Hybrid membrane-evaporative system for a near-ZLD utilization of coal mine brine

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ABSTRACT

Currently, in Poland, there is only one coal mine water utilization plant in operation, located in Czerwionka-Leszczyny, which uses energy-intensive ZOD technology, based on vapor compression and crystallization. To decrease the energy consumption, in this work a hybrid membrane-evaporative system for coal mine brine utilization has been proposed. The proposed technology consists of two-pass nanofiltration with intermediate gypsum crystallization (NFCr) and the reverse osmosis-electrodialysis concentration step (ROED). Assuming the proposed system utilizes the Piast-500 coal mine brine of total dissolved solids of 72.7 kg/m^3, the energy consumption and the amount of salt generated have been estimated for four cases: (1) the entirety of coal mine brine is utilized by the ZOD technology; (2) the ZOD system is preceded by the NFCr; (3) the coal mine brine is utilized in the NFCr-ROED-ZOD system; (4) the coal mine brine is utilized in the NFCr-ROEDCr system. The results show that implementing the NFCr before the ZOD alone can decrease the energy consumption by 22%, whereas the full NFCr-ROED-ZOD system shows 54% lower energy consumption than ZOD. The application of a hybrid membrane-evaporative system for coal mine brine utilization allows increasing the salt recovery from 62.9% up to over 90%.

Keywords: Nanofiltration; Coal mine brines; Desalination

1. Introduction

High amounts of saline waste streams are generated around the world, including the discharge from the brackish and seawater desalination, flow backs from shale gas fracturing, and other troublesome waters generated by many different branches of the industry. Disposal of saline wastewater is energy-intensive and costly. In the US, the costs of saline water utilization in inland desalination plants reach 5%–33% of total desalination costs and are estimated at 0.26–0.32 $/m^3 of desalinated water or 308–380 $/t of salt contained in the discharge [1]. The amount of sodium chloride contained in saline waters discharged into Polish rivers, including saline wastewater originating mainly from hard coal and copper mining, amounts to approximately 4 million tonnes annually. The discharge of saline wastewater into the rivers causes serious environmental problems. The only feasible solution for decreasing the salt load in waste streams is to use them in the production of evaporated salt.

Poland produces ca. 4–4.5 million tonnes of salt annually, of which about 1.0 million tonnes is the evaporated salt [2]. The largest salt producers in the country are CIECH Group (Janikowo), and ORLEN Group (Inowrocław). Evaporated salt is produced from a brine close to saturation with sodium chloride (ca. 310 g/dm^3 as NaCl), which is obtained by leaching the salt deposits. The brine is chemically purified from calcium and magnesium ions and then directed to the so-called crystallization evaporator. Multi-divisional evaporation systems with

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negative pressure in the last stage are used. The steam consumption is 0.4–0.5 t per tonne of condensate, whereas the electric energy consumption is approx. 0.25 kWh/t [3]. So far in Poland, there is one salt production plant in operation, which produces salt evaporated from saline mine waters, with an annual capacity of 100,000 tonnes [4,5]. In July 2015, this installation, previously owned by Zakład Odsalania Dębieńsko Sp. z o.o., was taken over by Przedsiębiorstwo Gospodarki Wodnej i Rekultywacji S.A. (PGWiR), which is a part of the Jastrzębska Spółka Węglowa (JSW) Group. The feed water for the plant comes from the "Budryk" mine, which is still in operation. Chemical treatment is not used. Two kinds of "Budryk" waters are used: brackish one total dissolved solid (TDS of 30.8 kg/m^3) and saline one (TDS of 72.7 kg/m^3). The brackish Budryk water is pre-concentrated by reverse osmosis (RO); the RO retentate is mixed with the saline Budryk water and fed to a vapor compression (VC) evaporator, where it's concentrated to approximately 290 g/dm^3 as NaCl. The energy consumption of VC is 44 kWh/m^3 of condensate. The brine is directed to the VC evaporative crystallization, which has an energy consumption of 66 kWh/m^3 of condensate. Fig. 1 for the general scheme of the reference technology. The solutions applied by the PGWiR are typical for the processing of highly saline wastewater; according to literature data, VC evaporators with an energy consumption of 39 kWh/m^3 of feed water are used to concentrate sodium chloride solutions to a concentration above 250 g/dm^3 and in VC evaporative crystallizers the energy consumption is 52–66 kWh/m^3 of feed water [6]. In the Wieliczka Salt Mine, where evaporated salt is produced from salt leachates of salinity of 111.8 g/dm^3, the energy consumption in the VC evaporator is 53.7 kWh/t of condensate and the total energy consumption is 78.3 kWh/m^3 of leachate, which corresponds to the energy consumption of 827.7 kWh/t of salt [7].

