Prediction of rejection properties and performance of nanofiltration membranes based on scaling prognosis in drinking water treatment

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Abstract. Reverse osmosis (RO) and nanofiltration (NF) are widespread for drinking water production from underground water sources; these techniques are used to reduce hardness, iron, fluoride, ammonium, strontium, nitrate, pesticides etc. At the same time, with high efficiency of removing iron, hardness, fluoride, ammonium from source water, nanofiltration membranes are much less exposed to the risk of calcium carbonate precipitation than the traditionally used low-pressure RO membranes. Usually it is important to predict the rejection properties of membranes not only at the launch time of RO/NF unit, but during all operation period and gradual membrane fouling/scaling. The article presents experimental data on determining membrane selectivity (nanofiltration membrane OPMN-K, Russia) for iron, fluoride and ammonium depending on the TDS, water hardness and the amount of calcium carbonate precipitate in the membrane module. Operational guidance has been developed that allow to determine the costs of chemicals for the operation of NF installations depending on the source water quality and membrane type. The above calculations show that the use of nanofiltration membranes instead of reverse osmosis can significantly reduce the cost of operating groundwater treatment facilities.

1. Introduction
Reverse osmosis and nanofiltration membranes are widely used to obtain drinking-quality water from groundwater with low mineralization. These membranes effectively remove hardness and iron from natural water, as well as fluorides, ammonium, strontium, nitrates, and other trace elements [1-9]. Reverse osmosis and nanofiltration are actually the only commercially available method for defluoridation [3, 5, 6]. Nanofiltration is also a common method for removal of arsenic and pesticides from drinking water [2, 10, 11, 12, 13]. Nanofiltration also has certain advantages for surface water treatment: reduction of disinfection by-products precursors [14], removal of micropollutants [15] and eventually NOM removal [16, 17]. Research conducted by Pervov [18, 19] towards the modernization of conventional spiral wound module allows us to expand the scope of reverse osmosis and nanofiltration, solving basic issues such as pretreatment and concentrate disposal, and making the method commercially more attractive for municipal applications [1, 9].

Membranes reject various ions differently depending on their nature, charge, and valence [3, 4, 7, 8, 12, 13, 20, 21], therefore, computer programs based on experimental data are used to predict filtrate composition [22]. When selecting membranes with various types and selectivity it is important to take into account the fact that these membranes not only reject ions differently, but they are also subject to different degrees of precipitation of slightly soluble salts. As a result, the period when contaminants
begin to pass into the filtrate and the operating time of the membrane facilities before chemical cleaning also differ. For example, reverse osmosis membranes provide high efficiency in reducing the concentration of fluoride ions, ammonium ions, and iron (by 90% or higher). However, due to the intensive formation of calcium carbonate scale on the membranes, selectivity for these ions can quickly fall down [23]. Nanofiltration membranes are poorly reject monovalent ions, but are less susceptible to scaling, providing a longer period of operation with more stable quality of treated water.

The authors set the objective of obtaining data allowing predicting the selectivity of nanofiltration membranes for a number of components: the main ions (Ca\(^{2+}\), Mg\(^{2+}\), Na\(^{+}\), Cl\(^{-}\), SO\(_4^{2-}\), HCO\(_3^{-}\)), and iron (II) and fluoride, which are often found in underground waters and are hazardous from a hygienic point of view. The aim of the experiments is to predict changes in purified water quality not only for new membranes, but also over time during the operation of membrane facilities [22, 24]. The multionic composition will significantly affect the selectivity of nanofiltration membranes [20], which is taken into account in computer programs, and the rate of sedimentation, but in some cases, to assess the change in membrane selectivity over time, it is sufficient to take into account only the total hardness of water and the total salinity; this was done in the described research.

2. Materials and methods

The study of the rejection properties of nanofiltration membranes was carried out on a laboratory unit, shown in Fig. 1. The experiments used 1812 spiral wound elements with nanofiltration composite membranes type OPMN-K based on polyvinyl alcohol provided by Vladipor Co, Russia and low-pressure reverse osmosis membranes type ESPA. The membrane had the following characteristics: salt rejection – 25% for 0.15% NaCl solution and 95% for 0.2% MgSO\(_4\) solution, maximum feed flow – 100 l/h·m\(^2\). The experiments were performed in a circulation mode with gradual concentration of feed solution. The feed water was placed in a tank 1, from where the pump 2 was fed to the nanofiltration membrane module 3. The filtrate was collected in tank 4, and the concentrate was returned to feed water tank 1. The operating pressure was set by a valve 6.

