

ELECTRODIALYSIS PHENOMENA OF AQUEOUS SOLUTIONS CONTAINING PHOSPHORIC ACID AND METAL IONS

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Abstract

The electrodialysis phenomena of aqueous solutions containing phosphoric acid, Al and Mo ions were investigated in this study. A feasibility study of electrodialysis for treatment of waste phosphoric acid containing metal ions was also carried out. The desalination percentage of various ions shows different values through a kind of ion-exchange membrane. The voltage, solution concentration and feed temperature mainly affect electrodialysis of phosphoric acid containing Al and Mo ions. Higher voltage and feed temperature are beneficial for desalination of Al and Mo ions. At least 30% of Al ions and 7% of Mo ions can be removed from the phosphoric acid by using CMX/AMX, CM1/AM1 and CMX-SB/ACS ion-exchange membranes. The electrodialysis process seems to be a promising one for use in treatment of waste phosphoric acid containing Al and Mo ions.

1. Introduction

Electrodialysis (ED) is an electrochemical separation process where ion-exchange membranes are used to separate ionic species from a mixed solution under an electrical potential difference¹⁾. The first application of electrodialysis in mass separation dates back to 1903. After development for many years, ED has become a mature technology. Up till now, the electrodialysis process has usually been applied to brackish water desalination²⁾, salt recovery from sea water³⁾, food processing including demineralization of cheese whey and skimmed milk, demineralization of soy sauce, sugar molasses and amino acid, de-acidification of fruit juice⁴⁻⁷⁾, wastewater treatment such as regeneration of waste acids used in metal pickling operations and removal of heavy metals from electroplating rinse waters^{8,9)}.

In this study, the electrodialysis process using ion-exchange membranes is employed to treat waste phosphoric acid containing Al and Mo ions discharged in a liquid crystal display (LCD) manufacturing process. In Japan, a LCD factory discharges 3000 t/y of waste solution, with about 10 mol/l phosphoric acid and about 500-1000 ppm Al and Mo ions. It is difficult to remove Al and Mo ions from this kind of waste solution due to the large difference in concentration between phosphoric acid and metal ions. If an ED process can be successfully applied to recycle the waste phosphoric acid, not only can this waste resource be reused, but also the disposal costs can be reduced. The objective of this paper is to study the electrodialysis

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phenomena of aqueous solutions containing phosphoric acid and metal ions through an ion-exchange membrane, and the feasibility of electrodialysis for the treatment of phosphoric acid containing a small amount of metal ions.

2. Principle of ED¹⁰⁾

The principle of ED is illustrated in Fig.1. The figure shows a schematic diagram of a typical electrodialysis cell arrangement consisting of a series of anion- and cation-exchange membranes, which are arranged in an alternating pattern to form individual cells between an anode and a cathode. A cell consists of a chamber with two adjacent membranes. When an ionic solution, such as aqueous salt solution, is introduced through these cells and an electrical potential is established between the anode and cathode, the positively-charged ions migrate towards the cathode and the negatively-charged cation-exchange membrane, but they are retained by the positively charged anion-exchange membrane. Likewise, the negatively-charged ions pass through the anion-exchange membrane, and are retained by the cation-exchange membrane. This results in an increase in the ion concentration in alternate compartments, while, simultaneously, the other compartments become depleted. The depleted solution is generally referred to as the 'dilute' and the concentrated solution is also referred to as the 'brine' or 'concentrate'. The driving force for the ion transport in such an electrodialysis process is the applied electrical potential between the anode and cathode.

