Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20578

75 (2017) 363–367
May

Electrodialytic utilization of coal-mine brines

Krzysztof Mitko*, Błażej Podleśny, Agata Jakóbik-Kolon, Marian Turek

Silesian University of Technology, Faculty of Chemistry, ul. B. Krzywoustego 6, 44-100 Gliwice, Poland, Tel. +48 32 237 28 05; email: krzysztof.mitko@polsl.pl

Received 2 August 2016; Accepted 7 February 2017

ABSTRACT

In order to decrease the environmental footprint of the coal mining industry, which produces vast amounts of saline wastewaters, desalination is required. In this work, a batch-mode electrodialysis of two coal-mine waters, having total dissolved salt content of 56.3 and 97 g/L, was performed using a module (MEGA EDR-Z) equipped with 10 pairs of Ralex CMH/AMH membranes and 0.8 mm thick spacers. The influence of the applied current density (100–400 A/m^2) on the energy consumption and the ionic composition of the diluate and concentrate was investigated. Based on the results, an integrated system for coal-mine water treatment was designed.

Keywords: Coal-mine waters; Desalination; Electrodialysis

1. Introduction

The coal mining industry in Poland produces vast amounts of waters, often highly saline, which generates the necessity of coal-mine water utilization [1]. High salinity of coal-mine waters occurs because the seams of the coalfield lie in predominantly sandstone strata in which waters within this aquifer gradually increase in salinity with increasing depth [2]. Various methods have been proposed for the coal-mine water treatment: application of nanofiltration as a thermal method pretreatment [3], electrodialysis and electrodialysis reversal for simultaneous desalination and production of concentrated brine [4–7], integrated reverse osmosis–forward osmosis system for treatment of low-salinity coal-mine water [8], and capacitive deionization [9].

Because some more concentrated coal-mine waters resemble seawater or seawater reverse osmosis (SWRO) brines, one could apply the same treatment methods. One of the possible methods for seawater and SWRO brines utilization is the production of evaporated salt. Application of membrane processes in evaporated salt production from seawater has been thoroughly studied, and various integrated designs have been proposed, such as integration of ultrafiltration, nanofiltration, reverse osmosis, distillation, and crystallization [10,11]; integration of nanofiltration, reverse osmosis, and membrane crystallization [12]; integration of reverse osmosis, electrodialysis, and crystallization [13,14], sometimes with additional nanofiltration [15,16]; and many others. Production of evaporated salt or concentrated brine is therefore a convenient method of the utilization of highly concentrated coal-mine waters, which resemble seawater. In Czerwionka-Leszczyny, Poland, the thermal desalination plant, formerly known as "Dębieńsko", treats waters 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 water is concentrated using vapor compression (VC) method; then the evaporated salt and gypsum are crystallized [1,17]. The evaporators are powered by electric energy, which makes them expensive; the energy consumption of brine concentrator (VC) is 44 kWh/m^3 of distillate, while the energy consumption of the brine crystallizer (RCC) is 66 kWh/m^3 of distillate [4,5,18].

---

* Corresponding author.

Presented at PERMEA 2016 (Membrane Science and Technology Conference of Visegrád Countries) and MELPRO 2016 (Membrane and Electromembrane Processes Conference), 15–19 May 2016, Prague, Czech Republic.

In this paper, we have investigated the electrodialysis as a method for the treatment of coal-mine waters. Two kinds of water were investigated – marked "A" and "B". The waters were collected in two coal mines located in Silesian Voivodeship, Poland. The water composition is presented in Table 1. The investigated coal-mine waters are particularly challenging for desalination, as they have high salinity and high amount of calcium and sulfate ions. On the other hand, the organic content is quite low and was never reported as a problem when the waters were subjected to a thermal treatment and crystallization despite no sophisticated pretreatment. If electrodialysis was to be applied for coal-mine water treatment, we expect microfiltration or even ultrafiltration pretreatment to be installed, which should remove most of the largest organic substances. Moreover, in the case of electrodialysis, the organic particles are either unaffected by the electric field if they are undissociated or, because of their size, have very low diffusion coefficient in the membrane. Thus, the organic content will not accumulate in the concentrate, contrary to what happens in pressure-driven methods.

