Glauconite	Filter "Tsarevin Kluch"
Odour, point	3/3	≤2	0/0	0/0	0/0	0/0
Colour,°	29/112	≤20	0/0	0/1.0	1.0/3.0	0/0
Opacity, units	4/5	≤2.6	0/0	0 / 1.0	1.0/1.0	0/0
pH	6/6.5	6–9	5.5/5.5	7.5/7.5	7.8/7.7	7.2/7.3

has been revealed according to exploratory drilling [1]. Power source is due to rainfall. Then, water filters through a thin layer of soil, weeps through the lens of shungite, filtered through fragmental limestone and falls into the water-bearing sand level. After that, pure water appears at the surface, forming a spring "Tsarevin Kluch".

The aim of the study was to determine experimentally the role of each of the constituent rocks in the mechanism of purification of water spring "Tsarevin Kluch." In the experiments shungite of the Zazhoginsky deposit was used, type IIIA, comprising $27.7 \pm 7\%$ C, $67 \pm 7\%$ SiO_2; 3.9% Al_2O_3; 0.6% FeO_3; 0.5% MgO, 1.4% K_2O, etc. Specific surface area 6–20 m^2 g^{-1}, total pore volume 0.05–0.15 cm^3 g^{-1} with the effective radius of 3–10 nm long. The mineral is milled to a grain size of 1 to 3 mm.

Further, the flint from deposits of the Smolensk region (West region of Russia) was used for comparison. Nodular black type flint (containing $10 \pm 0.5\%$ SiO_2, $10 \pm 0.5\%$ CO_3, $5 \pm 0.5\%$ K_2O, and Na_2O, Al_2O_3, Fe_2O_3, SO_4, BO_3, Cl, PO_4, Ca) was milled to a particle size of 1–5 mm. Glauconitic limestone from deposits of the Leningrad region was also studied, which contained not less than 50 wt.% $CaCO_3$ and CaO, and 40% of opal-crystobalite glauconite. In addition, the effectiveness of the filter "Tsarevin Kluch" presented at the consumer market was studied comprising a consistent composition of the three above mentioned NMSs in equal proportions. As a control comparison, activated carbon (AC) of BAC grade was used.

Effect of NMSs on the organoleptic properties of water. Water suitability for drinking is primarily deter-

mined by its organoleptic properties. Impact of NMSs on the indicators is demonstrated in Table. 4.

Effect of NMSs on chemical water composition (inorganic toxicants). When MAC is 0.3 mg l^{-1}, the tap water in the Moscow district of St. Petersburg contained (0.5 ± 0.1) mg l^{-1} of iron. Water samples from wells that supply villages Toksovo and Krasnitsy with drinking water contained iron in an amount exceeding the norm 15 and 134 times, respectively. After passing through the column with the NMSs the concentration of iron ions in all samples dropped to MAC (Table 5). Table 5 also shows that NMSs can effectively remove copper ions from water, being it soft or hard water: application of NMSs at tested copper concentrations resulted in a decrease of initial concentration 16 and 100 times: with 0.48 mg l^{-1} up to 0.03 mg l^{-1} for glauconite and filter "Tsarevin Kluch", and 10.0 mg l^{-1} to 0.10 mg l^{-1} for the same sorbents, respectively. The effectiveness of the NMSs is significantly higher than the efficiency of the AC, with the exception of the concentration of 5.40 mg l^{-1}, where efficiency and schungite and AC do not differ. NMSs are effective in highly-blooming water containing humic substances, unlike the AC, which is not effective in water of this sort.

