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Project Summary

Evaluation of Donnan Dialysis for Treatment of Nickel Plating Rinsewater

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A program to demonstrate the feasibility of metal salt recovery and pollution control by ion selective diffusion, also known as Donnan dialysis, was conducted on a Watts-type nickel plating line. The objective of the program was to demonstrate the Donnan dialysis system for recovery of nickel utilizing the tubular membrane configuration and to determine the suitable operating conditions for this equipment.

Several modules, consisting of tubular cation exchange membrane material mounted within a shell, were used to remove nickel ion from plating rinsewater with accompanying replacement of the nickel by hydrogen ion (supplied by sulfuric acid stripping solution). Recovery rates were determined at various operating conditions in order to specify the equipment for commercial use with emphasis on practicality, economics, reliability, and limitations.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, 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

Current concern over the presence of metallic ions in the watershed has caused the government to restrict and regulate wastewater discharge practices. This concern prompted industry to investigate certain recovery processes where the technology is sufficiently advanced to offer payback and compete with conventional disposal methods. Three processes depend on membranes for effecting separation: reverse osmosis, electrodialysis, and Donnan dialysis (also known as ion diffusion separation). Driving force for the first two processes are respectively pressure and electrical potential. Driving force for Donnan dialysis, however, is the membrane potential related to concentration differences across the membrane.

Utilizing the permselective properties of ion-exchange membranes one can cause an equilibrium to become established between two solutions of electrolytes separated by the membrane. In the case of the cation exchange membrane used in this project, the anionic species in the solutions are prevented from diffusing while the mobile cationic species will distribute themselves until at equilibrium:

$$\left(\frac{C_{il}}{C_{ir}}\right)^{1/z} = \left(\frac{C_{jl}}{C_{jr}}\right)^{1/z} = \left(\frac{C_{kl}}{C_{kr}}\right)^{1/z} = k$$

Where i, j, and k are cationic species, z is their respective valence, C is concentration, and l and r refer to left and right sides of the membrane. The driving force for the cation transfer from one side to the other is, therefore, the magnitude of the systems displacement from equilibrium, and this driving force can be affected by varying the solution concentrations. The extent that equilibrium conditions will be achieved depends on electrolyte concentration, membrane properties and operating conditions.

This program studied Donnan dialysis as a means of concentrating nickel ions from plating rinsewaters using hydrogen ions from dilute sulfuric acid as the other mobile cationic species.

Procedure

A series of preliminary tests was performed with the unit to determine operating characteristics and to prepare for later tests. Simulated nickel rinse solutions were dialyzed at flows between 0.063 and 3.78 l/m (0.017 and 1 gal/m). Feed solution concentrations, flowing on the tube side of the membranes, were varied between 0.025 and 0.164 g/l (0.0014 lb/gal.) of nickel. Feed flows were varied from 0.44 to 2.84 l/hr (0.12 to 0.75 gal./m). Strip solutions of 0.5 and 1 Normal sulfuric acid flowed at rates from 37.8 to 378 l/m (10 to 100 gal./m) on the shell side of the membrane. Flux increased both with increased feed flow and increased feed (rinse) concentration. Percent removal was in the 40 to 50% range for all operating conditions except extremely low feed flow rates where removal of 75 to 85% was achieved. Strip concentrations of 0.5 and 1.0 Normal sulfuric acid gave identical results as long as the acid concentration was maintained. Also the flow direction, counter-current or concurrent, had no effect on the removal rates.

After this testing was completed, all membrane modules were replaced with newly fabricated perfluorinated ion exchange membrane tubular modules. Reconstruction of the unit was carried out to accommodate these new modules as well as to provide greater flexibility in operating conditions. A total of six Nafion®* mass exchanges were supplied by DuPont and installed in two groupings designated front (F-1, F-2, F-3, and F-4) and rear (R-1 and R-2). Piping and valving allowed for choice of either parallel or series feed flow in the front exchangers each of which was fitted with a pressure gauge, sampling port, cartridge filter and flowmeter. The rear exchangers were piped for series flow only. All of these fittings were located downstream of the system to allow for product sampling. The accompanying feed side flow schematic (Figure 1) illustrates the piping and valving described above. Note that this schematic shows only the feed (rinse) flow which is always downflow and always on the tube (inner) side of the Nafion® membrane. The strip solution (not shown) is always counter-current and upflow and always in parallel for the front four exchangers and in series for the rear two.

