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Application of nanofiltration and electrodialysis for improved performance of a salt production plant

Marian Turek[a,*], Ewa Laskowska[a], Krzysztof Mitko[a], Marzena Chorążewska[b], Piotr Dydo[a], Krzysztof Piotrowski[a], Agata Jakóbik-Kolon[a]

[a]*Silesian University of Technology, Faculty of Chemistry, B. Krzywoustego 6, 44-100 Gliwice, Poland, Tel. +48 32 237 10 21; Fax: +48 32 237 22 77, email: marian.turek@polsl.pl*
[b]*Korea Fuel-Tech Poland Sp. z o.o., o/Żory, Przemysłowa 7, 44-240 Żory, Poland*

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ABSTRACT

Brines from coal mines are currently treated in a salt production plant with the use of thermal methods. To decrease the energy consumption and increase the salt recovery of the existing plant, the application of membrane processes – nanofiltration (NF), reverse osmosis (RO), electrodialysis (ED) – and chemical treatment was proposed. Based on the laboratory results, a hybrid NF-ED-RO system was designed, and the plant performance and the scaling risk were discussed. The result shows, that application of a membrane system could substantially improve the performance of a salt production plant.

Keywords: Evaporated salt production; Electrodialysis; Nanofiltration; Coal mine waters

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1. Introduction

Coal mining industry in Poland produces vast amount of brines, what generates the necessity of saline water utilization [1]. In Czerwionka-Leszczyny, Poland, the thermal desalination plant, formerly known as "Dębieńsko", treats water from nearby coal mines, simultaneously producing evaporated salt. The plant consists of two evaporators (brine concentrators) designed by the Resources Conservation Company in Seattle (RCC). Coal-mine brine is concentrated using vapor compression method, and next the evaporated salt and gypsum are crystallized [1,2]. Evaporators are powered with electrical energy, what makes their exploitation expensive; the energy consumption of brine concentrator (VC) is 44 kWh m^{-3} of distillate, while the energy consumption of brine crystallizer (RCC) is 66 kWh m^{-3} of distillate [3–5].

Membrane methods are widely considered in the production of the evaporated salts from brines, as they tend to be less energy consuming than conventional thermal methods. Turek et al. [6,7] have proposed an integrated ultrafiltration (UF) – nanofiltration (NF) – reverse osmosis (RO) – distillation – crystallization system for simultaneous production of desalinated water and evaporated salt. Drioli et al. [8,9] have proposed an integrated NF-RO-membrane crystallization system. Davis [10] has proposed a hybrid system, in which the RO retentate is treated by electrodialysis (ED). The ED diluate is then recycled back to the RO feed, whereas the ED concentrate is used for the crystallization of salt. Wallace [11] presented a similar system, in which NF-SWRO brine is treated by ED, after which the diluate is fed to a second stage of RO. Raman [12] has designed a NF-ED-RO system, in which the RO retentate is mixed with seawater and fed to the nanofiltration. Tanaka et al. [13] have described an integrated RO-ED-evaporation system, in which seawater RO brines are used for the production of edible salt.

To assess the performance of the plant, we have taken into account two brines, "A" and "B", resembling Polish coal mine waters especially problematic for the desalination and

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* Corresponding author.

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discharge to the environment. The composition of the coal mine brines is presented in Table 1. Brine "A" had total dissolved salts content (TDS) of 55 g L^{-1}, while for brine "B" it was TDS of 107 g L^{-1}. High salinity of coal mine waters occurs, because the seams of the coalfield lie in predominantly sandstone strata, in which waters gradually increase in salinity with increasing depth [14]. Based on brine composition, we have calculated the current situation at the plant, as depicted in Fig. 1. The salt recovery is limited by the amount of bivalent cations present in the brines. In the current solution, the crystallizer can only produce salt until the sum of calcium chloride and magnesium chloride concentrations is below 8% (w/w). As thermal methods do not affect the ratio of bivalent to univalent ions, the process is limited by the composition of the original brine. Membrane processes could alter the bivalent/univalent ratio, enhancing the performance of the salt production plant by increasing the salt recovery and possibly decreasing the energy consumption. Two membrane processes have been tested: electrodialysis and nanofiltration. Based on the results of the laboratory test, few cases of an integrated system have been discussed.

2. Experimental

Brines "A" and "B" were subjected to microfiltration (pore size of the membrane: 0.45 μm) before the experiments.

Table 1
Major components of "A" and "B" brines, equivalent amount of sodium not included

Brine	Concentration [g L^{-1}]			
	Cl^-	SO_4^{2-}	Mg^{2+}	Ca^{2+}
A	33.2	0.937	0.990	0.771
B	63.6	3.025	2.513	2.173

Ionic composition of brines and samples collected during was determined using ICS-5000 ion chromatograph (ThermoDionex, USA).