Effect of NMSs on chemical water composition (organic toxicants). The amount of water permanganate oxidation indicates the presence of easily oxidized organic matter. In the fresh waters the value of permanganate oxidation expressed as mg O_2 l^{-1} virtually coincides with level of organic carbon. Table 6 presents the results of the study on the effectiveness of NMSs for reducing the content of organic substances in water. Water after filtration

Table 5. The relative residual concentration of inorganic contaminant after a contact time with filler $\Delta t = 200$ min depending on the initial concentration $[X]_0$ and the type of a column filler Y_i

Inorganic contaminant (X)	$\dfrac{[X]_0}{MAC_X}$,[a]	$R_{X,Y_i}=[X]_{i,\Delta t}/[X]_0$				
		Shungite	Silica	Glaukonite	Filter "Tsarevin Kluch"	AC
Fe^{2+}	1.7±0.3	20± 5	20± 5	24 ± 6	20± 5	20± 5
	15 ± 0.7	3.3± 0.9	6.5± 1.7	5.4± 1.4	2.6± 0.7	3.0± 0.7
	134 ± 7	0.35±0.04	0.75±0.09	0.75±0.11	0.62±0.08	0.75±0.11
Cu^{2+}	0.58±0.02	34±4	0	7.0±0.7	0	34±12
	4.6±0.1	11±1	2.2±0.3	3.5±0.3	2.2±0.3	13.5±0.8
	9.95±0.5	5±1	1.0±0.2	0.50±0.03	0	3.0±0.3
Cu^{2+} [b]	0.49±0.02	16±2	8±2	14±1	12.3±2.5	41±4
	1.22±0.10	17±3	9±2	10.6±1.6	8.2±1.0	25±6
	9.95±0.5	6.5±0.6	1.5±0.5	1.0±0.2	1.0±0.1	11.0±2.4
Cu^{2+} [c]	0.48±0.02	0	21±3	6.2±0.4	6.2±0.8	42±6
	5.4±0.2	6.3±0.6	1.9±0.5	2.8±0.3	2.2±0.2	5.6±1.1
	10.0±0.5	6.5±0.6	1.5±0.5	1.0±0.2	1.0±0.1	31±3

[a] MAC = 0.3 mg l^{-1} for Fe^{2+}; MAC = 1.0 mg l^{-1} for Cu^{2+}; [b] Ca^{2+} with concentration $[Ca^{2+}] = 7.2$ mg-eq l^{-1} was in model water sample besides Cu^{2+}; [c] model water contained "colour" (humic substances) besides Cu^{2+}.

through a column with shungite, flint and glauconitic limestone, as well as "Tsarevin Kluch" filter met the requirement of SanPiN [4] in terms of permanganate oxidation (≤ 5.0 mg O$_2$ l^{-1}). Effectiveness of shungite and AC in reducing water oxidability was the same. So, shungite and filter "Tsarevin Kluch", as well as the AC, removed phenol from the water to the concentration lower than MAC.

Phenol at initial concentration of 0.05 mg l^{-1} was equally removed from highly-blooming water (to a value lower than MAC) by all the NMSs. At higher concentrations (1.5–34.5 mg l^{-1}) shungite, glauconitic limestone and filter "Tsarevin Kluch" removed phenol to lower limit values as effectively as the AC. Flint reduces phenol content down to 0.01 mg l^{-1} at the initial level of 1.5 mg l^{-1} and to 0.4 mg l^{-1} — at 34.5 mg l^{-1} (difference from control is proved). The effectiveness of shungite, glauconitic limestone and AC are almost identical for the highly-blooming water. Flint is inferior to all studied NMSs and the AC but in water rich with

humic substances its activity was higher than in other types of water (tap and hard).

Effect of NMS on the microbiological indicators of water. Drinking and sanitary water shall not contain any pathogenic agents. The safe drinking water supply is provided either by the use of groundwater of high quality under a sanitary control or by competent choice and proper operation of wastewater treatment plants. Bacteriological indicators of water may deteriorate in the distribution network. In addition, microbiological contamination occurs because of bacterial growth on building materials in contact with water (gaskets, tubes, plastics used in water pipes and taps). Therefore, local second-stage water treatment should effectively remove microbial contamination from water.

