

# Electrodialytic desalination and concentration of coal-mine brine

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## Abstract

Electrodialysis (ED) of coal-mine brine was investigated as the first stage of an ED–evaporation–crystallization system. Univalent ion permeable ACS and CMS membranes (Tokuyama) were applied in the first step while normal-grade CMV and AMV Asahi Glass membranes and electrodialysis reversal (EDR) were used in the second step (for the first step diluate treating). Electrodialysis in the countercurrent flow mode and electrodialysers with small intermembrane distances were applied to diminish problems that result from major differences in ED concentrate and diluate concentrations. A single-pass low residence operating time mode was applied to avoid gypsum crystallization in the EDR concentrate. A coal-mine brine with 32.8 g/L  $\text{Cl}^-$  content was desalinated and concentrated at a current density of 344–688 A/m<sup>2</sup> in the first step and 300 A/m<sup>2</sup> in the second. First step diluate was treated by EDR yielding 85% recovery. The total energy consumption found was equal to 7.8–14.4 kWh/m<sup>3</sup> inlet brine depending on the first step current density and the first step ED concentrate composition (TDS equal to 136–290 g/L). It was found that ED concentrate met requirements concerning low  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  concentrations to avoid gypsum crystallization during further evaporation. The comparison of RCC vapour compression evaporation and proposed electrodialytic concentration showed an advantage of ED treatment.

**Keywords:** Desalination; Salt production; Electrodialysis; Electrodialysis reversal; Evaporation; Integrated systems

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## 1. Introduction

Coal mines in Poland discharge ca. 550,000 m<sup>3</sup>/d of water containing 4000 t/d of chlorides and sulphates into the Vistula and Odra river basins, which makes ca. 2.4 million tons of salt load yearly (as sodium chloride) [1]. Several

ways of solving the problem of saline water are being considered, namely [2]:

- mining–geological methods of limiting saline water influx into mine workings;
- methods of saline water discharge reduction once water has been pumped up to the surface:  
(1) saline water recirculation, (2) underground

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reinjection, shallow and deep, (3) water underground storage, (4) hydraulic engineering method–retention, and (5) controlled discharge into rivers;

- saline water utilization.

Saline water utilization is the most effective way of avoiding environmental problems resulting from its disposal into water bodies. Sodium chloride, other chemical compounds, and desalinated water are the products of the typical utilization process. Saline mine water can also be directly used in the chemical industry [3].

Regardless of the ways saline mine waters are reused, they have to be preconcentrated since their salt concentration is much lower than that of natural saturated brines or brines obtained by leaching salt beds — a typical source of sodium chloride (NaCl concentration: 305–315 g/L). In the case of coal-mine brines, the evaporation method is used for concentrating [3–8], although reverse osmosis [5] and electrodialysis (ED) [2,5,9] have also been considered.

Despite the fact that the utilization of saline waters is considered to be the most adequate method of solving ecological problems caused by this kind of water in Poland, there is only one installation utilizing coal-mine waters. In 1994 an installation was put into operation for the processing of the Debiensko and Budryk coal-mine brines [4–8]. This plant replaced another one constructed by the Main Institute of Mining, equipped with a 12-stage expansion evaporator, which started in 1975 [5,7].

Brine with a TDS of about 80 g/L is concentrated making use of the vapour compression (VC) method in two evaporators (brine concentrators) designed by the Resources Conservation Company in Seattle (RCC). The evaporator is a seeded, falling film evaporator with vapour compression. Brine concentrators are designed to significantly reduce the volume of the feed without scaling of the heat transfer surface. The feed is concentrated to near the point at which

NaCl is precipitated. Calcium sulphate coming out of the solution is preferentially deposited on nucleation sites by recycled seed crystals instead of the heating surface [7]. This installation produces up to 100,000 t of salt and 10,000 t of discarded calcium sulphate per year. A disadvantage of the installation is the exclusive use of the most expensive form of energy, i.e., electricity. The energy consumption in the brine concentrator is as high as 30.4 kWh per 1 m<sup>3</sup> of distillate [7], while the total consumption of energy in the thermal installation comprising evaporators, a crystalliser and the utilization of lyes has been estimated not to exceed 45 kWh/m<sup>3</sup> of processed brine [8]; however, the problem of processing the lyes has not yet been solved.

