Recovery of Metals from Electroplating Waste Solutions and Sludge. Comparison of Donnan Dialysis and Pertraction Technique

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Abstract

An experimental study has been made on the recovery, separation and concentration of some metals from electroplating solutions and sludge. Two membrane methods (i.e. Donnan dialysis - DD - and the pertraction in a multimembrane hybrid system - MHS) were used and compared. Related ionic fluxes and separation coefficients for uni- and divalent cations were measured and discussed. It was found that the DD as a simple membrane technique can be used to permeate Zn^{2+} and Cu^{2+} with high fluxes associated with fluxes of other cations (Na^+, Ca^{2+}, Mg^{2+}). The selective recovery of Zn^{2+} at the presence of Mg^{2+}, K^+, and Na^+ was reached in the MHS composed of cation-exchange membranes and a liquid membrane containing di-(2-ethylhexyl) phosphoric acid (D2EHPA) or bis(2,4,4-trimethylpentyl) thiophosphinic acid (Cyanex 302) as a selective carrier. In the case of solutions remaining after zinc electroplating, the Zn^{2+} flux was 1.6×10^{-11} mol/cm^2s, and separation coefficients $\alpha^{Zn}_{\Sigma M}$ gained the value of 8-10. The use of the MHS for processing dissolved and acidified sludge (pH = 1) allowed recovery of Zn^{2+} with the transport stationary rate equal to 3.2×10^{-11} mol/cm^2s. According to the D2EHPA properties, other cations such as Cr^{3*} Fe^{3+}, Cu^{2+}, Mg^{2+}, and Na^+ were not transported to the stripping solution (1 M H_2SO_4). The use of Cyanex 302 instead of D2EHPA considerably lowers the flux of calcium and leads to the effective separation of Zn^{2+} over Ca^{2+}.

Keywords: electroplating waste solutions, sludge, membranes, Donnan dialysis, pertraction, multimembrane hybrid system, D2EHPA, Cyanex 302

Introduction

Industrial activity involving electroplating processes leads to the accumulation of large amounts of liquid and quasi-solid wastes containing heavy metals which can harm the environment. These wastes are produced in the form of acidic or alkaline solutions, rinse waters, and alkaline sludge which remains after chemical precipitation of heavy metals from effluents. (Note that the sludge after filtering is usually stored in huge amounts in dumping grounds. Such a typical example demonstrates the way in which wastewater problems are shifted to landfil problems.) The technology used nowadays [1, 2] requires more advanced methods for processing the waste water before its recycling or discharge into the environment. Similarly, the hydroxide sludge should be processed at the place in order to avoid further increase of stored precipitates containing heavy metals. Therefore, it is necessary to develop and test some new methods enabling simultaneous separation and concentration of metals from dilute aqueous solutions of complex composition. Besides conventional extraction, the most effective processes can be based on the application of membranes made of polymers or liquids [3, 4].

In general, membrane techniques of separation (including recovery, active concentration, purification, etc.) exploit physicochemical properties of any physical barrier

which is able either to discriminate some species present in the feed or to differentiate their permeation rates. The recovery of metal ions from aqueous solutions is possible with the use of polymer cation-exchange membranes or, alternatively, with hydrophobic liquid membranes containing a mobile ionic carrier. Specifically, among many methods the most promising are the Donnan dialysis (DD) and the liquid membrane (LM) technique based on coupled transport phenomena. These methods are recognized as applicable in the continuous and simultaneous metal recovery from dilute solutions. Moreover, they make possible the active concentration of target species in a small volume of the stripping phase. In this paper some laboratory studies concerning the efficiency of the DD and LM techniques in processing real electroplating waste solutions and sludge are presented and compared.

Characteristics of Donnan Dialysis (DD)

According to the scheme in Fig. 1 the Donnan dialysis of cations [5] is conditioned by an effective and directed cation exchange between two electrolyte solutions. This exchange occurs across a membrane made from crosslinked (water insoluble) and hydrophilic polyelectrolyte. Usually, divalent cations are transported from the dilute feed solution into the stripping solution containing an excess of univalent cations, which are most frequently hydrogen cations. The operation of the DD system makes reaching a stable flux of cations from dilute to concentrate phase possible. This uphill transport (or chemical pumping) is a result of coupled interdiffusion of M^{2+} and H^+ cations, which is driven in opposite directions by an excess of H^+ cations in the stripping solution. The final distribution of ions between two membrane adjacent solutions corresponds to the Donnan equilibrium principle, which takes the following form for the M^{2+}/H^+ ion exchange:

$$\frac{a_{M^{2+},f}}{a_{M^{2+},s}} = \left(\frac{a_{H^+,f}}{a_{H^+,s}}\right)^2 \qquad (1)$$

Symbols f and s represent the feed and strip solutions, respectively, and a_M^{2+}, a_H+ are the activities of the metal and hydrogen ions.

Donnan dialysis as the method that enables active concentration of ionic species has several attractive features. For example, high enrichment factors can be attained in a relatively short time [6] and the permeation rates are independent from the sample composition over a wide range of dialysis conditions [7]. On the other hand, free diffusion of electrolytes across the aqueous internal phase of the ion-exchange membrane can lower its selectivity [8, 9]. Nevertheless, it has been proven [9-12] that Donnan dialysis can be regarded as a feasible tool for the treatment of electroplating waste solutions.

Characteristics of Liquid Membranes

In a liquid membrane system the membrane itself is formed by a layer made of the hydrophobic liquid containing a selective reagent (carrier). For practical purposes
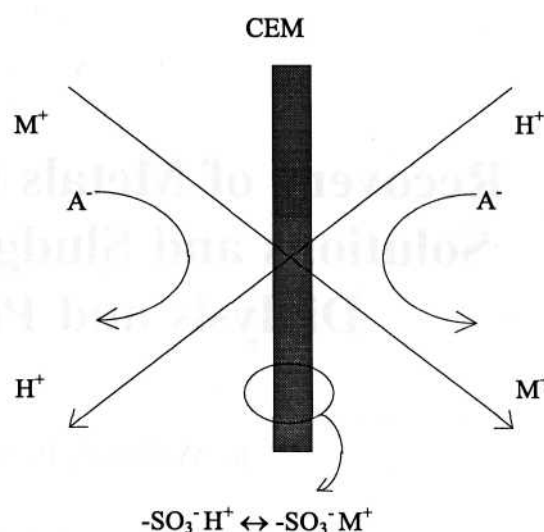

Fig. 1. Donan dialysis through cation exchange membrane (CEM).

liquid membranes are prepared as supported liquid membranes (SLM) or emulsion liquid membranes (ELM). The scheme of the simplest laboratory liquid membrane, i.e., a bulk liquid membrane (BLM), is shown in Fig. 2. According to this scheme, metal ions form a complex or salt with a carrier CH by the interfacial ion-exchange reaction. The neutral complex diffuses to the membrane/strip solution interface where protons from the strip solution displace the transported ions into this solution. As long as the strip solution is more acidic than the feed, metal ions are chemically pumped across the membrane. In the case of Zn^{2+} cations as target transport species, their permeation through the organic phase is enabled and facilitated typically by the presence of di(2-ethylhexyl) phosphoric acid (D2EHPA) [13]. This reagent can be used also for the transport of Cu^{2+} [14], Ni^{2+} [15], Sm^{3+} [16], Te^{4+} [17], and the separation of Co^{2+} and Ni^{2+} [18], or Cu^{2+} and Zn^{2+} [19]. In metal recovery processes, the technique of liquid membranes is of growing concern, and some industrial pilot plants are described [20]. In this context, several studies [15, 21-23] have demonstrated the LM feasibility in the treatment of electroplating solutions.