Testing for the presence of indicator-organisms for faecal contamination is the most reliable way of assessing the hygienic quality of water. None of the organisms can satisfy all the requirements of the ideal faeces

Table 6. The relative residual concentration of contaminant of organic nature depending on the initial concentration $[X]_0$ and the type of a column filler after a contact time with filler $\Delta t = 200$ min

Contaminant (X)	$\dfrac{[X]_0}{MAC_X}$, %[a]	R_{x_i}/%				
		Shungite	Silica	Glauconite	Filter "Tsarevin Kluch"	AC
Phenol	50±1	<2	<2	<2	<2	<2
	1500±100	<0.07	0.7±0.1	0.13±0.07	<0.07	<0.07
	34500±1500	<0.003	32±3	0.23±0.01	<0.003	<0.003
Phenol [b]	50±1	<2	<2	<2	<2	<2
	1500±100	<0.07	3.3±0.7	0.07	<0.07	<0.07
	34500±1500	<0.003	27±2	8.7±0.6	<0.003	<0.003
Phenol [c]	50±1	<2	<2	<2	<2	<2
	1500±100	<0.07	60±60	<0.07	<0.07	<0.07
	34500±1500	<0.003	1.2±0.4	<0.003	<0.003	<0.003
Organics oxidised with permanganate	1.36±0.10	14 ± 3	46 ± 7	46 ± 6	31 ± 4	18 ± 2
	2.32 ± 0.16	9.9±0.7	33 ± 5	32 ± 4	19 ± 3	15 ± 2
	3.12 ± 0.24	13.4±1.8	30 ± 4	26 ± 4	17.5±2.5	14 ± 2

[a] MAC = 0.001 mg l^{-1} for phenol; standard water oxidability for potable water not more than 5.0 mg l^{-1}; [b] Ca^{2+} with concentration [Ca^{2+}] = 7.2 mg-eq l^{-1} was in model water sample besides phenol; [c] MAC = 0.001 mg l^{-1} for phenol; model water contained "colour" (humic substances) besides phenol.

indicator. The best indicator is the *E. coli*. Tables 7–9 present the results of the study on the effectiveness of NMSs for the removal of cells *E. coli, B. subtilis* spores and *C. perfringens*. Tables show that the studied NMSs, as well as their complex in the filter "Tsarevin Kluch" effectively removed microbial contamination with a concentration of bacterial suspension of 1200–3500 cl ml^{-1}, not yielding a filter with the AC. Shungite and glauconitic limestone showed the greatest efficiency in the removal of the cells of microorganisms.

Toxico-hygienic assessment of water passed through filters with NMSs. Toxicity of water samples containing chemical toxicants (phenol, copper sulfate) before and after passing through filters with NMSs was determined using small crustaceans *Daphnia magna* and microalgae *Chlorella vulgaris*. The data in Table 10 show that the water before passing through filters with NMSs was toxic for crustaceans (*Daphnia magna* death rate in both cases exceeded 50%). After passing through filters with NMSs there was no visible toxic effect on *Daphnia magna* in all cases. Similar results were obtained for the microalgae *Chlorella vulgaris*.

APPROACH ON MECHANISM OF REGENERATION SHUNGITE-DOLOMITE WATER TREATMENT MODULE

To simulate the processes taking place under the day surface of the spring "Tsarevin Kluch", a transparent module (Scheme) filled consistently with shungite, glauconitic limestone and sand was made. The layers in the module were in reverse to natural order, since supply of the treated water and model solutions was carried out from the bottom upwards (in order to avoid air voids between the grains of filler). Within 47 days of the experiment A, namely, for 564 hours of operation of the circulation pump 1128 liters of water have been filtered through the layers, when 1504

Table 7. The number of microorganisms *E. coli* in water before and after filtration through filters (n = 5)

	Number of microorganisms, cl·ml^{-1} [a]				
Pristine water	Filter				
	Shungite	Silica	Glauconite	Filter "Tsarevin Kluch"	AC (control)
1200±100	0	0	0	0	0
3500±200	0	0	0	0	0
3200±200	800±100	1500±300	700±500	800±500	600±300

[a] Error is normal.

