



Project Summary

Fabrication and Pilot Scale Testing of a Prototype Donnan Dialyzer for the Removal of Toxic Metals from Electroplating Rinse Waters

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An initial program was conducted to develop anion-exchange membranes to be used in the removal of copper, cadmium, and zinc, as their complex cyanide anions, from cyanide process electroplating rinse waters by a Donnan dialysis process. For these laboratory studies, simulated rinse waters prepared by diluting electroplating bath solutions to the desired metal content were utilized.

A series of anion-exchange membranes based on radiation grafted polyethylene films were prepared. The grafting monomers used were vinylpyridines or vinylbenzyl chloride. These grafted membranes were converted to anion-exchange membranes by quaternization with alkyl halides or trialkylamines, respectively. The series of membranes exhibited varying ion-exchange capacities and varying hydrophilicity.

A follow-on program was conducted to fabricate a prototype Donnan dialyzer to be used in testing the previously developed anion exchange membranes. The prototype dialyzer was to be evaluated in actual electroplating shops in order to determine its engineering and economic feasibility for these rinse waters.

Synthesis of the required quantity of membranes for the dialyzer produced a product membrane which was unstable in the dialyzer stripping solution. Attempts to resolve the instability problem

were unsuccessful. An alternate membrane, therefore, was selected for use in the prototype dialyzer. The dialyzer was fabricated and laboratory tests were carried out prior to field evaluation. A series of technical problems were encountered with the plate and frame hardware for the dialyzer. The most serious involved development of internal leaks between the rinse water and stripping solution. These problems indicated that a major redesign of the dialyzer was required. After consideration of financial and time requirements for the redesign effort, a decision was made to terminate the program.

This Project Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, Ohio, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In the past several years, legislation has been passed at state and federal levels leading to the limiting of allowable emissions of many trace metals in water from industrial sites. Among the metals are copper, zinc, nickel, chromium, cadmium, lead, and mercury. Removal of these metals, present as ions, from the untreated industrial outflows will there-

fore be required. In certain cases, the removal may take place by using various means such as reverse osmosis, dialysis, and electrodialysis. All of these methods have certain advantages and disadvantages.

An approach which incorporates the advantages of ion-exchange systems is a membrane transfer process known as Donnan dialysis. This process is basically a continuous ion-exchange procedure utilizing an ion-selective membrane to establish a Donnan equilibrium between the two solutions of electrolytes separated by the membrane. In the case of an anion-exchange membrane, the cations in the two solutions are prevented from inter-diffusing across the membrane, but the anions will redistribute themselves between the two solutions until equilibrium is reached and the ratios of all similarly charged anions are equal. The driving force for anion exchange is the system's displacement from the equilibrium ratios and can be controlled by manipulation of the solution concentrations.

The simplest Donnan dialysis cell comprises an ion-selective membrane and a space on each side of the membrane. The toxic heavy metal ions in a rinse water feed can be extracted across the membrane and concentrated in a stripping solution. The only energy required in such a process is to pump the feed and stripping solutions across the cell. Large hydraulic pressures as required by reverse osmosis or large electric current flows as required by electrodialysis are not required in Donnan dialysis. A compact Donnan dialysis stack can be designed to contain many membrane-spacer units to economically treat large quantities of rinse water.

The application of Donnan dialysis is being extended to the removal of trace metals from electroplating wastes. Cadmium, copper, and zinc are important as they are present in electroplating wastes as their complex cyanide anions. Removal of these trace metals will therefore require the development of suitable anion-exchange membranes, in contrast to the removal of nickel, which is present as its free cation and could thus be removed with cation-exchange membranes. Conventional rinse water treatment involves chlorination for cyanide destruction, followed by precipitation of the metals as their hydroxides or sulfides. Donnan dialysis, provided high transport membranes are available, could provide a simple, efficient alternative electroplating rinse water treatment process.

