Heavy metals removal from wastewaters of phosphoric acid production: a comparison of hybrid liquid membrane (HLM) and aqueous hybrid liquid membrane (AHLM) technologies

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Abstract Selective removal of heavy metal ions from industrial wet-process phosphoric acid (WPA) was studied, using the two liquid membrane systems: Hybrid Liquid Membrane (HLM) and Aqueous Hybrid Liquid Membrane (AHLM). Monothiophosphinic acid (Cyanex 302) in kerosene (for the HLM) and Polyvinylsulfonic acid (PVSA) aqueous solution (for the AHLM) were used as a liquid membrane (LM), separated from the feed and strip streams by neutral or cation-exchange membranes.

On application of the HLM separation system, the permeation from the feed to the strip phase followed the selectivity sequence: Zn >> Cd > Cu with all types of membranes used. Results show that the selective separation of Cd and Zn from the WPA may be achieved by the HLM with cation-exchange membranes, using a single set-up installation at continuous processing. Copper is accumulated in the Cyanex 302, poisoning the carrier. So, this carrier and HCl as a strip solution can not be recommended for the HLM processing of WPA.

Using the AHLM separation system, heavy metals such as cadmium and copper, were successfully recovered from the WPA: average fluxes (in mol/m²sec) to the strip phase were $3.7 \times 10^{-7}$ and $6.7 \times 10^{-7}$. Satisfactory dynamic selectivity to copper (~16) was found. The transfer of iron and zinc species to the strip phase was below detection levels during the 144 hrs of the AHLM experiment. Contamination of the feed and strip solutions by PVSA was not observed during the 500 hrs of processing. The membranes were completely regenerable and used repeatedly.

In comparison with the HLM and other liquid membrane systems, the AHLM can potentially provide many operational, economic and environmental advantages, some of them being higher transport rates, low carrier losses and low contamination of the feed and strip solutions by water-soluble polymers, long membrane lifetime, ambient temperature, low energy requirements and chemical consumption, no special requirements for membrane resistance in organic solvents, and fewer limitations on the variability of membrane pore sizes, etc.

Keywords Liquid membrane; ion-exchange membranes; heavy metals separation; selectivity

Introduction
Water in the Mediterranean Region is an essential resource of limited availability. The Fertilizer Industries (FI), including phosphoric acid production plants, consume enormous amounts of water and form effluents containing various heavy metals some of which are highly toxic (see Table 1). With increasing Government restrictions on heavy metals outlet, these effluents have to be treated even at a high cost. Besides, there are increasingly strict geological, hydrological and other types of limitations imposed on potential distribution sites of durable storage. Removal of heavy metal impurities, together with anionic pollutants from the FI effluents, will allow their re-use in a closed-operation cycle.

Magnesium, calcium, aluminium and iron are the major metal constituents of the effluents. The main problem in recycling is the selective removal of minor but toxic heavy metals, such as Cd, As, Cu, Zn and some more transition metal ions, may be sufficient in saving on operating costs, as compared to complete removal of metal ions.
High selectivity for large industrial scale processing is achievable through chemical separation methods such as ion exchange, liquid-liquid extraction, membrane and liquid membrane technologies.

Two liquid membrane systems, Hybrid Liquid Membrane (HLM) (Kislik and Eyal, 1996a,b) and Aqueous Hybrid Liquid Membrane (AHLM) (Eyal and Kislik, 1999; Kislik and Eyal, 2000a,b), were developed for the separation of metal-ions and acids from aqueous solutions. Selective water-immiscible carriers in the HLM and water-soluble polyelectrolytes in the AHLM are used as circulating organic and aqueous liquid membranes, respectively. Neutral, cation- or anion-exchange membranes are used as barriers. Blocking the carrier leakage to the feed or to the strip is achieved through the membranes’ charge and through their pore size.

Theoretical models were developed for the simulation of HLM and AHLM transport kinetics and selectivity with the aim of designing different separation processes. A good correlation was found between the theoretically calculated and the experimental data.

The idea of dynamic selectivity and techniques for its determination were introduced (Kislik and Eyal, 2000b). Dynamic selectivity and the equations developed are helpful parameters for the process design.

