

Application of nanofiltration to produce water for drinking and industrial needs of urban economy

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Abstract. The issues associated with the operation of reverse osmosis plants at the water intake facilities (WIF) for the treatment of drinking water from groundwater sources are described. Ways of increasing reverse osmosis plants performance are considered. The technology of plants modernisation with the purpose of operational costs reduction and minimisation of concentrate discharges into sewerage system, consisting in replacement of reverse osmosis (RO) membranes with nanofiltration membranes, is provided. The use of nanofiltration membranes reduces the intensity of sedimentation and at the same time the concentrate flow without the sedimentation hazard. Also, nanofiltration membranes make it possible to reduce inhibitor dosage and operation costs respectively. Experimental studies on groundwater treatment and efficiency of the provided technology have been carried out. Rates of sedimentation in each device of the layout, as well as composition of water treated by each device depending on the volume reduction factor K (source water flow to the concentrate flow ratio) for the plant were determined. The feasibility comparative study considered the following parameters of the plant operation, without limitation: inhibitor dosage, membrane types, salt selectivity of membranes, source water volume reduction factor K.

Keywords: reverse osmosis; nanofiltration; sedimentation on membranes; membrane selectivity; membrane plant concentrates disposal; removal of lithium, fluorine and ammonium.

1 Introduction

The remoteness of standalone structures from a water supply source, or rather the remoteness of a water supply source from a centralised sewerage system and the lack of opportunities for wastewater discharge (water demand of a water treatment plant itself) form major issues for the creation of independent water supply systems. This led us to development of groundwater and surface water treatment processes that completely eliminate waste streams (as a demand of a water treatment plant itself). Such systems can divide source water into a stream of treated water of high quality and a sediment (concentrate) stream with the flow of 0.3-1% or less of the water incoming for treatment. Removal by road is feasible due to small volumes of sediment [1, 2].

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Creation of independent water supply systems requires a careful economic analysis as such systems operation is associated with drinking water costs, as well as hot water and sewerage costs for the consumer [3, 4, 5]. The analysis takes into account the cost of reagents, water consumption for the water treatment plant itself, electricity costs, and the cost of transporting sediment to a landfill. A system can be considered feasible if it provides low tariffs for the use of hot and cold water and for sewerage for a given quality of treated water.

Perhaps the most important aspect of the drinking water supply problem is the quality of drinking water and its composition compliance with modern hygienic requirements. In addition to the requirements for the removal of various dissolved contaminants, modern hygienic standards require “full physiological value” of water meaning the compliance for the minimum content of salts and hardness ions, as well as for the content of physiologically necessary elements like fluorine, selenium, etc. The paper presents a new type of plants for treatment of drinking water supplied from surface and underground water sources. The invented membrane technology makes it possible to minimize the concentrate flow (up to 5% of the incoming water for treatment or less), or, if necessary, to eliminate it completely (by removing it together with suspended solids or calcium carbonate crystalline precipitate). The invention is distinctive for its technology of staged application of membranes with different selectivity values depending on the composition of the source water and various contaminants in it (fluorine, strontium, ammonium, lithium, boron, bromine). At the same time, various challenging cases of dissolved contaminants in water (e.g., when the content of lithium exceeds the limit by factor of 10-20) are considered, when the application of reverse osmosis method in addition to removing contaminants causes a multiple reduction in total dissolved salts and total hardness. The invented technology of “ion separation” as it is called by the authors, makes it possible to achieve the intended level of concentration for the removed contaminant (e.g., lithium) while ensuring that the total dissolved salts and hardness ion concentration is increased in treated water [6, 7].

2 Materials and methods

The reverse osmosis is nowadays widely used to obtain high-quality drinking water from underground [7, 8] and surface sources [9, 10]. Reverse osmosis plants are effectively used in the “New Moscow” region (extended area of Moscow) for groundwater quality improvement. Several groundwater streams in the “New Moscow” area contains excessive amounts of fluorine, ammonium, lithium, strontium and even boron, exceeding WHO normative values, in addition to conventional calcium and iron. Reverse osmosis plants are used to remove these contaminants [11-13]. The value of the mixing ratio (the flow ratio of the permeate to the portion of the source water used for mixing) depends on the amount by which the concentration of the contaminant exceeds the regulatory limit [11, 13, 14]. Such an approach may be appropriate only if the concentration of contaminants exceeds the regulatory limits by 3-4 times or less. If the exceedance value is higher, there is no need for mixing, as in this case the entire amount of source water must pass through the membranes. Thus, in some instances the reverse osmosis application for obtaining water of drinking quality has the following disadvantages. To begin with, the hardness is decreased by 95-97% and in some cases we have to provide water conditioning by adding calcium ions. Second, treatment of very hard groundwater limits the set permeate yield (the flow ratio of the permeate to the source water) as calcium salts are formed in the membrane channels [15-17]. When using membrane plants for drinking water treatment, the choice of the permeate yield value of the plant has a significant impact on the price of treated water

supplied to consumers, since the amount of concentrate discharged to the sewerage increases the sewerage fee as well as the total cost of water produced by the membrane plant. And thirdly: when using reverse osmosis membranes, there is a risk of deposits of low water-soluble salts on the membranes, so the operation requires certain costs to prevent the formation of these deposits [18, 19].