![Figure 1. Flow diagram of a laboratory membrane unit:](image)

1 – feed water tank; 2 – pump; 3 – spiral wound membrane module; 4 – filtrate collection tank; 5 – pressure gauge; 6 – pressure control valve; 7 – heat exchanger

During the experiments, samples of purified water and concentrate are taken. The basic ionic composition (Na\(^{+}\), Ca\(^{2+}\), Mg\(^{2+}\), SO\(_4^{2-}\), HCO\(_3^{-}\), Cl\(^{-}\)) and the microelements required in specific experiments (F\(^{-}\), Fe\(^{2+}\) and NH\(_4^{+}\)) were determined in the water.

Depending on the amount of water in the tank 4 the recovery (concentration factor) is calculated. The maximum value of the concentration factor was set to 3. The higher the recovery, the higher the salt concentration in the filtrate, and at a certain value, the excess of the standard values for drinking
water begins. This method simulates the operation of a nanofiltration membrane unit and allows us to
determine the parameters of purified water depending on the specified recovery value.
Membrane selectivity for $F^-$, $Fe^{2+}$ and $NH_4^+$ ions was determined in a wide range of concentrations
of $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$, $HCO_3^-$ and $Cl^-$ ions. Experiments were performed on the Moscow tap water
with the addition of solutions of $FeSO_4$ and $NaF$, the concentration of $F^-$, $Fe^{2+}$ and $NH_4^+$ ions was 2
and 5 mg/l. For simulation of groundwater composition the salt solutions of $NaCl$, $CaCl_2$, $MgSO_4$,
$Na_2SO_4$, $NaHCO_3$ with a concentration of 5 and 10 mEq/L was added in the tap water.

3. Results
Figures 2 and 3 show the dependences of the concentrations of $F^-$ and $Fe^{2+}$ ions in the filtrate on the
concentration factor. When a scale forms on the surface of the membranes, concentration polarization
develops, due to which the concentration of ions near the membrane surface increases. The
development of this process leads to a deterioration in the quality of the filtrate [23].

Figure 4 shows the dependences of the concentration of various ions on the concentration factor at
different stages of the formation of a precipitate in a spiral wound membrane element (with a precipitate amount of 3000, 4800, and 6000 mEq/L).
The data obtained make it possible to predict a change in the filtrate composition over time
depending on the composition of the feed water and the selected recovery (concentration factor).
To predict changes in the rejection properties of nanofiltration membranes, it is necessary to use
experimentally obtained data to determine the growth rate of calcium carbonate scale in membrane
element depending on the source water composition. A series of experiments was carried out on a
laboratory unit at various hardness, alkalinity and TDS values [25, 26]. The obtained relationships
of scaling rate on the concentration factor are valid for the feed water of any composition with a hardness
of 1 to 30 mEq/L and a TDS value of 100-1000 mg/L. To determine the dependence of the scaling rate
on the concentration factor of a source water with given composition, the interpolation method is used,
according to which the desired curve is lies between the experimentally obtained curves for given
values of $Ca^{2+}$, $HCO_3^-$ and other ions [25, 26].

![Figure 2](image_url)

**Figure 2.** Dependence of fluoride concentration in the filtrate of nanofiltration element on the
concentration factor; a) initial fluoride concentration 2 mg/L; b) initial fluoride concentration 5 mg/L;
1 – $NaCl$; 2 – $MgCl_2$; 3 – $Na_2SO_4$; 4 – tap water
Figure 3. The dependence of iron concentration in the filtrate of nanofiltration element on the concentration factor: a) at the beginning of the work (the concentration of Fe$^{2+}$ in the feed water is 2 mg/L); b) after 300 hours (the concentration of Fe$^{2+}$ in the feed water is 5 mg/L); 1 – NaCl; 2 – MgCl$_2$; 3 – Na$_2$SO$_4$; 4 – tap water.

