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Nanofiltration enhancing the mine water treatment

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ABSTRACT

The use of reverse osmosis (RO) in water desalination often requires careful selection of the pretreatment methods to reduce scaling. One of them is nanofiltration (NF), which almost completely removes multivalent ions, whereas only 10%–50% of monovalent ones. The objective of the studies was to develop a two-stage membrane desalination process (NF + RO) to treat mine water. In the experiments, commercial membranes by Dow-Filmtec (NF-270, NF-90 and BW30FR-400) and Lanxess (PA00416 HR) were used in the NF and RO tests. The treatment efficiency (flux and permeate composition) and predicted scaling were determined. It was concluded that for both RO membranes and for the more compact NF membrane (NF90), the effectiveness of desalination was satisfactory. They achieved a high permeate flux and almost complete removal of most salts. It was necessary to apply a more compact nanofiltration membrane (NF-90) before RO. Application of the NF-90 membrane allowed to protect the RO membrane before scaling, that is, the precipitation of mineral compounds on the membrane surface.

Keywords: Nanofiltration; Mine water desalination; Reverse osmosis; Scaling

1. Introduction

One of the phenomena which is contributing to permanent deterioration of water pollution in Poland is the draining of saline water from the coal mines, mainly localised at Upper Silesia region. In most cases, the waters coming from mining operations are discharged, directly or indirectly, through settling tanks, into the river systems of the Oder and Vistula. High salinity impacts adversely on the biocoenosis of waters, contributing to their degradation and is toxic to the flora and fauna of the aquatic environment. In addition, the excessive salinity of the waters contributes to the corrosion of machinery and equipment that are in contact with the water [1]. The recommended maximum content of some of the indicators is exceeded by several times, including sodium, chlorides and the barium from a few hundred to a thousand times [2]. Hence, it is so important to take action focus on saving river ecosystems. Solutions which are mentioned here include the elimination of mining activities, which restrict the supply of salt water to the mines, and other solutions. These attempts, however, do not result in a significant reduction in the salinity of waters discharged into the rivers. It is necessary to find such methods, which can reduce the impact of mining water salinity on the environment. One of them is water desalination with the use of reverse osmosis (RO) process.

The problem in treatment/desalination by RO is an irreversible membrane scaling [3]. The intensity of scaling depends on the water recovery rate. When the water recovery

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rate is higher than 50% [4,5], scaling reduces the usefulness of RO for desalination of saline water. The introduction, therefore, of nanofiltration (NF) before the RO for water desalination may be a key solution, which can allow to achieve a high water recovery rate; this solution can eliminate the risk of crystallisation of calcium sulphate and other minerals in the concentrate stream [6]. The integrated system of NF with the RO process will allow to obtain a concentration of salt in the concentrate (brine) higher than in desalination by direct RO [7]. This solution is of particular importance, if further concentration of the concentrate should be carried out. NF membranes virtually remove the salts of polyvalent metals completely, while the salts of the monovalent metals are only rejected at a rate of 10%–50%, depending on the type of NF membrane. This creates a situation, in which the feed water transferred to the RO modules has a lower osmotic pressure than the raw water and thus, RO membranes can work under lower pressure and at a higher water recovery rate [6,7]. Such the solution sometimes enables to skip the second phase of RO, normally used in conventional desalination technology, because the concentration of dissolved substances in the first RO step permeate is approximately 200 mg/L.

The hypothesis of the planned research is based on the assumption that the introduction of the NF as a pretreatment in water desalination by the RO method will allow to obtain a concentration of salt in the concentrate (brine) much larger than the one generated in desalination exclusively based on the RO method, and in addition, it will allow to obtain a desalinated water and a concentrate with established concentration.

2. Materials and methods

2.1. Water

Water originating from the desalination plant, situated in the Silesian Voivodeship in southern Poland, was used in experiment. Samples of raw water were taken prior to their introduction to the RO installation, that is, after the standard initial preparation [8]. First, coagulation with alumina is carried out after correction of the pH, and disinfection with sodium hypochlorite. Then water is directed to the anthracite-sand bed filter, where the exact removal of the suspension takes place. For dechlorination, sodium metabisulphite is added to the decontaminated water, and the process is supported by the active carbon filters. Initially purified water is transferred to the RO installation, while desalinated waters are discharged into the river Bierawka and the concentrate is directed to the thermal processing installation.

The investigated water characterised with high degree of hardness of about 4,594 mg $CaCO_3$/L and total mineralisation of around 42 g/L. Investigated water also had a high content of magnesium (760 mg/L), barium (6.0 mg/L), bromides (55 mg/L), arsenic (0.026 mg/L), potassium (174 mg/L) and strontium (17 mg/L) and pH of approximately 6.76. Due to the Altowski–Szwiec system, the water was classified as SO_4-Cl-Na-Ca type [9].

2.2. Apparatus and membranes

NF and RO processes were carried out in 'cross-flow' mode using the large-laboratory module of the Osmonics SEPA type CF-HP in the high-pressure version. The scheme of the apparatus used in the process of RO and NF is displayed in Refs [8,10]. The raw water is pumped from the reservoir by a high-pressure pump and valve to the SEPA CF-HP membrane module. The membrane module has the shape of a rectangle (190 × 140 mm) and is installed at the bottom of the membrane cell. Part of the solution passes through the membrane to the permeate receiver, while the concentrate flows through the rotameter back to the raw water tank.

Commercial polyamide thin-film composite NF membranes produced by Dow-Filmtec (NF-270 and NF-90) and RO membranes type BW30FR-400 (Dow-Filmtec) and PA00416 HR (Lanxess) were used in the research. The physicochemical properties of the membranes are shown in Table 1.

The NF process was carried out at a trans-membrane pressure of 1.0–3.0 MPa, and the RO process at a pressure of 2.0–3.0 MPa. The active area of the membrane was 155 cm^2. The cross-flow velocity used in the measurements was 1 m/s and temperature 23°C ± 2°C. In the experiments, feed water pH was in the range of 6.1–6.45, and no additional pH adjustment was done. The new membrane was conditioned by filtration of deionised water to stabilise the permeate flux.

