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Recovery of Rinse Water and Plating Bath from Process Rinses Using Advanced Reverse Osmosis

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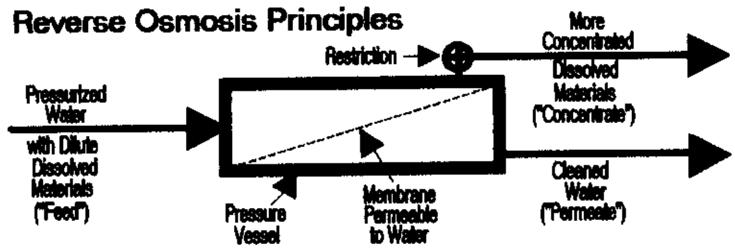
A. INTRODUCTION AND PROBLEM

Electronic parts makers, platers and other metal finishers require clean water rinses to remove plating chemicals from parts prior to the next process. The rinse water is sometimes expensive or in short supply. Furthermore, if the water is of poor quality, it must be pre-treated prior to use. The water is discarded after one use with conventional waste treatment, precipitation and clarification and a hazardous mixed metal sludge is generated which must be shipped to a hazardous waste landfill.

The cost for companies in terms of cash, possibly scarce water resources, ever tightening discharge limitations and perpetual liability for landfilled waste, requires that firms seek other solutions. The ideal solution is to develop economic point of use recycling and reuse systems. A technology that offers the potential for on-site recovery of a broad range of electronics and metal finishing applications is Advanced Reverse Osmosis (ARO).

B. ADVANCED REVERSE OSMOSIS EXPLAINED

WTI has modified and enhanced conventional reverse osmosis for use in plating applications. Reverse osmosis is a physical process whereby water containing dissolved materials can be cleaned by applying pressure to the solution and squeezing water through a membrane barrier which blocks other substances. The remaining material becomes more concentrated.



The ARO system design is very different from traditional reverse osmosis systems. With ARO, concentrations of 1,000 - 10,000 to 1 can be achieved using lower performance membranes. An ARO system can reconcentrate dilute solutions to at or near bath strength (typically a concentration of 40% to 70% is accomplished) without any evaporation or additional concentration technology.

This concentration is often sufficient for direct return to plating baths. Membrane materials and system components have been specially adapted to plating environments. Proper plastics and 316 SS (or Hastelloy C) components give the ARO system a long life in almost all plating operations. Custom designed sensors and controls manage the membranes. The degree of concentration, times of exposure, and pressures vary for every plating solution and membrane type. The variations are controlled by specialized software, the basic system remains standard.

In the ARO system, the cleaned water is returned to plating rinses while the concentrate is held in the ARO's internal storage tanks for further concentrating passes through the membrane until the required high concentrations are achieved. The schematic below (on the left) displays the "closed loop" nature of WTI's total recovery and recycle system. The diagram (on the right) shows a schematic of the pumps, sensors, membrane and internal storage tanks inside the ARO unit. Concentrate moves from the receiving tank to tank 3 and is finally returned for reuse to the bath.

ARO System Conceptual Schematic

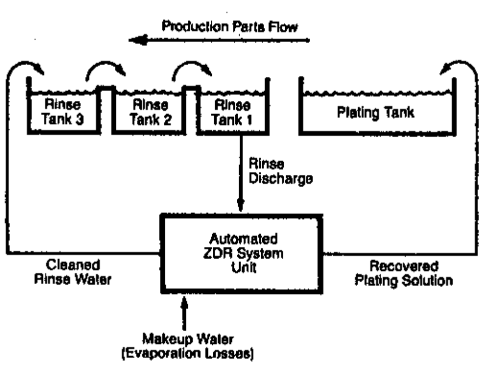
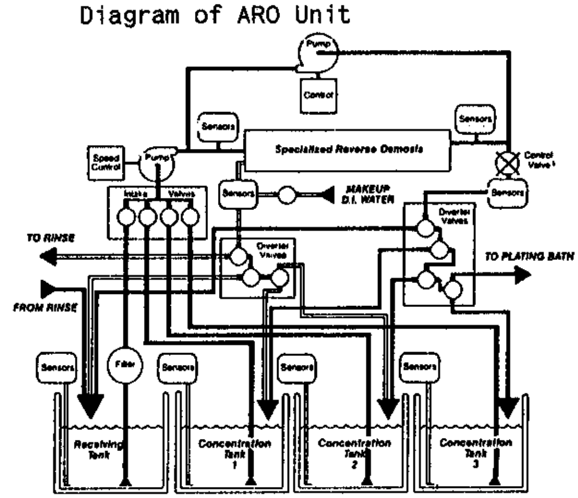