Table 8. The number of microorganisms *B. subtilis* in water before and after filtration through filters (n = 5) [a]

	Number of microorganisms, cl·ml^{-1} [a]				
Pristine water	Filter				
	Shungite	Silica	Glauconite	Filter "Tsarevin Kluch"	AC[a]
1500 ±100	0	0	0	0	0
3400±200	0	0	0	0	0
32000±1000	7 ± 1	15000±1000	7 ± 0.2	8 ± 0.2	8 ± 0.1

[a] Symbols in Tables 8 and 9 are the same as in Table 7.

mg of $FeCl_3$ $6H_2O$ or 266 mg of Fe were effectively strained out. During the experiment water pumped through the module had a concentration of iron (Fe) 0.235 mg l^{-1}, which is considerably lower than the MAC = 0.3 mg l^{-1}. Thus, shungite-dolomite module, represented in the Scheme, successfully removed iron salts at the beginning of its operating life even when their concentration was lower than MAC. It is easy to calculate that 1 liter of shungite filling can remove up to 31 mg of iron (in terms of metal) from the feed water. For further effective work shungite-dolomite module should be regenerated for further effective work. Regeneration was performed with a solution of oxalic acid.

DISCUSSION WITH TECHNICAL AND ECONOMICAL CALCULATION

Table 4 shows that both tap water and highly contaminated water of agricultural soil reclamation canal (in Petrodvorets district of St. Petersburg) release odor, color and turbidity being filtered through a layer of shungite chips. In contrast to the shungite, flint chips did not cope with cleaning the very dirty water from the reclamation canal and glauconite was not able to clean tap water completely, even in the Moscow district of St. Petersburg. This is explained by the fact that shungite is not just the adsorbent but also a strong acid [14] as well as an oxidation catalyst at access of atmospheric oxygen [15].
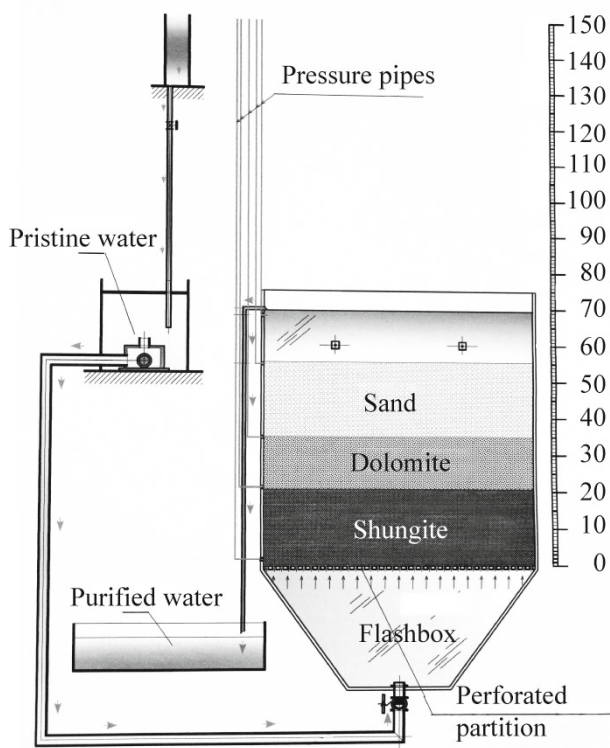
Scheme of the experimental device modelled the native process of water self-purification in "Tsarevin Kluch" area. Inside dimension in plane is 55×730 mm (sectional area is 400 cm²). The volume of the low flashbox is 9250 cm³. The volume of shungite charging is 8670 cm³ (layer thickness is 215 mm). The volume of dolomite charging is 5420 cm³ (layer thickness is 135 mm). The volume of sand charging is 8030 cm³ (layer thickness is 200 mm). The total charging volume is 22120 cm³ (subject to the low flashbox is 31370 cm³).

