Improvement of drinking water quality and reduction of concentrate discharges using nanofiltration membranes

Htet Zaw Aung, Dmitry Spitsov, and Alexei Pervov

Moscow State University of Civil Engineering, 26, Yaroslavskoe shosse, Moscow, 129337, Russia

Abstract. Reverse Osmosis method is efficiently and widely used in drinking water production. Treatment of ground water faces three main problems: scaling of membranes, concentrate handling and permeate ionic composition. A number of ionic pollutants (such as lithium, ammonia and boron) are poorly rejected by reverse osmosis membranes as compared to calcium and chloride ions. Thus, in cases when high lithium or ammonia concentrations are present in ground water, high rejection reverse osmosis membranes are usually used that provides a product water with low TDS and hardness values. Present article demonstrates results of research aimed at development of a new approach to change a ratio of monovalent and divalent ions in product water. An example of high boron water is discussed. A developed technique of ion separation is applied and experimental results are demonstrated, thus providing low boron concentration in product with increased TDS and calcium by 5 times as compared to the initial use of RO membranes. A flow diagram of the developed process is demonstrated based on experimentally obtained results.

Keywords: reverse osmosis; nanofiltration; membrane rejection; reduction of concentrate discharges; evaluation of scaling rates.

1 Introduction

Reverse osmosis today is widely used to produce a quality drinking water from ground [1, 2] and surface water sources [3,4]. New Moscow region (Expanded Moscow territory) efficiently uses Reverse Osmosis plants to improve water quality. A number of ground water intakes in New Moscow region contain, above conventionally meet calcium and iron, an excessive amounts of fluoride, ammonia, lithium, strontium and even boron that exceed WHO regulation values. To remove these species, reverse osmosis facilities are used [5-7]. Despite the high efficiency of reverse osmosis to remove dissolved ionic pollutants, it’s direct application for different ground water compositions seem unsuccessful. One of the main reasons is that reverse osmosis membranes provide high rejection of both monovalent ions (such as chloride, bicarbonate and fluoride) and divalent (such as sulphate, calcium,
strontium). In majority of cases we face the situation when concentrations of ammonia or lithium in ground water exceed regulation values only by 20-30 per cent. In these cases usually reverse osmosis is used to reduce all ingredients and total TDS by 95-96 per cent. After that product water is mixed with the feed (source) water. The part (mixing ratio) depends on the value, by which pollutant concentration exceeds regulation value [5, 7, 8]. This approach can be reasonable only on a condition when pollutant concentration exceeds regulation values no more than by 3-4 times. When the ratio value is higher, there is no reason of mixing as all water amount should pass through membranes. The use of reverse osmosis has certain disadvantages. First: we remove hardness by 95-97 per cent and in a number of cases should provide water conditioning by addition of calcium ions. Second: treatment of groundwater with high hardness limits the recovery value as calcium salts are formed in membrane channels [9-11]. In drinking water applications the recovery value has a significant influence on the product water price as the amount of concentrate discharged in the sewer increases total costs of water produced by membrane facility. Third: the use of reverse osmosis membranes has a hazard of scaling and their operation requires certain operational costs [14,15].

It was already mentioned that nanofiltration membranes provide efficient removal of monovalent pollutants [5- 8,], especially for the cases when concentrations of these pollutants should be reduced by three times and less [ 9-11]. Application of nanofiltration membranes not only provides efficient removal of monovalent pollutants but also reduction of operational costs as well. Moreover, additional use of nanofiltration stage can easily increase the recovery that significantly reduce total costs of supplied product water [1, 2, 6, 7]. Table 1 shows a typical ground water composition and results of its treatment with different types of membranes [1, 2].

Table 1. Results of well water treatment with different membranes.