Because of the serious environmental problems with saline discharges, there is a worldwide tendency to develop waste-free technologies of waste solution management, the so-called ZLD (zero liquid discharge); in such technologies, the water yield would have to be practically 100%. Recovery in the RO method is limited by the osmotic pressure of the retentate and the risk of crystallization of sparingly soluble species; its highest value in the case of seawater is 35%–50%. In the evaporation methods, the recovery is limited mainly by the risk of crystallization of sparingly soluble species and is typically 10%–30%. Numerous methods of increasing recovery in reverse osmosis are proposed: application of antiscalants [8,9]; new configurations of reverse osmosis, such as flow reversal reverse osmosis [10,11] or closed-circuit desalination reverse osmosis [12]; precipitation of hardly soluble salts between individual RO stages [13]; application of advanced pre-treatment [14,15].

In this work, we focus on designing the treatment for the Piast-500 coal mine water of TDS of 72.7 kg/m^3. The goal was to answer a question if the best case scenario is to replicate the technology already implemented in "Dębieńsko" to treat water from a different mine, or to use a new technology to mitigate the problems caused by the high energy consumption of the "Dębieńsko" evaporator–evaporative crystallizer system: the pre-treatment of brine by nanofiltration, carried

out in a manner developed by the authors in conditions of high saturation with calcium sulfate with partial retentate recirculation and controlled gypsum crystallization.

Four cases were modeled:

- Reference case: evaporator–evaporative crystallizer, the same technology as installed in the "Dębieńsko" plant (ZOD). The reference technology uses reverse osmosis to pre-concentrate part of the "Budryk" saline water (TDS of 30.8 kg/m^3) up to the TDS of 56 kg/m^3. As the Piast-500 water used for modeling already had TDS of 47 kg/m^3, the RO would no longer be practical and thus it was omitted.
- Application of the two-pass nanofiltration with intermediate crystallization as a pretreatment before the evaporator–evaporative crystallizer system (NFCr-ZOD).
- Application of the two-pass nanofiltration with intermediate crystallization, then further concentration of NF permeate in a hybrid reverse osmosis-electrodialysis system, followed by the VC evaporator and VC evaporative crystallizer (NFCr-ROED-ZOD).
- Application of the two-pass nanofiltration with intermediate crystallization, then further concentration of NF permeate in a hybrid reverse osmosis-electrodialysis system with crystallization from ED concentrate in evaporative crystallizer (NFCr-ROEDCr).

All of the modeling was performed using Piast-500 coal mine water as the feed water. The four cases were compared on the basis of energy consumption and recovery of salt and water. It was assumed that no additional salts are introduced into the system, other than the feed coal mine water.

2. Modeling

The model used in this study consisted of four systems: the two-pass nanofiltration with intermedia crystallization (NFCr), the hybrid reverse osmosis-electrodialysis (ROED), the hybrid reverse osmosis-electrodialysis with crystallization (ROEDCr), and the ZOD.

2.1. Feedwater

The feed water Piast-500 was collected at the "Piast-Ziemowit" coal mine and was analyzed with ThermoDionex ICS-500 ion chromatograph equipped with a CS-16 column for cations or an AS-19 column for anions. The full analysis is presented in Table 1; for the sake of simplicity, only chloride, magnesium, calcium, sodium and sulfate ions were taken into account in the modeling.

