Fundamental Research into the Treatment of the Chromic Plating Rinse by Reverse Osmosis

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Fundamental research into the treatment of the chromic plating rinse by reverse osmosis were carried out with Loeb-type skinned membranes. The effect of the pH on the transport of chromic acid was quantitatively investigated. With the increase in pH, chromic acid dissociates to form a divalent ion, CrO_4^{2-}, and the rejection by the membrane increases. For example, the rejection of 0.01 M chromic acid at pH 3 was 83%, while it was 96% at pH 7.25, both at 40 atm. The permeation behavior of additives such as sodium hexafluorosilicate and chromium (III) sulfate was also examined, mainly in connection with their dissociation in the solution. In the case of the concentration of chromic acid, the rejection remained constant up to about 15000 ppm, while the flux decreased considerably with an increase in the concentration.

In Japan as well as other developed countries, concern with pollution has been growing remarkably, and legislative restrictions on discharged harmful effluents are becoming stricter. In addition to national regulations, some more restrictions have been imposed in some local communities. At the same time, it is well recognized among the people concerned that pure water can no longer be treated as limitless natural resource.

The plating rinse effluents are regarded as among the most harmful wastes which contain numerous toxic constituents. In these circumustances, some studies[1,2] have been made on the application of reverse osmosis to the treatment of plating rinses with a view to the recovery of harmful substances and the reuse of the water. These experimental data give us much information for practical use. However, there have been few reports describing the relation between the state of the species in the solution and their permeation behavior. It may be necessary to consider even such a basic problem for a feasibility study. Therefore, simulated chromic plating rinse was chosen here and fundamental experiments were performed in order to clarify the relation mentioned above.

These fundamental experiments were carried out under the following conditions; a three-stage countercurrent rinse system had been chosen in which the concentration of the total dissolved solid in the first stage rinse was 2000 ppm. The concentrated solution (15000 ppm) of the first-stage rinse was returned to the plating bath for balance and the permeated water was used as the rinse. Golomb reported a scheme for the rinse system and the mass-balance of the Watts nickel plating rinse and should be referred to for the details.

Experimental

The modified cellulose acetate (E-398-3) membranes were prepared by the method reported by Loeb and Manjikian.[3] The casting solution was composed of 25 wt. % cellulose acetate, 65 wt. % acetone, and 10 wt. % phosphoric acid. The annealing temperatures of the Loeb-type membranes were 60, 65, 70, 75, and 78 °C. The evaporation temperature was 20±1 °C and the evaporation time was 40 s for all Loeb-type membranes. The membranes thus prepared had approximately 20% more fluxes, with the same rejections, as compared with standard (formamide-type) membranes. The effective membrane area in the desalination cell was 12.6 cm^2. The pressurized (40 atm) solution was circulated along the surface of the membrane at 1.2 l/min to reduce the concentration polarization.

Aqueous solutions of 0.01 M—0.2 M chromic acid, 0.005 M sodium-hexafluorosilicate, and 0.004 M chromic (III) sulfate were tested. Their pH was controlled by adding a suitable amount of 0.1 M NaOH or 0.1 M HCl to the solution. In all the experiments the permeated water was collected one hour after the beginning of the operation. The analysis of the chromic acid was performed by photo-absorption at 274 nm after adjusting the pH of the solution to 8. Sodium hexafluorosilicate was supposed to dissociate in the solution to form various species, so sodium, fluorine, and silicon were analyzed individually.

The sodium was determined by flame photo-absorption at 589 nm. The fluorine was measured by photo-absorption at 620 nm after color developing by a Dotite reagent, "Alfusone." The silicone was also analyzed by photo-absorption at 334 nm after treatment with ammonium molybdate. The properties of the membrane were shown by water flux (m^3/m^2·day) and salt rejection. The salt rejection is shown by;

$$R_e = (1 - C_p/C_f) \times 100 \qquad (1)$$

where C_p and C_f are the salt concentrations of the product and feed solutions respectively.

