Membrane Processes for Metal Recovery From Electroplating Rinse Water

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Investigations into the feasibility of two new applications of membrane processes for the recovery of plating metals from electroplating rinses have recently been initiated with the aid of EPA demonstration grants. These are the recovery of chromic acid from a decorative chrome plating line by electrodialysis and the removal of nickel from a Watts-type line via Donnan Dialysis. Both of these processes function by transferring metal ions or metal containing ionic complexes across ion-exchange membranes. This ionic transport is from the rinse water on one side of the membrane to a receiving solution on the opposite side. The enriched solution can then be returned to the plating tanks or otherwise treated more conveniently or economically than the rinse stream itself. A major difference between the two processes is that the driving force for electrodialysis is an impressed electrical potential across the membrane while Donnan dialysis depends on maintaining a cross-membrane concentration gradient. As normally operated, electrodialysis functions as a demineralization process, removing and concentrating both anions and cations from the treated solution. Donnan dialysis acts as a continuous ion-exchange process, replacing the ionic constituent of interest with an innocuous or a less valuable species of the same charge type. Lately, electrodialysis appears to have become more familiar to the electroplating industry but Donnan dialysis has seen little, if any, exploitation in this area. One of the goals of the demonstration programs is to make potential users aware of the technology and to indicate where it might best be applied. Each process will be discussed in more detail below and some of the laboratory and field results to date described.

Electrodialysis (ED) is a membrane process which can be used for the separation, removal or concentration of ionized species in water solutions. These operations are accomplished by the selective transport of the ions through ion-exchange membranes under the influence of an electrical potential (VDC) applied across the membrane. The ion-exchange membranes are the key to the process and two types are required. Cation-exchange membranes, which are permeable only to the positively charged cations in the solution, and anion-exchange membranes which permit only the passage of negative, anionic species. Physically, both membrane types are formed as thin sheets of ion-exchange material, usually reinforced by a synthetic fabric backing to provide the necessary strength. Thickness can vary between one-tenth to almost on millimeter and membrane sheets larger than one meter square are commonly used. The resin matrix is usually styrene or vinyl-pyridine copolymerized and cross-linked with divinylbenzene and the exchange capacity imparted by sulfonic acid, or quaternary ammonium or pyridinium groups covalently bonded to the polymeric backbone. In such membranes, 95-99% of any electric current flowing is carried by the mobile counterions.

In the usual configuration for electrodialysis, alternating cation- and anion-selective membranes are arrayed in parallel between two electrodes to form an ED multicell or membrane "stack" (1,2). Especially designed spacer/gaskets separate the membranes by forming leak-tight, flow directing compartments between adjacent membranes, and the whole assembly is held in compression by a pair of end plates and tie-rods or other clamping device. The compartments or cells formed by the spacers are typically 1-1.5 mm thick and direct the solution fed to the cell over the surfaces of the membranes either in a tortuous path or sheet flow pattern. The flow path usually contains a plastic screen or supporting baffles to ensure separation of the membranes and induce turbulent flow. A stainless steel sheet is commonly used for the cathode and platinized titanium for the anode. Other necessary equipment such as pumps, power supply, filters and piping is conventional, but plastic components are used wherever possible to avoid corrosion, stray electrical currents and contamination of the process streams.

Conventional arrangement and operation of an ED multicell are shown schematically in Figure 1. The process or feed solution which is to be depleted of ions is fed to the even-numbered or diluting cells and the ion-receiving or concentrating solution passes through the odd-numbered cells. Usually the same solution is used for both streams but the concentrating solution is volumetrically 10% to 20% of the feed and may be recycled to minimize the amount of discharge and better control the pressure differential. The repeating stack unit of a cation-selective membrane, a diluting spacer, an