Nanofiltration membranes are known to provide efficient removal of monovalent ions [11, 12, 14], which is particularly effective when concentrations of these contaminants need to be reduced by a factor of three or less [20-23]. Application of nanofiltration membranes provides effective removal of monovalent ions and also reduces operational costs due to slower formation of crystalline deposits in devices with low-selectivity membranes [8, 9, 12]. Moreover, the use of an additional nanofiltration stage can easily increase the permeate yield, which significantly reduces the overall cost of treated water production [7, 9, 12, 13]. Table 2 shows the typical composition of groundwater and the results of its treatment using different types of membranes [7, 8].

Table 1. Results of underground water treatment using different types of membranes.

No	Ingredients, Concentration values, mg/L	Concentration in the feed water, mg/L	Concentration in permeate, mg/L			
			Membrane model / K (coefficient of initial volume reduction)			
			BE/3	BLN/4	90 NE/4	70 NE/5
1	Calcium	70	0.23	0.5	4.6	10.8
2	Alkalinity	366	5.4	9.5	26.5	8.5
3	Sulphates	34	0.5	1.2	2.3	5.4
4	Chlorides	56	0.6	1.2	6.0	12.1
5	Lithium	0.05	0.002	0.003	0.007	0.016
6	Fluoride	1.6	0.015	0.03	0.14	0.53
7	TDS	527	10.0	20.3	52.0	164.0
8	pH	7.5	5.7	6.0	6.7	7.0

It is not uncommon that the concentration of some monovalent ions (e.g., lithium) can exceed WHO standards by a factor of 20-24 [23, 24]. Table 2 shows the composition of groundwater in Yakutia. The lithium concentration is 0.48 milligrams per litre. It means that the lithium concentration needs to be reduced by a factor of 24 to achieve the compliance with SANPiN requirements. Table 2 also shows the results of groundwater treatment using different membranes. Fig. 1 provides values of membrane selectivity for different ions as a function of the initial value of the volume reduction factor K, based on published results [18, 19].

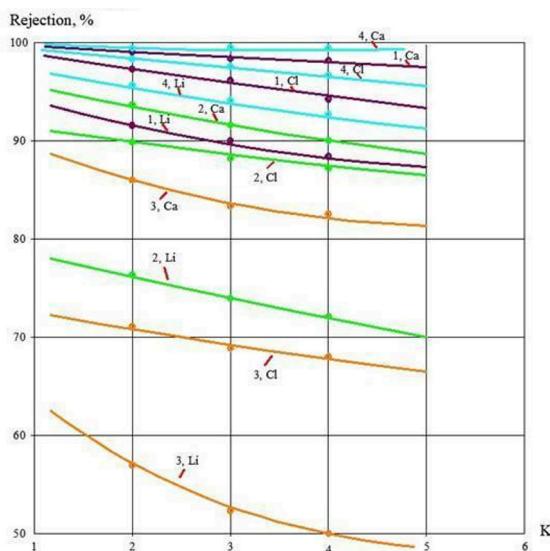
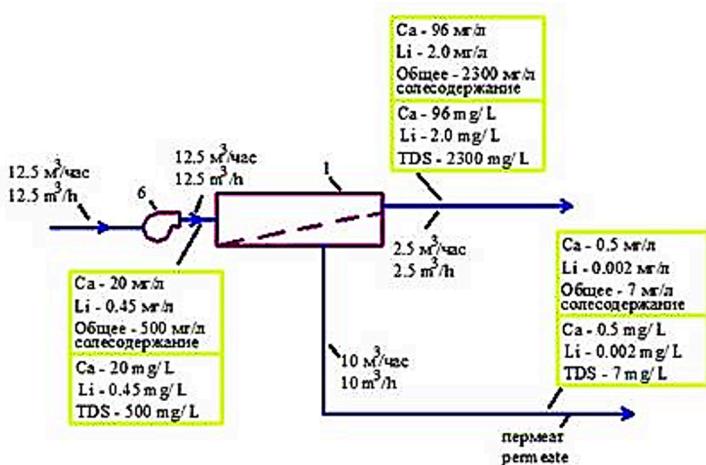


