Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22601

128 (2018) 96–105
October

Integration of nanofiltration and reverse osmosis in desalination of mine water

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Received 3 April 2018; Accepted 5 June 2018

ABSTRACT

The research with natural mine waters coming from Desalination Plant 'Dębieńsko' (Southern Poland), taken before reverse osmosis (RO) installation, that is, after standard pretreatment, was carried out. Commercial nanofiltration (NF) membranes produced by the Dow-Filmtec (NF-90) and RO membranes (SW30-2521 of Dow-Filmtec and AD HR-90 by GE) were used in the test. The NF process was carried out at a transmembrane pressure of 1.0 and 1.5 MPa and the RO process at a pressure of 2.5 and 3.0 MPa, depending on the system used. Tests were conducted using the Osmonics Inc. company's SEPA CF-HP type membrane module, in the high-pressure version in crossflow mode and in some cases in the dead-end mode system. A two-stage treatment system combining NF and RO for the desalination of mine water was used. The desalination efficiency (flux and composition of permeate and concentrate) was determined. The obtained results proved that NF could be an ideal pretreatment step for mine waters during RO desalination process. It enabled to increase the permeate flux of the RO membrane, eliminated the scaling problem and increased the concertation of salt in RO retentate. The use of the NF-90 membrane in the NF + RO desalination system resulted in a lower permeate flux in the NF process, while the flux in the RO process was higher in comparison to the system without NF. Taking into consideration the membrane efficiency results, one can conclude that permeates coming from mine water corresponded to the permissible values for drinking water standard. In addition, water was nontoxic.

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

1. Introduction

Draining of saline water from the coal mines of the Upper Silesia (south part of Poland) to the river systems of Oder and Vistula (Poland) contributes to permanent deterioration of water pollution. So high salinity impacts the biocenosis of water, its degradation and it is toxic to flora and fauna of the aquatic environment. The salinity of waters, which are drained from mines, is varied, but the main components are sodium, potassium, calcium, magnesium, chlorides, sulphates, carbohydrates, iodides and bromides ions, and also a variety of micropollutants, which are toxic for the life of the hydrosphere. Among the 30 indicators, which are used to assess the quality of the mines waters in Silesia, 9 of them are listed: nitrogen in the ammonium form, sodium, iron, potassium, chlorides, sulphates, bar, boron and pH, as their content usually is exceeded by several times, including sodium, chlorides and bar from a few hundred to a thousand times [1–4]. Since 2007, an increase in the amount of chlorides and sulphates discharged by the mines has been noticed and its maximum has reached 4,183.2 T/d. In 2008, 3,496.9 T/d of salt was introduced to surface waters, and 2/3 of it was deposited to the Vistula river basin [1–4].

The salinity in the water first of all creates the adverse effect not only on the aquatic environment (direct impact),

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Presented at the XII Scientific Conference 'Membranes and Membrane Processes in Environmental Protection' – MEMPEP 2018 13–16 June 2018, Zakopane, Poland.

but also on the economy (direct and indirect impacts). It reduces the amount of microorganisms, which are responsible for water self-cleaning, decreases their enzymatic activity and increases the activity of microorganisms resistant to salinity. In addition, excessive salinity of water contributes to the corrosion of machinery and equipment, which are in contact with water [2]. It should be therefore concluded that pit mining waters, especially those strongly salted, cause significant changes to surface water biocenosis in relation to the environmental conditions that are considered natural. There are measurable losses, which, however, are extremely difficult to estimate and these results of the uselessness of such waters for economic purposes, agriculture and forestry. For example, the drinking water supplied to the regions of Upper Silesia and Cracow (south part of Poland) already has to be transported from great distances.

Considering the earlier, it is necessary to apply a variety of methods to reduce the impact of mining waters salinity on the environment. One of them is water desalination.

Reverse osmosis (RO) is a membrane separation process, in which the membrane is permeable to fresh water, while it is resistant to soluble salts permeation. The resistant is assured by the use of pressure higher than the osmotic pressure of sea or brackish water. During the process, two fractions are obtained: pure water (permeate) and concentrated salts solution (retentate or concentrate). The effectiveness of the process depends on operational parameters, membrane properties and raw water characteristics [5–9]. The transmembrane pressure, which is necessary, reaches the values up to 5–6 MPa for strongly saline water and approximately 2 MPa for brackish water. The operating problem with the RO process, related to its performance, is an irreversible persistence limiting membrane permeability, so-called fouling, which is a deposition of a substance (suspended particles, colloids, soluble macromolecular compounds and salts) on the surface of the membrane and/or in the pores. Therefore, the initial cleaning of raw water and optimization of this procedure are required and essential for the correct operation of the RO modules. The second operating problem of desalination by RO is the membrane scaling, that is, deposition of $CaCO_3$, $CaSO_4$ and $BaSO_4$ on the membrane surface. The intensity of scaling depends, first of all, on water recovery rate. When this parameter is below 50%, the phenomenon can be effectively limited by adding the antiscalants into the water. Scaling reduces the usefulness of RO for desalination when water recovery rate is higher than 50% [10–14]. The application of RO for desalination of waters with salinity greater than 70 g/L and generation of a concentrate of salts concentration of more than 90 g/L is not justified [4]. Therefore, the introduction of nanofiltration (NF) for water desalination, before the RO, may be a key solution, which can allow to achieve a high water recovery rate, because it can eliminate the risk of crystallization of calcium sulphate and other minerals in the concentrated stream. The integrated system of NF and RO processes will allow to obtain in the concentrate (brine) of the concentration of salt, at least 150 g/L [4,5]. This solution is important, if the concentrate from the RO is further concentrated in evaporators, and crystallization of salts takes place. NF membranes remove almost all polyvalent ions, while the monovalent ones are rejected only at 10%–50%, depending on the type of membrane NF. In such a situation, water transferred to the RO modules has lower osmotic pressure than the raw water and thus, RO membranes can work at a lower pressure and a higher water recovery rate. Due to this solution it will be possible eventually resign of the second degree of RO, normally applied in the conventional desalination system, because the concentration of solute substances in the permeate produced by the first RO step is approximately 200 mg/L. The use of the NF in the desalination technology, before the main process of desalination, is particularly justified in the case of higher content of bivalent ions.