2.2. Two-pass nanofiltration with intermediate crystallization (NFCr)

The scheme of the proposed system is presented in Fig. 2. The feed (coal mine water) is subjected to a nanofiltration (NF1) working at high gypsum saturation in the retentate. The permeate is then fed to the second pass of nanofiltration (NF2). The gypsum precipitates from the supersaturated NF1 retentate in an external crystallizer; the post-precipitation solution is mixed with the NF2 retentate and recycled
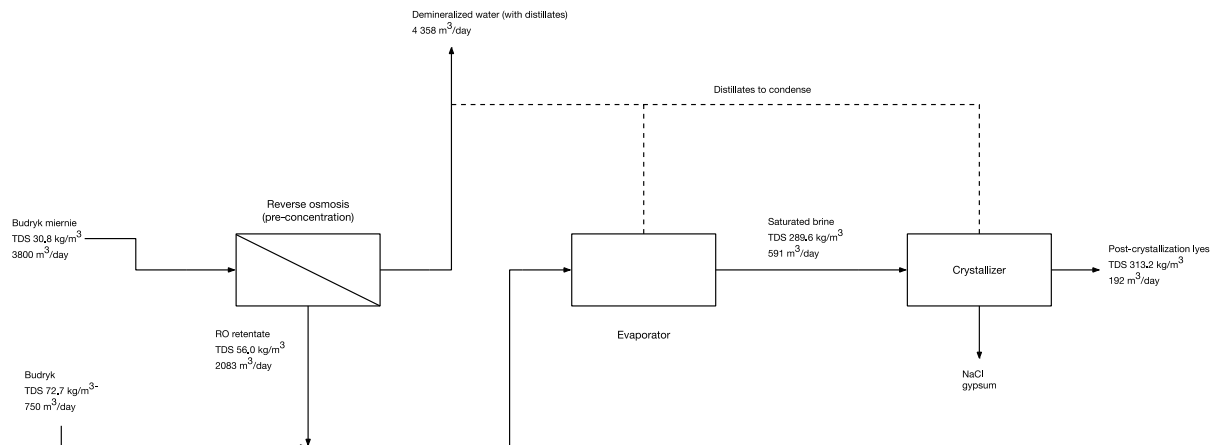
Fig. 1. The general scheme of the "Dębieńsko" plant.

back to NF1. The entire system can reach relatively high permeate recovery. The two-pass nanofiltration was tested in the 400 L/h NF-RO-ED pilot plant operating between July 2019 and March 2020 in the "Bolesław Śmiały" coal mine in Łaziska Górne, Poland [16,17]; the intermediate gypsum crystallization is being tested in the NF-crystallization pilot plant operating at the premises of "Dębieńsko" plant in Czerwionka-Leszczyny, Poland.

Following assumptions have been made when modeling the NFCr system:

- the rejection coefficients in the nanofiltration step are based on the results obtained in the pilot plant using Trisep TS40 nanofiltration membranes [16,17] and were as follows: R_{Cl^-} = 23.5%, $R_{Ca^{2+}}$ = 90.3%, $R_{Mg^{2+}}$ = 95.6%, $R_{SO_4^{2-}}$ = 97.3%,
- the sodium content in all streams are calculated based on electroneutrality condition,
- the energy consumption [kWh/m³ of permeate] of each of the NF units are calculated using the equation derived from equations presented in [20,21]:

$$E = 0.02724 \cdot \frac{P_f}{Y \cdot 0.88 \cdot 0.96} - 0.02724 \cdot (P_f - 2) \cdot \frac{1-Y}{Y} \cdot \frac{0.94}{0.96} + 0.05 \tag{1}$$

where Y is the permeate recovery and P_f is the required pressure [bar] given as:

$$P_f = 0.448175 \cdot (TDS_f - TDS_p + TDS_r - TDS_p) + 24 \tag{2}$$

where TDS_f, TDS_p, and TDS_r are the salinity (kg/m³) of feed, retentate, and permeate, respectively.

- saturation of gypsum in all streams are calculated according to the procedure described in [22,23]
- the gypsum can be precipitated down to saturation level of 163% in the crystallizer of a reasonably low hydraulic residence time [24],
- as the gypsum precipitates spontaneously, it does not contribute to the energy consumption,

Table 1
Ionic composition of Piast-500 coal mine water

Ion	Concentration (kg/m³)
Cl⁻	28.106
Na⁺	16.948
SO₄²⁻	1.495
Mg²⁺	1.046
Ca²⁺	0.919
K⁺	0.185
Br⁻	0.077
NO₃⁻	0.024
Sr²⁺	0.018
Li⁺	0.00135

- 95% of the NF1 retentate and 100% of NF2 retentate are recycled, meaning 5% of feed water is discarded as "waste" stream (Fig. 2),
- maximum gypsum saturation level in NF1 retentate is 320%,

2.3. Hybrid reverse osmosis-electrodialysis

The scheme of the proposed system is presented in Fig. 3. The feed (NFCr permeate) is fed to the reverse osmosis unit; the RO retentate is further concentrated in an electrodialyzer, which produces concentrated sodium chloride solution (feed for the ZOD) and the diluate, which is completely recycled to the RO. This system was tested in the 400 L/h NF-RO-ED pilot plant operating between July 2019 and March 2020 in the "Bolesław Śmiały" coal mine in Łaziska Górne, Poland [16,17].