The objectives of this research included the development of optimized anion-exchange membranes for the removal of copper, zinc, and cadmium, as their complex cyanide anions, from electroplating rinse waters and the fabrication and field evaluation of a prototype Donnan dialyzer for field evaluation in electroplating shops. It was intended for this research to provide engineering data to allow technical and economic analysis of Donnan dialysis as a means of removing toxic metals from electroplating rinse waters.

During the course of this laboratory study, all membrane evaluations were conducted with simulated electroplating rinse waters. These were prepared by diluting plating bath formulations to give the desired metal ion concentration (50 ppm or 500 ppm).

Experimental Procedures Film Grafting Procedures

A desired length of the polymer films was backed with absorbent crepe paper toweling or cheesecloth and rolled onto a 12.7-mm aluminum pipe that was capped at one end. The roll of film and backing material were placed in a hydrometer jar, which was connected to a vacuum system and pumped down to approximately 10 to 12 Torr Hg. A grafting solution of the desired monomer in a suitable solvent (usually benzene, methanol, or water) was drawn into the evaluated jar. The jars were placed on turntables in the irradiation facility and exposed to a uniform cobalt-60 source adjusted to give the desired dose rate.

The film was removed from the reactor, unrolled, and separated from the paper toweling or cheesecloth. The film was then washed in solvents suitable for removing homopolymer, which was deposited on the film and allowed to dry on paper toweling.

Film Quaternization Procedures

Vinylpyridine films were quaternized with methyl iodide (2% in methanol, 48 hours) or with 1-bromobutane (2% in methanol, 48 hours). Vinylbenzyl chloride films were quaternized with trimethylamine (10% in water, 24 hours) or with tri-*n*-butylamine (10% in methanol, 48 hours). After quaternization, the films were washed with 5% hydrochloric acid, washed with deionized water, and air dried.

Film Characterization

The membranes were characterized for equilibrium water content, ion-exchange capacity, osmotic water transport, and metal complex anion transport. The membranes were pneumatically leak tested.

The metal complex anion transport rate constants were determined on a Donnan dialysis system. A schematic of the test system is shown in Figure 1. The feed solution (simulated rinse water) was pumped through the cells on a once-through basis to waste, and the strip solution was pumped through the system to the strip reservoir for recycle. The rate constant for metal ion transport was calculated using the expression:

$$k = \frac{1n \frac{C_0}{C}}{t}$$

where C_0 is the concentration of metal ion in the cell inlet, C is the metal concentration in the cell outlet, and t is the residence time in the cell.

Initial membrane evaluations indicated that flow rates were too short to give metal complex anion removal rates capable of being accurately determined. The membrane test system was modified to provide cell contact times on the order of 0.5 to 0.7 minute. With the modified test system, variable metal ion transport rates