Nanofiltration experiments were performed using dead-end Sterlitech® HP 4750X Stirred Cell module of effective membrane area of 14.6 cm^2. Commercial nanofiltration flat-sheet membranes were tested: Desal 5-DL (GE Osmonics) and NF270 (Dow Filmtec). All experiments were conducted at 21°C and 40 bars of pressure. A high stirring speed (1,200 rpm) was applied to avoid concentration polarization. During the experiments, the permeate was collected by every 10% of the feed volume recovery, until the flux dropped below 50% of the initial value.

3. Results

Tables 2 and 3 present the effect of water recovery, defined as the volume of the collected permeate per the feed volume, and ion rejection coefficients, calculated basing on analysis results of samples collected during the nanofiltration.

The results of the nanofiltration experiments enabled to conclude that ions rejection coefficients decreased in the order $SO_4^{2-} > Mg^{2+} > Ca^{2+} > Cl^-$, what was an expected behaviour. Rejection coefficient of SO_4^{2-} ions was lower than the predicted one, due to high Cl^- ions concentration. Water recovery strongly affected the rejection coefficients. Generally, as the recovery increases, concentration at the active side of the membrane rises making diffusional flux higher and decreasing the rejection coefficient. In our experiments, this was especially seen at higher recoveries, but not at lower recoveries. NF270 membrane showed lower rejection coefficients than Desal 5-DL membrane. Additionally, Desal 5-DL membranes showed very high rejection coefficients of divalent ions at high water recovery.

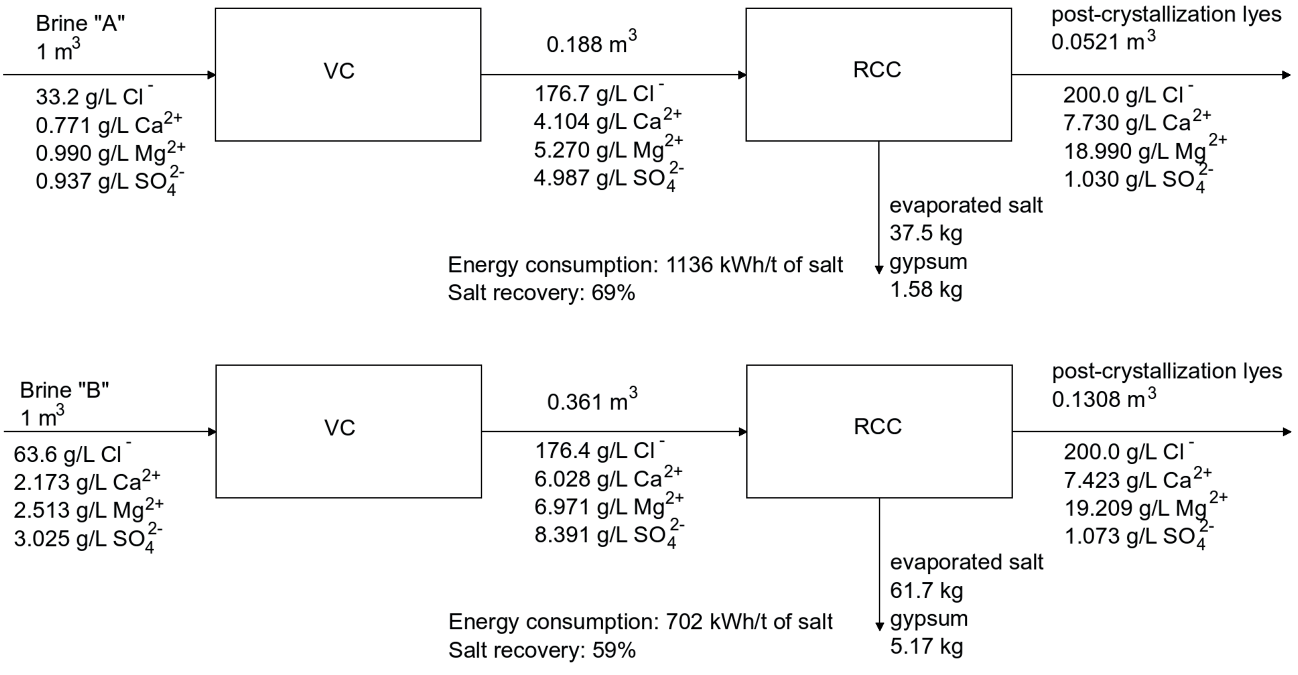

Fig. 1. A scheme of the current situation at the desalination plant treating brine "A" or "B".

