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The application of electrodialysis to the treatment of industrial copper and zinc electrolytes

Marek Dubrawski*, Marianna Czaplicka, Jan Mrozowski

Environment Protection, Institute of Non-Ferrous Metals, Sowinskiego 5, Gliwice 44-100, Poland, Tel. +48322380200; Fax: +48322316933; email: marek.dubrawski@imn.gliwice.pl

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ABSTRACT

The zinc electrolyte obtained from a zinc smelting process and the copper electrolyte from an electrorefining process were treated with application of the electrodialysis. Three anion exchange membrane types ACM, PC Acid 60 and PC Acid 100 combined with the cation exchange membrane CMS were tested. Up to 99% Zn, Mg and Mn retention factors were obtained. The majority of chloride ions are being transferred from the diluate to the concentrate stream. Up to 25% of the arsenic can be removed from the copper electrolyte feed solution.

Keywords: Electrodialysis; Membrane; Sulphuric acid; Copper; Zinc; Separation

1. Introduction

During the process of copper electrorefination, accompanying metal ions (Fe, Ni, As, Sb, Cu) accumulate in the solution. A common practice is to bleed a portion of the electrolyte from the circuit to keep their amount at a constant level. Then the most concentrated elements (copper and nickel) are recovered from this bleed solution using a deep decopperisation followed by crystallisation of nickel [1]. Decrease of sulphuric acid concentration by electrodialysis would allow to retrieve useful elements with high efficiency and to become alternative to commonly applied methods [2,3].

Similarly in the course of the zinc production with application of the roast-leach-electrowinning process [4], part of the zinc electrolyte has to be refreshed due to accumulation of elements like magnesium, manganese or chlorides. A frequently utilised method is to withdraw fraction of the working solution from the main circuit and consecutive neutralisation with calcium hydroxide solution. Such process produces a large amount of highly hydrated post-neutralisation precipitate which has to be returned to the process due to high zinc content.

In the past, different membrane processes like diffusion dialysis [5], nanofiltration [6] and membrane electrolysis [7] were successfully applied to the treatment of such complex solutions. The main advantage of the membrane separation compared to common separation methods is low energy consumption, ease of system configuration, low maintenance requirement and theoretically unlimited possibility to scale up due to modular construction.

The electrodialysis (ED) is one of the methods of acid separation from solutions containing metal ions. Many publications were devoted to separation of selected elements present in industrial copper and zinc electrolytes but only few dealt with genuine industrial electrolytes.

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*Corresponding author.

Cifuentes et al. [8] removed the sulphuric acid from a synthetic solution containing As and Sb impurities. Examined membranes were MC3470 (cation exchange) and MA3475 (anion exchange) installed in a laboratory-scale electrodialyser. They observed that the direction of the As transport depends on the formed ionic species charge during the electrodialysis process. As(III) compounds at low pH values form mainly $H_4AsO_3^+$ cation and the As(V) exist in undissociated forms. In refining solutions, arsenic exists in the form of undissociated arsenic acid H_3AsO_4 [9]. Mainly diffusive transport of undissociated arsenic acid H_3AsO_4 due to concentration gradient is expected between the process streams. Chang et al. [10] studied the electrodialysis of the Cu^{2+} model solution under electroconvection conditions. Tested membranes were CMI 7000 (cation exchange) and AMI 7001 (anion exchange). They reported formation of a deposit on the anion exchange membrane which caused increase of the power consumption. The deposit has been identified as copper hydroxide and copper oxide. Boucher et al. [11] focused mainly on examination of sulphuric acid recovery rate, water transport, metal leakage and energy intake for the CMS cation exchange membrane coupled with the Morgane ARA 17-10 anion exchange membrane. The composition of the treated solution was 200 g/l H_2SO_4, 10 g/l Zn, 10 g/l Mg and 5 g/l Mn. Obtained results confirmed CMS membrane's impermeability towards co-ions and permselectivity to monovalent cations. It was also discovered that soaking of previously used membranes prior the consecutive test in 50 g/l sulphuric acid for at least 14 h, decreases CMS membrane-bivalent cation transport number in the initial stage of the process (for up to 4 h of run). Baltazar et al. [12] examined application of the electrodialysis for separation of sulphuric acid from a nickel sulphate industrial stream containing copper, arsenic, bismuth and antimony in addition to nickel. Tested membranes were CMS and ACM (low proton leakage anion exchange). It was reported that up to 99% of sulphuric acid can be removed from the diluate stream (from 193 to 6 g/l). The final nickel concentration in the concentrate stream did not exceed 3 g/l from feed levels up to 20 g/l. The rate of metal transfer from the diluate to the concentrate stream increased noticeably after 60% of sulphuric acid removal.

The aim of this study was to investigate application of electrodialysis to the treatment of industrial copper and zinc electrolytes. These electrolytes are highly acidic and contaminated with multiple compounds. The experiments were conducted with application of different types of membranes and process parameters. An attempt to selectively remove undesired contaminants like arsenic and chlorides from diluate stream while retaining the others was performed. The process was evaluated mainly by energy consumption, sulphuric acid transport rate and retention factors of accompanying constituents.

2. Materials and methods

2.1. Electrolytes

The chemical compositions of examined zinc and copper electrolytes are shown in Tables 1 and 2, respectively. Both of them are highly acidic and characterised by high concentration of dissolved metals. Initial studies with application of zinc electrolyte were performed with a synthetic (S) solution of composition similar to the industrial zinc electrolyte (Table 1). The same conditions were applied during the consecutive studies of the industrial zinc electrolyte. In the case of industrial copper electrolyte, all the tests were performed with application of industrial one.

