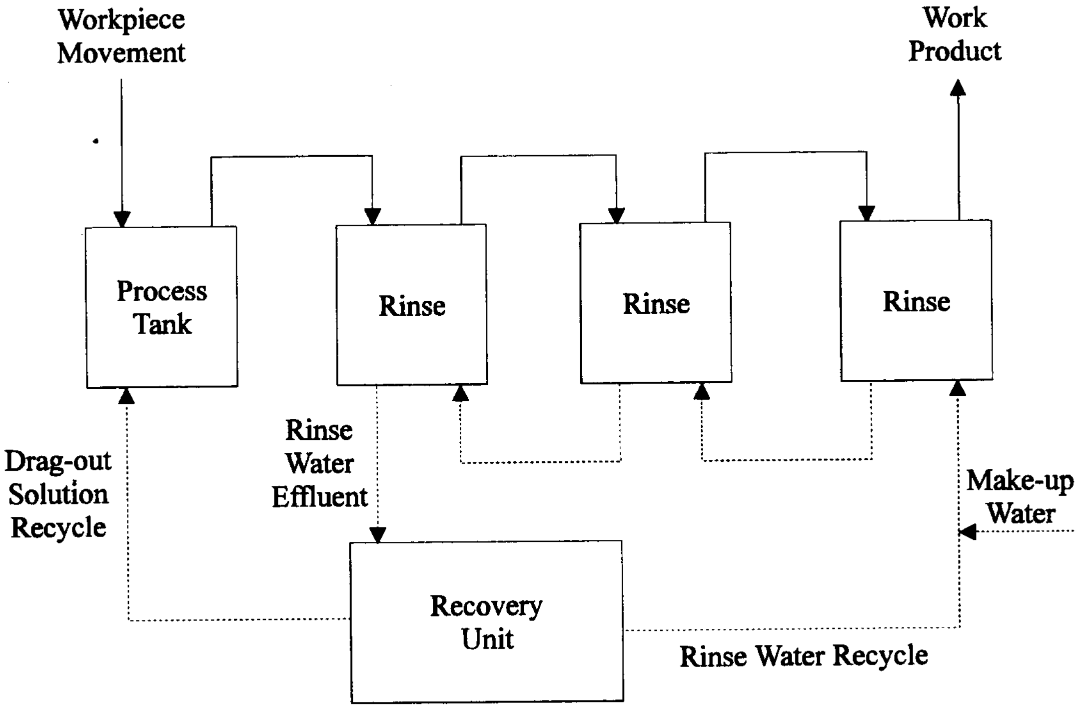
12/9/96

Metal Finishing: Metal Recovery and Water Reuse

Pollution Prevention Information Packet



September 1995

Prepared by

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Metal Finishing: Metal Recovery and Water Reuse
Pollution Prevention Information Packet

Can you use more information about making your metal finishing operations more profitable? More likely to be in compliance, or better? More environmentally friendly, using pollution prevention? And, who sells the necessary equipment and materials? Would you like to get the basics in one place? Ohio EPA's Office of Pollution Prevention has done some of that work for you. This packet has several of the best, most beneficial and commonly referenced technical papers available in this area. We are pleased to provide this information to help make your job easier.

Pollution prevention offers you some of the best opportunities to reach each of your objectives above. Please use these references as guidance, and contact the Office of Pollution Prevention if you would like further information.

The information packet contains the following **articles**:

Overview

✓1. Ohio EPA. 1994. *Source Reduction and Metal Recovery Techniques for Metal Finishers.* Fact Sheet No. 24. Office of Pollution Prevention, Ohio Environmental Protection, Columbus. 6pp.

Ion Exchange

✓2. Cushnie Jr., G.C. 1994. Pollution Prevention and Control Technology for Plating Operations. *Chemical Recovery. Ion Exchange.* National Center for Manufacturing Sciences, Ann Arbor, Michigan. pp. 97-118.

✓✗ 3. Wilk, L.F and R.S. Capaccio. 1992. *Application of Ion Exchange Technology in Pollution Prevention.* Metal Finishing 90(11): 25-28.

