Recovery of NaCl from Saline Mine Water in an Electrodialysis—Evaporation System*

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A system comprising electrodialysis (ED), evaporation, and crystallization was proposed as an alternative for comprehensive utilization of low-salinity mine waters. The profitability of the system was analyzed using experimental data from a cascade of four electrodialyzers equipped with membranes of low transport number for divalent ions. The ED concentrate composition was optimized taking into account the corresponding environmental legislation, technological requirements, and plant efficiency. For mine waters with chloride content of 7.27 g dm^{-3}, the value of 90 g of Cl$^-$ per dm^3 of ED concentrate was obtained.

Coal mines in Poland discharge daily about 550 000 m^3 of water containing 4000 t of chlorides and sulfates into Vistula and Odra river basins. Every year the salt load (as sodium chloride) becomes about 2.4 million tons [1]. Several ways of solving the problem of saline water are being considered [2], including saline water utilization. Moreover, a part of these waters can be directly used in the chemical industry [3].

The analysis of the projects undertaken so far and planned to solve the problem of saline mine water shows that the most important way of lowering the salt load being discharged with water is its utilization. All water types belonging to the group IV, the so-called coal-mine brines with concentration of Cl$^-$ and SO$_4^{2-}$ higher than 42 g dm^{-3}, and a part of the group III waters, low-salinity waters containing between 1.8—4.2 g dm^{-3} of Cl$^-$ and SO$_4^{2-}$, should be included in the utilization program. Sodium chloride, desalinated water, and other chemicals are the products of the typical utilization process.

Regardless of the way the 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 with NaCl content of 305—315 g dm^{-3}. In the case of coal-mine brines, the concentration of which (as NaCl) is 70—140 g dm^{-3}, water evaporation is used to concentrate them [4], although reverse osmosis (RO) [5] and electrodialysis (ED) [3, 6] is also considered.

Preconcentration of saline mine waters by evaporation is characterized by high energy consumption.

Moreover, the presence of calcium and sulfate ions in water limits seriously application of low-energy evaporation processes, *e.g.* multistage flash (MSF). Composition of saline water submitted to evaporation should comply with the following condition:

$$c_{\text{Ca}^{2+}} c_{\text{SO}_4^{2-}} < 1.45 \times 10^{-3}(c_1/c_2) \qquad (1)$$

$c_{\text{Ca}^{2+}}$ and $c_{\text{SO}_4^{2-}}$ being molar concentrations of calcium and sulfate ions, whilst c_1 and c_2 denote NaCl concentration in the saline water prior and after water evaporation, respectively.

In order to avoid gypsum crystallization, nanofiltration was proposed to reduce the concentration of calcium or sulfate ions in coal-mine brines, meanwhile, electrodialysis with membranes of low transport number for divalent ions was recommended for lower-salinity waters [6].

Desalination of low-salinity waters (3—9 g dm^{-3} of chlorides) in a cascade of three electrodialyzers was studied recently [2]. Current densities of 50 A m^{-2}, 150 A m^{-2}, and 500 A m^{-2} were applied in the respective electrodialyzer cells at 12 cm s^{-1} linear flow velocity. At given conditions, the Cl$^-$ content in diluate dropped to 0.3 g dm^{-3}, whereas in concentrate 100 g dm^{-3} of chlorides were found (165 g dm^{-3} as NaCl), energy consumption peaked at 12.4 kWh per m^3 of processed water, and total process costs amounted to 1.99 \$ m^{-3}. These results indicate economic prevalence of ED over RO and MSF for desalination of mine waters belonging to the tested salinity range.

In the present paper, the efficiency of electrodialysis, a part of comprehensive low-salinity mine water

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utilization process, is discussed. The whole process consists of preconcentration of saline mine water by ED, and further concentration of this concentrate by water evaporation up to a concentration of 300 g dm^{-3} of NaCl, *i.e.* 182 g dm^{-3} of Cl$^-$. Simultaneously with mine water being concentrated, the concentrations of calcium and sulfate ions should decrease in the concentrate of electrodialysis. Therefore, membranes with the transport number for divalent ions lower than that for univalent ions, CMS and ACS membranes supplied by Neosepta, were applied [7].

EXPERIMENTAL

Water from "Janina" mine was selected for the investigations; its composition is given in Table 1. The salt concentration in this water is in the upper range of values deemed optimum in the electrodialysis process; it is stated that ED may compete with RO or thermal methods in the range of feed water salinity up to 10 g dm^{-3} [8].

Four-step electrodialysis in countercurrent flow mode was proposed to diminish the problems connected with a high difference between the ED concentrate and diluate salt concentrations such as high values of back electromotive force, back diffusion, and osmotic water transport [9]. Membrane-to-membrane distance of 0.4 mm was used for each stage. Because of the low cost of electric energy obtained from

Table 1. Ions Content in the Saline Water from "Janina" Mine

Ion	$\rho/(\text{g dm}^{-3})$
Cl$^-$	7.27
SO$_4^{2-}$	0.442
Na$^+$	4.47
Ca^{2+}	0.176
Mg^{2+}	0.136

co-generation system, it was assumed that electrodialysis should be carried out at as high values of current densities as possible to diminish investment costs. The limiting current densities were determined at 12 cm s^{-1} linear velocity for solutions with 4.5, 3.0, 1.7, and 1.1 g dm^{-3} Cl$^-$ concentration; these values were assumed as diluate concentrations in cascade of electrodialyzers. Electrodialysis process was carried out at current densities values equal to 80 % of their limiting values. Fig. 1 represents the current density applied at each individual cascade stage as well as the steady-state Cl$^-$ content variation in both concentrate and diluate along the electrodialyzer. The values of Cl$^-$ concentrations in ED concentrates presented in Fig. 1 are valid for one of seven series which were investigated. The complete list of concentrate concentrations values is presented in Table 2.
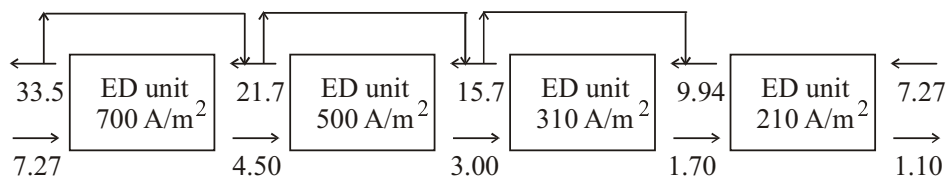