A comparison between HLM and AHLM technologies, noting their advantages and disadvantages, are presented in this paper. The comparison was conducted using the results of heavy metals removal from industrial or simulated phosphoric acid (WPA) solutions.

### Experimental

#### Materials

Filtered industrial wet-process phosphoric acid (WPA, 40 wt% H$_3$PO$_4$) was used as a feed solution. The WPA composition is presented in Table 1.

<table>
<thead>
<tr>
<th>Species (or ions)</th>
<th>Concentr. units</th>
<th>Concentration</th>
<th>Maximum permissive limits, EPA-IARC</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Sewerage syst.</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>g/l</td>
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<td>–</td>
</tr>
<tr>
<td>Ca</td>
<td>g/l</td>
<td>0.50</td>
<td>–</td>
</tr>
<tr>
<td>Al</td>
<td>g/l</td>
<td>1.6</td>
<td>–</td>
</tr>
<tr>
<td>Mg</td>
<td>g/l</td>
<td>1.4</td>
<td>–</td>
</tr>
<tr>
<td>Fe</td>
<td>g/l</td>
<td>1.1</td>
<td>–</td>
</tr>
<tr>
<td>Cl</td>
<td>g/l</td>
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<td>–</td>
</tr>
<tr>
<td>F</td>
<td>g/l</td>
<td>1.5</td>
<td>–</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>g/l</td>
<td>22</td>
<td>–</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Minor components</th>
<th>Concentr. units</th>
<th>Concentration</th>
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</thead>
<tbody>
<tr>
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<td></td>
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<td>Sewerage syst.</td>
</tr>
<tr>
<td>As*^</td>
<td>mg/l</td>
<td>5–10</td>
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</tr>
<tr>
<td>Cd*^</td>
<td>mg/l</td>
<td>8–50</td>
<td>0.05</td>
</tr>
<tr>
<td>Cu*^</td>
<td>mg/l</td>
<td>20–100</td>
<td>1.0</td>
</tr>
<tr>
<td>Ni*^</td>
<td>mg/l</td>
<td>50–100</td>
<td>1.0</td>
</tr>
<tr>
<td>V*</td>
<td>mg/l</td>
<td>100</td>
<td>0.5</td>
</tr>
<tr>
<td>Zn*</td>
<td>mg/l</td>
<td>300–400</td>
<td>1.0</td>
</tr>
<tr>
<td>Mn*</td>
<td>mg/l</td>
<td>N.A.</td>
<td>–</td>
</tr>
<tr>
<td>U*</td>
<td>mg/l</td>
<td>N.A.</td>
<td>–</td>
</tr>
<tr>
<td>Cr*</td>
<td>mg/l</td>
<td>50</td>
<td>0.01</td>
</tr>
<tr>
<td>Organic</td>
<td>mg/l</td>
<td>50</td>
<td>–</td>
</tr>
</tbody>
</table>

**Notes:** * – hazardous (EPA); ^ – carcinogenic (IARC-EPA); N.A. – not analyzed

EPA: Environmental Protection Agency. IARC: International Agency for Research on Cancer
Phosphoric acid, extra pure, 85–87%, a product of Baker Chemicals Co, Ferric sulfate, 99.5%, a product of BDH Chemicals Ltd., and Cadmium sulfate (3CdSO₄·8H₂O), extra pure, >99%, a product of Merck, were used for the preparation of model feed solutions and standards.

A 25 wt% aqueous solution of poly(vinylsulfonic acid) sodium salt (PVSNa) (Molymeux, 1984) with molecular weight range of 30,000–60,000, was obtained from Aldrich Chem. Co. and used as a carrier for the AHLM; PVSNa solution (pH = 8.2) was converted into PVSA (acid form, pH = 3.5) by dialysis through a cation-exchange membrane, with 1 mol/kg HCl solution on the other side. The concentration of polyelectrolyte is expressed by the number of sulfur moles (for PVSA or PVSNa) per kg of solution (Molymeux, 1984; Eisenberg and Ram, 1959). In order to remove low molecular weight components, the polyelectrolyte solutions were diafiltered extensively through the membranes used in the experiments.