Table 2
Effect of water recovery (*Y*) on rejection coefficient (*R*) using Desal 5-DL membrane

Feed brine	*Y* [%]	*R* [%]			
		Cl^-	SO_4^{2-}	Mg^{2+}	Ca^{2+}
"A"	50.8	19.7	95.0	90.0	80.9
	59.3	17.9	95.2	89.7	79.8
	67.8	16.3	95.4	89.3	78.3
	76.3	14.3	95.5	88.6	76.1
	84.7	11.7	95.6	87.3	72.5
"B"	50.8	2.5	96.1	92.0	83.0
	61.0	0.4	96.2	91.5	81.2
	71.2	–1.3	96.3	90.2	79.4

Table 3
Effect of water recovery (*Y*) on rejection coefficient (*R*) during nanofiltration using NF-270 membrane

Feed brine	*Y* [%]	*R* [%]			
		Cl^-	SO_4^{2-}	Mg^{2+}	Ca^{2+}
"A"	51.2	23.4	94.9	83.9	64.0
	61.4	20.5	95.3	83.3	62.0
	71.5	17.4	95.2	82.1	59.1
	81.7	13.3	95.0	80.0	54.6
	91.9	7.9	94.3	74.8	45.0
"B"	50.8	5.4	86.4	78.1	62.1
	61.0	3.1	87.0	77.4	60.5
	65.4	1.9	87.3	77.1	59.7

4. Process simulation

Experimental results were the basis for following cases of an integrated NF-ED-RO-vapor compression (VC)-crystallization (RCC) system design:

(1) Brine concentration with a thermal method, then feeding to a crystallizer. This is the current state of the operation at the plant.
(2) Brine treatment with nanofiltration followed with NF permeate treatment with electrodialysis. Gypsum and magnesium hydroxide precipitation from the NF retentate, which is then recycled and mixed with NF feed. The possibility of magnesium hydroxide production from coal mine brines has been tested before in the pilot plant [3]. Magnesium hydroxide can next be used to obtain magnesium oxide, an important raw material for basic refractories used in the cement and steel industry. The ED concentrate is fed to the crystallizer. The ED diluate is treated with RO, which produces potable water. The RO retentate is mixed with brine and post-crystallization effluents from $Mg(OH)_2$ precipitation and fed back to NF unit.

Both cases were designed to work on two different brines, "A" and "B", and using two different NF membranes, NF-270 and Desal 5-DL.

Following assumptions were made:

- The maximum concentration of bivalent ions in the post-crystallization effluents was 8% (w/w) as $MgCl_2$+$CaCl_2$ –the actual limit of the crystallizer in the existing plant.
- The maximum chloride concentration in the post-crystallization effluents was 200 g L^{-1}.
- The solubility product of calcium sulphate was $4.302 \cdot 10^{-6}$ mol^4dm^{-6} — value calculated on the basis of the composition of post-crystallization effluents from the plant and corresponding to the temperature and ionic strength of the liquid in the existing crystallizer.
- Energy consumption of the electrodialytic desalination was 120 kWh t^{-1} of transported salt — such a low energy consumption was reached in the laboratory due to the application of novel spacers, which lowered the membrane stack electric resistance by decreasing the concentration polarization and shortening the intermembrane distance.
- Rejection coefficients of a RO membrane were assumed as follows [15]: $R_{Cl^-} = 99.22\%$, $R_{Mg^{2+}} = 99.90\%$, $R_{Ca^{2+}} = 99.85\%$, $R_{SO_4^{2-}} = 99.72\%$
- The required pressure drop [bar] in RO unit, the energy consumption in RO and NF were calculated as discussed in [16,17].
- The maximum total dissolved salts content (TDS) of the RO concentrate was 60 g L^{-1}.
- Ion concentration in ED diluate and concentrate was estimated basing on the assumption, that the change in sulphate, calcium, and magnesium concentration was proportional to the change in chloride concentration, with respective ratios of Cl^- concentration change/ion concentration change calculated on the basis of our previous results describing the transport of ions and water during electrodialysis of concentrated solutions and the production of saturated brine [18,19].
- ED could produce concentrate of TDS higher than 270 g L^{-1} (up to 300 g L^{-1}), what meant that the vapor compression unit was no longer required.
- ED could work either with NF retentate being fed to both, diluate and concentrate compartments, or with no preliminary concentrated solution.
- Because the precipitation of gypsum was slow, during the $Mg(OH)_2$/gypsum precipitation step the saturation level with respect to gypsum was not reached. Instead, reaching gypsum saturation level of ca. 160% was assumed to be possible [20].
- The energy consumption in the $Mg(OH)_2$/gypsum precipitation step was neglected, as no external heating was applied here, only addition of chemicals.