The refitted dialysis unit was installed at Seaboard to treat the first of three counterflow rinses that follow the plating tanks and a spray rinse on a Watts-type nickel electroplating line. Rinse water from a second nickel line was also discharged through the circulating counterflow tank giving a total rinse water input to this tank of approximately 1136 l/hr (300 gal./hr). The Donnan system was installed on this first rinse tank, pumping nickel-contaminated rinsewater through the Donnan system and returning the product (slightly acidic because of the exchange of H^+ for Ni^{++}). The sulfuric acid strip tank (not shown in Figure 1) constantly recirculated acid stripping solution through the strip side of the Donnan modules and back into the strip tank. Because of osmotic flow through the membrane, the volume of a stripping solution slowly increased, necessitating a periodic return of the nickel-laden stripping solution back to the nickel bath. The bath could accommodate the volume because of evaporative losses.

The next series of tests was designed to determine the performance of the exchangers and to decide on the most convenient method for handling the strip and rinse solutions. Initial operations were undertaken with parallel feed flow to the four front exchangers. The resulting data (Table 1) showed that both increases in feed concentration and feed flow rate caused an increase in the transport rate, recorded as flux, which at 1136 l/hr (300 gal./hr) was greater than at 681 l/hr in spite of a slightly lower feed concentration. These

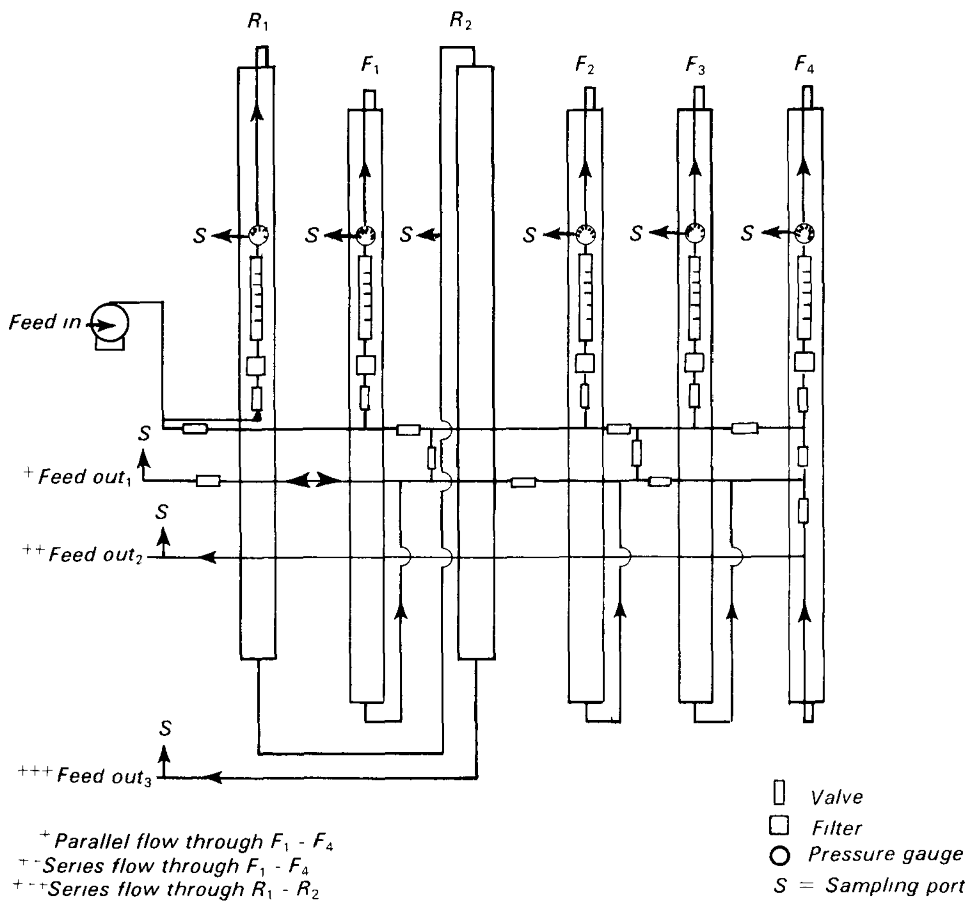

Figure 1. *Feed side flow schematic*

*Mention of trademarks or commercial products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency

Table 1. *Initial On-Site Results*

Feed Flow Rate (l/hr)	Average Feed Concentration (g/l)	Average Nickel Transport (g/hr)	Average Flux (g/hr/m^2)
681	0.72	163	2.15
1136	0.66	176	23.7
454	0.80	210	28.0

variations did not seem to affect transport rate as long as the strip solution (H_2SO_4) concentrations remained at 1 Normal or above.