Diagram of ARO Unit

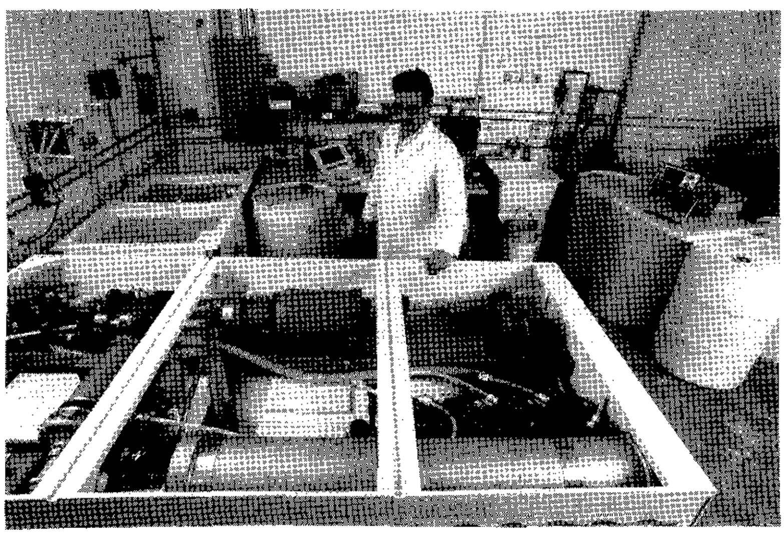


The ARO system's internal microprocessor changes operating parameters for each pass of concentrate through the membrane. Pressures and process times are controlled in order to achieve long membrane lifetimes and very high concentrations of dilute metal salts.

Meanwhile, because the ARO system is completely automated and simple to operate, the plater can concentrate on plating production. There is a simple switch with "Auto" and "Service" positions. In "Auto" position, the ARO microprocessor automatically monitors all remote rinse and internal sensors and initiates ARO processing whenever the final rinse exceeds the operator's preset rinse quality standard. In the "Service" position, the ARO system purges itself and depressurizes to allow the operator to service the rinse tanks or the ARO system.

Among the most significant features of the ARO unit are its ability to be remotely monitored and controlled, and its ability to automatically call for help, both accomplished through a modem and telephone connection. These features allow for rapid diagnosis and service response.

The picture below shows the interior of the ARO system and indicates its key components. The ARO system is in the foreground, other tanks, barrels and equipment are used to simulate customer applications prior to ARO installation. All operating components are located on the top of the system for easy repair or replacement. Membrane changes can be accomplished in 15 to 20 minutes.



Interior of ARO System Showing Pressure Vessel (across front), Pressure Pump (at back), Recycle Pump, Valves and Plumbing

C. TESTING AND CASE STUDIES OF ARO

WTI has completed testing on over 50 plating and metal finishing solutions in a wide range of pH. Test results for selected plating, etching and coating solutions are listed in the table on the next page.

Plating Solutions Tested in ARO Bench Scale System

Plating	Bath pH	Concentration Ratios	Passes to Required Strength	Membrane Life(mos)
Acid Copper Sulfate	0	40	3	6+
Copper Pyrophosphate	8	200	2-3	6+
Tin/Lead Fluoborate	0	10	4	6+
Tin and Tin/Lead Methane Sulfonic	3.6	100	2-3	6+
Electroless Copper	12	1000*	1*	6+
Electroless Nickel	10	250	2	6+
Bright Nickel	4.3	110	2-3	6+
Nickel Sulfamate	4	250	2-3	6+
Watts Nickel	4.4	100	2-3	6+
Zinc Chloride	4.9	30	3	6+
Zinc Cyanide	12	25	3	6+
Copper Cyanide	13.5	30	3	6+
Cadmium Cyanide	12	25	3-4	6+
Hexavalent Chrome	-.14	100	2-3	1
Etchants				
Peroxy-Sulfuric	0	30	4	1-2
Ammonium Chloride	8	60	3	6+
Chromic-Sulfuric Acid	-.5	70	2-3	1
Sulfuric Acid	0	40	3-4	6+
Hydrochloric Acid	.5	20	4	6+
Coatings/Sealers/ Passivators/Cleaners				
Chelated Lead Brightener	13.5	80	2	4+
Chrome Iridite	2	10.8	2-3	1+
Nickel Acetate	5.5	150	2	6+
Nitric Acid	1	30	4	1
Sodium Hydroxide	13.5	20	4	3+

*Special membrane, selective separation.