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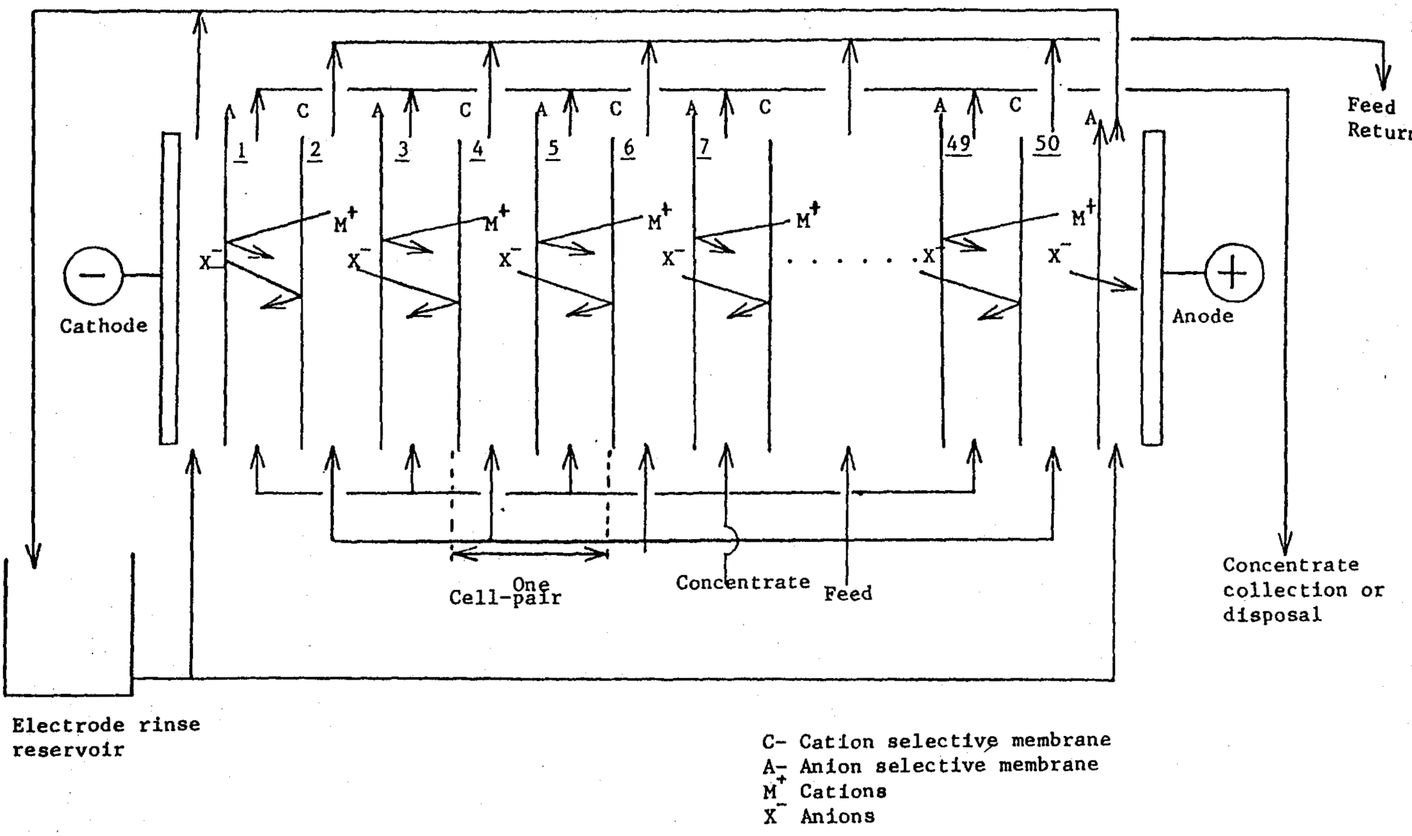

Fig. 1—ED Multicell Schematic.

anion-selective membrane, and a concentrating spacer is termed a cell-pair, and ED equipment can be characterized by indicating the number of cell-pairs comprising a multicell. Industrial stacks generally contain 50-300 cell-pairs although a recent report has described a multicell containing over 900 cell-pairs especially designed for large-volume brackish water demineralization. Solution is distributed to, and collected from, the cells by two internal hydraulic circuits; one for the concentrating cells and one for the diluting cells. As indicated in Figure 1, the passage of a direct current through the stack causes the ions in the solutions flowing through the stack to move in the direction of the oppositely charged electrode. Positive cations in the feed stream are attracted to the negative cathode and pass from the diluting compartments, through the cation-exchange membranes on the cathode side of the cell, into the concentrating compartments, where they accumulate, since their further transport is prevented by interposed anion-selective membranes. Negative anions move in the opposite direction, traversing the adjacent anion-exchange membranes but blocked by the cation-exchange membrane next encountered. Flow velocity of the solutions in the cells varies with the stack type within the range 5-50 cm/sec. A hydraulically separate stream is used to rinse the electrode compartments and remove the gases formed by the electrode reactions:

at the cathode: $2\ H_2O + 2e^- \rightarrow H_2\uparrow + 2OH$

at the anode: $H_2O - 2e^- \rightarrow 1/2\ O_2\uparrow + 2\ H^+$ or
$Cl^- - e^- \rightarrow 1/2\ Cl_2\uparrow$

The electrode rinse is usually acidified to prevent increases in pH and resulting precipitation of insoluble species. Part of the feed or concentrate solutions can be used as the rinse or a special rinse solution prepared and recycled independent of the process streams. Use of the electrodialysis multicell concept makes it possible to obtain a deionizing effect equal to many times the electrical equivalents passed. This feature and the availability of physically strong and highly selective ion-exchange membranes combine to make electrodialysis economically viable, notably for the desalination of water.

Ohm's and Faraday's Laws apply to the electrochemical phenomena occuring within the multicell and several mathematical relationships can be used to characterize electrodialysis equipment and to compare different types of apparatus. Current efficiency, also called coulomb efficiency, indicates the effective utilization of the current passing through the membrane stack for transfer of the ion of interest. It is calculated from feed stream flow rate and inlet and outlet concentrations, current through the stack, and number of cell pairs.

Another important consideration is the relationship of the stack limiting current density to solution concentration and flow velocity. If the limiting current density is exceeded, polarization at the membrane surface will occur due to local ion depletion and pH changes, precipitation in the cells, high electrical resistance and loss of current efficiency may result. To avoid polarization operating current densities are held at conservative levels, often one-half the limiting value. Turbulance promoters and high fluid velocities in the feed cells are used in an effort to maximize the allowable current through the stack.

