

## Recovery of NaCl from saline mine water in the ED-MSF system

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A considerable part of water obtained by drainage of Polish coal-mines is saline which creates substantial ecological problems. The load of salt (mainly sodium chloride) amounts to 5 mln t/year. Despite the utilisation of saline coal-mine waters is considered to be the most adequate method of solving ecological problems caused by this kind of water in Poland there are only two installations utilising coal-mine waters and producing 100,000 t salt per year. In the case of the most concentrated waters, the so-called coal-mine brines, the method of concentrating by evaporation in twelve-stage expansion installation or vapour compression is applied, after which sodium chloride is manufactured. In the case of low salinity waters they are preconcentrated first by RO method. High energy consumption in above-mentioned methods of evaporation is a considerable restriction in the utilisation of coal-mine brines. An obstacle in the application of low energy evaporation processes, e.g. multi-stage flash, is the high concentration of calcium and sulphate ions in the coal-mine waters.

A method of pre-treatment of coal-mine saline waters is proposed consisting in reducing the concentration of calcium or sulphate ions. The product of the concentrations of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions, expressed in  $\text{kmol/m}^3$ , in saline water being evaporated should not exceed  $(c_1/c_2)^2 \cdot 1.45 \cdot 10^{-3}$  (where:  $c_1$  - concentration of salt (NaCl) in saline water before evaporation,  $c_2$  - concentration of salt in concentrated brine). Electrodialysis with membranes of low transport number for divalent ions is proposed for low salinity waters and nanofiltration for so-called coal-mine brines. Saline water treated in this way may be evaporated without any risk of sulphate crystallisation. Low energy evaporation process may be then applied, resulting in a reduction of the unit costs of the concentration process.

In the case of ED the efficiency of separation of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions from NaCl has been tested. The cascade of electrodialysers and the concentration of the ED concentrate have been optimised, the latter being the input solution to the MSF process, in order to minimise the costs of a comprehensive utilisation.

### 1. INTRODUCTION

Coal-mines in Poland discharge ca 900 thou  $\text{m}^3/\text{d}$  of water containing 6960 t/d of chlorides and sulphates into Vistula and Odra river basins which makes ca 4.2 million tons of salt load yearly (as sodium chloride) [1]. Several ways of solving the problem of saline water are being considered and namely [2]:

- a) mining-geological methods of limiting saline water influx into mine workings,
- b) methods of saline water discharge reduction once water has been pumped up to the surface:
  - saline water recirculation;
  - underground reinjection, shallow and deep;
  - water underground storage;

- hydraulic engineering method – retention and controlled discharge into rivers;
- saline water utilisation.

The analysis of the projects undertaken so far and of the plans that mines have aiming at solving the problem of saline water shows that the most important way of lowering the salt load being discharged with water is its utilisation. All water types belonging to the group IV, i.e. saline mine waters with a concentration of anion sum  $\text{Cl}^- + \text{SO}_4^{2-} > 42 \text{ kg/m}^3$  (so-called coal-mine brines) and a part of water types belonging to the group III or so-called low salinity waters – having an anion sum concentration  $\text{Cl}^- + \text{SO}_4^{2-}$  of 1.8-42  $\text{kg/m}^3$  have to be included in the utilisation program. Sodium

chloride, other chemical compounds and desalinated water are the products of the typical utilisation process. Saline mine water can also be directly used in the chemical industry [2]. Total sodium chloride load in water types that should be utilised is ca 2.5 million tons yearly.

Regardless of the way of saline mine waters reuse 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 kg/m<sup>3</sup>). In the case of coal-mine brines, whose concentration (as NaCl) is 70-140 kg/m<sup>3</sup>, the evaporation method is used for concentrating [3], although reverse osmosis [4] and electrodialysis [2,4] is also considered.