The NF is considered to be as one of the most promising techniques for production of high-quality water from surface and brackish waters, and there are many examples of the use of this method in practice, especially in the drinking water industry [15,16]. NF belongs to the pressure membrane processes and involves membranes of a cut-off between the RO and ultrafiltration. The retention usability of NF membranes depends not only on the pore size (0.5–1.5 nm), but also of their electric charge [17,18]. The mechanism of NF membrane retention can be a combination of the spherical effects, the Donnan phenomenon and dielectric effects. NF has a few advantages over RO, such as lower operating pressure, higher flux and lower investment and exploitation costs. Due to these properties, the NF is considered to be a proper process for initial treatment of water for desalination, especially for waters with high hardness and high concentration of sulphates and carbonates [19–24].

The objective of the work is based on the assumption that the introduction of NF process to water desalination by RO will allow to obtain the concentration of salt in the concentrate (brine) much larger than by the desalination by using the RO method only. Furthermore, it will allow to obtain the desalinated water and the concentrate of the composition, which can be set in advance.

2. Experimental

The research was carried out using the natural mine water coming from the Desalination Plant 'Dębieńsko,' situated in the Silesian Voivodship at South of Poland, characterized by a relatively high hardness. Samples of raw water were taken prior to their introduction to RO installation, that is, after the standard initial preparation (Fig. 1). These treatments are designed to protect the RO membranes against fouling. Raw waters are heavily contaminated biologically and physically (mainly by clay – carbon suspended matters) therefore, their preparation requires application of series of operations. After correction of the pH, a coagulant (alumina) and a polymer P-26 are added to the mixing chamber to assist the process of flocculation, followed by the addition of sodium hypochlorite to disinfect the water. Build-up of flocs takes place in four flocculation chambers equipped with slow speed mixers. After the initial mechanical purification, water is directed to the two anthracite-sand bed filters, where the exact removal of the rest of suspension takes place. Sodium metabisulphite is added to the decontaminated water, in order to eliminate the excess of free chlorine, because the maximum chlorine content, which is tolerated by the membrane material, may not exceed 0.05 mg/L. In addition, the process of water dechlorination is supported by the active

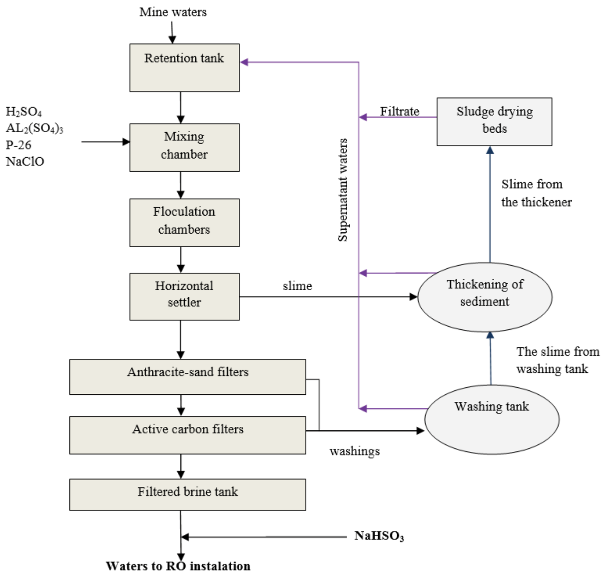

Fig. 1. Diagram of mine water pretreatment.

carbon filters, which, like two bed filters, are periodically washed in countercurrent by filtered brine. Initially purified waters are transferred to the RO installation, while desalinated waters are discharged into the river Bierawka and the concentrate is directed to the thermal installation.

The water used to tests characterized by a relatively high hardness of about 170 mval/L and mineralization around 42 g/L. Complete physical characteristics of the tested water are presented in Table 2. According to the Altowski–Szwiec classification, the examined water was included to the type of SO_4-Cl-Na-Ca [25]. In addition, the water contained high content of magnesium (1,124 mg/L), strontium (16.0 mg/L), bromides (118 mg/L), potassium (135 mg/L) and strontium (16 mg/L) and has pH in the range of approximately 6.6.

Mine water desalination was carried out in the two-stage system, integrated NF and RO processes. At first, the NF of raw water was carried out, and the resulting permeate was introduced to the RO module, as a feed water. Both processes, NF and RO, were carried out to obtain the designed water recovery rate. Desalination efficiency was specified by measuring the permeate flux (process efficiency) and physicochemical composition of feed water, permeate and concentrate.