Di-(2,4,4-trimethyl-pentyl)monothiophosphinic acid, C₁₆H₃₅OPS (Sole and Hiskey, 1995), Cyanex 302, 83–87%, M.W. = 306, a product of CYTEX Canada Inc. was used as a carrier for the HLM. Low aromatics kerosene (Parasol), a product of PAZ, Israel, was used as a diluent.

All other chemicals: copper(II) and zinc chloride hydrates, products of Merck, and the mineral acids, bases, were of analytical grade.

The neutral (Celgard®) or cation-exchange (Neosepta®) membranes used, and their properties, were described previously (Eyal and Kislik, 1999; Kislik and Eyal, 1996a).

**Procedures**

Two kinds of experimental modules, that were used, have been described in detail previously (Eyal and Kislik, 1999; Kislik and Eyal, 1996a,b, 2000a,b): the module with circulating through compartments feed (F), carrier (E) and strip (R) solutions and the mechanically shaken module with the same but stationary filled compartments. In the latter, the shaken rate varied in the range of 50–200 rpm; solution quantities were Vₕ = Vₐ = 28 g and Vₐ = 7.0 g in all experiments. In the circulating module, the liquids (feed, carrier and strip solutions) circulated through the module and supplied reservoirs at flow rates varying from 15 to 100 cm³/min; the initial quantities of the solutions in all experiments were the same: Vₕₐ₉ = Vₚₐₐ = 250 g and Vₜₐ₉ = 100 g.

To avoid organic phase leakage in the HLM to the feed and strip aqueous phases, a pressure differential of 20–30 mm Hg was maintained (Kislik and Eyal, 1996a).

Procedures for the determination of individual mass-transfer coefficients and distribution coefficients were described previously (Kislik and Eyal, 1996a, 2000a,b).

Industrial wet-process 40 wt% phosphoric acid (Density at 25°C, d₂₅ = 1.38 ± 0.01 g/cm³), or model phosphoric acid solution (d₂₅ = 1.35 ± 0.01 g/cm³), containing cadmium (50 ppm), copper (50 ppm) and Zn (300 ppm), were used as a feed phase. 2.0–3.0 mol/kg HCl solutions (d₂₅ = 1.11 ± 0.01 g/cm³) were used as a strip phase. The carrier solutions used were 0.5–0.7 mol/kg of Cyanex 302 in kerosene (d₂₅ = 0.80 ± 0.01) or PVSA in water (d₂₅ = 1.05 ± 0.01 g/cm³).

Reproducibility of the transport results was tested by repeating experiments at the same conditions.

Analytical and calculation techniques were described elsewhere (Eyal and Kislik, 1999; Kislik and Eyal, 1996b, 2000a,b).

**Results and discussion**

Selective removal of Cd, Cu and Zn from industrial or simulated WPA solutions was investigated, using both HLM and AHLM technologies.
The main objectives of this experimental study were:
• evaluation of the HLM and AHLM systems’ feasibility for selective separation of cadmium,
• laboratory scale testing of cadmium removal from industrial wet-process phosphoric acid, using the HLM and AHLM systems with cation-exchange membranes.

Metal distribution at equilibrium extraction by Cyanex 302
Equilibrium extraction (forward and backward) experiments were conducted to determine selectivity at equilibrium conditions. Samples of model or industrial wet-process phosphoric acid, containing 40 wt% $\text{H}_3\text{PO}_4$, 50 ppm Cd (or 8,800 ppm, only in model solutions), 50 ppm Cu, 200–350 ppm Zn, 50 ppm Pb and 1,000–2,000 ppm Fe(III) were equilibrated with 0.7 mol/kg Cyanex 302 in kerosene at different aqueous/organic (wt) ratios. The results of some tests are given in Table 2.