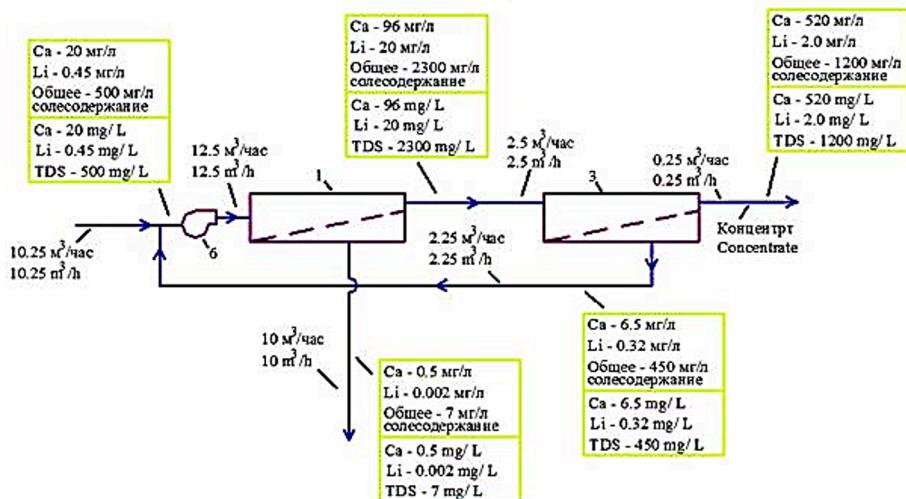
Fig. 1. Selectivity values for calcium ions, chloride ions and lithium ions in different membranes as a function of the volume reduction factor K: 1 = BLN membranes (low pressure RO membranes); 2 = 90NE membranes (nanofiltration membranes, 90% total salt selectivity); 3 = 70NE membranes (nanofiltration membranes, 70% total salt selectivity); 4 = BE membranes (medium pressure RO membranes).

3 Results

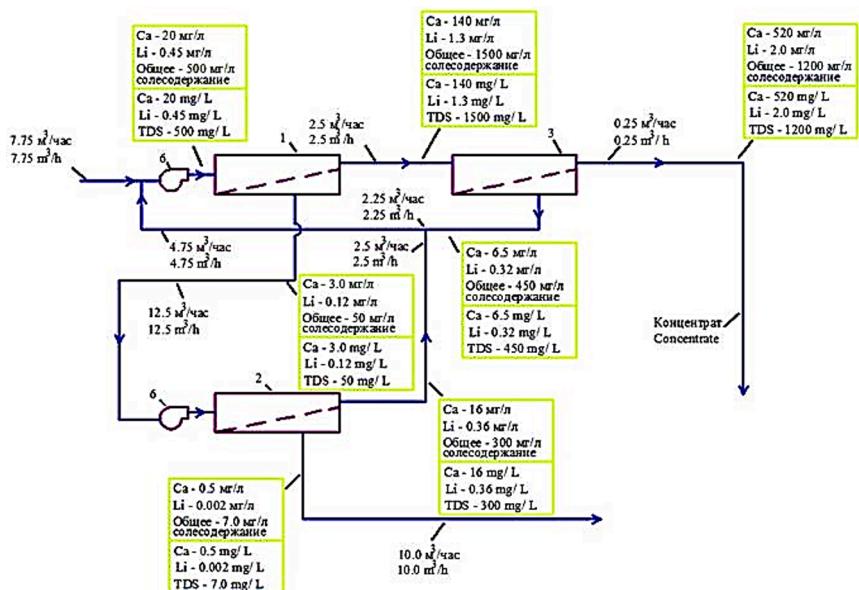
Many reverse osmosis systems are used to remove monovalent ions such as ammonium and lithium [23, 24]. Obtaining drinking water from groundwater sources in many cases requires the removal of dissolved contaminants in ionic form, mainly in the form of monovalent ions [15-17]. The methods of concentrate flow reducing in membrane plants are also based on the use of nanofiltration membranes [22-24], which are less sensitive to the formation of low-soluble salts sediments [18, 19]. Possible process flow diagrams for groundwater treatment using membranes are shown in Fig. 2. Fig. 2(a) shows the traditional approach to the groundwater treatment challenge, the process flow diagram of a membrane plant using RO membranes with high selectivity and low permeate yield. This approach results in high costs of reagents and concentrate disposal [19, 25].



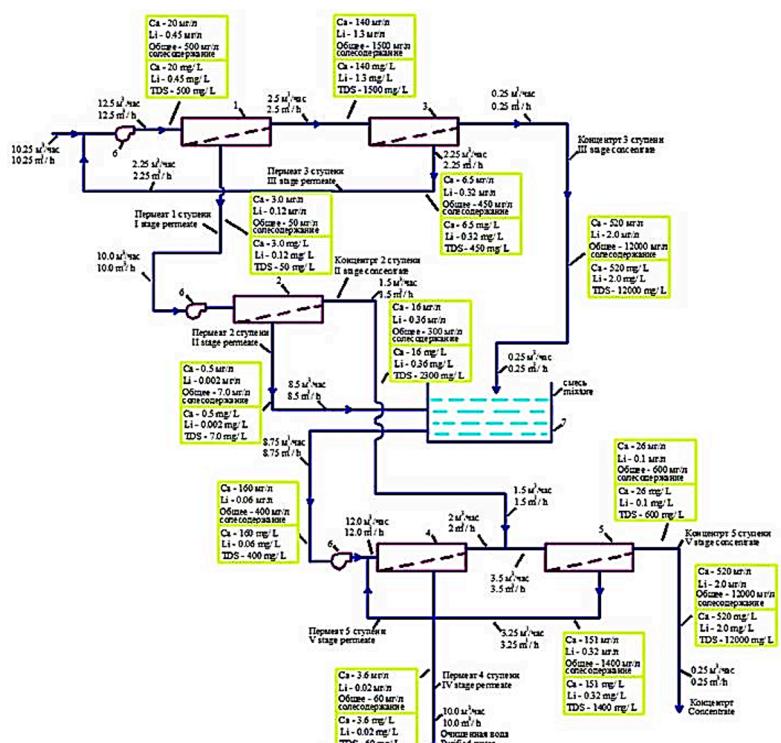
a



b



b



d

Fig. 2. The process flow diagrams for obtaining drinking water from an underground water source and basic process flow diagrams for obtaining high-quality drinking water and reducing concentrate flow: (a) a traditional approach of using RO membranes with high selectivity value; (b) application of RO