2.3. Methodology of the membrane processes and physicochemical analysis

A two-stage system, which integrated the NF and RO processes (NF + RO), was used for mine water processing. Raw water was introduced to NF process, and the resulting permeate was used as the feed to the RO process. Both processes, NF and RO, were carried out until 50% water

Table 1
Membrane characteristics (manufacturers' data)

Membrane	NF-270	NF-90	RO BW30FR-400	RO PA00416 HR
Producer	Dow Filmtec	Dow Filmtec	Dow Filmtec	Lanxess
Cut-off (Da)	200–400	200–400	–	–
Operating pressure (MPa)	Max. 4.1	Max. 4.1	Max. 4.1	Max. 8.3
pH range	2–11	2–11	1–13	2–11
Max. operating temp. (°C)	45	45	45	45
Retention coefficient	>98% $MgSO_4$	>98% $MgSO_4$	99.65% NaCl	Max. 99.8% NaCl
	50% NaCl	90%–96% NaCl		Min. 93.0% NaCl

recovery rate was obtained. The effectiveness of mine water treatment was determined by measuring the permeate flux and physicochemical composition of feed water, permeate and concentrate.

The quality of particular process streams was permanently measured online and included temperature and pH and specific electrical conductivity, immediately after sampling water from the installation. Determination of the inorganic components was carried out in an accredited laboratory in the Institute of Environmental Engineering, Polish Academy of Sciences, Poland.

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 total disolved solids (TDS) in the brine and the differences in the salt permeability of scalants the scaling potential of the brine stream is generally quite different from one of the feed solution. The saturation state of raw water with reference to minerals that could potentially pose a membrane scaling was performed using program PHREEQC (*Phreeqc Interactive 3.3.3-10424* – PHREEQCI – Wateq4f minerals database) [11]. The value of the saturation index (SI) of each mineral was calculated from the chemical activity of dissolved substances [11].

The SIs were calculated for the raw mine water introduced to the NF process and the permeates after the NF (NF-270 and NF-90 membranes) and before the RO using both BW30FR-400 and RO PA00416 HR membranes.

3. Results and discussion

3.1. Process efficiency

Figs. 1–3 show changes of relative permeate flux (J/J_0). J_0 is the volumetric flux of deionised water and J is the volumetric permeate flux obtained during the mine water treatment with NF and RO.

Experimental data indicated that the permeability (performance) of the NF-270 membrane was rather stable throughout the whole period of its operation (Fig. 1). The minimum loss of membrane efficiency during the NF process indicated on a slight reduction in performance, and the value of the relative permeate flux at the level of 0.75 attested to the low degree of scaling of the NF membrane. We could, however, assume that, in the long-term process, the phenomenon of membrane scaling would probably occur.

For the integrated NF + RO system the permeate flux was significantly reduced. After 26 h of operation (Fig. 1), relative permeate flux (for RO membrane) decreased to the value of 0.025, therefore to a value which deviated slightly from the flux, which was characteristic for the RO membrane used in the single process (Fig. 2). Such a big difference in the performance of both processes (NF and NF + RO) indicated on the significant scaling caused by the tested mine waters, which contained a large amount of solutes (TDS) (approx. 42 g/L) and had a significant degree of hardness of approximately 4.6 g $CaCO_3$/L (Table 2). The permeate after NF had only slightly smaller values of these parameters (TDS – 40 g/L, hardness – 4 g $CaCO_3$/L).

Permeate flux for NF-90 membranes (Figs. 3 and 4) was much lower than for the NF-270 membrane (Fig. 2). In the case of membrane NF-90_1 (i.e. operated at 1–3 MPa and combined with DOBW30FR-400 membrane), the flux was more stable, however, the values of the relative flux were in the range of 0.05–0.02, which resulted from the changes of transmembrane pressure during operation (Fig. 3). During about 6 h of operation, with the use of the NF-90_2 membrane, relative permeate flux decreased from about 0.2 to about 0.1 (mean flux about 10 L/m^2 h) (Fig. 4), which

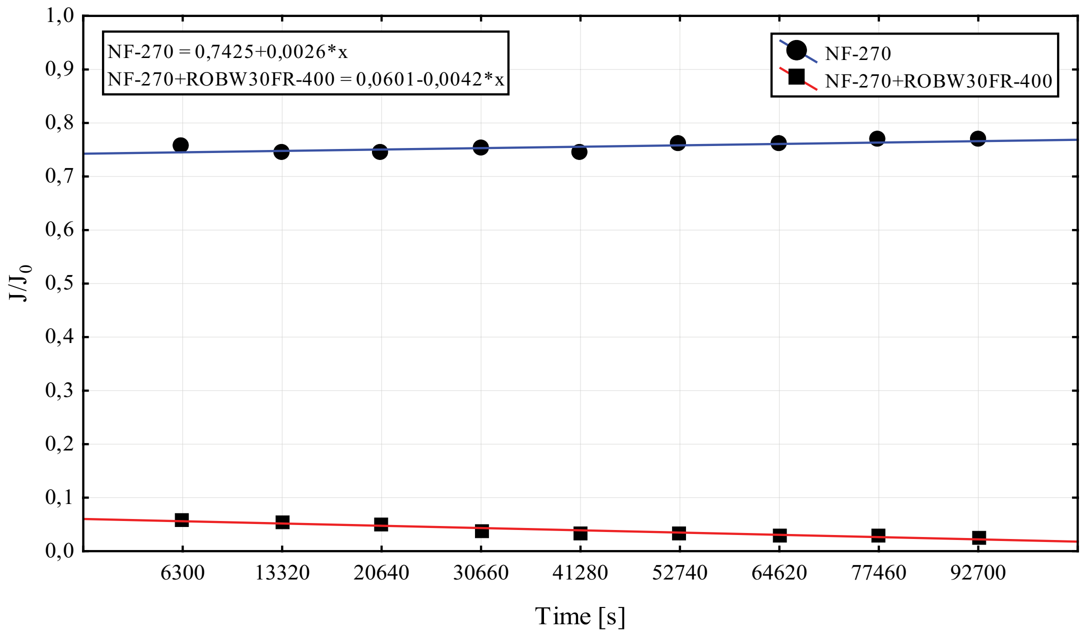

Fig. 1. Changes in the relative permeate flux during the nanofiltration process and a two-stage mine water desalination system (NF + RO) using NF-270 and RO BW30FR-400 membranes (transmembrane pressure: 1.0 MPa for NF, 2.0 MPa for RO, temp. 23°C for NF and 23.5°C for RO).