Following assumptions have been made when modeling the ROED system:

- the rejection coefficients in the reverse osmosis step are based on the literature data of seawater reverse osmosis plants [25] and were as follows: R_{Cl^-} = 99.22%, $R_{Ca^{2+}}$ = 99.85%, $R_{Mg^{2+}}$ = 99.9%, $R_{SO_4^{2-}}$ = 99.72%,
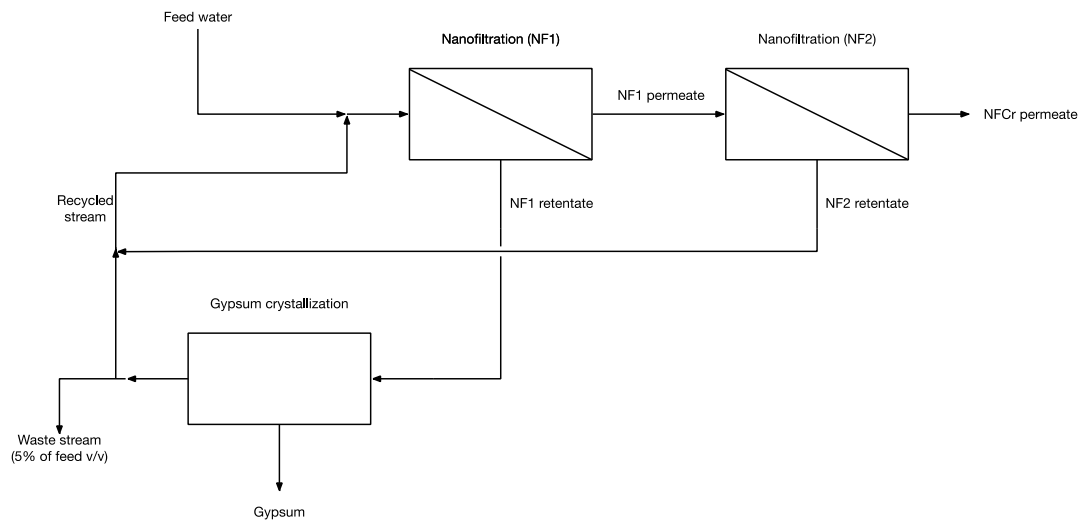
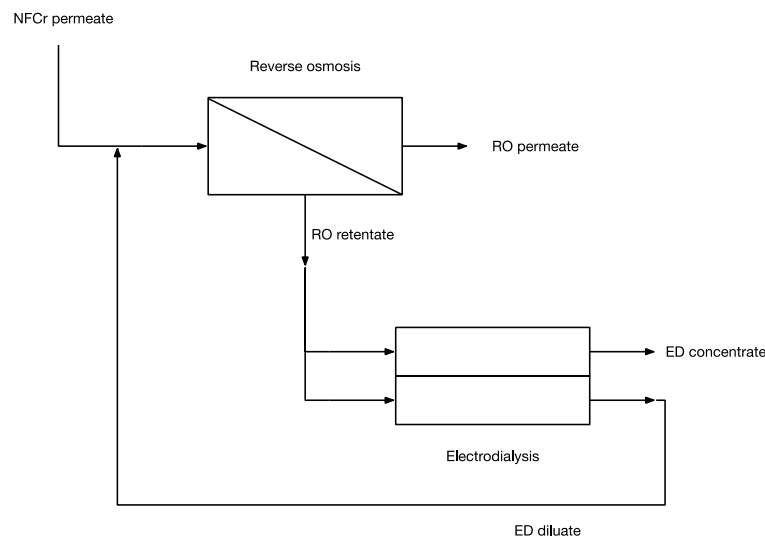Fig. 2. The two-pass nanofiltration with intermediate crystallization (NFCr) – patent-pending [18,19].

Fig. 3. The hybrid reverse osmosis-electrodialysis system (ROED).

- the sodium content in all streams are calculated based on electroneutrality condition,
- the maximum pressure required by RO is 70 bar,
- the maximum chloride concentration in ED concentrate is 111 kg/m^3, as observed in the pilot plant using membranes PC-Cell PC-SK/SA with 0.35 mm thin spacers [16,17],
- the energy consumption of the reverse osmosis unit is calculated using the same method as in NFCr –Eqs. (1) and (2),
- the energy consumption of the electrodialyzer is 0.3 kWh/kg of salt transported across the membrane [16,17],

2.4. Evaporator–evaporative crystallizer

The ZOD system has been implemented on an industrial scale in Czerwionka-Leszczyny, Poland. It consists of two evaporators: (1) vapor compression evaporator, which accepts saline water and pre-concentrates it up to ca. 290 kg/m^3 as NaCl, (2) crystallizer – second vapor compression unit – which concentrates the brine further and crystallizes evaporated salt and gypsum (Fig. 4).