For the treatment of plating rinse water, rather small, mobile ED modules have been developed for use in the usually space-limited plating rooms. A commercial unit is shown in Figure 2. It measures approximately 42″ × 52″ × 27″ and contains all controls and equipment necessary for operation. Feed and return piping for recirculation of a still or reclaim rinse and a single electrical connection are all that are necessary to complete installation. The membrane stack shown at the lower right of the module contains 35 cell-pairs and can vary in size in order to provide the capacity required to remove an amount of plating salts equal to that dragged into the rinse from the plate tank(s) and thus hold the reclaim solution at a constant metal concentration. The multi-cell differs from conventional ED equipment in that the concentrate cells are dead-ended for maximum concentration and simplified operation.

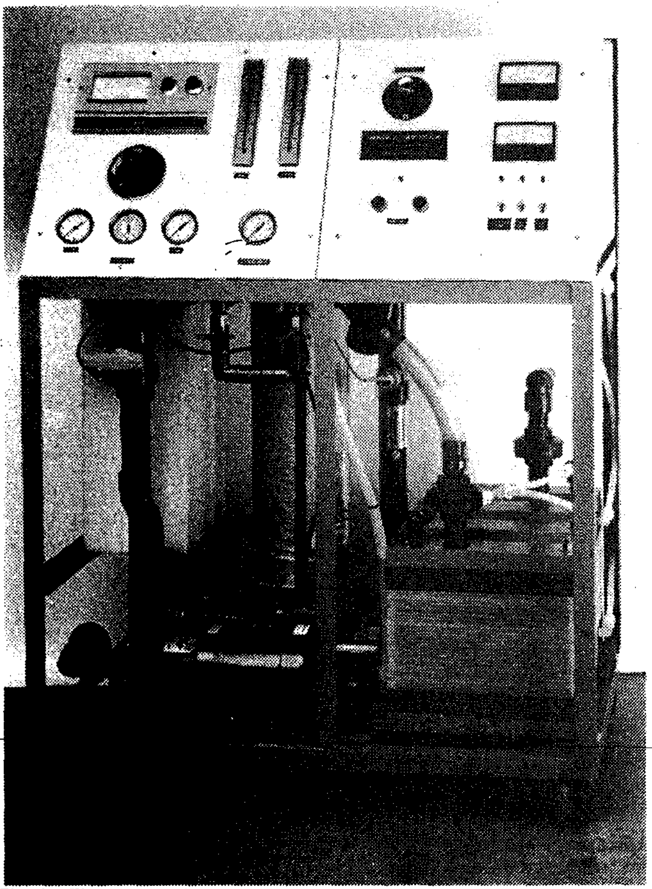

Fig. 2—Electrodialysis Module for Metal Recovery.

In order to extend the electrodialysis concept to the treatment of chrome plating rinses, one of the first considerations was the chemical resistance of the membranes. To check this, commercially available anion-exchange membranes were immersed at room temperature in chromic acid plate solution and sections removed for testing after 7, 14, 42, and 69 days. All sections were leak-tight and appeared to have lost none of their physical strength although there was a slight roughening of the surface. Exchange reactions indicated that the ion-exchange groups were not affected by the acid. Laboratory electrodialysis experiments were then conducted with a five cell-pair stack similar in size and operating characteristics to the multicell shown in Figure 2. Simulated chromic acid rinse solutions were prepared by dissolving chromium trioxide in tap water. Electrodialysis of these solutions over a range of current densities gave the representative results in Table I. All samples were taken after several hours operation at each operating condition. Rinse temperature was 78-91° F. The data indicate that chromic acid can be concentrated from dilute aqueous solutions at least to about 70% of the strength of many chrome plate solutions and may be useful for direct return to the plate tanks. Figure 3 plots the increase in product concentration with current through the stack, a result consistent with data from other electrodialysis concentration experiments. (3) The attainable chromic acid concentration in the product appears to be leveling off at 170-180 g/l and the product/feed concentration ratio decreases with increasing feed concentration. During the course of these experiments the membranes were in contact with varying concentrations of chromic acid over a period of 2-3 months without obvious deterioration or loss of selectivity; tending to confirm the life test results described above.

A fifty cell-pair demonstration module was next constructed for testing on an actual chrome plating line operated by Seaboard Metal Finishing Co. of West Haven, CT. This module is shown on-site in Figure 4 and was installed to recirculate a dead rinse located between the plate tanks and the counterflow rinses. Figure 5 is a schematic of this arrangement. Recirculation rate through the ED stack was 20-25 GPM and dilute sulfuric acid was used an an electrode rinse solution. Initially, the objective was to determine if the membranes and other materials of construction would be sufficiently resistant

Table I
Electrodialysis of Simulated Chromic Acid Rinses

Run	*Current Density*	*Feed Conc. g/l CrO_3*	*Product Conc. g/l CrO_3*	*Product/ Rinse Ratio*
1	10 ma/cm^2	.37	61	165
2	12	.32	106	331
3	14	1.24	143	115
4	16	.98	167	170
5	18	.70	174	249