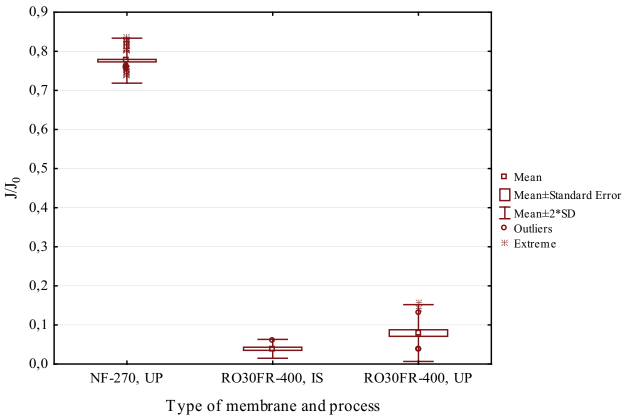

Fig. 2. The comparison of the relative permeate flux for the NF and RO processes and NF + RO system using NF-270 and RO BW30FR-400 membranes (UP-unit process, IS – integrated system).

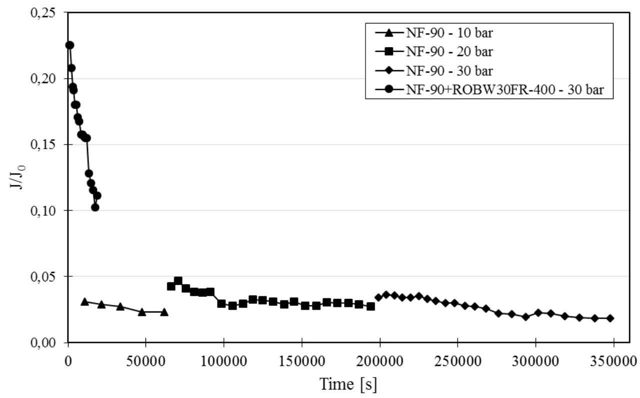

Fig. 3. Changes to the relative permeate flux during the two-stage mine water desalination system (NF + RO) using NF-90_1 and RO BW30FR-400 membranes (transmembrane pressure: 1.0/2.0/3.0 MPa for NF, 3.0 MPa for RO, temp. 24°C for NF and 26°C for RO).

Table 2
The results of a two-stage treatment system (NF + RO) (water: mine water after the initial treatment, NF membrane: NF-270, RO membrane: BW 30 FR-400, water recovery rate: 50%, transmembrane pressure: 1.0 MPa for NF, 2.0 MPa for RO, temp. 23°C ± 0.5°C for NF and 23.5°C for RO)

Parameter	Raw water	Nanofiltration			Reverse osmosis			
		Concentration		*R* (%)	Concentration		*R* (%)	
		Permeate	Retentate		Permeate	Retentate	To NF permeate	To raw water
pH	6.10	6.80	7.49		6.66	7.98	–	–
Eh (mV)	130	217	223		214	252	–	–
Conductivity (mS/cm)	59.5	57.4	65.6	3.5	20.8	80.4	63.8	65.0
TDS (g/L)	42.1	39.3	45.3	6.65	13.0	62.8	67.7	69.1
Total hardness (mg $CaCO_3$/L)	4,594	3,978	5,633	–	2,443	8,696	38.6	46.8
Total hardness (mval/L)	91.9	79.6	113		48.9	174	38.6	46.8
Na^+ (g/L)	16.8	11.0	22.0	34.5	3.52	190	66.9	79.0
Ca^{2+} (mg/L)	589	80.25	857	86.4	65.3	1,340	18.7	91.4
Mg^{2+} (mg/L)	760	510	850	32.9	198	1,300	61.2	73.9
Ba^{2+} (mg/L)	0.566	0.494	0.61	12.7	0.067	0.777	86.4	88.2
Sr^{2+} (mg/L)	16.8	13.6	17.7	19.0	1.52	27.7	88.8	91.0
Fe^{2+} (mg/L)	<0.05	<0.05	<0.05	–	<0.05	0.61	–	–
Mn^{2+} (mg/L)	1.01	0.812	1.02	19.6	0.104	1.46	87.2	89.7
Cl^- (g/L)	32.5	19.8	45.2	39.1	6.74	39.7	66.0	79.3
Br^- (mg/L)	55.0	54	51	1.8	22	76	59.3	60.0
SO_4^{2-} (mg/L)	1,110	707	1,557	36.3	606	510	14.3	45.4
HCO_3^- (mg/L)	2.3	2	2.5	13.0	0.5	–	75.0	78.3
SiO_2 (mg/L)	8.03	7	7.06	12.8	1.4	6.8	80.0	82.6
B (mg/L)	1.51	1.27	1.32	15.9	1.15	1.25	9.4	23.8
Alkalinity (mval/L)	2.3	2.5	2.0	–	–	–	–	–
Acidity (mval/L)	0.18	0.1	0.1	–	0.3	–	–	–

R – Retention coefficient.

indicated on a significant compactness of the NF-90 membrane. This was confirmed by the high retention rates of most water physicochemical parameters obtained for this membrane (Table 4).

For the NF + RO system (using the NF-90 membrane), relative permeate flux in the RO process was approximately 0.5 (Fig. 4). It was significantly higher than in comparison with the integrated process with the use of the NF-270 membrane

