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APPLICATION OF ELECTRODIALYSIS TO
WATER AND ACID RECOVERY

Studies on water and acid recovery from the effluent after metal etching rinse are presented. Water recovery was investigated using two alternative systems: electrodialysis 1 (ED1) – cation exchange – electrodialysis 2 (ED2) (System 1) and cation exchange – ED1 – ED2 (System 2). System 1 yielded acid-free water which contained trace amounts of metal salts and had a conductivity of 30 µS/cm. System 2 provided water of a better quality – with no acid and metal salts content and its conductivity amounted to 3 µS/cm only.

In order to recover hydrochloric acid from the ED1 concentrate, monoselective electrodialysis (Ed_{mon}) was applied. Its was found that the acid solution recovered from the concentrate obtained in System 1 was 49 times concentrated comparing to raw wastewater, whereas the acid recovered in System 2 was 74 times concentrated.

The calculated cost of water and acid production amounted to 0.4 DEM/m^3 and 1.55 DEM/m^3 in System 1 and System 2, respectively.

1. INTRODUCTION

Electrodialysis is widely applied in saline and brackish water desalination. The process is often referred to as *classical electrodialysis*. It requires two kinds of ion-exchange membranes: anion-exchange membranes with positively charged groups and cation-exchange membranes with negatively charged groups. The membranes, separated with spacers, are put in a constant electric field (figure1).

The ionic groups reject co-ions present in the solution, whereas counter-ions are transported through the membrane. By this mean every second cell is depleted of ions and in the rest of cells ions are concentrated.

Sometimes the aim of the process is to separate the ions of various valency in order to reuse valuable ionic components. In this process, monoselective membranes are used and they are preferentially permselective with respect to monovalent ions. Monoselective membranes are characterized by markedly reduced transport numbers

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with respect to divalent ions [1]–[3]. In the case of CMS membranes (TOKUYAMA), the leakage of divalent cations varies from 3 to 5%.
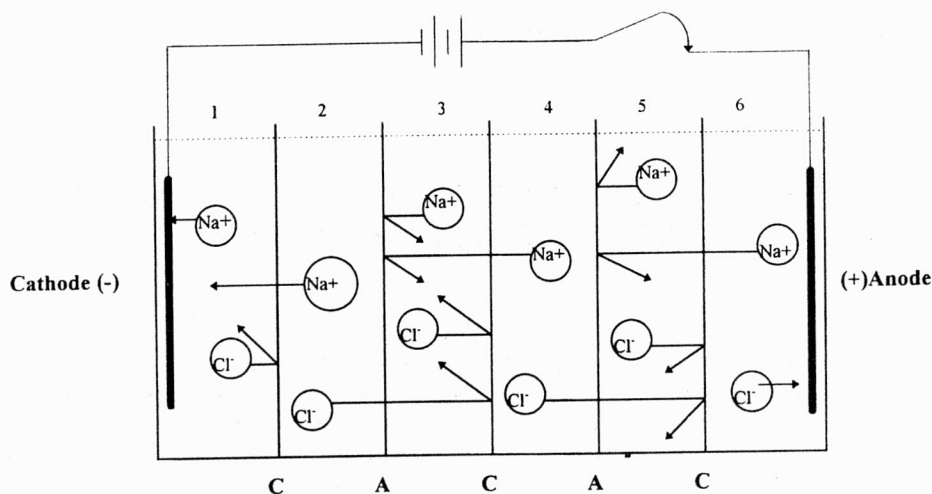

Fig. 1. Scheme of electrodialysis: anion-exchange membrane, cation-exchange membrane, 2, 4 – dilutate compartment, 3, 5 –concentrate compartment, 1, 6 – electrode compartments

We applied both of the above-mentioned processes to recover high-quality water and acid from the after metal-etching rinse. Effluents from the after metal-etching operations contain diluted acid and metal salts. The effluents are generally treated by neutralization, which has the disadvantage of producing large amounts of sludge and high-salinity wastewater.

In order to recover high-quality water and concentrated pure acid from the after etching rinse, it is necessary to design an appropriate treatment train. In this particular case, it will combine classical electrodialysis, ion exchange and monoselective electrodialysis. Such a combination of membrane techniques and ion-exchange processes is also advantageous in terms of deionization costs [4].

In the present study, water recovery was investigated using two alternative treatment trains (referred to as System 1 and System 2, respectively):

- electrodialysis 1 (ED1) + cation exchange + electrodialysis 2 (ED2),
- cation exchange + ED1 + ED2.