Salt recovery and energy consumption for each of the simulated cases are presented in Table 4. The proposed system decreased the energy consumption of the plant; this was caused by the high costs of a current thermal setup. Figs. 2–5 present the calculated composition of process streams, energy consumption, and salt recovery in each of the investigated cases. The application of nanofiltration, intermediate precipitation of gypsum and magnesium hydroxide, and electrodialysis decreased the amount of bivalent cations introduced to the crystallizer, which led to higher amount of evaporated salts being produced and lower volume of the post-crystallization effluents. Moreover, reverse osmosis unit produced potable water. Application of Desal 5-DL (GE Osmonics) membrane enabled higher salt recovery than NF-270. The energy consumption could be decreased 2–3 times, when compared with conventional, thermal treatment.

5. Scaling risk assessment

To assess the scaling risk during electrodialysis and nanofiltration, a previously described algorithm [21], binding crystallization kinetics and hydrodynamics of the module, was applied. As it turned out, the application of NF shifted the scaling risk to the NF retentate. The process streams, which showed the supersaturation with respect to calcium sulphate, and corresponding induction times, are presented in Table 5. The induction time was calculated by semi-empirical correlation [22,23]:

$$t_{ind} = K\sigma^{-r} \tag{1}$$

where, σ denotes the saturation level, $K = 1.3{\cdot}10^5$ *s* and $r = 5.6$ [24]. The gypsum saturation level was calculated using the equation [23]:

$$\sigma = \frac{a_{\mathrm{Ca}^{2+}} a_{\mathrm{SO}_4^{2-}} a^2_{\mathrm{H_2O}}}{K_{sp}} \tag{2}$$

where, a_i denotes the activity of *i*-th species, calculated basing on the Bromley equation for a high ionic strength solution [24], K_{sp} denotes calcium sulphate dihydrate solubility product, calculated using the equation [23]:

$$\ln\left(K_{sp}\right) = 390.9619 - 152.624\log T - \frac{12545.62}{T} + 0.0818493\,T \tag{3}$$

In the case of brine "A", only NF retentate and effluents from $Mg(OH)_2$ precipitation were supersaturated with respect to calcium sulphate. The effluents from magnesium

Table 4
Comparison of salt recovery and energy consumption in each of the investigated cases

System	Brine	NF membrane	Salt recovery [%]	Energy consumption [kWh t^{-1} of salt]
Current system	A	–	69.0	1,136
Current system	B	–	59.0	702
NF-ED-RO	A	NF-270	91.9	425
NF-ED-RO	A	Desal 5-DL	92.6	426
NF-ED-RO	B	NF-270	89.9	365
NF-ED-RO	B	Desal 5-DL	91.3	362