Figure 4. An example of predicting an increase in the concentration of F$^-$ ions in the filtrate of nanofiltration element: a) depending on the scale amount; b) over time; concentration factor: 1 – 3; 2 – 2; 3 – 1.5

The methodology for predicting changes in membrane selectivity during its operation includes the following steps:
- for each composition of the source water, it is necessary to determine scaling rate (to obtain the dependence of scaling rate on concentration factor);
- for specified operating conditions (at selected values of the concentration factor and the corresponding scaling rate) obtain the dependence of scale amount on the operating time;
- to build the dependence of the content of various ions in filtrate on the amount of accumulated scale at different values of the concentration factor;
- the change in the concentration of various ions in the filtrate can be represented as a function of the operating time, since each value of scale amount corresponds to a certain operating time of membrane facility.

An example of forecasting based on experimental data is presented in Figure 5.

4. Discussion

Based on this research, the operating conditions were generalized and calculated depending on the composition of the source water and the type of membranes used.

To determine the optimal operating mode, it is necessary to identify the composition of the source water in accordance with Table 1. Alphanumeric indices are determined based on the concentrations of calcium and bicarbonate ions, pH and total salinity. The optimal operating mode is determined according to Table 2 for obtained from the Table 1 index values. The intervals between chemical
cleanings were calculated taking into account the values of the scale growth rate for concentration factors of 1.7 and 2.5 (respectively for recovery of 40 and 60%).

Figure 5. Forecast of an increase in the concentration of various ions in the filtrate during the operation of membrane facility (using the OPMN and ESPA membranes)
Table 1. Identification of the source water composition

| pH     | TDS, mg/L | Total alkalinity, mEq/L | Total hardness, mEq/L |
|--------|-----------|-------------------------|-----------------------|
|        |           | 4–6                     | 6–8       | 8–10 | 6–8 | 8–10 |
| 7.2–7.7| 500–800   | A1                      | B1        | C1   | D1  | E1  |
|        | 800–1200  | A2                      | B2        | C2   | D2  | E2  |
|        | 1200–1800 | A3                      | B3        | C3   | D3  | E3  |
|        | 500–800   | A4                      | B4        | C4   | D4  | E4  |
| 7.8–8.4| 800–1200  | A5                      | B5        | C5   | D5  | E5  |
|        | 1200–1800 | A6                      | B6        | C6   | D6  | E6  |

Table 2. Chemical cleaning schedule recommendations (K – concentration factor, α – recovery)

| Source water index | Recommended interval between chemical cleanings |
|-------------------|-------------------------------------------------|
|                   | ESPA membranes | OPMN membranes |
|                   | K = 1.7 (α = 0.4) | K = 2.5 (α = 0.6) |
|                   | K = 1.7 (α = 0.4) | K = 2.5 (α = 0.6) |
| A1                | 600 400         | 1000* 750       |
| A2                | 1000 800        | 1500* 1000      |
| A3                | 1500 1200       | 2000* 1200*     |
| A4                | 500 –           | 900 500         |
| A5                | 700 –           | 1200 800        |
| A6                | 1000 300        | 1500 1000       |
| B1                | 500 400         | 500* 600        |
| B2                | 800 500         | 800* 800        |
| B3                | 1200 1500       | 1200* 1200      |
| B4                | 250 –           | 400 250         |
| B5                | 400 250         | 800 400         |
| B6                | 800 500         | 1200 800        |
| C1                | 400 –           | -- 400          |
| C2                | 900 400         | 800* 900        |
| C3                | 1200 800        | 1100* 1200      |
| C4                | 300 –           | 400 300         |
| C5                | 700 –           | 800 700         |
| C6                | 100 –           | 1400 1200       |
| D1                | 500 –           | 500* 500        |
| D2                | 800 250         | 1800* 800       |
| D3                | 1200 400        | 1200* 1200      |
| D4                | 300 –           | 500* --         |
| D5                | 400 –           | 600* 500        |
| D6                | 700 250         | 900* 800        |
| E1                | 300 –           | 500 300         |
| E2                | 500 –           | 750 500         |
| E3                | 700 –           | 1000 700        |
| E4                | – –             | 300 –           |
| E5                | 300 –           | 500 350         |
| E6                | 400 –           | 800 400         |

The cases when dosing of the antiscalant is not required are marked with * (in all other cases 10 mg/L of AMINAT-K antiscalant is used)
These calculations were made for membrane facilities with OPMN-K membranes using the “Aminat-K” inhibitor (the mixture of methyliminobis-methylene phosphonic and nitrilotrimethyl phosphonic acids) dosing (dose 1 mg/L) and for specified cases – without inhibitor dosing.

