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Prevention of scaling during the desalination of geothermal water by means of nanofiltration

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ABSTRACT

Geothermal water which is discharged into surface waters following use has a negative impact on the water biocenosis. For this reason, the desalination of geothermal waters using membranes can not only be considered as a means of providing water for irrigation purposes, but also as a possible source of drinking water supply. Geothermal water has a high content of divalent ions, and in such conditions scale is formed on the membrane. Scaling causes a decrease in membrane capacity and permeate quality. The use of the reverse osmosis process in water desalination often requires careful selection of the pre-treatment methods. One of them is nanofiltration which almost completely removes multivalent salts, whereas only 10–50% of single-valent metal salts are removed. The objective of the studies was to develop a two-stage membrane desalination (NF + RO) process for geothermal water that has a high degree of hardness. In the experiments carried out, two different geothermal waters were tested, one from the Podhale basin (southern Poland) and the second from Uniejow (central Poland). Commercial membranes from the Dow-Filmtec company were used in the NF and RO test. The desalination efficiency (flux and permeate composition) and scaling prognosis were determined. Based on the results, an innovative approach to the role of membrane processes in the desalination of very hard geothermal water is proposed. It was concluded , that for water of high hardness (Uniejow) there should be applied a more compact nanofiltration membrane (NF90) before reverse osmosis, due to this method, it was achieved close to 100% removal of most analyzed ions. In the case of water with a lower hardness (Banska) there should be applied a less compact nanofiltration membrane (NF-270) before reverse osmosis obtaining by this method similar results of ions removal as in the case of NF-90 membrane, at the level close to 100% with a higher permeate flux.

Keywords: Geothermal water; Desalination; Integrated system; Nanofiltration; Reverse osmosis

1. Introduction

Water desalination is a separation process in which fresh water is removed from saline water. Thus, the salts and multivalent ions, hardness, are retained in the retentate causing an increase in hardness and total dissolved solids. Due to the low solubility of hardness salts in saline water, and depending on the conditions used, the hardness salts can precipitate on the desalination membranes and equipment (scaling), creating a serious problem in desalination plants [1].

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Used geothermal water, which is then discharged into surface waters, has a negative impact on the freshwater biocenosis because it is toxic to the flora and fauna in the aquatic environment. Geothermal waters often exhibit high concentrations of silica, sulphates, calcium, magnesium, strontium, barium and carbonate which may affect the membrane's desalination due to scaling. Elevated contents of undesirable elements such as boron, arsenic and fluorine may significantly restrict the possibility of discharging geothermal water into surface waters and reduce its economic use [2,3]. Hence the effective removal of these elements is significant not only from the point of view of meeting the quality standards required for drinking water, but also from that of resolving problems in its exploitation [4].

Scaling causes a decrease in both, membrane capacity and permeate quality, and the intensity of the phenomenon depends on the water recovery rate (WRR). The phenomenon may be controlled by the addition of anti-scalants such as polyphosphates or polycarboxylic acids, but even then there are inorganic substances in the water produced which cause fouling. An additional factor which can encourage scaling of the membrane can be the tendency to precipitate sulphate and silica deposits and increase feed water temperature [4,5]. The use of the reverse osmosis (RO) process in water desalination often requires careful selection of the methods of pre-treatment [6–8]. One of them is nanofiltration (NF).

Cheaper seawater desalination processes had been developed by integrating NF with various types of desalination technologies including reverse osmosis (RO), forward osmosis (FO), electrodialysis (ED), multistage flash (MSF) and multi-effect distillation (MED), membrane distillation (MD) and ion exchange (IX) [9]. The application of NF as a pre-treatment in water desalination has so far primarily been applied to sea water [10–15]. The hybrid NF-RO multistage flash distillation (MSF) system for seawater desalination was developed in Saudi Arabia [16–18]. Song et al. [19] applied NF as a seawater reverse osmosis pretreatment in order to eliminate scaling in the reverse osmosis module. Also Kaya et al. [20] showed that the integration of NF and RO in seawater desalination can increase the water recovery rate from 27.8% to 55.1%.

Analysis of world literature leads to the conclusion that the use of an NF pretreatment of seawater in desalination plants has such benefits as: [13–15,20]: (1) prevention of RO membrane fouling by the removal of turbidity and bacteria, (2) elimination of scaling in RO by the reduction of scale forming hardness ions, (3) lowering the required operating pressure in RO plants by reducing seawater feed TDS by 30–60% depending on the type of NF membrane and operating conditions, (4) allowing a high WRR to be obtained through avoiding the risk of crystallisation of scaling substances in the concentrated stream.

The research was carried out in order to look into the feasibility of an integrated process combining NF and RO using geothermal waters from two water sources characterised by relatively elevated levels of hardness. The desalination efficiency (flux and composition of permeate) was determined.

2. Materials and methods

2.1. Apparatus and membranes

A schematic diagram of the apparatus used in the NF and RO system is shown in Fig. 1. Tests were conducted using the American Osmonics Inc. company's SEPA CF-HP type membrane module, in the high-pressure version in cross-flow mode. The feed stream is pumped from the water tank, through a high-pressure pump and valve to the membrane cavity of the SEPA CF-HP module. From the cavity, the solution flows tangentially across the membrane surface. Solution flow is fully controlled and can be laminar or turbulent depending on the feed spacer and the fluid velocity used. A single piece of rectangular-membrane (190 × 140 mm) is installed in the bottom