membranes for obtaining high-quality drinking water (first stage) and decrease of concentrate flow by using nanofiltration membranes (third stage); (c) obtaining high-quality drinking water by a two-stage process using nanofiltration membranes with low selectivity value (first and second stage) and decrease of concentrate flow by using nanofiltration membranes (third stage); (d) improvement of treated water quality (increase of hardness ion concentration and total dissolved salts values) using the proposed ion separation method: 1 – 1st stage membranes; 2 – 2nd stage membranes; 3 – 3rd stage membranes; 4 – 4th stage membranes; 5 – 5th stage membranes; 6 – pumps; 7 – mixing tank.

4 Discussion

A groundwater sample of 25L with high lithium content was used for the experiments. The experiment was aimed at obtaining the main specification of the process flow diagram of Fig. 2(d) and experimentation for providing ground of the effective water purification potential with simultaneous achievement of high volume reduction coefficient K. The composition of groundwater used for experimentation comprised calcium (3.5 mg-equ/L), alkalinity (6.1 mg-equ/L); lithium (0.05 mg/l); chlorides (56 mg/l); sulfates (35 mg/l); total dissolved salts (527 mg/l) and pH of 7.2.

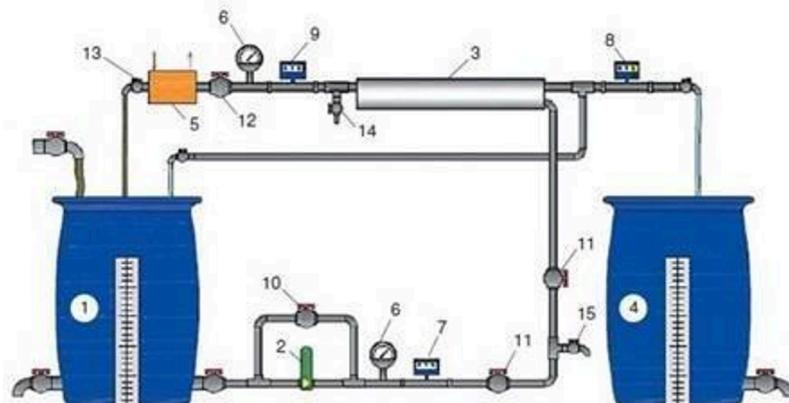


Fig. 3. Experimental laboratory unit layout diagram: 1 = source water tank; 2 = pump; 3 = membrane element in the pressure vessel; 4 = filtrate tank; 5 = heat exchanger; 6 = pressure gauge; 7-9 = flow meters; 10 = check valve; 11 = source water flow control valve; 12 = operating pressure and concentrate flow control valve; 13 = cooling water flow control valve; 14, 15 = samplers.

The scheme of the experimental unit is shown in Fig. 3. Nanofiltration membrane elements of 1812 nominal size with nanofiltration membranes of 70 NE and 90 NE grades (developed by CSM Company, Korea) purchased from Raifil Company (Moscow) were used. The experimental procedure consisted of circulating the source water through membrane apparatus 3 by pump 2 wherein the permeate was withdrawn to a separate tank 4 and the concentrate was returned back to the source water tank 1.

Application of the second stage provides lithium reduction by 27-30 times (which corresponds to the selectivity value of 96.5-96.7%). This ensures a high quality of purification similar to that achieved with BE grade RO membranes (Fig. 4). As shown in Fig. 4, mixing the second-stage permeate and the third-stage concentrate provides purified water with higher values of total dissolved salts and calcium concentration in the fourth stage than in the first-stage permeate (curves 2 and 3).

Fig. 4 shows the results of the mixture treatment using 70NE membranes. As can be seen from Fig. 4(a), the calcium concentration in the permeate increased by factor of 6 compared to that of the second stage permeate (curve 2), and the total dissolved salts value increased by factor of 5.

In this paper, a feasibility comparative study of water treatment process flows has been carried out, shown in Fig. 5 (a, b, c, d). The results of the calculations are provided in Table 5. The main performance characteristics of the considered process flows are determined using the data listed in Fig. 5.