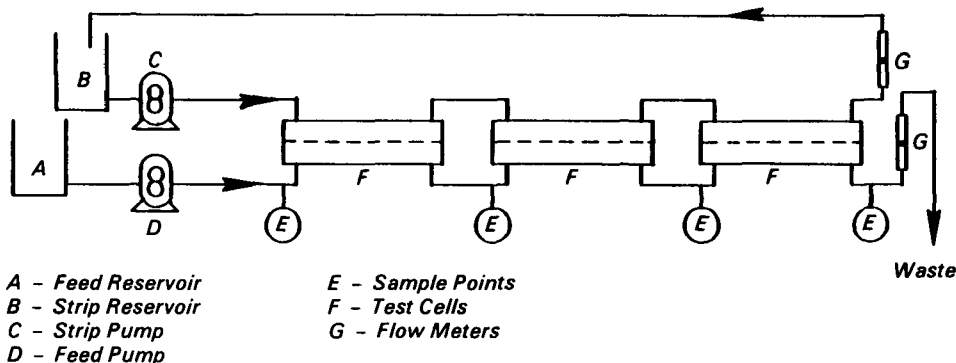
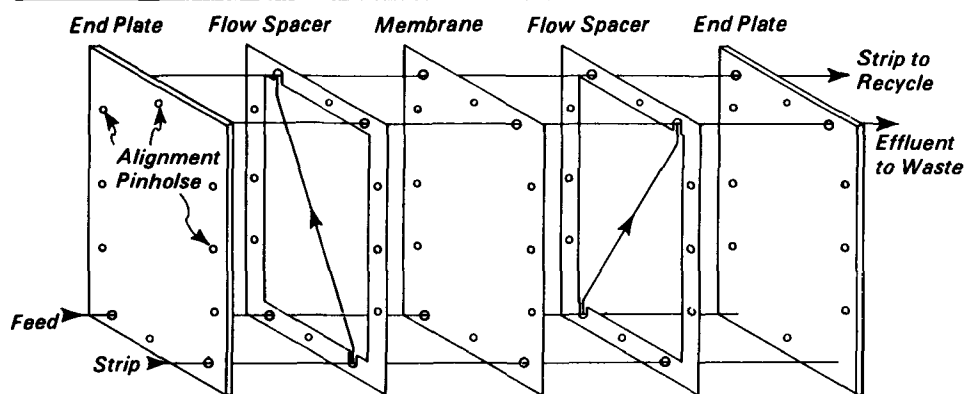


Figure 1. Membrane test system.



Note: The assembly bolt holes in the end plates are not shown.

Figure 2. Details of dialysis stack components.

were encountered during the initial period of each run until the system came to steady-state conditions.

Prototype Dialyzer Design

The prototype dialyzer was based upon a plate and frame design and was a scaled-up version of a design reported in the literature. The unit consists of two end plates, flow spacers, and sheet membranes. The flow spacers were fabricated using polypropylene mesh. The border of each spacer was impregnated with silicone rubber and was faced on each side with neoprene rubber gaskets. Entry and exit ports were cut into the gaskets so inlet and outlet manifolds were formed upon assembly of the dialysis stack. Holes were also cut into the gasketed edges of the spacers to accommodate locating pins. Matching ports and locating pinholes were cut in the membranes. It was found necessary to use a liquid rubber adhesive to assemble the

unit to avoid leaks. Details of the dialysis stack component design are shown in Figure 2.

The assembled dialysis unit used two positive displacement gear pumps with variable speed electric motors. Each feed pump was connected to a 5-micron in-line filter, a flow meter, a pressure gauge and was connected to the appropriate inlet port on the dialyzer stack. The entire unit was mounted on a base designed for handling with a forklift. The assembled unit is shown in Figure 3.

Results and Discussion

Several membranes were evaluated for metal ion transport. Results are shown in Table 1.

The trend that is readily apparent in the data in Table 1 is a positive correlation of metal ion transport rate with ion-exchange capacity. Increased ion-exchange capacity appears to lead to increased metal ion transport rates. Additionally, it

was determined that there was a positive correlation between osmotic water flow rate and ion-exchange capacity.

The four membranes that showed the highest metal ion transport rate constants when operating with low levels of metal ion (about 50 ppm) in the feed were selected for further evaluation with higher concentrations of metal ion in the feed. These four membranes, whose properties are shown in Table 2, all have ion-exchange capacities in excess of 2 milliequivalents per gram. Two membranes are based on vinylpyridine-grafted polyethylene, and two are based on vinylbenzyl chloride-grafted polyethylene film. The results obtained with the four membranes are presented in Table 3.

All four membranes showed good transport rate constants with the low level feed solutions. However, Membranes E12Q4 and E16Q1 showed significantly lower rate constants with the high level feeds. Membrane E11Q4 showed decreased rate constants with the high level feed, but the rate constants still are acceptably high.

This membrane was selected for use in the prototype dialyzer. Preparation of a sufficient quantity for dialyzer fabrication was undertaken.

