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Salt production from coal-mine brine in ED–evaporation–crystallization system

Marian Turek[a]*, Piotr Dydo[a], Romuald Klimek[b]

[a]Silesian University of Technology, Faculty of Chemistry, ul. B. Krzywoustego 6, 44–100 Gliwice, Poland
email: Marian.Turek@polsl.pl
[b]"Debiensko" Desalination Plant, ul. Mlynska 24, 44–230 Czerwionka-Leszczyny, Poland

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Abstract

ED-EDR double step electrodialytic pre-treatment and pre-concentration of "Debiensko" coal-mine brine was examined. Univalent ion permeable Tokuyama Co. ACS and CMS membranes were applied in the first electrodialysis step and normal grade CMV, AMV Asahi Glass membranes in the second. Coal-mine brine with 32.8 g/L Cl^- content was desalinated and concentrated at a current density of 344–688 A/m^2 in the first step and 300 A/m^2 in the second. The total ED-EDR energy consumption found was in the range for 9.4–14.4 kWh/m^3 of inlet brine depending on applied electric current density. The performance of crystallization step was then estimated based on chemical compositions of ED concentrates and compared with data from the "Debiensko" Desalination Plant, where currently a salt crystallizer is supplied with brine concentrated by RCC evaporation method. This comparison shows that unit energy consumption decreases from ca 970 kWh per 1 ton of evaporated salt for brine treated by RCC method to ca 500 kWh/t in the case of ED-EDR treated brine. At the same time the amount of salt in lye decreases from 110 kg per 1 ton of evaporated salt produced to 20 kg/t.

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

1. Introduction

Coal-mines in Poland discharge ca 550 m^3/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 discharged yearly (as sodium chloride) [1]. Several ways of solving the problem of saline water were recently considered and described [2,3].

Saline water utilization is the most effective way of avoiding environmental problems

*Corresponding author.

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resulting from its disposal into water bodies. Regardless of the ways saline mine waters are utilized, they have to be preconcentrated. In the case of high-salinity waters (so called coal-mine brines) the evaporation method is used for concentrating [4–9], although reverse osmosis [5] and electrodialysis [2,3,6,10] are also considered.

2. Process description

In 1994 the "Debiensko" and "Budryk" coal-mine brines treatment plant operation was started [5–9]. There the brine with a TDS of about 60 g/L is concentrated using the vapour compression 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. The feed is concentrated to near the point at which NaCl would precipitate. Calcium sulphate coming out of the solution is preferentially deposited on the nucleation sites by recycled seed crystals instead of the heating surface [8].

The brine product from the evaporators is collected in the waste/seed tank and transferred to the clarifier for separation of calcium sulphate. The overflow from the clarifier is transferred to another tank for pH adjustment with caustic soda and then fed to the crystallizer.

The crystallizer is a forced circulation submerged tube evaporator equipped with a mechanical vapor recompressor. The resulting steam is mechanically compressed and condenses in the twin crystallizer heaters, supplying all the heat normally required. The salt slurry is drained in the centrifuge thickener vessel and then dewatered in two pusher-type centrifuges operating in parallel.

The "Debiensko" Desalination Plant produces up to 100,000 t of salt per year. A disadvantage of the installation is the exclusive use of the most expensive form of energy, i.e. electric energy. According to project data the energy consumption in the brine concentrator should be equal to 30.4 kWh per 1 m^3 of distillate [8] while the total consumption of energy in the thermal installation comprising evaporators, a crystalliser and the utilization of lye has been estimated not to exceed 44 kWh/m^3 of processed brine [8]. The actual operating data are as follows: the energy consumption in the brine concentrator is equal to 44 kWh per 1 m^3 of distillate while the energy consumption in the brine crystalliser is equal to 66 kWh per 1 m^3 of distillate [9,11]. The problem of processing the lye however has not been solved so far. The magnesium ions concentration in the crystallizer may not exceed the value of 2110 meq/L, and the operating range is 1800–2110 meq/L [11]. Thus the inlet brine magnesium concentration strongly affects the amount of lye and, as the consequence, the salt recovery.

High energy consumption in the above-described method of evaporation is a considerable restriction in the utilization of saline-mine waters. An obstacle in the application of low energy evaporation processes is the high concentration of calcium and sulphate ions in the coal-mine saline waters.

3. Electrodialytic pre-treatment and pre-concentration

A method of pre-treatment of coal-mine saline waters has been proposed [6] consisting in reducing the concentration of calcium or sulphate ions to avoid gypsum crystallization during further evaporation. The product of the concentrations of Ca^{2+} and $SO_4{}^{2-}$ 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 — concentration of salt (NaCl) in the saline water before evaporation, c_2 — concentration of salt in the concentrated brine). Nanofiltration and electrodialysis with low transport number membranes for divalent ions are proposed as pre-treatment methods.

In our previous research the profitability of low salinity mine water utilization in the electrodialysis evaporation system was proved [10]. The advantages of electrodialytic seawater desalination [12] and dual propose desalination-salt production electrodialysis [13] were also demonstrated.