2.2. Testing equipment

The experiments were performed in a laboratory-scale electrodialyser PCCell 200 (PCCell, Germany). The electrodialyser cell is composed of five membrane cell pairs, platinum-coated titanium electrode as anode and a stainless steel cathode. According to literature [13] a cell pair is defined as two membranes (cation and anion exchange) separating the two process streams (diluate and concentrate). In the membrane stack (Fig. 1) two cation exchange membranes are next to electrodes compartments. There is no contact of diluate and concentrate streams on both side of a membrane. Treating these as a part of fully operational

Table 1
Zinc electrolyte composition

Electrolyte	H_2SO_4 (g/l)	Zn (g/l)	Mg (g/l)	Mn (g/l)	Cl^- (g/l)
Synthetic	130	57.0	15.9	4.1	600
Industrial	150	56.8	14.4	3.6	580

Table 2
Copper electrolyte composition

H_2SO_4 (g/l)	Ni (g/l)	As (g/l)	Sb (g/l)	Cu (g/l)	Fe (g/l)
215	8.2	4.0	0.30	0.20	0.14

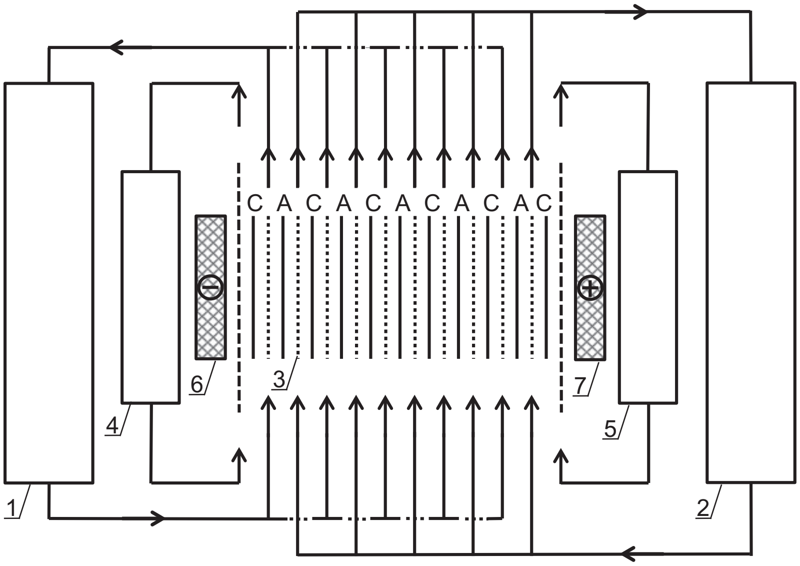

Fig. 1. Electrodialysis system scheme: 1—diluate stream; 2—concentrate stream; 3—membrane spacer; 4—catholyte stream; 5—anolyte stream; 6—cathode; 7—anode; A—anion exchange membrane; C—cation exchange membrane.

membrane cell pair is questionable. For convenience two side membranes were neglected during the calculations. The system was treated as four membrane cell pairs.

Three anion exchange membranes (AEM): ACM (ASTOM corp., Japan), PC Acid 60 and PC Acid 100 (PCCell, Germany) were tested. All of the mentioned membranes were combined with the CMS cation exchange membrane (ASTOM corp., Japan). According to producers' specification and described application [13–18] each one of tested membrane is able to resist acidic conditions. The crucial parameter of CMS membrane is permselectivity towards monovalent ions [12,15]. The hydrogen ions responsible for majority of electric charge transport across the membrane stack can freely permeate through a membrane. The cations possessing higher electric charge are retained. Due to that selectivity CMS membrane is suitable for installation in membrane stack and also as a separation membrane for electrode compartments. The ACM membranes application for electrodialysis of acidic solutions are widely described in literature [16,17]. The PC acid 100 and 60 membrane are less common but according to description [15,18] they are specially designed for acid separation.

Tested membranes' parameters are presented in Table 3. The specifications provided by manufacturers are very similar and it is hard to predict which of the membranes is best suited for the process. In case of AEM ACM is described as possessing the highest ion exchange capacity equal to 1.5 eq/g. The ACM membrane is also a bit thicker compared to PC Acid 100 and 60 membranes. The size of membrane is 12.5 × 26.2 cm with active area equal to 210 cm^2. The total volume of concentrate or diluate compartments is 15 ml, meaning 3 ml per single channel. The volumetric flow rate relation with retention time in membrane stack and linear velocity are presented in Table 4.

The electrode compartments were continuously rinsed with 0.15 M sulphuric acid solution prepared from analytical grade acid. The stream's flow rate (Q) was controlled at a chosen value by a set of installed rotameters. The voltage was applied using a regulated direct current power supply.

2.3. Methods

The deionised water was pumped in each system stream for 20 min prior each test to check for possible leaks. If no disturbances were noticed during that time, proper solutions were introduced into the electrodialyser after complete deionised water discharge from the circuit. The process started at the moment of power supply connection to the system. Constant value of the electric current was maintained throughout the whole testing period. Three different electric current values were analysed 12 A (equivalent to 570 A/m^2), 18 A (equivalent to 860 A/m^2) and 24 A (equivalent to 1,140 A/m^2). All the streams were periodically sampled for chemical analysis (25 ml samples). At each sampling interval, current, voltages,

Table 3
Ion exchange membranes properties [13–18]

Membrane	Unit	ACM	CMS	PC Acid 60	PC Acid 100
Type		Anion exchange Strongly alkaline	Cation exchange Strongly alkaline	Anion exchange Strongly alkaline	Anion exchange Strongly alkaline
Area resistance	Ω cm^2	4.0–5.0	1.5–2.5	n.a.	n.a.
Ion exchange capacity	eq/g	1.5	2	0.35–0.1	0.37–0.57
Selectivity		n.a.	n.a.	0.95	0.88
Thickness	mm	0.15	0.2	0.08–0.1	0.08–0.1
Burst strength	kg/cm	n.a.	n.a.	4–5	4–5
Water content	%	15	38	15	18
Maximum temperature	℃	n.a.	n.a.	60	60
pH stability	pH	n.a.	n.a.	0–9	0–10
Additional information		Proton blocker	Univalent selective	Designed for monovalent acid treatment	Designed for multivalent acid treatment

Note: n.a.—not available.