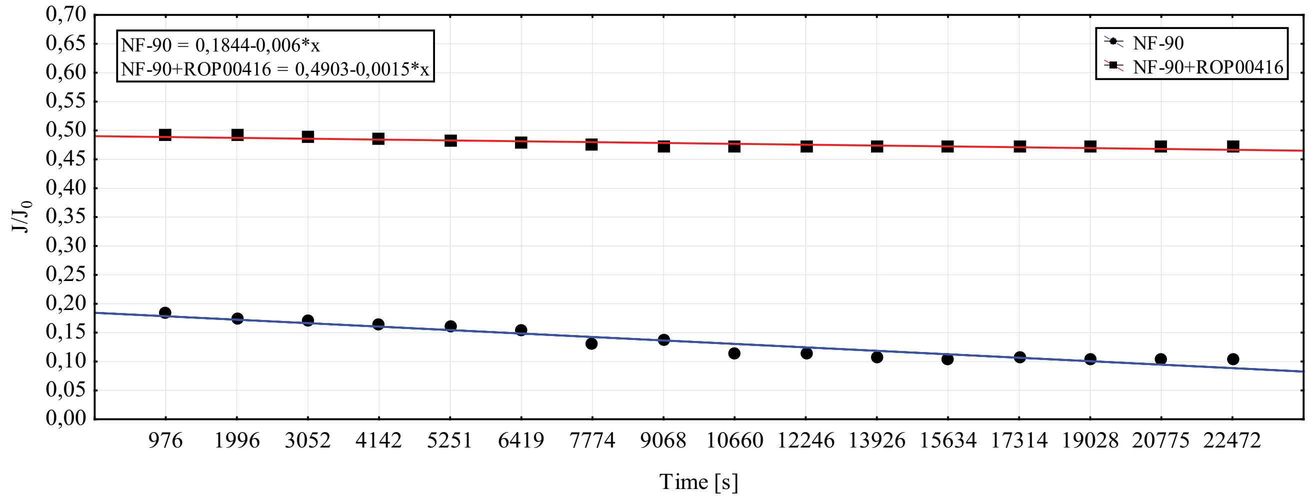

Fig. 4. Changes of the relative permeate flux during the nanofiltration process and a two-stage mine water desalination system (NF + RO) using NF-90_2 and RO P00416 membranes (transmembrane pressure: 3.0 MPa for NF, 3.0 MPa for RO, temp. 25°C for NF and 25°C for RO).

(Fig. 1). In addition, contrary to the integrated process with use of the NF-270 membrane (Fig. 1), the integrated process (NF + RO) with the NF-90 membrane (Figs. 3 and 4) had a higher permeate flux than the individual NF process. The reason was the greater compactness of the NF-90 membrane and lower values of the TDS (31.5 and 16.2 g/L) and hardness (931 and 747 mg $CaCO_3$/L) in the streams introduced to the RO treatment (Table 3 and 4). For the NF-270 membrane, these parameters were significantly higher (39.3 g/L for TDS and 3,978 mg $CaCO_3$/L for total hardness) (Table 2). Similar differences were observed in the case of Na^+, Cl^- and SO_4^{2-} ions.

It should be noted, that permeate flux in the RO process (RO POO416 membrane) in the integrated system NF-90 + RO was much higher (J/J_0 approximately 0.5) than the flux obtained for the same RO membrane in a single process, J/J_0 approximately 0.1 (Fig. 5).

In summary, it can be concluded that, the use of the NF-90 membrane in an integrated desalination system (NF + RO) gave a lower permeate flux in the NF process, while the flux in the RO process was higher compared with the system operated with the NF-270 membrane.

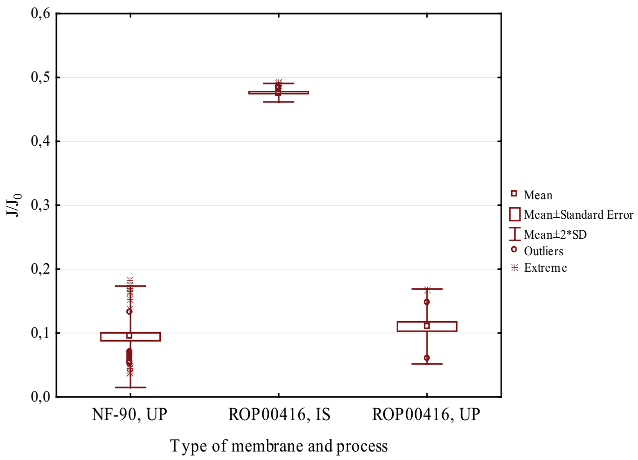

Fig. 5. The comparison of the relative permeate flux for the NF, RO and NF + RO system using NF-90_2 and RO P00416 membranes (UP-unit process, IS – integrated system).

3.2. Effectiveness of water purification

Tables 2–4 show the results of physicochemical analysis of mine water during NF and RO.

In the first stage of treatment (NF), the retention coefficients of bivalent ions, Ca^{2+}, Mg^{2+}, Sr^{2+} and Mn^{2+}, and hardness and SO_4^{2-}, were 86.4%, 33%, 19% 19.6% and 36.3%, respectively (Table 2). The removal of monovalent ions, that is, Na^+ and Cl^-, amounted to 34.5% and 39.1%, while the removal of HCO_3^- was at a lower level of 13%. Similar values were obtained for boron and silica (Table 2). These are typical results observed for the process of NF.

In the second stage of treatment (RO) almost all ions were removed to a large extent, for example, TDS and conductivity retention was 69% and 65%, respectively, sodium and chloride – 79%, other bivalent ions (Mg^{2+}, Sr^{2+}, Mn^{2+} and Ba^{2+}) – 74%–91%, and HCO_3^- and SiO_2, respectively, 78.3%, 82.6%.

These results provided real reduction of the scaling phenomenon in the second phase of desalination, that is, during the RO process, but at the same time, the obtained water did not meet the conditions of water intended for human consumption [12]. This was, first of all, due to the concentration of such components as sodium, calcium, magnesium, sulphates and boron. For this reason, a more compact membrane than the NF-270 should be used as a first stage of mine water treatment, for example, the NF-90 membrane.

Tables 3 and 4 show the results of mine water NF, obtained for the NF-90 membrane in the first stage of the treatment and for BW 30 FR-400 and PA00416 HR RO membranes in the second stage.