✗4. Ragosta, J.M. 1991. *Using Your Ion Exchange Wastewater Treatment Equipment.* Metal Finishing 89(11): 7-9.

✓✗5. Karrs, S., D.M. Buckley, and F.A. Steward. 1986. *Ion Exchange for Metal Recovery: A Discussion of Trade-Offs.* Plating and Surface Finishing 73(4): 60-66.

✓6. Gavaskar, A.R., R.F. Olfenbuttel, and J.A. Jones. 1994. *Cadmium and Chromium Recovery from Electroplating Rinsewaters.* Project Summary. EPA/600/SR-94/050. Risk Reduction Engineering Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio. 5pp.

Pollution prevention means the use of source reduction techniques in order to reduce risk to public health, safety, welfare and the environment and, as second preference, the use of environmentally sound recycling to achieve these same goals. Pollution prevention avoids cross-media transfers of waste and/or pollutants and is multi-media in scope. It addresses all types of waste and environmental releases to the air, water and land.

Electrolytic Recovery

✓7. Cushnie Jr., G.C. 1994. Pollution Prevention and Control Technology for Plating Operations. *Chemical Recovery. Electrowinning.* National Center for Manufacturing Sciences, Ann Arbor, Michigan. pp. 118-138.

8. Gavaskar, A.R., R.F. Olfenbuttel, and J.A. Jones. 1994. *Cadmium and Chromium Recovery from Electroplating Rinsewaters.* Project Summary. EPA/600/SR-94/050. Risk Reduction Engineering Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio. 5pp.

✓9. Ehrmmann, I. 1993. *Electrolytic Effluent Treatment for Acid or Cyanide Zinc Plating Baths.* Metal Finishing 91(5): 36-37.

10. Wiaux, J.P. and T Nguyen. 1990. *Recovered Value from Electroplating Industry Waste.* Metal Finishing 88(6): 85-92.

X 11. Shaulys, J. and B. Rovinelli. 1991. *Cadmium Compliance Achieved with Electrowinning.* Plating and Surface Finishing 87(9): 42-44.

✓ 12. U.S. EPA. 1991. *Recovery of Metals from Sludge and Wastewater.* Project Summary. EPA/600/S2-91/041. Risk Reduction Engineering Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio. 6pp.

X 13. Beninati, C.A. and W.J. McLay. 1983. *Electrolytic Metal Recovery Comes of Age.* Plating and Surface Finishing 70(3): 26-28.

Reverse Osmosis

✓ 14. Cushnie Jr., G.C. 1994. Pollution Prevention and Control Technology for Plating Operations. *Chemical Recovery. Reverse Osmosis.* National Center for Manufacturing Sciences, Ann Arbor, Michigan. pp. 143-154.

X 15. Lindsey, T.C. 1993. *Recycling Nickel Electroplating Rinse Waters by Low Temperature Evaporation and Reverse Osmosis.* Project Summary. EPA/600/SR-93/160. Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio. 6pp.

Evaporation

✓ 16. Cushnie Jr., G.C. 1994. Pollution Prevention and Control Technology for Plating Operations. *Chemical Recovery. Atmospheric Evaporators.* National Center for Manufacturing Sciences, Ann Arbor, Michigan. pp. 66-80.

✓ 17. Cushnie Jr, G.C. 1994. Pollution Prevention and Control Technology for Plating Operations. *Chemical Recovery. Vacuum Evaporators.* National Center for Manufacturing Sciences, Ann Arbor, Michigan. pp. 80-97.

X 18. Lindsey, T.C. 1993. *Recycling Nickel Electroplating Rinse Waters by Low Temperature Evaporation and Reverse Osmosis.* Project Summary. EPA/600/SR-93/160. Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio. 6pp.

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Electrodialysis

✓ 21. Cushnie Jr., G.C. 1994. Pollution Prevention and Control Technology for Plating Operations. *Chemical Recovery. Electrodialysis.* National Center for Manufacturing Sciences, Ann Arbor, Michigan. pp. 138-143.

✓ 22. Folsom, D.E., J.A. Jones, and R.F. Olfenbuttel. 1994. *Evaluation of an Electrodialytic Process for Purification of Hexavalent Chromium Solutions.* Project Summary. EPA/600/SR-94/071. Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio. 6pp.