## 2. Membrane pre-treatment of saline waters

High energy consumption in the above-mentioned methods of evaporation is a considerable restriction in the utilization of saline mine waters. An obstacle in the application of low energy evaporation processes, e.g., multi-stage flash (MSF) or VC, is the high concentration of calcium and sulphate ions in the coal-mine waters.

A method of pre-treatment of coal-mine saline waters was proposed [5] consisting of reducing the concentration of calcium or sulphate ions to avoid gypsum crystallization during further evaporation. The product of the concentrations of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> ions, expressed in mol/L, in the saline water being evaporated should not exceed:

$$(c_1/c_2)^2 \cdot 1.45 \cdot 10^{-3} \quad (1)$$

where  $c_1$  is the concentration of salt (NaCl) in the saline water before evaporation and  $c_2$  is the concentration of salt in the concentrated brine. Nanofiltration and ED with membranes with a low transport number for divalent ions are proposed as pre-treatment methods.

In our previous research the profitability of low-salinity mine water utilization in the ED–evaporation system was proved [9]. The efficiency of electrodialytic seawater desalination [10] and dual-purpose desalination–salt production ED [11] were also demonstrated.

### 3. Experimental

Results are presented for the investigations of the efficiency of using ED as an element of a comprehensive Debiensko coal-mine brine utilization process. It was assumed that ED is used for a pre-concentration of the coal-mine brine as an alternative to high energy consumption evaporation with the RCC method. The concentrate obtained in the ED step was further concentrated using a low-cost evaporative method up to a concentration of 290 g/L NaCl. Simultaneously, with coal-mine brine being concentrated, the concentrations of calcium and sulphate decreased against sodium chloride in the process of ED, and therefore membranes with the transport number for divalent ions lower than that for monovalent ions were applied. Concentration to 290 g/L by ED alone was also considered to eliminate the evaporative brine concentration step. ED was investigated at the laboratory ED stand (Fig. 1).

Univalent ion permeable ACS and CMS membranes (Tokuyama) were applied in the first step and normal-grade CMV, AMV Asahi Glass membranes in the second step (for the first step diluate treating). An ED stack developed by the author equipped with a 0.19 mm spacer was used. [10]. A single-pass low residence operating time mode was used to avoid gypsum crystallization in the EDR concentrate [11,12]. The Debiensko coal-mine brine was treated at a current density of 344–688 A/m<sup>2</sup> in the first step and 300 A/m<sup>2</sup> in the second. The composition of coal-mine brine and ED diluates and concentrates are presented in Table 1.

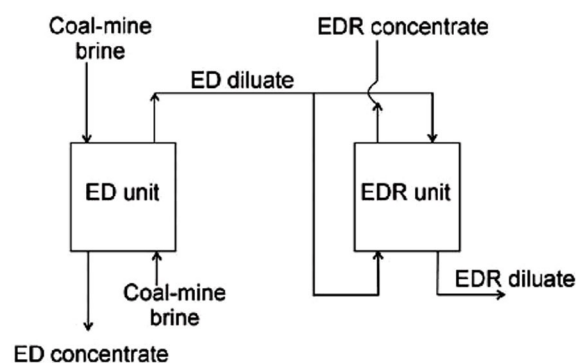


Fig. 1. Scheme of coal-mine brine pre-concentration by electro dialysis.