Being filtered through a layer of shungite chips, water became significantly acidified (see the last line in Table 4) and required conditioning before using as drinking water. This problem was solved by a three-layer module shown in Scheme, after which water acquired physiologically acceptable value of pH = 7.25 ± 0.05.

Table 7 shows that lower is the initial concentration of contaminant in water model, the higher is the efficiency of water purification from organic pollutants. Such pattern is almost obvious: the more completely adsorbing filler purifies water, the less organic pollutant it has.

Purification of water model from mineral content (Table 5) is entirely different: the lower the inorganic

contaminants remain in the water model, the harder this contaminant is removed from the water by a mineral adsorbent. The mineral adsorbent is no longer effective for metal cations, as soon as their concentration is comparable with their MAC.

It follows therefrom that excessive lowering of inorganic impurities concentration is harmful to animals. Therefore, ultra-pure distilled or frozen out water, is entirely unsuited both for unicellular and multicellular organisms. This ultra-pure water should be conditioned in accordance with mineral composition by adding inorganic compounds to a level close to their MAC. The water purified in shungite-dolomite modules is automatically conditioned by mineral composition and can be recommended as the best option of drinking water.

The result of experiment A implies that 1 t of mineral material costing about 15000 rub t⁻¹ allows to purify 22 m³ of water before its "breakdown". Mineral material is recovered without unloading at least 10–20 times, so using a single load 450 m³ of water can be safely purified.

The result of experiment B showed that regeneration of 1 t of mineral material requires 20 kg of oxalic acid costing about 6000 rub. 20 cycles of regeneration will require 400 kg of oxalic acid costing about 120000 rub. Thus, the regeneration operations essentially contribute into the cost of water purification by shungite-dolomite modules. The final price of such drinking water:

$$\frac{135000 \text{ rub}}{450 \text{ m}^3} = 0.3 \text{ rub } l^{-1}$$

On the other hand, the distillation of 1 liter of water requires 500 calories of heat, or 0.6 kW h of electricity costing 2 rubs. Thus, the purification and conditioning of drinking water in multi-mineral shungite-dolomite modules is 10 times cheaper than its purification by distillation. Moreover, production of shungite-dolomite purifiers can be based entirely on national raw materials.

EXPERIMENTAL PART

The effectiveness of sorption by NMSs was studied under current conditions. The mineral, crushed into particles of the required size, was placed into a plastic column with a diameter 6 cm and a height 23 cm between two polypropylene gaskets at the top and at the bottom (to eliminate the leaching of small particles from the column). The amount of material was 500 cm³. The rate of water supply to the column within the limits of 2–3 ml min⁻¹ (1 drop per 1–2 s), i.e. the duration of contact of treated water with a layer of the

Table 9. The number of microorganisms *S. perfringens* in water before and after passing through the filters (n = 5)

Pristine water	The number of microorganisms, cl ml^{-1}				
	Filter				
	Shungite	Silica	Glauconite	Filter "Tsarevin Kluch"	AC
1300±100	0	0	0	0	0
3200±200	0	0	0	0	0
31000±2000	6 ± 0.1	16 ± 14	8 ± 0.4	7 ± 0.3	7 ± 0.5

Table 10. Lethality (*L*, % to control [a]) in the colony *Daphnia magna* (numerator) or *Chlorella vulgaris* (the denominator) depending on the degree of water purification from the model toxicant (n = 5)