Tests were carried out using the large laboratory module of the company Osmonics Inc. (USA) SEPA type CF-HP, in its high-pressure version in a 'cross-flow' system. The diagram of the apparatus used in the process of RO and NF is displayed in Fig. 2. Transmembrane pressure for NF was 1–2 MPa, and for RO it was 2–3 MPa, while the linear velocity above the surface of the membrane was 1 m/s and the temperature 23°C ± 3°C. The raw water was pumped from the reservoir by high pressure pump and valve to the membrane module SEPA CF-HP. The membrane module had the shape of a rectangle (190 × 140 mm) and it was installed at the bottom of the membrane cell. Part of the solution passed through the membrane and it was directed to the permeate receiver, while concentrate flew through the rotameter back to the raw water tank. The membrane process was also carried out in the dead-end mode. For this purpose, the pressure device

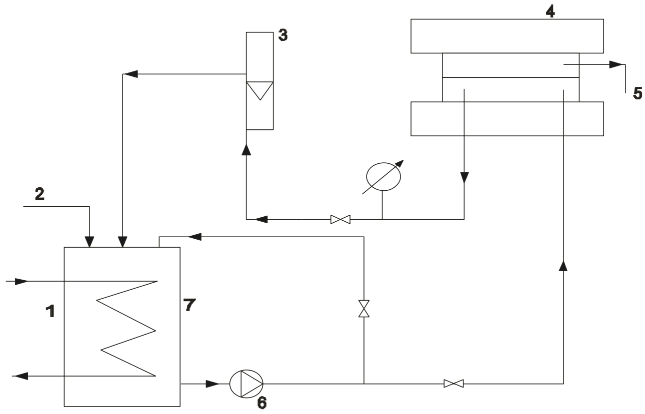

Fig. 2. The diagram of the apparatus for NF and RO experiments performance in 'crossflow' mode (1-heat exchanger; 2-raw water; 3-rotameter; 4-membrane cell; 5-permeate outflow; 6-pump and 7-raw water tank).

consisting of a steel cell with a capacity of 400 cm^3 (Fig. 3) and a magnetic stirrer was used.

Commercial NF membranes produced by Dow-Filmtec (NF-90) and two RO membranes type SW30-2521 (Dow-Filmtec) and AD HR-90 (General Electric) were used in

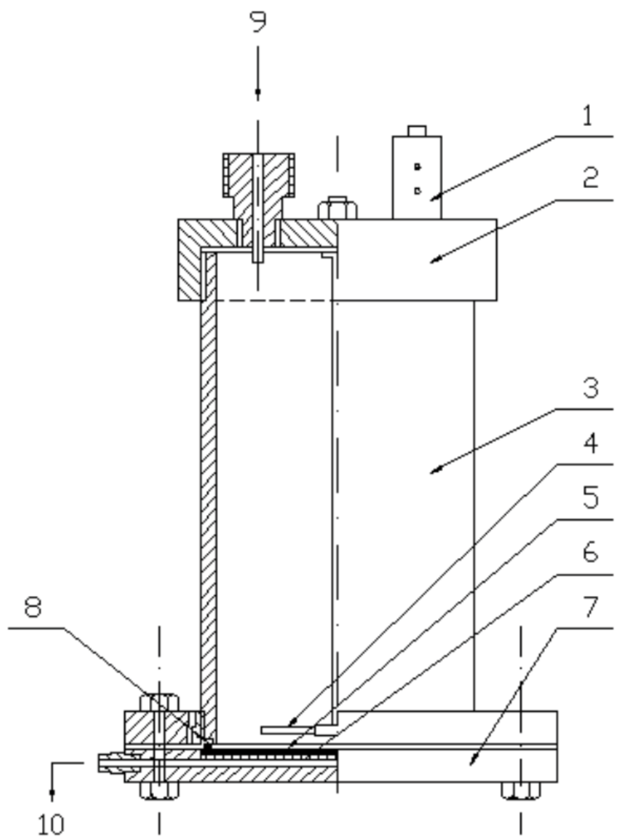

Fig. 3. The schematic diagram of the stirred cell device used in the reverse osmosis process (1-safety valve; 2-top cover; 3-pressure cylinder; 4-magnetic stirrer; 5-membrane; 6-perforated plate; 7-lower cover; 8-gasket; 9-gas supply and 10-permeate discharge).

the research. Physicochemical properties of membranes are shown in Table 1.

The quality of the feed and desalinated water was measured by the permanent 'on-line' analysis of unstable physical parameters, that is, temperature, pH and specific electrical conductivity. The measurement of the pH was made by the electromagnetic method, immediately after sampling water from the installation. Determinations of inorganic components were made in an accredited laboratory in the Institute of Environmental Engineering, Polish Academy of Sciences, Zabrze, Poland by using ion chromatography, while the content of Fe and Mn by the atomic absorption spectrometry method. Alkalinity and acidity of water were determined by titration method, in accordance with the test procedures, while the dry residue was determined by the weight method.

Purified water coming from integrated NF + RO processes and RO unit processes was also assessed for the toxicity using Microtox® biotest. The test procedure is based on the measurement of the intensity of bioluminescence of the indicator bacteria in the relation to the control sample that contains no toxicants (2% NaCl). As bioluminescence organisms, bacteria *Aliivibrio fisheries* of sensitivity to a broad range of toxic substances were used. During exposure of the indicator microorganisms to toxic substances in the aquatic environment, reduction of microorganisms' populations takes place, which in turn changes the intensity of the light emitted by the bacteria [26]. The analysis was performed using Microtox Analyzer Model 500 company Tigret (Warsaw, Poland). The exposure of bacteria to test samples was 15 min.