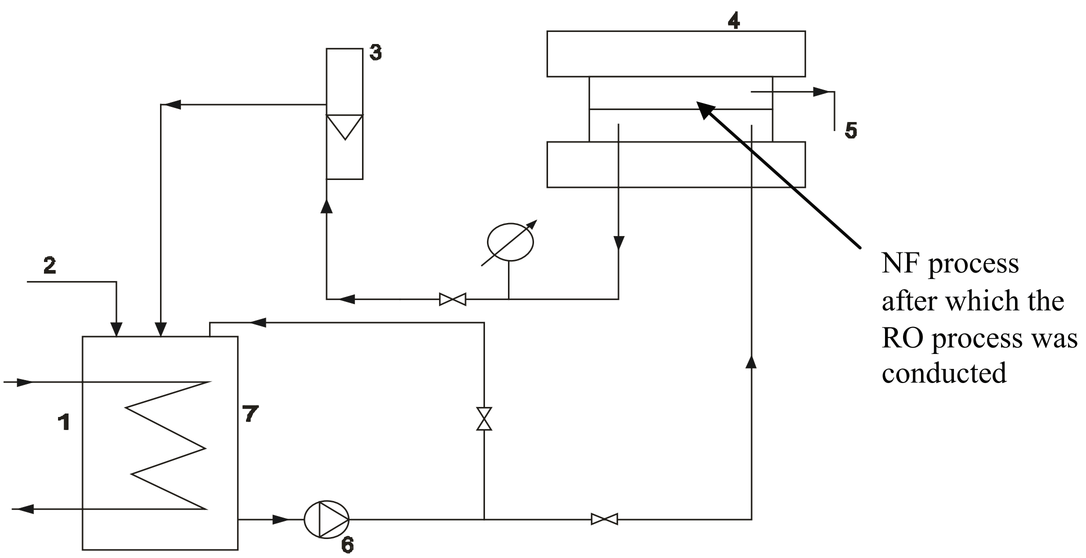

Fig. 1. Diagram of the apparatus for carrying out nanofiltration and reverse osmosis experiments in "cross-flow" mode (1-heat exchanger; 2-raw water inflow; 3-rotameter; 4-membrane cell; 5-permeate outflow; 6-pump; 7-raw water tank).

of the cell body on top of the feed spacer. A portion of the solution permeates the membrane and flows through the permeate carrier, which is located in the top of the cell body and then flows out through the permeate outlet connection into a permeate collection vessel. The concentrate stream, which contains the material rejected by the membrane, continues sweeping over the membrane and collects in the manifold. The concentrate then flows through the concentrate flow control valve and rotameter back into the feed vessel.

In this study, the NF-270 and NF-90 membranes were used for the NF process, while the BW30FR-400 (FilmTec™ membrane of Dow Chem. Company) was used as the RO membrane. The physicochemical properties of the membranes were shown in Table 1.

The NF process was carried out at a transmembrane pressure of 1.0 MPa, and the RO process at a pressure of 1.5 MPa. The active area of the membrane was 155 cm^2. The cross-flow velocity used in these measurements was 1 m/s. In the experiments, feed water pH was in the range of 7.4–6.5, and no additional pH adjustment was done. The new membrane was conditioned by filtration of deionised water to stabilise the permeate flux.

A two-stage treatment system (NF-RO) for the desalination of geothermal water was used. At first, NF of the raw water was carried out and the permeate obtained was fed to the RO process. Both processes, NF and RO, were carried out to obtain 50% recovery of feed water.

2.2. Geothermal waters

Two different geothermal waters were tested in the experiments, one from the Podhale basin (Banska PGP-1) (southern Poland) and the second from Uniejow PIG/AGH-2 (central Poland) (Fig. 2). The waters are characterised by a relatively high hardness of about 691 and 400 mg $CaCO_3$/L and mineralisation of about 2500 and 5900–6100 mg/L for the Banska PGP-1 and Uniejow waters respectively. The full physicochemical characteristics of the waters investigated are presented in Tables 2–4. The feed water had a temperature of 23 ± 2°C. According to the Szczukariewa-Piklonskiego classification [21], the Banska PGP-1 water possesses a hydrogeochemical type SO_4–Cl–Na–Ca, while the Uniejow PIG/AGH-2 waters have a Cl-Na hydrogeochemical character.

2.3. Methodology of physicochemical analysis

To produce an assessment of the quality of the raw water, permeate and retentate after the NF and RO processes, an analysis of the content of the basic mineral components was determined and the rejection coefficients were calculated. Also the permeate flux was measured and calculated.

Water pH and temperature was measured using the electrometric method immediately after sampling water from the system. Inorganic components were determined in an accredited laboratory of the Department of Hydrogeology and Engineering Geology of the AGH University of Science and Technology in Krakow (PCA certificate No AB 1050) using both the inductively coupled plasma mass spectrometry (ICP-MS) and inductive plasma optical emission spectrometry (ICP-OES) methods. Chloride ion content was determined by titration in accordance with accredited testing procedures.

2.4. Membrane scaling prognosis

In the design and operation of NF/RO installations, it is important to predict the scaling potential of the brine stream. Because of the increase of TDS in the brine stream and the differences in the salt permeability of scalant ions, the scaling potential of the brine stream will generally be quite different from those of the feed solution.

The saturation indices (*SI*) of the solution, 1) for geothermal feed waters before the NF processes, and 2) for permeate after the NF and before the RO processes, were calculated using the *Phreeqc Interactive 3.3.3-10424* program (PHREEQCI) using the Wateq4f minerals database [22]. The calculations include:

1. Banska PGP-1: 1) feed water before the NF process (10 bar): temperature 22°C, pH 6.46 and 2) permeate after the NF-270 membrane and before the RO process (15 bar): temperature 22°C, pH 7.33;
2. Uniejow PIG/AGH-2: 1) feed water before the NF process (10 bar): temperature 23°C, pH 7.30 and 2) permeate after the NF-270 membrane and before the RO process (15 bar): temperature 23°C, pH 7.91;
3. Uniejow PIG/AGH-2: 1) feed water before the NF process (10 bar): temperature 23°C, pH 7.39 and 2) permeate after the NF-90 membrane and before the RO process (15 bar): temperature 23°C, pH 6.81.