Table 4
Volumetric flow rate relation with linear velocity and retention time

Parameter	Unit			
Volumetric flow rate	l/h	30	70	100
Linear velocity	cm/s	1.23	2.87	4.09
Retention time	s	17.9	7.68	5.37

flow rates, temperatures and fluid volumes were monitored. A rapid increase of the voltage required to keep the electric current at constant level determined the final point of the experiment. An increased voltage across the stack caused warming of the streams that could damage the membranes. The sulphuric acid content in the samples was determined using direct titration by sodium hydroxide, while metal analyses were performed by complexometric titration using the ethylenediaminetetraacetic acid and flame atomic absorption spectrometry. The Mohr method was used for determination of chlorides concentration. The current efficiency (Eq. (1)) of the process was calculated using the following equation:

$$\eta_{\%}^{H^+} = \frac{z \times F(C^C_{\mathrm{final}} \times V^C_{\mathrm{final}} - C^C_{initial} \times V^C_{\mathrm{initial}})}{n \times I \times t} \times 100 \tag{1}$$

where z is electric charge of acid, F is Faraday's constant (26.8 A h/mol), C^C is concentration of concentrate stream (g/l), V^C is volume of concentrate stream respectively before and after the experiment (l), n is number of membrane cells, I is electric current (A) and t is time of the process (h). The mass of compound transferred from diluate to concentrate stream, compared to the amount of this compound introduced in diluate stream at the beginning of the process is defined as retention factor. It is evaluated by a formula:

$$R = \left(1 - \frac{C^C_{\mathrm{final}} \times V^C_{\mathrm{final}} - C^C_{\mathrm{initial}} \times V^C_{\mathrm{initial}}}{C^D_{\mathrm{initial}} \times V^D_{\mathrm{initial}}}\right) \times 100 \tag{2}$$

where C^D is concentration in diluate stream (g/l).

3. Results and discussion

3.1. Limiting current density

The limiting current density (LCD) of the system can be determined by plotting the relationship between the current and corresponding potential [19]. The electrodialysis system was temporary modified in order to perform determination. The diluate and concentrate streams were connected to one single tank. This solution provided constant mixing of streams hence concentration of streams was kept at a fixed level. The test was performed with flow rate 70 l/h with application of CMS ACM membrane set for zinc and copper electrolytes. The obtained results are presented in Fig. 2 for zinc electrolyte and Fig. 3 for copper electrolyte.

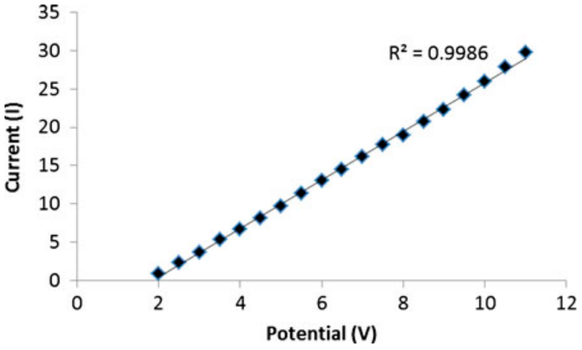

Fig. 2. Determination of LCD with zinc electrolyte.

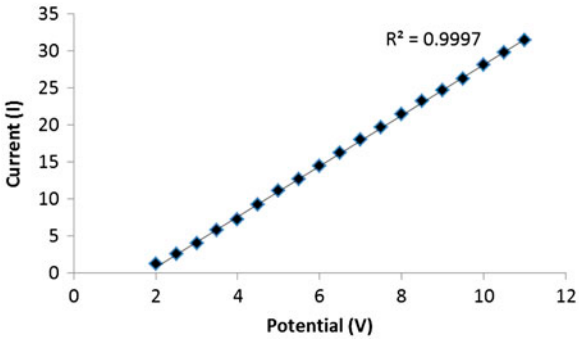

Fig. 3. Determination of LCD with copper electrolyte.

The inflexion of a characteristic curve is not visible up to a value of 30 A. The examination at higher electric current was not possible due to overload of the power supply. It was assumed that even the maximum current 24 A used during the proper experiments is below LCD hence it was not investigated any further. Linear dependency of current/potential suggests that the system is working in Ohmic region. The increase of voltage results is directly proportional to increase of current.

3.2. Zinc electrolyte

The obtained results for the process performed on the synthetic solution with flow rate 70 l/h and current density 570 A/m^2 indicated relatively low current efficiencies (Table 5). The lowest value 53.3% was obtained for the PC Acid 60 membrane, 58.9% for the PC Acid 100 membrane and the highest 61.6% for the ACM membrane. It can be explained by conducting the process at high current densities compared to other electrodialysis systems [20,21]. The rapid oxygen evolution at the anode causes competing transport of hydrogen ions across the membrane. Tzanetakis et al. [22] reported that the lower current density resulted in better current utilisation and, hence, transport properties. However, change of the current density for the industrial zinc electrolyte treatment in the range from 570 to 1,140 A/m^2 did not cause noticeable change of current efficiency (Table 6). During the experiment with application of industrial electrolyte, performed at 570 A/m^2 current density and 70 l/h, 61.1% current efficiency was obtained. The same process conducted at current density 1,140 A/m^2 resulted in 63.3% current efficiency. The possible reason of no significant changes is that the experiments were performed at much higher current densities compared to the ones conducted by Tzanetakis (in the range from 200 to 400 A/m^2). Also the acid concentration of working solutions should be taken into consideration. The analysed zinc electrolyte concentration is around 1.5 M of H_2SO_4 compared to 0.01 M of solution used by Tzanetakis. A higher ionic strength of a solution prevents the effect of concentration polarisation even at elevated current densities. The concentration polarisation occurs when the ions migrate through the membrane faster than they move through the solution. The solution near the membrane surface can become depleted in ions that are responsible for the electric charge transport [23]. As a result current efficiency decreases.

