



## *Project Summary*

# Demonstration of Zinc Cyanide Recovery Using Reverse Osmosis and Evaporation

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A field test was conducted to demonstrate closed-loop recovery of zinc cyanide rinsewater at a job shop plating facility. Since the zinc cyanide bath operates at room temperature with very little evaporation from the bath, reverse osmosis (RO) treatment of the rinsewater must be supplemented by evaporation in order to achieve the volume reduction necessary for return of a concentrate to the plating bath. The permeate from the RO unit was recycled to the first rinse after plating, while the distillate from the evaporator was recycled to the second rinse after plating. Continuous, unattended operation of this system was demonstrated with no adverse effects on plating quality.

Spiral-wound PA-300 membrane modules were used in the RO unit. Periodic tests were conducted throughout the demonstration to characterize membrane performance under standard conditions. These tests indicated a gradual loss in membrane flux and rejection. After 3,000 hours of exposure to the rinsewater, the membranes were cleaned by flushing with a cleaning solution. The cleaning resulted in nearly complete restoration of flux and rejection. The gradual loss in membrane performance is thus attributable to fouling of the membrane by particulates in the rinsewater. Such fouling can be reduced by better pre-

filtration and reversed by periodic cleaning.

The economics of the combined RO evaporation system were assessed for a system designed to provide rinsing equivalent to the present two-stage counter-current rinse at the demonstration site. The analysis showed that the total operating cost (including amortization) was somewhat less for the combined RO evaporation system than for evaporation alone. The minimum cost occurred for 90% water recovery in the RO system. However, credits for rinsewater recovery were insufficient to completely off-set the total operating cost of the recovery system.

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*This Project Summary was developed by EPA's Industrial Environmental 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

Wastewater treatment technologies for the electroplating industry can be broadly classified as end-of-pipe destruction processes or in-plant recovery processes. The end-of-pipe destruction processes treat a total shop effluent to remove a mixture of heavy metals. At present it is neither technically nor economically feasible to recover and recycle metals from the end-of-pipe processes (1). In-plant recovery processes, however, treat rinsewater from a specific plating bath (or other operation) making it possible to recover and return the heavy metals to the plating bath.

Because of the inherent disadvantage of end-of-pipe treatment — loss of valuable plating chemicals, cost of treatment chemicals, cost of sludge disposal — increasing attention has been focused on closed-loop recovery methods. In many cases, the economics of closed-loop recovery have been very favorable, resulting in rapid payback on the capital investment for recovery equipment (2).

Aside from a few applications in which closed-loop recovery can be achieved by countercurrent rinsing alone, some technique must be used to remove the dissolved plating chemicals from the rinsewater. Although other techniques are under development, evaporation, reverse osmosis (RO), and ion exchange are the most commonly used processes for rinsewater recovery (1,3). Each of these techniques has particular advantages and disadvantages and the best technique or combination of techniques will depend on factors specific to each application.

A number of advantages can be cited for the use of RO in rinsewater recovery. These include low capital cost, low energy and operating costs, and minimal space requirements. However, there are also some limitations. The major limitations for RO are:

1. The membrane modules deteriorate with time and require periodic replacement. The rate of deterioration depends on the type of membrane, the rinsewater pH and temperature, and the concentration of other reactants in the rinsewater such as oxidants.
2. Reverse osmosis cannot produce a highly concentrated stream for recycle to the plating bath. Thus for ambient temperature baths, RO must be supplemented with

some other concentration technique, such as evaporation, in order to close the loop.

To date, RO has been applied primarily to the recovery of nickel rinsewaters. For nickel, the rinsewaters are relatively mild in pH (4-6) resulting in acceptable life for the conventional commercial membranes (cellulose acetate and aromatic polyamide). In addition, nickel baths operate at elevated temperatures where substantial evaporation occurs, and closed-loop operation can be achieved with RO alone.