Table 1
Membrane characteristics (manufacturers' data)

Membrane	NF-270	NF-90	RO BW30FR-400
Producer	Dow Filmtec	Dow Filmtec	Dow Filmtec
Membrane material	Polyamide thin-film composite	Polyamide thin-film composite	Polyamide thin-film composite
Molecular weight Cut-off, Da	200–400	200–400	–
Operating pressure, MPa	Max. 4.1	Max. 4.1	Max. 4.1
pH range	2–11	2–11	1–13
Max. operating temp., °C	45	45	45
Retention coefficient	>98% for $MgSO_4$ 50% NaCl	>98% for $MgSO_4$ 90–96% NaCl	99.65% for NaCl

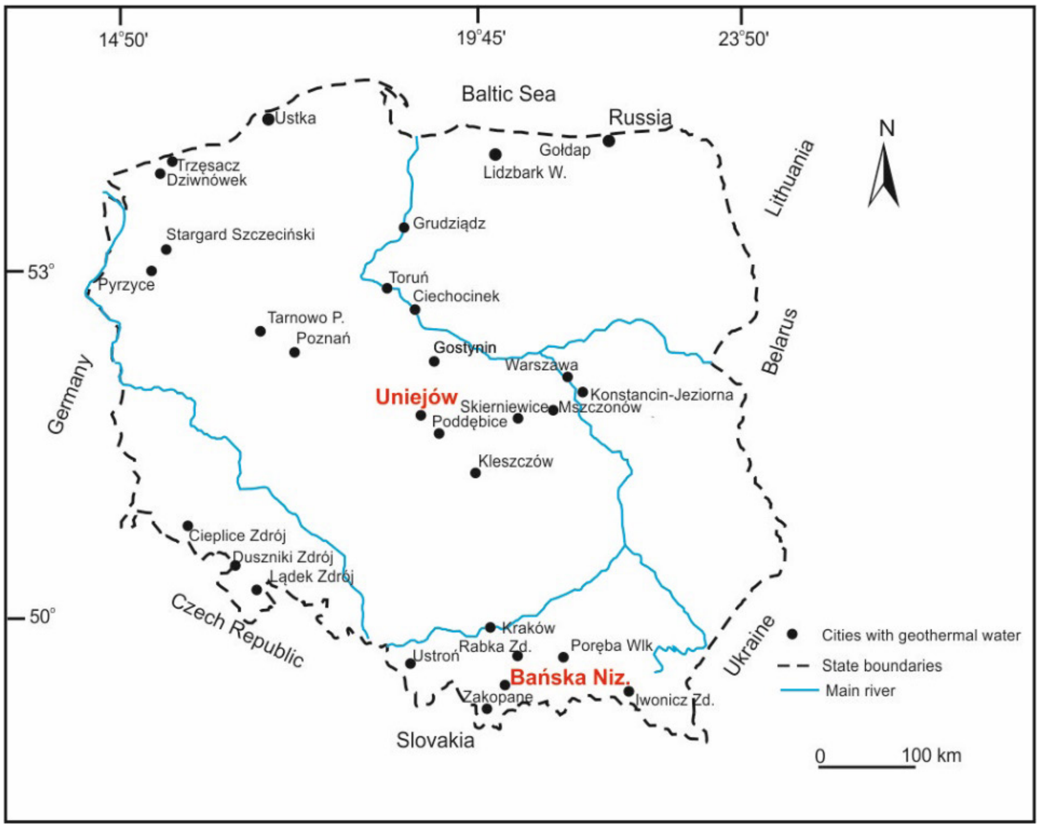

Fig. 2. The sources of geothermal water in Poland.

Table 2
The results of studies of a two-stage NF-RO system (water: Banska PGP-1, NF membrane: NF-270, RO membrane: BW 30 FR-400, recovery rate 50%, transmembrane pressure:10 bar for NF, 15 bar for RO)

Parameter	Raw water	NF permeate		NF permeate introduced to RO	Average permeate after RO		
		Concentration	R, %		Concentration	R, %, to NF permeate	R, %, to raw water
pH	6.46	7.60	–	7.33	6.23	–	–
Conductivity, µS/cm	2910	1612	44.6	1323	21.7	98.4	99.3
TDS, mg/L	2388	998.4	58.2	850.9	36.8	95.7	98.5
Mineralisation, mg/L	2530	1120	55.7	925.0	40.0	95.7	98.4
Total hardness*, mg/L	690.9	134.0	80.6	111.6	0.0	100	100
Na^+, mg/L	504.4	276.1	45.3	235.8	2.68	98.9	99.5
K^+, mg/L	49.1	25.3	48.4	22.0	0.21	99.0	99.6
Li^+, mg/L	1.09	0.568	47.9	0.473	0.005	98.9	99.5
Ca^{2+}, mg/L	206.6	40.8	80.2	34.2	10.0	70.8	95.2
Mg^{2+}, mg/L	42.6	7.80	81.7	6.37	0.100	98.4	99.8
Sr^{2+}, mg/L	6.31	1.18	81.3	1.01	0.20	80.2	96.8
Fe^{2+}, mg/L	0.15	<0.01	93.3	0.01	0.01	0	93.3
Mn^{2+}, mg/L	<0.005	<0.005	–	<0.005	<0.005	–	–
Cl^-, mg/L	469.6	424.6	9.58	385.6	5.9	98.5	98.7
Br^-, mg/L	1.2	0.7	41.7	0.8	0.1	87.5	91.7
SO_4^{2-}, mg/L	844.6	6.84	99.2	5.76	3.00	47.9	99.6
HCO_3^-, mg/L	284.4	243.2	14.5	148.2	6.4	95.7	97.7
H_2SiO_3, mg/L	80.9	62.0	23.4	54.9	0.31	99.4	99.6