In the first stage of desalination (membrane NF90_1), the attention was drawn to the high retention of hardness (approximately 80%) and the majority of the bivalent ions

Table 3
The results of a two-stage treatment system (NF + RO) (water: mine water after the initial treatment, membrane for NF: NF-90_1, RO membrane: BW 30 FR-400, water recovery rate: 50%, transmembrane pressure: 1.0/2.0/3.0 MPa for NF, 3.0 MPa for RO, temp. 24°C ± 0.5°C for NF and 26°C ± 0.5°C for RO)

Parameter	Raw water	Nanofiltration			Reverse osmosis			
		Concentration		*R* (%)	Concentration		*R* (%)	
		Permeate	Retentate		Permeate	Retentate	To permeate after NF	To raw water
pH	6.45	6.52	6.79	–	6.80	7.22	–	–
Eh (mV)	130	147	261	–	227	238	–	–
Conductivity (mS/cm)	58.4	48.7	151.4	16.6	1.79	53.5	96.3	96.9
TDS (g/L)	42.1	31.5	103.7	25.2	0.948	34.5	97.0	97.5
Total hardness (mg $CaCO_3$/L)	4,594	931.5	14,980	79.7	16.6	1,040	98.2	99.6
Total hardness (mval/L)	91.9	18.6	300	79.8	0.332	20.9	98.2	99.6
Na^+ (g/L)	16.8	12.1	34.9	28.0	0.374	13.4	96.9	97.8
K^+ (mg/L)	174	151	417	13.2	8	212	94.7	95.4
Ca^{2+} (mg/L)	589	169	1,910	71.3	5	194	97.0	99.2
Mg^{2+} (mg/L)	760	124	2,484	83.7	1	136	99.2	99.9
Ba^{2+} (mg/L)	0.566	0.098	0.683	82.7	<0.05	0.187	49.0	91.2
Sr^{2+} (mg/L)	16.8	2.1	53.8	87.5	<0.05	4.21	97.6	99.7
Fe^{2+} (mg/L)	<0.05	<0.05	0.139	–	<0.05	0.056	–	–
Mn^{2+} (mg/L)	1.01	0.108	1.56	89.3	<0.05	0.203	53.7	95.05
Cl^- (g/L)	32.5	22.1	70.7	32.0	0.644	25.0	97.1	98.0
Br^- (mg/L)	55.0	49	127	10.9	2	54	95.9	96.4
SO_4^{2-} (mg/L)	554	235	2,067	57.6	8	238	96.6	98.6
HCO_3^- (mg/L)	2.3	0.75	2.2	67.4	0.15	2.2	80.0	93.5
SiO_2 (mg/L)	8.03	2.06	6.05	74.3	0.199	3.3	90.3	97.5
B (mg/L)	1.51	1.4	1.62	7.28	0.839	1.53	40.1	44.4
Alkalinity (mval/L)	2.3	0.75	2.2	–	0.15	2.2	–	–
Acidity (mval/L)	0.18	0.075	0.6	–	0.05	0.1	–	–

R – Retention coefficient.

(approximately 80%–90%) as well as to the decrease of conductivity, TDS (respectively,16.5% and 25.2%), chloride and sodium ions (respectively, 32% and 28%). High degrees of removal of the bicarbonate ion (67.4%) and silica (74.3%) were also noticed, while boron removal was poor (Table 3). These are typical results observed for compact NF membranes.

Table 4 shows the results for mine water NF obtained for NF-90_2 and RO for the PA00416 HR membranes.

Very high retention rates of bivalent ions (Mg^{2+}, Sr^{2+}, Mn^{2+} and Ba^{2+}) were found for the NF90_2 membrane amounting to above 90%, slightly lower for calcium and sulphate ions (68% and 70%, respectively), moderate for Na^+ and Cl^- ions (62.2% and 64.3%), TDS and specific conductivity (61.5% and 50.6%, respectively). The high retention rate of hardness and silica and the bicarbonate ion amounting to >80% was also noticed. Low retention of boron for both NF-90 membranes resulted from the low values of the pH of raw water. For the acidic pH of raw water, the membrane selectivity was insufficient to achieve high degrees of boron removal [13].

In summary, it can be concluded that the NF-90 membrane manufactured by the Dow Filmtec™ company, USA, provided high efficiency in removal of salts at low transmembrane pressures. A comparison of the two NF membranes shows that the NF-90 membrane enabled partial (significant) demineralisation, while the NF-270 membrane characterised with none or very poor water demineralisation rate. The NF-90 membrane is usually used in water softening, due to the high values for bivalent ion removal. This membrane has a moderate sodium chloride retention, while the NF-270 membrane is characterised by NaCl retention usually amounting to <50%. Both NF membranes have high rates of removal of magnesium sulphate [14].

Tables 5 and 6 show the results achieved during the integrated process of NF-90 membrane and the two RO membranes: BW 30 FR-400 and PA00416 HR (Table 5) and for direct, single-stage RO process with the use of investigated membranes (Table 6). The retention rates for integrated systems with both osmotic membranes and all water physicochemical parameters, with the exception of boron, exceeded 90%, and in many cases reached values of 99%–100%. In permeate, only the content of sodium ions and chlorides was slightly exceeded in comparison with the permissible values for drinking water standards [12] (Table 5). Both, the retention rates and concentrations of chlorides and sodium were much higher in the case of single-stage desalination

Table 4
The results of a two-stage desalination system (NF + RO) (water: mine water after the initial treatment, membrane for NF: NF-90_2, RO membrane: PA00416 HR, water recovery rate: 50%, transmembrane pressure: 3.0 MPa for NF, 3.0 MPa for RO, 25°C ± 0.5°C for NF and RO)

Parameter	Raw water	Nanofiltration			Reverse osmosis			
		Concentration		*R* (%)	Concentration		*R* (%)	
		Permeate	Retentate		Permeate	Retentate	To permeate after NF	To raw water
pH	6.33	6.92	7.62	–	6.86	6.49	–	–
Eh (mV)	130	244	239	–	234	252	–	–
Conductivity (mS/cm)	56.5	27.9	96.9	50.6	1.25	32.2	95.5	97.8
TDS (g/L)	42.1	16.2	70.7	61.5	0.640	19.9	96.0	98.5
Total hardness (mg $CaCO_3$/L)	4,594	747	9,110	83.7	16.6	1,610	97.8	99.6
Total hardness (mval/L)	91.9	14.9	182	83.8	0.331	32.1	97.8	99.6
Na^+ (g/L)	16.8	6.35	22.7	62.2	0.248	7.76	96.1	98.5
K^+ (mg/L)	174	151	274	13.2	4	108	97.4	97.7
Ca^{2+} (mg/L)	589	189	1,275	67.9	5	545	97.4	99.2
Mg^{2+} (mg/L)	760	67	1,441	91.2	1	60	98.5	99.9
Ba^{2+} (mg/L)	0.566	<0.05	0.865	91.2	<0.05	0.089	–	91.2
Sr^{2+} (mg/L)	16.8	0.682	36.8	95.9	<0.05	1.226	92.7	99.7
Fe^{2+} (mg/L)	<0.05	<0.05	<0.05	–	<0.05	0.222	–	–
Mn^{2+} (mg/L)	1.01	<0.05	0.847	95.0	<0.05	0.131	–	95.0
Cl^- (g/L)	32.5	11.6	51.9	64.3	0.439	14.6	96.2	98.6
Br^- (mg/L)	55.0	29	90	47.3	1	33	96.6	98.2
$SO4^{2-}$ (mg/L)	554	166	1,417	70.0	5	462	97.0	99.1
HCO_3^- (mg/L)	2.3	0.4	3.85	82.6	0.2	1	50.0	91.3
SiO_2 (mg/L)	8.03	1.45	6.82	81.9	0.177	3.8	87.8	97.8
B (mg/L)	1.51	1.16	1.36	23.2	0.655	1.25	43.5	56.6
Alkalinity (mval/L)	2.3	0.4	3.85	–	0.2	1	–	–
Acidity (mval/L)	0.18	0.05	0.225	–	0.05	0.075	–	–