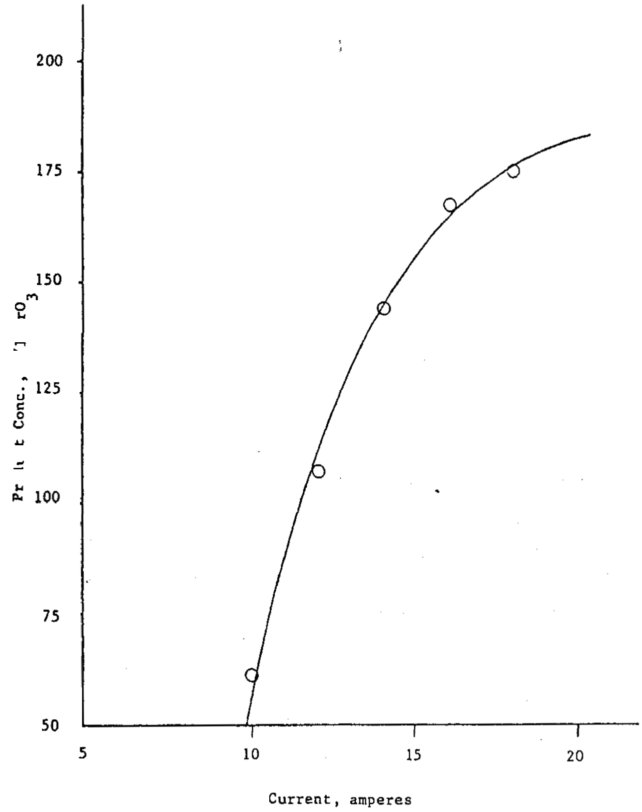

Fig. 3—Chromic Acid Electrodialysis

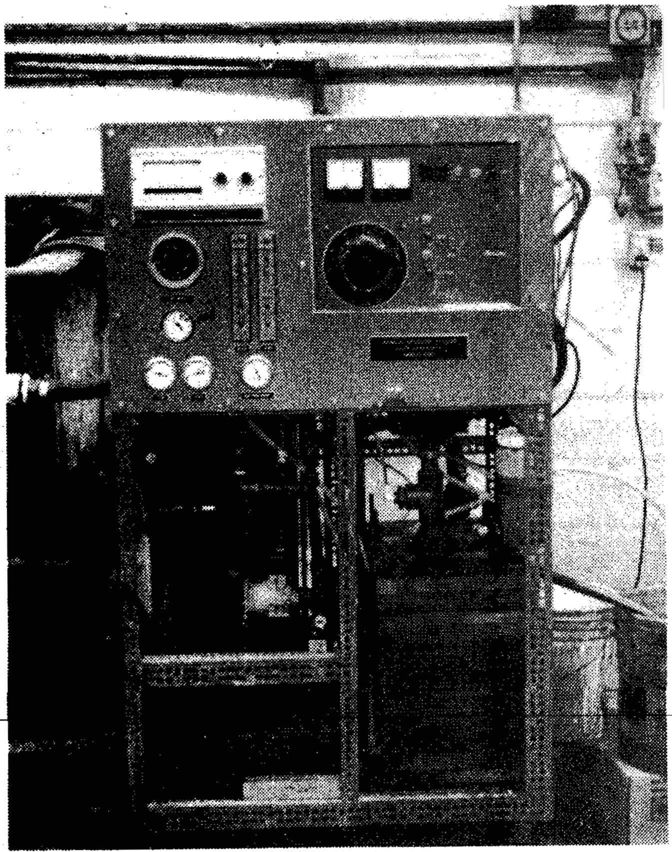

Fig. 4—Electrodialysis Unit on Chrome Line.

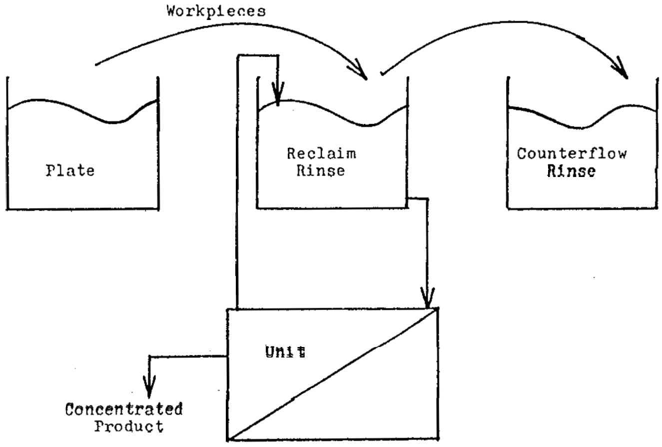

Fig. 5—ED Treatment of Chrome Line.