Table 1  
Composition of coal-mine brine and ED diluates and concentrates (g/L)

Item	Coal-mine brine	Series 1		Series 2		Series 3	
		Diluate	Conc.	Diluate	Conc.	Diluate	Conc.
Ca <sup>2+</sup>	0.462	0.386	0.598	0.351	0.773	0.446	0.558
Mg <sup>2+</sup>	0.383	0.354	0.434	0.325	0.547	0.378	0.411
Cl <sup>-</sup>	32.8	4.36	87.75	3.04	117.1	8.52	175.93 <sup>a</sup>
SO <sub>4</sub> <sup>2-</sup>	1.824	2.208	1.152	2.05	1.181	1.944	1.109
Vol. per 1 m <sup>3</sup> of inlet brine		0.637	0.363	0.739	0.261	0.855	0.145

<sup>a</sup>–290 g/L as NaCl.

Table 2  
Performance of the first step electrodialysis

Item	Series 1	Series 2	Series 3
Current density, A/m <sup>2</sup>	344	516	688
Voltage drop per cell pair, V	0.300	0.405	0.639
Current efficiency, %	89	89	90
Power consumption, kWh/t NaCl transferred through the membrane	162	222	307
Power consumption, kWh/m <sup>3</sup> of inlet brine	6.3	7.7	12.4

Table 3  
Composition of EDR diluate and concentrate (g/L)

Item	Diluate	Conc.
Ca <sup>2+</sup>	0.0701	1.942
Mg <sup>2+</sup>	0.0649	1.795
Cl <sup>-</sup>	0.567	17.06
SO <sub>4</sub> <sup>2-</sup>	0.576	10.40
Vol. per 1 m <sup>3</sup> of inlet brine	0.85	0.15

Diluate from the first step ED was treated by EDR (Table 2). The composition of EDR diluate and concentrate, obtained by Series 2 ED diluate treating, is presented in Table 3.

The power consumption in the EDR step was equal to 2.35 kWh per 1 m<sup>3</sup> of ED diluate. The calcium sulphate scaling potential of the EDR concentrate was then characterized as previously described [12]. Scaling did not occur despite a 411% calcium sulphate saturation level and 93 s induction time of gypsum nucleation.

The sum of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> concentrations in the EDR diluate (Table 3) is equal to 1.143 g/L. According to Polish regulations, water having such a salt concentration (below 1.5 g/L) may be discharged; it can also be used in some mining processes.

The EDR concentrate may be treated with

Table 4  
Power consumption per 1 m<sup>3</sup> of coal-mine brine in the process of its concentration to 290 g/L of NaCl

	Method		
	ED	Evaporator	Total
RCC	—	24.7	24.7
Series 1 ED+evaporator <sup>a</sup>	6.3	2.0	8.3
Series 2 ED+evaporator <sup>a</sup>	7.7	1.0	8.7
Series 3 ED	12.4	—	12.4
Series 1 EDR+evaporator <sup>a</sup>	7.8	2.0	9.8
Series 2 EDR+evaporator <sup>a</sup>	9.4	1.0	10.4
Series 3 EDR	14.4	—	14.4

<sup>a</sup>Low-cost evaporation method, e.g., VC; 11 kWh/1 m<sup>3</sup> of distillate power consumption was assumed.

lime to remove Mg<sup>2+</sup> as magnesium hydroxide and SO<sub>4</sub><sup>2-</sup> as gypsum. Such a treated solution, consisting mainly of NaCl, may be recycled to the feed brine stream.

The energetic efficiency of electrodialytic pre-concentration of coal-mine brine was then estimated. Power consumption in the processes of brine concentration in (1) the RCC evaporator, (2) ED followed by low-cost evaporation, and (3) ED alone was compared. The results are presented in Table 4.

#### 4. Conclusions

The results presented in Table 4 show that in each method involving ED power consumption in the process of coal-mine concentration, it is significantly lower than for the RCC evaporation method. The power consumption increased when ED concentrate salinity increased, but the purity of concentrated brine was improved at the same time (i.e., low Ca<sup>2+</sup>, Mg<sup>2+</sup>, and SO<sub>4</sub><sup>2-</sup> concentration as related to NaCl; see Table 1). This results in high salt recovery in the crystallization step but only a small amount of post-crystallization lye.

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