During the process with synthetic solution conducted at 570 A/m^2 current density and 70 l/h flow rate the lowest energy consumption of 1.04 Wh/g was observed for the PC Acid 100 membrane. The highest values of 1.27 Wh/g for the PC Acid 60 and 1.15 Wh/g for the ACM were observed (Table 5). Boucher et al. [11] reported energy consumption in the range from 0.72 to 1.14 Wh/g during the tests with application of a membrane stack composed of six ACM CMS membrane pairs and similar process conditions, but slightly different membranes' configuration in the stack. An expansion of the membrane stack to 10 membrane pairs reduced power consumption to 0.50 Wh/g. It was reported [11] that the anolyte and catholyte compartment contribute in a significant way to the energy consumption of the electrodialysis cell. Hence, membrane stack composed of larger number of membrane pairs should affect lower net power consumption.

Mohammadi et al. [20] recommended application of a low flow rate (0.07 ml/s using electrodialyser cell composed of two membrane pairs) to obtain the best performance of ED system. In the presented studies, change of the flow rate in the range from 30 to 100 l/h during the tests with ACM membranes and at 570 A/m^2 current density had almost no effect on the metal retention factor or the acid removal rate. During

Table 5
Parameters of synthetic zinc solution electrodialysis at 70% acid removal

Membrane	Unit	PC Acid 60	PC Acid 100	ACM	ACM	ACM
Flow rate	l/h	70	70	30	70	100
Time	h	7	5.5	5.5	6	5.5
Current density	A/m^2	570	570	570	570	570
Acid removal	%	70	70	70	70	70
Current efficiency	%	53.3	58.9	64.3	61.6	64.8
Energy consumption	Wh/g	1.27	1.04	1.16	1.15	1.08
Concentrate volume increase	l	0.25	0.25	0.27	0.30	0.23
H_2SO_4 transport	mole/(m^2 h)	5.68	6.28	6.85	6.57	6.91
Zn transport	mole/(m^2 h)	0.122	0.086	0.074	0.117	0.068
Mg transport	mole/(m^2 h)	0.057	0.062	0.071	0.025	0.057
Mn transport	mole/(m^2 h)	0.010	0.008	0.009	0.005	0.008
Zn retention	%	97.2	98.3	98.6	97.6	98.9
Mg retention	%	99.5	99.5	99.5	99.8	99.6
Mn retention	%	99.8	99.9	99.9	99.9	99.9

Table 6
Parameters of industrial zinc electrolyte electrodialysis at 70% acid removal

Membrane	Unit	ACM	ACM
Flow rate	l/h	70	70
Time	h	6.5	3
Current density	A/m^2	570	1,140
Current efficiency	%	61.1	63.3
Energy consumption	Wh/g	1.15	2.36
Concentrate volume increase	l	0.32	0.39
H_2SO_4 transport	mole/(m^2 h)	6.51	13.50
Zn transport	mole/(m^2 h)	0.093	0.213
Mg transport	mole/(m^2 h)	0.047	0.114
Mn transport	mole/(m^2 h)	0.005	0.011
Zn retention	%	97.9	97.9
Mg retention	%	99.6	99.6
Mn retention	%	99.9	99.9

the run at 100 l/h flow rate, slightly lowered energy consumption was noticed, equal to 1.08 Wh/g. The observed power consumptions at 30 l/h and at 70 l/h flow rate were equal to 1.16 Wh/g and 1.15 Wh/g, respectively.

The results of the ED process with application of the ACM membranes for the industrial zinc electrolyte and the synthetic zinc solution treatment were very similar. At 570 A/m^2 current density and 70 l/h flow rate for industrial electrolyte, 61.1% current efficiency and 1.15 Wh/g energy consumption were obtained, while for synthetic solution 61.6 and 1.15 Wh/g, respectively, were observed. During the following test with application of industrial electrolyte at current density 1,140 A/m^2 (Table 6) the power consumption of the system doubled and was equal to 2.36 Wh/g. At the same time transport of sulphuric acid to the concentrate stream increased from 6.51 to 13.50 mol/(m^2 h). The transport rate values of zinc, magnesium and manganese obtained during the industrial zinc electrolyte ED at 570 and 1,140 A/m^2 are presented in Fig. 4.

The obtained data indicate that doubling of the current density cause approximately twice higher power consumption. At the same time sulphuric acid's and analysed metal ions' (Zn, Mg and Mn) transport to the concentrate stream is increased by the same extent. It was also noticed that the ratio of a zinc charge to a sulphuric acid charge transferred to concentrate stream are approximately the same regardless of a current density applied or treated solution type (Fig. 5).

An intensive water transport across the ED streams was noticed. The concentrate stream volume continuously increased during each conducted process independently of the membrane type used, current density value or treated solution. During the test with synthetic solution at 570 A/m^2 current density and 70 l/h flow rate, the highest increase of concentrate stream volume (Table 5) was noticed for the ACM membrane, equal to 0.30 l. In the case of PC Acid 60 and 100 0.25 l volume change was observed. During the industrial electrolyte ED at 570 A/m^2 current density with application of the ACM membrane the concentrate stream volume increased by 0.32 l, and at 1,140 A/m^2 current density by 0.39 l. The highest values of water transport were observed during the tests with application of the ACM membrane. The ACM membrane is often described [14,15] as a proton blocker meaning that the proton transfer across the membrane is greatly

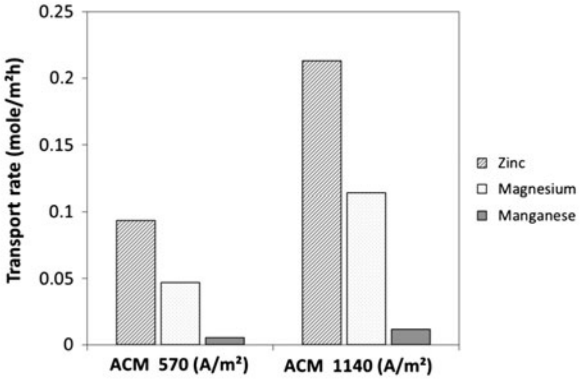

Fig. 4. Transport rates of Zn, Mg, and Mn during the industrial electrolyte electrodialysis.