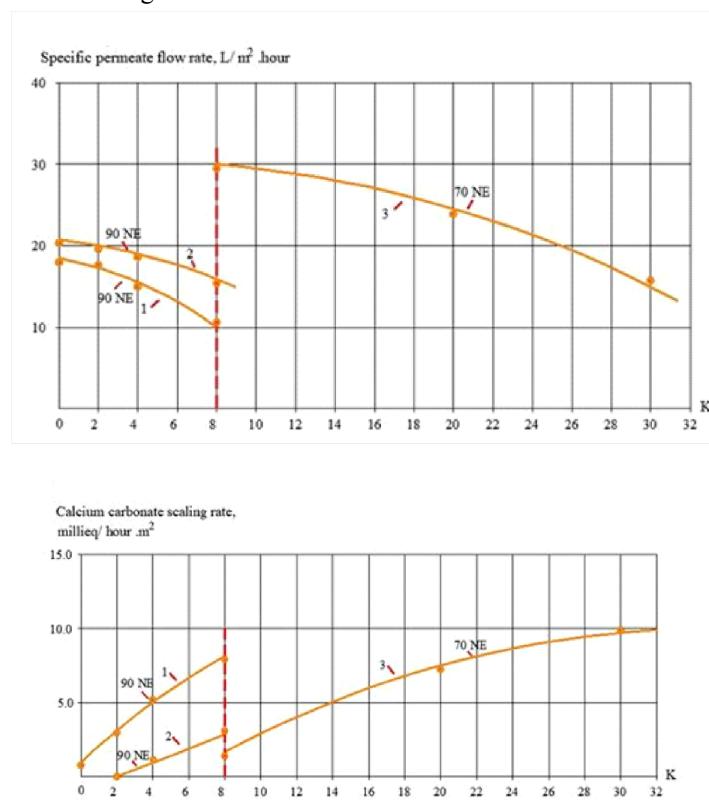


Fig. 4. The observed results of membrane operation during test runs: (a) dependencies of specific product flow on K values; (b) dependencies of calcium carbonate sedimentation rates on K at different stages of membrane units' operation.

Fig. 4 and 5 show the dependencies of Ca, Li, Cl ion concentrations in concentrate and permeate of the first and third stages as a function of K. Fig. 5 shows the concentrations of these ions in the second-stage permeate and in the fourth-stage permeate. Upon obtaining of the second-stage permeate it was mixed with the third-staged concentrate. As a result of mixing the water with the following composition was obtained: calcium concentration 76 mg/l; lithium concentration 0.08 mg/l; chloride concentration 440 mg/l. The value of total dissolved salts was 760 mg/l.

The results of treatment of the second stage permeate with the third stage concentrate mixture are provided in Fig. 5. The conductivity of the permeate and permeate flow were continuously measured during the experimentation for plotting the decrease in membrane element performance correlation with increasing salt concentration in the source water. Calcium ion concentrations were also measured in order calculate calcium carbonate sediment growth rates in the membrane elements channels during concentration the source water. The results of decreasing specific performance of the membrane and acceleration of calcium carbonate formation on the membranes with K coefficient increasing are shown in Fig. 7 (a, b). Rates of calcium carbonate deposit formation were acquired by material balance calculation as previously described in [8]. The methodology for calculating

sedimentation rates is based on determining of the derivatives of the formed calcium carbon amount as a function of time.

Fig. 5 (a) shows the decrease in membrane performance depending on the K coefficient. Fig. 16 (b) shows the results of calcium carbonate formation rates as a function of K coefficient, as well as the dependence of the brand of membranes used, composition of treated water and inhibitor application.

All diagrams provided in Fig. 5 show the balance of permeate and concentrate flow. The concentrations of different contaminants in concentrate and permeate determined during the experimental tests are described below (Fig. 4-6).