It may be expected that System 1 will allow a reduction of operating costs for the ion-exchange bed, because ED1 yields a considerable separation of metal salts. System 2 is supposed to provide recovered water of a better quality.

The acid and metal salt concentrate produced in the course of ED1 was subjected to monoselective electrodialysis (Ed_{mon}) for the recovery and further concentration of

the acid. It was anticipated that there would be some differences between the compositions of concentrates in System 1 and System 2. This implied that there might also occur differences in the concentrations of the acid recovered by Ed_{mon} and in the purity of the acid.

2. EXPERIMENTAL

The experiments were carried out on samples of after-etching rinse with hydrochloric acid. The parameters of the wastewater are listed in table 1.

Table 1

Parameters of the wastewater

Parameter	Value
pH	2.81
Conductivity	8.40 mS/cm
Acidity	24.00 eq H^+/m^3
Total iron	99.50 g Fe_{tot}/m^3
Nickel	2.70 g Ni^{2+}/m^3
Chromium	0.58 g Cr^{3+}/m^3

Metal cations were removed using a macroporous cation exchanger of Amberlyst 15 type. The ED process was run in a GOEMASEP 136 System equipped with 20 pairs of cells with Neosepta AMX and CMX membranes. The ratio of diluate volume to concentrate volume was 27 dm^3/1.8 dm^3, which was equivalent to 93.75% water recovery. The Ed_{mon} process was run with the same electrodialyser, which involved 20 pairs of cells with Neosepta ACS abd CMS membranes. The ratio of diluate volume to concentrate volume was 9 dm^3/1.8 dm^3.

3. RESULTS AND DISCUSSION

Water recovery train in System 1 yielded two streams: desalinated water and the concentrate stream (figure 2). It was found that the parameters of the concentrate obtained in the course of the ED2 process were similar to those of the raw wastewater, thus enabling recirculation of the solution and its reuse as a concentrate for ED1. In this way, it was possible to reduce the wastewater volume and to enhance water recovery.

Water recovered via System 1 was acid-free, with trace amount of metal salts, and its conductivity amounted to 30 µS/cm. Water recovery exceeded 91% (including water consumption for preparation of the cation exchanger).

SYSTEM 1
ED1 - CATION EXCHANGE -ED2

WATER FOR REGENERATION
SOLUTION AND FOR RINSING
$(0.13dm^3 + 0.72dm^3 = 0.85dm^3)$

EFFLUENT

$135.7 dm^3$

$135 dm^3$

$9 dm^3$
$(8.3 dm^3 + 0.7 dm^3)$

ED1

$135 dm^3$ CATION EXCHANGE

$133.2 dm^3$

$124.9 dm^3$(WATER)

ED2

$124.05 dm^3$

$8.3 dm^3$

$1.8 dm^3$

EDmon

$1.8 dm^3$(HCl)
$9 dm^3$
(WASTEWATER)

$9 dm^3$

RECIRCULATION ($8.3dm^3$)

WASTEWATER AFTER
REGENERATION AND RINSING

$0.85dm^3$

NEUTRALIZATION

Ca(OH)$_2$

TO SEWERAGE
SYSTEM

$$R_{H_2O} = \frac{124.05}{135.7} = 0.914 \qquad R_{HCl} = \frac{1.8}{135.7} = 0.013 \qquad WASTEWATER = \frac{9.85}{135.7} = 0.073$$

Fig. 2. Scheme of fluxes in System 1

SYSTEM 2
CATION EXCHANGE - ED1 -ED2

WATER FOR REGENERATION SOLUTION AND FOR RINSING ($1.2dm^3 + 6.8dm^3 = 8dm^3$)

EFFLUENT $137.4dm^3$

CATION EXCHANGE

$135.6 dm^3$

$135dm^3$

$9 dm^3$

ED1

$135 dm^3$ ED2

$126.6dm^3$
(WATER)

$118.6dm^3$

$8.4dm^3$

$9 dm^3$

RECIRCULATION ($8.4dm^3$)

$1.8dm^3$

EDmon $\longrightarrow$ $1.8dm^3$HCl

$9 dm^3$
(WASTEWATER)

WASTEWATER AFTER
REGENERATION AND
RINSING

$8 dm^3$

NEUTRALIZATION

Ca(OH)$_2$

TO SEWERAGE
SYSTEM

$$R_{H_2O} = \frac{118.6}{137.4} = 0.86 \qquad R_{HCl} = \frac{1.8}{137.4} = 0.013 \qquad WASTEWATER = \frac{17}{137.4} = 0.129$$

Fig. 3. Scheme of fluxes in System 2

The concentrate obtained in the course of ED1 contained hydrochloric acid (260 eq H^+/m^3) and iron salts (850 g Fe_{tot}/m^3). It was subjected to monoselective electrodialysis for the recovery and further concentration of the acid. Concentration of the recovered acid was 49 times as high as it was in the raw wastewater and it was slightly contaminated with iron salt-impurities amounted to 0.16%.