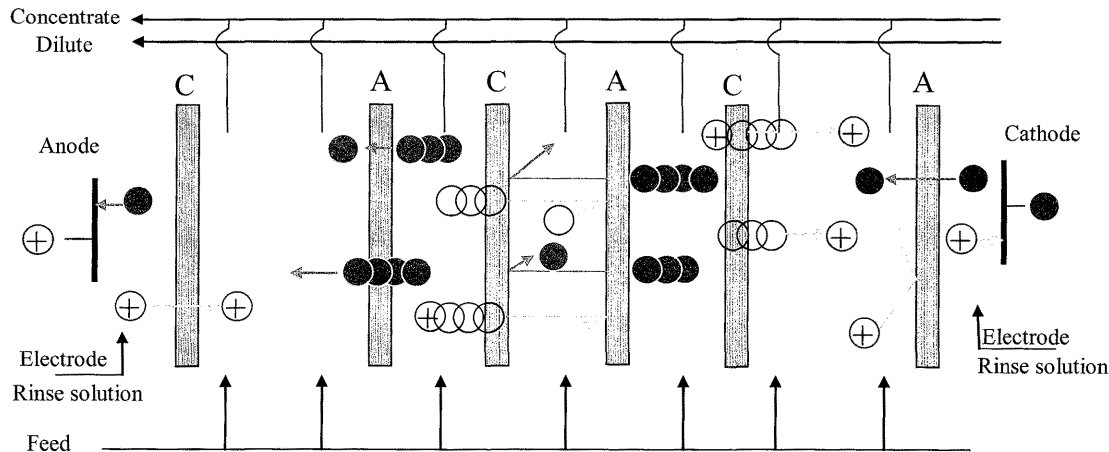


Fig. 1 Schematic diagram illustrating the principle of desalination by electrodialysis in a stack with cation- and anion-exchange membranes in alternating series between two electrodes.

3. Experimental

As shown in Fig. 2, an electrodialysis apparatus is employed (Micro Acilyzer S3 produced by Astom Co. Japan), equipped with ten pairs of cation- and anion-exchange membranes with an effective area of 71 cm². In this study, CM1, CM2, CMX CMX-SB, CMS cation-exchange

membranes and AM1, AM3, AMX, ACS anion-exchange membranes (Astom Co. Japan) are used. The properties of these membranes are listed in Table 1. The spacer between membranes is set at 1 mm. Three solution tanks are prepared for holding the feed solution, the recovery solution and the solution for the electrode cell; three pumps set in the equipment

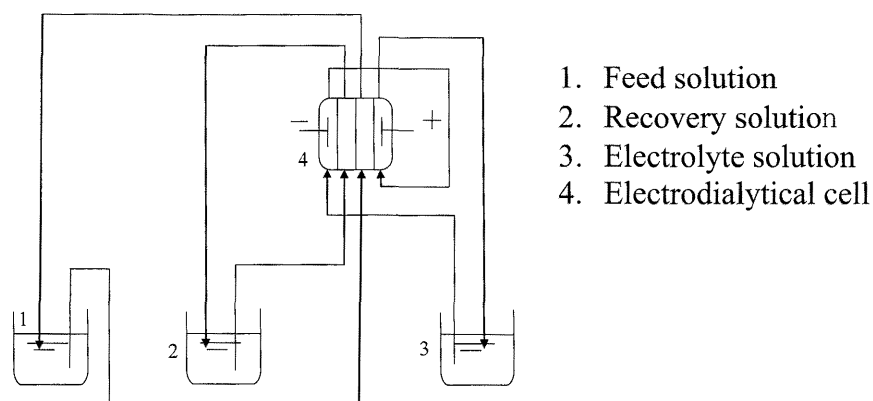


Fig. 2 Electrodesialysis set-up used in this experiment

Table 1 Properties of cation-exchange membrane and anion-exchange membrane.