Multimembrane Hybrid System (MHS)

During the practical application of liquid membranes some problems concerning their instability and short time-life were encountered. Details of various phenomena underlying these disadvantages are discussed widely in literature [20, 24, 25]. Therefore, it was proposed to combine liquid membranes with ion exchange polymer membranes in some new membrane systems called "multimembrane hybrid systems" (MHS) [26-32]. The scheme and functioning of a simple MHS are presented in Fig. 3. The MHS operation involves a series of ion-exchange -diffusion processes (in CEMs), and the transport mediated by a carrier in the BLM. The presence of polymer membranes stabilizes the liquid membrane system and enhances the interfacial ion-exchange reactions because of high and specific sorption of cations by the CEM polyelectrolyte. The liquid membrane provides the selectivity towards a given cation - according to the properties of a carrier used. By the
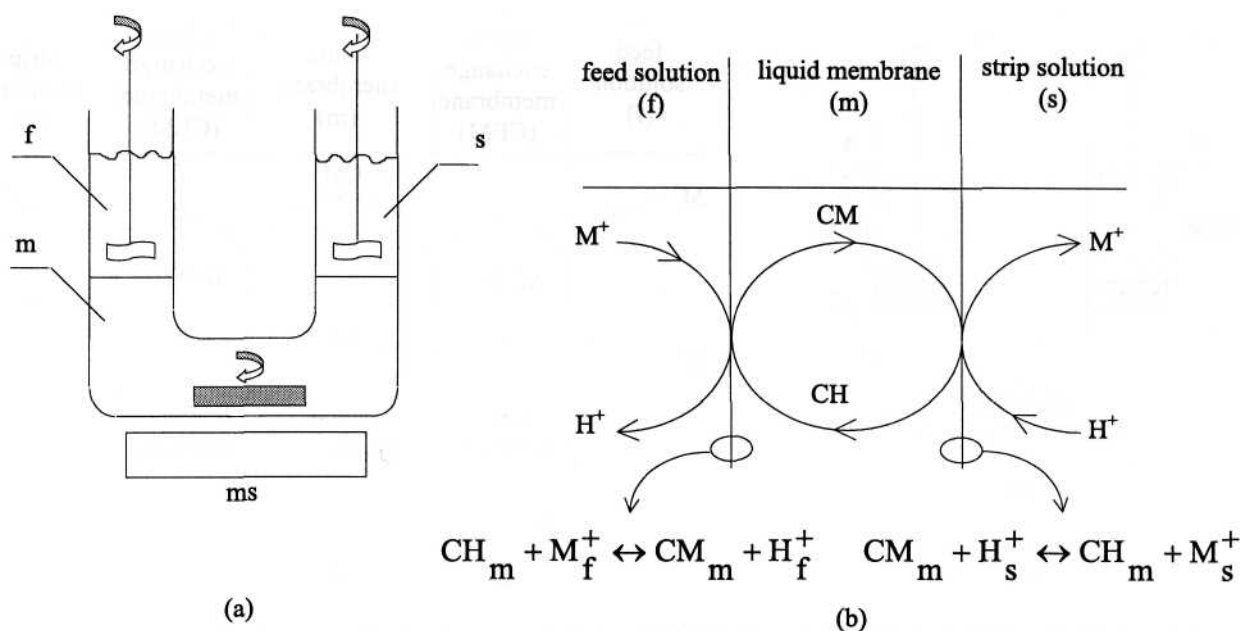
Fig. 2. Idea of agitated bulk liquid membrane (a), and carrier transport system (b); f - feed solution, s - strip solution, m - liquid membrane, CEM - cation exchange membrane, ms - magnetic stirrer.
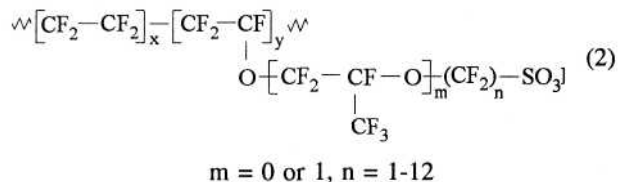
analogy to extraction and diffusion phenomena, the overall liquid membrane system (including the MHS) can be called henceforth the pertractor and the realized process - the pertraction [33].

Experimental

Reagents and Materials

Membranes

The Nafion-120 cation-exchange membrane was used in the DD and the MHS experiments. The membrane is commercially available from Du Pont De Nemours, USA. The Nafion polymer contains ionomer of the following composition:

$$\sim\!\!\left[CF_2\!-\!CF_2\right]_x\!\!\left[CF_2\!-\!CF\right]_y\!\!\sim \atop O\!\!\left[CF_2\!-\!CF\!-\!O\right]_m\!\!(CF_2)_n\!-\!SO_3\right] \quad (2) \atop CF_3$$

$$m = 0 \text{ or } 1, n = 1\text{-}12$$

Before transport experiments, the membrane (0.028 cm thickness, cation exchange capacity 1.1 mol H^+/dm^3) was conditioned in boiling water for over 3 hours and prepared in its H^+ form by standard methods. All experiments were carried out with the same Nafion membrane samples. After each experimental transport run, the membranes were regenerated by the ion exchange in the 0.5 M solution of sulfuric acid, and washed in distilled water. The 0.1 M solution of D2EHPA (Chemical Co. Sigma, 95%) in kerosene (prod. Maker, Poland, b.p. 124-174°C, viscosity 6.9 x 10^{-3} Paxs) was used as the liquid membrane in the MHS. In some experiments D2EHPA was replaced by bis(2,4,4-tri-methylpentyl) thiophosphinic acid, Cyanex 302, (Fluka,

85%). This reagent is recommended for the Zn^{2+} separation in the presence of Ca^{2+}.

Feed and Strip Solutions

Three different industrial feed solutions, taken from the electroplating installation of Apator S.A. Torun, were used in this study. Acidic solution produced during copper etching was applied as the feed in the membrane systems without any pre-treatment. Alkaline solution remaining after zinc electroplating was used both in its initial form and after neutralization and acidification. Alkaline sludge in the form of suspension (100 g/dm^3) was treated with sulfuric acid to dissolve hydroxides and attain acidic solution. The composition and pH of feeds (except as noted) are listed in Tab. 1. A solution of sulfuric acid (reagent grade, POCh, Gliwice) at concentration 1 M was used as the stripping phase in each transport system.