*in mg $CaCO_3$/L, R – retention coefficient

Table 3
The results of studies of a two-stage NF-RO system (water: Uniejow PIG/AGH-2, NF membrane: NF-270, RO membrane: BW 30 FR-400, recovery rate 50%, transmembrane pressure: 10 bar for NF, 15 bar for RO)

Parameter	Raw water	NF permeate		NF permeate introduced to RO	Average permeate after RO		
		Concentration	R, %		Concentration	R, %, to NF permeate	R, %, to raw water
pH	7.30	7.91	–	7.42	6.08	–	–
Conductivity, μS/cm	11330	9800	13.5	8000	3760	53.0	62.5
	6086	5380	11.6	5341	192.7	96.4	97.1
TDS, mg/L	6251	5506	11.9	5444	198.4	96.4	97.0
Mineralisation, mg/L	406.4	304.6	25.0	309.7	3.6	98.8	99.1
Total hardness*, mg/L	2132	1863	12.6	1989	67.4	96.6	97.2
Na^+, mg/L	19.88	89.45	–	16.5	1.73	89.5	91.4
K^+, mg/L	0.178	0.156	12.4	0.142	<0.005	96.5	97.1
Li^+, mg/L	125.6	97.16	22.6	98.8	1.14	98.8	99.1
Ca^{2+}, mg/L	22.6	15.11	33.1	15.4	0.184	98.8	99.1
Mg^{2+}, mg/L	5.04	3.63 (3.8	28.0	3.66	<0.20	94.5	96.0
Sr^{2+}, mg/L	1.64	0.02	98.8	0.02	<0.01	–	98.0
Fe^{2+}, mg/L	0.042	0.048	–	0.033	<0.005	–	86.8
Mn^{2+}, mg/L	3485	3139	9.92	3063	110	96.4	97.0
Cl^-, mg/L	5.4	5.7	–	1.58	0.1	93.7	92.9
Br^-, mg/L	83.1	5.41	93.5	17.7	<3.00	83.0	95.9
SO_4^{2-}, mg/L	330.4	250.1	24.3	206.1	11.3	94.5	95.9
HCO_3^-, mg/L	37.5	33.9	9.60	27.9	0.64	97.7	98.1
H_2SiO_3, mg/L							

*in mg $CaCO_3$/L, R – retention coefficient

Table 4
The results of studies of a two-stage NF-RO system (water: Uniejow PIG/AGH-2, NF membrane: NF-90, RO membrane: BW 30 FR-400, recovery rate 50%, transmembrane pressure: 10 bar for NF, 15 bar for RO)

Parameter	Raw water	NF permeate		NF permeate introduced to RO	Average permeate after RO		
		Concentration	R, %		Concentration	R, %, to NF permeate	R, %, to raw water
pH	7.39	6.81	–	6.98	6.13	–	–
Conductivity, μS/cm	10390	1860	82.1	1610	32.8	98.0	99.7
	5891	1003	83.0	853.7	19.7	97.7	99.7
TDS, mg/L	6029	1016	83.1	867.3	22.6	97.4	99.6
Mineralisation, mg/L	395.2	1.8	99.5	3.6	0.3	91.7	99.9
Total hardness*, mg/L	2061	378.2	81.6	327.8	4.2	98.7	99.8
Na^+, mg/L	18.39	3.84	79.1	4.81	0.93	80.7	94.9
K^+, mg/L	0.170	0.024	85.9	0.02	0.005	96.5	97.0
Li^+, mg/L	123.6	2.85	97.7	1.00	0.11	89.0	99.9
Ca^{2+}, mg/L	21.1	0.427	97.8	0.260	0.015	94.2	99.9
Mg^{2+}, mg/L	4.70	0.20	95.7	0.20	0.20	–	95.7
Sr^{2+}, mg/L	0.48	0.01	97.9	0.01	0.01	–	97.9
Fe^{2+}, mg/L	0.008	0.005	–	0.005	0.005	–	–
Mn^{2+}, mg/L	3407	593.6	82.6	495.5	5.8	98.8	99.8
Cl^-, mg/L	6.0	0.4	93.3	0.4	0.1	75.0	98.3
Br^-, mg/L	70.45	3.00	95.7	3.00	3.00	–	95.7
SO_4^{2-}, mg/L	275.0	25.9	90.6	27.3	5.8	78.8	97.9
HCO_3^-, mg/L	36.1	2.95	91.8	2.98	0.03	99.0	99.9
H_2SiO_3, mg/L							

*in mg $CaCO_3$/L, R – retention coefficient

3. Results and discussion

3.1. Variation of permeate flux

In this study, two different geothermal waters (Banska PGP-1 and Uniejow PIG/AGH-2) with different mineralisation characteristics were employed. The NF and RO permeability was calculated using the permeate flow rates and effective membrane area. Figs. 3–5 show the change in relative permeate flux (J/J_0) with time during nanofiltration and reverse osmosis of the geothermal waters from both intakes.