Toxicant X	$[X]_0$, mg l^{-1}	L [b] in pristine water	L in water after filtration through the filter [c]				
			Shungite	Silica	Glauconite	"Tsarevin Kluch"	AC
CuSO$_4$	10	85.5±5.0 95.0±5.0	5.0±0.5 7.0±0.4	4.0±0.2 4.5±0.4	3.0±0.2 5.0±0.5	4.0±0.1 6.0±0.3	5.0±0.2 6.5±0.5
	5	59.0±3.0 64. 0±3.0	4.0±0.2 4.5±0.5	3.0±0.1 3.0±0.3	3.0±0.2 5.5±0.4	3.0±0.2 5.0±0.5	4.0±0.2 7.0±0.4
phenol	1.5	73.0±2.5 75. 0±5.0	3.0±0.2 3.0±0.2	11.0±0.5 18.0±1.5	4.0±0.3 7.0±0.6	3.5±0. 4.5±0.2	3.5±0.2 6.0±0.3
	0.05	57.0±1.5 56. 0±3.0	2.5±0.1 3.5±0.3	3.0±0.2 9.0±0.6	3.0±0.1 4.5±0.5	4.0±0.2 3.5±0.3	4.0±0.3 5.5±0.5

[a] The control is the water in vessels, where *Chlorella vulgaris* was cultivated; [b] error is normal; [c] in all variants of the experiment the pH of water was fitted within 7.0-7.2 after passing through columns.

NMSs was about 200 min. The efficiency of different sorbents in water treatment was evaluated by comparing organoleptic, physical, chemical, microbiological and toxicological parameters of the original and the treated water in accordance with standard nomenclature and methodology [17].

For studying the effectiveness of various NMSs in the processes of straining out pollutants the cupric ions are selected as a model for heavy metals. Concentration of copper in the model solutions was as follows:

Cu^{+2} 0.5 mg l^{-1}, 5.0 mg l^{-1} and 10.0 mg l^{-1} making the necessary amount of 1 M solution of copper sulfate. The copper content in water was determined by colorimetric method with sodium diethyldithiocarbamate using a FEK-M tester. Phenol concentration in the model solutions was 0.05 mg l^{-1}, 1.5 mg l^{-1}, or 34.5 mg l^{-1} adding the necessary amount of standard solution of phenol with a concentration of 100 mg l^{-1}. The content of phenol in water was determined after distillation by colorimetric method with 4-aminoantipyrine using the FEC-1 tester [18].

The influence of a number of physicochemical factors on the effectiveness of the NMSs as water purifying material was studied as a function of:

• variations of water hardness. Tap water (hardness 0.8–0.9 mg-eq l^{-1}) as well as a model water with desired amount of $CaCl_2$ solution to create a higher level of hardness (up to 7 mg-eq l^{-1}) was used.

• variations in the color of water due to the presence of humic substances; the results of impact of the NMSs on tap water (color 10–15°) and on the model water with a higher color index, which was prepared by adding a solution of humic substances into the tap water (commercial product "Ideal"), were compared.

• preparation mode (activation) of the sorbent for the process. Various ways to activate NMSs, i.e. graining, acid treatment and heating, were studied.

Sorbents were grained with conical inertia crushers. The desired fraction was obtained by screening out with further washing with water to remove dust fraction. Acid treatment was carried out by a mixture of 10% oxalic acid and hydrogen peroxide (1:1). After chemical activation the sorbents were washed with distilled water to pH 7. Experiments were performed under uncurrent conditions: NMSs particles of 5–10 mm in size were placed in a flask with a solution containing ions of Cu^{2+} (volume ratio 1:15) at constant stirring to avoid diffusion limitations for transportation of a contaminant model molecules to the surface of the sorbent.

Developing the scheme of regeneration of schungite-dolomite modules, the rocks were spalled at a jaw crusher, then fractions of 1–2 mm were sifted by the laboratory sieve. Grains were got the dust particles off with running tap water and then air-cured. The developed rocks were put into tester in level layers. Pressure between the layers was measured with piezo-thermal tubes. The process of purification and regeneration was studied using a model solution of ferric chloride $FeCl_3$ with a concentration 10 mg l^{-1} (per Fe), which corresponded to 30 MAC (equal to 0.3 mg l^{-1} [4]).