Transport and Separation Experiments

Donnan Dialysis

Experiments were carried out in a laboratory set-up composed of a three-chamber transport cell, feed reservoir, pumps and magnetic stirrer. The scheme of the apparatus and respective flow diagram are presented in Fig. 4. The Nafion membrane was clamped between two cell halves made of plexiglass. A transport cell was connected with the external reservoirs by PVC tubing. The system was filled with 1 dm^3 of the feed solution (pH = 2.11 or 8.75) and 145 cm^3 of the 1 M H_2SO_4 as the stripping solution. The solutions were circulated between cell chambers and reservoirs by running peristaltic pumps. The working area of the membrane was 25 cm^2. Periodically, samples (1 cm^3) were taken out from the feed and stripping solutions to be analyzed by the A AS method (ABQ Varian). The pH of the feed
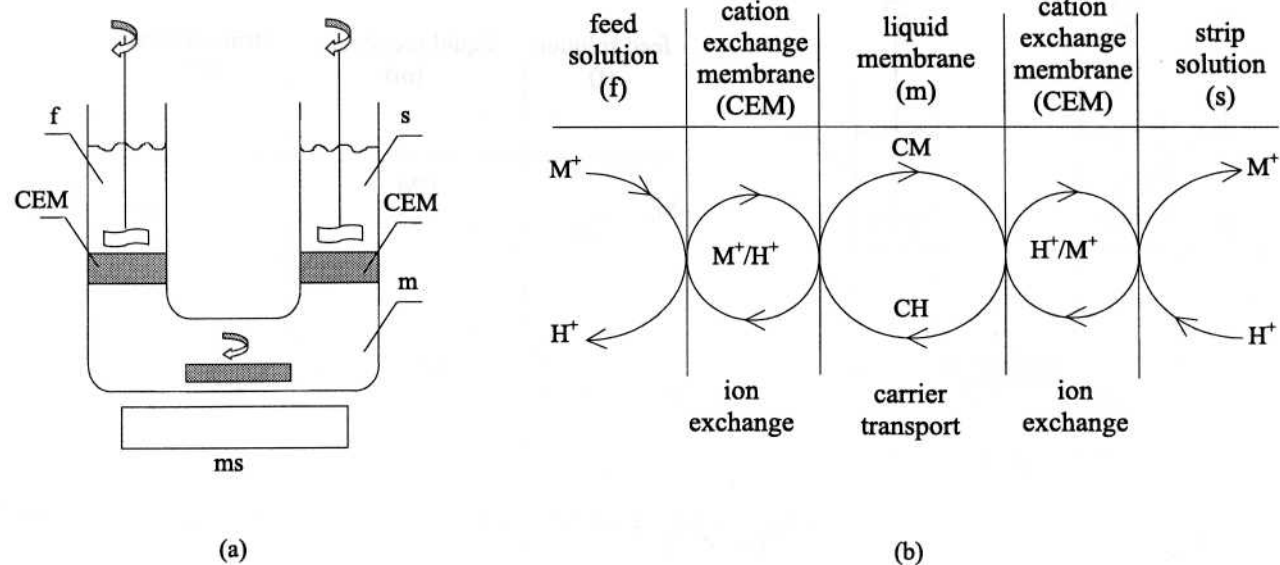
Fig. 3. Idea of multimembrane hybrid system (a), and scheme of operation (b): f - feed solution, s - strip solution, m - liquid membrane, CEM - cation exchange membrane, ms - magnetic stirrer, CM,CH - salt and acid carrier species.

was monitored on line with a pH-meter (Elmetron CX-721) and a glass body combination electrode (Hydromet ERH-11).

Pertraction in the multimembrane hybrid system

The scheme of the experimental set-up for the MHS pertraction is shown in Fig. 5. The transport cell (pertractor) was composed of five chambers separated by two Nafion membranes and one liquid membrane. The working area of each polymer membrane was 12.6 cm^2. The feed was pumped throughout external chambers (f) by a peristaltic pump from an external reservoir of 1 dm^3 volume. The central chamber contained 144 cm^3 of 1 M H$_2$SO$_4$ as the stripping solution (s). This solution was agitated magnetically (300-500 rpm.). Throughout the two intermediating chambers (LM in Fig. 5) the flowing liquid membrane of volume 125 cm^3 was circulated (470 cmVmin) by a teflon

piston pump (OSI, France). The experiments were made at room temperature (18-26°C). Metal content and pH were measured as described above.

Results and Discussion

In order for pertraction in any MHS to be a practical industrial technology, the method should be stable and comparable to other membrane techniques. Therefore, the results concerning the MHS and DD experiments are presented herein in parallel to reveal possible differences and to compare respective concentration factors and separation coefficients. From primary data, i.e. from instantaneous concentrations of metal species (M = Zn, Cu, Ca, Fe, Cr, Mg, K, Na) in the feed and strip solution, the cumulative transport curves Q = f(t) were calculated and drawn in respective figures. Each value of Q was calculated as the amount (in moles) of M species transported into the strip-
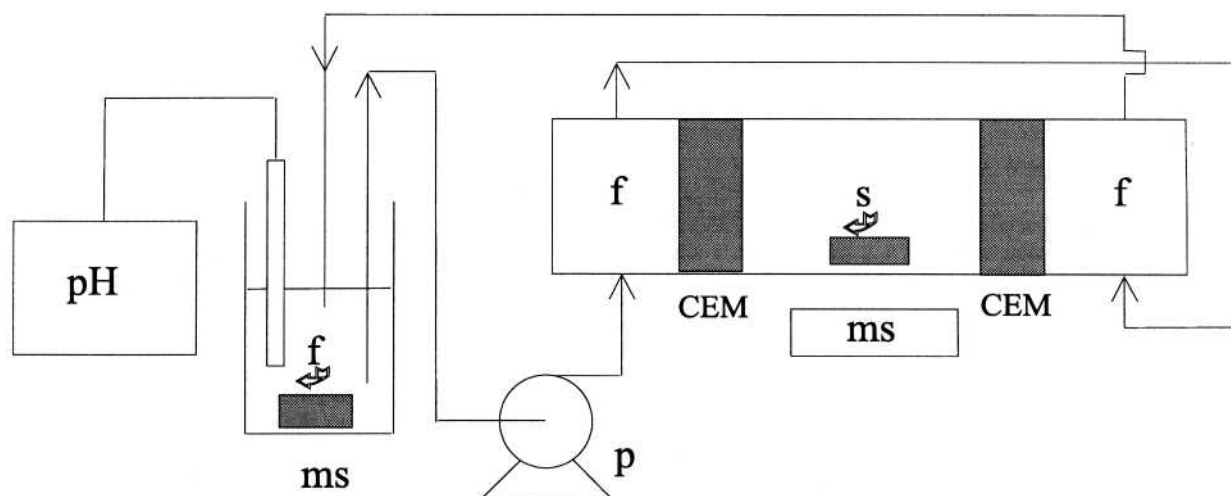

Fig. 4. Scheme of experimental system for Donnan dialysis: f - feed, s - strip solution, CEM - cation exchange membrane, m - magnetic stirrer, p - peristaltic pump, pH - pH-meter.

ping solution (s) after the time t through 1 cm² of the working membrane area:

$$Q_M = \frac{[M]_s V_s}{1000 A_s} \quad (mol/cm^2) \quad (3)$$

In Eq.3, V_s is the volume of the stripping (s) solution (cm³), $[M]_s$ is the concentration of M metal species after transport time t (mol/dm³), and A_s (cm²) is the area of the strip solution/membrane interface. The slope of tangent of the cumulative curve at any t-point determines the instantaneous output flux of M, i.e., $J_{M,t=t}$ (mol/cm²s). In the case of Q vs. t linear dependence, the $J_{M,t=t}$ is equivalent to the quasi-stationary flux J_M, usually calculated from Eq.4:

$$J_M = \frac{\Delta[Q]_{M,s}}{\Delta t} \quad (mol/cm^2 s) \quad (4)$$

In order to compare transport rates of uni- and mono-valent cations, the fractional fluxes N_M can be calculated from Eq. 5:

$$N_M = \frac{z_M J_M}{\sum_i z_i J_{M,i}} \quad (5)$$

According to the properties of Donnan dialysis and MHS pertraction, the concentration $[M]_s$ can reach the value of $[M]_f$. Further permeation occurs as the uphill transport with characteristic unequality $[M]_s > [M]_f$. In practice, this effect is characterized by the concentration factor (CF):

$$CF_M = \frac{[M]_s}{[M]_{f,0}} \quad (6)$$

where "0" denotes the initial concentration (t = 0) of M in the feed. Note that this quantity depends both on the ionic fluxes and volume of the stripping solution.