The assessment of the saturation state of mine water in relation to minerals, that could potentially cause membranes scaling, was performed by using program PHREEQC (*Phreeqc Interactive 3.3.3-10424* – PHREEQCI – Wateq4f minerals database) [27].

The SI (*saturation index*) value of each mineral was calculated from the activities of dissolved species: simple ions, ionic pairs and complexes. The overall formula for any mineral represented as '*k*' is given in Eq. (1) [26]:

$$\mathrm{SI} = \log\left(\frac{Q}{K}\right)_k = \log Q_k - \log K_k$$

where SI – saturation index of each mineral, Q – the product of the real ionic concentration of components participating in a dissolution/precipitation reaction of a given mineral, K – the equilibrium constant resulting of the law of mass action and/or the solubility product for a specific temperature of reaction between a mineral and its solution. To determine saturation state (equilibrium, undersaturation and supersaturation), the value of SI for each mineral is used. The mineral is at the thermodynamic equilibrium between the precipitate and solution when SI = 0. The SI values above and below 0 refer to supersaturation and undersaturation states, respectively. It is assumed that in natural conditions, the equilibrium state between water and mineral corresponds to SI values ±5% log K (SI = 0 ± 0.05 log K). The supersaturation state indicates on a trend of precipitation of a given mineral from water, while the undersaturation state corresponds to the dissolution of a given mineral and a transition of its components from reservoir rock to water [27,28].

The SIs for mine raw water before NF and for permeate after NF and before process RO were calculated. The calculations were included for:

- mine raw water used in the NF process;
- permeate after the NF using membranes NF-90 and before the RO process using membranes RO SW 30-2521 and
- permeate after the NF using membranes NF-90 and before the process of RO using membranes RO AD HR-90.

3. Results and discussion

3.1. Process efficiency

Our previous studies have shown that NF is an appropriate mean for pretreatment of mine water in the process of desalination with RO method [29,30]. Such a solution increases the permeate flux of RO membranes, eliminating the scaling problem. Hence, during the NF, the multivalent ions and, to some extent, sodium chloride removal occurs, and water directed to RO process characterizes by much lower ionic strength than the raw water. The consequence is lower osmotic pressure and, therefore, we can apply lower transmembrane pressure, which leads to a reduction of the energy consumption and increases the degree of water recovery rate. Taking into account the results of the efficiency of the membrane and the prediction of scaling phenomenon, with two NF membranes (open NF-270 and compact NF-90), it was found that in the first stage of the desalination more compact

Table 1
Membrane characteristics (manufacturers' data)

Membrane	NF-90	RO SW30-2521	RO AD HR-90
Producer	Dow Filmtec	Dow Filmtec	General Electric
Membrane material	Polyamide thin-film composite	Polyamide thin-film composite	Polyamide thin-film composite
Molecular weight, cut-off (Da)	200–400	–	–
Operating pressure (MPa)	Max. 4.1	Operating 5.5 max. 6.9	Max. 8.27 operating 5.5
pH range	2–11	2–11	4–11
Max. operating temp. (°C)	45	45 35 (pH > 10)	50
Retention coefficient	>98% $MgSO_4$ 90%–96% NaCl	99.4% NaCl	Average 99.75% NaCl Min. 99.3% NaCl

NF membrane (NF-90 company Dow Filmtec) should have been used [29,30]. NF-90 membrane characterized with high retention rates and lower performance compared with the membrane of the NF-270 [29,30]. However, in the second stage of desalination stage, with the use of RO membrane for brackish water desalination, the received permeate exceeded content of the sodium and chloride ions compared with the standards for drinking water [31].

Thus, at this investigation, a more compact NF membrane (NF-90 Dow Filmtec) and two more compact RO membranes for desalination saline waters (sea) (SW30-2521-Dow-Filmtec and AD HR-90 General Electric) to the desalination of mine water in a two-stage system were used. Figs. 4–6 show changes of relative permeate flux (J/J_0). Experimental data of the permeability of the NF-90 membrane showed that relative permeate flux was rather low and throughout the whole period of its operation decreased from 0.06 to about 0.02 (Fig. 4). This was confirmed by the high retention rates of most water physicochemical components obtained for this membrane (Tables 2 and 3). The results of the NF conducted in the crossflow and the dead-end modes were similar, though a bit higher fluxes were obtained in the dead-end mode, which was due to the higher transmembrane pressure used.

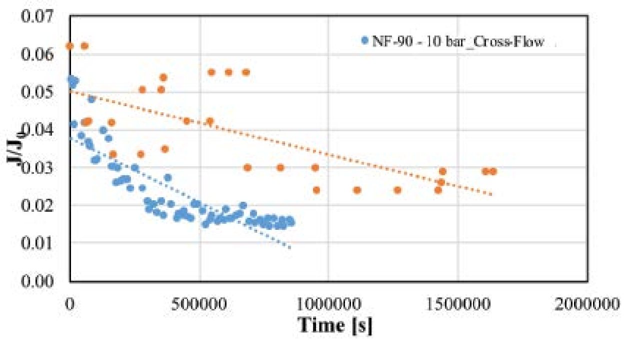

Fig. 4. Changes of the relative permeate flux during nanofiltration process using NF-90 membrane carried out in crossflow and dead-end mode; J_0–volumetric flux of deionized water, J–volumetric permeate flux during the mine water treatment with NF and RO.