Results

Rejection of Chromic Acid. It is well known[4,5] that, in the case of electrolytes, fluxes of a given solute through the membrane are closely related to the charged state of the molecules in the solution. Since chromic acid dissociates in the solution, chromic acid solutions with pHs of 2, 3, 5, 6, and 7 were tested in order to clarify the effect of pH on the permeation of chromic acid. The rejection of chromic acid was considerably influenced by the pH of the solution, as had been expected. For instance, the rejection of chromic acid was 83% and 96% at pH 3 and 7.25 respectively for the membrane annealed at 70 °C, as is shown in Fig. 1. As it is known that the cellulose acetate membrane is deteriorated rapidly, with a loss

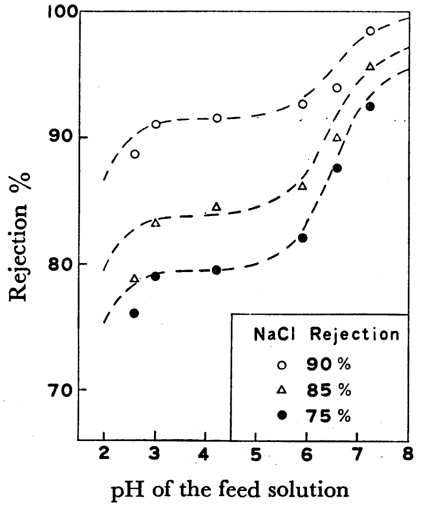

Fig. 1. The effect of pH on the rejection of chromic acid.

of performance, by a strong acidic solution,[6] experiments were carried out as rapidly as possible. That there was no loss of performance of the membrane during the experiment was verified by the fact that there was no change in the water flux or NaCl rejection between before and after the experiment, as is shown in Table 1.

TABLE 1. MEMBRANE PERFORMANCE BEFORE AND AFTER EXPERIMENT

	Memb.					
	●[a)]		△		○	
	NaCl rej. %	Water flux m³/m²·day	NaCl rej. %	Water flux m³/m²·day	NaCl rej. %	Water flux m³/m²·day
Before	74.0	1.55	85.3	1.14	90.0	1.07
Intermediate	76.2	1.55	84.1	1.18	90.6	1.09
After	76.8	1.52	84.4	1.18	90.5	1.09

a) Symbols in Table 1 correspond to those in Fig. 1.

Rejection of Additives. The permeation behavior of chromium(III) sulfate and sodium hexafluorosilicate as additives was also examined.

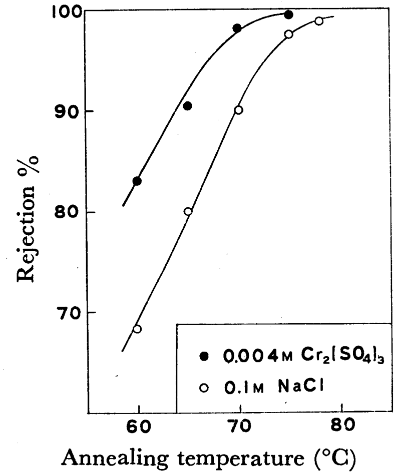

Fig. 2. Rejections of $Cr_2(SO_4)_3$.

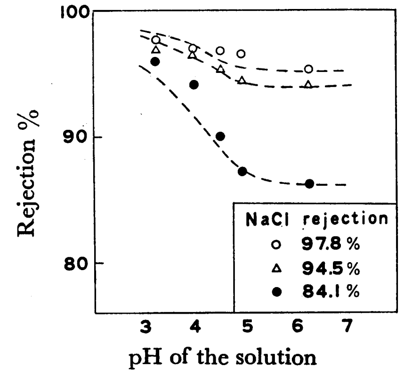

Fig. 3. Rejection of Si in Na_2SiF_6.
------: Calculated rejection.

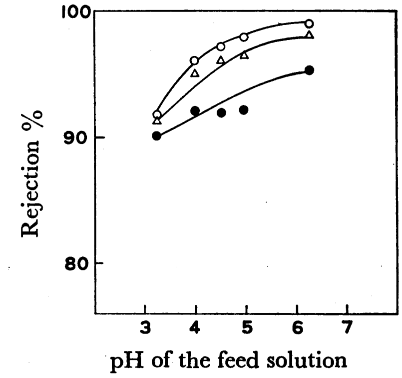

Fig. 4. Rejections of F in Na_2SiF_6.