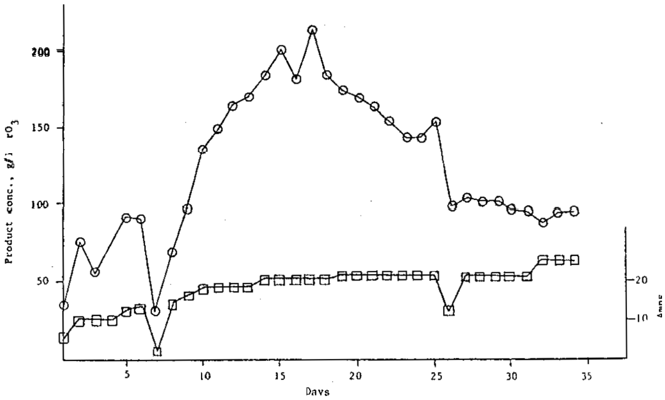

Fig. 6—Chrome Product Concentration.

to exhibit a reasonable life, to see what operating conditions must be used, to decide what modifications must be made to optimize chrome recovery during later stages of the project and to familiarize the plating room personnel with operation of the electrodialysis equipment. The recovery unit was to run directly on the drag-out solution without any adjustment in or accommodations by the normal plating operation. During this time the unit was run for approximately 250 hours over a period of more than two months. Operation was during the day shift of a three-shift operation. Concentrations of product samples taken at the end of each operating run together with the operating currents are plotted in Figure 6. During the first part of the period the current on the stack was increased slowly to a maximum of 20-21 amps at Day 10, where it was maintained for the remainder of the period. Product concentration also increased, as expected from the laboratory data, and remained relatively high in the 160-212 g/l chromic acid range until Day 26 when it fell sharply. The chief operating difficulty during the period was the high temperature acquired by the rinse solution due to heating by the pumps and the DC current applied to the stack. Most of the time it was significantly greater than 100° F, the recommended maximum operating temperature, and caused extensive slippage between the stack spacers and membranes, eventually leading to external and internal leakage. It is to this leakage that the sharp drop in product concentration is attributed and, indeed, the highest observed rinse temperature of 118° was reached on the previous day. Rinse concentration data during this operating period are incomplete but were in the 50-70 g/l CrO_3 range, giving product/feed concentration ratios of 2-4. These ratios can, of course, be markedly improved by operating simultaneously with the plating operation to prevent chrome buildup in the rinse and/or increasing the stack capacity as required.

At this point the test program was interrupted for equipment inspection and evaluation, construction and installation of a new stack designed to minimize slippage problems, and installation of a cooler in the rinse tank. Disassembly of the stack revealed no general failure of the membranes but several were torn and wrinkled due to displaced spacers. Others had developed pin-holes. Some spacers had extruded to partially block the flow path and manifolds and there was a general misalignment of the stack plies, again, probably attributable to the high temperatures. At this time, or at subsequent re-startup attempts, all wetted stainless-steel flowmeter fittings had to be replaced, viton "O" installed in all unions and filters and a replacement plastic impeller housing for the feed pump was required. The second test period was started a few weeks ago but no correlated data is yet available. Plans are for the ED unit to run concurrently with the plating shifts and to increase recovery capacity by increasing membrane area with a larger stack or additional units. Lower rinse concentrations should then be able to be maintained. With the addition of the cooler in the rinse solution, higher current densities can also be explored. The outlook for use of ED for chromic acid recovery is promising but it appears that high current densities will be required to obtain a product of plating concentration, that cooling will be necessary and that, relative to treatment of other bath types, more membrane area will be needed for equivalent metal recovery.

The second membrane system being examined for potential usefulness to the electroplating industry is Donnan dialysis. This process uses the permselective properties of ion-exchange membranes to establish a Donnan equilibrium between two solutions of electrolytes separated by the membrane. In contrast to electrodialysis, only one type of membrane is used; either cation- or anion-permeable. For example, in the case of a cation-exchange membrane, the anions in the two solutions are prevented from inter-diffusing across the membrane but the mobile cations will redistribute themselves between the two solutions on either side of the membrane until equilibrium is reached and the ratios of all similarly charged cations are equal:

$$(C_{il}/C_{ir})^{1/z} = (C_{jl}/C_{jr})^{1/z} = (C_{kl}/C_{kr})^{1/z} = K$$

where i, j, and k are cationic species, z their valence, C their concentration and r and l refer to the left sides of the membrane.

Any multivalent ions present in the solutions will equilibrate at higher ratios than the monovalent ions. The driving force for the cation exchange is the system's displacement from the equilibrium ratios and can be controlled by manipulation of the solution concentrations. If the concentration of one cation species is substantially increased in, say, the left or stripping solution, the total cation concentration is maintained due to the impermeability of the membrane for anions and the principle of electroneutrality as applied to the solutes. However, in order to approach equilibrium, the net effect is the diffusion of any other cationic species in the right-hand solution from right to left across the membrane, against the concentration gradient, to ultimately reach a concentration many times that remaining in their original solution. They are replaced by counter-diffusion of the added cation. The major variables affecting the transfer rate are temperature, concentration and solution flow characteristics at the membrane face. In practice, membrane configuration can be plate-and-frame (similar to the ED multicell), tubular or hollow fiber and the process regarded as a continuous ion-exchange system.