2. Experimental

Coal-mine waters "A" and "B" were subjected to microfiltration (pore size of the membrane: 0.45 μm) prior to the experiments. Ionic composition of coal-mine waters and the samples collected during the experiments was determined using ICS-5000 ion chromatograph (ThermoDionex, USA).

The batch-mode, constant current experiments were performed in a plate-and-frame electrodialyzer (MEGA EDR-Z) equipped with 10 pairs of Ralex CMH/AMH membranes and 0.8 mm thick spacers. The properties of the applied membranes are presented in Table 2. The membrane effective area was 64 cm^2. The linear flow velocity of both diluate and concentrate was 2 cm/s. Initially, both diluate and concentrate tanks were filled by either "A" or "B" water. The applied current density range was 100–400 A/m^2. During the experiments, samples of diluate and concentrate were collected, and the volume change in both diluate and concentrate tank was measured.

3. Results

The results are presented in Tables 3 and 4. The results show that the water flux across the membranes is quite high, especially at higher current densities. This may limit the application of electrodialysis in production of concentrated brine. In previous experiments [19], we were able to reach sodium chloride saturation in the concentrate, although we used thin, homogenous membranes and very high current densities. Casas et al. [20] have modeled a pilot electrodialysis plant for SWRO brine concentrations. Based on the Nernst–Planck equation and mass balance equations, they have developed a model describing the plant performance with respect to the transport of sodium chloride; however, calcium and magnesium transport was neglected. Although the desired chlor-alkali feed concentration of 300 g/L as NaCl was not reached in the experiments because current density was not high enough, the model predicted that such concentrations should be reached in the investigated plant at ca. 600–700 A/m^2 after 25–28 h of operation (inlet concentration ca. 65 g/L as NaCl). Based on experimental results presented in Tables 3 and 4, we predict that the water flux across Ralex CMH/AMH membranes will be too high to achieve sodium chloride saturation. The water flux measured in [19] was in the range of 5.9–8.7 × 10^{-7} m/s (current density range of 368–617 A/m^2), whereas the water flux measured during the experiments with Ralex CMH/AMH membranes was in the range of 2.1–11.2 × 10^{-5} m/s (calculated as $\Delta V/(At)$, where ΔV is the mean change in diluate and concentrate volume; A is the effective membrane area, 64 cm^2; and t is the time of the experiment). The maximum concentrate total dissolved salt (TDS) can be calculated knowing the ratio of ion flux to water flux (in other words, ratio of ions passing through the membrane to water passing through the membrane can be treated as the concentration of the stream being added to the concentrate).

The energy consumption during the experiments was very high, as presented in Table 5. To compare electrodialysis directly with the VC utilized in "Dębieńsko" plant, we have calculated equivalent energy of the thermal method as follows: (1) calculate the amount of water that would have to be evaporated to obtained water of the same TDS as the electrodialysis diluate using the evaporative method; (2) multiply it by 44 kWh/m^3 to obtain the energy consumption of the thermal method; and (3) divide it by mass of salt transported in electrodialysis to get the comparable value. The results show that to produce electrodialysis concentrate by the thermal method one would need to spend more energy, which means electrodialysis can be a good replacement in this case.

Table 1
Main components of the investigated coal-mine waters

Brine	Concentration (g/dm^3)					TDS (g/dm^3)
	Cl$^-$	SO$_4^{2-}$	Mg^{2+}	Ca^{2+}	Na$^+$	
A	33.9	0.973	0.978	0.773	19.7	56.3
B	57.8	2.85	2.33	2.03	32.0	97.0

Table 2
Selected properties of the applied membranes

Membrane		Ralex CMH	Ralex AMH
Type		Cation exchange	Anion exchange
Electrical resistance in 0.5 M NaCl (W/cm^2)		9.0 ± 0.5	7.5 ± 0.5
Transport number		>0.98	>0.97
Ion-exchange capacity (meq/g)		2.2	1.8
Thickness in medium (μm)	Dry	430 ± 10	430 ± 10
	Demineralized water	610 ± 10	580 ± 10
	10 g/dm^3 NaCl	600 ± 10	570 ± 10
	100 g/dm^3 NaCl	550 ± 10	530 ± 10
	300 g/dm^3 NaCl	490 ± 10	510 ± 10