Experiment A to determine the service life of shungite-dolomite unit. The model solution of hexaqua trichloride iron $FeCl_3·6H_2O$ with a concentration of 16.0 mg l^{-1}, that is in terms of iron was 3.3 mg l^{-1}, which amounted to 11 MAC was pumped to the lower zone of radiator feed tank with the help of circulation pump, then diluted to lower concentrations in the side tank. Through a horizontal perforated diaphragm (underneath shungite) the model water entered the bottom of filter filler, rose up, and being purified, flowed back into the tank with circulating pump. A concentrated solution of ferric chloride (16 mg l^{-1} $FeCl_3·6H_2O$) at the rate of 160 ml hr^{-1}, 2.7 ml min^{-1}, 1 drop per 5 s was constantly pumped from the upper flask into the purified water. The rate of water filtration was 2 l h^{-1}.

Within a day at a 12-hour continuous operation of the circulation pump 2 l of the model solution from the upper flask was used. 24 liters of water amounting to 32 mg of $FeCl_3·6H_2O$, 6.6 mg in terms of iron passed through the filter fillings. At the end of the day 200 ml of purified water were bled, where 2–4 drops of potassium rhodanate solution were poured to. By the absence of red staining concluded that the iron in the treated water was completely absent.

The next day in the morning the upper flask was charged with 2 l of regular solution model containing 32 mg $FeCl_3 6H_2O$. The new experiment was performed during 12 h within 47 days. The pH value in different module layers were the following:

pH = 6.2 was in the water under a shungite layer;

pH = 5.2 was in the water under a shungite layer up to a dolomite layer;

pH = 7.05 ± 0.05 was over and underneath a sand layer.

On the 48th day of the experiment a "breakdown" of the module occured. Iron hydroxides penetrated into the treated water at the outlet of the sand. Jelly-like gel rapidly went up from the sand layer and deposited on a top of it. The experiment was completed with the following pH values in the layers:

pH = 6.2 was in the water under a shungite layer;

pH = 5.2 was in the water under a shungite layer,up to a dolomite layer;

pH = 6.35 ± 0.15 was over and underneath a sand layer.

Experiment B on testing the undischarge method of regeneration of shungite-dolomite unit. To regenerate the exhausted resource of the module an aqueous solution of oxalic acid ($H_2C_2O_4 2H_2O$, 5 g l^{-1}) was used. A single refill compounds 12 l, which required 60 g of oxalic acid. Every 24 hours at 6:00 the regenerative solution passes through the module at the rate of 2 l h^{-1}. The experiment passed for 18 days

during which 216 l of an aqueous solution containing 1080 g of oxalic acid passed through the unit. On the 19th day the module was almost completely cleared (95%). The following pH values were observed in the course of regeneration:

pH = 2.0 was in the water at the entrance (underneath shungite);

pH = 3.75 ± 0.25 was over a sand layer.

Being washed with clean water the module was ready for the next cycle [18].

ACKNOWLEDGMENTS

REFERENCES

1. Skorobogatov, G.A. and Kalinin, A. I., *Ostorojno! Vodoprovodnaya Voda* (Carefull! Potable Water.), St. Petersburg: St. Petersburg State University, 2003.

2. *Okhrana okrujayuschey sredy, prirodopol'zovanie i obespechenie ekologicheskoy bezopasnosti v Sankt-Peterburge v 2005 godu* (Environmental Protection, Nature Management and Ecological Safety Control in St. Petersburg in Year 2005), Ed. by D.A. Golubev and N.D. Sorokin, St. Petersburg, 2006.

3. *Pit'evaya Voda. Gigienicheskie trebovaniya k kachestvu vody centralizovannykh system pit'evogo vodosnabjeniya. Kontrol' kachestva* (Potable Water. Water Quality Sanitary Standards for the Centralized Water-Supply Systems. Quality Control), SanPiN 2.1.4.559-96, Moscow: Russian State Board for sanitary and epidemic inspection, 1996.