Several programs, jointly sponsored by EPA and AES, have been conducted to evaluate the applicability of RO to plating baths other than nickel (4,5,6). Laboratory tests were conducted with a variety of newly developed membranes and rinsewaters with extreme pH levels (6). These tests indicated that of the membranes tested, the PA-300 was superior to the other membranes for treatment of copper cyanide, zinc cyanide, and chromic acid rinsewaters. The PA-300 membrane has since been commercialized (currently designated TFC-PA; manufactured by Fluid Systems Division of UOP) and is available in a spiral-wound modular configuration.

A field test was undertaken to evaluate the PA-300 membrane module for recovery of zinc cyanide rinsewater under realistic conditions. Zinc cyanide was selected because of the large volume of zinc cyanide plating done by the industry and because the high pH of the rinsewaters would provide a "worst case" test of the membrane for resistance to alkaline conditions. Since the zinc cyanide bath operates at room temperature, it was necessary to use an evaporator to supplement RO treatment and achieve the level of concentration necessary for closed-loop operation. This report summarizes and discusses the results of this field test.

## Methods and Materials

A mobile RO test system was leased from Abcor, Inc., and an evaporator was leased from Wastesaver Corporation for the duration of the field test. These two units were installed on an automatic rack, zinc cyanide plating line at New England Plating Co. in Worcester, Massachusetts. The overall schematic of the installation is shown in Figure 1. Feed to the RO system was withdrawn from Rinse Tank #1 and separated by the RO system into a permeate stream and a concentrate stream. For purposes

of design, it was assumed that the RO system would produce about 7.5 lpm (2 gpm) of permeate and would operate at 90% conversion. (Conversion is defined as the ratio of permeate flow to feed flow.) Thus the RO system would be fed at the rate of 8.4 lpm (2.22 gpm) and would produce concentrate at the rate of .8 lpm (0.22 gpm). The permeate was returned to Rinse Tank #1 and the concentrate was fed to the evaporator.

Since drag-in and drag-out were essentially identical for the plating bath and the rate of evaporation was negligible, there was no room in the plating bath for a concentrate stream. If the evaporator were fed only RO concentrate, it would have to evaporate it to dryness in order to prevent eventual overflow of the bath. In order to prevent precipitation of plating chemicals in the evaporator a 3.8 lpm (1 gpm) purge stream was circulated from the plating bath through the evaporator and carried the plating salts introduced with the RO concentrate back to the plating bath. That is, the evaporator concentrate was higher in concentration than the plating bath by the amount added by the RO concentrate. The distillate from the evaporator was collected in a holding tank and added at a controlled rate to Rinse Tank #2. A float valve operating off the level in Rinse Tank #1 insured that the rate of RO concentrate production was exactly balanced by the rate of distillate returned to Rinse Tank #2. A slight excess of distillate was produced to insure that the holding tank would always remain full; and the excess was permitted to overflow into the plating bath (.08 lpm). The steam rate was cut back to minimize overflow from the holding tank.

A flow schematic of the RO system is shown in Figure 2. Feed from the first rinse tank was withdrawn by a booster pump and passed through two string-wound cartridge filters in parallel. Both 1- $\mu$  and 20- $\mu$  filters were used at different times during the field test. Excess flow from the booster pump was returned to the rinse tank. After pre-filtration, the feed was pressurized to 48.6 atm (700 psi) with a multi-stage centrifugal feed pump and passed through three 102 mm (4-inch) diameter, spiral-wound, PA-300 modules arranged in series. Most of the concentrate from the third module was recycled to the suction of the feed pump in order to maintain the required feed flow rate through the modules. A heat exchanger