Grade	Material	Characteristics	Electric resistance (Ω/cm^2)	Density (g/cm^3)	Thickness (mm)
CM1	Cross-linked styrene-divinylbenzen copolymer with sulfonic acid group	Cation permselective	0.8~2.0	0.9~1.4	0.12~0.17
CM2	Cross-linked styrene-divinylbenzen copolymer with sulfonic acid groups	Cation permselective	2.0~4.5	0.9~1.4	0.11~0.16
CMX	Cross-linked styrene-divinylbenzen copolymer with sulfonic acid groups	Cation permselective	1.8~3.8	0.9~1.4	0.14~0.20
CMS	Cross-linked styrene-divinylbenzen copolymer with sulfonic acid groups	Mono-cation permselective	1.5~3.5	0.9~1.4	0.12~0.17
AM1	Cross-linked styrene-divinylbenzen copolymer with quaternary ammonium	Anion permselective	1.2~2.0	0.9~1.4	0.10~0.15
AMX	Cross-linked styrene-divinylbenzen copolymer with quaternary ammonium	Anion permselective	2.0~3.5	0.9~1.4	0.12~0.18
ACS	Cross-linked styrene-divinylbenzen copolymer with quaternary ammonium	Mono-anion permselective	3.0~6.0	0.9~1.4	0.12~0.2
AM2	Cross-linked styrene-divinylbenzen copolymer with quaternary ammonium	Anion permselective	2.0~3.0	0.9~1.4	0.13~0.16

are used to circulate these solutions, and each pump has a maximum flow rate of $31 \text{ cm}^3/\text{s}$.

The feed solutions were NaCl , CaCl_2 , AlCl_3 , NaNO_3 and Na_2SO_4 solutions and phosphoric acid containing Al and Mo ions. Pure water was used as the recovery solution. A 5wt% NaSO_4 solution was used as the solution for the electrode cell. Each solution were 500 ml by volume. Experiments were performed at different temperatures, voltages and concentrations of feed solution.

The electrodialysis behavior was expressed by a desalination percentage, which is calculated as follows: $\text{desalination \%} = (C_0 - C_t)/C_0 \times 100$, where C_0 and C_t are the initial feed concentration and the concentrations of feed solution at each treatment time, respectively.

4. Results and Discussion

4.1 Electrodialysis of mixed solution containing different valent ions

The experimental results of electrodialysis of different valent cations such as Na^+ , Ca^{2+} and Al^{3+} using several ion-exchange membranes, CMX-SB/ACS and CMS/ACS, are shown in Fig. 3 (a) and (b). As shown in Fig. 3 (a), the desalination percentage of monovalent (Na^+), divalent (Ca^{2+}) and trivalent ions (Al^{3+}) with the CMX-SB/ACS membrane is about 40%, 70% and 80%, respectively, after 30 min. treatment. The CMX-SB/ACS membrane shows a better desalination performance for monovalent, divalent and trivalent ions. It is obvious from Fig. 3 (b) that CMS/ACS membrane has a very low desalination percentage compared with CMX-SB/ACS membrane. Only 30% of Na^+ and about 10% of Ca^{2+} and Al^{3+} are desalinated. The CMS/ACS membrane does not give a high desalination percentage for monovalent ion, although it is