The ability of the system to separate cations is characterized by separation coefficients, which indicate how far the composition of the stripping solution is more profitable than the composition of the feed. In the case of multicomponent mixtures the overall separation coefficient α^jij can be calculated from Eq. 7.

Table 1. Feed solutions used in Donnan dialysis and pertraction processes.

Cation	Initial concentration $[M]_{f,t=0} \times 10^3$, mol/dm³		
	Solution after zinc electroplazing	Solution after copper etching	Solution prepared of sludge*⁾
Cr^{3+}	–	–	0.77
Fe^{3+}	–	–	2.72
Zn^{2+}	1.5	0.30	48.9
Cu^{2+}	–	7.11	1.96
Ca^{2+}	1.43	1.80	9.82
Mg^{2+}	0.91	0.45	8.21
Na^+	2.95	0.40	0.99
pH	11.5	1.5	1

*⁾ Analyzed after dissolving in sulfuric acid, (100 g/dm³)

$$\alpha_{\Sigma M}^{M_k} = \frac{[M]_{k,s} \sum_{i \neq k}[M]_{i,f}}{[M]_{k,f} \sum_{i \neq k}[M]_{i,s}} \quad (7)$$

Alkaline Solution after Zn Electroplating

In order to asses the DD as an independent membrane process and its potential contribution to the MHS process, the respective experiments with the DD system were carried out. In the introductory experiment, real alkaline electroplating solution (pH = 11.5) remained after zinc electroplating was used. The results are presented in Figs. 6 a and b as the transport cumulative curves, and the dependence of overall separation coefficients vs. time. In this experiment the prevailing flux of sodium cations was observed. As can be expected, only these cations are able to exchange freely between the alkaline feed solution and the cation-exchange membrane. Consequently, the respective separation coefficients indicate fast and active transportation of Na^+ during the DD process. On the other hand, hydrogen ions transported at least in the equivalent amount in the opposite direction, neutralize the feed solution. This process liberates cations from insoluble hydroxides, and as
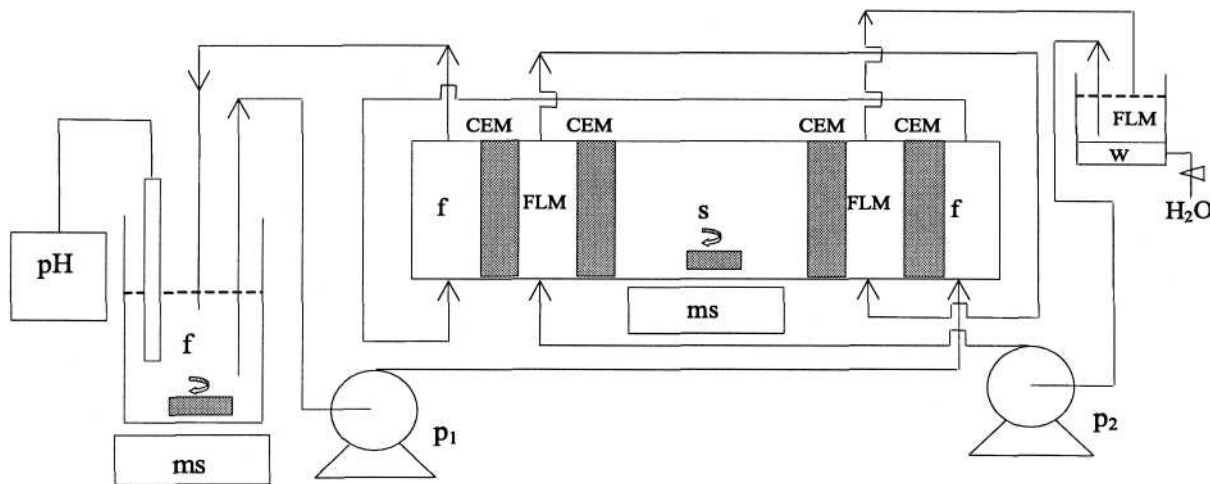

Fig. 5. Scheme of experimental set-up for pertraction in multimembrane hybrid system: f - feed solution, s - stripping solution, FLM - flowing liquid membrane, CEM - cation exchange membrane, m - magnetic stirrer, p_1 - peristaltic pump, p_2 - teflon made piston pump, pH - pH-meter.

a result, even Zn^{2+} transport in some small quantities can be observed (see Tab. 2). The selectivity order for the DD system found from the values of separation coefficients is Na » Ca > Zn > Mg. Thus, the effective recovery of Zn^{2+} is practically impossible when using the DD technique for treating alkaline feeds.

The results of pertraction with the use of MHS are presented in the same way in Figs. 7 a,b. It can be seen that the course of respective plots and relationships between fluxes observed for the DD and MHS working with the alkaline feed are similar. However, the additional disadvantage of the MHS method is a progressive emulsification of the liquid membrane during the pertraction process. Among many factors which can cause this phenomenon, the surface-active properties of sodium salt of D2EHPA [34-36] seem to be fundamental for forming water in-oil-emulsions and reversed micelles. This can be associated with a very high flux of sodium cations and the permeation of water from aqueous solutions into the organic LM phase. In our study these effects were further eliminated by acidification of the feed (pH = 2.8) resulting in considerable changes in both fluxes and separation coefficients (see Fig. 7 c,d, and Tab. 2). The selectivity order changes to, Zn, Ca » Mg,Na, that is the MHS selectivity coefficient $\alpha^{Zn}_{\Sigma M}$ increases from 0.1 (alkaline feed) to 8 (t = 200 hours) with a tendency to further increase in time. However, due to a high affinity of D2EHPA towards Ca^{2+}, the unfavourable transport of calcium cations was observed. The problem can be solved (see below) by using a carrier with higher

separation coefficients etc", e.g., some sulfur containing analogues of D2EHPA [20]. The results listed in Tab. 2 indicate that the relative flux of sodium ions (N_{Na}) is considerably reduced from 0.9 down to 0.02, that is to *2% of the overall flux*, when pertraction is carried out with an acidic feed.

Rinse Solution after Cu Etching

The rinse solutions produced during the process of Cu etching, as a part of electroplating technology, contain two target metals which should be recovered and/or separated: Zn^{2+} and Cu^{2+}. Both of these metals can be transported and separated with the use of D2EHPA also in a multimembrane hybrid system [37]. The comparison of cumulative curves (see Fig. 8) corresponding with the DD and MHS processes allows us to conclude that the fluxes of Zn^{2+} and Cu^{2+} in the pertraction are 20-fold and 4-fold higher than those resulting from dialysis (see Tab.2). Contrary to the DD, in the case of MHS, the flux of sodium is considerably diminished, i.e. ca. 1000 times. A similar effect is seen in respect to magnesium cations. The plots of the overall separation coefficients vs. time (see Fig. 8) show that during dialysis mainly sodium cations are preferentially transported with the uphill transport effect (CF > 1). Some amount of copper was also transported, but not actively. In this case, the DD selectivity order is: Na > Cu > Mg, Zn > >Ca.

Table 2. Donnan dialysis and pertraction of metals from electroplating solutions.