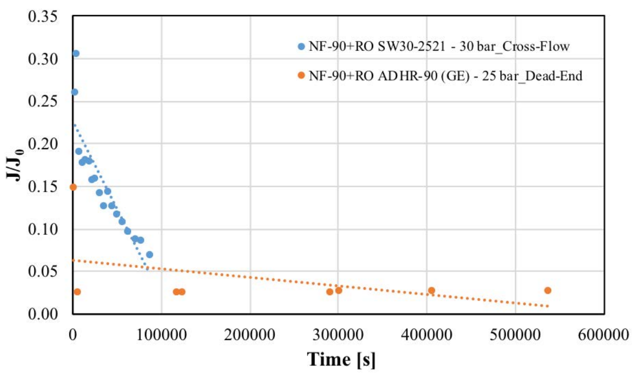

Fig. 5. Changes of the relative permeate flux during two-stage mine water desalination (NF + RO) using RO membranes.

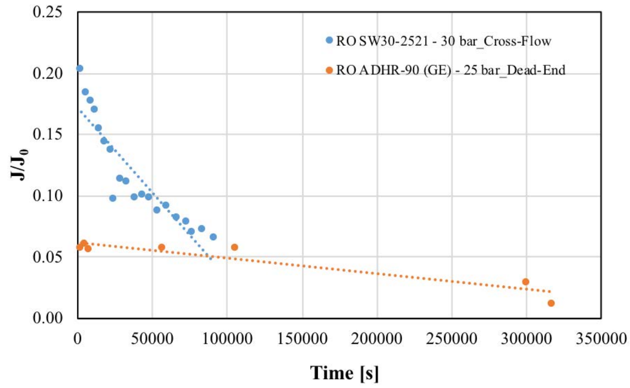

Fig. 6. Changes of the relative permeate flux during desalination of mine water using RO SW30-2521 (transmembrane pressure: 30 bar) and RO AD HR-90 (transmembrane pressure: 25 bar).

For the integrated NF + RO system, conducted in the crossflow mode (NF-90 and SW30-2521 membranes), the relative permeate flux amounted to 0.1–0.25 and was significantly higher compared with the integrated process carried out in dead-end mode using NF-90 and AD HR-90 General Electric membranes (Fig. 5). The crossflow process differs from the filtration in the dead-end mode. In the latter, the raw water (retentate) flows perpendicular to the surface of the membrane, which promotes the formation of filter cake on the membrane surface. In crossflow filtration mode, the feed flows tangentially to the surface of the membrane. The main advantage of this method of operation is that the filter cake (which may cause fouling) is washed out during the filtration process, increasing the lifetime of the membrane.

Additionally, it should be noted that the permeate fluxes in RO process in the integrated NF90 + RO were higher than ones obtained for the same RO membranes in a unit RO process (Figs. 4 and 5).

3.2. *The efficiency of desalination*

Tables 2–4 show the physicochemical parameters of raw mine water and permeate obtained during NF in first stage of desalination and osmotic membranes SW 30-2521 and AD HR-90 in second stage, including the retention rates of particular contaminants.

In the first stage of desalination (NF-90 membrane), the retention coefficients of bivalent ions were high and, in general, ranged between 70% and 90%, with slightly lower removal of sulphate ion (SO_4^{2-} – 65.5% in crossflow and 46.8% in dead-end mode). It should be noted to the high removal of total hardness (86.5%–88.5%) as well as calcium and magnesium (89.7%–91.4% and 83.9%–86.1%, respectively). The removal of monovalent ions was lower, that is, chloride 20% (crossflow) and 30% (dead-end), while rejection of HCO_3^- exhibited a higher level of approximately 54% (crossflow) and 42% (dead end) (Tables 2 and 3). NF-90 membrane manufactured by the Dow Filmtec™ company provides high efficiency removal of salts, at low transmembrane pressure, which corresponds to a partial demineralization of water. It is usually used in water softening, due to the high value of

Table 2
The results of a two-stage desalination system using NF and RO membranes (raw water: mine water after the initial treatment, NF membrane: NF-90, RO membrane: SW 30-2521, water recovery rate: 50% and transmembrane pressure: 10 bar for NF, 30 bar for RO); *R* – retention coefficient

Parameter	Raw water	Nanofiltration			Reverse osmosis			
		Concentration		*R* (%)	Concentration		*R* (%)	
		Permeate	Retentate		Permeate	Retentate	To NF permeate	To raw water
pH	6.60	7.56	7.24	–	7.00	7.44	–	–
Eh (mV)	231	236	–25.5	–	–55.3	6.5	–	–
Conductivity (mS/cm)	58.2	52.8	104	9.27	4.15	55.4	92.1	92.9
TDS (g/L)	42.0	37.2	82.1	11.4	2.16	37.7	94.2	94.9
Total hardness (mval/L)	171	23.0	236	86.5	0.81	26.3	96.5	99.5
Na^+ (g/L)	13.1	12.3	25.1	6.10	0.827	13.0	93.3	93.7
K^+ (mg/L)	196	135	666	31.1	13.3	289	90.1	93.2
Ca^{2+} (mg/L)	1,575	162	1,430	89.7	6.58	186	95.9	99.6
Mg^{2+} (mg/L)	1,124	181	2,002	83.9	5.86	207	96.8	99.5
Ba^{+2} (mg/L)	0.504	0.171	0.719	66.1	0.05	0.149	70.8	90.1
Sr^{2+} (mg/L)	15.8	4.53	44.8	71.4	0.143	5.1	96.8	99.1
Fe^{2+} (mg/L)	<0.05	<0.05	7.80	–	<0.05	0.186	–	–
Mn^{2+} (mg/L)	0.464	0.127	0.731	72.6	<0.05	0.29	60.6	89.2
Cl^- (g/L)	25.2	22.1	54.0	12.3	1.44	23.5	93.5	94.3
Br^- (mg/L)	118	100	42.4	15.2	1.1	25.6	98.9	99.1
SO_4^{2-} (mg/L)	524	279	1,264	46.8	33.2	206	88.1	93.7
HCO_3^- (mg/L)	121	56.1	165.0	53.6	13.4	76.3	76.1	88.9
SiO_2 (mg/L)	7.48	1.46	6.39	80.5	<0.1	2.42	93.2	98.7
Boron (mg/L)	0.947	1.0	11.1	–	0.42	1.22	58.0	58.0