The feasibility of the process has been examined in the laboratory for the separation and concentration of uranyl and lanthanum ions (4), water softening (5), nutrient removal from secondary sewage effluents (6) and, in the present case, nickel removal from plating rinses. The early tests of nickel solutions were performed on plate-and-frame apparatus adapted from the ED membrane stack shown on the module in Figure 2 and schematically in Figure 1. Commercial cation-exchange membranes in sheet form were used. Dilute nickel feed solution was pumped repeatedly through a single feed cell and 0.5-1 N H_2SO_4 stripping solution recirculated through two flanking concentrating cells. Typical results are shown in Table II.

As can be seen, a 20% reduction (% cut) in nickel per pass through the unit was realized in the feed solution by exchange with strip solution hydrogen ions and the recovered nickel was concentrated in the strip solution up to 50 times its original feed concentration. In another experiment a sulfuric acid stripping solution was recirculated for 40 hours against a once-through feed solution held between 25 and 50 mg/l nickel. The strip was maintained at 1.0 - 1.5 normal by the periodic addition of acid but no other adjustments were made. At the end of the experiment the nickel concentration in the

TABLE II
NICKEL RECOVERY BY DONNAN DIALYSIS

Ni Feed Conc., mg/l				
in	*out*	*% Cut*	*Ni Strip Conc. mg/l*	*Strip/Feed (in) Conc. Ratio*
30	24	20	710	24
24	19	21	780	33
20	16	20	830	42
13	10	23	870	67

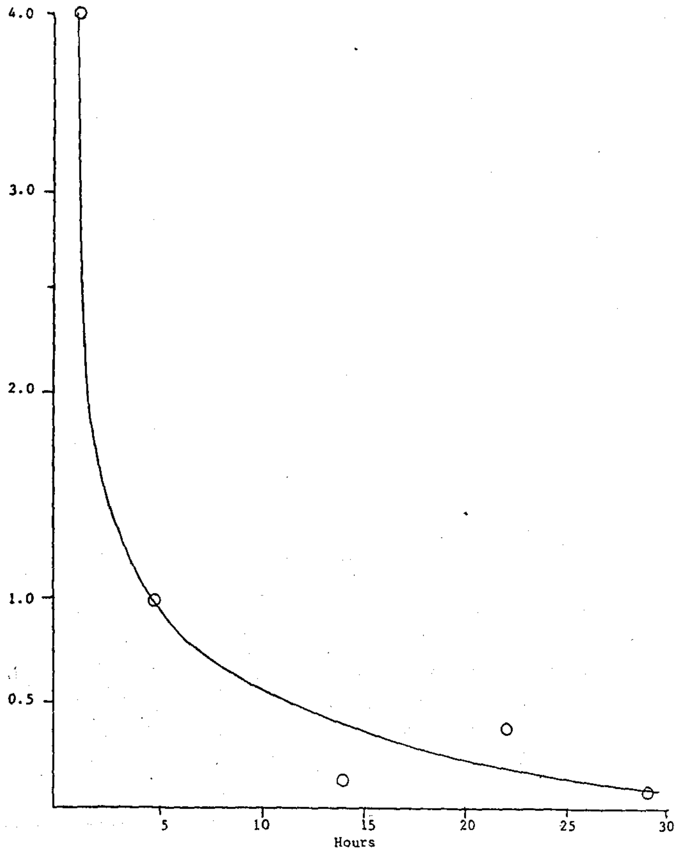

Fig. 7—Nickel Recovery by Donnan Dialysis.

strip had increased to 14 g/l, a concentration ratio of 300, without any decrease in transfer rate or percent removal, indicating no significant decrease in driving force. Feed pH was 1.75 to 6.0 during the experiment.

If, in addition to the strip, the rinse or feed solution is also recirculated, extremely low residual nickel concentrations can be attained with Donnan dialysis. Figure 7 is a plot of the nickel concentration in a simulated rinse where an initial concentration of 4 mg/l nickel was reduced to .07 mg/l after 29 hours continuous dialysis. Again, only a single cell was used and much more rapid removal rates would be anticipated with an increase in membrane area. Higher initial concentrations could also be easily treated at the expense of additional treatment time or equipment size. It is, of course, possible and perhaps sometimes desirable to flow both feed and strip solutions through the exchanger on a once-through basis. The data demonstrate the possibility of polishing some plating effluents to fractional ppm with a very simple technique and offers the hope of meeting very low effluent standards.

We have also performed some Donnan dialysis work using ion-exchange membranes in tubular form. The tubes were made by DuPont from their Nafion ion-exchange resin and had an inside diameter of .025". A shell and tube exchanger containing about 380 individual tubes, or 13 ft² of membrane area, was used. The aim was to verify the effects of certain operating variables on nickel transport rate. Results are shown in Figure 8 where flux in g/hr/380-tube module is plotted versus total feed flow rate. Each curve represents a fixed nickel concentration and at each concentration level the flux increases with flow rate. This is typical of film-controlled membrane processes where the thickness of the stagnant layer at the membrane surface can be reduced by increasing fluid velocity. The increase in flux with bulk solution concentration at equivalent flow is also consistent with a film controlled process where diffusion to the membrane face is critical.