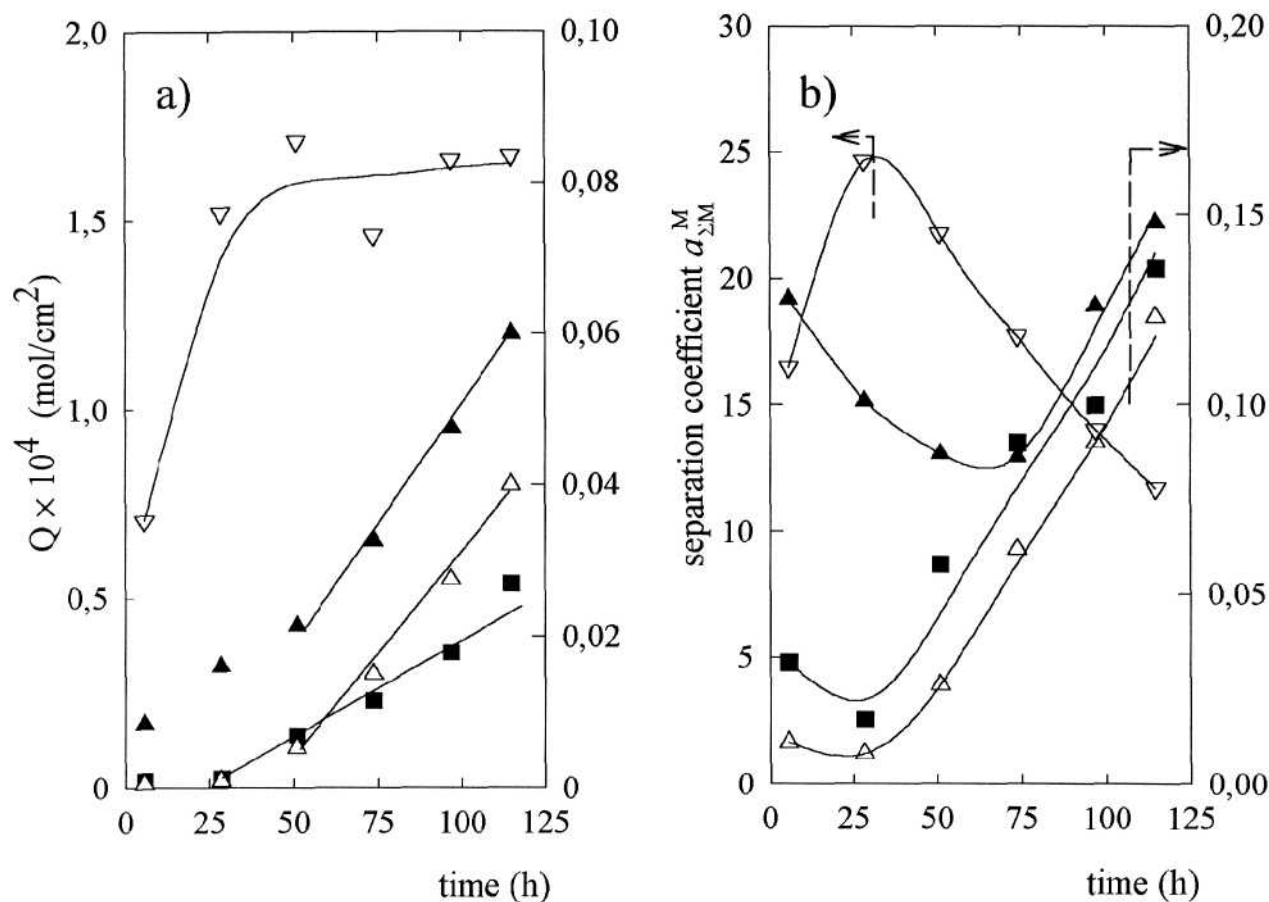| Cation	Donan dialysis			Pertraction in multimembrane hybrid system		
	Flux $J_M \times 10^{12}$ mol/cm²s	Fractional flux N_M	Concentration factor $CF^{*)}$	Flux $J_M \times 10^{12}$ mol/cm²s	Fractional flux N_M	Concentration factor $CF^{*)}$
solution after zinc electroplating (pH = 11.5)						
Zn^{2+}	3.63	0.01	3.3	0.57	0.01	< 0.1
Ca^{2+}	7.96	0.03	4.1	5.69	0.07	0.9
Mg^{2+}	2.89	0.01	3.6	1.15	0.02	< 0.1
Na^+	613	0.95	8.3	1.39	0.90	1.6
$\Sigma z_i J_i$ eqv./cm²s	642	1		154	1	
acidified solution after zinc electroplating (pH = 2.8)						
Zn^{2+}				16.2	0.55	1.3
Ca^{2+}				11.9	0.40	1.4
Mg^{2+}				0.90	0.03	0.2
Na^+				1.28	0.02	0.1
$\Sigma z_i J_i$ eqv./cm²s				59.3	1	
solution after copper etching (pH = 1.5)						
Cu^{2+}	4.20	0.40	2.8	17.20	0.61	0.2
Zn^{2+}	0.14	0.01	2.3	3.03	0.11	1.2
Ca^{2+}	2.06	0.20	1.8	7.89	0.28	0.6
Mg^{2+}	0.77	0.07	2.4	0.05	< 0.01	< 0.1
Na^+	6.7	0.32	3.9	0.06	< 0.01	0.3
$\Sigma z_i J_i$ eqv./cm²s	21.0	1		56.4	1	

*) after 120 hours.

Fig. 6. Donnan dialysis of alkaline solution after Zn electroplating: (a) - cumulative transport curves, (b) - separation coefficients; (■) Zn, (▲) Ca, (△) Mg, (∇) Na.

According to the D2EHPA properties, very different effects are observed during the pertraction in the MHS, i.e. the separation coefficients indicate the preferential transport of Zn^{2+} with a negligible transport of sodium ions. The respective separation order is Zn > Ca > Na > Cu > Mg. That is, the calcium permeation remains as an unfavourable effect. Alternatively, as demonstrated elsewhere [38], copper can be selectively transported instead of zinc in the same system by using Acorga P50 (2-hydroxy-5-nonylbenzaldehyde oxime) as a selective carrier for Cu^{2+}.

Electroplating Sludge

Electroplating sludges as a final by-product of electroplating activity are usually stored in the form of filtered quasi-solid wastes in dumping grounds. In opposition to liquids, which can be processed currently at the place, after appropriate modification of the applied technology, the solid wastes exist in huge amounts and wait for reasonable utilization. As rule, the precipitates contain mainly hydroxides of very low solubility in water. This makes the immediate treatment of their suspension by membrane technique practically impossible. Thus, in order to increase the content of cations allowed to exchange with hydrogen ions and to permeate the membrane system, the feed phase was acidified with concentrated sulfuric acid down to pH in the range 1-2. The results concerning dialysis (starting pH = 2.1) and pertraction (starting pH = 1) are shown in Fig.

9 and Tab. 3. Qualitatively, the results resemble these presented above for experiments carried out with electroplating solutions. This means that Zn^{2+} cations are transported preferentially in the MHS with the selectivity order Zn > Ca, Na » Cr >Fe, Mg. As compared to this result, the DD process seems completely ineffective because of its low separation ability and the predominating flux of sodium ions. On the other hand, a very high concentration of calcium in the feed leads to its high flux and the precipitation of Ca sulfates on the cation exchange membranes contacted with the strip solution. This effect sometimes can reduce considerably overall fluxes of the other cations (see Fig. 9).