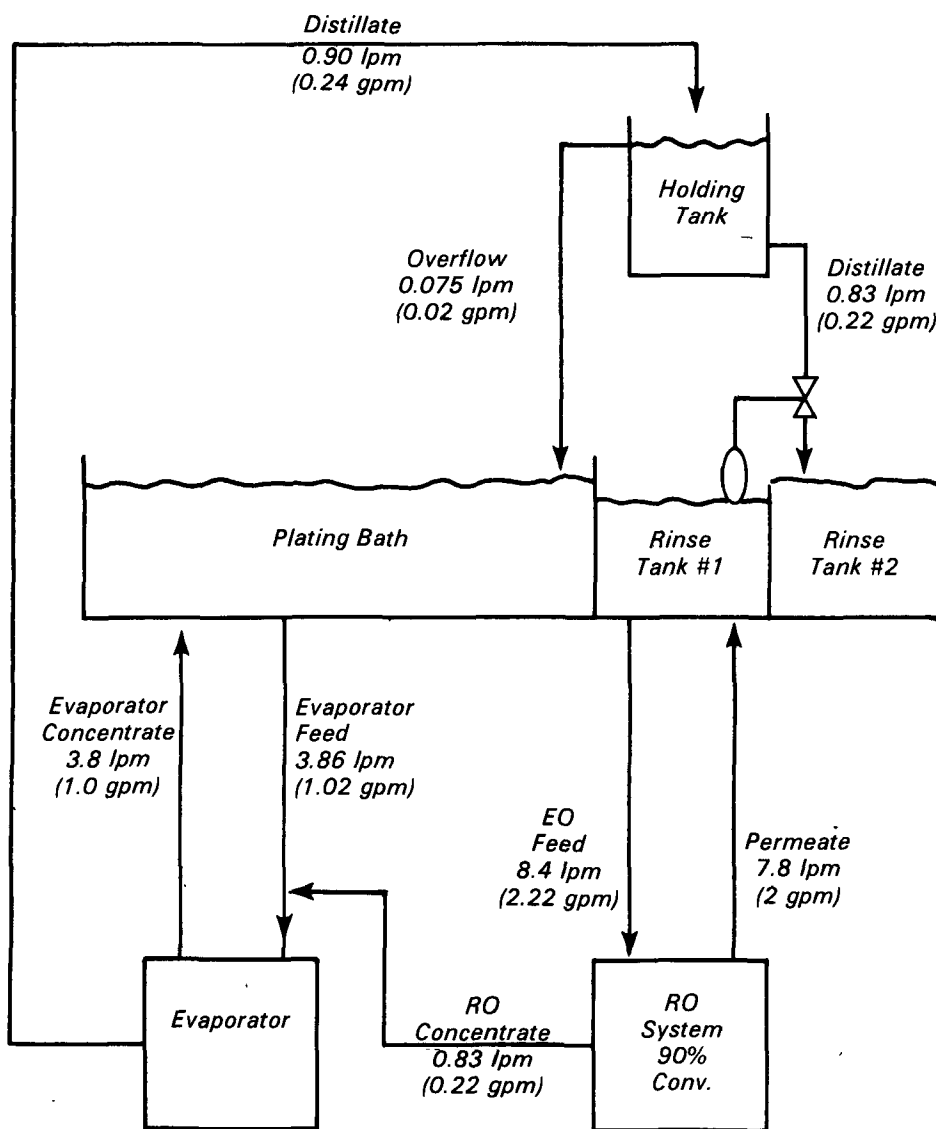


Figure 1. Overall schematic of RO/evaporator operation.

in the recirculation loop removed heat generated by the energy input of the pumps. A small flow of concentrate from the third module was fed to the evaporator (see Figure 1), and the permeate from the three modules was combined and returned to the first rinse tank. The instrumentation and controls for the RO system are shown in Figure 2.

In order to characterize membrane performance with a standard feed solution, the RO system was periodically operated in a total recycle mode using the auxiliary feed tank. For this mode of operation, the booster pump recycle line

was closed off, the concentrate line to the evaporator was opened, and the permeate was returned to the auxiliary tank rather than the rinse tank. The standard solution (generally a portion of plating bath diluted to 10% by volume or original bath strength) was charged to the auxiliary tank and the system was operated with total recycle until steady state was achieved. At steady state, the permeate flow rate for each module was measured, and samples of the feed and permeate from each module were obtained for analysis.