Based on the operating boundaries of this plant, the following assumptions have been made when modeling the ZOD system:

- The maximum concentration of bivalent ions in the post-crystallization lyes is 8% (w/w) as $MgCl_2 + CaCl_2$,
- The maximum chloride concentration in the post-crystallization lyes is 200 kg/m^3,
- The maximum chloride concentration in the VC concentrate is 176 kg/m^3,
- The solubility product of calcium sulfate in the post-crystallization lyes is 4.302×10^{-6} mol^2/dm^6,
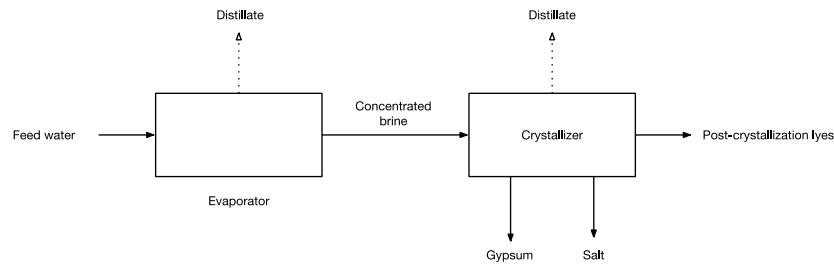
Fig. 4. A scheme of vapor compression with crystallization system (ZOD).

- The energy consumption is 44 and 66 kWh/m³ of evaporated water for the evaporator and evaporative crystallizer, respectively,

2.5. Reverse osmosis-electrodialysis with VC evaporative crystallizer

The proposed system is almost identical with ROED, with the only difference being that the produced concentrate is already saline enough that it can be directly fed to the evaporative crystallizer. To confirm it can be done, the laboratory experiment at a current density of 300 A/m² was performed in a CS-0 (Asahi Glass Co. Ltd) electrodialyzer equipped with 10 pairs of Selemion CSV/ASV membranes with an effective area of 172 cm², 0.75 mm thin spacers. The initial diluate volume was 2.458 dm³ and the final volume was 2.354 dm³ while the volume of the concentrate was 0.114 and 0.220 dm³, respectively. The electrodialyzer was able to concentrate model NaCl solution from 36.5 kg/m³ as Cl⁻ to 176 kg/m³ as Cl⁻ and simultaneously desalinate model NaCl solution from 36.5 kg/m³ as Cl⁻ to 23.5 kg/m³ as Cl⁻. The given concentration values were obtained after 101 min of the experiment which means that the current efficiency was 90%. The energy consumption during the bench-scale studies was 0.24 kWh/kg of transported salt, 6 moles of water were transported per every mole of chlorides. The ED concentrate (176 kg/m³ as Cl⁻) would be directly fed to the same evaporative crystallizer as used by the ZOD system.

2.6. Benchmarking parameters

Three important parameters were used to compare the proposed cases: energy consumption, salt recovery, and water recovery. The energy consumption of each system was calculated as the sum of energy consumption in each of the unit operations divided by the mass of recovered salt. The salt recovery was defined as:

$$Y_{salt} = \frac{m_{NaCl}}{\left(\dfrac{C_{Cl^-}}{M_{Cl}} M_{NaCl}\right)} \cdot 100\% \qquad (3)$$

where m_{NaCl} is the mass of the salt produced by the ZOD, C_{Cl^-} is the chloride concentration in the feed Piast-500 water (28.106 kg/m³), M_{Cl} and M_{NaCl} are the molar masses of chloride and sodium chloride, respectively. The water recovery was the sum of RO permeate from the ROED part (if present) and the condensed distillates from the evaporator and the evaporative crystallizer of the ZOD. It was assumed that the condensation and mixing with RO permeate does not consume additional energy.

3. Results

Tables 2–5 present the calculated ionic composition and flow rate of the process streams in each of the investigated cases. Table 6 presents the amount of recovered solids and the key benchmarking parameters of each of the proposed systems. The application of NFCr pretreatment alone decreases the energy consumption by 22% and increases the salt recovery from 62.9% up to 91.2%. This is caused by the increase in the amount of salt produced in the crystallizer. The evaporative crystallizer used in the ZOD is sensitive to high magnesium and calcium contents, the mass percent of CaCl₂ + MgCl₂ in the post-crystallization lyes cannot exceed 8%. Removing calcium and magnesium allows pushing the technology further. This is a major problem of the "Dębieńsko" salt production plant,