A listing of **potential vendors** can be found at the end of the information packet. This list is not necessarily a complete listing of vendors, but is being provided to help identify and locate vendors of pollution prevention equipment and supplies. Ohio EPA does not endorse any of these vendors, but provides this information as a service to Ohio businesses.

Besides this information packet, the Office of Pollution Prevention (OPP) of Ohio EPA provides other types of technical assistance. OPP provides industry specific pollution prevention from over-the-phone consultations to on-site pollution prevention assessments. All services are non-regulatory and provided free-of-charge. OPP also coordinates voluntary pollution prevention programs such as Green Lights and Ohio Prevention First. In cooperation with the Ohio Department of Development, OPP administers a pollution prevention loan program. This program loans funds for existing facilities to acquire or renovate machinery and equipment for pollution prevention practices. For further information on any of OPP's program contact OPP at **(614) 644-3469**, or point your Internet World Wide Web browser to: http://www.epa.ohio.gov/opp/oppmain.html.

OhioEPA

State of Ohio
Environmental Protection Agency

Fact Sheet

Pollution Prevention

Source Reduction and Metal Recovery Techniques for Metal Finishers

Number 24
September 1994

> *Both market and regulatory forces are increasing the pressure on platers to make the right decisions on pollution prevention and control technology, and are aggravating the consequences of bad choices.*
>
> **George C. Cushnie, Jr., CAI Engineering**

High waste management costs and strict disposal regulations have demanded the attention of many Ohio businesses and a significant portion of their profits. For metal finishing operations to remain competitive and in compliance with environmental requirements, these companies must focus their efforts on pollution prevention to reduce waste generation and disposal costs, limit liability and restore maximum profits.

This fact sheet summarizes some of the opportunities for metal finishers to reduce wastes while maintaining profitability and achieving compliance. By applying the pollution prevention concept, metal finishers can reduce the generation of metal-bearing wastes at the source. When waste cannot be reduced in the process, recycling offers a good alternative for process residues. Current technologies applicable to recycling and summarized in this fact sheet include evaporation, reverse osmosis, ion exchange, electrodialysis and electrolytic recovery.

Source Reduction

According to the hierarchy of preferred approaches to waste management established by the Pollution Prevention Act of 1990, source reduction options should be investigated first, followed by environmentally sound recycling, treatment, and disposal. Before turning to methods to recover metals from wastewater, metal finishers should examine processes and operations for opportunities to reduce the generation of waste at the source.

Source reduction techniques for metal finishers include:

1. Slow down - Reduce the speed of parts removal and allow drain time above tanks to reduce dragout. Dragout is the solution pulled from one tank in a plating operation into another. Racks for hanging parts to drain while workers move to another task can help. Automation also can help.

2. Counter-current rinsing - Fresh water is fed into the rinse tank farthest from the plating tank and overflows backwards through the flowing rinse tanks until it reaches the rinse tank immediately after the plating tank. For example, the part moves from process bath, to rinse #1, to rinse #2, then to #3. Rinse water should flow from rinse #3, to rinse #2, then to #1, as in *Figure 1*.

3. Static rinse - The first rinse after a process bath should be a static rinse that builds up a concentration of "drag-in" and is used to replenish the process bath (instead of fresh water). Make up this static rinse with purified water.

4. Rack to reduce drag-out - Position part so that fluid will flow together and off the part by the quickest route. Don't position parts directly over one another. Tilt parts to avoid fluid pockets.