The procedure for calculating the technological performance of membrane facility:
1. Identification of the composition of water according to Table 1.
2. The membrane type selection according to Table 2, determination of the concentration of Ca²⁺, Fe²⁺, F⁻ ions at the start time of membrane facility operation.
3. The selection and creation the dependency for predicting the concentrations of various ions in the filtrate as a function of time.
4. Determination of annual chemical consumption based recommended interval between chemical cleanings and specific consumption for one 8040 membrane element.

These recommendations allow us to compare the performance of nanofiltration (OPMN-K) and low-pressure reverse osmosis (ESPA) membranes for drinking water treatment from various underground sources. Depending on the hardness, alkalinity, pH and TDS of the source water, as well as the recovery according to the Table 2, you can determine: the composition of purified water and its change over time, the consumption of antiscalant and reagents for chemical leaching. As can be seen from the Tables 1 and 2, for most groundwater sources, the use of OPMN-K membranes (as compared to ESPA reverse osmosis membranes) provides significant savings in the cost of service chemicals and production of drinking water of stable high quality.

The calculation results show that the use of nanofiltration membranes for water purification of certain composition is preferable due to lower operating costs (absence of antiscalant dosing, longer period between chemical cleanings). When determining the economic effect of nanofiltration membranes application, the results of calculating operating costs and choosing their optimal value were used.

**Table 3. Economic comparison of different groundwater treatment methods**

| Costs                          | Ion exchange – deferrization | NF (OPMN-K) | RO (ESPA) |
|-------------------------------|-----------------------------|-------------|-----------|
| Capital costs, EUR:           |                             |             |           |
| ion-exchange deferrization (BIRM) | 17,500                 | 34,000      | 32,500    |
| RO / NF unit                  | 14,000                      |             |           |
| Σ                              | 31,500                      | 34,000      | 32,500    |
| Operating costs:              |                             |             |           |
| Electricity, kWh/year (EUR/year): | 36,000 (1,800)              | 66,000 (3,300) | 66,000 (3,300) |
| Chemicals, kg/year (EUR/year): 90,000 (10,000) | 300 (1,500)         | 1000 (5,000) | 156 (1,560) |
| salt NaCl                     |                             |             |           |
| antiscalant (Aminat-K)        |                             |             |           |
| cleaning solutions             |                             |             |           |
| Materials and filter media, EUR/year: | 1,150                  | 2,100       | 2,000     |
| resin replacement              | 625                         |             |           |
| BIRM filter bed replacement    |                             |             |           |
| membrane replacement           |                             |             |           |
| Σ                              | 13,575                      | 6,900       | 11,860    |
| Reduced costs = Capital costs x 0.16 + Operating costs | 18,615                  | 12,340      | 17,060    |

The calculations of the capital and operating costs and the value of the economic effect for the selected method of water treatment and the type of membranes are presented in Table 3. The
calculations were carried out for a groundwater treatment facility (reducing hardness, iron and fluoride in the drinking water) with a capacity of 25 m$^3$ per hour. Feed water composition is: Ca $\approx$ 7.1 mEq/L; HCO$_3$ $\approx$ 6.2 mEq/L; Mg $\approx$ 2 mEq/L; Cl $\approx$ 4.3 mEq/L; Na $\approx$ 3.5 mEq/L; SO$_4$ $\approx$ 2.1 mEq/L; Fe $\approx$ 0.9 mEq/L. Compared water treatment methods are; deferrization (aeration and filtration) and sodium cation exchange; reverse osmosis with ESPA membranes and nanofiltration with OPMN-K membranes (recovery is 75 %). Calculations of the costs of the service chemicals were performed based on data from Tables 1 and 2.