Distribution of lead and iron into the organic phase was not observed.
Copper was practically completely extracted by Cyanex 302, but could not be stripped by 2–4 mol/kg HCl. It is accumulated in the organic phase and prevents extraction of cadmium. Recovery of 94% copper from the loaded Cyanex 302 organic solution may be achieved only by 8 mol/L HCl strip solution during 30 hrs (Ortiz et al., 1996). However, after contact with strong acidic media, Cyanex 302 loses its complexation ability. Copper causes oxidation/reduction phenomena, resulting in the formation of Cu(I) complex and extractant that cannot be regenerated (Sole and Hiskey, 1995).

Metal distribution at membrane-based equilibrium extraction by PVSA
Distribution coefficients at equilibrium conditions were determined by membrane-based forward and backward extraction experiments in the shaken two compartment module. In the forward extraction, the mentioned above composition samples of the industrial WPA were used as a feed solution and 0.5 mol/kg PVSA aqueous solution were used as a strip. In the backward extraction, the organic solution of PVSA with loaded metal ions, was used as a feed and 2.0 mol/kg HCl was used as a strip. The experiments lasted up to equilibrium conditions, when the concentration of the metal ions in every compartment did not change in time. The experimental results are presented in Table 3.

Selectivity at the HLM transport
The HLM transport tests were carried out in the shaking and flowing modules, using the same feed, organic LM and strip solutions. Polypropylene Celgard neutral hydrophobic (C 2400, thickness 25 µm; C 4400, thickness 175 µm), hydrophilic (C 5401, thickness 175 µm), and cation-exchange membranes (CEM), Neosepta CM-1, CM-2 and CMS, were used as barrier. Transport rates of cadmium, copper, zinc and dynamic selectivity data were determined. Some examples are presented in Figures 1 and 2.

Table 2 Metal ions distribution at Equilibrium Extraction by Cyanex 302
Feed: 40% $\text{H}_3\text{PO}_4$, 50 ppm Cd, 50 ppm Cu, 50 ppm Pb, 230 ppm Zn, 1000 ppm Fe(III)
Extractant: 0.66 mol/kg Cyanex 302 in kerosene. Strip: 2.0 mol/kg HCl. Aq./Org. ratio =5/1

<table>
<thead>
<tr>
<th>Ions</th>
<th>Concentration mg/kg</th>
<th>Distribution</th>
<th>Concentration mg/kg</th>
<th>Distribution</th>
<th>Concentration mg/kg</th>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forward</td>
<td>130</td>
<td>25.0</td>
<td>5.2</td>
<td>249</td>
<td>0.51</td>
<td>488</td>
</tr>
<tr>
<td>Backward</td>
<td>8.1</td>
<td>22.4</td>
<td>3.0</td>
<td>245</td>
<td>0.5</td>
<td>0.002</td>
</tr>
</tbody>
</table>

* In the forward extraction: $D = C_{\text{Org}}/C_{\text{Aq}}$; in the backward extraction: $D = C_{\text{Aq}}/C_{\text{Org}}$.
As expected, because of the weak complexation affinity to zinc, Cyanex 302 did not show strong influence on the zinc transport: zinc is driven through the HLM system with neutral membranes mostly by its concentration gradient in the feed and strip solutions. Its average selectivity to cadmium was equal to 3.6. In the case of the HLM with cation-exchange membranes, the Zn/Cd selectivity was increased by about one order.

The thickness of the neutral hydrophobic membranes does not have a strong influence on the transport kinetics of cadmium and copper. Dramatic differences in mass transfer rates were found when using organic-filled (neutral hydrophobic) and aqueous-filled pore membranes (neutral hydrophilic or cation-exchange). For example, when processing with cation-exchange, CM-2 (in this case the best) membranes, the decrease of the cadmium flux to the strip is about one order, as compared with the data of hydrophobic membranes.

The drop in the metal ions transport rates to the carrier solution is not as strong as it is to the strip solution. This means that the limiting step of the transport may be the kinetics of the metal-carrier decomplexation reaction at the strip-side interface of the hydrophilic or cation-exchange membrane.