The initial synthesis utilized 11 rolls of film. The film was grafted and quaternized as described above. Laboratory evaluation indicated nonuniform grafting was obtained.

A second grafting run utilized six rolls of film. Infrared spectra of film samples indicated uniform grafting was obtained. These films were quaternized and subjected to laboratory evaluation.

It was found that the metal ion transport rate constant decreased with time. Initial values of 1.4-1.6 min^{-1} were obtained, but these values declined to $<0.5 \text{ min}^{-1}$ in several hours of dialyzer operation.

Infrared spectra of the unused samples of the membranes showed very strong absorption bands for the quaternized polyvinylpyridine.

Samples of the quaternized membrane were washed with 10% hydrochloric acid and with 10% sodium hydroxide. Acid washing produced no change in the infrared spectra, but caustic washing led to loss of most of the absorption band intensity of quaternized polyvinylpyridine.

It was concluded that the films had not grafted appreciably. The strong infrared absorption bands were attributed to occluded polyvinylpyridine homopolymer within the film. After quaternization, the resulting water-soluble polyvinyl-N-

Table 1. Membrane Transport Data

Membrane number	Ion-exchange capacity meq/dry g	Osmotic water flow rate mL/hr/cm ² *	Metal complex anion transport rate constant** min ⁻¹		
			Cu	Cd	Zn
E11Q4	2.5	0.040	3.1	2.8	1.9
E12Q4	2.6	0.053	2.3	2.2	2.9
E12Q5	1.1	0.010	0	--	--
E14Q4	0.7	0.010	1.1 (1.1)†	0.3	0.2
E15Q1	1.1	0.012	1.0	0.4	0.1
E16Q1	2.2	0.102	2.5	--	--
E16Q2	1.2	0.016	0	--	--
E18Q1	2.2	0.054	2.2	1.4	0.6
E18Q2	1.4	0.009	0	--	--

*0.2N NaCl versus deionized H₂O—cell effective area 122 cm².

**Feed-nominal 50 ppm in metal of interest; stripping solution 0.2N NaCl.

†Duplicate determinations of the rate constant.

methylpyridinium iodide leached out of the film.

Inasmuch as good membranes were prepared on the previous project by grafting 4-vinylpyridine onto polyethylene followed by quaternization with methyl iodide using the above procedures, a review of possible differences in this work and the previous work was undertaken. The results of this review follow.

1. Polyethylene Film—The film used in the previous and present studies was from a special lot purchased several years ago.
2. Cheesecloth Interleaving—The cheesecloth used in the present and previous studies was from a lot purchased several years ago.
3. Solvent—ACS grade methanol was used as the grafting solvent. GC/MS analysis of the methanol did not reveal any significant impurities which might affect the grafting reaction.
4. Monomer—Monomer on the current program was from a different source than the monomer on the previous program. GC/MS analysis indicated 99.8% plus 4-vinylpyridine with no differences in impurities (mostly alkylpyridines).
5. Radiation Dose Rate—The dosimetry at SwRI had been done for several years using the Bausch and Lomb cobalt chip technique. Dosimetry was changed to lithium fluoride crystal dosimeters when Bausch and Lomb discontinued production of cobalt glass chips. A comparison of dosimetry measurements was made using a few remaining cobalt glass chips and the lithium fluoride dosimeters to ensure that dose rates in the previous work and current were the same. Identical results were obtained.

A series of experiments were conducted in an attempt to resolve the problem of membrane stability. Study parameters involved included the effect of source of the monomers, irradiation dose rate and total dose, inclusion of small amounts (1-4%) of other monomers known to enhance grafting in the grafting solution, and crystalline/amorphous ratio of the polyethylene. None of these parameters affected the stability of the product membranes.