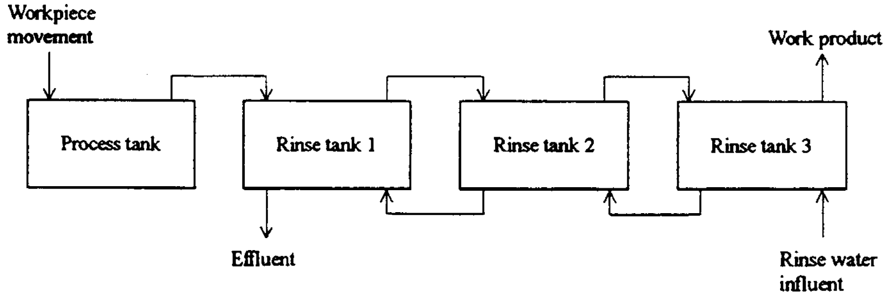

Figure 1 - Counter-current Rinsing

Office of Pollution Prevention, Ohio Environmental Protection Agency, 1800 WaterMark Dr., P.O. Box 163669, Columbus, OH 43216-3669, (614) 644-3469

5. Bath chemistry - Regularly monitor bath chemistry. Testing methods are available from your supplier. Sometimes supplier specifications for concentration levels are set high. By experimenting and lowering levels to just above the point when defects start to occur, you can reduce chemical costs and the costs associated with disposal or treatment.

6. Restrict Water Flow - Simple in-line flow restrictors can limit the water flow rate. Turn off flowing rinses when not in use.

7. Drain Boards -Place a drain board over the lips of two adjacent tanks to catch dragout. Slope the board back to the first tank (this also keeps the solutions off the floor).

8. Agitate Baths - Agitation can be done by manually moving the part (better if part is completely removed and then re-immersed), with a mechanical agitator, or with forced air or solution in an immersion tank. You may need to filter baths to remove sediment prior to agitation.

9. Fogging/Spray/Air Knives - After a part is removed from a bath, these devices can force some of the dragout off the part and back into the bath (*WRAP*, 1993).

Dragout recovery is one of the most important source reduction practices. It is a simple technology used by metal finishers to return plating chemicals to their original bath before they become integrated into a wastestream. It involves using drain boards, drip tanks, fog-spray tanks or rinse tanks separately, or in combination, to capture chemicals dragged out of plating tanks. Drain boards are widely used throughout the metal finishing industry to capture plating solutions. These boards are suspended between process tanks and are constructed of plastic, or plain or teflon-coated steel. Solutions drip on the boards and drain back into their respective processing tanks.

In contrast, a drip tank recovers process chemicals by collecting dragout into an empty tank from which it can be returned to the process as needed.

Another dragout recovery option is a fog-spray tank, where plating chemicals clinging to parts are recovered by washing them with a fine water-mist. The solution that collects in the fog-spray tank is returned to the process tank as needed. The added water helps to offset evaporative losses from the process tanks.

Another option is a dragout tank. Dragout tanks are essentially rinse tanks. Dragout chemicals are captured in a water solution, which is returned to the process tank as needed.

There are advantages and disadvantages to dragout recovery. The presence of airborne particles and other contaminants in recovered plating chemicals may necessitate treatment of collected solution to remove the contaminants prior to solution reuse. Depending upon the solution, up to 60 percent of the materials carried out of a plating tank can be recovered for reuse, thus lowering material and waste management costs. However, reusing dragout can affect metal deposition and surface finish quality. Impurities can concentrate in the solutions causing a deteriorating effect on the plating process when returned to the plating bath.

Recovery Techniques

After utilizing the source reduction methods previously mentioned, recovery techniques can be used to recover metal for reuse. Recovery should begin with segregation.

Waste Stream Segregation

Segregation of waste streams is essential for most recycling and resource recovery technologies. To reuse a waste material for another process, recover valuable chemicals from a waste stream, or recycle rinse water, the waste stream must be kept separate from other wastes that will disturb the reuse or recycling process. Therefore, implementation of recycling and resource recovery technologies will typically require process piping modifications and additional holding tanks to provide appropriate material segregation (PRC Environmental Management, Inc., 1989).

Once the waste solutions have been isolated as much as is feasible, there are a variety of methods that can be used to remove the metals or process chemicals.

Evaporation

Heat or natural evaporation is used to evaporate water from the rinse water containing dilute plating chemicals. Once sufficient concentration of the plating chemicals is achieved, the solution can be reused in the plating bath.

There are essentially two types of evaporators: those that operate at atmospheric pressure and those that operate under vacuum. Atmospheric evaporators, the most commonly used units, are less expensive to purchase than vacuum evaporators. They are open systems that use process heat and warm air to evaporate water. The source of air is important because the bath may absorb impurities from air. A packed bed evaporator is an example of an atmospheric evaporator.