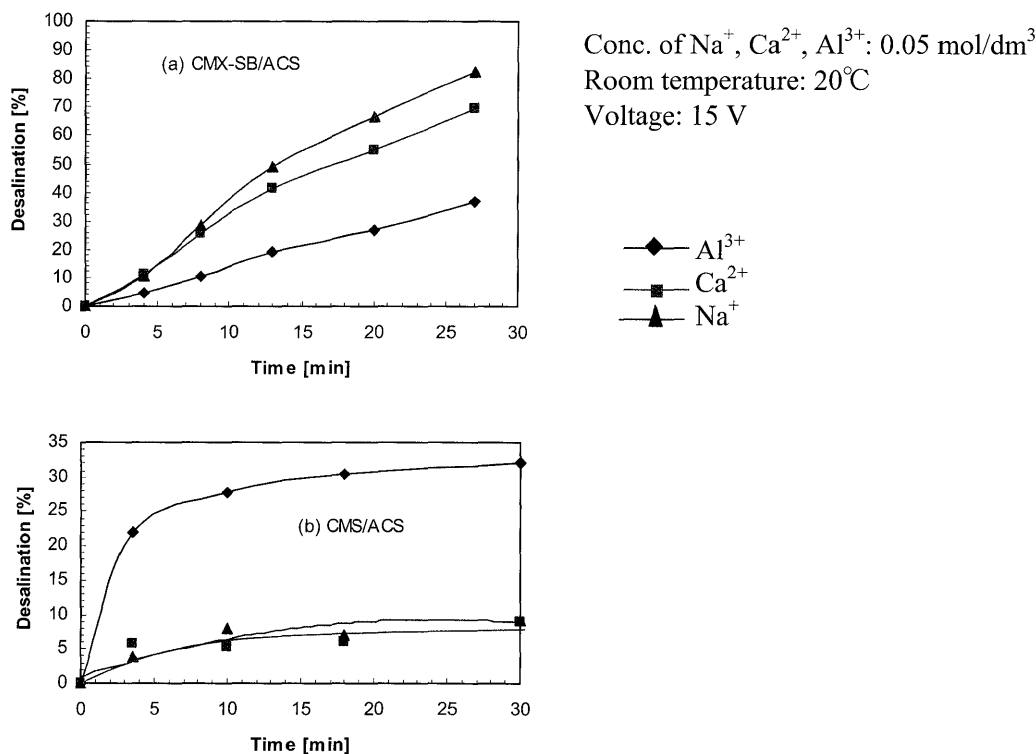


Fig. 3 Electrodialysis of different valent cations using different ion-exchange membrane.

a monovalent cation permselective ion-exchange membrane. Possibly this is caused by the existence of mixed ion solution and the low diffusion coefficient of ions through the CMS/ACS membrane.

Electrodialysis of monovalent and divalent anions through the CMX-SB/ACS membrane is shown in Fig. 4. The desalination percentage of both monovalent anions, Cl^- and NO_3^- , reaches about 70%, while that of divalent anion, SO_4^{2-} , is about 10% for 10 min.. It is evident that monovalent anions transport through the membrane prior to divalent anions in this region. The monovalent anion permselective characteristic of ACS membrane appears abundantly. The desalination percentage of monovalent anion reaches almost 100% for 30 min., while that of divalent anion reaches about 80%.

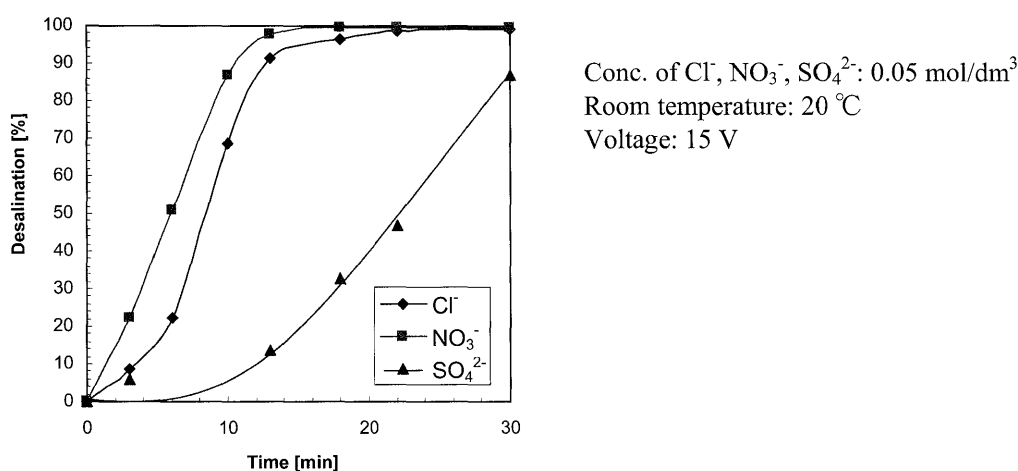


Fig. 4 Electrodialysis of different valent anion using CMX-SB/ACS ion-exchange membrane.