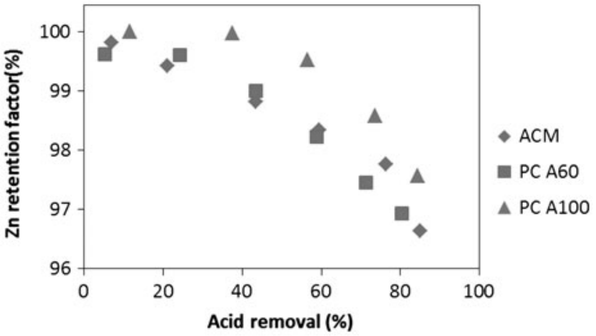

Fig. 6. Change of Zn retention factor as a function of acid removal degree at 570 A/m^2 and 70% of acid removal.

reduced compared to standard AEM. Robbins et al. [24] reported that the water flux is directly connected with the proton leakage across the membranes and improvement of one leads to deterioration of the other.

During the experiments with either synthetic solution or industrial electrolyte, the retention factors of analysed metal ions (Zn, Mg and Mn) are very high (around 99%). The retention factors start to decrease for each examined membrane after 60% sulphuric acid is removed from the diluate stream (Figs. 6–8). Baltazar et al. [12] reported similar phenomenon.

The mass balance for metal ions (Table 7) is at least 90%. The values exceeding 100% of mass initially introduced to the system are caused by experimental errors and uncertainty. The electrode streams analysis after the process showed only trace amounts of analysed ions (less than 1% of total mass introduced to the system) in anolyte and catholyte stream. The possible electrodeposition on electrodes was assumed to be negligible.

The obtained data (Table 8) indicate that majority of chloride ions are being transferred from diluate to concentrate stream irrespective of the current density applied or membrane type used. Such occurrence was observed for both synthetic solution and industrial electrolyte.

3.3. Copper electrolyte

All the experiments were conducted with application of industrial copper electrolyte at 70 l/h flow rate and constant current throughout the whole

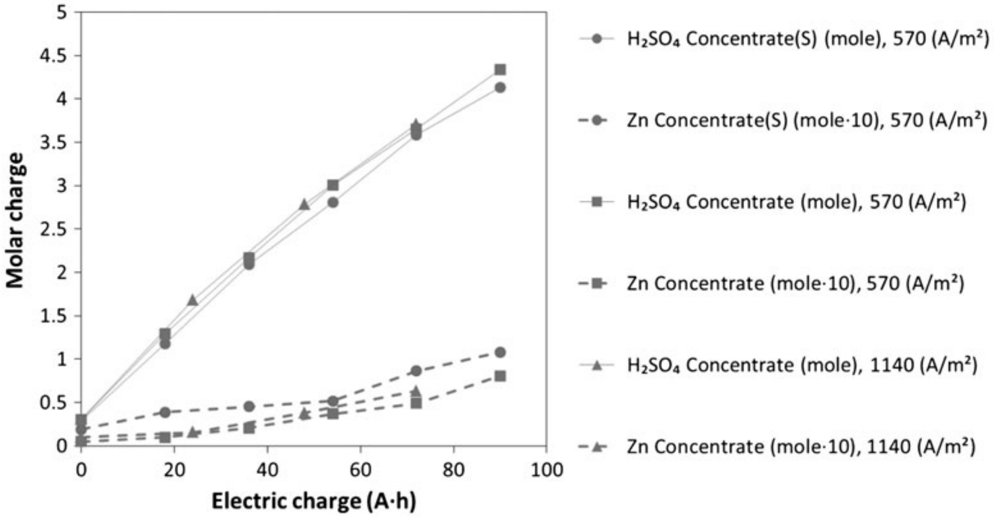

Fig. 5. Change of zinc and sulphuric acid molar charge as a function of electric charge obtained for CMS ACM membrane set.

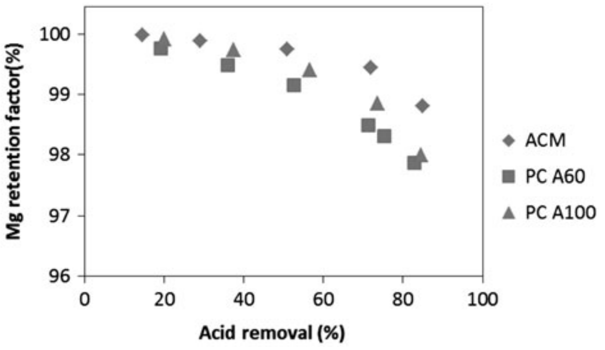

Fig. 7. Change of Mg retention factor as a function of acid removal degree at 570 A/m^2 and 70% of acid removal.