Typical operating conditions for both closed-loop and total recycle were:

Feed Pressure 48.6 atm (700 psi)  
 Recirculation  
 Flow Rate 37.8 lpm (10 gpm)  
 Temperature 21-32°C (70-90°F)  
 Concentrate 0.75 lpm (0.2 gpm)  
 Flow Rate closed-loop only

The flow schematic for the evaporator is shown in Figure 3. Steam was fed through a pressure reducing valve to a tube bundle submerged in the boiler section of the evaporator, and steam condensate was returned to the plant boiler. For most installations, a cooling tower is used to cool the water which is recirculated through the condenser section of the evaporator. However, for this installation it was more convenient to use recirculated chilled water since it was readily available at the installation site and the chiller had sufficient excess capacity. The evaporator was maintained under vacuum by circulating water through an eductor. Cooling water was added to the eductor tank to remove the energy input of the eductor circulation pump. Feed to the evaporator was controlled by a level switch (LS) and solenoid valve. Upon low level signal, the solenoid valve opened and feed was drawn by vacuum into the evaporator. The distillate from evaporation of the feed condensed, was collected in a tray below the condenser, and was continuously pumped back to the second rinse after plating (see Figure 1). The concentrate from the boiler section of the evaporator was continuously pumped back to the plating bath.

Typical operating conditions for the evaporator were:

Vacuum 0.87 atm abs.  
 (26-27 in. Hg)  
 Temperature 38-43°C  
 (100-110°F)  
 Steam <1.3 atm abs.  
 Pressure <19.7 psig  
 Concentrate  
 Flow Rate 3.8 lpm (1 gpm)

During the field test, the RO modules were cleaned using a cleaning sequence recommended by the membrane manufacturer. The modules were first flushed with 189 liters (50 gal) of water to remove the plating chemicals. A 0.1% by volume solution of Triton X-100, a non-ionic surfactant, was prepared and recirculated through the modules at a pressure of 48.6 atm abs (700 psi), a flow rate of 37.9 lpm (10 gpm), and a temperature of 49°C (120°F) for 45 minutes. After flushing with another