Despite the utilisation of saline coal-mine waters is considered to be the most adequate method of solving ecological problems caused by this kind of water in Poland, there are only two installations utilising coal-mine waters and producing 100,000 t salt per year. The first one, started in 1975, operates at the "Debiensko" coal-mine and processes about 2,000 m<sup>3</sup> of brine per day, containing about 100 kg/m<sup>3</sup> of salt; this yields 40,000 t of salt every year. This brine is concentrated in a 12-stage expansion installation [4]. Selectively, sodium chloride and calcium sulphate are crystallised by means of a method developed at the Main Institute of Mining. In this way high-quality table salt (99.5% NaCl) is obtained. This technique does not require any preliminary purification of brine in order to remove calcium and magnesium ions. For each cubic meter of brine 0.3 t of steam at a pressure of 0.3 MPa is consumed as well as 10 kWh of electric energy. As a result of processing of end lyes magnesium chloride, carnallite or potassium chloride and alkaline solution of iodine and bromine are obtained. The processing of lyes requires 1 t of steam at a pressure of 0.5 MPa and 75 kWh of electric energy for 1 m<sup>3</sup> of lye. Related to 1 m<sup>3</sup> of brine, the consumption of energy for the processing of lyes amounts to 0.06 t of steam and 4.7 kWh of electric energy [4].

In 1994 an installation was put in operation for processing of brines from the coal-mines "Debiensko" and "Budryk" [3]. Brine with a TDS of about 90 kg/m<sup>3</sup> is concentrated making use of the vapour compression method in evaporators designed by the Resources Conservation Company in Seattle (RCC). This installation produces 100,000 t of salt and 10,000 t of

discarded calcium sulphate per year. Total consumption of energy in the thermal installation comprising evaporators, a crystalliser and the utilisation of lyes has been estimated not to exceed 45 kWh/m<sup>3</sup> of processed brine, however the problem of processing the lyes has not been solved so far. The installation is based on the latest achievements in the field of the evaporation of untreated mine waters, the removal of calcium sulphate, heat exchange and the minimisation of energy consumption. A disadvantage of the installation is the exclusive use of the most expensive form of energy, i.e. electric energy.

The construction of an installation with a capacity of 1.2 million t/year has been planned, to process about 33,000 m<sup>3</sup>/day of brine from the coal-mines "Piaś", "Ziemowit" and "Czeczott" [5,6]. According to the plans, concentrating of saline mine water nearly up to the saturation level using five-stage evaporators or the VC method is being considered to be effected on this plant.

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

## 2. DESALINATION AND CONCENTRATION OF LOW SALINITY MINE WATER

Because of a varied composition of saline mine water types their utilisation requires the use of various techniques. Multi-stage evaporation (namely multi-stage flash - MSF), reverse osmosis (RO) and electrodialysis (ED) are considered for use in desalination and concentration of low salinity mine waters. Resulting concentrate is further processed by evaporation. In Poland only a single RO plant processing low salinity water is in operation at the moment. Apart from coal-mine brine, concentrated using the evaporation method not preceded by any preconcentrating treatment, at the KWK „Debiensko” Desalination Plant mentioned earlier low salinity waters are also utilised following a preliminary RO treatment. Water, with the salt concentration of 14-15 g/dm<sup>3</sup>, is subjected to a three-stage reverse osmosis (RO) treatment plus additional recycling of a part of the concentrate. The concentrate with a concentration

of 65-70 kg/m<sup>3</sup> is obtained in this way. Power consumption is 5 kWh per 1 m<sup>3</sup> of input water, whilst the cost is estimated to be 1.43 PLN/m<sup>3</sup> (according to the prices as of August '96, assuming the capacity of 10 thou m<sup>3</sup>/d).

Desalination and concentration of low salinity water using the electrodialysis method have also been investigated. After optimisation of conditions for ED process in a cascade of three electrodialysers the process was implemented to waters with Cl<sup>-</sup> concentration 3.0, 6.0 and 9.0 kg/m<sup>3</sup>. The linear velocity in the electrodialyser cells was 12 cm/s and current densities were 50, 150 and 500 A/m<sup>2</sup> in respective stages. As a result of the ED, a diluate of 0.3 kg/m<sup>3</sup> of Cl<sup>-</sup> and concentrate of 100 kg/m<sup>3</sup> (TDS of 165 kg/m<sup>3</sup>) were obtained. For the tested Cl<sup>-</sup> concentrations energy consumption was 7.1, 7.4 and 12.4 kWh/m<sup>3</sup> processed water and total costs: 0.91, 1.40 and 1.99 \$/m<sup>3</sup> respectively. The ED effectiveness was then compared with RO and MSF. The analysis of the literature data shows that the energy consumption of about 10 kWh/m<sup>3</sup> in RO process in the above-mentioned range of Cl<sup>-</sup> concentration is expected. However no cost data is available. For MSF as designed by the Main Institute of Mining in Katowice, in the case of concentration to TDS of 140 kg/m<sup>3</sup> the costs of 2.29, 2.22 and 2.15 \$/m<sup>3</sup> are expected respectively. Comparison of available data indicates the economic prevalence of ED in the tested salinity range.