Table 3
The results of a two-stage desalination system using NF and RO membranes (raw water: mine water after the initial treatment, NF membrane: NF-90, RO membrane: AD HR-90, water recovery rate: 50% and transmembrane pressure: 10 bar for NF, 25 bar for RO); *R* – retention coefficient

Parameter	Raw water	Nanofiltration			Reverse osmosis			
		Concentration		*R* (%)	Concentration		*R* (%)	
		Permeate	Retentate		Permeate	Retentate	To NF permeate	To raw water
pH	6.60	7.57	7.15	–	6.91	7.74	–	–
Eh (mV)	231	–71.8	–84.4	–	57.1	21.1	–	–
Conductivity (mS/cm)	58.2	40.6	72.9	30.2	11.3	62.7	72.2	80.6
TDS (g/L)	42.0	26.45	56.0	37.0	6.32	44.5	76.1	85.0
Total hardness (mval/L)	171	19.6	156	88.5	2.87	34.7	87.4	98.3
Na^+ (g/L)	13.1	9.11	16.25	30.5	2.34	17.7	74.3	82.1
K^+ (mg/L)	135	199	292	–	31.3	364	84.3	76.8
Ca^{2+} (mg/L)	1,575	136	1,030	91.4	23.8	240	82.5	98.5
Mg^{2+} (mg/L)	1,124	156	1,279	86.1	20.4	277	86.9	98.2
Ba^{+2} (mg/L)	0.504	0.149	0.944	70.4	<0.05	0.237	66.4	90.1
Sr^{2+} (mg/L)	15.8	3.03	31.4	80.9	0.485	6.62	84.0	97.5
Fe^{2+} (mg/L)	<0.05	<0.05	0.332	–	<0.05	0.155	–	–
Mn^{2+} (mg/L)	0.464	0.074	0.386	98.4	<0.05	0.151	32.4	89.2
Cl^- (g/L)	25.2	17.5	33.7	30.6	4.35	29.3	75.1	82.7
Br^- (mg/L)	118	11.3	25.6	90.4	5.9	25.8	47.8	95.0
SO_4^{2-} (mg/L)	524	181	967	65.5	72.0	369	60.2	86.3
HCO_3^- (mg/L)	99.0	57.4	167	42.0	17.7	84.8	69.1	82.1
SiO_2 (mg/L)	7.48	3.88	13.6	48.1	0.89	6.5	77.1	88.6
Boron (mg/L)	0.947	1.02	1.11	–	0.66	1.26	35.3	30.3

Table 4
Results of single stage desalination using RO membranes (raw water: mine water after the initial treatment, water recovery rate: 30%–50% and transmembrane pressure 25–30 bar); *R* – retention coefficient

Parameter	Raw water	RO membrane SW 30-2521			RO membrane AD HR-90		
		Permeate	Retentate	*R* (%)	Permeate	Retentate	*R* (%)
pH	6.60	7.08	7.80	–	7.35	7.91	–
Eh (mV)	231	62.4	22.4	–	41.1	11.5	–
Conductivity (mS/cm)	58.2	11.1	68.1	80.9	35.0	78.2	39.9
TDS (g/L)	42.0	6.53	51.9	84.5	22.8	59.3	45.7
Total hardness (mval/L)	171	7.85	106	95.4	38.3	127	77.6
Na^+ (g/L)	13.1	2.28	15.1	82.6	7.33	14.9	44.0
K^+ (mg/L)	135	31.1	354	77.0	94.2	405	30.2
Ca^{2+} (mg/L)	1,575	56.3	651.5	96.4	270	796	82.9
Mg^{2+} (mg/L)	1,124	61.3	897	94.5	302	1,067	73.1
Ba^{2+} (mg/L)	0.504	0.063	0.607	98.75	0.282	0.764	94.4
Sr^{2+} (mg/L)	15.8	1.37	19.2	91.3	7.6	24	51.9
Fe^{2+} (mg/L)	<0.05	<0.05	1.61	–	<0.05	0.082	–
Mn^{2+} (mg/L)	0.464	<0.05	0.384	89.2	0.12	0.344	74.1
Cl^- (g/L)	25.2	4.23	29.6	83.2	14.8	33.5	41.3
Br^- (mg/L)	118	4.6	22.6	96.1	14.1	38.9	88.0
SO_4^- (mg/L)	524	72.3	699	86.2	160	765	69.5
HCO_3^- (mg/L)	99.0	20.7	120	79.1	60.4	150	39.0
SiO_2 (mg/L)	7.48	0.59	4.16	92.1	3.56	12.2	52.4
Boron (mg/L)	0.947	0.51	1.08	46.1	0.72	1.21	24.0

the removal of bivalent ions. Additionally, it has a moderate sodium chloride retention (>50%), while the NF-270 membrane is characterized by NaCl retention amounting most often to <50% [29,30].