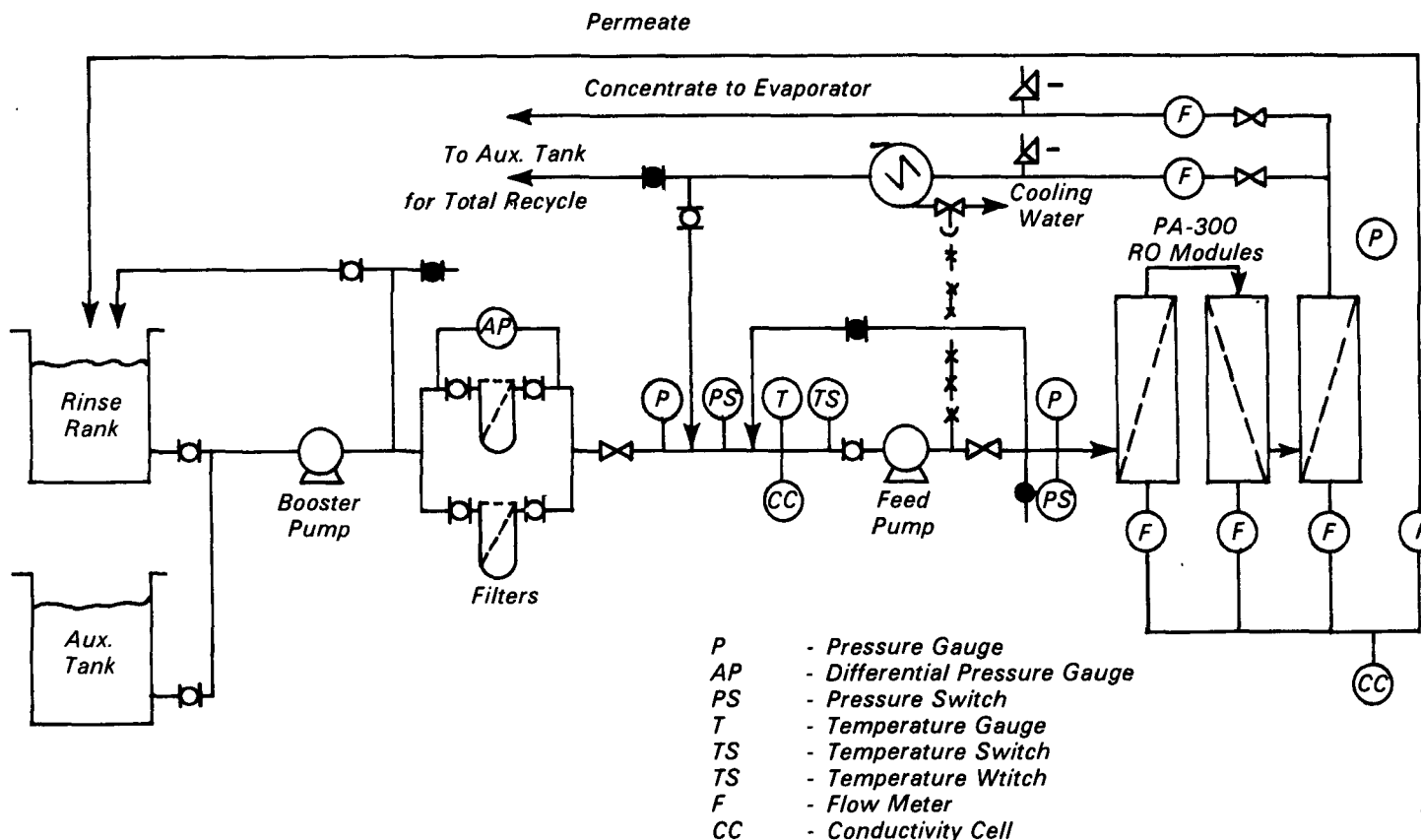


Figure 2. Flow schematic for RO demonstration system.

189 liters<sup>2</sup> of water, a 2% citric acid solution was prepared and adjusted to pH 3.0 with ammonium hydroxide. This solution was recirculated through the modules at the same conditions and for the same time as the Triton X-100. Following the citric acid cleaning the system was again flushed with water and returned to treatment of zinc cyanide rinsewater. Since the PA-300 membrane is rapidly degraded by chlorine, all water used for flushing and preparing cleaning solutions was dechlorinated by the addition of sodium sulfite.

Samples collected during the field test were analyzed for zinc (atomic absorption), free cyanide (selective ion electrode), total solids (gravimetric determination of residue), conductivity (conductivity bridge), and pH (electrode).

The nominal composition of the plating bath was:

Zn (as metal) 20,000 mg/l  
2.7 oz/gal

CN (as NaCN) 60,000 mg/l  
8.0 oz/gal  
Caustic 75,000 mg/l  
10.0 oz/gal  
Brightener 4 ml/l  
(700 Special) 4 gal/1000 gal

In addition to these compounds, polysulfide was regularly added to the bath for purification, and the bath also contained a large quantity of carbonates. The total solids concentration of the bath was in the vicinity of 350,000 mg/l (35% by weight).

### Conclusions

Closed-loop recovery of zinc cyanide rinsewaters can be achieved with a combined RO/evaporator system. Continuous and unattended operation of the system was demonstrated over one-week periods (Monday through Friday, three shifts per day). No adverse effects on plating quality were noted during the demonstration.

The single-effect vacuum evaporator was operated at about one-half of its rated capacity, and the vacuum was sufficient to keep the vaporization temperature below 43°C (110°F). The quality of the distillate was considered quite suitable for final rinsing.