The experimental data indicated that when the operating time was over 7 h, the NF-270 membrane permeability was, on the whole, stable. Studies have shown a minimum loss of membrane efficiency with time during the NF process which indicates a limited decrease in efficiency but, over a longer timescale, that scaling phenomena will indeed be observed, especially for Uniejow PIG/AGH-2 water. As can be seen, these two waters exhibited different permeate flux at the same operating pressure. At 10 bar, the NF-270 membrane gave an average flux of 46 L/m^{2}h with 29.2 L/m^{2}h for the Uniejow PIG/AGH-2 and Banska PGP-1 water, respectively. For the RO process, the permeate flux was lower (average 30.2 L/m^{2}h and 13.7 L/m^{2}h for the Banska PGP-1 and Uniejow-1 waters, respectively) than for NF, despite the fact that a higher pressure (15 bar) was applied than for the NF process. In an opposite manner to the NF-270 membrane, permeate flux was lower for the Uniejow PIG/AGH-2 water because the mineralisation after NF was much higher than for NF permeate coming from the Banska PGP-1water.

The NF flux of Banska PGP-1 water was higher than Uniejow PIG/AGH-2 water using NF-270. The differences between the permeabilities observed for both waters can be attributed to the use of different feed water. The TDS for the Banska feed water was almost 3 times lower than for the Uniejow water, and this was also the situation in the NF permeate (the RO feed). The TDS for the Uniejow PIG/AGH-2 water is much higher than for the Banska PGP-1 geothermal water (Tables 2 and 3). In addition, pH values in the brine streams of the NF stage increased more distinctly than those in the feed streams. According to the experimental data, the pH value of raw Banska PGP-1 water was 6.46 and it increased to 7.6 in permeate and retentate at a 50% recovery rate. For Uniejow PIG/AGH-2 water the pH changed from 7.30 in feed to 7.91 in permeate and 8.15 in brine. The pH values of both feed and brine streams in the BWRO stage only increased from 7.33 to 7.52 for PGP1 and 7.34 to 7.42 for Uniejow PIG/AGH-2, so the apparent difference was not observed in the experimental range. These values also attest to the usefulness of applying a two-stage desalination system of geothermal water, especially for Banska PGP-1 water.

For the NF-90 membrane, the flux was much lower than for the NF-270 membrane. During approx. 22 h of operation, the relative flux lowered from 0.5 to 0.2 (average flux approx. 10 L/m^{2}h), indicating both the compactness of the NF-90 membrane and the significant scaling induced by the geothermal water tested. The Uniejow PIG/AGH-2 water is characterised by a high mineralisation of approx. 6 g/L and a severe degree of hardness – approx. 400 mg $CaCO_3$/L. The pH change for the NF-90 membrane streams was similar to that obtained for the NF-270 membrane and for the same water. The pH values of the stream increased from 7.39 in feed to 8.40 in retentate. For the RO process the relative permeate flux was higher (approx. 0.9; average flux – approx. 20 L/m^{2}h) than in the case of the NF-270 membrane (0.6–0.7; average flux – approx. 14 L/m^{2}h). The reason is the lower TDS (854 mg/L), mineralisation (867 mg/L) and hardness (3.6 mg $CaCO_3$/L) of the feed introduced to the RO membrane (Table 4). For the NF-270 membrane (Uniejow water) the concentration amounted to 5341 mg/L, 5444 mg/L and 310 mg $CaCO_3$/L, respectively. Similar differences were observed in the case of Na^+, Cl^- and SO_4^{2-} ions.

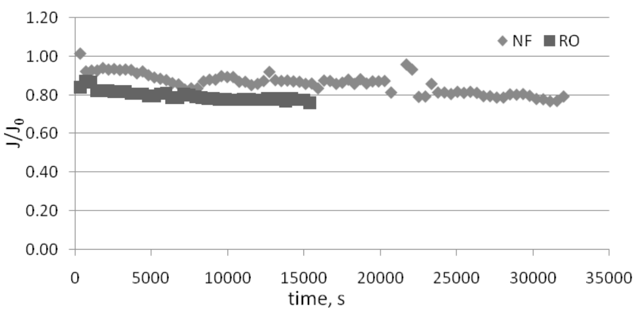

Fig. 3. Changes of relative permeate flux during the NF-270 and RO of Banska PGP-1 geothermal water.

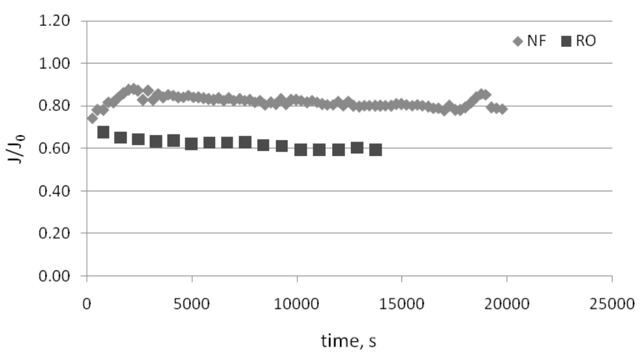

Fig. 4. Changes of relative permeate flux during the NF-270 and RO of geothermal water from Uniejow PIG/AGH-2.

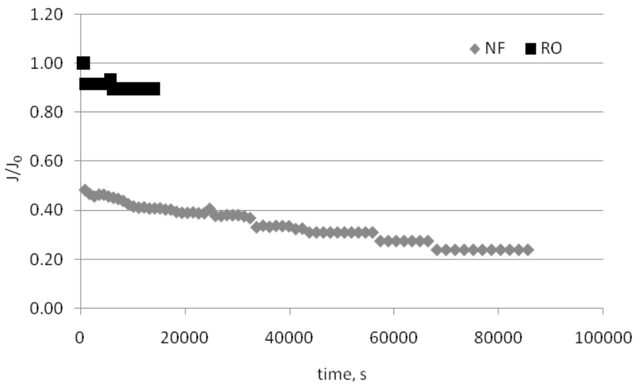

Fig. 5. Changes in relative permeate flux during the NF-90 and RO of geothermal water from Uniejow PIG/AGH-2.

In summary, it can be concluded that the use of the NF-90 membrane in the NF + RO desalination system results in a lower permeate flux in the NF process, while the flux in the RO process is higher compared to the system using the NF-270 membrane.