<table>
<thead>
<tr>
<th>No.</th>
<th>Characteristics</th>
<th>Concentration in Feed Well Water, ppm</th>
<th>Concentration values in permeate</th>
<th>Membrane type / K value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>BE/3</td>
<td>BLN/4</td>
</tr>
<tr>
<td>1</td>
<td>Ca$^{2+}$</td>
<td>70</td>
<td>0.23</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>HCO$_3^-$</td>
<td>366</td>
<td>5.4</td>
<td>9.5</td>
</tr>
<tr>
<td>3</td>
<td>SO$_4^{2-}$</td>
<td>34</td>
<td>0.5</td>
<td>1.2</td>
</tr>
<tr>
<td>4</td>
<td>Cl$^-$</td>
<td>56</td>
<td>0.6</td>
<td>1.2</td>
</tr>
<tr>
<td>5</td>
<td>Li$^+$</td>
<td>0.05</td>
<td>0.002</td>
<td>0.003</td>
</tr>
<tr>
<td>6</td>
<td>F$^-$</td>
<td>1.6</td>
<td>0.015</td>
<td>0.03</td>
</tr>
<tr>
<td>7</td>
<td>TDS</td>
<td>527</td>
<td>10.0</td>
<td>20.3</td>
</tr>
<tr>
<td>8</td>
<td>pH</td>
<td>7.5</td>
<td>5.7</td>
<td>6.0</td>
</tr>
</tbody>
</table>
There are a lot of cases where certain monovalent pollutant (like lithium) concentration can exceed WHO regulation values by 20-24 times [12,13]. Table 1 shows ground water composition in Yakutia. The lithium concentration is 0.48 milligrams per liter. This means that lithium concentration should be reduced by 24 times to reach drinking water standards. Table 1 shows results of treatment of ground water using different membranes. Rejection values of different ions depending on initial volume reduction coefficient K value, basing on the already published results [14,15] are presented on Figure 1.

Table 1 shows results of treatment of ground water using different membranes. Rejection values of different ions depending on initial volume reduction coefficient K value, basing on the already published results [14,15] are presented on Figure 1.

<table>
<thead>
<tr>
<th>Rejection, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
</tr>
<tr>
<td>90</td>
</tr>
<tr>
<td>80</td>
</tr>
<tr>
<td>70</td>
</tr>
<tr>
<td>60</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>40</td>
</tr>
<tr>
<td>30</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>0</td>
</tr>
</tbody>
</table>

Figure 1. Dependencies of rejection values of calcium, chloride and lithium ions by different membranes on the initial volume reduction coefficient K value: 1 - BLN membranes (low pressure reverse osmosis membranes); 2 - 90NE membranes (nanofiltration membranes, total salt rejection is 90%); 3 - 70 NE membranes (nanofiltration membranes, total salt rejection is 70%); 4 - BE membranes (medium pressure reverse osmosis membranes).

As it can be seen, even application of low pressure BLN membranes does not guarantee efficient removal of lithium at pressure of 10-12 Bars and recovery of 70%. High efficiency can be reached using BE high rejection medium pressure membranes. Meanwhile, calcium concentration of product water is less than 0.05 mg/l and TDS is about 5 ppm. These results are questionable as BE membranes require high pressure and therefore power costs, and membrane product flux is significantly lower than of BLN membranes. Additionally we should mention high scaling rates and low recovery.

A lot of applications with RO are used to reject monovalent pollutants, such as ammonia and lithium [12,13]. Drinking water production also requires reduction of monovalent ions in many cases [9-11]. Moreover, membranes are selected only owing to their ability to reject monovalent ions. As a result, when we reduce monovalent ions we produce deionized water which as not applicable for drinking. This article proposes a new approach to provide drinking water quality using the developed ion separation techniques based on different rejection of ions. This new technique is used together with developed
concentrate reduction techniques. Principles of concentrate reduction are based on application of nanofiltration membranes [16-18] that are less susceptible to scaling [14,15]. Figure 2(a) shows a typical solution for ground water treatment: using high rejection membranes with low value of recovery. This approach requires costs for chemicals and concentrate disposal [15,19].
**Figure 2.** Flow diagrams to produce drinking water from the groundwater intake and techniques to reduce concentrate flow rate: a) conventional approach using reverse osmosis membrane with high rejection; b) application of reverse osmosis membranes to produce quality drinking water (on the first stage) and reduce concentrate flow using nanofiltration membrane (on the second stage); c) production of quality drinking water using a double stage low selection membranes (first and second stages) and reduction of concentrate flow using nanofiltration membrane (on the third stage); d) improvement of the product water quality (increase of hardness and TDS) using a developed ion separation techniques: 1 – membranes of the 1st stage; 2 – membranes of the 2nd stage; 3 – membranes of the 3rd stage; 4 – membranes of the 4th stage; 5 – membranes of the 5th stage; 6 – pumps; 7 – mixing tank.