Separation of Zn^{2+} and Ca^{2+} with Cyanex 302

In order to check the MHS ability to separate Zn^{2+} and Ca^{2+}, the carrier D2EHPA was replaced by Cyanex 302. Two transport runs were carried out. The first experiment was carried out with the use of a simulated industrial solution containing Zn, Cu, Ca, Mg, K, Na nitrates of the concentration 0.01 mol/dm^3 each. The second one was made with the actual industrial solution after zinc electroplating containing Zn (9.25 x 10^{-5}), Ca (1.32 x 10^{-3}), Mg (4.13 x 10^{-4}), Na (2.92 x 10^{-3}) and K (1.43 x 10^{-4} mol/dm^3). This solution was acidified to pH = 2.86 before using it as feed for the pertraction procees. The corresponding experimental results are presented in Fig. 10 and Tab. 4. The values
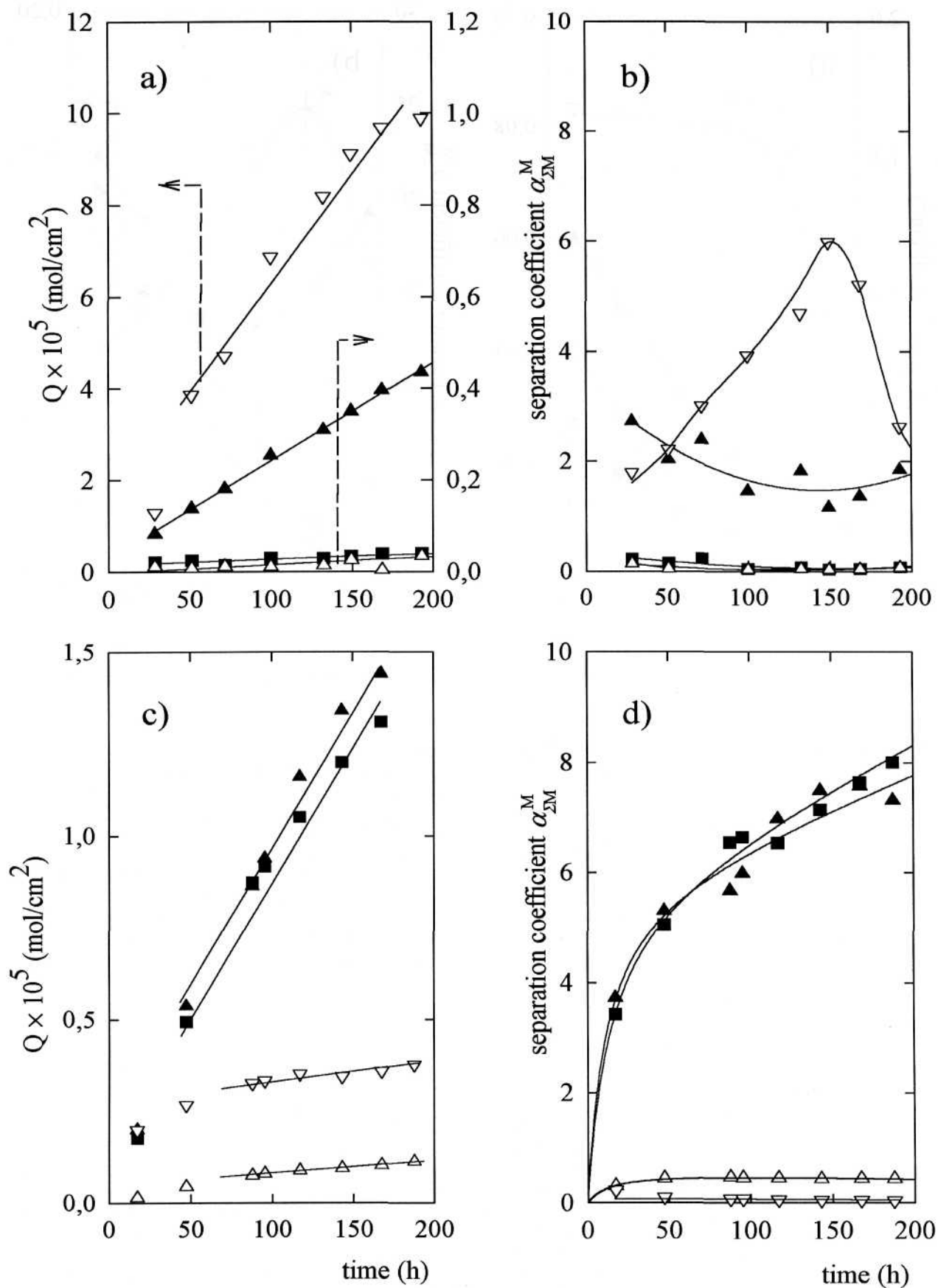