3.2. Salt rejection

Nanofiltration is considered to be a most promising technique for the production of high quality water from surface and brackish water and there are many examples of its use in practice, especially in the drinking water industry [23,24]. NF is a pressure-driven membrane process which has a molecular weight cut-off between reverse osmosis and ultrafiltration. The rejection ability of NF membranes depends not only on the pore size (0.5–1.5 nm) but also on the charge on the membrane [10,11]. Rejection of NF membranes may be attributed to a combination of steric, Donnan, dielectric and transport effects. NF presents several advantages as compared to RO, such as low operating pressures, higher fluxes, lower investment, operation and maintenance costs. Due to these properties, NF is considered a suitable pre-treatment process for the desalination of waters with a high degree of hardness and a high concentration of sulphates and carbonates [12–16,20].

Tables 2–4 present the results of the physicochemical parameters during the nanofiltration and reverse osmosis of all geothermal waters.

In the first stage of desalination (NF), a low retention of chlorides was found with the NF-270 membrane, but there was a very high retention of SO_4^{2-} and a significant retention of bivalent and hardness cations (Tables 2 and 3). For Banska PGP-1, the water retention coefficients of hardness and divalent ions (SO_4^{2-}, Ca^{2+}, Mg^{2+}, Sr^{2+}, and Fe^{2+}) were above 80%, and mineralisation and TDS were 56–58%. For monovalent cations, i.e. Na^+, K^+, rejection amounted to 45–48% and for the anions Cl^-, HCO_3^- removal was lower at 10–14%. Such results ensure a significant reduction in the scaling phenomenon during the second phase of desalination, i.e. during the RO process. Treatment of the Uniejow PIG/AGH-2 water in the NF process using an NF-270 membrane resulted in a lower reduction in the concentration of SO_4^{2-} ions (93.5%), while the TDS was only reduced by about 11.6%. The reduction that was obtained in the calcium and magnesium ion content, as well as in hardness, was also lower, i.e. 22.6%, 33.1% and 25% respectively. Monovalent ions were reduced to a lesser extent, i.e. only about 10%. The reason was the high TDS content of the Uniejow PIG/AGH-2 water compared to that of Banska PGP-1. As a first step in the desalination of the Uniejow water, a more compact membrane than the NF 270 was also used, i.e. NF-90 membrane.

Table 4 shows the results of the NF process obtained for NF-90 membranes and Uniejow PIG/AGH-2 water. Note the very high retention rates of both hardness and bivalent ions (95–97%) and lower, but also high values for TDS and monovalent ions (80–83%). The reason is that the Dow Filmtec™ NF-90 membrane provides high productivity performance while removing a high percentage of salts, nitrate, and iron, and also organic compounds such as pesticides, herbicides and THM precursors [25]. The low net driving pressure of the NF-90 membrane allows the removal of these compounds at low operating pressures. So the comparison between the NF-90 and NF-270 is between partial (significant) demineralisation vs. none or very little demineralization. The NF-90 membrane is typically used in water softening. NF-90 has a sodium chloride rejection of between 90–96% while the NF-270 membrane has approximately 50% rejection. Both NF membranes have high magnesium sulphate rejections (>98) [26].

The NF permeate coming from the Banska PGP-1 water changed its hydrogeochemical type from sulphate-chloride-sodium-magnesium-calcium to chloride-sodium-bicarbonate (TDS: 1000 mg/L, sulphate 7 mg/L, calcium 41 mg/L, HCO_3^- 240 mg/L). The raw water contained 2400 mg/L of dissolved substances and 850 mg/L of sulphate ions, 200 mg/L of calcium ions and 285 mg/L of bicarbonate ions. The hydrochemical type of Uniejow waters didn't change.

In the second stage of desalination (RO), almost all ions were retained to a great extent – e.g. mineralisation was retained to 96%, hardness to 99%, and monovalent ions to 99% for the Banska PGP-1water and to approx. 97% for the NF-270 membrane and to approx. >99% for the NF-90 membrane when Uniejow waters were tested. Similar data were obtained for both membranes for hardness and divalent ions. It was apparent that the permeate quality of the integrated system combinations was very high and better than single NF membranes (Tables 2–4) and SW30 FR-400 membranes (Table 5). The feed characteristics were also listed for a single SW30–RO membrane and integrated system combinations.

Drioli et al. [27] proposed a system of combined NF-RO-membrane crystallisation to increase the water recovery rate up to 93% [28]. Turek et al. [29,30] have proposed an integrated UF-NF-RO-distillation-crystallisation system for the production of desalinated water and evaporated salt at a water recovery rate of 77.2%. Macedonio et al. [28] analysed seven different integrated membrane

Table 5
The results of the Banska PGP-1 geothermal water using a BW30FR-400 Dow Filmtec reverse osmosis membrane (transmembrane pressure 15 bar, R-retention coefficient)

Parameter	Raw water	Permeate	R [%]	R (NF + RO) [%]
pH	6.80	6.55	–	–
Conductivity[1]	3.35	0.088	97.4	99.3
Total hardness[2]	655.4	3.2	99.5	100
Na^+, mg/L	488.7	10.7	97.8	99.5
K^+, mg/L	47.6	3.0	93.8	99.6
Ca^{2+}, mg/L	194.1	0.799	99.6	95.1
Mg^{2+}, mg/L	41.6	0.285	99.3	99.8
Sr^{2+}, mg/L	6.24	0.2	96.8	96.8
Cl^-, mg/L	487.9	12.2	97.5	98.7
SO_4^{2-}, mg/L	854.7	12.5	98.5	99.6
H_2SiO_3, mg/L	79.4	1.76	97.8	99.6
Fe^{2+}, mg/L	0.232	0.010	95.6	93.3