The main constraints on ARO at this time are highly concentrated, oxidative solutions like chromic acid, nitric acid and peroxy-sulfuric etchant. Their process rinses can be recovered and metals separated; but, reconcentrating to near (40-70% of) bath strength, achievable with other solutions, shortens membrane life. WTI is working to develop membranes and operating procedures to improve system economies. Right now a life of 4-6 months is typical in most applications.

WTI currently has ARO systems operating in three categories of metal finishing - Electronic parts and circuit board manufacture, functional (cyanide) plating and aluminum coating and finishing.

WTI has had systems operating on the following electronic and circuit board solutions: acid copper plating, chelated lead brightening, and nickel sulfamate plating. Tin-lead fluoboric and electroless copper systems are to be installed in June, 1989. The systems have been or are to be installed at Cray Research, Control Data and Vitramon (a Thomas and Betts subsidiary).

WTI, with Ensco Environmental Services, has recently won a Farr Grant to install two ARO systems in the Bay Area for long term testing and evaluation. One is to be installed at Hewlett Packard (on acid copper and nickel sulfamate) and the other, at Domain Technologies (on electroless nickel and electroless cobalt). The project should begin in late Summer, 1989.

In general, the firms' objectives for the ARO systems they purchased or installed were and are to:

- o Gain or remain in compliance with EPA, state and local water discharge standards
- o Gain additional capacity for existing treatment plants without extensive modification
- o Determine if on-site recovery using ARO is economical
- o Reduce water consumption while maintaining or improving parts quality
- o Monitor and provide rinse water of acceptable quality
- o Process "drag over" from plating baths to acceptable purity and concentration for reuse
- o Maintain economic membrane lives in standard applications of 4-7 months (and one month in specialized applications)
- o Offer inexpensive installation and operating returns versus competing systems

Specific case studies applications are:

Electronic and Circuit Board Plating

Acid Copper. In July, 1987, a 1 gallon per minute (gpm) ARO system was installed at Cray Research's printed circuit board facility. Cray produces multilayer boards for its supercomputers. The acid copper bath has a pH of 0. The ARO's remote conductivity sensor was immersed in the final rinse and the system was set to maintain approximately a 38 ppm conductivity. (Rinse quality can be set at any level in the system's software.) The concentrate is reconcentrated to approximately 60% of bath strength which provides for makeup of the evaporative loss from Cray's plating bath. During five months of testing the concentrate was found to have excellent plating characteristics. Since that time, the concentrate return has been plumbed directly into the bath. Cray's savings accrue from reduces costs related to waste treatment, labor, and plating chemicals. A payback of less than two years is anticipated.

Chelated lead brightener. Cray requested a second ARO system to recover and recycle a rinse and bath for a heavily chelated lead brightener (pH 13.5). The chemical was expensive ($13 to $15 per gallon) and 240 gallons per month were being consumed. Further, the chemical was very difficult to waste treat, because it complexed with other metals in their existing precipitation/clarification treatment system. The ARO was able to clean the rinses (to 4.1 ppm lead) and recover the chelated chemical cutting Cray's chemical use to only 20 gallons per month. Payback was realized in less than one year.

Nickel Sulfamate. Vitramon, a Thomas and Betts subsidiary, installed a 1 gpm ARO system to recover rinses and recycle nickel bath used to plate electronic capacitors. Previously, Vitramon had used an ion exchange system to remove the nickel. Ion exchange regenerant was shipped to a reclaimer. Water was reused. Ion exchange cost of operation was $4,000 per month. The ARO system maintains the rinse at less than 40 ppm nickel. Savings from nickel recovery and avoided treatment cost will provide a payback of approximately 10 months.

Results from electroless copper, tin-lead (solder) fluoboric and tin-lead (solder) sulfonic applications will be discussed as they become available from installations planned for June and July, 1989.