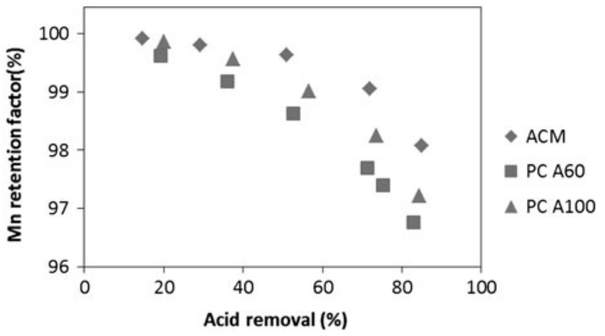

Fig. 8. Change of Mn retention factor as a function of acid removal degree at 570 A/m^2 and 70% of acid removal.

experiment. During the examination of ACM, PC Acid 60 and 100 membrane sets at 570 A/m^2 current density, the highest current efficiency (Table 9) was obtained with application of the ACM membrane which was equal to 68.1%. The lowest current efficiency was observed for the PC Acid 60, equal to 51.8%; and for the PC Acid 100 value of 60.8% was obtained. During the following tests with the ACM membrane set conducted at the current density 860 and 1,140 A/m^2, obtained current efficiencies were 65.9 and 67.8%, respectively. Similar values of current efficiency resulted in higher net power consumption when the higher current density was used. The lowest power consumption for the ACM membrane set was obtained at 570 A/m^2 and was equal to 0.90 Wh/g. At the current density of 860 A/m^2 and 70% of acid removal, power consumption increased to 1.16 Wh/g and at 1,140 A/m^2 it increased to 1.37 Wh/g.

Table 7
The mass balance of analysed metal ions

	Unit	Zinc	Magnesium	Manganese
PC Acid 60	%	107.0	100.7	97.8
PC Acid 100		103.0	102.3	98.9
ACM Q30		104.3	103.8	100.9
ACM Q70		94.7	93.5	94.3
ACM Q100		94.1	101.5	98.9
ACM industrial 570		94.9	98.6	93.1
ACM industrial 1140		95.1	92.5	92.2

Table 8
Chlorides concentration after electrodialysis of zinc electrolyte

Membrane	Current density (A/m)	Cl^- concentration in diluate stream mg/l	
		Initial	Final
PC A60	570 (S)	598	168
PC A100	570 (S)	626	113
ACM	570 (S)	588	172
ACM	570 (S), Q100	676	163
ACM	570	544	118
ACM	1,140	609	252

During the experiments performed at 570 A/m^2, gradual decrease of nickel retention factor for each examined membrane set was noticed as the sulphuric acid content in diluate stream decreased (Fig. 9).

The analysis of other metal ions (As, Sb, Cu and Fe) indicated relatively low arsenic and copper retention factors (Fig. 10). At 570 A/m^2 current density arsenic retention factor for the PC acid 60 membrane was the highest and equalled 83.9% and for ACM membrane it equalled 80.2%. During the consecutive tests with ACM membrane at 860 and 1,140 A/m^2 current densities, arsenic retention factors were 74.9 and 74.4%, respectively. Baltazar et al. [12] reduced arsenic content in the diluate stream at 600 A/m^2, below 60% of the initial value. The metal ions-transport rates analysis (Fig. 11) also indicates high copper transport across the membrane independently of used membrane type or current density.

During the following tests with ACM membrane set, increase of current density from the 570 to 860 A/m^2 and 1,140 A/m^2 (Table 10) changed the transport rate of sulphuric acid from 7.3 to 10.2 mol/(m^{2}h) and 14.1 mol/(m^{2}h), respectively. Obtained nickel transport rates at 570 A/m^2 and 70% of acid removal are higher compared to results obtained even at 80% acid removal

Table 9
Parameters of copper electrolyte electrodialysis

Membrane	Unit	PC A60	PC A100	ACM	ACM	ACM	ACM	ACM
Current density	A/m^2	570	570	570	860	860	1,140	1,140
Time	h	6.5	5.5	5	3	4	2.5	3
Acid removal	%	70	70	70	70	80	70	80
Current efficiency	%	51.8	60.8	68.1	65.9	63.5	67.8	66.4
Energy consumption	Wh/g	1.09	0.94	0.90	1.16	1.37	1.37	1.47
Concentrate volume increase	l	0.28	0.27	0.26	0.31	0.45	0.37	0.43

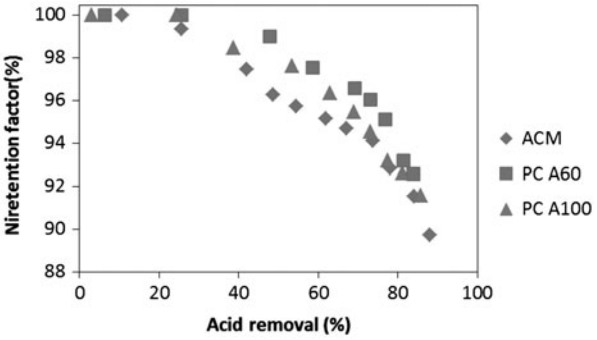

Fig. 9. Change of Ni retention factor as a function of acid removal degree.

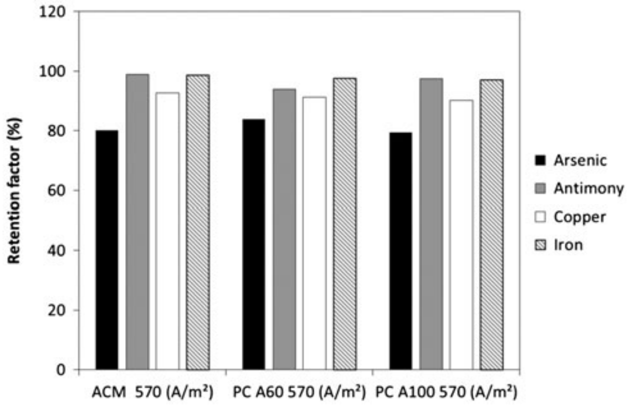

Fig. 10. Comparison of As, Sb, Cu and Fe retention factors at 70% acid removal.

at 860 and 1,140 A/m^2 current density (Fig. 12). It is uncommon phenomenon because increased permeability of metal ions is expected as the acid content in diluate stream is reduced [11,12]. At higher current density a lower transport rate resulted in lower nickel content in the concentrate stream at the end of the ED process.