[1]conductivity in mS/cm; [2]Total hardness in mg $CaCO_3$/L

systems for seawater desalination namely: (1) only the RO unit; (2) NF-RO; (3) MF-NF-RO; (4) MF-NF-RO and a membrane crystalliser module on NF brine; (5) MF-NF-RO and a membrane crystalliser module on RO brine; (6) MF-NF-RO and a membrane crystalliser module on both NF and RO brines; and (7) MF-NF-RO and a membrane crystalliser module on NF brine and membrane distillation on RO brine. From this analysis, adoption of integrated membrane systems appears to provide interesting possibilities for improving desalination operations and meeting the increasing demand for pure water. They also stated that the overall desalination process also becomes very attractive from an economic point of view [28]. Other configurations of desalination plants include NF-RO-MD [31]. Integration of RO with forward osmosis [32] or pressure retarded osmosis [33] for energy recovery has also been investigated.

3.3. Scaling prognosis

The scaling forecast prepared using geochemical modelling and taking into account the physicochemical properties of the geothermal waters (feeds) studied and the pressure used in the process in question (10 bar during NF and 15 bar during RO processes) yielded the following results for both the geothermal waters analysed (Figs. 6, 7 and 8):

1. Feed water before the NF process: a) the supersaturation of solutions and a tendency of the following minerals to precipitate: barite ($BaSO_4$), chalcedony, quartz (SiO_2), iron oxides and hydroxides such as goethite (FeOOH), magnetite (Fe_3O_4) and aluminium hydroxide – gibbsite ($Al(OH)_3$) (Fig. 6); b) a state of equilibrium with respect to aragonite, calcite

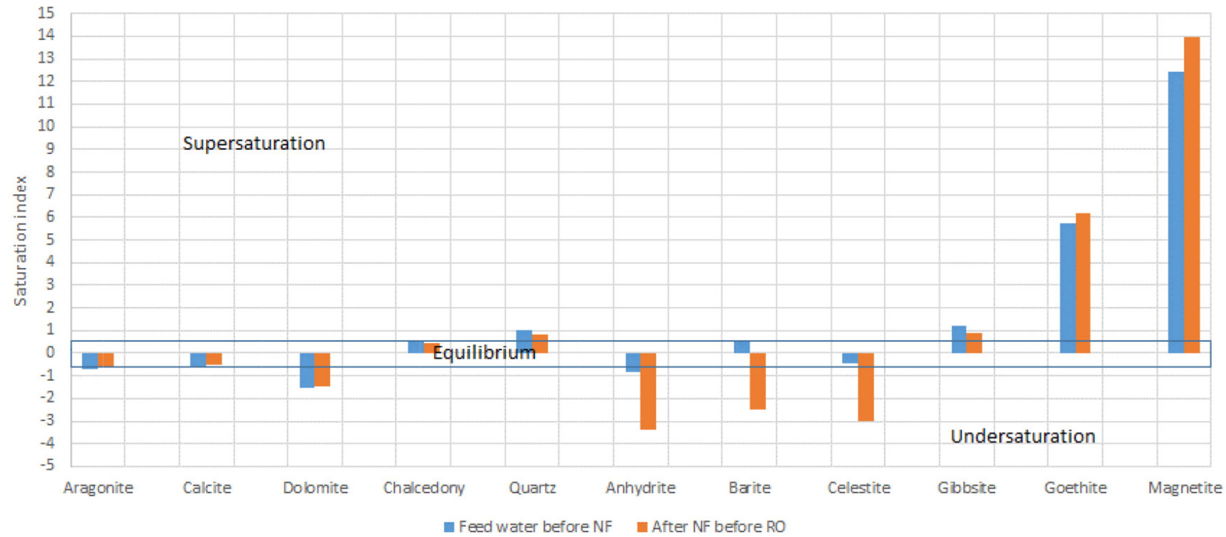

Fig. 6. Mineral saturation of the Banska PGP-1 geothermal water.

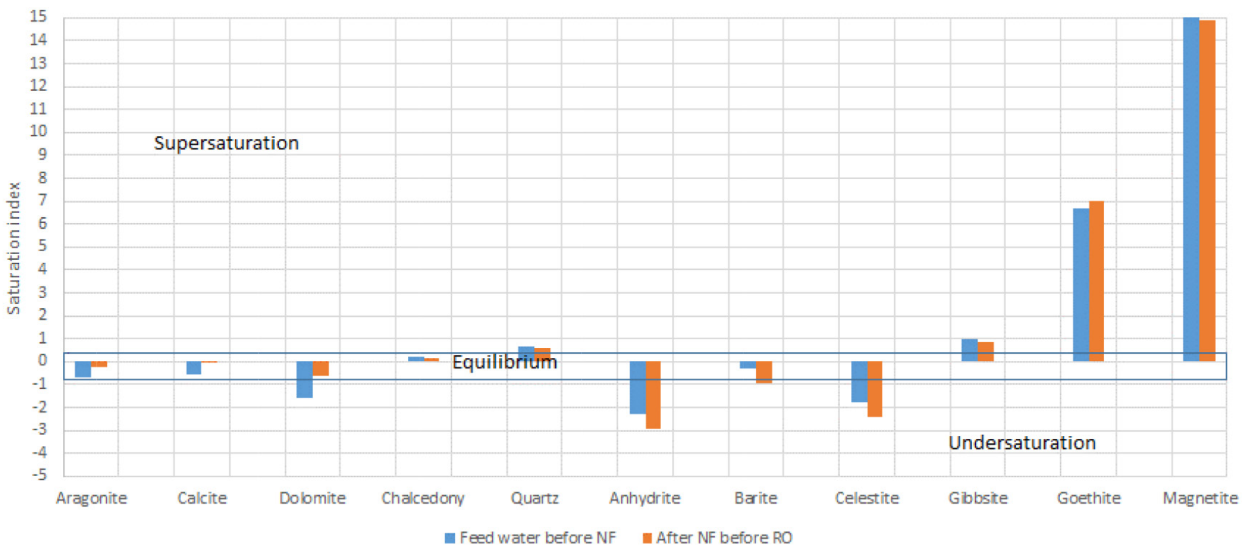

Fig. 7. Mineral saturation of the Uniejow PIG/AGH-2 geothermal water in a test with membrane NF-270.