4.2 Electrodialysis of phosphoric acid containing Al and Mo ions

Applied voltage plays an important role in the electrodialysis process. The effect of voltage on electrodialysis of P, Al and Mo ions is shown in Fig. 5. As applied voltage increases, the desalination percentage of P, Al and Mo ions rises. Increasing the applied voltage is beneficial for the desalination of ions, because the driving force for ion transport is the electrical

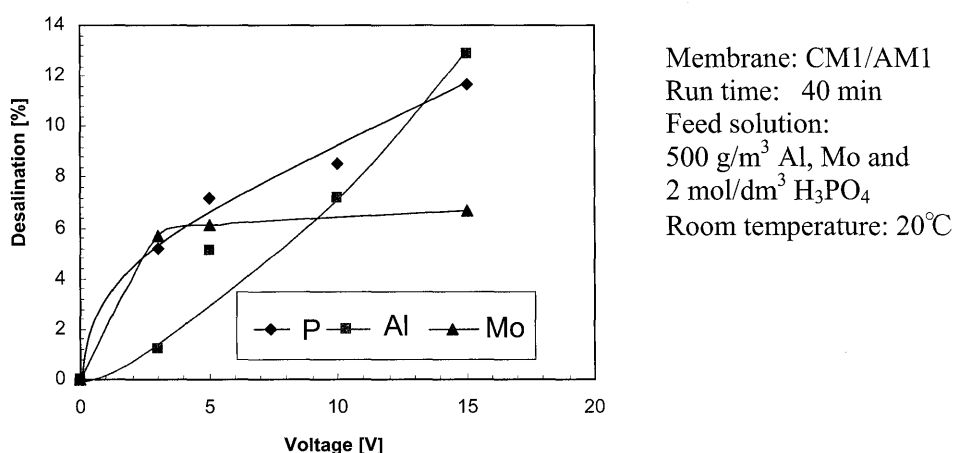


Fig. 5 Effect of voltage on electrodialysis of P, Al and Mo ions.

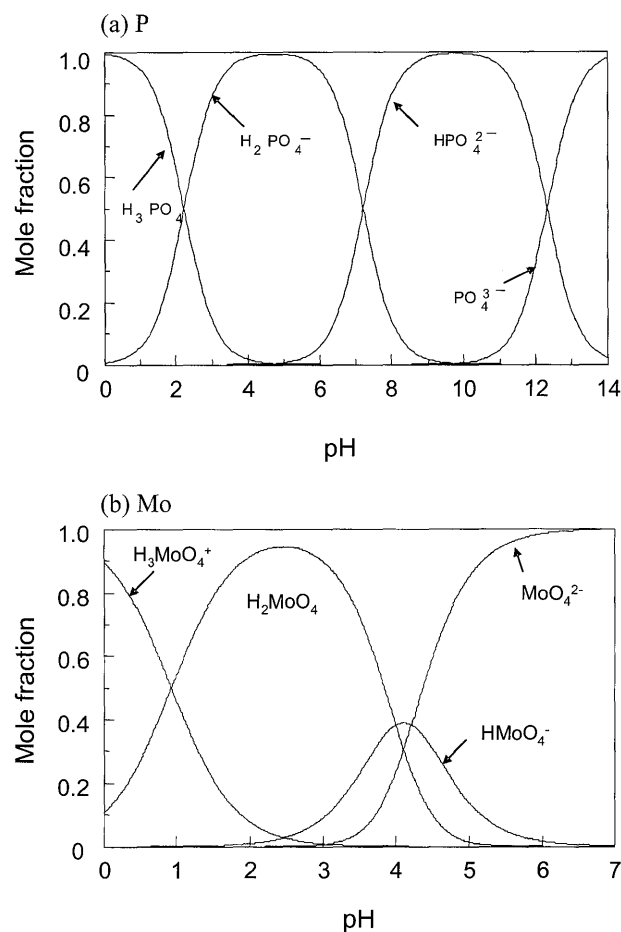


Fig. 6 Relationship between mole fraction and pH.

potential. It is worth noting that when the voltage is below 10 V, the effect of pH should be considered. The distribution diagrams of phosphate and Mo species are shown in Fig. 6. When the applied voltage is below 10 V and the pH of the feed solution is about 2, most of the P and Mo ions may exist in the form of $H_2PO_4^-$ and H_2MoO_4 , which transport through the membrane. On the other hand, according to other studies^{11, 12)}, when the voltage is above 10 V, the dissociation rate of water molecules decreases and the pH effect may be negligible. In the following experiments, the applied voltage is set at 15 V and the Mo ions mainly exist in the form of $Mo_2O_4^{2-}$.