Table 3
The experimental conditions (current density, *I*; time, *t*; initial volumes, V_d and V_c), ionic composition of the obtained diluate and concentrate, and the mean change in diluate and concentrate volume, ΔV, during the experiments with coal-mine water "A"

i (A/m²)	*t* (min)	C_d (g/dm³)						C_c (g/dm³)						V_d (dm³)	V_c (dm³)	ΔV (dm³)
		Cl^-	SO_4^{2-}	Mg^{2+}	Ca^{2+}	Na^+	TDS	Cl^-	SO_4^{2-}	Mg^{2+}	Ca^{2+}	Na^+	TDS			
102	15	19.6	0.945	0.332	0.221	12.3	33.4	37.3	1.08	0.998	0.773	21.9	62	0.15	0.15	0.02
102	30	9.18	0.723	0.124	0.045	6.00	16.1	39	1.09	1.05	0.818	22.8	64.8	0.15	0.15	0.041
202	15	14.8	0.822	0.256	0.137	9.33	25.3	40.8	0.923	0.934	0.73	24.2	67.3	0.202	0.194	0.028
202	30	0.335	0.092	0.005	0.006	0.245	0.683	48.8	1.17	1.12	0.887	29.0	81	0.202	0.194	0.055
299	10	13.9	0.823	0.252	0.162	8.73	23.9	40.8	1.1	1.11	0.876	23.8	67.7	0.198	0.202	0.027
299	18	1.89	0.275	0.028	0.014	1.29	3.49	47.1	1.26	1.29	1.03	27.5	78.1	0.198	0.202	0.054
403	10	7.32	0.603	0.153	0.077	4.65	12.8	49.2	1.33	1.41	1.15	28.5	81.6	0.2	0.198	0.043

Table 4
The experimental conditions (current density, *I*; time, *t*; initial volumes, V_d and V_c), ionic composition of the obtained diluate and concentrate, and the mean change in diluate and concentrate volume, ΔV, during the experiments with coal-mine water "B"

i (A/m²)	*t* (min)	C_d (g/dm³)						C_c (g/dm³)						V_d (dm³)	V_c (dm³)	ΔV (dm³)
		Cl^-	SO_4^{2-}	Mg^{2+}	Ca^{2+}	Na^+	TDS	Cl^-	SO_4^{2-}	Mg^{2+}	Ca^{2+}	Na^+	TDS			
102	10	58	3.23	2.36	1.88	32.4	97.9	70.5	3.36	1.97	2.03	41.2	119	0.198	0.198	0.008
102	20	58.7	3.63	2.54	1.8	32.8	99.5	76.9	3.24	1.95	1.96	45.4	129	0.198	0.198	0.016
102	30	51.7	3.74	2.22	1.54	29.3	88.5	79.1	3.31	2.09	1.97	46.6	133	0.198	0.198	0.024
203	10	46.4	2.9	1.23	1.24	27.7	79.4	60.3	2.52	2.04	1.97	34.1	101	0.202	0.202	0.019
203	20	33.1	2.65	1.35	0.909	19.1	57.1	63.6	2.41	2.04	1.72	36.5	106	0.202	0.202	0.037
203	30	13	1.47	0.539	0.303	7.75	23.1	67.9	2.37	2.1	1.79	39.0	113	0.202	0.202	0.056

Table 5
Comparison of energy consumption in electrodialysis and thermal method

Coal-mine water	*i* (A/m²)	Energy consumption in electrodialysis (kWh/kg)	Equivalent energy consumption in thermal method (kWh/kg)
A	102	0.308	1.75
A	202	0.661	1.34
A	299	0.864	1.40
A	403	0.987	1.60
B	102	0.188	1.50
B	203	0.606	1.51