5. Conclusions
The rejection properties of nanofiltration membranes (OPMN-K type) for iron (II) and fluorides and their changes depending on the formation of calcium carbonate and others scales were obtained. Recommendations for selecting operating conditions and service procedures for membrane facilities for groundwater of various qualities (pH, hardness, alkalinity, total salinity, recovery) were developed.

The use of nanofiltration membranes in drinking water treatment systems can significantly reduce the cost of operating membrane installations by extending their operation time before chemical washings, as well as reducing the cost of sedimentation inhibitors and detergents.

References
[1] Yu Dan Su, Pervov A G and Golovesov V A 2018 Vestnik MGSU 13 8 (119) 992-1007.
[2] Van der Bruggen B, Everaert K, Wilms D and Vandecasteele C 2001 J. of Membr. Sci. 193 (2) 239-248.
[3] Ben Nasr A, Charcosset C, Ben Amar R and Walha K 2013 J. of Fluorine Chem. 150 92-97.
[4] Košutić K, Novak I, Sipos L and Kunst B 2004 Separ. and Purif. Technol. 37 (3) 177-185.
[5] Elazhar F, Tahaikt M, Achatéi A, Elmidaoui F, Taky M, El Hannouni F, Laaziz I, Jariri S, El Amrani M and Elmidaoui A 2009 Desalination 249 (1) 154-157.
[6] Tahaikt M, El Habbani R, Ait Haddou A, Achary I, Amrani M and Elmidaoui A 2007 Desalination 212 (1-3) 46-53.
[7] Owusu-Agyeman I, Reinwald M, Jeihanipour A and Schäfer A I 2019 Chemosphere 217 47-58.
[8] Reig M, Licon E, Gibert O, Yaroshchuk A And Cortina J L 2016 Chem. Eng. J. 303 401-408.
[9] Pervov A. and Efremov R. 2018 IOP Conf. Series: Materials Sci. and Eng. 365 062025.
[10] Košutić K., Furač L., Sipos L., Kunst B. 2005 Separ. and Purif. Technol. 42 (2) 137-144.
[11] Van der Bruggen B, Schaep J, Maes W, Wilms D and Vandecasteele C. 1998 Desalination 117 (1-3) 139-147.
[12] Yu Y, Zhao C, Wang Y, Fan W abd Luan Z 2013 J. of Environ. Sci. 25 (2) 302-307.
[13] Saitúa H, Campderrós M, Cerutti S and Padilla A P 2005 Desalination 172 (2) 173-180.
[14] Lin Y-L, Chiang P-C, Chang E-E 2006 J. of Hazardous Mater. 137 (1) 324-331.
[15] Cuhorka J, Wallace E and Mikulášek P 2020 Sci. of The Total Environ. 720 137474.
[16] Orečkí A, Tomaszchuk M, Karakuški L and Morawski A W 2004 Desalination 162 47-54.
[17] Pervov A G, Kozlova Y V , Andrianov A P and Motovilova N B 2006 Membranes 1 20.
[18] Pervov A G 2015 Desal. and Water Treat. 55 (9) 2326-39.
[19] Pervov A. 2016 MATEC Web of Conf. 86 03006.
[20] Wang X-L, Shang W-J, Wang D-X, Wu L and Tu C-H 2009 Desalination 236 (1-3) 316-326.
[21] Wang D-X, Su M, Yu Z-Y, Wang X-L, Ando M and Shintani T 2005 Desalination 175 (2) 219-225.
[22] Pervov A G, Andrianov A P, Kondratyev V V and Spitsov D V 2008 Kriticheskie tehnologii. Membrany 1(37) 9-18.
[23] Pervov A G, Makarov R I, Andrianov A P and Efremov R V 2002 Water supply and Sanitation Technique 10 26-29.
[24] Pervov A G 1991 Desalination 83 77-118.
[25] Pervov A G, Efremov R V, Andrianov A P and Makarov R I 2004 Membrany 3(23) 3-13.
[26] Pervov A G, Rudakova G Y and Efremov R V 2009 Water supply and Sanitation Technique 7 21-28.