A peer review was conducted to assess the status of the program and to make

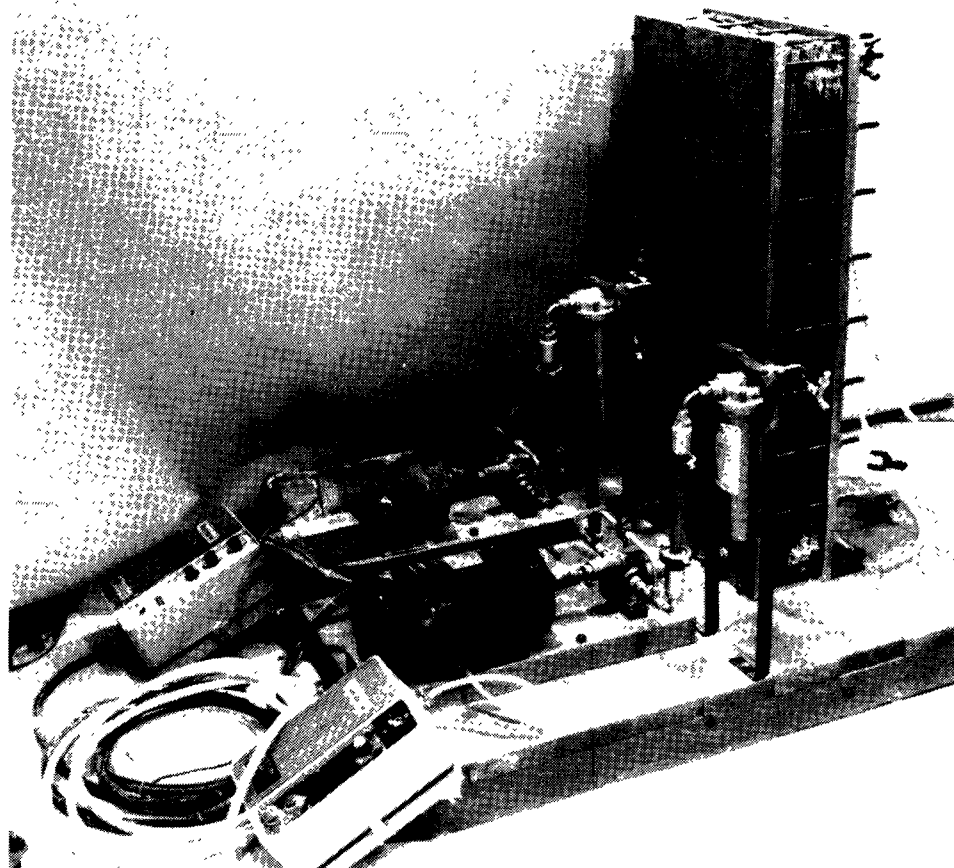


Figure 3. Prototype Donnan dialysis unit.

recommendations for further work. The review group included two representatives of the U.S. Environmental Protection Agency, a representative of the American Electroplaters Society, two industry consultants, and two representatives of Southwest Research Institute. It was concluded that the reasons for the instability of all 4-vinylpyridine-grafted membranes prepared subsequent to the synthesis of Membrane E11Q4 were not known. The peer reviewers also concluded that while the above-described attempts at resolving the problem were reasonable and diligently pursued, further

efforts at resolving the problem were not justified at the present time. It was recommended that no further work on the problem of membrane instability be undertaken. It was further recommended that the best available, stable SwRI membranes be compared with representative, commercially available membranes. The best membrane available, either SwRI produced or commercially available, should be selected. The prototype should be fabricated using this membrane and the field evaluation conducted. Three commercially available membranes were obtained from the manufacturer. These

Table 2. Properties of High Transport Rate Membranes

Membrane number	Membrane type	Equilibrium water content g H ₂ O/g	Ion-exchange capacity meq/dry g	Osmotic water flow rate* mL/hr/cm ²
E11Q4	(4-VP) CH ₃ I	1.08	2.5	0.040
E12Q4	(4-VP/N-VP) CH ₃ I	2.45	2.6	0.048
E16Q1	(VCB)(CH ₃) ₃ N	1.52	2.2	0.102
E18Q1	(VBC/N-VP)(CH ₃) ₃ N	1.00	2.2	0.090

*0.2N NaCl versus deionized H₂O—cell effective area 122 cm².