Fig. 7. Pertraction of metals in multimembrane hybrid system with alkaline (a,b) and acidified (c,d) feed solution after zinc electroplating: (a,c) - cumulative transport curves, (b,d) - separation coefficients; (■) Zn, (▲) Ca, (△) Mg, (▽) Na.
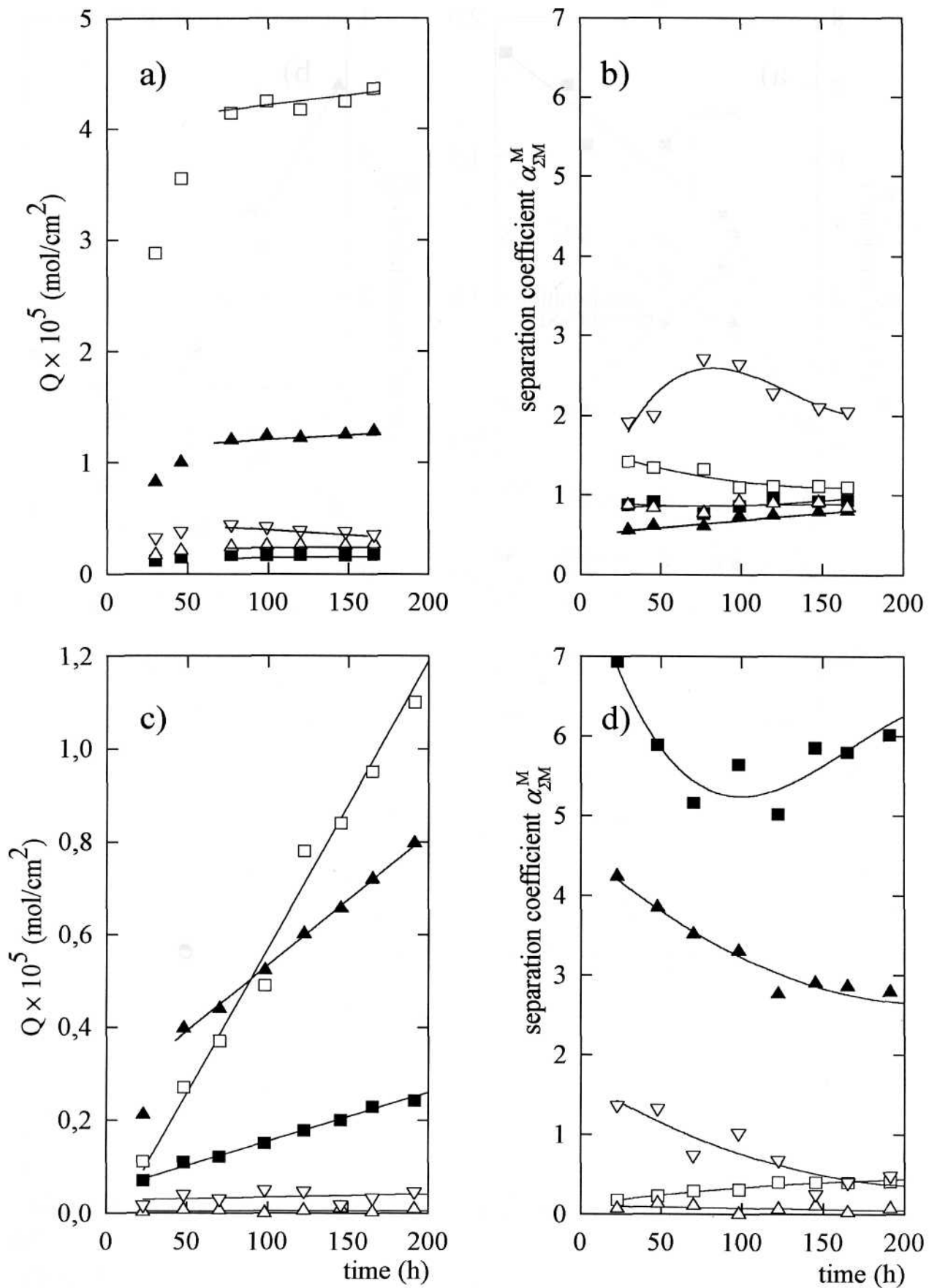
Fig. 8. Donnan dialysis (a, b) and pertraction (c, d) of metals: from feed solution after copper etching: (a, c) - cumulative transport curves, (b, d) - separation coefficients; (■) Zn, (▲) Ca, (Δ) Mg, (∇) Na.
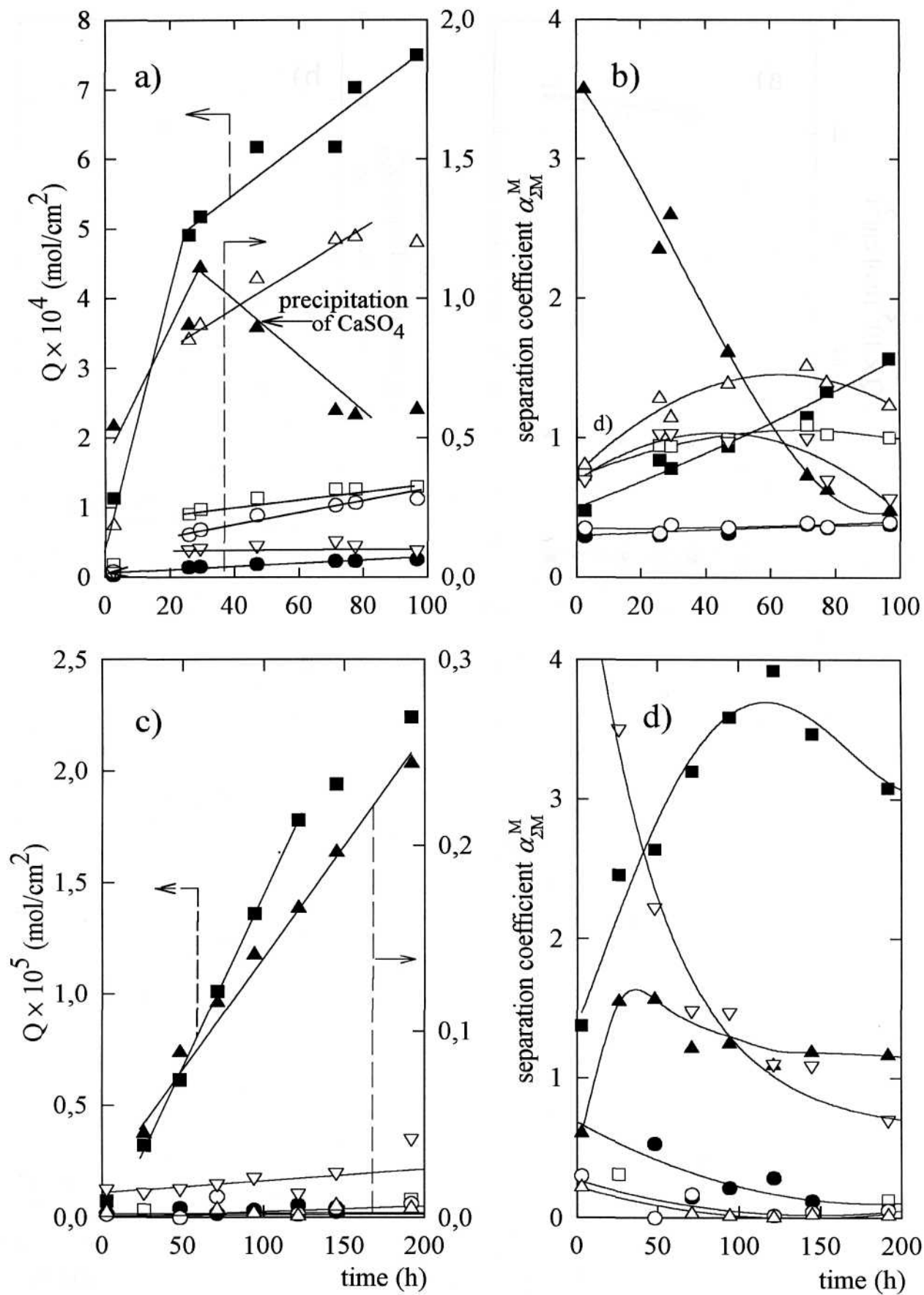
Fig. 9. Donnan dialysis (a,b) and pertraction (c,d) of metals from feed solution prepared of electroplating sludge: (a,c) - cumulative transport curves, (b,d) - separation coefficients; (■) Zn, (□) Cu, (●) Cr, (○) Fe, (▲) Ca, (Δ) Mg, (V) Na.
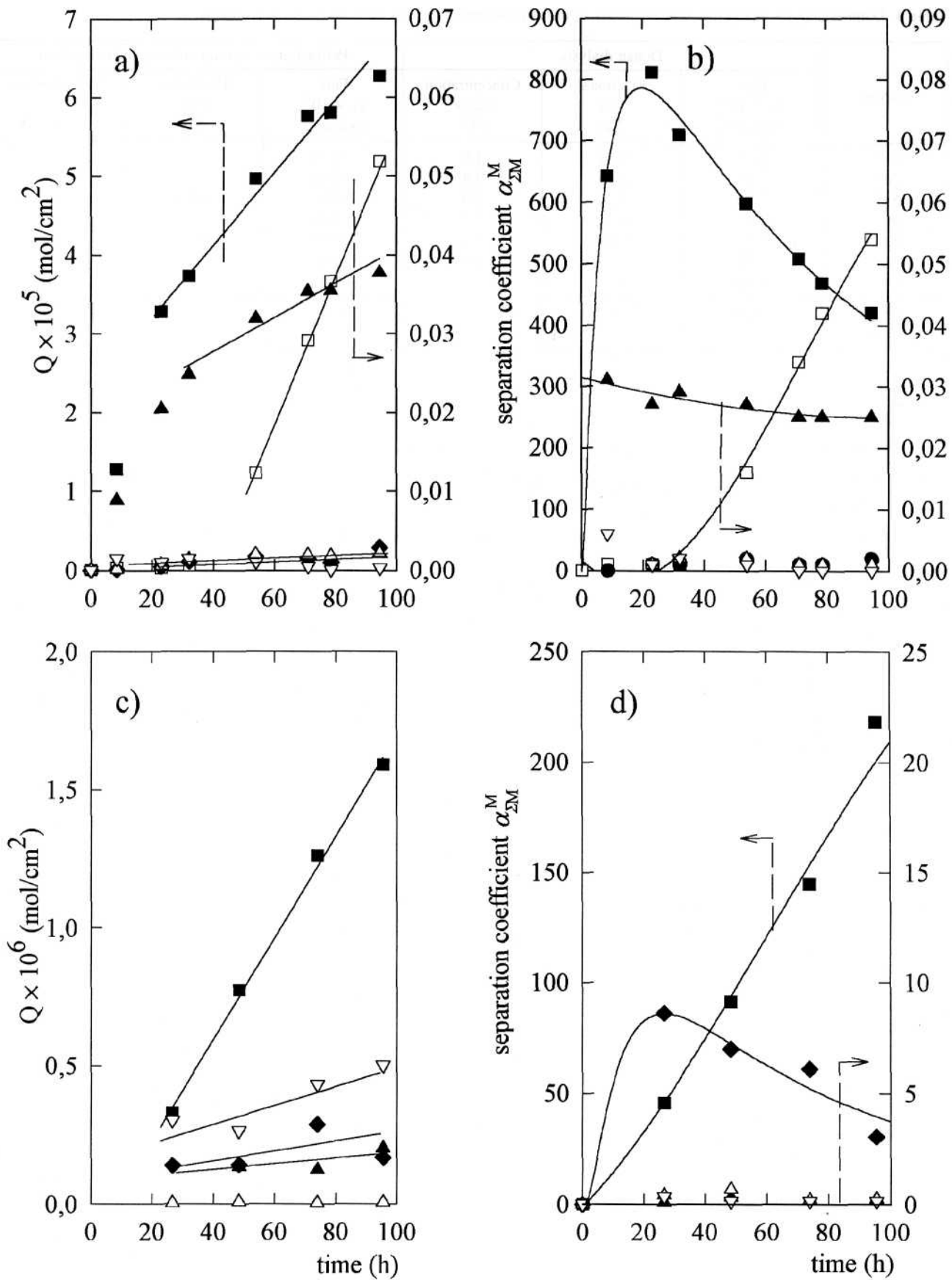
Fig. 10. Pertraction of metals with Cyanex 302: (a,b) model solution, (c,d) solution after zinc electroplating, (a,c) cumulative transport curves, (b,d) separation coefficients: (■) Zn, (□) Cu, (▲) Ca, (△) Mg, (∇) Na, (◆) K.