Fig. 1. Scheme of saline mine waters preconcentration by electrodialysis; numbers indicate chloride ions concentration in g dm^{-3}.

Table 2. ED Concentrate Composition and Evaluation of the Possibility of Gypsum Crystallization during Evaporation (Eqn (*1*))

Series	ED concentrates Cl$^-$ contents (g dm^{-3}) at individual cascade stages				Final ED concentrate composition			$\dfrac{c_{\text{Ca}^{2+}}c_{\text{SO}_4^{2-}}\cdot 10^5}{\text{mol}^2\ \text{dm}^{-6}}$	$\dfrac{1.45\times 10^2(c_1/c_2)}{\text{mol}^2\ \text{dm}^{-6}}$
	I	II	III	IV	$\dfrac{c_{\text{Cl}^-}}{\text{g dm}^{-3}}$	$\dfrac{c_{\text{Ca}^{2+}}}{\text{g dm}^{-3}}$	$\dfrac{c_{\text{SO}_4^{2-}}}{\text{g dm}^{-3}}$		
1	13.8	10.9	9.28	7.85	13.8	0.232	0.488	2.95	0.84
2	24.1	16.8	12.6	8.95	24.1	0.334	0.599	5.21	2.55
3	33.5	22.1	15.7	9.94	33.5	0.438	0.721	8.22	4.92
4	47.9	30.2	20.4	11.5	47.9	0.593	0.896	13.80	10.02
5	60.0	37.6	24.9	13.0	60.0	0.739	1.069	20.60	15.80
6	77.4	46.71	30.6	15.0	77.4	0.911	1.284	27.70	26.20
7	94.0	57.8	37.6	17.5	94.0	1.015	1.383	36.56	38.68
*8**					85.0	0.947	1.305	32.18	31.63

*Optimum Cl$^-$ content in ED concentrate.

RESULTS AND DISCUSSION

The preconcentration of saline mine waters by electrodialysis was tested for various salt concentrations in the concentrate (Table 2). The data from Table 2 were used to calculate the overall costs of saline water comprehensive utilization, including the water evaporation from ED concentrate to increase the Cl^- content up to 182 g dm^{-3}. Moreover, additional requirements imposed on the quality of the effluent water stream were considered. According to Polish regulations, only waters containing less than 1.5 g dm^{-3} of salt can be discharged, or reused in some mining processes.

Table 3 presents the particular costs assumed for costs evaluation of the ED-MSF system. Subsequently, the costs of further evaporation accompanied by salt crystallization were estimated. Taking into account "Ecosol" plant construction study, these costs were assumed to be 8 $ per ton of salt obtained [11, 12]. Results of economic calculations are summarized in Table 4.

The optimum concentration of chloride ions in ED concentrate was then determined assuming minimum cost of utilization (including ED, evaporation, and crystallization, Table 4) as optimization criterion. Calculations were based on quadratic equation formula estimated using the least-squares method. This value was equal to 85 g dm^{-3}. On the other hand, only ED concentrate with Cl^- content higher than *ca.* 90

Table 3. Assumed Investment and Operation Costs of Desalination Plant Based on Electrodialysis – MSF Saline Water Treatment

Effective membrane surface area/%	70
Energy costs/($ kWh^{-1})	0.03
Pump efficiency/%	85
Membrane life/y	10
Total investment costs per membrane surface area/ ($ m^{-2})	320
Maintenance costs per membrane surface area*/ ($ m^{-2})	80
Evaporation costs per m^3 of condensate [10]/($ m^{-3})	1

*25 % of the total investment costs.

g dm^{-3} was suitable for further increase of salt concentration by water evaporation, fulfilling the condition (*1*).

The desalination plant profitability was estimated assuming the salt price of 30 $ t^{-1} [13] at 85 % salt recovery from the saline mine waters. The plant economy would profit, apart of the sold salt income, from a decrease of charges paid for chloride and sulfate discharge (about 33.2 $ per ton of salt). Thus, the total benefit, 63.2 $ per ton of salt obtained, would be higher than the salt recovery costs (Table 4).

Table 4. Salt Recovery Costs

Series	Concentrate Cl^- content g dm^{-3}	Concentrate volume per 1 m^3 of saline water/m^3	ED costs/($ m^{-3}) Energy	ED costs/($ m^{-3}) Capital & others	Evaporation costs /($ m^{-3})	ED + evaporation + crystallization costs per 1 ton of salt/$
1	13.8	0.479	0.079	0.068	0.443	73.2
2	24.1	0.263	0.120	0.114	0.228	60.0
3	33.5	0.189	0.133	0.129	0.154	54.9
4	47.9	0.132	0.145	0.141	0.097	51.2
5	60.0	0.104	0.151	0.149	0.070	50.3
6	77.4	0.083	0.155	0.153	0.047	47.4
7	94.0	0.067	0.159	0.156	0.033	47.4

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