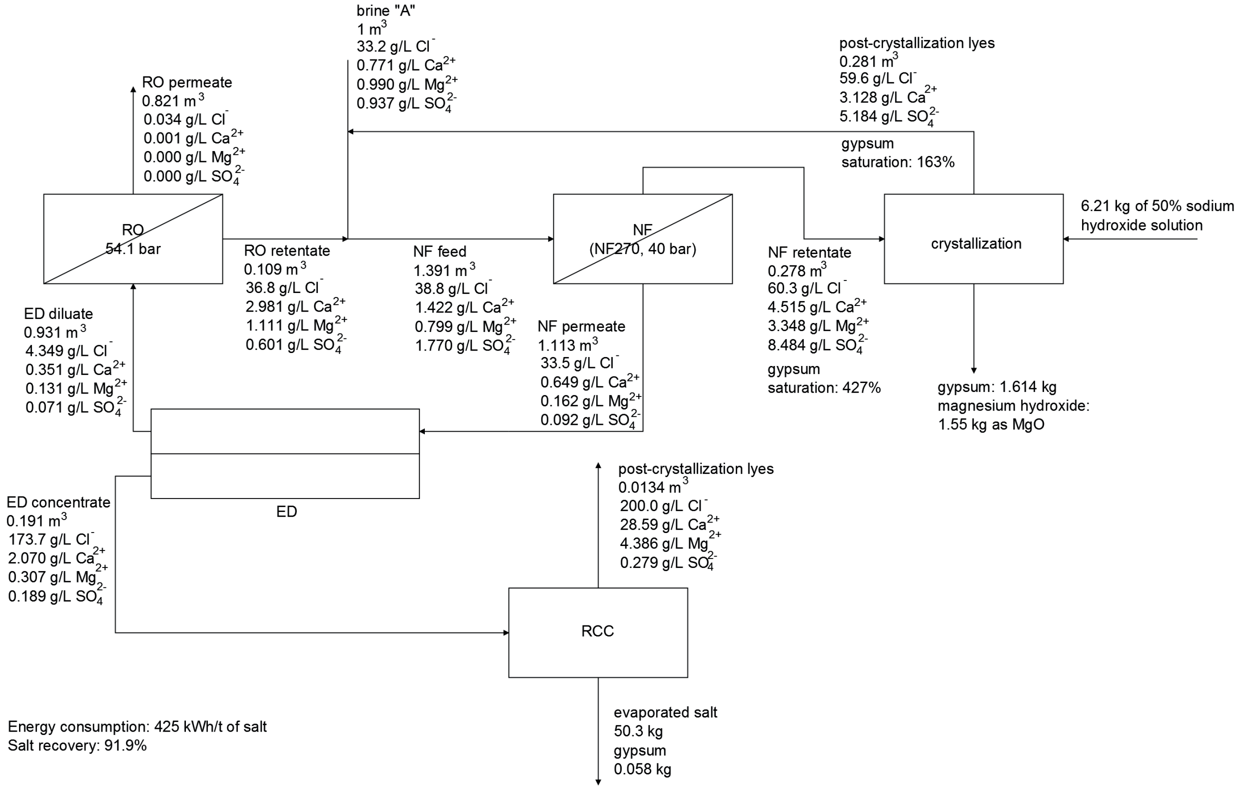

Fig. 2. Composition of process streams, energy consumption, and salt recovery in a NF (NF-270 membrane)-ED-RO system treating brine "A" (change lyes into effluents).

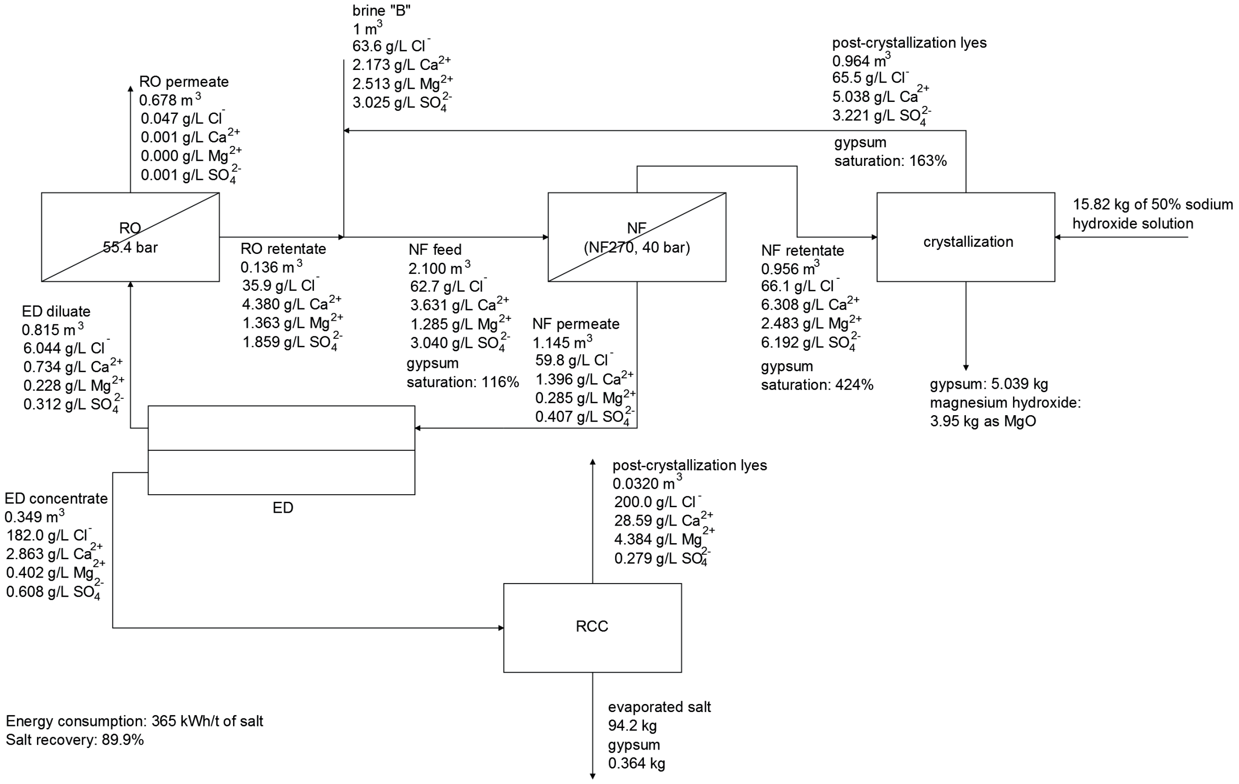

Fig. 3. Composition of process streams, energy consumption, and salt recovery in a NF (NF-270 membrane)-ED-RO system treating brine “B” (change lyes into effluents).