Table 3. Effect of Metal Ion Concentration on Ion Transport

Membrane	Metal ion transport rate, min ⁻¹					
	Low concentration*			High concentration**		
	Cu	Cd	Zn	Cu	Cd	Zn
E11Q4	3.1	2.8	1.9	1.5	1.5	1.5
E12Q4	2.3	2.2	2.9	0.7	0.8	0.6
E16Q1	2.5	1.6	0.7	0.6	0.9	--†
E18Q1	2.2	1.4	0.6	1.41	0.6	0.4

* Nominal 50 ppm in metal ion.
 **Nominal 500 ppm in metal ion.
 † Membrane ruptured.

membranes, along with several SwRI membranes, were evaluated in the laboratory dialysis system. Results are presented in Table 4.

SwRI Membrane SW-3-3 was selected for use in the dialysis unit.

Six rolls of film were grafted using a solution of 4-vinylpyridine (24.4%) and styrene (3.6%) in methanol. After quaternization, samples (SW-R-3 and SW-R-5) were evaluated. Osmotic water transport rates were slightly lower than for SW-3-3, and the copper transport rate constant was about 25% higher, as shown in Table 4.

These membranes were selected for incorporation into the prototype dialyzer. The membranes were cut to size and leak tested. Assembly of the dialyzer stack was completed, and the dialysis unit was assembled.

After assembly the unit was checked for operability by pumping water through both the feed and stripping solution pumps. After a short period of operation, leaks developed in the dialyzer stack. The stack was disassembled and examined. It was found that the leaks developed in the

flow spacer gaskets. These gaskets are a laminated structure consisting of neoprene rubber/silicone rubber/neoprene rubber, the silicone rubber serving to impregnate and seal the periphery of the polypropylene mesh flow spacers. The neoprene rubber/silicone rubber interfaces had delaminated in some areas and led to leaks.

The flow spacers were reassembled using a liquid rubber adhesive. Additionally, as each flow spacer-membrane assembly was placed in the dialysis stack, the adhesive was used to ensure good spacer-to-spacer bonding.

The reassembled dialysis stack was subjected to flow testing at 1.0 to 1.2 gpm flow rate through both the feed and stripping solution pumps. There were no initial problems; however, after approximately 33 hours of operation (5 to 6 hours per day), it was noticed that the volume of water in the strip tank was increasing and the volume of water in the feed tank was decreasing, indicating internal leaks. The pressure drop across the dialysis stack was 35 to 40 psi at flow rates of 1.0 to 1.2 gpm. It was not possible to control the

feed and strip pressure at identical values with the manually controlled feed pumps. A pressure differential between the feed and strip of about 3 to 5 psi was normally seen, and the leaks were from the high pressure stream to the low pressure stream.

It was not determined whether the leaks were due to defects in the spacer assemblies or due to physical defects developing in the membranes. Since the spacer-membrane assemblies were bonded together during reassembly of the dialysis unit, an attempt to disassemble the unit would probably result in a certain amount of physical damage to the components and would obscure the cause of the leaks; however, it does appear that the present design is not viable for a dialysis unit with the dimensions employed.

Review of the project led to the conclusion that a major redesign of the dialysis unit would be required. After consideration of both the financial and time factors involved in such a redesign effort, it was decided to terminate the project.

Conclusions

The results obtained in the initial study indicated that anion-exchange membranes with transport properties suitable for removal of metal complex anions from electroplating rinse waters by Donnan dialysis can be prepared by irradiation grafting of polymer films.

The results further indicate that membranes prepared by grafting with 4-vinylpyridine followed by quaternization with methyl iodide are superior to membranes prepared by grafting with vinylbenzyl chloride followed by quaternization with trimethylamine.