Vacuum evaporators are also used to recover plating chemicals. They are closed systems that use steam heat to evaporate water under a vacuum. The water vapor is condensed for reuse as rinse water. These evaporators operate by removing rinse water from the first rinse tank and boiling it at a reduced pressure. A climbing file evaporator is an example of a vacuum evaporator.

A typical evaporative recovery system consists of an evaporator, a feed pump and a heat exchanger. Plating solution or rinse water containing dilute plating chemicals is circulated through the evaporator. The water evaporates and concentrates the plating chemicals for reuse. In open evaporator systems, the water evaporates and mixes with air and is released to the atmosphere. (Note: It may be necessary to vent the contaminated air stream to a ventilation/scrubber treatment system prior to release.) In enclosed evaporators, the water is condensed from the air and can be reused in rinses, which further increases savings. Water reuse is preferred whenever possible.

As with all process equipment, the design and size of an evaporator system is dependent upon volumetric flow, specifically the rinse water flow rate required and the volume of process solution dragout. In order to reduce sludge waste, the volume of water used to rinse the parts must be reduced. Therefore, rinsing efficiency becomes an important factor. Manufacturers can improve rinsing efficiency in several ways. First of all, turbulence can be utilized to reduce the amount of water needed to rinse the part. Turbulence includes spray rinsing and water agitation. Furthermore, the contact time between the part and the rinse bath can be increased. This usually is achieved by multi-stage rinse baths and counter-current rinse systems.

Advantages:
- recovered chemicals can be reused
- reduced volume to waste treatment facility
- self operating
- low maintenance
- widely applicable
- atmospheric evaporators are inexpensive
- vacuum evaporators recycle rinse water

Disadvantages:
- evaporators increase impurities
- impurities require further treatment
- energy intensive
- vacuum evaporators are capital intensive
- needs accompanying system for recycling
- plating chemicals corrosive to evaporator
- may require pH control
- evaporation can degrade or volatilize bath additives

Ion Exchange

Ion exchange is a molecular exchange process where metal ions in solution are removed by a chemical substitution reaction with an ion-exchange resin. The metal salt produced can sometimes be returned to the plating bath for reuse. Ion exchange can be used with most plating baths. The ion exchange unit's size (volume of resin) is determined by the amount of metal to be removed from the recovered solutions.

Advantages:
- recycles process water
- recovers process chemicals
- efficient in removing ions from dilute solutions, handles dilute feed
- resins can be selected to remove certain ions
- low energy demands

Disadvantages:
- produces a concentrated solution which needs to be further treated
- usually run as a batch process
- difficult to find a suitable resin for treatment of a waste solution containing mixed metal ions
- needs accompanying systems for metal recycling
- sensitive to temperature, solids, and organics
- requires tight operation maintenance, equipment complex
- limited concentration ability
- excess regenerate required
- feed concentration must be closely monitored
- ion exchange column takes time to regenerate

Reverse Osmosis

Reverse osmosis (RO) recovers plating chemicals from plating rinse water by removing water molecules with a semi-permeable membrane. The membrane allows water to pass through but blocks metals and other additives.

Diluted or concentrated rinse waters are circulated through the membrane at pressures greater than aqueous osmotic pressure. This action results in the separation of water from the plating chemicals. The recovered chemicals can be returned to the plating bath for reuse and the permeate, which is similar to the condensate from an evaporator, can be used as make-up water. RO units work best on dilute solutions. The design and capacity of an RO unit is dependent on the type of chemicals in the plating solution and the dragout solution rate. Certain chemicals require specific membranes. For instance, polyamide membranes work best on zinc chloride and watts nickel baths, while polyether/amide membranes are suggested for chromic acid and acid copper solutions. The flow rate across the membrane is very important: It should be set at a rate to obtain maximum product recovery. RO systems have a 95 percent recovery rate with some materials and with optimum membrane selection (CMF, 1991).