R – Retention coefficient.

Table 5
The comparison of parameters for desalinated water (permeate) with permissible values for drinking water

Parameter	Integrated system NF + RO			Limit values for drinking water acc. norm [12]
	NF-270 + BW 30 FR-400	NF-90 + BW 30 FR-400	NF-90 + PA00416 HR	
Chlorides (mg/L)	6,740	644	439	250
Manganese (mg/L)	0.104	<0.05	<0.05	0.05
Conductivity (mS/cm)	20.8	1.79	1.25	2.5
Sulphate (mg/L)	606	8	5	20
Sodium (mg/L)	3,520	374	248	200
Iron (mg/L)	<0.05	<0.05	<0.05	0.2
Magnesium (mg/L)	32.9	1	1	30
Hardness (mg $CaCO_3$/L)	2,443	16.6	16.6	6–500

system by the RO method using the same membranes (Table 6).

3.3. Results of the scaling prognosis

The prediction of membrane scaling was carried out for the selected mining water streams. The results are shown in Figs. 6–8.

The raw mining water (after the initial treatment) showed undersaturation relative to the carbonate minerals, that is, aragonite ($CaCO_3$), calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), and therefore it was not dangerous for the membrane lifetime. This was confirmed by the scaling prediction for raw mine water (Figs. 6–8). At the same time, the mine water showed an equilibrium in relation to the siliceous forms of minerals such as: chalcedony (SiO_2), quartz

Table 6
Parameters of desalinated water produced during single-stage RO desalination system (raw water: mine water after the initial treatment, water recovery rate: 50%, pressure 3.0 MPa, temp. 25°C)

Parameter	Raw water	Membrane RO: BW 30 FR-400			Membrane RO: PA00416 HR		
		Permeate	Retentate	*R* (%)	Permeate	Retentate	*R* (%)
pH	6.27[a]; 5.90[b]	6.66	6.79	–	6.04	7.22	–
Eh (mV)	130	244	268	–	275	250	–
Conductivity (mS/cm)	53.7[a]; 51.4[b]	6.77	72.3	87.4	11.1	69.3	78.4
TDS (g/L)	42.1	3.54	47.8	91.6	6.2	47.8	85.3
Total hardness (mg $CaCO_3$/L)	4,594	527	9,864	88,5	432	5,845	90,6
Total hardness (mval/L)	91.9	10.5	197	88.6	8.64	117	90.6
Na^+ (g/L)	16.8	1.45	22.9	91.4	2.0	17.2	85.7
K^+ (mg/L)	174	24	340	86.2	38	217	78.2
Ca^{2+} (mg/L)	589	170	1,356	71.1	99	754	83.2
Mg^{2+} (mg/L)	760	25	1,576	96.7	45	964	94.1
Ba^{2+} (mg/L)	0.566	<0.05	0.547	91.2	<0.05	0.516	91.2
Sr^{2+} (mg/L)	16.8	0.306	18.2	98.2	0.642	18.5	96.2
Fe^{2+} (mg/L)	<0.05	<0.05	<0.05	–	<0.05	<0.05	–
Mn^{2+} (mg/L)	1.01	<0.05	0.289	95.05	<0.05	0.624	95.05
Cl^- (g/L)	32.5	2.55	5.53	92.2	4.15	35.1	87.2
Br^- (mg/L)	55.0	7	105	87.3	10	61	81.8
SO_4^{2-} (mg/L)	554	43	1169	92.2	62	802	88.8
HCO_3^- (mg/L)	2.3	0.4	2.46	82.6	0.34	2.12	85.2
SiO_2 (mg/L)	8.03	0.609	6.91	92.4	0.988	5.86	87.7
B (mg/L)	1.51	0.9	1.1	40.4	0.938	1.05	37.9
Alkalinity (mval/L)	2.3	0.4	2.4	–	0.34	2.12	–
Acidity (mval/L)	0.18	0.05	0.2	–	0.105	0.16	–

R – Retention coefficient.
[a]Membrane BW 30 FR-400, [b]membrane PA00416 HR.