Tests were conducted periodically to determine the flux and rejection performance of the three PA-300 spiral wound modules used in the RO system. Results for Modules #1 and #2 were in close agreement throughout the demonstration. Module #3 was concluded to be defective from the outset of the program and was removed after 3,000 hours.

The flux and rejection of Modules #1 and #2 gradually declined during the demonstration. Over the first 3,000 hours of exposure, the flux declined to about one-half of its original value and the zinc rejection, for example, declined from 99% to 97%. At 3,000 hours, the membranes were cleaned by flushing with a cleaning solution. The clean

- T - Temperature Gauge  
 P - Pressure Gauge  
 F - Flow Meter  
 LW - Level Switch

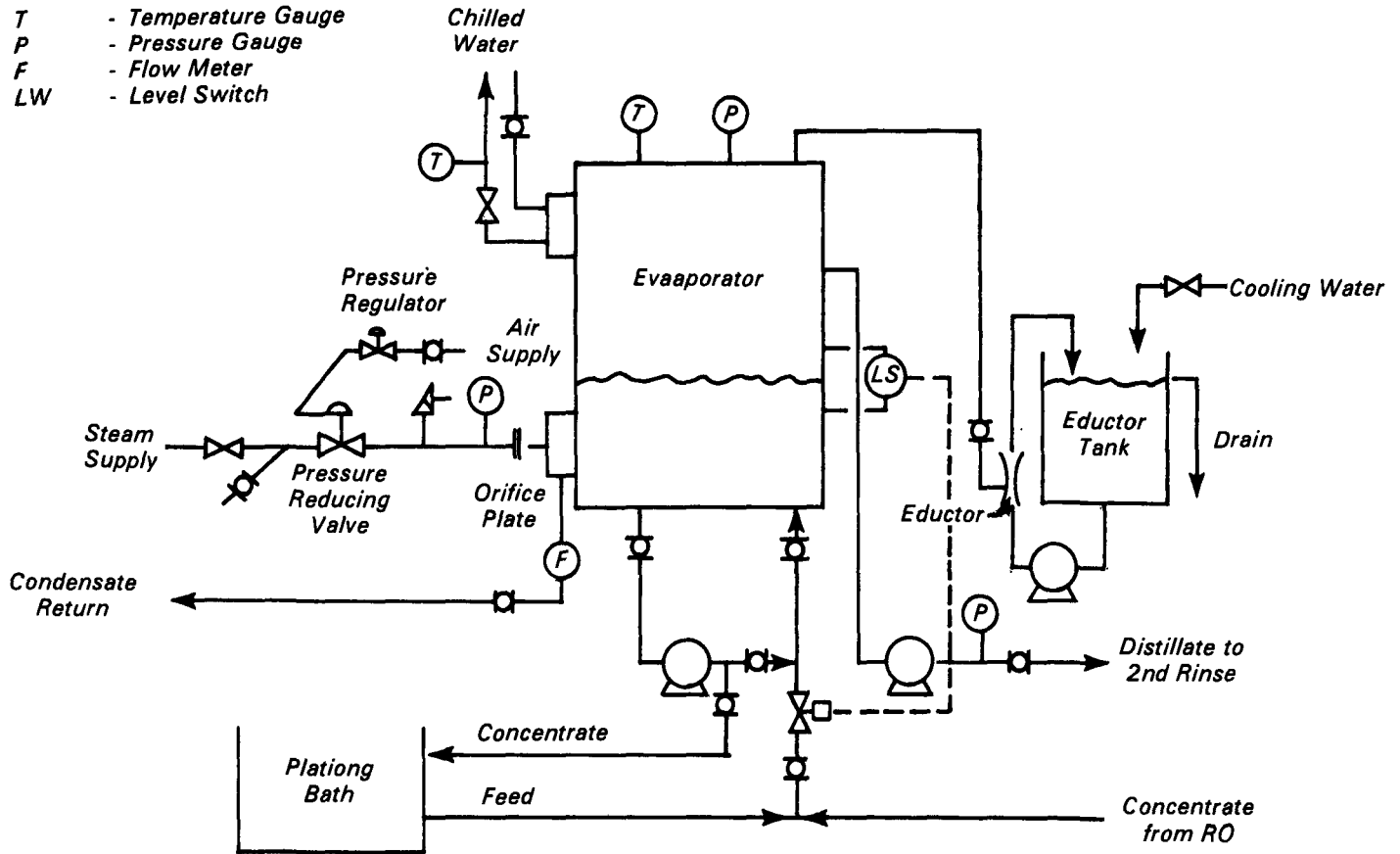


Figure 3. Flow schematic for evaporator.

resulted in nearly complete restoration of flux and rejection. The gradual loss in membrane performance is thus attributable to fouling of the membrane by particulates in the rinsewater. Such fouling can be reduced by better pre-filtration and reversed by periodic cleaning.

Following the field test, Module #2 was cut open and unwound for inspection. The membrane was fouled with a thin layer of what appeared to be sulfide sludge. (Polysulfide is used as a bath purifier). Examination of the module internals revealed that some deterioration in the strength of the membrane backing material had occurred. However, this produced no gross effects on the performance of the modules as observed during the field test.

The economics of the combined RO evaporation system were assessed for a system designed to provide rinsing equivalent to the present two-stage counter-current rinse at the demonstra-

tion site. The analysis showed that the total operating cost (including amortization) was somewhat less for the combined RO evaporation system than for evaporation alone. Total operating costs were calculated for various RO system water recoveries, and the minimum cost occurred for 90% water recovery in the RO system. However, credits for rinsewater recovery were insufficient to completely off-set the total operating cost of the recovery system. Energy costs for evaporation using a double effect evaporator were 4-5 times greater than those for RO. Continuing escalation of energy costs would provide further incentive for a combined RO evaporation system.