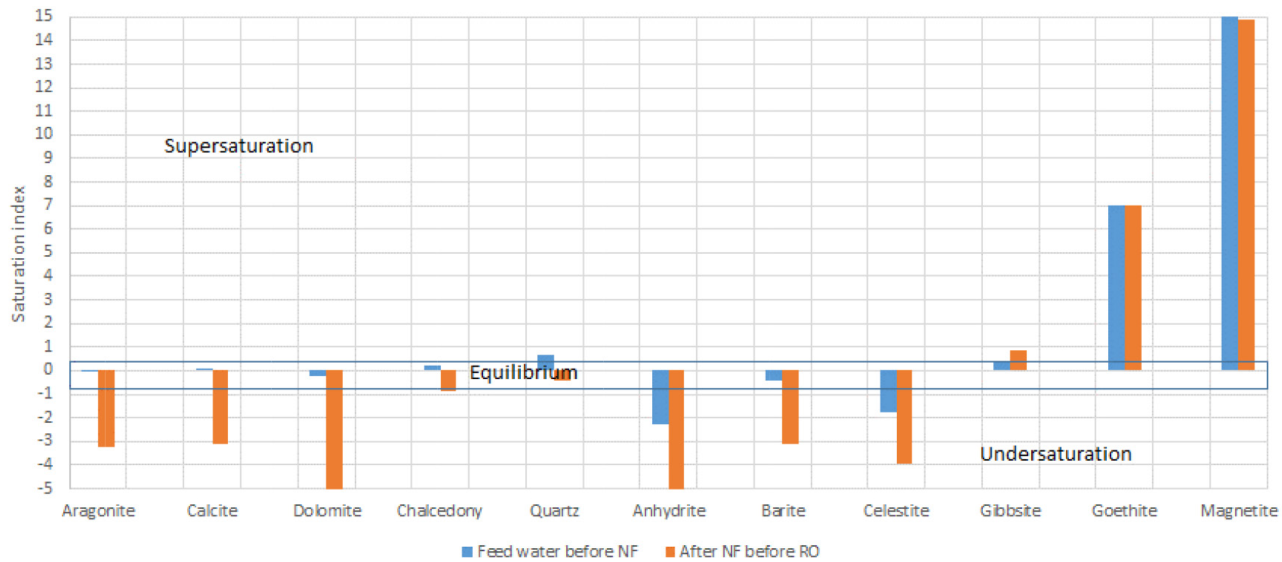

Fig. 8. Mineral saturation of the Uniejow PIG/AGH-2 geothermal water in a test with membrane NF-90.

($CaCO_3$), gypsum ($CaSO_4$) and in the case of Banska PGP-1: anhydrite ($CaSO_4$) and celestite ($SrSO_4$); c) undersaturation with dolomite ($CaMg(CO_3)_2$) and in the case of Uniejow PIG/AGH-2: anhydrite ($CaSO_4$) and celestite ($SrSO_4$).

2. The permeate from the NF-270 membrane followed on to the RO process and presents a) really strong undersaturation of solutions and a smaller tendency to precipitate sulphate forms, anhydrite, gypsum and celestite (Fig. 7); b) a state of equilibrium still persisting or supersaturation of the permeate from the geothermal water solutions tested and a tendency of the following minerals to precipitate: silicates such as chalcedony, quartz, and also iron and aluminium oxides and hydroxides, ex. goethite, magnetite gibbsite. However, in the case of the test with an NF-90 membrane and water from Uniejow PIG/AGH-2, a really strong undersaturation of solutions with respect to carbonate and sulphate minerals has been analysed (Fig. 8). These results are connected with a significant retention of bivalent and hardness cations during the test with the NF-90 membrane (Table 4).

One can observe the differences between the tendency to precipitate found with some minerals from the raw geothermal waters and that of those in permeate from the NF (feed for RO). It also justifies the application of a two-stage desalination system of geothermal waters.

4. Conclusions

It was determined that NF could be an ideal pre-treatment step for geothermal waters during the desalination process. This increases the permeate flux on the BWRO membrane and reduces the cost of the desalination process by eliminating the scaling problem. An NF stage before RO removes the multivalent ions plus some sodium chloride, leaving a feed that has a much lower ionic strength than the original raw water for the RO system which follows. The consequence is that there is a smaller osmotic pressure effect and therefore lower need to apply pressure, leading to lower energy use and higher water yield. That is also why the RO process can be carried out with a stable permeate flux and with a high rate of removal of all inorganic salts.

Taking into consideration the membrane efficiency results and an analysis of the scaling prognosis, one can conclude that permeates coming from both the geothermal waters tested present a tendency to precipitate some minerals, especially with the NF-270 membrane. To avoid this situation, a more compact NF membrane (e.g. NF-90 from DowFilmtec) should be applied in the first stage of desalination, especially for water with higher mineralisation (e.g. Uniejow PIG/AGH-2 water), regardless of whether antiscalants will be introduced to the second stage of the integrated process. According to the desalination results obtained, the NF-90 membrane gave a high rate of rejection and lower flux while the NF-270 exhibited lower rejection and higher flux.

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