4. Effectiveness of the ED–evaporation-crystallization system

Our present paper deals with the efficiency of coal-mine brine utilization system comprising ED-EDR pre-concentration and pre-treatment as an element of a comprehensive "Debiensko" coal-mine brine utilization process.

It has been assumed that the electrodialysis will be used for a pre-concentration of coal-mine brine, as an alternative to high energy consumption evaporation by RCC method. The concentrate obtained in the electrodialysis step will be further concentrated using a low energy evaporative method up to a concentration of 290 g/L NaCl. Simultaneously with coal-mine brine being concentrated the concentrations of calcium sulphate and magnesium should decrease against sodium chloride in the process of electrodialysis, and therefore membranes with the transport number lower for divalent than monovalent ions were applied. Concentration to 290 g/L by electrodialysis alone was also considered to eliminate evaporative brine concentration step.

The electrodialysis was investigated in laboratory ED stand. Univalent ion permeable Tokuyama Co. ACS and CMS membranes were applied in the first step and normal grade CMV, AMV Asahi Glass membranes in the second step (electrodialysis reversal (EDR), for the first step diluate treating). A single-pass low residence time mode of operating was applied to avoid gypsum crystallization in the EDR concentrate [13,14]. The "Debiensko" coal-mine brine was treated at current density 344–688 A/m^2 in the first step and 300 A/m^2 in the second. The detailed description of the electrodialysis stage, compositions of coal-mine brine as well as ED and EDR diluates and concentrates were presented in our previous paper [3].

The EDR concentrate is treated with lime to remove Mg^{2+} as magnesium hydroxide and SO_4^{2-} as gypsum. This treated solution, consisting mainly of NaCl, is recycled to feed brine stream. The salinity of the EDR diluate is below 1.5 g/L (as $Cl^- + SO_4^{2-}$) and, according to Polish regulations, may be discharged to rivers; it can be also used in some mining processes.

The scheme for the proposed system is presented on Fig. 1.

The effectiveness of proposed system was then calculated and compared to the presently operated plant performance. Results are presented in Tables 1–4.

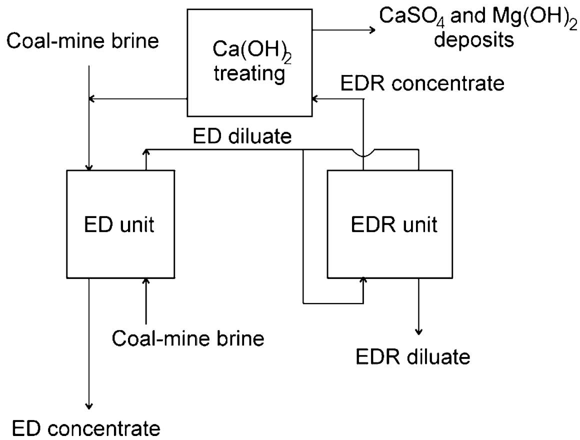

Fig. 1. Scheme of coal-mine brine pre-treatment and pre-concentration by electrodialysis.

Table 1
The present "Debiensko" Plant performance

Item	Inlet brine	RCC evaporator	Crystallizer	Salt (t per 1 m^3) of inlet brine	Salt in lye (kg/t salt produced)	Total energy consumption
Item 1						
Volume, L	1000	186.402	14.9289	—	—	—
Mg^{2+}, meq/L	31.5	169	2110	—	—	—
Cl^-, meq/L	925	4962.4	5800	0.049	103.6	—
Volume, m^3/t salt produced	20.409	3.804	0.305	—	—	—
Energy consumption, kWh/t salt	—	730.6	231.0	—	—	961.6
Item 2						
Volume, L	1000	186.402	17.5000	—	—	—
Mg^{2+}, meq/L	31.5	169	1800	—	—	—
Cl^-, meq/L	925	4962.4	5800	0.048	123.6	—
Volume, m^3/t salt produced	20.779	3.873	0.364	—	—	—
Energy consumption, kWh/t salt	—	743.9	231.6	—	—	975.5

Table 1 presents the present "Debiensko" Plant performance. Table 2 presents the predicted performance of the "Debiensko" Plant, modified by coal-mine brine pre-treatment and pre-concentration by ED-EDR. Table 3 presents a system with coal-mine brine pre-treatment and pre-concentration by ED-EDR and low energy evaporator instead of RCC one. Table 4 presents predicted data for ED concentration to NaCl content equal to 290 g/L; the evaporation step is then omitted. In each table the "1" and "2" items (column 1) differ in magnesium ions concentration in the crystallizer.