All drawings presented on Figure 2 contain flow diagrams with flow and concentration values determined throughout experiment test runs described below. To improve the situation, a reduction of concentrate can be applied. Figure 2(b) demonstrates concentrate reduction technique using low rejection nanofiltration membrane on the second stage. The second stage permeate is forwarded to the inlet of the first stage. This approach enables us to reduce concentrate flow by 5-10 times. This flow diagram provides a solution of concentrate disposal problem. But scaling problem and high operational costs to escape it are still not solved. Figure 2(c) demonstrates the solution of drinking water quality using low pressure and low rejection nanofiltration membranes. It was already discussed that application of low rejection membranes reduces calcium carbonate scaling [15, 19]. Nanofiltration membranes also provide higher flux at a lower pressure values [21-23]. Thus, the use of the double stage of nanofiltration membranes provides the same quality of product water. Due to high product flow rate, the double stage scheme can use smaller amount of membrane modules, than the single stage scheme. And lower scaling propensities of nanofiltration membranes make this approach economically reasonable [20, 24-26]. Concentrate flow reduction in this scheme is implemented, using the additional nanofiltration stage to treat first stage concentrate. The second stage concentrate is forwarded at the entrance to the first stage. The only concern is low hardness and low TDS of product water that can require additional costs for conditioning. In present article a new technique is studied: the possibility to increase TDS and hardness of product water using ion separation with nanofiltration membranes [1, 15, 27]. Principles of product TDS increase with high lithium rejection are demonstrated on Figure 2(d). The double-stage scheme is used previously shown on Figure 2(c). Concentrate flow is reduced by 30 times as compared to the feed water flow. As rejection values of calcium ion and TDS are higher than rejection of lithium, calcium concentration and TDS value increase in concentrate are higher than concentration value increase. We can apply mixing of the concentrate and the second stage product. After mixing (addition of 30 parts of permeate to one part of concentrate we can obtain the following concentrations of calcium, lithium and TDS in the mixture:

- Calcium: 160 milligrams per liter;
- Lithium: 0,06-0,07 milligrams per liter;
- TDS: 400 milligrams per liter.

As it can be seen at Figure 2(c), lithium concentration in the first stage product water that enters the second membrane stage is equal to lithium concentration in the mixture. Thus, the purpose of this article was to develop production of quality drinking water technique with low costs, low concentrate disposal.

## 2 Materials and Methods

To perform experiments, a 25 liter sample was delivered. The experiment was aimed at obtaining main technical parameters that correspond to scheme shown on Figure 2(d) and
Figure 3. Laboratory test unit flow diagram: 1 - source water tank; 2 - pump; 3 – membrane element in the pressure vessel; 4 – filtrate tank; 5 – heat exchanger; 6 - manometer; 7–9 – flow meters; 10 - bypass valve; 11 - valve for adjusting the flow of source water; 12 - valve for adjusting the working pressure and concentrate flow; 13 - valve for adjusting the flow of cooling water; 14, 15 – samplers.

A test unit flow diagram is shown in Figure 3. Nanofiltration membrane elements were used of 1812 standard tailored with 70 NE and 90 NE membranes (developed by CSM company, Korea) and supplied by Raifil Company (Moscow). The test procedure consisted of the circulation of the feed water in membrane module with collection of permeate in the separate permeate tank and concentrate returned back to the feed water tank.