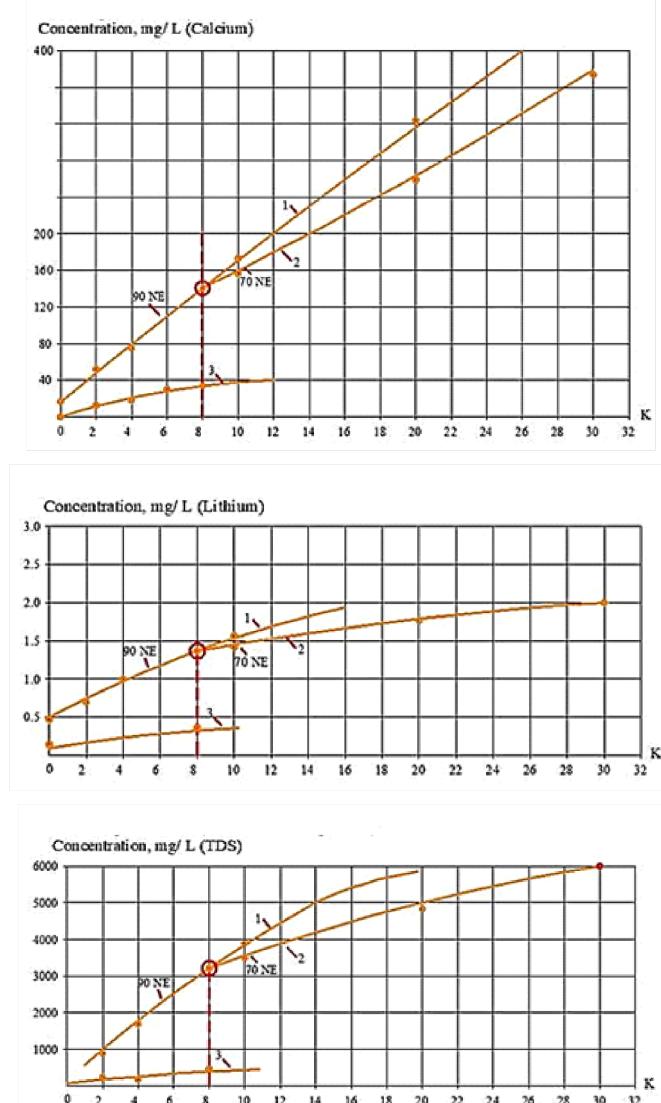


Fig. 5. Dependencies of calcium (a), lithium (b) and chloride (c) ion concentration values on K in the concentrate of 90NE and 70NE nanofiltration membranes at different stages of the process flow (Fig. 2, d): 1: 90NE membranes at the first stage (drinking water production); 2: 70NE membranes at the third stage used to reduce concentrate flow; 3: 70NE membranes at the second stage (used to improve drinking water quality and reduce lithium content).

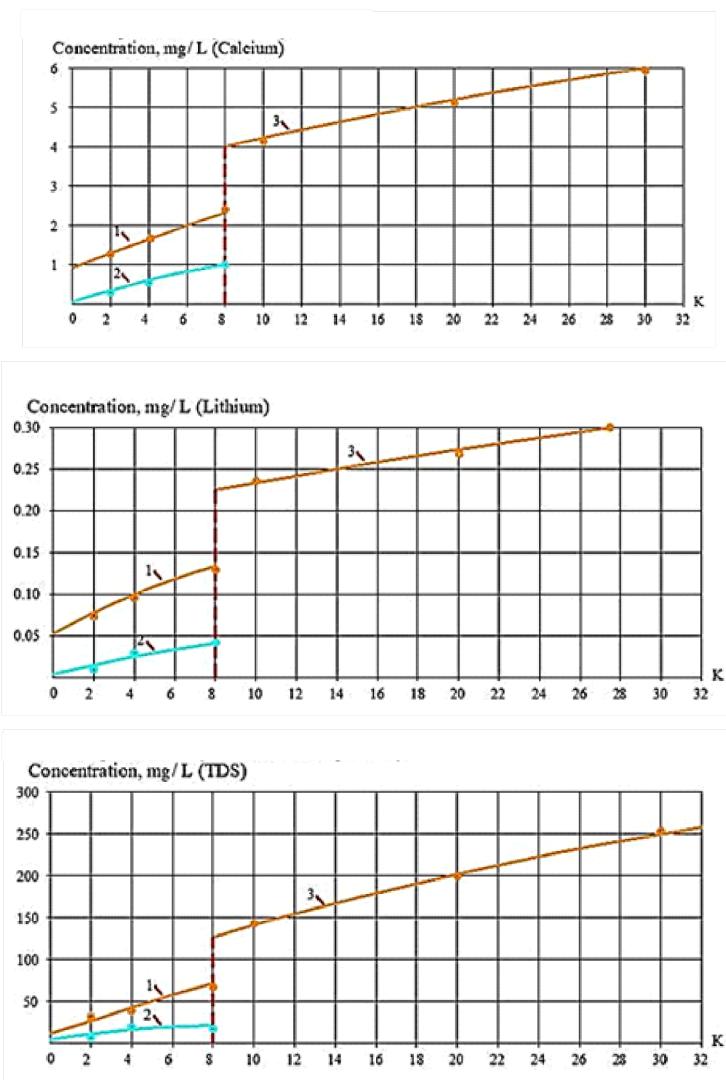


Fig. 6. The calcium (a), lithium (b) and chloride (c) ion concentration as a function of K in the permeate of 90NE and 70NE nanofiltration membranes at different stages of the water process flow (Fig. 2, d): 1: 90NE membranes at the first stage; 2: 70NE membranes at the third stage; 3: 70NE membranes at the second stage.