5. Conclusions

The comparison of results presented in Table 1 and Tables 2–4 shows that in each system involving electrodialysis the total power consumption, per 1 ton of salt obtained, is significantly lower than in the present system. In the case of ED pre-treatment and pre-concentration, the power consumption increased when ED concentrate salinity increased (Tables 3 and 4) but at the same time the purity of concentrated brine is improved (i.e. low Mg^{2+} concentration as related to NaCl). This results in high salt recovery in the crystallization step and a small amount of post-crystallization lye resulting in small amount of salt in lye per 1 ton of salt produced. The lowest total energy consumption was attained in the case of ED-EDR-low energy evaporation combination (Table 3). The advantage of this system is the result of both: low $CaSO_4$ and low Mg^{2+} concentrations in the ED treated brine as related to NaCl. The first enables the application of low energy evaporator, as the risk of $CaSO_4$ scaling is eliminated, while the second enables high salt recovery that is limited by final Mg^{2+} concentration in the crystallizer. The amount of salt in lye per 1 ton of salt produced in this case is however not as small as in the case of ED only brine concentration (Table 4) because in the latter pre-treatment is extremely effective, i.e. lowest Mg^{2+} concentration as related to NaCl.

Table 2
The predicted performance of the "Debiensko" Plant, modified by coal-mine brine pre-treatment and pre-concentration by electrodialysis

Item	Inlet brine	ED concentrate	RCC evaporator	Crystallizer	Salt (t per 1 m^3) of inlet brine	Salt in lye (kg/t salt produced)	Total energy consumption
Item 1							
Volume, L	1000	363	170.7	6.1418	—	—	—
Mg^{2+}, meq/L	31.5	35.7	76	2110	—	—	—
Cl^-, meq/L	925	2334[a]	4962.4	5800	0.047	44.0	—
Volume, m^3/t salt produced	21.083	7.653	3.600	0.129	—	—	—
Energy consumption, kWh/t salt	—	198.9[b]	178.4	229.0	—	—	606.3
Item 2							
Volume, L	1000	363	170.7	7.1995	—	—	—
Mg^{2+}, meq/L	31.5	35.7	76	1800	—	—	—
Cl^-, meq/L	925	2334[a]	4962.4	5800	0.047	52.0	—
Volume, m^3/t salt produced	21.244	7.712	3.627	0.153	—	—	—
Energy consumption, kWh/t salt	—	200.5[b]	179.7	229.3	—	—	609.5

[a] 136.4 g/L as NaCl
[b] ED(R) energy consumption is equal to 9.4 kWh/m^3 of inlet brine

Table 3
The predicted performance of the "Debiensko" Plant, modified by coal-mine brine pre-treatment and pre-concentration by electrodialysis and low energy evaporator instead of RCC one

Item	Inlet brine	ED concentrate	Low energy evaporator	Crystallizer	Salt (t per 1 m^3) of inlet brine	Salt in lye (kg/t salt produced)	Total energy consumption
Item 1							
Volume, L	1000	363	170.7	6.1418	—	—	—
Mg^{2+}, meq/L	31.5	35.7	76	2110	—	—	—
Cl^-, meq/L	925	2334[a]	4962.4	5800	0.047	44.0	—
Volume, m^3/t salt produced	21.083	7.653	3.600	0.129	—	—	—
Energy consumption, kWh/t salt	—	198.9[b]	44.6	229.0	—	—	472.5
Item 2							
Volume, L	1000	363	170.7	7.1995	—	—	—
Mg^{2+}, meq/L	31.5	35.7	76	1800	—	—	—
Cl^-, meq/L	925	2334[a]	4962.4	5800	0.047	52.0	—
Volume, m^3/t salt produced	21.244	7.712	3.627	0.153	—	—	—
Energy consumption, kWh/t salt	—	200.5[b]	44.9	229.3	—	—	474.7

[a] 136.4 g/L as NaCl
[b] ED(R) energy consumption is equal to 9.4 kWh/m^3 of inlet brine
[c] energy consumption 11 kWh/m^3 of distillate

Table 4
The predicted performance of the "Debiensko" Plant, modified by coal-mine brine pre-treatment and pre-concentration by electrodialysis

Item	Inlet brine	ED concentrate	Crystallizer	Salt (t per 1 m^3) of inlet brine	Salt in lye (kg/t salt produced)	Total energy consumption
Item 1						
Volume, L	1000	145	2.7228	—	—	—
Mg^{2+}, meq/L	31.5	33.8	1800	—	—	—
Cl^-, meq/L	925	4962.4[a]	5800	0.041	22.5	—
Volume, m^3/t salt produced	24.315	3.526	0.066	—	—	—
Energy consumption, kWh/t salt	—	350.4[b]	228.3	—	—	578.7
Item 2						
Volume, L	1000	145	2.3227	—	—	—
Mg^{2+}, meq/L	31.5	33.8	2110	—	—	—
Cl^-, meq/L	925	4962.4[a]	5800	0.041	19.1	—
Volume, m^3/t salt produced	24.235	3.514	0.056	—	—	—
Energy consumption, kWh/t salt	—	349.2[b]	228.2	—	—	577.4

[a]290 g/L as NaCl; the evaporation step is then omitted.
[b]ED(R) energy consumption is equal to 14.4 kWh/m^3 of inlet brine.

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