The effect of initial concentration of H_3PO_4 on the desalination percentage of P, Al and Mo ions is shown in Fig. 7. With an increase in initial concentration of H_3PO_4 , the desalination percentage of Al ions falls while that of Mo ions increases. The higher concentration of H_3PO_4 inhibits the transport of Al ions and PO_4 ions through the membrane, whereas it accelerates transport of Mo ions. As anion species, $Mo_2O_4^{2-}$ and PO_4^{3-} transport through the anion membrane. The $Mo_2O_4^{2-}$, with higher mobility than PO_4^{3-} , transports through the anion membrane prior to PO_4^{3-} . Within the same run time, the concentration of residual PO_4^{3-} in the feed solution increases as the initial concentration of phosphoric acid increases.

The effect of temperature on the electrodialysis of P, Al and Mo ions is shown in Fig. 8. Change in feed temperature drastically affects the electrodialysis of Al ions. The desalination

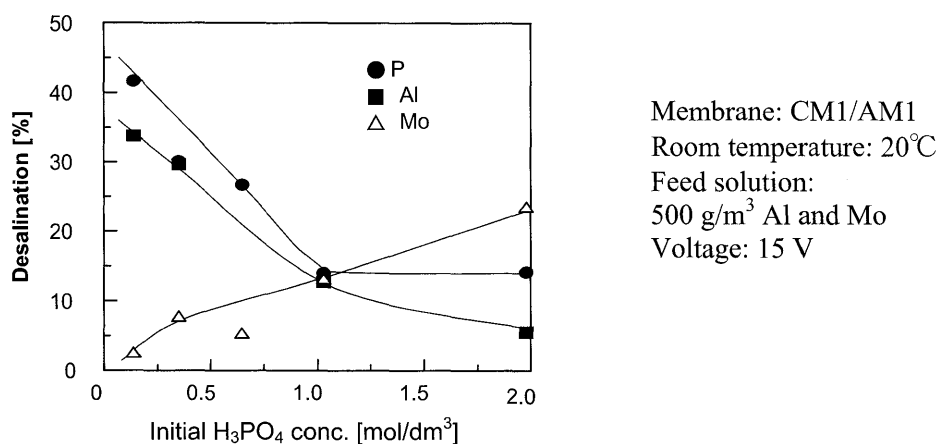


Fig. 7 Effect of initial concentration of H_3PO_4 on electrodesalination of P, Al and Mo ions.

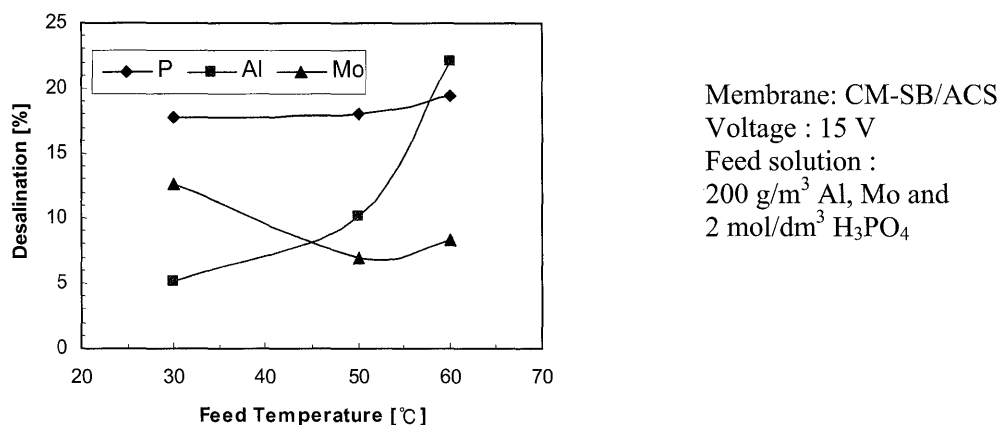


Fig. 8 Effect of feed temperature on electrodesalination of P, Al and Mo ions.