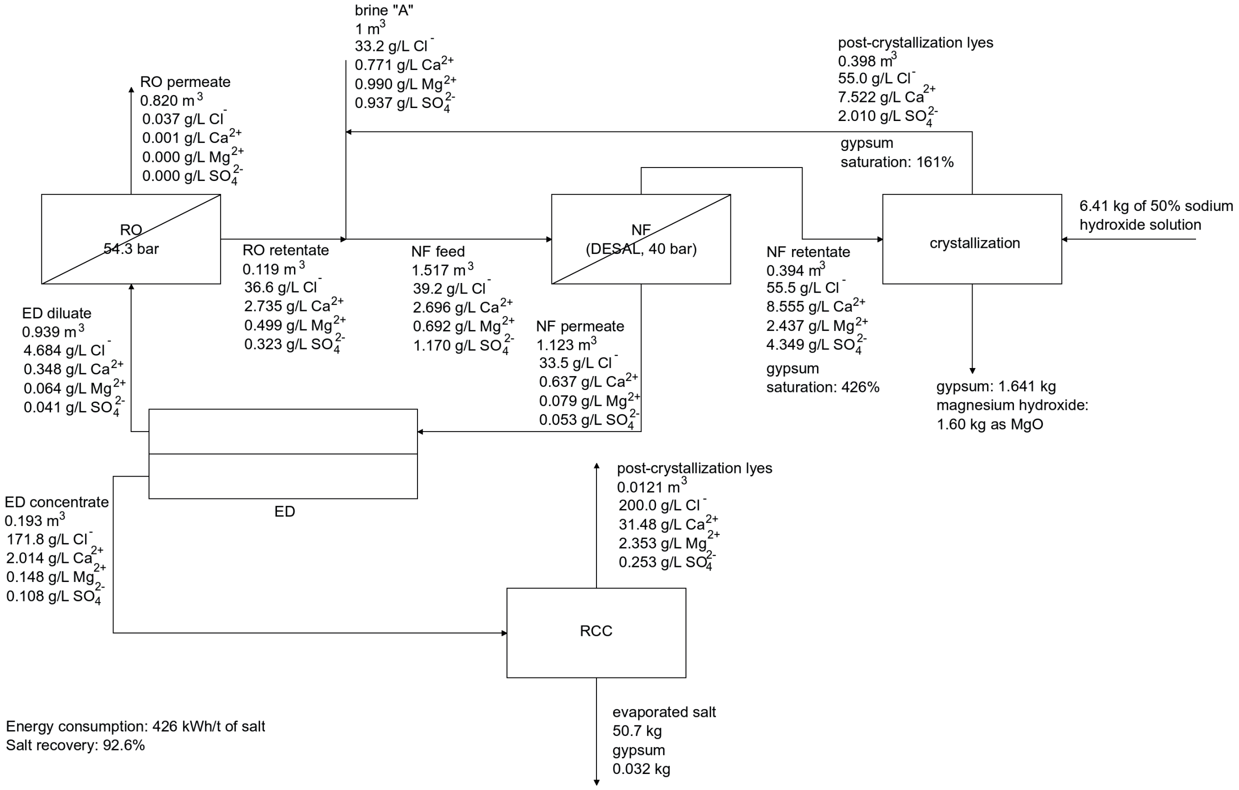

Fig. 4. Composition of process streams, energy consumption, and salt recovery in a NF (Desal 5-DL membrane)-ED-RO system treating brine “A” (change lyes into effluents).