In the case of inorganic salts, the order of separation is usually consistent with the order of the lyotropic property.[7] In that sense, the rejection of chromium (III) sulfate, which is composed of cations and anions with a high valency, was remarkably higher than that of NaCl, as is shwon in Fig. 2. Since sodium hexafluorosilicate was supposed to dissociate to form various type of species, the rejection was calculated by taking into account the existence of each species.

The analytical data of silicon and fluorine indicate that the rejection of species which contain silicon decreased with the increase in pH, while in the case of species which contain fluorine the opposite is true, as is shown in Figs. 3 and 4.

Discussion

Rejection of Chromic Acid. Chromic acid dissociates in an aqueous solution as follows.

$$H_2CrO_4 \overset{K_1}{\rightleftharpoons} H^+ + HCrO_4^- \qquad (2)$$

$$HCrO_4^- \overset{K_2}{\rightleftharpoons} H^+ + CrO_4^{2-} \qquad (3)$$

The literature values[7] of the dissociation constants K_1 and K_2 are 1.8×10^{-1} and 3.2×10^{-7} respectively.

The amounts of H_2CrO_4, $HCrO_4^-$, and CrO_4^{2-} in 0.01 M chromic acid solution were calculated using the values of K_1 and K_2. The calculation indicated that at pH 3, most of the chromic acid exists in the solution in the form of $HCrO_4^-$, while at pH 7.25, $HCrO_4^-$ and CrO_4^{2-} exist in the solution in portions of 14.8% and 85.2% respectively. Over the pH range from 2 to

7, the amount of H_2CrO_4 is too small to affect the rejection of chromic acid. Based on the calculation, the expected values of rejection were calculated in the following manner:

(1) The rejection of chromic acid at pH 3 was supposed to be the rejection of $HCrO_4^-$.

(2) Taking into account the existence ratio of CrO_4^{2-} and $HCrO_4^-$, the rejection of CrO_4^{2-} was calculated from the observed rejection at pH 7.25 by using the calculated rejection of $HCrO_4^-$.

(3) The rejection at pH values from 2 to 8 was expressed by the following equation:

$$R = \frac{a(H_2CrO_4) + b(HCrO_4^-) + c(CrO_4^{2-})}{(H_2CrO_4) + (HCrO_4^-) + (CrO_4^{2-})} \tag{4}$$

where a, b, and c are the expected rejections of H_2CrO_4, $HCrO_4^-$, and CrO_4^{2-} respectively. As the amount of H_2CrO_4 was insignificantly small, the value of a is not very important and is supposed to be zero here.

The calculated values of a, b, and c for each membrane are shown in Table 2.

Table 2. Calculated values of a,b, and c

Membrane		a[a)]	b	c
NaCl Rej.	75%	0	79.5	96.0
	85%	0	84.0	97.6
	90%	0	91.5	99.7

a) Not calculated but determined in advance.

The calculated rejections are thus in fair agreement with the experimental values, as is shown in Fig. 1. At pH 2.5 the observed rejections were several percent lower than the ones expected for each membrane. It can be considered that the amount of species with no charge, H_2CrO_4, became richer at the surface of the membrane, when the concentration of chromic acid increased there due to concentration polarization thereby displacing the equilibrium.

Rejection of Sodium Hexafluorosilicate. The dissociation of sodium hexafluorosilicate is expressed as follows:

$$Na_2SiF_6 \rightleftharpoons 2Na^+ + SiF_6^{2-} \tag{5}$$

$$SiF_6^{2-} \overset{K_1}{\rightleftharpoons} SiF_4 + 2F^- \tag{6}$$

$$SiF_4 + 2H_2O \overset{K_2}{\rightleftharpoons} SiO_2 + 4HF \tag{7}$$

$$HF \overset{K_3}{\rightleftharpoons} H^+ + F^- \tag{8}$$

where K_1, K_2, and K_3 are the dissociation constants; their literature values[9)] are 1.0×10^{-6}, 1.0×10^{-8}, and 4×10^{-4} respectively.