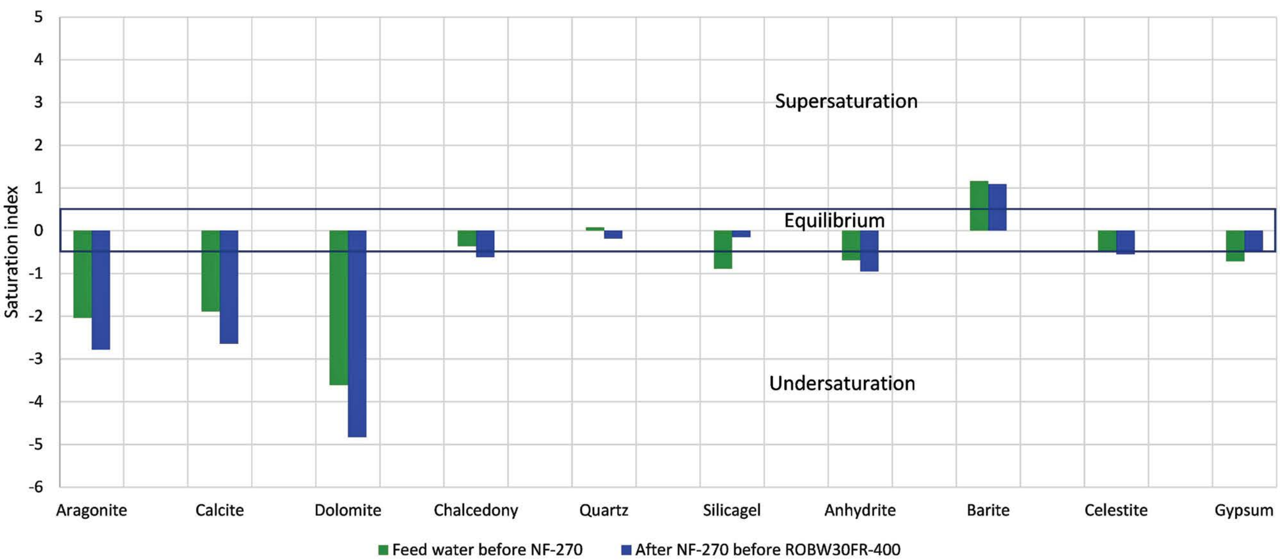

Fig. 6. The saturation index in relation to the carbonates (aragonite, calcite and dolomite), siliceous forms (chalcedony, quartz and silica gel) and sulphate mineral forms (anhydrite, barite, celestite and gypsum) for the raw mine water fed to the NF-270 membrane, and water after NF fed to the RO BW30FR-400 membrane (transmembrane pressure: 1.0 MPa for NF, 2.0 MPa for RO, water temperature, respectively, 23°C for NF and 23.5°C for RO).

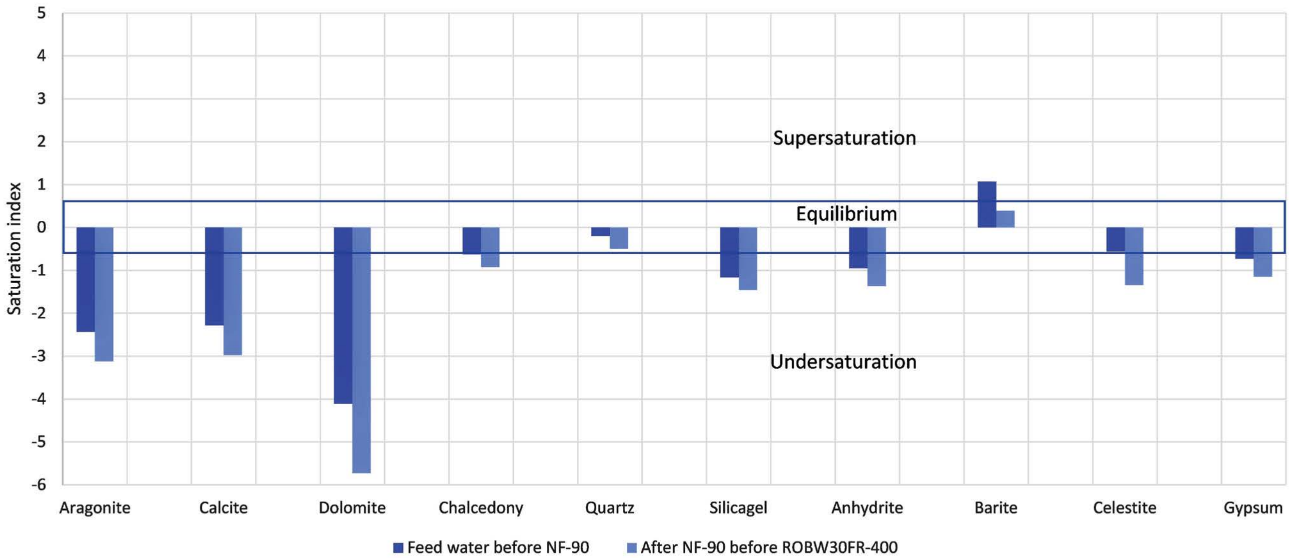

Fig. 7. The saturation index in relation to the carbonates (aragonite, calcite and dolomite), siliceous forms (chalcedony, quartz and silica gel) and sulphate mineral forms (anhydrite, barite, celestite and gypsum) for raw mine water fed to the NF-90 membrane, and water after NF fed to the RO BW30FR-400 membrane (transmembrane pressure: 1.0/2.0/3.0 MPa for NF, 3.0 MPa for RO, the temperature of the water, respectively, 24°C for NF and 26°C for RO).