percentage of Al ions increases with an increase in feed temperature. The desalination percentage of P ions does not change very much, although it also increases with increasing feed temperature. An increase in feed temperature is not helpful for the desalination of Mo ions. This result is unexpected, because the transport rate of the ions is determined by kinetic as well as by thermodynamic parameters¹³; namely, it is relative to the diffusion coefficient and the driving force. Increasing feed temperature makes the diffusion coefficient larger. At the present time, we cannot explain why the behavior of Mo ions does not follow this tendency.

Experiments were performed with different ion-exchange membranes in order to test whether the electrodesalination process can be applied to the treatment of waste phosphoric acid containing Al and Mo ions. The experimental results are shown in Fig. 9. The CMX/AMX, CM1/AM1 and CMX-SB/ACS membranes exhibit a comparable desalination percentage of Al ions, while the desalination percentage of Mo ions is low. When the CMX-SB/ACS membrane is used, the desalination percentage of Al ions reaches about 45% and that of Mo ions reaches about 7%. At the same time about 15% of the phosphoric acid is removed. In this case, separation between the Al-rich solution and the P- and Mo-rich solution can be achieved, though the purity and recovery percentage of target materials are not particularly high.

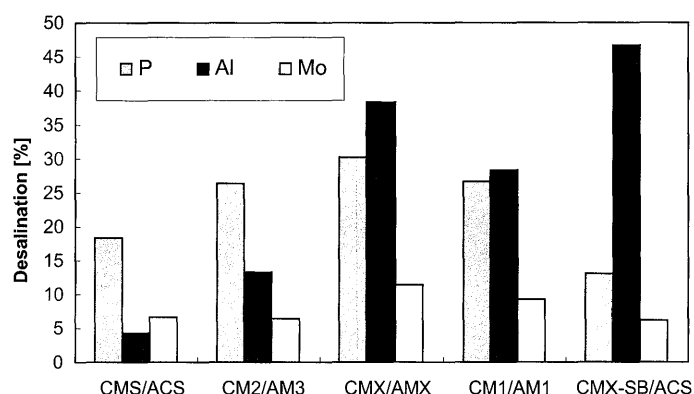


Fig. 9 Electrodialysis of P, Al and Mo using different ion-exchange membranes.

Engineering problems still remain to be solved in a practical application, but the electrodialysis process suggests the possibility of treating waste phosphoric acid containing Al and Mo ions. For example, if the second stage treatment by an ED process is applied to the P and Mo rich solution with a suitable membrane such as the CMS/ACS, it could prove successful.

5. Conclusion

The electrodialysis phenomena of aqueous solutions containing phosphoric acid and metal ions were investigated. The feasibility of an electrodialysis process applied to treat phosphoric acid was evaluated.

When different ion-exchange membranes are used, the desalination percentage of several ions are dependent on the valency of particular ions. Of the membranes used in this study, the CMX-SB/ACS ion-exchange membrane showed the best desalination performance for monovalent, divalent and trivalent ions.

The voltage, concentration and feed temperature affect electrodialysis of phosphoric acid containing Al and Mo ions. Higher voltage is beneficial for desalination of the Al and Mo ions. An increase in feed temperature will cause an increase in the desalination percentage of Al ions, while lowering the desalination percentage of Mo ions. A higher initial concentration of phosphoric acid obstructs the desalination of Al and P ions, but promotes the desalination of Mo ions.

By using the following three kinds of the ion-exchange membranes, at least 30% of Al ion and 7% of Mo ion could be removed from the waste solution: CMX/AMX, CM1/AM1 and CMX-SB/ACS. The electrodialysis process shows promise as a way of treating waste phosphoric acid containing Al and Mo ions if using a the combination of the ED process.

Acknowledgement

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