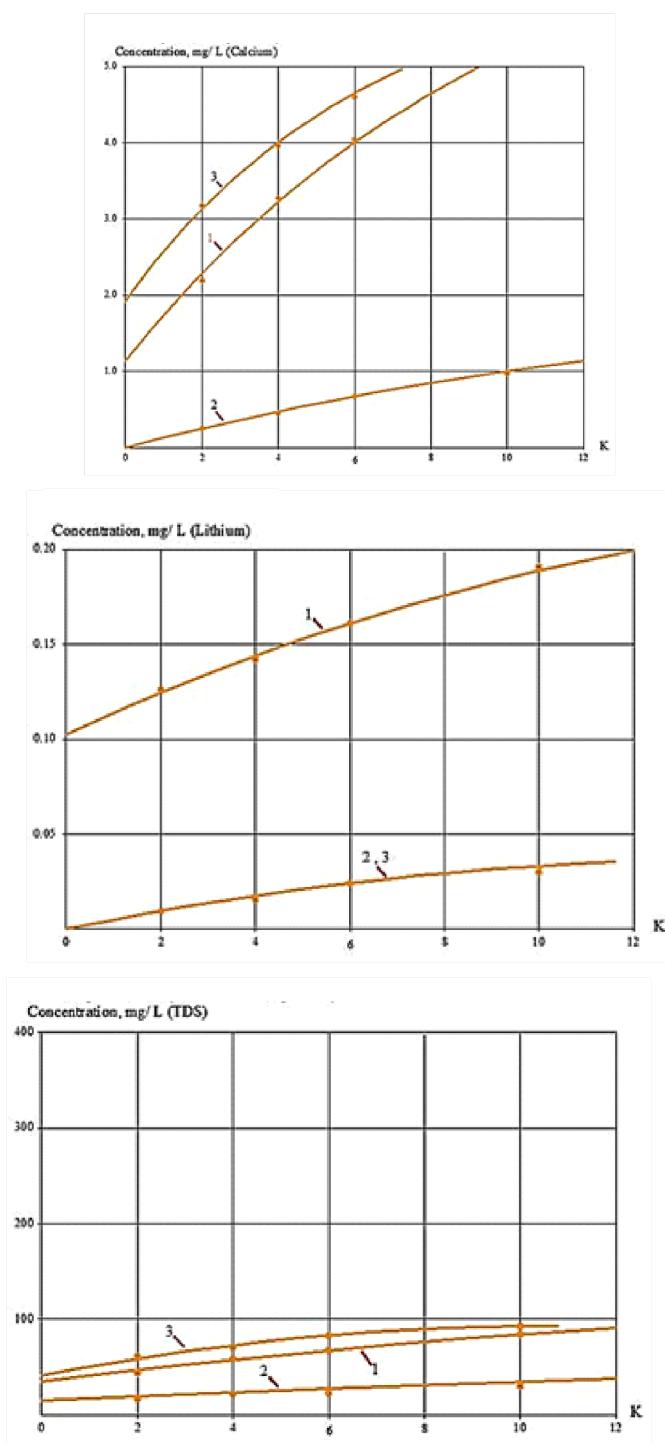


Fig. 7. The calcium (a), lithium (b) and chloride (c) ions concentration as a function of K in the permeate of 90NE and 70NE membranes at different stages of the process flow (Fig. 2,d): 1: at the first stage; 2: at the second stage; 3: at the fourth stage (after treatment of the third-stage concentrate and second-stage permeate mixture).

As several published study results show, the use of membranes with low selectivity rates reduces the intensity of calcium carbonate sedimentation [19, 25]. Nanofiltration membranes also have higher permeability (performance) at lower operating pressures [27-29]. Thus, the two-staged treatment of natural water using nanofiltration membranes provides the same quality of permeate (the same level of monovalent ions removal) as in the case of low-pressure RO membranes. Due to the high performance of nanofiltration membranes, fewer membrane elements can be used in a two-stage scheme than in a single-stage scheme. And higher resistance of nanofiltration membrane elements to the formation of crystalline deposits confirms the feasibility of the discussed approach to the development of water treatment process flow [30-34].

According to Table 3, the use of additional ion separation provides better water product quality. Significant decrease of operational costs can also be achieved through savings in electricity and reagent consumption (lime, descaling and cleaning chemicals).

Table 2. Main operational characteristics of a membrane plant with a capacity of 10 cubic meters per hour and comparison of economic and technical parameters of different approaches to the provision of high-quality drinking water.

No .	Parameters	Scheme 1 (Fig. 2, a)	Scheme 2 (Fig. 2, b)	Scheme 3 (Fig. 2, c)	Scheme 4 (Fig. 2, d)
1	The number of membrane elements 8040, membrane type / annual membrane replacement costs, pcs/rubles	18, BE /180000	20, BE, 70NE/200000	17 (70NE)/170000	23 (70NE)/230000
2	Annual antiscalant consumption/ annual antiscalant purchase costs, kg/rubles	400/400000	400/400000	80/80000	80/80000
3	Annual cleaning chemicals consumption/ annual cleaning costs, kg/rubles	120/120000	50/50000	50/50000	50/50000
4	Total pump power, kW	10	10	11	12.5
5	Total annual power consumption/ annual power consumption costs, kW × hour/rubles	70000/350000	70000/350000	77000/350000	87500/437500
6	Concentrate discharge flow rate/ total annual discharge/ annual discharge costs, (m ³ /hour)/m ³ /rubles	2.5/17500/35000 0	0.25/1750/3500 0	0.25/1750/3500 0	0.25/1750/3500 0
7	Lime consumption for product water conditioning/ annual lime consumption costs,	1.0/50000	1.0/50000	1.0/50000	---

	tons/rubles				
8	Annual operational costs, rubles	1450000	1085000	735000	832500

5 Conclusion

1. A new technology is provided using nanofiltration membranes with low selectivity. The proposed technology makes it possible to reduce concentrate flow and rate of sedimentation on the membranes of crystalline deposits, as well as to increase the concentration of hardness ions and the value of dissolved salts content of the permeate without compromising lithium-ion content in treated water.

2. The developed ion separation method demonstrated high feasibility related to the operational costs' reduction compared to the traditional approach to groundwater treatment using reverse osmosis membranes.