The data show that the ion transport rates across the membrane are proportional to membrane ion-exchange capacity, i.e., the higher the ion-exchange capacity, the higher the transport rate. However, equilibrium water content also increases the increasing ion-exchange capacity.

Two major technical problems were encountered in fabrication and evaluation of the prototype dialyzer. The first involved the inability to reproduce the high transport rate membrane developed in the initial study. All attempts to prepare this membrane led to a product which was unstable in the basic stripping solution. The problem of the membrane stability was not resolved.

The second problem encountered involved the development of internal leaks

Table 4. Membrane Evaluation

Membrane number	Source	Type	Osmotic water transport* mL/hr/cm ²	Copper removal rate constant** min ⁻¹
C-1	Commercial	VBC	0.026	0.20
C-2	Commercial	VBC	0.017	0.31
C-3	Commercial	4-VP	--†	--†
SW-3-3	SwRI	4-VP/ST	0.071	0.61
SW-3-6	SwRI	4-VP/ST	0.068	0.28
SW-3-2	SwRI	2-VP	0.052	0.30
SW-3-4	SwRI	VBC	0.054	0.18
SW-R-3	SwRI	4-VP/ST	0.059	0.75
SW-R-5	SwRI	4-VP/ST	0.061	0.77

*Deionized H₂O versus 1.0N NaCl
 **500 ppm Cu feed; 1.0N NaCl strip
 †Not determined—membrane unstable

VBC vinylbenzyl chloride
 4-VP 4-vinylpyridine
 2-VP 2-vinylpyridine
 ST styrene

in the dialysis unit. The exact cause of these internal leaks could not be ascertained but probably was due to insufficient support for membranes under the applied hydraulic loads resulting in damage to the membranes.

As a result of these problems, no field evaluation data on metals removal from electroplating rinse waters were obtained. Therefore, no technical or economic evaluation of Donnan dialysis for this application can be made.

Recommendations

The data obtained in the initial study indicate that the best membranes prepared in this study show acceptable performance for removal of metal-cyanide complex anions from simulated electroplating rinse waters under laboratory conditions.

It was recommended that further studies be conducted to evaluate the most promising membranes under field conditions.

A prototype dialyzer would be evaluated on electroplating rinse waters in commercial plating shops to obtain engineering data. These data would allow technical and economic evaluation of Donnan dialysis as a means of controlling effluent levels of copper, cadmium, and zinc from commercial plating lines. It would also provide field experience on membrane life and maintenance. Quantities of spent stripping solution would be available for characterization and study as to the best means of disposal.

The results of the follow-on study did not allow the technical or economic evaluation of Donnan dialysis as a pollution control device in electroplating shops.

The lack of success of this program is attributable to inability to reproduce high transport rate membranes and to mechanical problems with the dialysis unit. The dialyzer problems were probably due in part to the complexity of the dialyzer design.

Any future work in this area would benefit from careful consideration of dialyzer design. Tube- and shell-type units, fabricated from bundles of small diameter ion-exchange tubing sealed into a tubular housing at the ends, would minimize seal problems. Procedures for isolating leaks within individual ion-exchange tubes followed by plugging of any leaking tubes could provide a relatively simple and easy means of eliminating internal leaks. Finally, the technology for preparing ion-exchange tubular membranes by irradiation-initiated grafting of small diameter, thin wall polyolefin

tubing exists and could be readily optimized. This approach should provide a dialyzer which is more easily constructed and maintained and is less susceptible to internal leaks. Consideration of a system of this type is recommended for consideration in any future program in this area.

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The complete report, entitled "Fabrication and Pilot Scale Testing of a Prototype Donnan Dialyzer for the Removal of Toxic Metals from Electroplating Rinse Waters," (Order No. PB 85-227 890/AS; Cost: \$8.50, subject to change) will be available only from:

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