Table 2
The ionic composition and flow rates of process streams in the ZOD case

		C_{Cl^-} (kg/m³)	$C_{Ca^{2+}}$ (kg/m³)	$C_{Mg^{2+}}$ (kg/m³)	$C_{SO_4^{2-}}$ (kg/m³)	C_{Na^+} (kg/m³)	V (m³/h)
Feed water	Piast-500	28.1060	0.9190	1.0460	1.4950	25.6156	1.0000
	Feed	28.1060	0.9190	1.0460	1.4950	15.8642	1.0000
Evaporator	Distillate	0.0000	0.0000	0.0000	0.0000	0.0000	0.8403
	Concentrate	175.9829	5.7542	6.5494	9.3608	99.3320	0.1597
Evaporative crystallizer	Feed	175.9829	5.7542	6.5494	9.3608	99.3320	0.1597
	Distillate	0.0000	0.0000	0.0000	0.0000	0.0000	0.1076
	Concentrate	199.9942	6.2132	20.0631	1.2819	84.5885	0.0521

Table 3
The ionic composition and flow rates of process streams in the NFCr-ZOD case

		C_{Cl^-} (kg/m³)	$C_{Ca^{2+}}$ (kg/m³)	$C_{Mg^{2+}}$ (kg/m³)	$C_{SO_4^{2-}}$ (kg/m³)	C_{Na^+} (kg/m³)	V (m³/h)
Feed water		28.106	0.919	1.046	1.495	25.616	1.0000
Nanofiltration 1	Feed*	45.867	3.599	0.563	1.523	30.336	1.9096
	Permeate	35.088	0.349	0.025	0.041	22.304	1.2030
	Retentate	64.220	9.132	1.479	4.047	30.210	0.7065
Nanofiltration 2	Feed	35.088	0.349	0.025	0.041	22.304	1.2030
	Permeate	26.843	0.034	0.001	0.001	17.350	0.9624
	Retentate	68.071	1.610	0.119	0.201	42.119	0.2406
Evaporator	Feed	26.843	0.034	0.001	0.001	17.350	0.9624
	Distillate	0.000	0.000	0.000	0.000	0.000	0.8156
	Concentrate	175.983	0.222	0.007	0.007	113.752	0.1468
Evaporative crystallizer	Feed	175.983	0.222	0.007	0.007	113.752	0.1468
	Distillate	0.000	0.000	0.000	0.000	0.000	0.1458
	Concentrate	199.607	33.095	1.077	0.241	89.315	0.0010

*mixture of feed water, recycled NF2 retentate and recycled NF1 retentate after gypsum precipitation.

Table 4
The ionic composition and flow rates of process streams in the NFCr-ROED-ZOD case

		C_{Cl^-} (kg/m³)	$C_{Ca^{2+}}$ (kg/m³)	$C_{Mg^{2+}}$ (kg/m³)	$C_{SO_4^{2-}}$ (kg/m³)	C_{Na^+} (kg/m³)	V (m³/h)
Feed water		28.1060	0.9190	1.0460	1.4950	25.6156	1.0000
	Feed*	45.8672	3.5986	0.5628	1.5232	30.3360	1.9096
Nanofiltration 1	Permeate	35.0884	0.3491	0.0248	0.0411	22.3041	1.2030
	Retentate	64.2202	9.1317	1.4790	4.0467	30.2104	0.7065
	Feed	35.0884	0.3491	0.0248	0.0411	22.3041	1.2030
Nanofiltration 2	Permeate	26.8426	0.0339	0.0011	0.0011	17.3505	0.9624
	Retentate	68.0715	1.6099	0.1195	0.2012	42.1187	0.2406
	Feed**	24.7911	0.0458	0.0021	0.0020	16.0062	2.2103
Reverse osmosis	Permeate	0.1934	0.0001	0.0000	0.0000	0.1252	0.7316
	Retentate	36.9612	0.0684	0.0031	0.0030	23.8636	1.4787
	Feed	36.9612	0.0684	0.0031	0.0030	23.8636	1.4787
Electrodialysis	Diluate	23.2117	0.0549	0.0029	0.0027	14.9712	1.2477
	Concentrate	111.2235	0.1408	0.0045	0.0046	71.8919	0.2310
Evaporative crystallizer	Feed	111.2235	0.1408	0.0045	0.0046	113.7506	0.2310
	Distillate	0.0000	0.0000	0.0000	0.0000	0.0000	0.0850
	Concentrate	175.9829	0.2228	0.0072	0.0073	113.7506	0.1460
Crystallizer	Feed	175.9829	0.2228	0.0072	0.0073	113.7506	0.1460
	Distillate	0.0000	0.0000	0.0000	0.0000	0.0000	0.1450
	Concentrate	200.0993	33.1037	1.0754	0.2406	89.6266	0.0010