The front four exchangers were next run in series. These runs showed generally lower nickel transport. This was expected since the initial rinse concentrations were gradually reduced on passing through each successive exchanger and, as expected, the flux rate decreased when the nickel concentration in the feed (rinse) decreased.

Results of further tests showed that exchanger F-4 was more efficient than the other three front exchangers. Subsequent investigation showed this tube was of an improved design that indicated the possibility of upgrading the total performance of this type of equipment in the future. Additional testing was performed to assess the effects of increased acidity in the strip solution, to evaluate the rear exchangers, which were hard piped for series flow, and to investigate the effects of operating the mass exchangers with the rinse on the shell side and the strip on the tube side of the membranes.

In all, approximately 71 completed runs were performed to assess the performance of this dialysis unit under various operating conditions. In summary, the modes of operation were the following:

Strip solution on the shell side, and:
- front 4 exchangers in parallel
- front 4 exchangers in series
- investigation of single exchanger
- rear exchangers only

Strip solution on tube side, and:
- front 4 exchangers in parallel
- front 4 exchangers in parallel with rear exchangers in series

No less than three runs were performed to establish average flux values. All data used in the project report, summarized here, are listed in the appendix of the full report.

Results and Discussion

An investigation of parallel versus series flow through the membrane modules showed significant differences in performance. In all cases parallel operation gave at least 15% higher nickel flux values, confirming that the process is concentration sensitive. Combined parallel-series operation gave lower flux values than would be expected and suggests that series operation should probably be restricted to polishing applications while parallel operation is particularly indicated for higher recovery rate systems.

The most effective operations were those runs in which the exchangers were piped in parallel configuration with a feed concentration of 0.5 g/l (0.004 lb/gal.) or greater and with feed flow rates equal to or greater than 795 l/hr (210 gal./hr). With the exchangers used in these tests, flux was significantly greater when feed was circulated through the tubes and strip was circulated on the shell side of the membrane (outside of the tubes).

Applications certainly exist for Donnan dialysis treatment of plating rinsewaters utilizing either tubular membrane modules or plate and frame multi-cell stacks. The exchange of H^+ ions for Ni^{++} ions will produce a slightly acidic effluent, which must be neutralized in an end-of-pipe treatment system before discharge. The stripping solution containing the nickel may, in most cases, be returned directly to the plating bath. Donnan dialysis should also be considered as a treatment complementing other technologies as part of the overall recovery and pollution control facility.

Conclusions and Recommendations

Donnan dialysis is an effective process for recovery of nickel ion from electroplating rinse water.

By recirculating rinse water from a Watts-type nickel plating line through a Donnan dialysis unit fitted with permselective cation exchange membranes and utilizing a strip solution of 1 Normal sulfuric acid as the source for other cation species, it was possible to remove over 6.6 grams of nickel per square meter of membrane per hour (0.004 lb/ft^2/hr) from the rinse water thus prolonging the life of the rinse solution. This process generates a concentrated solution with nickel ion levels in excess of 30 grams per liter (0.25 lb/gal.) and is useful to replace the nickel removed from the electroplating bath and to help control the plating batch pH.

Economic advantages lie in the savings of raw material cost, the reduction of conventional disposal costs, reasonable capital investment costs, and lower operating costs than the electrical and high-pressure-driven dialyses processes.

Variables affecting the rate of recovery of nickel ion from wastewater have been throughly examined both in controlled laboratory tests and in actual onsite operations of the Donnan dialysis unit. Separation in this unit was accomplished using modular hollow tube cation exchange resin of the perfluorosulfonic acid type. This process also can be carried out using the conventional plate or frame configuration, such as is typical of the electrodialysis multicell.

Plate and frame multicells, while larger than tubular modules, have been shown to enjoy long life expectancy in nickel recovery operations. Such stacks should be tested in series and parallel combinations under operating conditions similar to those described herein. Techniques for nickel recovery by this method should then be adapted for recovering other ionic species.

The Donnan dialysis system generates a mildly acidic effluent because of the exchange of H^+ for Ni^{++} that can be combined with other flows to the end-of-pipe neutralization system.

The full report was submitted in fulfillment of Grant No. R-804655 by the Seaboard Metal Finishing Company, Inc. The report covers the period March, 1978 to June, 1979, and work was completed as of June, 1981.

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***Mary K. Stinson** is the EPA Project Officer (see below).*
The complete report, entitled "Evaluation of Donnan Dialysis for Treatment of Nickel Plating Rinsewater," (Order No. PB 85-200 046/AS; Cost: $8.50, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
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