In this case, the dissociation is so complex that it is very difficult to explain the rejction of each species. The species were, therefore, classified into three groups, containing sodium, fluorine, and silicon respectively.

There are numerous reports[7)] seeking to explain the permeation behavior of sodium ions, and so nothing will be mentioned about it here. The species which contain silicon are SiF_6^{2-}, SiF_4, and SiO_2. Calculations based on Eqs. (6), (7), and (8) suggest that at pH 6, the amounts of SiF_6^{2-} and SiF_4 are vanishingly small, while at pH 3 suggests that SiO_2 and SiF_6^{2-} exist in the solution in portions of 30.0 mol.% and 66.6 mol.%. Considering the charged state of the species, SiF_6^{2-} seems to have a much higher rejection rate than the other two species. Just as in the previous section, the rejection of SiO_2 was calculated assuming the amount of SiO_2 to be 5×10^{-3} M at pH 6.25.

Then the rejections of SiF_6^{2-} were calculated considering the existence ratio of each species at pH 3.15. In calculating, it was assumed that the rejection of SiF_4 was almost the same as that of SiO_2, since both of them are the same type of nonelectrolyte. The rejections thus calculated are shown by dotted lines in Fig. 3, and they agree with experimental values. In the case of the separation of the species containing fluorine, it is very difficult to describe the permeation behavior of each species, since there are too many species in the solution.

It may be said, however, that, with an increase in the pH of the solution, HF was enhanced to produce charged species, H^+ and F^-, and that the rejection of the fluorine-containing species became higher, as is shown in Fig. 4. As is shown in this case, the species in the permeated solution are sometimes different from those in the feed solution.

Particular attention should be paid to the cases when species with small solubilities are concentrated or produced in the feed or permeated solution.

Concentration of Chromic Acid. Experiments on the concentration were carried out using a batched-type cell with an effective membrane area of 12.6 cm². To avoid concentration polarization, an impeller was rotated over the membrane at 300 r.p.m. The cell was initially charged with 4 l of a chromic acid solution; then it was pressurized with nitrogen gas, which was maintained at 40 atm during the experiment. The permeated solution was collected every hour by using a fraction collector. The initial concentrations of the chromic acid solutions were 0.01—0.05, and each solution was concentrated by a factor of 3—4.

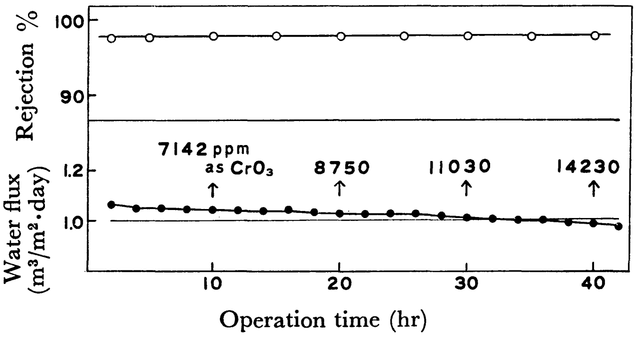

Fig. 5. Concentration of chromic acid. Initial concentration of the feed; 4560 ppm, pH of the feed; 7.1.

Results obtained with an initial concentration of 0.05 M are shown in Fig. 5. Figure 5 indicates that water flux decreased with the increase in the concentration of the feed, while the rejection of chromic acid remained approximately constant. According to those results, the concentration of the permeate was in linear proportion to that of the feed.

When the rejection remains constant, the extent of the concentration can be calculated from the following equation,[10] which corresponds to the concentration process by evaporation:

$$C/C_0 = (V_0/V)^R \qquad (9)$$

where C is the concentration of the feed and V is the residual volume of the feed. C_0 and V_0 indicate the initial concentration and volume of the feed.

Later, hexavalent chromium in the permeate should be removed by a method such as ion-exchange resin if the permeate is to be drained off.

The addition of NaOH to control the pH of the feed may be troublesome in that the concentrated solution must be returned to the plating bath. A new type of membrane which has a high resistance to chemicals is expected to be developed.

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