Based on the ionic composition of the diluates and concentrates obtained at various applied current densities, we have designed an integrated system for coal-mine water treatment. In the designed system, the electrodialysis treats the coal-mine water, producing desalinated water and concentrated brine. The brine is then further concentrated by a VC unit and passed to a crystallizer (RCC), similar to the "Dębieńsko" plant [1,4,5,17,18]. For comparison, a VC–RCC system without electrodialysis unit has been designed as well (Fig. 1). The design of a VC and RCC units has been described elsewhere [21] – a following set of assumptions has been made:

- The maximum concentration of bivalent ions in the post-crystallization lyes is 8% (w/w) as $MgCl_2$ + $CaCl_2$ – this is the actual limit of the crystallizer in the existing plant.
- The maximum chloride concentration in the postcrystallization lyes is 200 g/L.
- The solubility product of calcium sulfate is 4.302×10^{-6} mol⁴/dm¹² – value calculated based on the composition of postcrystallization lyes from the plant and corresponding to the temperature and ionic strength of the liquid in the existing crystallizer.

The simulation procedure was as follows:

- Take the composition and volume of concentrate obtained during the laboratory tests of the electrodialysis.
- Calculate the composition of the VC unit output using mass balances, assuming the limiting condition is the chloride content <176 g/dm³ – the same as in the existing plant.
- Calculate the composition of the crystallizer using mass balances, taking into account three boundary conditions (Ca + Mg limit, NaCl limit, gypsum solubility limit).

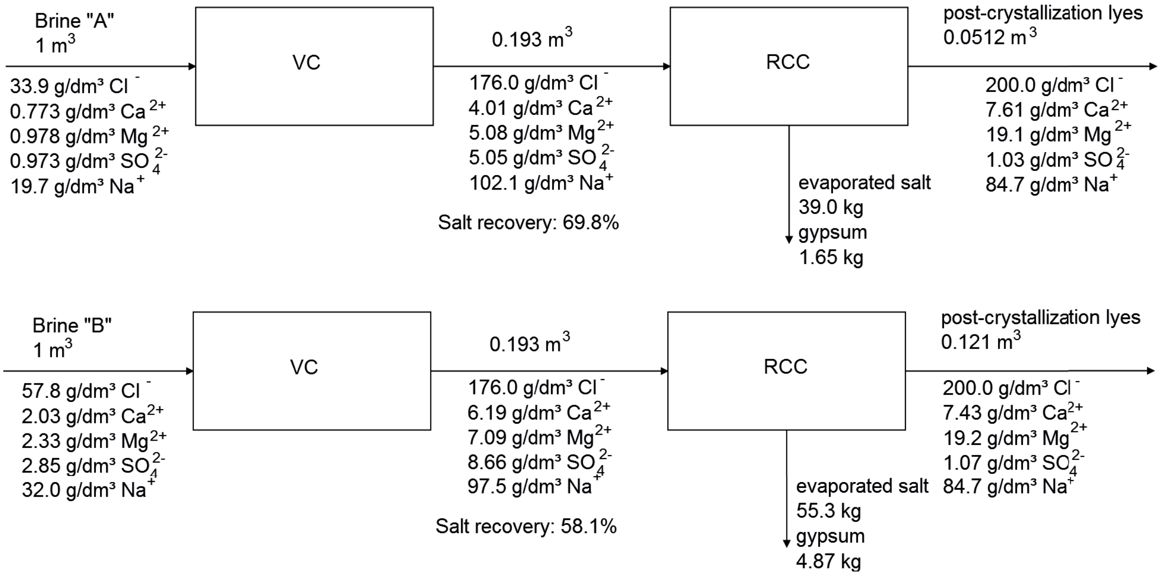

Fig. 1. A scheme of thermal desalination plant treating waters "A" and "B".

Table 6
The overall salt recovery calculated for each applied current density investigated

Coal-mine water	i (A/m^2)	Salt recovery (%)
A	102	76.7
A	202	77.9
A	299	71.2
A	403	59.3
B	102	47.3
B	203	50.6

- Calculate the overall salt recovery as the ratio of the amount of chlorides in the evaporated salt to the amount of chlorides in the electrodialysis feed water.