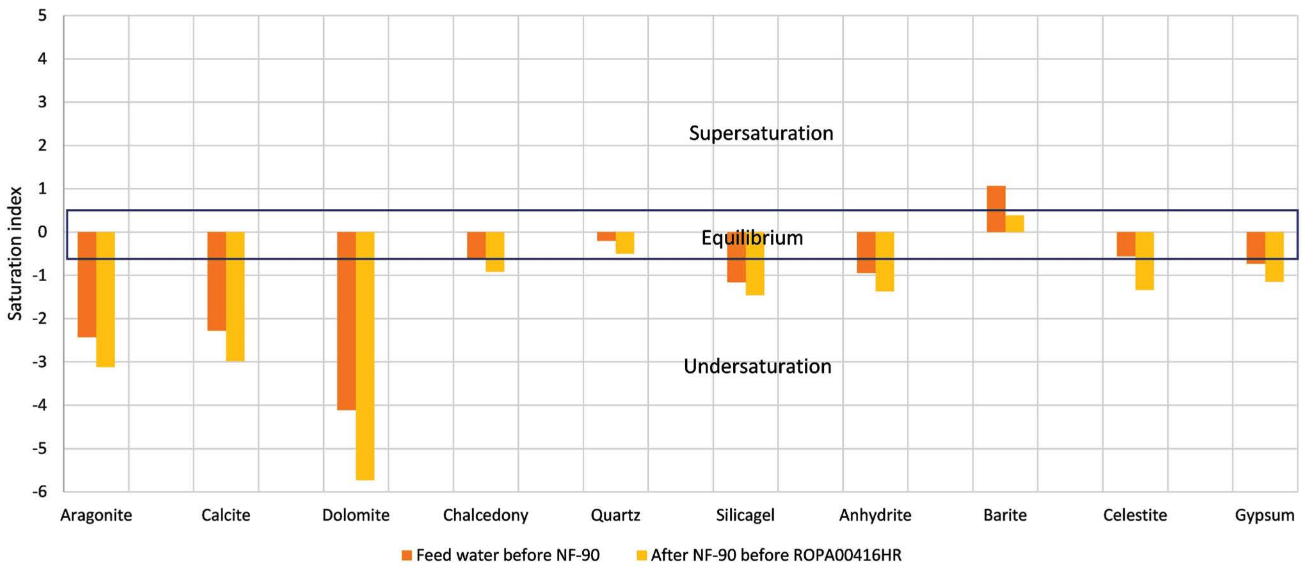

Fig. 8. The saturation index in relation to carbonates (aragonite, calcite and dolomite), and siliceous forms (chalcedony, quartz and silica gel) and sulphate mineral forms (anhydrite, barite, celestite and gypsum) for raw mine water fed to the NF-90 membrane, and water after NF fed to the PA00416HR RO membrane (transmembrane pressure: 3.0 MPa for NF, 30 bar for RO, water temperature, respectively, 25°C for NF and 25°C for RO).

(SiO_2) and undersaturation in relation to silica-gel (SiO_{2gel}) (Figs. 6–8).

Application of the NF as a pretreatment method allowed to reduce the concentration of bivalent ions before second stage treatment using RO membrane, but it did not contribute to significant changes in terms of the possibility of potential membrane scaling by silica compounds, and, in particular, by the minerals as chalcedony and quartz. The equilibrium of the water in relation to these minerals could result in the precipitation of secondary siliceous deposits and polarisation in the case of a high concentration [9]. Modelling of the geochemical state of saturation of mine waters after treatment with NF membranes showed a supersaturation of the concentrate solution in relation to hardly soluble barite ($BaSO_4$) (Fig. 6–8) and an equilibrium relative to other sulphate mineral forms, such as celestine ($SrSO_4$) and gypsum ($CaSO_4$). Therefore, there is a risk of precipitation of barium sulphate (Fig. 9) on the NF membrane.

The results of the research on the efficiency of rejection of sulphate and other ions in the NF process showed a much

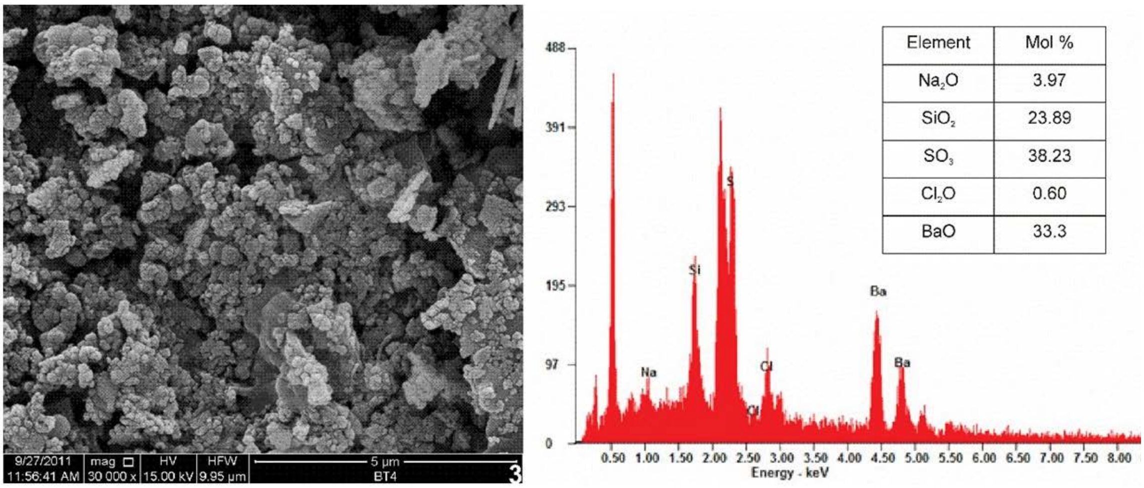

Fig. 9. Example of barium sulphate ($BaSO_4$) sediment precipitated on the RO membrane (on the basis [9]).

higher effectiveness of the NF-90 membrane compared with the NF-270 membrane. The performed experiments agreed with the predicted membrane scaling. The application of NF using the NF-90 membrane would allow to protect the membranes used in water desalination by means of an RO process from a secondary precipitation of sediments from a group of sulphate minerals (Figs. 7 and 8) on their surface. The application of the membrane NF-270 would not allow one to obtain such beneficial effects (Fig. 6).

An estimate of membrane scaling, taking into account the physical conditions during the implementation of laboratory tests (pressure, temperature, pH, Eh), was carried out. There was no confirmed impact of the operating pressure on the saturation state of relevant minerals. On the other hand, the temperature of the treated water, pH and Eh had a significant impact on the predicted results. These factors guide the course of thermodynamic reactions. Previous studies of the authors, implemented on the basis of the geothermal waters [8,15], showed a high correlation of geochemical modelling results with identified sediments on the membranes after the filtration processes.

4. Conclusions

- The NF could be an appropriate pretreatment step in the treatment of mine water using the RO process.
- NF membranes used should be more compact compared with the standard NF membrane.
- A comparison of the two NF membranes shows that NF-270 membrane allowed for non or very poor water demineralisation, while the NF-90 membrane enabled partial (significant) demineralisation, especially in regard to divalent ions.
- Among tested NF membranes of different compactness (NF-270 and NF-90), the more compact membrane (NF-90) should be used, because it should prevent scaling.
- The use of these membranes as a pretreatment step for RO membrane (NF + RO) gives lower permeate flux in the NF process, while the flux in the RO process is improved in reference to single-stage RO system.
- Water obtained after the second stage of the treatment (RO membrane) almost meets the requirements for drinking water and it can be used as a technological water.
- The scaling prognosis showed that the application of the NF, equipped with a more compact membrane, for example, Dow Filmtec NF-90, allowed to protect the RO membranes against a secondary precipitation the carbonate, silicate and sulphate minerals on their surface, while barite shows supersaturation.

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