*Mixture of feed water, recycled NF2 retentate and recycled NF1 retentate after gypsum precipitation;
**Mixture of NF2 permeate and ED diluate.

limiting the amount of product obtained in the installed evaporative crystallizer. Gypsum saturation of the NF1 retentate is 319%, which according to the laboratory experiments [16] should be manageable without antiscalants if NF modules were equipped in thin intermembrane spacers of narrow residence time distribution. The slightly smaller amount of produced gypsum in the NFCr-ZOD and NFCr-ROED-ZOD cases can be explained as a result of

discarding 5% of supersaturated solution before the recycle in the NFCr a (depicted as waste stream in Fig. 2). The application of nanofiltration membranes also increases the magnesium concentration in the NF1/NF2 retentate, which opens up the possibility of magnesium recovery.

The application of ROED can decrease the energy consumption even further, by 54% compared to the reference ZOD-only case. The root cause is the very high

Table 5
The ionic composition and flow rates of process streams in the NFCr-ROEDCr case

		C_{Cl^-} (kg/m³)	$C_{Ca^{2+}}$ (kg/m³)	$C_{Mg^{2+}}$ (kg/m³)	$C_{SO_4^{2-}}$ (kg/m³)	C_{Na^+} (kg/m³)	V (m³/h)
Feed water		28.1060	0.9190	1.0460	1.4950	25.6156	1.0000
Nanofiltration 1	Feed*	45.8672	3.5986	0.5628	1.5232	30.3360	1.9096
	Permeate	35.0884	0.3491	0.0248	0.0411	22.3041	1.2030
	Retentate	64.2202	9.1317	1.4790	4.0467	30.2104	0.7065
Nanofiltration 2	Feed	35.0884	0.3491	0.0248	0.0411	22.3041	1.2030
	Permeate	26.8426	0.0339	0.0011	0.0011	17.3505	0.9624
	Retentate	68.0715	1.6099	0.1195	0.2012	42.1187	0.2406
Reverse osmosis	Feed**	24.2559	0.0488	0.0026	0.0024	15.6552	2.3439
	Permeate	0.1892	0.0001	0.0000	0.0000	0.1225	0.8157
	Retentate	37.1013	0.0748	0.0039	0.0037	23.9457	1.5282
Electrodialysis	Feed	37.1013	0.0748	0.0039	0.0037	23.9457	1.5282
	Diluate	22.4463	0.0592	0.0036	0.0033	14.4693	1.3824
	Concentrate	175.9673	0.2227	0.0072	0.0073	113.7407	0.1459
Evaporative crystallizer	Feed	175.9673	0.2227	0.0072	0.0073	113.7407	0.1459
	Distillate	0.0000	0.0000	0.0000	0.0000	0.0000	0.1449
	Concentrate	199.9615	33.2746	1.0816	0.2392	89.3282	0.0010

*Mixture of feed water, recycled NF2 retentate and recycled NF1 retentate after gypsum precipitation;
**Mixture of NF2 permeate and ED diluate.

Table 6
Recovery of resources in the four compared cases

Case	Recovered solids (kg/h)		Energy consumption (kWh/t of salt)	Salt recovery (%)	Water recovery (%)
	Salt	Gypsum			
ZOD	29.13	2.559	1,513	62.9	94.0
NFCr-ZOD	42.25	2.416	1,176	91.2	96.1
NFCr-ROED-ZOD	42.02	2.416	694	90.7	96.2
NFCr-ROEDCr	41.98	2.416	596	90.6	96.1

energy consumption of the evaporators used in the ZOD system – 44 kWh/m³ for concentration and 66 kWh/m³ for crystallization. Fig. 5 presents the breakdown of energy consumption for each of the proposed systems. The energetically-ineffective evaporator is responsible for the majority of the energy costs (83.9% and 72.7% of the total energy consumption for the ZOD and NFCr-ZOD, respectively). In the NFCr-ROED-ZOD system, the largest energy consumers are the electrodialyzer and the evaporative crystallizer (32.6% and 29.4% of the total energy consumption, respectively).

Application of less energy-consuming electrodialyzer can decrease the energy consumption even further. Although the electrodialyzer modeled in the ROED case is already energy-efficient (0.3 kWh/kg of transported salt), there is room for improvement by using more selective membranes with lower electric resistance and spacers with increased mass transfer coefficients and narrower boundary layers. Such possibility was confirmed in the bench-scale experiments (ROEDCr), when the electrodialyzer was able to reach a salinity of 176 kg/m³ as Cl⁻.