## 2.1. Membrane pre-treatment of saline waters

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

A method of pre-treatment of coal-mine saline waters has been proposed [4] consisting in reducing the concentration of calcium or sulphate ions. The product of the concentrations of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> ions, expressed in kmol/m<sup>3</sup>, 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 is proposed for so-called coal-mine brines and electrodialysis with membranes of low transport number for divalent ions for low salinity waters.

## 2.2. Utilisation of saline mine water in the ED-MSF system

In the present paper, the results are presented of the investigations on the efficiency of using the electrodialysis as an element of a comprehensive low salinity mine water utilisation process. It has been assumed that the electrodialysis will be used for a preconcentration of saline mine water, whilst the concentrate obtained from electrodialysis will be further concentrated using the evaporative method up to a concentration of 300 kg/m<sup>3</sup> NaCl, i.e. 182 kg/m<sup>3</sup> Cl<sup>-</sup>. Simultaneously with mine water being concentrated the concentrations of calcium and sulphate should decrease against sodium chloride in the process of electrodialysis, and therefore membranes with the transport number for divalent ions lower than that for monovalent ions, of Neosepta CMS and ACS type were adopted [7].

Water from „Janina” mine was selected for the investigations; the composition is given in Table 1.

Table 1  
Composition of saline water from „Janina” mine

Component	Concentration, kg/m <sup>3</sup>
Cl <sup>-</sup>	7.27
SO <sub>4</sub> <sup>2-</sup>	0.442
Na <sup>+</sup>	4.47
Ca <sup>2+</sup>	0.176
Mg <sup>2+</sup>	0.136

Salt concentration in this water is in the upper range of values deemed optimum in the electrodialysis process [8].

The electrodialysis process was investigated at various concentrate concentrations in order to determine the optimum value, at which the cost of concentrating up to the level of 182 g/dm<sup>3</sup> Cl<sup>-</sup> or 300 g/dm<sup>3</sup> as NaCl, with the evaporative method being taken into account, will be lowest. In the first series of tests it was assumed, that as a result of electrodialysis a diluate with Cl<sup>-</sup> concentration of 1.7 g/dm<sup>3</sup> would be obtained. In the second series it



was assumed, that as a result of electrodialysis a diluate would be obtained with such a concentration of  $\text{Cl}^-$ , which upon dilution of the diluate with the condensate from the evaporation would give  $\text{Cl}^-$  concentration below  $1.0 \text{ g/dm}^3$ . According to the Polish regulations, water having such salt concentration may be discharged as an effluent; it can also be used in some mining processes. The electrodialysis in the first series of tests was effected in a cascade of 3 electrodialysis units. In the

individual cascade stages current densities were: 700, 500 and  $310 \text{ A/m}^2$  correspondingly. In the second series, due to lower final concentration of the diluate, an additional fourth electrodialysis stage was used, operated at a lower current density. The electrodialyser of the author's design, with the membrane-to-membrane distance of 0.4 mm was used in the investigations.

On the basis of the results obtained, the costs of a comprehensive saline mine water utilisation

Table 2  
Salt recovery cost, series No 1

Item	Cl <sup>-</sup> concentration in ED solutions, $\text{kg/m}^3$		Volume of ED solutions from 1 $\text{m}^3$ of saline water, $\text{m}^3$		ED costs, $\$/\text{m}^3$			Evaporation costs, $\$/\text{m}^3$	ED + evaporation costs, $\$/\text{m}^3$	ED + evaporation + crystallisation costs per 1 ton of salt, \$
	Concentrate	Diluate	Diluate	Concentrate	Energy	Capital & others	Total			
1	13.8	1.70	0.521	0.479	0.079	0.028	0.108	0.443	0.551	58.6
2	24.1	1.70	0.751	0.249	0.113	0.040	0.153	0.216	0.369	45.4
3	33.5	1.70	0.825	0.175	0.125	0.044	0.168	0.143	0.311	40.1
4	47.7	1.70	0.879	0.121	0.133	0.047	0.179	0.089	0.269	36.3
5	60.4	1.70	0.905	0.095	0.137	0.048	0.185	0.063	0.248	34.2
6	77.0	1.70	0.926	0.074	0.140	0.049	0.189	0.042	0.231	32.6