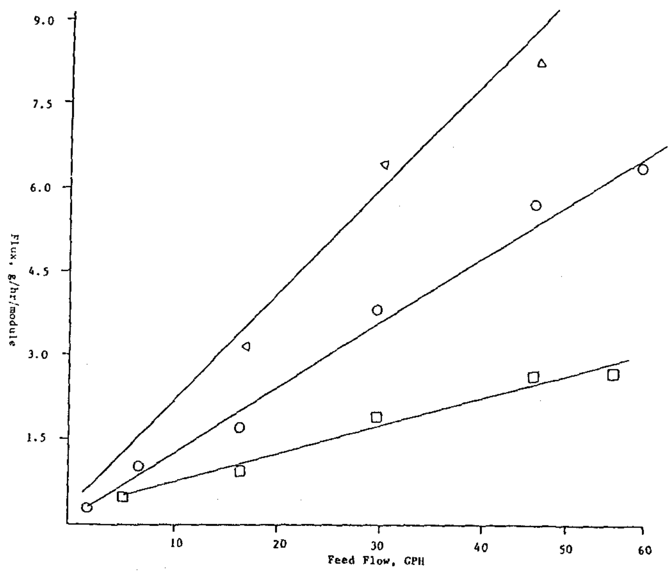

Fig. 8—Donnan Dialysis Transport Rate vs. Flow Rate.

On the basis of the laboratory results a Donnan dialysis unit was constructed for field testing to demonstrate nickel recovery from the rinse water on a Watts-type nickel plating line. The unit consists of four vertically mounted shell and tube Nafion exchangers fabricated by DuPont and piped to be able to run in parallel or in series, plus two auxiliary tubes arranged for series flow only. Each tube provides 20 ft² of membrane area. A schematic of the feed side hydraulics only is shown in Figure 9. Strip solution is always up,

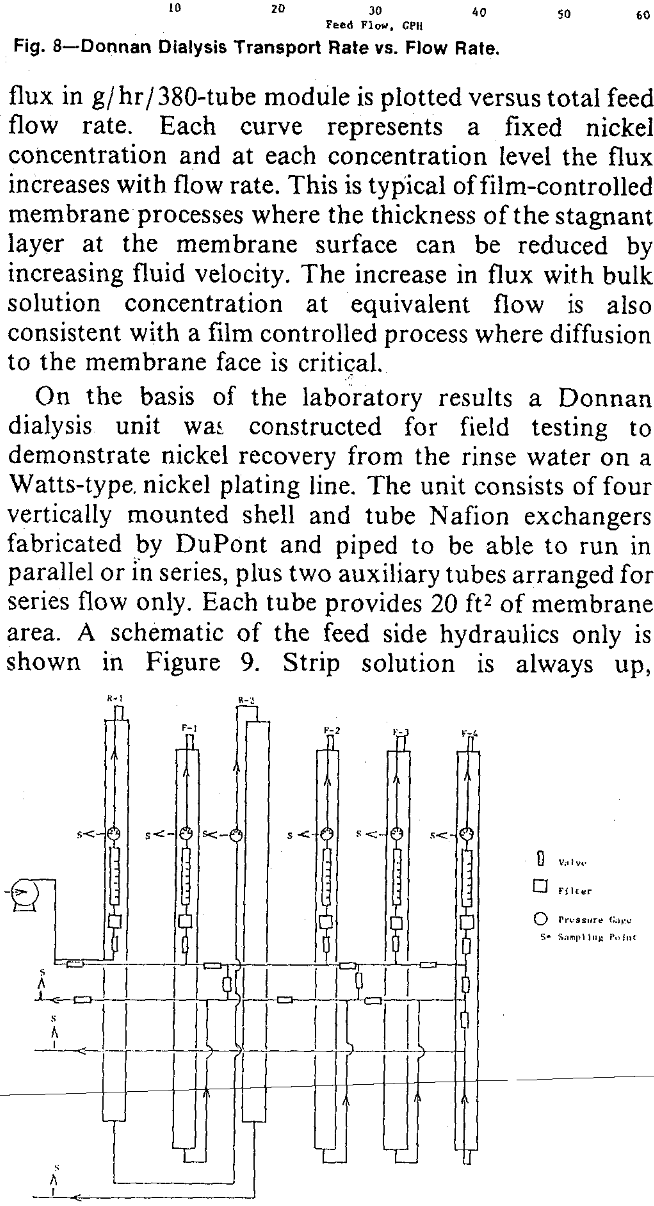

Fig. 9—Feed Side Flow Schematic.