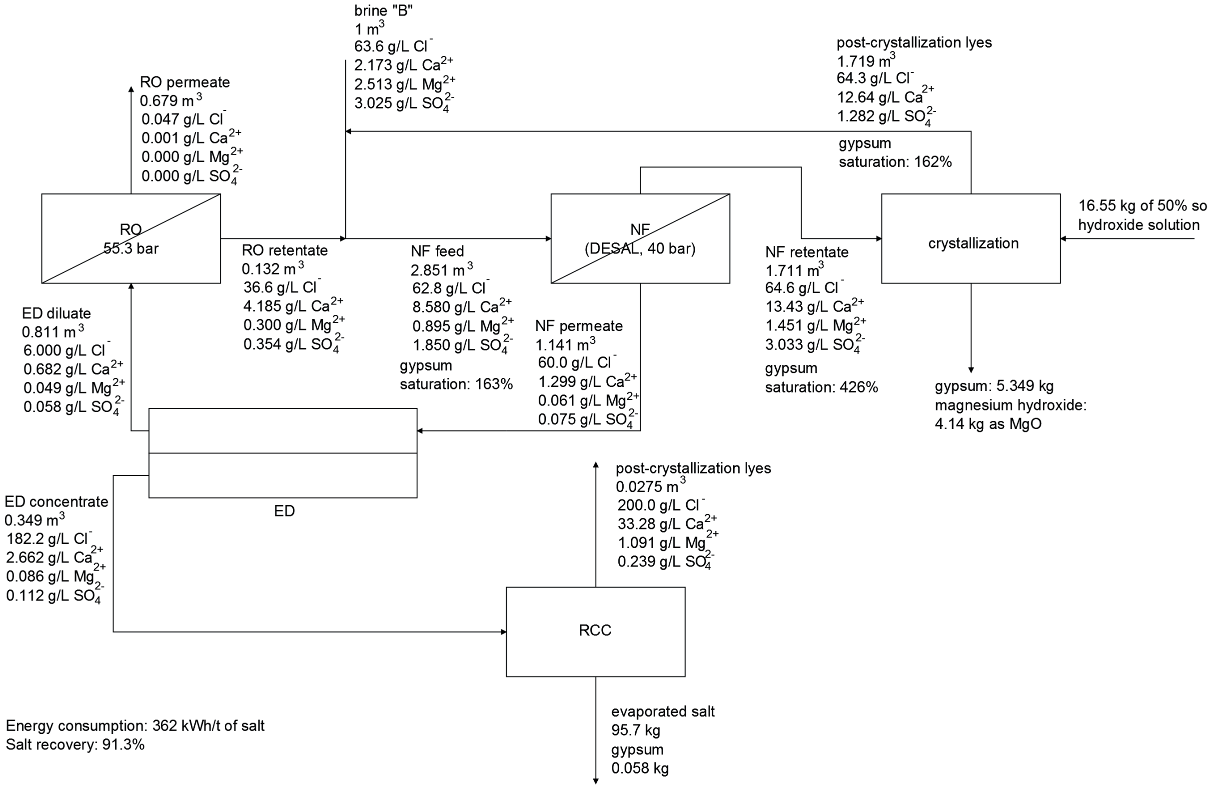

Fig. 5. Composition of process streams, energy consumption, and salt recovery in a NF (Desal 5-DL membrane)-ED-RO system treating brine "B" (change lyes into effluents).

Table 5
Gypsum saturation and corresponding induction time of the supersaturated process streams in the integrated system

Brine	NF membrane	Process stream	Gypsum saturation [%]	Induction time [*s*]
A	NF-270	NF retentate	427	77
		Post-crystallization effluent	163	9,600
	Desal 5-DL	NF retentate	426	78
		Post-crystallization effluent	161	10,000
B	NF-270	NF retentate	424	80
		Post-crystallization effluent	163	9,500
		NF feed	116	53,000
	Desal 5-DL	NF retentate	426	78
		Post-crystallization effluent	162	9,800
		NF feed	163	9,400

hydroxide precipitation, having gypsum saturation level of ca. 160%, were mixed with fresh portion of brine "A" and RO retentate, which were both not supersaturated. It removed the supersaturation from the NF feed. In the case of NF retentate, it was possible to design a scaling-free nanofiltration even at relative saturation of ca. 430%. Application of intermembrane spacers of low residence time variance could allow to operate a single-pass NF module without the membrane scaling. A possibility of such an operation had already been proved experimentally in previous research [16] in a single-pass nanofiltration using a specially designed two-sided flat laboratory module [25] with a woven 0.26 mm spacer. Single-pass nanofiltration was performed for several hours at various overall recoveries to evaluate the maximum possible recovery. The flow conditions were set up as it was previously described for electrodialysis [21]: as long as the residence time of the supersaturated solution was longer than the nucleation induction time, no scaling inside the module was expected. Single-pass experiments confirmed, that maximum NF water recovery was equal to 84.4% — see Fig. 6.

The situation was more complicated in case of the treatment of brine "B", which contained more calcium and sulphate ions. The RO retentate, NF feed, NF retentate and effluent from $Mg(OH)_2$ precipitation were supersaturated.

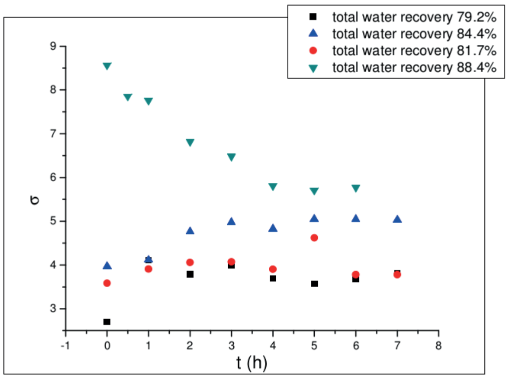

Fig. 6. Changes in calcium sulphate relative saturation during the high recovery NF experiments.

NF retentate reached very high supersaturation with respect to calcium sulphate. However, because gypsum precipitation is relatively slow, and the supersaturation of NF feed is not high, the scaling risk should appear only in NF retentate, as in the case of brine “A”.

6. Conclusions

The application of nanofiltration and electrodialysis in an evaporated salt production plant was investigated. Two kinds of coal mine waters were tested – brine “A”, having TDS of 55 g L^{-1}; and brine “B”, having TDS of 107 g L^{-1}. On the basis of laboratory results, a hybrid system consisting of nanofiltration, electrodialysis, reverse osmosis, and precipitation was proposed. The results showed, that the proposed system could increase the salt recovery and decrease the energy consumption; moreover, both potable water and magnesium hydroxide were produced. The salinity of the obtained ED concentrate was high enough to eliminate the need of costly vapor compression unit.