In the second stage of desalination, using RO SW 30-2521 membrane, almost all ions were removed to a large extent, for example, TDS and conductivity retention was 95% and 93%, sulphates – 94%, chloride and bromide – 94% and HCO_3^- – 90% (Table 2). Slightly lower results were obtained for RO AD HR-90 GE membrane. Practically all retention rates were below 90%, that is, conductivity – 81%, TDS – 85%, chloride – 83%, bicarbonate ion – 82% and sulphates 86% (Table 3).

Both, the retention rates and values of particular physicochemical parameters were much lower in the case of a single-stage desalination system using RO process with the same membranes (Table 4). It showed the benefits of the application of two-stage system for water desalination (NF + RO), resulting of the initial removal of hardness and bivalent ions from water.

The obtained results provided a reduction of the scaling phenomenon in the second stage of desalination, that is, in the RO process, and at the same time the enabling the final water to meet the conditions set in the regulation on drinking water quality (Table 5) [31]. For this reason, at the first stage of mine water desalination, a relatively compact NF membrane, for example, membrane NF-90, should be applied and in the second stage, the membrane for desalination saline waters, is recommended.

This was also confirmed by the results of toxicological analyses of purified water samples obtained in the integrated NF + RO and single-stage RO processes, applied in the crossflow and in the dead-end systems. They showed a

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

Parameter	Integrated system NF + RO		Limit values for drinking water acc. norm [31]
	NF-90 + SW30-2521	NF-90 + AD HR-90	
Chloride (mg/L)	1.44	4.35	250
Manganese (mg/L)	<0.5	<0.5	0.05
Conductivity (mS/cm)	4.15	11.3	2.5
Sulphates (mg/L)	33.2	22.0	250
Natrium (mg/L)	0.810	2.340	200
Iron (mg/L)	<0.5	<0.5	0.2
Magnesium (mg/L)	5.86	20.4	30

Table 6
The change in toxicity of the samples

Sample	Inhibition of bioluminescence (%)		
	Dead-end mode	Cross-flow mode	Toxicity class [32]
Raw water	32.03		25.01–50.00 Low toxicity
NF-90 permeate	0	19.44	<25.00 No toxicity
NF90 + RO permeate: RO-SW30-2521 cross-flow mode RO-ADHR-90 dead-end mode	0	6.83	<25.00 No toxicity
RO permeate, unit process: RO-SW30-2521 cross-flow mode RO-ADHR-90 dead-end mode	0	1.19	<25.00 No toxicity

marked reduction in bioluminescence inhibition of the test organisms (Table 6).

3.3. The results of scaling prognosis

The study of membrane scaling prognosis was carried out for all tests of mining water desalination. Results are shown in Figs. 7–8.

The raw mining waters after the initial treatment show the saturation equilibrium related to the scaling minerals, that is, carbonate minerals: aragonite ($CaCO_3$), calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) and siliceous forms of minerals: chalcedony, quartz and the silica gel (SiO_{2gel}). It should not, therefore, constitute to a significant threat to the membrane scaling. The degree of saturation was only noted in respect of barite ($BaSO_4$). The applied process of initial treatment using NF-90 membrane, contributed to water softening, and in addition, the significant reduction of the saturation in respect to all the analysed forms of minerals: carbonates, siliceous and sulphates. In particular, the saturation reduction related to barite and quartz, that is, minerals that are difficult to remove from the membrane surface forming a sludge/shell, was obtained.

4. Conclusions

- NF process could be an appreciate pretreatment step for the RO desalination process of mine water.