Several stages vs. time were observed in the cadmium and copper transport to the carrier phase: first, where the values of the fluxes are close; then the flux of Cu dramatically increases, but the cadmium flux does not change, or even monotonously decreases. The stability of the cadmium flux shows that the complexation mechanism and the kinetics do not change with the increase of Cd concentration. At this stage of transport to the carrier phase, the Cu/Cd selectivity reaches a maximum. The last stage indicates that the Cyanex 302

### Table 3 Metal distribution at membrane-based equilibrium extraction by 0.5 mol/kg polyvinylsulfonic acid (PVSA) aqueous solution (averaged data)

<table>
<thead>
<tr>
<th>Ions</th>
<th>Extraction operation</th>
<th>Cd Distribution</th>
<th>Cu Distribution</th>
<th>Zn Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Forward</td>
<td>4.7</td>
<td>41.4</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>Backward</td>
<td>0.29</td>
<td>0.1</td>
<td>0.16</td>
</tr>
</tbody>
</table>

**Figure 1** Transport rates of cadmium, copper and zinc to the strip phase for the treatment of industrial WPA, composed of 50.5 ppm Cd, 52.6 ppm Cu and 340 ppm Zn, in the HLM circulating module, with neutral hydrophobic Celgard 2400 and cation-exchange Neosepta CM-2 membranes.
carrier phase approaches its saturation (at high initial concentrations of copper and/or cadmium in the feed phase) or that the HLM closed system approaches the steady state transport.

The same as in equilibrium extraction experiments, copper at the HLM transport is almost completely extracted by Cyanex 302, but cannot be stripped by 2 mol/kg HCl: as a rule, the copper concentration in the strip phase of the HLM with different types of membranes was found to be under the detection level or close to it. This means that copper is accumulated in the organic phase, poisons it and prevents the complexation of cadmium.

**Selectivity at the AHLM transport**

Application of organic solutions as carriers has some drawbacks. Those are mainly membrane blinding or fouling, concentration polarization, possible contamination of the effluent and product aqueous solutions by the carrier organic components due to leakage through the membranes, etc. Application of water-soluble complexants as carrier is expected to overcome these drawbacks.

Selective separation of copper and cadmium from the industrial, wet process phosphoric acid (WPA) containing 55.6 ppm Cd and 50.6 ppm Cu, was tested in the shaken and circulating AHLM modules with 0.5 mol/kg polyvinylsulfonic acid (PVSA) aqueous solution as carrier, 2 mol/kg HCl as stripping solution, and Neosepta CM-2 membranes. Results are presented in Figures 3 and 4.

The fluxes to the strip phase during the 144 hrs of the transport are: \( J_{\text{Cd}} = 3.7 \times 10^{-7} \text{ mol/m}^2\text{sec} \) and \( J_{\text{Cu}} = 6.7 \times 10^{-7} \text{ mol/m}^2\text{sec} \).

Analysis of the experimental data shows different kinetics of mass transfer to carrier and strip for Cd, Cu and Zn: affinity of PVSA to complex formation is strongest with Cu, then with Cd and much weaker with Zn. So, for Cu and Cd the limiting step is decomplexation kinetics and diffusion on the strip side of the AHLM system, but for Zn, the limiting step is the diffusion kinetics on the feed side of the AHLM.

The peaks of the metal concentration profiles in the LM phase are resolved well in time (for details Kislik and Eyal, 2000a,b). As a rule, the peak in the circulating module is located at a higher processing time than in the shaken module. This can be explained by the differences in the feed:carrier:strip ratios and by the differences in the hydraulic properties of the shaken and circulating flows.

Fluxes of proton from the WPA feed are \( 1.0 \times 10^{-5} \text{ mol/m}^2\text{sec} \) to the HCl strip solutions.

The diffusion rate of polyelectrolyte molecules in the liquid membrane solution is very low. 

**Figure 2**  Dynamic selectivity data, obtained by treating industrial WPA, composed of 50.5 ppm Cd, 52.6 ppm Cu and 340 ppm Zn, in the HLM circulating module with CM-2 membranes.
Spectroscopic study of Cyanex 302-cadmium complexes

In order to understand better the mechanisms of cadmium complexation by Cyanex 302, UV-VIS spectra of aqueous and organic phases were studied after equilibration and separation of the phases. Figures 5 and 6 present examples of the spectra.