4. *Pit'evaya Voda. Gigienicheskie trebovaniya k kachestvu vody centralizovannykh system pit'evogo vodosnabjeniya. Kontrol' kachestva* (Potable Water. Water Quality Sanitary Standards for the Centralized Water-Supply Systems. Quality Control), SanPiN 2.1.4.1074-01, Moscow: Russian State Board for sanitary and epidemic inspection, 2001.

5. *Okhrana okrujayuschey sredy, prirodopol'zovanie i obespechenie ekologicheskoy bezopasnosti v Sankt-Peterburge v 2004 godu* (Environmental Protection, Nature Management and Ecological Safety Control in St. Petersburg in Year 2004), Ed. by D. A. Golubev, and N. D. Sorokin, St. Petersburg, 2005.

6. *Virusnye gepatity v Rossiyskoy Federazii. Analiticheskii obzor. 6-i vypusk.* (Hepatitis Viruses in Russion Federation. Analytical review. 6th Issue.), Ed. by A.B. Zhebrun, St.Petersburg: "Boston–spectrum", 2006. 110 pp.

7. Skorobogatov, G.A., Bakhtiarov, A.V., Kalinin, A.I. and Savilova, L.M., *Ekol. Khim.*, 2007, vol. 16, no. 3, p. 182.

8. *Guidelines for drinking-water quality*, 3d Ed., Vol. 1. Recommendations, WHO: Geneva, 2004.

9. Donchenko, V.K. *Nauchno-informazionnyi bulleten' NICEB RAN* (Scientific Bulletin by Scientific Research Centre of Ecological Safety, Russian Academy of Science), St. Petersburg, 1996, no. 5, p. 5.

10. *Okhrana okrujayuschey sredy, prirodopol'zovanie i obespechenie ekologicheskoy bezopasnosti v Sankt-Peterburge v 2007 godu* (Environmental Protection, Nature Management and Ecological Safety Control in St. Petersburg in Year 2007), Ed. by D.A. Golubev, and N.D. Sorokin, St. Petersburg, 2008.

11. Kalinin, Yu.K., Kalinin, A.I. and Skorobogatov, G.A., *Schungity Karelii – dlya novykh stroymaterialov, v khimicheskom sinteze, gazoochistke, vodopodgotovke i medizine* (Karelian Schungites for new Building Materials, in the Chemical Synthesis, Gas Cleaning, Water Treatment, and Medicine), St. Petersburg: Dept. of Chemistry, St. Petersburg State University, 2008.

12. Meilakhs, A.G., Skorobogatov, G.A. and Novikaite, N.V., *Ekol. Khim.*, 2001, vol. 10, no. 3, p. 198.

13. Skorobogatov, G.A., Kalinin, A.I. and Kalinin, Yu.K., *Zh. Org. Khim.,* 1995, vol. 31, no. 6, p. 947.

14. Tanabe, K., *Solid asids and bases*, Russian translation, Ed. by K.V. Topchiev, Moscow: Mir, 1973.

15. Zenkevich, I.G., Ischenko, E.V., Makarov, V.G., Makarova, M.N. and Selezneva, A.I. *Zh. Obsch. Khim.,* 2008, vol. 78, no. 9, p. 1449.

16. Zakharov, I. D., Kalinin, A.I., Semkovich, M.Ya. and Yakovlev, A.V., *Sbornik nauchnykh trudov Nauchno-Issledovatel'skoy gruppy №1 VITU Ministerstva Oborony RF*, St. Petersburg, 2003, iss. 5, p. 366.

17. *Pit'evaya Voda. Metody analiza.* (Potable Water. Analytical Methodology.), Moscow: Standards Publishing House. 1984.

18. Lur'e, Yu. Yu., *Analiticheskaya khimiya promyshlennykh stochnykh vod* (Analytical chemistry of industrial sewage), Moscow: Khimiya, 1984.