The results of the process design, presented in Table 6, shows that in case of water "A", the presented system reaches highest overall salt recovery (defined as the mass of the crystallized sodium chloride per amount of sodium chloride carried by 1 m^3 of the feed brine) at relatively low current density applied in the electrodialysis. The electrodialysis increased the overall salt recovery thanks to changes in ion composition of the concentrate. This is because the current density strongly influences the selectivity of ion-exchange membranes, thus influencing the ratio of sulfate to calcium ions in the produced concentrate and the amount of gypsum precipitated in the RCC. When the amount of the crystallized gypsum is high, more salt can be produced before reaching the 8% bivalent ions content limit. In case of water "B", however, the overall salt recovery has been decreased.

4. Conclusions

Electrodialysis was applied as a coal-mine water treatment method. Based on the laboratory results, the integration of electrodialysis into a thermal plant producing evaporated salt was investigated. The results show that electrodialysis can increase the overall salt recovery if the less concentrated water (TDS of 56.3 g/dm^3) is to be treated at low current densities.

Acknowledgment

The presented research was funded within the Iuventus Plus framework of the Polish Ministry of Science and Higher Education (project no. IP2014 031273).

References

[1] B. Ericsson, B. Hallmans, Treatment and disposal of saline wastewater from coal mines in Poland, Desalination, 98 (1994) 239–248.
[2] M. Andersson, Change and Continuity in Poland's Environmental Policy, Springer, Dordrecht, Netherlands, 1999.
[3] M. Turek, M. Gonet, Nanofiltration in the utilization of coal-mine brines, Desalination, 108 (1997) 171–177.
[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, Comprehensive utilization of brackish water in ED — thermal system, Desalination, 221 (2008) 455–461.
[7] J. Chromíková, V. Matúšková, J. Thomas, P. Malíková, L. Volavková, Application of membrane processes for mine water treatment, Miner. Eng., 15 (2014) 181–186.
[8] R. Thiruvenkatachari, M. Francis, M. Cunnington, S. Su, Application of integrated forward and reverse osmosis for coal mine wastewater desalination, Sep. Purif. Technol., 163 (2016) 181–188.
[9] X. Sun, J.-Y. Hwang, Desalination of Coal Mine Water with Electrosorption, Chapter 21, J. Drelich, Ed., Water in Mineral Processing, Society for Mining, Metallurgy, and Exploration (SME), Englewood, CO, USA, 2012.
[10] M. Turek, P. Dydo, Hybrid membrane–thermal versus simple membrane systems, Desalination, 157 (2003) 51–56.
[11] M. Turek, M. Chorążewska, Nanofiltration process for seawater desalination-salt production integrated system, Desal. Wat. Treat., 7 (2009) 178–181.

[12] E. Drioli, A. Criscuoli, E. Curcio, Integrated membrane operations for seawater desalination, Desalination, 147 (2002) 77–81.

[13] T.A. Davis, Production of Purified Water and High Value Chemicals from Salt Water, Patent No. US2004055955, 2004.

[14] 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.

[15] P.S. Wallace, Membrane and Electrodialysis Based Seawater Desalination with Salt, Boron and Gypsum Recovery, Patent No. US8999171, 2015.

[16] A. Raman, Process and System for Producing Sodium Chloride Brine, Patent Application No. WO2013023249, 2012.

[17] B. Ericsson, B. Hallmans, Treatment of saline wastewater for zero discharge at the Debiensko coal mines in Poland, Desalination, 105 (1996) 115–123.

[18] M. Turek, J. Mrowiec-Białoń, W. Gnot, Utilization of coal mine brines in the chlorine production process, Desalination, 101 (1995) 57–67.

[19] 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.

[20] S. Casas, N. Bonet, C. Aladjem, J.L. Cortina, E. Larrotcha, L.V. Cremades, Modelling sodium chloride concentration from seawater reverse osmosis brine by electrodialysis: preliminary results, Solvent Extr. Ion Exch., 29 (2011) 488–508.

[21] M. Turek, E. Laskowska, K. Mitko, M. Chorążewska, P. Dydo, K. Piotrowski, A. Jakóbik-Kolon, Application of electrodialysis and nanofiltration for better performance of a salt production plant, Desal. Wat. Treat., 64 (2017) 244–250.