The results show that there is a significant dissolution of Cyanex 302 (peak at 271 nm) in the aqueous phosphoric acid solution (see Figure 5c). The value of the peak, hence solubility, is proportional to the concentration of the free Cyanex 302 in the organic phase (compare Figures 5c and d). There is a possibility to develop an analytic technique of Cyanex 302 determination in the aqueous phase. On the other hand, we cannot consider the dissolution of Cd-Cyanex 302 complex in the aqueous phase because its peak is out of UV detection range.

UV-VIS spectra of the organic phase are introduced in Figure 6. Cyanex 302 in parasol has a peak at 315 nm (Figure 6a, peak 2). This peak decreases after equilibration with 40 wt% H₃PO₄ solution, and a new peak appears at 212 nm (Figure 6b, peak 1). After equilibration of 0.66 mol/kg Cyanex 302 in kerosene with 40 wt% H₃PO₄ containing 50 ppm Cd at aq./org. ratio = 100/1 wt (cadmium concentration in the organic phase was equal to 4.3*10⁻² mol/kg), peak 1 moves to 235 nm (Figure 6c, peak 1’). Peak 2 also moves a little: from 315 to 318 nm (Figure 6c, peak 2’). With increasing cadmium concentration in the organic phase, the magnitude of peak 1’ (235 nm) is increased and that of peak 2’ (318 nm) is decreased. When Cd concentration in the organic phase reaches 0.2–0.29 mol/kg (Figure 6d,e) peak 1’ grows and widens, while peak 2’ is close to disappear. So, we can conclude that Cyanex 302 is saturated with cadmium. It proves the assumption that Cd-Cyanex 302 species, forming at these conditions, are something like CdL₂*2HL, in which Cd/HL = 1/4. Broad peaks are typical for aggregates, where different but close in energy bonds, are formed.

To understand the complexation mechanisms, further studies are necessary.

Spectroscopic study of PVSA-copper complexes

In order to understand the complexation mechanisms of copper complexation by PVSA, UV-VIS spectroscopy was applied. An aqueous solution of 0.2 M CuHPO₄ in H₃PO₄ has low (Molymeux, 1984). The high fluxes of cations through that medium may indicate the transport mechanism by hopping steps diffusion.
absorption peaks at 800 and 230 nm. These absorptions are related, respectively, to copper in the cationic form – bound through the first coordination sphere and copper in the anionic form – bound through the second coordination sphere (Molymeux, 1984). Below, these complexes will be referred to as Types (I) and (II), respectively.

In the spectra of aqueous Cu-PVSA solutions, these peaks are shifted to 780 and 280 nm, respectively.

The effect of copper concentration was studied, using 0.5 mol/kg PVSA solution as a reference. The correlation between the values of the peaks is very much dependent on the Cu/PVSA ratio and the pH of the solution. At low copper concentrations in the Cu/PVSA mixture, the value of the 780 nm peak preferentially increases and shifts to the lesser wavelengths. At such (small) copper concentrations in the AHLM membrane solution, the copper transport rate to the strip is low.

At Cu/PVSA ratios that are higher than 1/4 (Meq/Meq), the growth of the second peak (280 nm) begins to dominate and shifts to the higher wavelengths. This is the stage in the AHLM processing when the copper transport rate to the strip sharply increases.

At Cu/PVSA = 1/2 the values of both peaks are about equal.

The following model of copper-PVSA complexation and copper transport across the polymer functional groups may be proposed. At low Cu/PVSA ratios, the dominant species

![Figure 5 UV-VIS spectra of the aqueous phase samples: a) 40% wt. synthetic solution of phosphoric acid; b) solution a), containing 769 ppm Cd (6.84x10^{-3} mol/kg); c) solution a) after equilibration with 0.66 mol/kg Cyanex 302 in kerosene (aq./org. ratio = 5/1); d) solution b) after equilibration with 0.66 mol/kg Cyanex 302 in kerosene (aq./org. ratio = 5/1) and containing 206 ppm Cd (1.83x10^{-3} mol/kg). References – deionized water.](https://iwaponline.com/ws/article-pdf/1/5-6/119/477269/119.pdf)