An alternative approach may be to use ultra-high pressure reverse osmosis. The retentate salinity in reverse osmosis is limited because of the high osmotic pressure of the concentrated solutions. Electrodialysis is not hindered by this limitation, but the simulation results showed ca. 4 times higher energy consumption than the RO. In this paper, the upper limit for RO pressure was assumed as 70 bar; however, RO systems working at higher pressures are possible. It is possible that RO working at 90 bars might help decrease the energy consumption even further.

Finally, the application of a less energy-consuming crystallizers may be a big improvement. The ZOD uses mechanical vapor compression and is entirely powered by electric energy. There are many alternative crystallizer designs possible, for example, using steam for heating.

The investment costs were not taken into account in this study. In the case of more complex, integrated and hybrid ZLD systems the investment costs may be prohibitive compared to relatively simpler systems, such as ZOD. On the other hand, the decrease in energy consumption may be more important when a long-term operation is
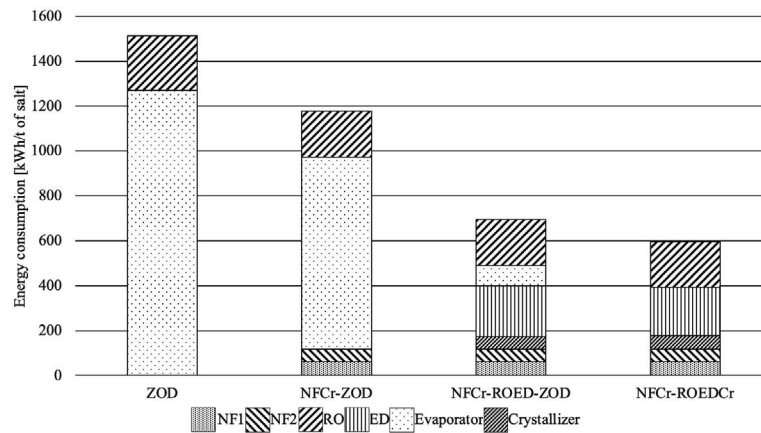
Fig. 5. Breakdown of energy consumption in each of the proposed cases.

envisioned – for example, the Dębieńsko salt production plant has been in continuous operation since the 1980s. The decreased energy consumption also helps in mitigating the CO_2 emissions associated with coal mine water treatment. Since Poland's energy sector largely relies on coal, emissions caused by electricity generation 719 g CO_2/kWh [26]; application of the proposed near-ZLD system would save up between 589–660 kg of CO_2/t of produced salt and help to achieve national emission goals. While in the context of saline coal mine waters the priority is to mitigate the problems caused by salinization of surface waters, it should be also noted that the application of near-ZLD systems allows for recovery of demineralized water. The demineralized water can be either discharged to the rivers safely, as the salt has been removed, or it can be reused by the industry. Generally, the volume of discharged water is too high to be completely reused by the coal mine, but a lot of them are located in the industrial clusters, so the other water-intensive industries (e.g., energy industry, textile industry, agriculture) could reuse the generated water. The quality of the water generated by the near-ZLD systems described in this work should be comparable with potable water in terms of salinity.

4. Conclusions

The possibility of decreasing energy consumption and increasing the salt recovery was investigated by simulating four cases: evaporation-crystallization, the reference case modeled after the "Dębieńsko" salt production plant operating in Czerwionka-Leszczyny, Poland; the application of two-pass nanofiltration with intermediate crystallization before the evaporation-crystallization system; the near-ZLD hybrid membrane-thermal system consisting of two-pass nanofiltration with intermediate crystallization, reverse osmosis, electrodialysis, evaporator and evaporative crystallizer; the application of two-pass nanofiltration with intermediate crystallization followed by hybrid reverse osmosis-electrodialysis system capable of reaching high enough salinity that the produced concentrate can be directly fed to the evaporative crystallizer. The results show that the application of a near-ZLD system can substantially decrease energy consumption by removing the bivalent impurities in the pretreatment step and saving up the energy of the concentration step. The NFCr-ROEDCr is the best configuration out of the tested ones from the point of view of the economics of the process: it exhibits the lowest energy consumption (596 kWh/t of salt) with a high salt recovery (90.6%). From the point of view of avoiding salt discharge to the environment, the NFCr-ZOD offers higher salt recovery (91.2%); however, it achieves that with significantly higher energy consumption (1176 kWh/t), meaning small environmental benefits in decreasing water salinization would likely be defeated by an increase in emissions related to electricity production. There was no significant difference between water recovery in the existing ZOD technology and in the proposed near-ZLD systems.

Acknowledgment

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