The volume of the feed water was 25 liters. Experimental program consisted of five steps (stages):

- On the first stage feed water was treated using 90 NE membranes to achieve 80 per cent recovery;
- On the second stage 90 NE concentrate was further treated with 70 NE membranes to reduce concentrate value by 5-6 times to reach concentrate volume of 1 liter.
- On the third stage the collected first stage permeate (18 liters) was treated by 70 NE membranes to reach 80-85 per cent recovery and to reach desired value of lithium concentration (0.02 mg/l);

Concentrations of Calcium, Lithium and TDS in Concentrate and permeate were evaluated throughout all test runs. The final stages of experimental program included:

- On the fourth stage we have mixed the second stage permeate of 70 NE membranes and the third stage concentrate obtained using 70 NE membranes on the second stage of experiment and determined concentration values of calcium, lithium as well as TDS value;
- On the fifth stage the mixture was again treated by 70 NE membranes to produce a product water and concentrate achieving 80 per cent recovery; Membrane spiral wound modules (models 1812-70 NE with nanofiltration membranes and 1812-BLN with reverse osmosis low pressure membranes) were supplied by Toray Advanced Materials Korea Inc. (the manufacturer of CSM Membrane Technologies, Korea, Seoul company CSM). Membrane area in spiral wound elements was equal to 0.5 square meters.

Permeate and concentrate samples were withdrawn from tanks 1 and 2. Calcium, chloride, lithium concentrations as well as pH and TDS values were determined. Calcium
and magnesium concentrations were determined by titration. Sulphate ion concentrations were determined using turbidimetric method. Sodium ion concentrations were evaluated using the atomic adsorption method. Lithium was determined by atomic-emission analysis method using atomic adsorption spectrophotometer operated in emission mode. Electric conductivity, TDS and temperature values were determined using the electrical conductivity meter (model Cond.730, WNW "Inolab-Akvilon", Moscow, Russia). pH values were determined using laboratory pH meter HI 2215 (Hanna Instruments, Vohringen, Germany).

Figure 4 shows dependencies of Ca, Li, Cl concentrations in concentrate on the first stage and on the third stage as functions of K. Figure 5 shows concentrations of these ions in product on the second stage as dependencies on K. We used 70NE membranes on the first stage and 90NE on the second stage. After we produce permeate on the second stage, we implemented mixing with concentrate produced on the third stage. After mixing we get the water with calcium concentration: ppm; lithium concentration. ppm; TDS value ppm. Results of treatment of mixture of the second stage permeate with the third stage concentrate are presented on the Figure 6. During experiment conductance, product flow rate were constantly measured to detect membrane flux reduction during the feed water concentration increase. Also calcium concentrations were measured to calculate calcium carbonate growth rates in membrane modules during constant recovery increase. Results of membrane specific product rate reduction and calcium carbonate scale increase with coefficient K value growth are demonstrated on the Figure 7 (a,b). Calcium carbonate deposition rates were determined using mass balance techniques described earlier [2]. The techniques are based on determination of derivatives of the function of the amount of deposited calcium on time.
Figure 4. Dependencies of Calcium (a), Lithium (b) and Chloride (c) ion concentration values on K in concentrate of 90 NE and 70 NE nanofiltration membranes on the different stages of water flow diagram (Figure 2,d): 1 - 90 NE membranes on the first stage (producing drinking water); 2 - 70NE membranes on the third stage used for concentrate flow reduction; 3 - 70 NE membranes on the second stage (for drinking water quality improvement and lithium reduction).
Figure 5. Dependencies of Calcium (a), Lithium (b) and Chloride (c) ion concentration values on K in permeate of 90NE and 70NE nanofiltration membranes on different stages of water flow diagram (Figure 2,d): 1 - 90 NE membranes on the first stage; 2 - 70NE membranes on the third stage; 3 - 70NE membranes on the second stage.
(a) Concentration, mg/L (Calcium)