### Recommendations

On the basis of this field test and previous laboratory tests (6) the PA-300 membrane can be recommended for the treatment of cyanide rinsewaters on a commercial scale. Application to copper cyanide recovery appears to be partic-

ularly attractive because of: 1) the lower pH of copper cyanide relative to zinc cyanide, 2) the higher value of copper relative to zinc, and 3) the higher evaporation rate from the copper bath which would permit closed-loop operation with RO alone (no evaporator required).

Additional development of the PA-300 or similar membranes is recommended with particular emphasis on the development of modules containing materials which are highly resistant to pH extremes. In particular, a more alkaline-resistant membrane backing material should be developed for cyanide applications.

Data should be obtained on the life of PA-300 (or similar) modules for longer exposure times (>4,200 hours). This data can be conveniently and inexpensively obtained by "soaking" the module in a solution of the plating bath diluted to simulate concentrated rinsewater. The flux and rejection of the modules can then be determined

periodically. These soak tests will provide information on the resistance of various module components to attack by the major constituents of the bath (e.g. OH<sup>-</sup>).

In view of the good acid resistance exhibited by the PA-300 membrane in laboratory tests (6), it is recommended that a field test and long-term soak tests be conducted using PA-300 modules and low pH rinsewater such as acid copper. (In future field tests, the feed to the modules should be pretreated by passage through a 1 $\mu$  filter. The objective of these tests would be to extend the applicability of RO to pH levels below 2.5 (the lower limit for cellulose acetate membranes).

For evaporative recovery, development of a low capacity, low cost, mechanical vapor recompression evaporator is recommended. This type of evaporator is highly efficient and could be operated at a significantly lower cost than the combined RO/evaporator system tested in this program.

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*The complete report, entitled "Demonstration of Zinc Cyanide Recovery Using Reverse Osmosis and Evaporation," (Order No. PB 81-231 243; Cost: \$6.50, subject to change) will be available only from:*

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