References

1. A.G. Pervov, Technologies of natural water treatment (ASV Publisher, Moscow, 2016)
2. A.G. Pervov, A.P. Andrianov, D.V. Spitsov, L.V. Rudakova, Water Supply Sanit. Equip. **7**, 12-19 (2009)
3. A. G. Pervov, V. I. Bondarenko, G.G. Zhabin, Energy Sav. Water Treat. **5** (2004)
4. A. G. Pervov, A. P. Andrianov, D. V. Spitsov, Energy Sav. Water Treat. **11** (2008)
5. A. G. Pervov, A. P. Andrianov, R. V. Efremov, V. A. Golovesov, Memb. Memb. Tech. **11(6)**, 202-210 (2021)
6. A. G. Pervov, V. A. Golovesov, G. Ya. Rudakova, D. V. Spitsov, MGSU Bul. **15(11)** (2020)
7. W. B. Suratt, D. R. Adrews, V. J. Pujals, S. A. Richards, Desalination **131(1-3, 20)**, 37-46 (2000). [https://doi.org/10.1016/S0011-9164\(00\)90004-3](https://doi.org/10.1016/S0011-9164(00)90004-3)
8. D. Spitsov, H.Z. Aung, A. Pervov, Membranes **13**, 85 (2023). <https://doi.org/10.3390/membranes13010085>
9. B.M. Watson, C. Hornburg, Desalination **72**, 11-22 (1989)
10. C.N. Lopes, J.C.C. Petrus, H.G. Riella, Desalination **172**, 77-83 (2005)
11. E.H.H. Al-Qadami, A. Ahsan, Z. Mustafa, A.S. Abdurrasheed, K.W. Yusof, S.M.H. Shah, J. Desal. Water Purif. **18**, 3-9 (2020). <http://abilpub.com/download/jdwp18-2/>
12. J. Tian, X. Zhao, Sh. Gao, X. Wanng, R. Zhang, Membranes **11(9)**, 662 (2021). <https://doi.org/10.3390/membranes11090662>
13. H. Guo, W. Yang, X. Li, Z. Yao, Front. Chem. Sci. Eng. **15**, 681-698 (2021)
14. S. Li, X. Wang, Y. Guo, J. Hu, S. Lin, Y. Tu, L. Chen, Y. Ni, L. Huang, J. Clean. Prod. **333**, 130171 (2022)
15. S. Jamaly, N. N. Darwish, I. Ahmed, S. W. Hasan, Desalination **354**, 30-38 (2014). <https://doi.org/10.1016/j.desal.2014.09.017>
16. P. S. Goh, W. J. Lau, M. H. D. Othman, A. F. Ismail, Desalination **425**, 130-155 (2018). <https://doi.org/10.1016/j.desal.2017.10.018>
17. S. Jiang, Y. Li, B. P. Ladewig, Sci. Total Environ. **595**, 567-583 (2017). <https://doi.org/10.1016/j.scitotenv.2017.03.235>

18. A.W. Mohammad, N. Hilal, N. Darwish, H. Al-Zoubi, J. Memb. Sci. **289**(1), 40-50 (2006). <https://doi.org/10.1016/j.memsci.2006.11.035>.
19. A.G. Pervov, Membr. Technol. **3**, 192-205 (2017)
20. W. Xu, D. Liu, L. He, Zh. Zhao, Membranes **10**(12), 371 (2020). <https://doi.org/10.3390/membranes10120371>
21. X. Li, Y. Mo, W. Qing, S. Shao, Ch. Y. Tang, J. Li, J. Memb. Sci. **591**, 117317 (2019). <https://doi.org/10.1016/j.memsci.2019.117317>
22. M. Hedayatipour, N. Jaafarzadeh, J. Environ. Manag. **203**(1), 151-156 (2017)
23. S.F. Ahmed, A. Momtahin, F. Mehejabin, N. Tasannum, Chemosphere, **306**, 135527 (2022)
24. N. Voutckov, Desalination **273**, 205-219 (2011)
25. A. Alghamdi, Energy Proc. **150**, 205-211 (2017)
26. A.G. Pervov, A.P. Andrianov, V.A. Golovesov, M.N. Danilycheva, Memb. Memb. Tech. **9**(6), 1-15 (2019)
27. I. Koyuncu, F. Yalcin, I. Ozturk, Water Sci. Technol. **40**, 241-248 (1999)
28. M.C. Collivignarelli, A. Abbà, M.C. Miino, S. Damiania, J. Environ. Manag. **236**, 727-745 (2019)
29. Y. Zheng, S. Yu, S. Shuai, Q. Zhou, Q. Cheng, M. Liu, C. Gao, Desalination **314**, 89-95 (2013)
30. N. Najid, S. Fellaou, S. Kouzbour, B. Gourich, A. Ruiz-Garcia, Process Saf. Environ. Prot. **156**, 373-390 (2021)
31. S. Jafarinejad, M.R. Esfahani, Separations **8**, 206 (2021)
32. M. Turek, K. Mitko, P. Dydo, E. Laskovska, A. Jakobic-Kolon, Desalination **401**, 180-189 (2017). <https://doi.org/10.1016/j.desal.2016.07.047>
33. S. Bunani, G.E.Y. Sert, Ü. Yüksel, N.M.Y. Kabay, Desalination **315**, 33-36 (2013)
34. M. Talaeeipour, J. Nouri, A.H. Hassani, A.H. Mahvi, J. Envir. Health Sci. Eng. **15**, 18 (2017). <https://doi.org/10.118/s402010170279>