Table 3  
Salt recovery cost, series No 2

Item	Cl <sup>-</sup> concentration in ED solutions, $\text{kg/m}^3$		Volume of ED solutions from 1 $\text{m}^3$ of saline water, $\text{m}^3$		ED costs, $\$/\text{m}^3$			Evaporation costs, $\$/\text{m}^3$	ED + evaporation costs, $\$/\text{m}^3$	ED + evaporation + crystallisation costs per 1 ton of salt, \$
	Concentrate	Diluate	Diluate	Concentrate	Energy	Capital & others	Total			
1	13.8	1.70	0.521	0.479	0.079	0.028	0.108	0.443	0.551	58.6
2	24.1	1.25	0.737	0.263	0.120	0.047	0.167	0.228	0.395	45.8
3	33.5	1.15	0.811	0.189	0.133	0.053	0.186	0.154	0.340	40.6
4	47.9	1.10	0.868	0.132	0.145	0.058	0.203	0.097	0.300	36.8
5	60.0	1.05	0.896	0.104	0.151	0.061	0.212	0.070	0.282	35.4
6	77.4	1.03	0.917	0.083	0.155	0.063	0.218	0.047	0.265	33.0

process using electrodialysis were then estimated. It was assumed that for concentrating of the concentrate up to the level of 300 g/dm<sup>3</sup> NaCl or 182 g/dm<sup>3</sup> Cl<sup>-</sup> the MSF or other effective method would be used. Evaporation cost of 1.0\$ per 1 m<sup>3</sup> of condensate was assumed [9]. The costs of further evaporation accompanied by salt crystallisation were estimated based on the study on the construction of the plant according to the technological concept of „Ecosol” and were assumed to be 8 \$ per 1 ton of salt obtained [10,11].

The cost of obtaining the salt in the systems described above is given in Tables 2 and 3. In Tables 4 and 5 ED concentrate composition is shown.

Table 4  
ED concentrate composition. Items as in Table 2

Item	ED concentrate composition, kg/m <sup>3</sup>		[Ca <sup>2+</sup> ][SO <sub>4</sub> <sup>2-</sup> ] kmol <sup>3</sup> /m <sup>6</sup> × 10 <sup>5</sup>	"x" value × 10 <sup>5</sup>
	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>		
1	0.488	0.232	2.95	0.84
2	0.559	0.321	4.67	2.53
3	0.626	0.402	6.55	4.92
4	0.725	0.525	9.91	9.98
5	0.814	0.634	13.40	16.30
6	0.930	0.776	18.78	61.30

"x" - results from the formula (1)

Table 5  
ED concentrate composition. Items as in Table 3

Item	ED concentrate composition, kg/m <sup>3</sup>		[Ca <sup>2+</sup> ][SO <sub>4</sub> <sup>2-</sup> ] kmol <sup>3</sup> /m <sup>6</sup> × 10 <sup>5</sup>	"x" value × 10 <sup>5</sup>
	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>		
1	0.488	0.232	2.95	0.84
2	0.599	0.334	5.21	2.55
3	0.721	0.438	8.22	4.92
4	0.896	0.593	13.80	10.02
5	1.069	0.739	20.60	15.80
6	1.284	0.911	27.70	26.20

"x" - results from the formula (1)

As results from the data presented in Tables 2-5, in order to meet the condition of the formula (1)

electrodialysis has to be carried out up to a concentration of Cl<sup>-</sup> in the concentrate of at least 47.7 kg/m<sup>3</sup> (series No 1) and ca 80 kg/m<sup>3</sup> (series No 2). From the analysis of the data in Tables 2 and 3 it results that in the ED-MSF system no minimum of the concentration cost can be observed within the concentration range of the ED concentrate. Therefore, osmosis and electroosmosis limit the possibilities of ED concentrate concentration beyond a certain level.

In a profitability estimation, it was assumed that the value of salt obtained is 40 \$/t [10,11]. On the benefit side of the balance, apart from the value of salt, it was assumed that payment of the charge paid for chloride and sulphate discharge is effectively eliminated (0.2057 PLN/kg). Thus, a total benefit is 71.2 \$/t of salt obtained and is much higher than its recovery cost (Tables 2 and 3). This can ensure a profitability of the salt production in the described system.

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