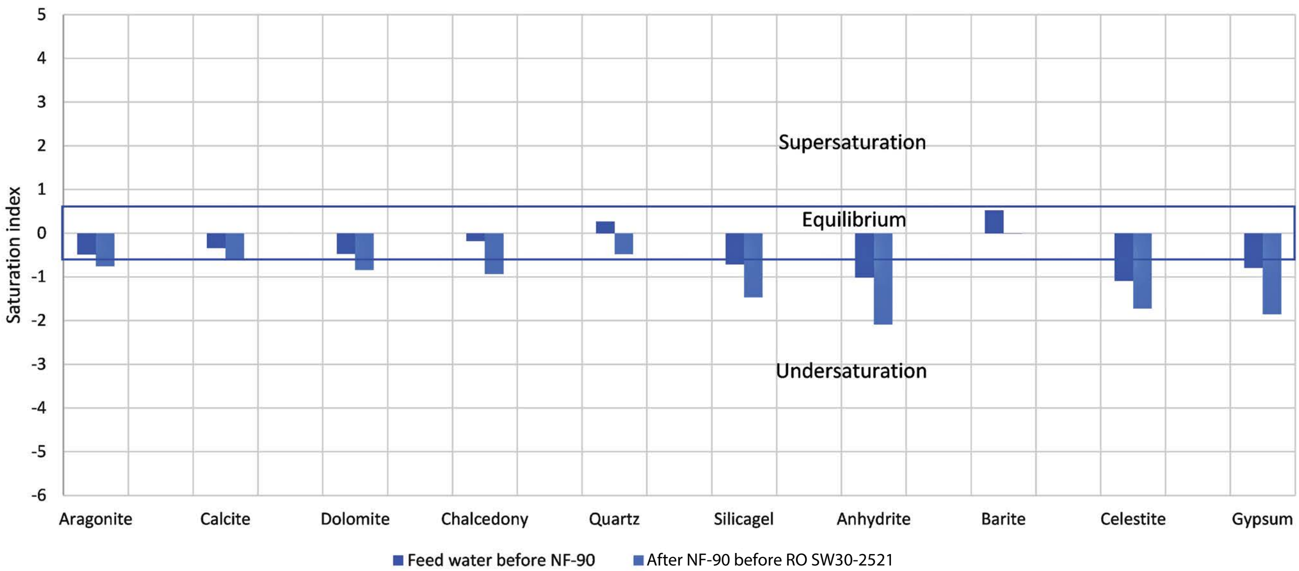

Fig. 7. The saturation index in relation to the carbonates (aragonite, calcite and dolomite), siliceous (chalcedony, quartz and silica gel) and sulphate mineral forms (anhydrite, barite, celestite and gypsum) for the raw mine water directed to the NF-90 membrane, and water after NF directed to the RO SW 30-2521 membrane, (water recovery 50% for NF and 30% for RO, transmembrane pressure: 10 bar for NF, 20 bar for RO).

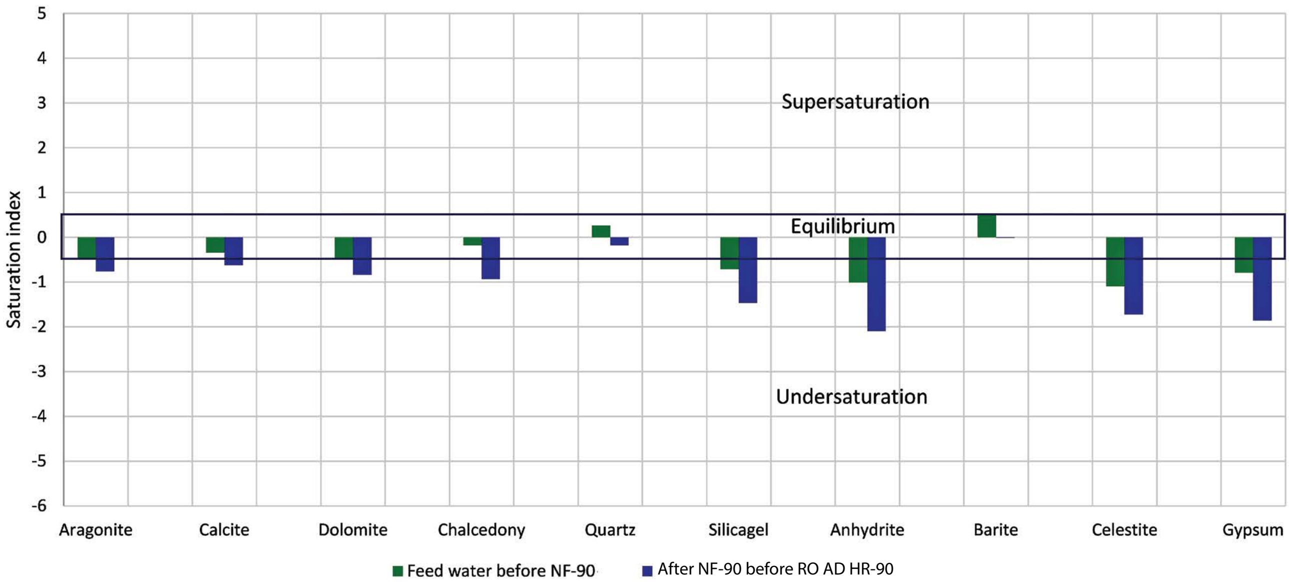

Fig. 8. The saturation index in relation to the carbonates (aragonite, calcite and dolomite), siliceous (chalcedony, quartz and silica gel) and sulphate mineral forms (anhydrite, barite, celestite and gypsum) for the raw mine water directed to the NF-90 membrane, and water after NF directed to the RO AD HR-90 membrane (water recovery 50%, transmembrane pressure: 10 bar for NF, 25 bar for RO).

- The selection of NF membranes, which should be more compact compared with standard NF membrane, is very important. For example, NF-90 membrane characterizes with partial (significant) demineralization, especially it removes divalent ions.
- The use of NF-90 membrane in integrated desalination system (NF + RO) gives lower permeate flux in the NF process, while the flux in the RO process is higher compared with the desalination system using single stage RO.
- In the second stage of desalination membrane for seawater desalination should be used.
- Scaling prognosis shows that application of the NF, equipped with more compact membrane, for example, Dow Filmtec NF-90, allows to protect the RO membranes against a secondary precipitation of carbonate, silicate and sulphate mineral forms on membranes surface.
- Obtained water after second stage of the desalination (RO membrane) meets the requirements for potable water or it can be used as a technological water.

Acknowledgements

This work was financed by statutory research of the Institute of Environmental Engineering Polish Academy of Sciences (Project no 1a-113/17) and by Ministry of Science and Higher Education Republic of Poland within statutory funds to the Institute of Water and Wastewater Engineering of the Silesian University of Technology. Part of the work was financed from AGH University of Science and Technology statutory research 11.11.140.031.

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