Functional (cyanide) plating

Copper cyanide. In February, 1988, Joyner's, a mid sized zinc diecasting and plating facility, installed an ARO system on copper cyanide (pH 13.5) after reviewing ion exchange and atmospheric evaporation technologies. The system has saved an estimated 6,000 gallons of water per day compared with former operating procedures with no loss in rinse or parts quality. All the copper cyanide bath concentrate is returned to the bath; no cyanide goes to waste treatment. Payback versus the evaporation or ion exchange systems also considered was estimated to be about one year.

Zinc cyanide. In August, 1988, Plating Inc., a subsidiary of Superior Plating, installed a 5 gpm ARO system on one of its automated zinc cyanide plating lines to recover rinse and bath after zinc cyanide plating. In a seven month study funded by the Minnesota Waste Management Board, the ARO system achieved objectives for waste reduction and compliance with federal and local regulations. The system monitored and maintained rinse quality to Plating Inc.'s exacting standards, recovered 2,480 gallons of plating solution, avoided shipment of thousands of gallons of dead rinse for central treatment and is projected to eliminate the need for shipment of 700 cubic feet per year of resins containing cyanide for off-site regeneration. Payback from the system is expected to be less than one year versus centralized treatment and recovery.

Cadmium cyanide. In January, 1989, API Industries in Chicago, installed a 5 gpm ARO system to evaluate cadmium cyanide recovery. Complete results are not available at this time. Laboratory tests and economic projections indicate that the rinses and bath are reclaimable and payback from ARO should be one year or less.

Other applications

Chrome iriditing. WTI has installed a 1 gpm ARO system on a chrome iriditing process at Fotomark in Minneapolis. The system has recovered several hundred gallons of chrome solution for recovery and recycling and the ARO has maintained rinse quality, while eliminating water discharges from their iriditing process rinse.

Process modification requirements

The companies which have installed WTI's ARO systems have generally found that only minimal plating and process modifications were required from previous practice. The modifications include:

- Deionized water for rinsing and bath make-up. Rinse tanks using ARO recovery are charged once with de-ionized water which is continuously monitored and cleaned by the ARO system. Evaporative losses are automatically made up by the ARO. De-ionized water use avoids contamination, prevents precipitants from forming, and usually improves rinse quality. Bath make-up should also use de-ionized water to minimized contaminate build-up.

- Bath filtration and cleaning. Filtering and carbon trading plating baths is standard practice with most applications to remove spent organics and any precipitants which might affect a high quality finish. Usually filtration of 5-10 microns is sufficient. Some baths do present unique issues requiring special equipment or chemistry.

- Rinse pH monitoring. Some rinse waters require pH monitoring and adjustment to protect following processes (the de-ionized water is unbuffered).

- Counterflow rinsing and drag out reduction. Lower capital cost for ARO recycling and recovery equipment can sometimes be achieved through relatively simple rinsing and dragout steps -- adding a delay timer to hold barrels over the bath for an added 10 seconds reduced drag out by 42% in one application; changing to counter flow rinses and using a one gallon per minute ARO system cut water usage by 6,000 gallons per day in another application.

- Bath monitoring. Firms can maximize recovery by monitoring bath quality and making selective bath additions.

- Good housekeeping. Removing parts from baths containing corrosive plating solutions, using cleaners to remove oil and grease from parts, proper rinsing prior to the plating bath, etc. all should be practiced.

Nearly total recycle and recovery of rinse water and bath is possible using these and other techniques. Practices will vary somewhat among applications; but common sense steps and bath management will provide substantial economic benefits from ARO application.

D. CONCLUSIONS

On-site recovery technologies like ARO which can be applied at the point of use to remove dissolved hazardous metal salts from process rinses offer:

- Environmental benefits. Hazardous waste generation is reduced or eliminated. Sludge is avoided. Handling, transport and storage of hazardous wastes can be eliminated.

- Economic benefits. Long-term liability for landfill is reduced or eliminated. Labor, chemical, capital, and transport costs are saved.

On-site recovery can thus meet regulatory goals at a lower cost. Given WTI's experience, it appears that combinations of technologies can achieve waste minimization goals and allow individual systems to be more efficient - ARO works best on rinse water and dilute solution recovery; ion exchange is excellent as a polisher of treated water; electrowinning and electrodialysis operate most effectively on concentrated solutions; and central treatment facilities are useful for small volumes of concentrates or other plating wastes for which economies of scale are required.