![Figure 6 UV-VIS spectra of the organic phase samples: a) 0.66 mol/kg Cyanex 302 in kerosene; b) solution a) after equilibration with 40% wt. H_3PO_4 aqueous solution (aq./org. ratio = 5/1); c) solution a) after equilibration with 40% wt. H_3PO_4 aqueous solution, containing cadmium, [Cd]_{org} = 4.3x10^{-2} mol/kg; d) solution a) after equilibration with 40% wt. H_3PO_4 aqueous solution, containing cadmium, [Cd]_{org} = 0.2 mol/kg; e) solution a) after equilibration with 40% wt. H_3PO_4 aqueous solution, containing cadmium, [Cd]_{org} = 0.29 mol/kg. Reference – kerosene.](https://iwaponline.com/ws/article-pdf/1/5-6/119/477269/119.pdf)
formed is of Type I, possibly $[\text{Cu(PVS)}_2(\text{PVSH})_2]$. The copper in this complex is too strongly bound to allow effective cation exchange interaction between $\text{Cu}^{2+}$ and proton at the membrane solution – strip solution interface. As a result, the transport rate of the copper to the strip phase is low.

With increasing copper concentration in the membrane solution, Type II complex starts to form (Eisenberg and Ram, 1959). Here, copper is coordinated in the second sphere, maybe through water molecules. The type I complex behaves as a complexant, in analogy with proton-ionizable macrocyclic polyethers ("crown ethers"), which are both coordinators and countercations (McDowell et al., 1992). Energetically, it is considered a good carrier for alkali and alkali-earth cations. The problem of transferring an anion is avoided. Such an exchange, taking place at the membrane-strip solution interface, facilitates the transport of copper ions and explains the drastic increase in copper flux. We can assume that this type of complexant (Cu-PVSA complex of Type I) may be acceptable in the transport of cations from a medium containing high concentration of mineral acids.

Cadmium complexes do not absorb in the UV-VIS range and are, therefore, more difficult to follow. Apparently, cadmium ions form Type I complexes with PVSA under experimental conditions (in the presence of copper), but do not form Type II ones. Similar to the case with copper ions, cadmium Type I complex is too strong to allow efficient exchange with protons. As a result, the flux of cadmium ions is relatively low and does not change much during the trial.

The complexation and transport mechanisms, presented here, are in agreement with the UV-VIS data and explain the selectivity and flux profiles found in the AHLM experiments. Additional experimental work is required to validate these explanations, to better identify the nature of the complexes and to understand why cadmium ions do not form Type II complexes at the chosen conditions.

Comparison of HLM and AHLM transport parameters

The HLM and AHLM transport rate and selectivity data are compared in Table 4.

During the first 144 hrs of AHLM treatment, the average cadmium flux and Cu/Cd selectivity are equal to $7 \times 10^{-7}$ mol/m²sec and about 10, respectively. The next 100 hrs of treatment show more than 2 times less flux and 5 times less selectivity. The maximum of Cu/Cd dynamic selectivity, located at the 21st hour after beginning of the trial, is equal to 15.8.

The cadmium flux at the AHLM treatment is about twice as high, compared with the HLM treatment data. Selectivity results cannot be compared because the copper practically did not strip at the HLM treatment.

Comparatively low selectivity results can be explained by the competitive transport of zinc and other metal ions such as Mg, Ca, Al, whose transport was not studied.

Table 4 Comparison of cadmium transport rates and selectivity data for the circulating HLM and AHLM modules with cation-exchange membranes at the feed, carrier, and strip flow rates equal to 6 ml/min

<table>
<thead>
<tr>
<th>Process. time</th>
<th>Average Cd flux to strip</th>
<th>Average selectivity</th>
<th>Maximum in dynamic selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HLM</td>
<td>AHLM</td>
<td>HLM/ AHLM</td>
</tr>
<tr>
<td>hrs</td>
<td>mol/m²sec</td>
<td>mol/m²sec</td>
<td>Cu/Cd</td>
</tr>
<tr>
<td>0–144</td>
<td>$3.7^* \times 10^{-7}$</td>
<td>$7.0^* \times 10^{-7}$</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>144–240</td>
<td>$1.1^* \times 10^{-6}$</td>
<td>$3.0^* \times 10^{-7}$</td>
<td>3.7</td>
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<td></td>
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<td>48</td>
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</table>

Comparison of HLM and AHLM transport parameters

The HLM and AHLM transport rate and selectivity data are compared in Table 4.