Table 3. Donnan dialysis and pertraction of metals from feed solutions prepared from electroplating sludge.

Cation	Donan dialysis			Pertraction in multimembrane hybrid system		
	Flux $J_M \times 10^{10}$ mol/cm^{2}s	Fractional flux N_M	Concentration factor CF[*]	Flux $J_M \times 10^{12}$ mol/cm^{2}s	Fractional flux N_M	Concentration factor CF[*]
Cr^{3+}	0.26	0.01	1.9	< 0.01		
Fe^{3+}	1.29	0.04	3.4	< 0.01		
Zn^{2+}	32.30	0.72	2.9	5.56	0.65	0.01
Cu^{2+}	1.52	0.03	3.2	< 0.01		
Ca^{2+}	2.51	0.06	3.1	2.97	0.35	0.06
Mg^{2+}	5.69	0.13	2.5	< 0.01		
Na^+	0.60	0.01	1.8	< 0.01		
$\Sigma z_i J_i$ eqv./cm^{2}s	89.29	1		17.1	1	

[*] after 100 hours.

Table 4. Pertraction characteristics for multimembrane hybrid system with Cyanex 302.

Cation	Model solution (pH = 2.1)			Acidified solution after zinc electroplating (pH = 2.8)			Mass transfer coefficient k cm/s	
	Flux $J_M \times 10^{12}$ mol/cm^{2}s	Fractional flux N_M	Concentration factor CF[*]	Flux $J_M \times 10^{12}$ mol/cm^{2}s	Fractional flux N_M	Concentration factor CF[*]	Cyanex 302	D2EHPA[**]
Zn_2^+	150.5	0.98	3.6	4.51	0.76	1.8	5.0×10^{-5}	1.1×10^{-5}
Cu^{2+}	1.74	0.01	0.03	–	–	0.02	–	–
Ca^{2+}	0.87	< 0.01	0.02	0.55	0.09	–	4.2×10^{-7}	8.3×10^{-6}
Mg^{2+}	0.06	< 0.01	< 0.01	0.02	< 0.01	0.01	3.3×10^{-8}	9.9×10^{-7}
Na^+	< 0.01	< 0.01	< 0.01	1.50	0.13	0.03	6.7×10^{-7}	4.3×10^{-7}
K^+	0.07	< 0.01	< 0.01	0.15	0.01	0.12	1.0×10^{-6}	–
$\Sigma z_i J_i$ eqv./cm^{2}s	306	1		11.8	1			

[*] after 120 hours
[**] calculated from fluxes in Tab. 2.

of separation coefficients drawn vs. time in Figs. 10 b,d prove that it is possible to separate effectively Zn^{2+} from electroplating waste solutions containing high amount of Ca^{2+} with the separation order Zn»K>Ca>Na>Mg. At the presence of Cu^{2+} (simulated solution) this sequence changes to Zn»Cu>Ca>K, Na, Mg, i.e., Cyanex 302 like D2EHPA could transport and separate Cu^{2+} from the other cations in the case of Zn^{2+} free solutions. The fractional flux of Zn calculated from fluxes expressed in eqv./cm^{2}s attains 0.76-0.98, which indicates Cyanex 302 as very efficient reagent in the recovery of Zn^{2+} from both equimolar Zn^{2+}-Ca^{2+} solutions and these containing considerable excess of Ca^{2+} (e.g. for industrial soln. [Ca]/[Zn] ≈ 15). To compare the properties of D2EHPA and Cyanex 302, the overall mass transfer coefficients (k, cm/s) were calculated using Eq. 8:

$$k_M = \frac{1000 J_M}{[M]_{f,0}} \quad (cm/s) \qquad (8)$$

The values of coefficients presented in Tab. 4 show that the k_{Zn} for Cyanex is comparable with that of D2EHPA,

that is both values are of the same order 10^{-5} (cm/s), which is typical for many membrane transports. The considerable differences appear in the case of k_{Ca}, whose values for Cyanex are much lower (4.2×10^{-7}) than those corresponding with D2EHPA (8.3×10^{-6} cm/s).

Conclusions

The results concerning Donnan dialysis and pertraction technique applied for the utilization of electroplating sludge and waste solutions enable us to formulate the following conclusions and remarks:

1. The membrane system constructed as the combination of polymer and liquid membranes in series can be successfully applied for the recovery of metals from acidic or acidified electroplating waste solutions (as a part of more general proecological technology). In the case of zinc or copper recovery the use of D2EHPA as a carrier is possible after the pre-removal of Ca^{2+} from feeds.

2. The Donnan dialysis allows rapid concentration of some metals from very different feeds. However, the effective separation of valuable metals can be achieved only with the use of a selective liquid membrane.

3. Troublesome (low selectivity and fouling effects) content of calcium in the feed can be overcome by chan ging a liquid membrane composition, i.e. by the choice of an appropriate carrier and solvent. The reagent suitable for the Zn^{2+} and Ca^{2+} separation is Cyanex 302.

4. After successful pertraction processes, the concent rated strip product containing zinc or copper should be recycled. Because the pertraction is usually carried out into a strongly acidic phase (required for maintaining constant driving force for coupled permeation), further recycling of metals needs the deacidification of the product. This can be made by diffusion dialysis of the strip solution, which is now realized in our laboratory [39].

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