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References

[1] B. Ericsson, B. Hallmans, Treatment and disposal of saline wastewater from coal mines in Poland, Desalination, 98 (1994) 239–248.
[2] B. Ericsson, B. Hallmans, Treatment of saline wastewater for zero discharge at the Debiensko coal mines in Poland, Desalination, 105 (1996) 115–123.
[3] M. Turek, J. Mrowiec-Białoń, W. Gnot, Utilization of coal mine brines in the chlorine production process, Desalination, 101 (1995) 57–67.
[4] M. Turek, Electrodialytic desalination and concentration of coal-mine brine, Desalination, 162 (2004) 355–359.
[5] M. Turek, P. Dydo, R. Klimek, Salt production from coal-mine brine in ED-evaporation-crystallization system, Desalination, 184 (2005) 439–446.
[6] M. Turek, P. Dydo, Hybrid membrane–thermal versus simple membrane systems, Desalination, 157 (2003) 51–56.
[7] M. Turek, M. Chorążewska, Nanofiltration process for seawater desalination-salt production integrated system, Desal. Wat. Treat., 7 (2009) 178–181.
[8] E. Drioli, A. Criscuoli, E. Curcio, Integrated membrane operations for seawater desalination, Desalination, 147 (2002) 77–81.
[9] F. Macedonio, E. Curcio, E. Drioli, Integrated membrane systems for seawater desalination: energetic and exergetic analysis, economic evaluation, experimental study, Desalination, 203 (2007) 260–276.
[10] T.A. Davis, Production of purified water and high value chemicals from salt water, Patent no. US2004055955 (2004).
[11] P.S. Wallace, Membrane and electrodialysis based seawater desalination with salt, boron and gypsum recovery, Patent no. US8999171 (2015).
[12] A. Raman, Process and system for producing sodium chloride brine, Patent application no. WO2013023249 (2012).
[13] Y. Tanaka, R. Ehara, S. Itoi, T. Goto, Ion-exchange membrane electrodialytic salt production using brine discharged from a reverse osmosis seawater desalination plant, J. Membr. Sci., 222 (2003) 71–86.
[14] M. Andersson (Ed.), Saline Waste Water from the Hard Coal Sector, Change and Continuity in Poland’s Environmental Policy, Springer Netherlands, Dordrecht, 1999, pp. 153–174.
[15] N. Voutchkov, Introduction to Reverse Osmosis Desalination, Available from: https://s3.amazonaws.com/suncam/npdocs/053.pdf. Accessed on (February 27, 2016), 2010.
[16] M. Turek, K. Mitko, E. Laskowska, M. Chorążewska, K. Piotrowski, A. Jakóbik-Kolon, P. Dydo, Energy Consumption and Gypsum Scaling Assessment in Hybrid Reverse Osmosis-Electrodialysis System for Seawater Desalination, 2nd International Conference on Desalination and Environment, Doha, Qatar, 2016.
[17] M. Wilf, Fundamentals of RO-NF Technology, International Conference on Desalination Costing, Middle East Desalination Research Center, Limassol, 2004 pp. 18–31.
[18] M. Turek, K. Mitko, M. Chorążewska, P. Dydo, Use of the desalination brines in the saturation of membrane electrolysis feed, Desal. Wat. Treat., 51 (2013) 2749–2754.
[19] K. Mitko, W. Mikołajczak, M. Turek, Electrodialytic concentration of NaCl for the chlor-alkali industry, Desal. Wat. Treat., 56 (2015) 3174–3180.
[20] A. Rahardianto, B.C. McCool, Y. Cohen, Accelerated desupersaturation of reverse osmosis concentrate by chemically-enhanced seeded precipitation, Desalination, 264 (2010) 256–267.
[21] M. Turek, J. Waś, K. Mitko, Scaling prediction in electrodialytic desalination, Desal. Wat. Treat., 44 (2012) 255–260.
[22] A. Packter, The precipitation of sparingly soluble alkaline-earth metal and lead salts: nucleation and growth orders during the induction period, J. Chem. Soc. A, (1968) 859–862.
[23] A. Lancia, D. Musmarra, M. Prisciandaro, Measuring induction period for calcium sulfate dihydrate precipitation, AIChE J., 45 (1999) 390–397.
[24] M. Prisciandaro, A. Lancia, D. Musmarra, Calcium sulfate dihydrate nucleation in the presence of calcium and sodium chloride salts, Ind. Eng. Chem. Res., 40 (2001) 2335–2339.
[25] M. Turek, M. Chorążewska, Laboratory cross-flow membrane filtration module, patent application no. EP2564919A1 (2013).