During the first 144 hrs of AHLM treatment, the average cadmium flux and Cu/Cd selectivity are equal to $7 \times 10^{-7}$ mol/m²sec and about 10, respectively. The next 100 hrs of treatment show more than 2 times less flux and 5 times less selectivity. The maximum of Cu/Cd dynamic selectivity, located at the 21st hour after beginning of the trial, is equal to 15.8.

The cadmium flux at the AHLM treatment is about twice as high, compared with the HLM treatment data. Selectivity results cannot be compared because the copper practically did not strip at the HLM treatment.

Comparatively low selectivity results can be explained by the competitive transport of zinc and other metal ions such as Mg, Ca, Al, whose transport was not studied.
It should be mentioned that the AHLM, in this case, does not result in any significant transport rate improvements, in comparison with the HLM, however, membrane fouling is practically avoided.

**Carrier leakage**

For the HLM system: visible dissolution of Cyanex 302 in the 40 wt% H₃PO₄ treating aqueous solution leads to its strong contamination. The concentrations of the carrier in the strip solution samples were under the detection level (1 ppm) in all measured solutions.

For the AHLM system: the concentrations of PVSA in the feed and strip solutions were close to or under the detection level (2 ppm) of the UV spectrophotometric technique (Eyal and Kislik, 1999). The reference was de-ionized water.

**Membrane lifetime**

At the HLM and AHLM processing the membrane stability tests were followed through the mass transfer rates.

For the HLM: membrane fouling was observed. This may be explained by the accumulation of copper in the liquid membrane, inside the pores of the membrane. After 150–200 hrs of trial the gel layers were visible on the membrane surfaces, contacting with aqueous phases. After washing in water or acid solutions, the membrane samples did not regenerate to their original state.

For the AHLM: membranes showed very stable fluxes of solutes during 300 hrs of experiment. After washing in water, the membrane samples were used repeatedly and the fluxes were stable. The working time of some membrane samples was more than 600 hrs. We tend to think that the fouling or blinding problems, that were encountered in the liquid membrane processes with various organic solutions, are not critical in the case of the AHLM processing.

**Conclusions**

1. Wet-process phosphoric acid (WPA) treatment by the HLM showed high transport rates and Zn/Cd selectivity. The Cu/Cd selectivity cannot be judged because of copper accumulation in the carrier solution.
2. Application of Cyanex 302 as carrier in the HLM system is questionable because of:
   - visible dissolution of Cyanex 302 in the phosphoric acid solution;
   - poisoning of the carrier by copper, which is always present in industrial WPA;
   - membrane fouling by strong copper-carrier complexes formed.
3. AHLM experimental tests of cadmium and copper separation from WPA showed high transport rates at relatively low selectivity. The low selectivity results are explained by the low selectivity of PVSA as a carrier and competitive transport of many other metal ions, such as Ca, Mg, Al, Zn.
4. In comparison with other liquid membrane systems and affinity dialysis the AHLM process has some decisive advantages, such as:
   - high transport rates;
   - the feed and strip solutions are not contaminated by water-soluble polymers used as carriers;
   - long membrane lifetime; no fouling and blinding was observed. The membranes were completely regenerable and used repeatedly. No special requirements are needed for membrane stability in organic solutions;
   - the AHLM modules may be based on commercially available ion-exchange hollow-fiber or spiral membrane modules and equipment.
5. The AHLM is an environmentally friendly and economical technology due to operation
at ambient temperature, low energy requirements, low chemical consumption and no parasitic by-products formation.

6. The AHLM separation technologies may be based on commercially available ion-exchange spiral or hollow-fiber membrane modules and equipment.

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References

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