System 2 provided water of a better quality. Water was acid-free, with no metal salts, and its conductivity amounted to 3 µS/cm only. The composition of the concentrate from ED2 enabled its reuse as a concentrate for ED1 (figure 3). But water recovery (86%) was much lower than that in System 1 because of much higher consumption of water necessary for the rinsing of the ion exchanger.

The concentrate produced in the course of ED1 showed a higher content of the acid (410 eq H^+/m^3) and a lower content of iron salt (48 eq Fe_{tot}/m^3) than the concentrate obtained in the ED1 process in System 1. As a result, the acid solution recovered by Ed$_{mon}$ in System 2 was more concentrated than that in System 1. The acid concentration was 74 times as high as that of the raw wastewater, and the level of impurities proved to be very poor (0.03%).

The parameters of the water obtained in the two Systems are gathered in table 2, whereas those of the recovered hydrochloric acid are presented in table 3.

Table 2

Parameters of the recovered water

Parameter	System 1	System 2
Acidity, eq H^+/m^3	0	0
Total iron, g Fe_{tot}/m^3	0.02	0
Nickel, g Ni^{2+}/m^3	0.001	0
Chromium, g Cr^{3+}/m^3	0.01	0
pH	4.39	5.55
Conductivity, µS/cm	30	3
Recovery, %	91.4	86.3

Table 3

Parameters of the recovered hydrochloric acid

Parameter	System 1	System 2
Hydrochloric acid, eq H^+/m^3	1180	2000
Total iron, g Fe_{tot}/m^3	70	24
Nickel, g Ni^{2+}/m^3	0.02	0.037
Chromium, g Cr^{3+}/m^3	0.01	0.01
Acid concentration compared to raw wastewater	49 times higher	74 times higher

We decided to calculate the operating costs for the two systems. We took into consideration the following items:

- the cost of HCl for the regeneration of the cation exchanger,
- the cost of lime for the neutralization of the wastewater,
- the cost of energy for ionic transport during the ED processes,
- dues for the wastewater volume, charges for chlorides in the wastewater and fines for exceeding TDS level.

The calculated costs of water production in System 1 and System 2 amount to 0.4 DEM/m^3 and 1.55 DEM/m^3, respectively. The high operating cost in System 2 should be attributed to the cost of HCl for the regeneration of the cation exchanger and the cost of energy required in the ED processes.

What is more, System 2 produces larger quantities of wastewater than System 1. It should be noted, however, that the quality of the recovered products is much better in System 2 than in System 1.

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ZASTOSOWANIE ELEKTRODIALIZY DO ODZYSKU KWASU I WODY

Przedstawiono wyniki badań nad odzyskiem wody i kwasu ze ścieków pochodzących z płukania metali po trawieniu. Do odzysku wody wykorzystano dwa alternatywne układy technologiczne: elektrodializę 2 (ED2) (system 1) oraz wymianę kationów – ED1 – ED2 (system 2). W systemie 1 otrzymano wodę pozbawioną kwasu, ze śladową zawartością soli metali, o przewodności 30 µS/cm. W systemie 2 otrzymano wodę o lepszej jakości (pozbawioną kwasu i soli metali), a jej przewodność wynosiła 3 µS/cm.

Aby odzyskać kwas solny z koncentratu po procesie ED1, zastosowano elektrodializę monoselektywną (Ed$_{mon}$). Stwierdzono, że roztwór kwasu otrzymany z koncentratu w systemie 1 był zatężony 49-krotnie w stosunku do ścieków surowych, roztwór kwasu natomiast odzyskany w procesie Ed$_{mon}$ w systemie 2 był zatężony 74-krotnie.

Obliczony koszt wody i kwasu wyniósł 0,4 DEM/m^3 wody w systemie 1 i 1,55 DEM/m^3 wody w systemie 2.