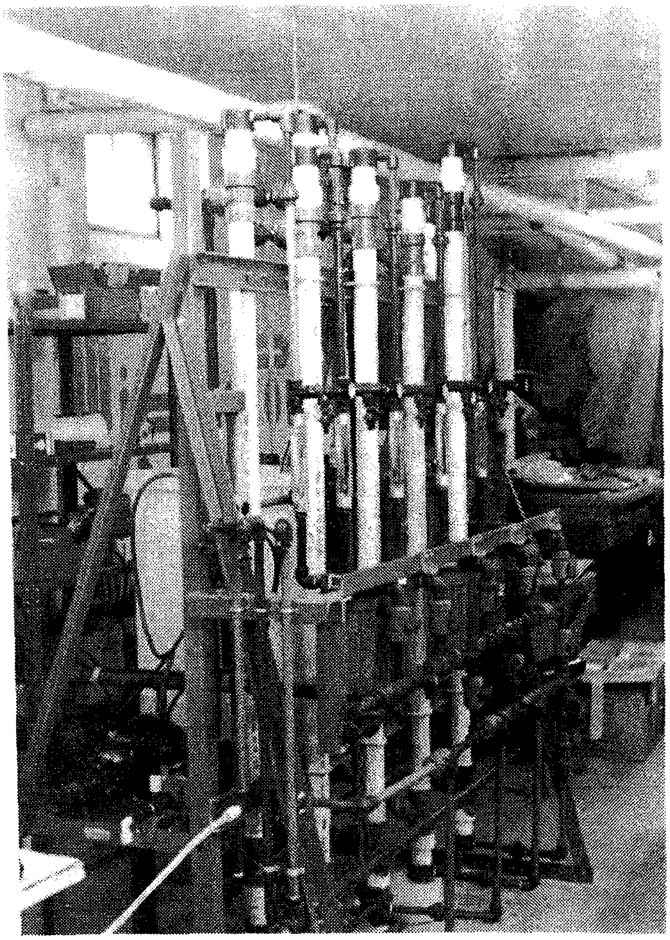

Fig. 10—Tubular Donnan Dialysis System.

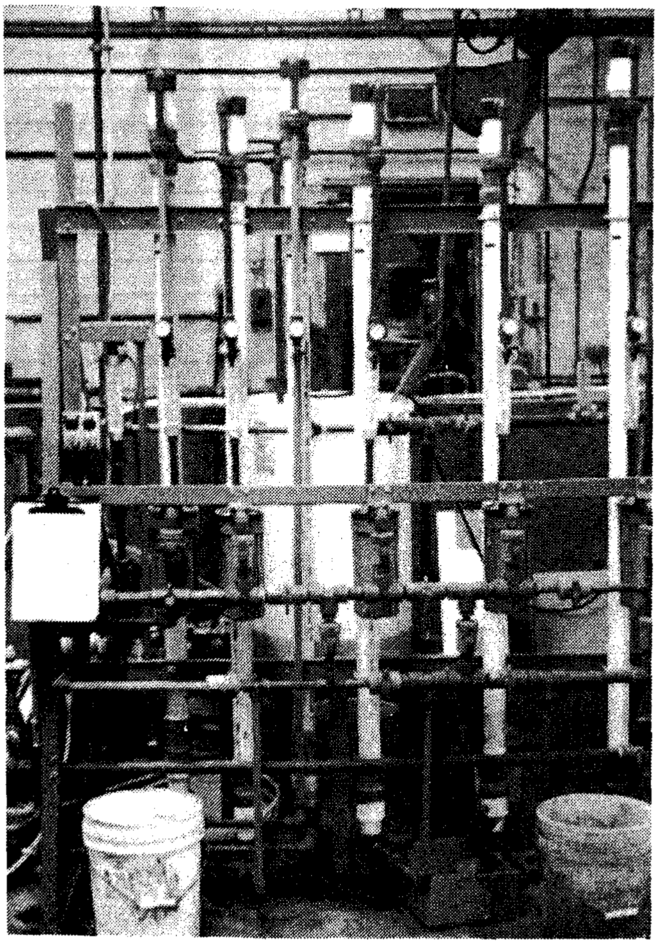

Fig. 11—Donnan Dialysis System on-site.

counterflow and parallel. Individual valves, pressure gages, flowmeters and filters control the flow through each tube. A photo of the completed unit undergoing hydraulic testing is shown in Figure 10. Pumps for feed and strip solutions are mounted at the rear of the unit. Installation on-site was completed only about two months ago. In operation, the first rinse of a counterflow sequence, currently averaging 0.5 g/l nickel, is recirculated through the tube-side of the modules and a 1-2 normal acid strip pumped through the shell side from a separate reservoir. Nickel-laden strip solution is to be used to replenish the plate tanks, as required, and the acid concentration renewed daily. Figure 11 is a view of the installed unit. The strip reservoir can be seen in the rear. Preliminary results are consistent with the laboratory tests in yielding a nickel transfer rate of about 2 g/hr/ft^2 depending chiefly on variation in rinse concentration.

After collecting preliminary data on the performance of the individual tubes and checking the several possible operating modes, the unit will be adjusted to optimize nickel recovery and minimize counterflow volume. The final results will be used to determine what type of recovery operation is best suited for Donnan dialysis and as a basis for design of a prototype commercial unit. One interesting concept is to use Donnan dialysis as the final step in a sequence of treatment processes to produce very low contaminant levels in the final effluent. Processes such as electrodialysis, which have relatively higher recovery rates and more concentrated products would do most of the reclaim work. In any event, Donnan dialysis seems certain to become a useful metal recovery and pollution control technique.

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