(b) Concentration, mg/L (Lithium)
Figure 6. Dependencies of Calcium (a), Lithium (b) and Chloride (c) ion concentration values on K in permeate of 90NE and 70 NE membranes on the different stages of water flow diagram (Figure 2.d): 1 - on the first stage; 2 - on the second stage; 3 - on the fourth stage (after treatment of the mixture of the third stage concentrate and the second stage permeate).
3 Discussion of results

Treatment of feed water with nanofiltration membranes (Figures 4 and 5) using two stages of concentrate reduction provides increase of calcium ion concentration only by 40 times and TDS value increase by 50 times despite the 99% recovery.

The second stage membrane quality provides reduction of Lithium by 27-30 times (96.5-96.7 % rejection) to provide permeate quality similar to permeate quality achieved by the use of reverse osmosis BE membranes. Mixing of the second stage permeate and the third stage concentrate provides water with higher TDS and calcium concentration values than of the first stage permeate (Scheme shown on Figure 2,d).

Figure 6 shows results of the mix blend treatment with 70 NE membranes. As it is shown on Figure 6, calcium concentration in permeate increased by 6 times as compared with the second stage permeate and TDS value increased by 5 times. When permeate flow value achieved 1000 liters per hour and concentrate flow value achieved 10 liters per hour (100 times reduction), concentrate TDS value reached 50 grams per liter that is substantially lower than in case Schemes 1-3 shown on the Figure 2 can reach. Comparison of water treatment schemes is performed and results are shown in Table 2. Main operational characteristics of discussed technological schemes are determined using the data presented on the Figure 7.
Table 2. Main operational characteristics of the 10 $m^3$/hour membrane facility and Comparison of economical and technical parameters of different approaches to provide a quality drinking water

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameters</th>
<th>Scheme 1 (Fig. 2, a)</th>
<th>Scheme 2 (Fig. 2, b)</th>
<th>Scheme 3 (Fig. 2, c)</th>
<th>Scheme 4 (Fig. 2, d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Number of membrane elements, membrane type (8040 type)</td>
<td>18, BE</td>
<td>20, BE, 70NE</td>
<td>17 (70NE)</td>
<td>23 (70NE)</td>
</tr>
<tr>
<td>2</td>
<td>Annual antiscalant consumption kilograms per year</td>
<td>400</td>
<td>400</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>Annual cleaning agents consumption kilograms per year</td>
<td>120</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>Total power of the pumps, KW</td>
<td>10</td>
<td>10</td>
<td>11</td>
<td>12.5</td>
</tr>
<tr>
<td>5</td>
<td>Total energy consumption (annual): KW.H/year</td>
<td>70 000</td>
<td>70 000</td>
<td>77 000</td>
<td>87 500</td>
</tr>
<tr>
<td>6</td>
<td>Concentrate discharge $m^3$/hour</td>
<td>2.5</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>7</td>
<td>Lime consumption for conditioning, tons/year</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>---</td>
</tr>
</tbody>
</table>

As it can be seen in Table 2, application of additional ion separation provides better product water quality. Also, a substantial reduction of operational costs can be achieved due to savings in power and reagent consumption (lime, antiscalant and cleaning chemicals).

4 Conclusion

1. In many cases (such as removal of poorly rejected monovalent pollutants like ammonia and lithium) the use of reverse osmosis to produce drinking quality water seems not reasonable as very low TDS water is produced that requires additional operational costs for conditioning.
2. Reverse osmosis membrane have high scaling propensities and their use increase operational costs spent for scale prevention and concentrate handling.
3. A new technique is proposed that uses low pressure and low rejection nanofiltration membranes to reduce concentrate disposal and scaling potential, as well as to increase permeate hardness and TDS.
4. The developed nanofiltration technique has demonstrated considerable cost savings as compared to conventional reverse osmosis due to reduction of power and reagent consumption.
References