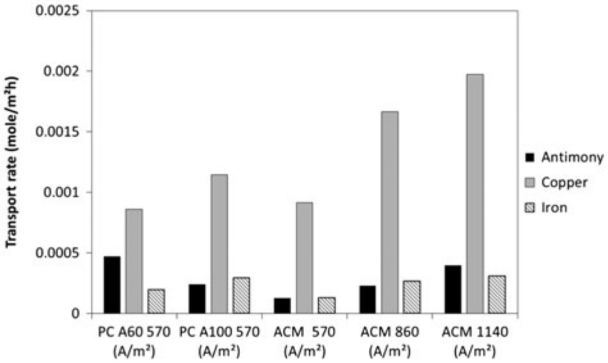

Fig. 11. Comparison Sb, Cu and Fe transport rates of at 70% acid removal.

The cause of nickel retention factor improvement at higher current densities needs further examination. The current density applied to the system has direct influence on time of the process (Table 9). A decreasing amount of transported arsenic from diluate to concentrate stream at higher current density can be explained by shorter time of contact between the process streams. Only a diffusive transport of undissociated arsenic acid H_3AsO_4 due to concentration gradient is expected. A smaller amount of arsenic will be able to permeate through a membrane during the shorter process. ED at lower current density is advised in order to transport the largest amount of arsenic from diluate stream. In such case lower nickel retention factor is expected.

The mass balance for metal ions (Table 11) is at least 90% in each experiment. Similarly to the zinc electrolyte the values exceeding 100% of mass are caused by experimental errors and uncertainty. Only a trace amount of analysed ions were found in anolyte and catholyte stream. The possible electrodeposition on electrodes was assumed to be negligible.

Similarly to the ED conducted with application of zinc electrolyte (Tables 5 and 6), increased volume of the concentrate stream was observed at the end of

Table 10
Retention and transport parameters for copper electrolyte

Membrane	Unit	PC A60	PC A100	ACM	ACM	ACM
Current density	A/m^2	570	570	570	860	1,140
Acid removal	%	70	70	70	80	80
Ni retention	%	96.0	94.5	94.1	96.5	96.9
As retention	%	83.9	79.4	80.2	74.9	74.4
Sb retention	%	93.8	97.6	98.8	98.2	97.7
Cu retention	%	91.3	90.2	92.7	89.6	90.6
Fe retention	%	97.7	97.1	98.8	98.1	98.3
H_2SO_4 transport	$mole/(m^2 h)$	5.5	6.5	7.3	10.2	14.1
Ni transport	$mole/(m^2 h)$	0.018	0.031	0.036	0.025	0.030
As transport	$mole/(m^2 h)$	0.036	0.055	0.058	0.092	0.123
Sb transport	$10^4 mole/(m^2 h)$	4.7	2.4	1.3	2.3	4.0
Cu transport	$10^4 mole/(m^2 h)$	8.6	11.4	9.2	16.7	19.8
Fe transport	$10^4 mole/(m^2 h)$	1.9	2.9	1.3	2.6	3.1

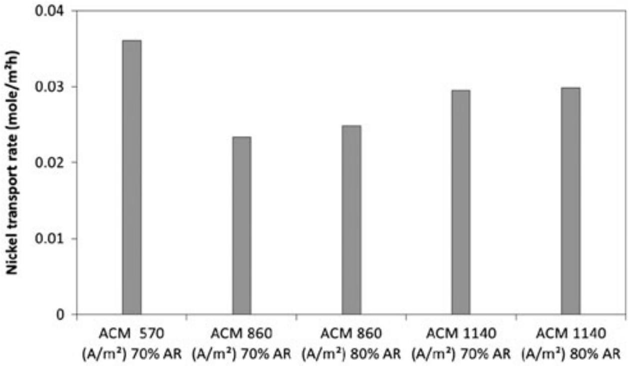

Fig. 12. Comparison of nickel transport rates during the nickel electrolyte electrodialysis.

process. During the experiment conducted at $570\,A/m^2$ the volume increase was in the range from 0.26 to 0.28 l for each tested membrane set. Transported water amount increased when the higher current density was applied to the system. At 70% of sulphuric acid removal during the test at $860\,A/m^2$ current density, concentrate stream volume increased by 0.31 l and at $1{,}140\,A/m^2$ increased by 0.37 l. When 80% of the acid was removed even more rapid volume change was observed. During the test at $860\,A/m^2$ current density concentrate stream volume increased by 0.45 l and at $1{,}140\,A/m^2$ by 0.43 l. The obtained results indicate increased water transport as the sulphuric acid content in the diluate stream decreases. Not all of the electric current introduced to a electrodialyser is utilised for acid ion transport. Part of this current is also responsible for water transport across the membrane. The obtained CMS ACM current efficiencies (Table 9) are very similar at different current densities. Over 30% of introduced current is dissipated in each experiment. In case of current density $570\,A/m^2$ a quantitative amount of the electric charge that is not utilised on acid transport is estimated to be $170\,A/m^2$ and for $1{,}140\,A/m^2$ estimated to be $340\,A/m^2$. This increase of dissipated current is believed to be responsible for the different amounts of transported water between the process streams.

Table 11
The mass balance of analysed metal ions

	Unit	Nickel	Arsenic	Antimony	Copper	Iron
PC Acid 60	%	98.4	93.4	92.0	93.5	95.9
PC Acid 100		101.2	100.6	105.0	102.5	100.6
ACM 570		93.8	96.2	91.6	95.6	97.3
ACM 860		96.8	95.3	98.0	96.1	92.3
ACM 1140		94.4	96.7	102.7	97.0	96.2

4. Conclusions

Electrodialysis process was successfully used in the treatment of industrial zinc and copper electrolytes. The studies indicate:

- the process was conducted below the LCD for both industrial electrolytes,
- calculated mass balances of analysed ions are over 90% for both tested electrolytes,
- only a small amount of contaminants are transferred to anolyte and catholyte streams during the electrodialysis process,
- it is possible to perform a steady ED process with application of the industrial zinc electrolyte with current efficiency up to 63.3%,
- the power consumption of the industrial zinc electrolyte and synthetic solution ED is approximately equal,
- the flow rate change in the range from 30 to 100 l/h had negligible effect on metal retention factor and rate of acid removal,
- the increased current density did not diminish membrane separation selectivity or performance in the case of zinc electrolyte ED,
- the Zn, Mg and Mn retention factors are of high value (99%) till the 60% sulphuric acid removal from the diluate stream,
- the majority of chloride ions are being transferred from the diluate to the concentrate stream during the course of the process, irrespective of current density applied or membrane type used,
- it is possible to perform a steady ED process with application of copper electrolyte up to 80% acid removal maintaining satisfactory metal ion retention,
- a lowered arsenic and copper retention factors compared to other analysed metal ions (Ni, Sb and Fe) were observed,
- at the 860 and 1,140 A/m^2 current densities an increased arsenic transport with simultaneous decreased nickel transport to the concentrate stream were observed, and
- up to 25% of the arsenic can be removed from the copper electrolyte feed during the electrodialysis.

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References

[1] S. Wang, Impurity control and removal in copper tankhouse operations, JOM 56 (2004) 34–37.

[2] J.E. Hoffmann, The purification of copper refinery electrolyte, JOM 56 (2004) 30–33.

[3] A. Agrawal, D. Bagchi, S. Kumari, V. Kumar, B.D. Pandey, Recovery of nickel powder from copper bleed electrolyte of an Indian copper smelter by electrolysis, Powder Technol. 177 (2007) 133–139.

[4] R.B. Gordon, T.E. Graedel, M. Bertram, K. Fuse, R. Lifset, H. Rechberger, S. Spatari, The characterization of technological zinc cycles, Resour. Conserv. Recycl. 39 (2003) 107–135.

[5] J. Jeong, M.-S. Kim, B.-S. Kim, S.-K. Kim, W.-B. Kim, J.-C. Lee, Recovery of H_2SO_4 from waste acid solution by a diffusion dialysis method, J. Hazard. Mater. 124 (2005) 230–235.

[6] J. Tanninen, M. Nyström, Separation of ions in acidic conditions using NF, Desalination 147 (2002) 295–299.

[7] F. Rögener, M. Sartor, A. Bán, D. Buchloh, T. Reichardt, Metal recovery from spent stainless steel pickling solutions, Resour. Conserv. Recycl. 60 (2012) 72–77.

[8] L. Cifuentes, G. Crisóstomo, J.P. Ibáñez, J.M. Casas, F. Alvarez, G. Cifuentes, On the electrodialysis of aqueous H_2SO_4–$CuSO_4$ electrolytes with metallic impurities, J. Membr. Sci. 207 (2002) 1–16.

[9] M.B. Bogacki, M. Wiśniewski, J. Szymanowski, Effect of extractant on arsenic(V) recovery from sulfuric acid solutions, J. Radioanal. Nucl. Chem. 228 (1998) 57–61.

[10] J.-H. Chang, A.V. Ellis, C.-H. Tung, W.-C. Huang, Copper cation transport and scaling of ionic exchange membranes using electrodialysis under electroconvection conditions, J. Membr. Sci. 361 (2010) 56–62.

[11] M. Boucher, N. Turcotte, V. Guillemette, G. Lantagne, A. Chapotot, G. Pourcelly, R. Sandeaux, C. Gavach, Recovery of spent acid by electrodialysis in the zinc hydrometallurgy industry: Performance study of different cation-exchange membranes, Hydrometallurgy 45 (1997) 137–160.

[12] V. Baltazar, G.B. Harris, C.W. White, The selective recovery and concentration of sulphuric acid by electrodialysis, Hydrometallurgy 30 (1991) 463–481.

[13] W. Ho, K. Sirkar, Membrane Handbook, Van Nostrand-Reinhold, New York, NY, 1992.

[14] R.K. Nagarale, G.S. Gohil, V.K. Shahi, Recent developments on ion-exchange membranes and electro-membrane processes, Adv. Colloid Interface Sci. 119 (2006) 97–130.

[15] T. Xu, Ion exchange membranes: State of their development and perspective, J. Membr. Sci. 263 (2005) 1–29.

[16] S. Cattoir, D. Smets, A. Rahier, The use of electro-electrodialysis for the removal of sulphuric acid from decontamination effluents, Desalination 121 (1999) 123–130.

[17] S. Koter, Separation of weak and strong acids by electro-electrodialysis—Experiment and theory, Sep. Purif. Technol. 60 (2008) 251–258.

[18] PCCell GmbH, Technical Datasheet of Ion Exchange Membranes, Available from: http://www.pccell.de/

[19] H.J. Lee, H. Strathmann, S.H. Moon, Determination of the limiting current density in electrodialysis desalination as an empirical function of linear velocity, Desalination 190 (2006) 43–50.

[20] T. Mohammadi, A. Moheb, M. Sadrzadeh, A. Razmi, Separation of copper ions by electrodialysis using Taguchi experimental design, Desalination 169 (2004) 21–31.

[21] L. Cifuentes, I. García, P. Arriagada, J.M. Casas, The use of electrodialysis for metal separation and water recovery from $CuSO_4$–H_2SO_4–Fe solutions, Sep. Purif. Technol. 68 (2009) 105–108.

[22] N. Tzanetakis, W.M. Taama, K. Scott, R.J.J. Jachuck, R.S. Slade, J. Varcoe, Comparative performance of ion exchange membranes for electrodialysis of nickel and cobalt, Sep. Purif. Technol. 30 (2003) 113–127.

[23] P. Murray, Manual of Water Supply Practices–M38, 1st ed., American Water Works Association, Denver, CO, 1999.

[24] B.J. Robbins, R.W. Field, S.T. Kolaczkowski, A.D. Lockett, Rationalisation of the relationship between proton leakage and water flux through anion exchange membranes, J. Membr. Sci. 118 (1996) 101–110.