Advantages:
- recovers process chemicals
- recycles process water
- high separation rate can be achieved
- no chemicals used
- small floor space requirement

Disadvantages:
- membrane durability problems
- sensitive to hard water salts
- fouling of membranes due to feeds high in suspended solids; feed filtration essential
- returns ionic impurities to plating bath
- limited concentration range of operation

Electrodialysis

In electrodialysis, electromotive forces selectively drive metal ions through an ion-selective membrane (in reverse osmosis, pressure is the driving force; in ion exchange, the driving force is chemical attraction). The membranes are thin sheets of plastic material with a series of alternatively placed cationic- and anionic-permeable membranes (PRC Environmental Management, 1989).

Advantages:
- energy efficient
- only ionic materials are recovered, organics not concentrated, minimal return of unwanted inorganic material
- achieves higher concentration than reverse osmosis or ion exchange

Disadvantages:
- membranes sensitive to clogging and ruptures, flow distribution, pH, and suspended solids
- efficiency drops as purity increases
- feed must be filtered
- equipment uses multi-cell stacks
- membrane life uncertain

Electrolytic Recovery

In electrolytic recovery, metal ions are plated-out of solution electrochemically by reduction at the cathode. There are essentially two types of cathodes used for this purpose: a conventional metal cathode (electrowinning) and a high surface area cathode (HSAC). The HSAC cathode can effectively plate-out metals, such as gold, zinc, cadmium, copper, nickel, etc. Therefore, electrolytic recovery can be used with most plating baths.

Advantages:
- metals are recycled
- no chemicals used
- recovers only metals
- results in salable, nonhazardous product
- energy efficient
- low maintenance

Disadvantages:
- energy inefficient at very low concentrations

Deionized Water

Using deionized water to prepare plating bath solutions is an effective way to prevent waste generation. Some ground water and surface water contains high concentrations of calcium, magnesium, chloride and other soluble contaminants that may build up in process baths, possibly shortening bath life. By using deionized water, build-up of contaminants can be more easily controlled. Technologies such as reverse osmosis and ion exchange also can be used to effectively remove soluble contaminants from incoming water.

Case Study

Walbridge Coatings

Walbridge Coatings, Walbridge, Ohio, has installed a metal recovery system. Its system returns 95 percent of the metals found in the waste stream back to the process, and Walbridge has developed secondary sources for the use of the remaining 5 percent.

Walbridge Coatings produces electrogalvanized zinc and zinc-nickel cold rolled steel, primarily for the automotive industry. In 1989, the company embarked on an aggressive metals recovery and reclamation program. After over a year of engineering work, it was decided that recovery of zinc and nickel was possible through ion exchange.

Initial tests indicated that over 90 percent metals recovery was possible. It was estimated that initial recovery efforts would result in approximately a 500-ton reduction in sludge generation. After proving the system on the zinc-nickel stream, expansion to the zinc process had the potential to further reduce sludge generation by an additional 350 tons.

During 1991, the project resulted in eliminating 515 tons of sludge. During 1992, with improved methods, and the addition of the zinc stream, the system accounted for the elimination of over 892 tons of sludge. This exceeded the engineering expectations of this project by 5 percent.

During this same time period, extensive efforts were made to find uses for the remaining metals which were not recoverable by the ion exchange method. Walbridge Coatings was successful in its efforts and in 1991 placed 600 tons of material as feedstock for other industrial operations. Further development of secondary sources resulted in placing more than 925 tons in 1992. The total impact of the Walbridge coatings waste minimization project was an annual reduction of more than 1,800 tons of sludge.

The total project costs were $3,167,573, while the annual savings were $2,035,000. Therefore, the payback period for the project, based solely on cost avoidance, was 1.5 years. However, when such issues as long-term liability and corporate responsibility to the community were considered, it was immediately apparent to Walbridge Coatings that this was a worthwhile project to undertake.

For more information contact:

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University of Tennnessee. 1993. *WRAP (Waste Reduction Assistance Program),* page 5. University of Tennessee. Vol. 3, No. 3. Nashville, TN. Fall 1993.

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Further Information Available

The following are a few of the relevant documents available from the Ohio EPA Office of Pollution Prevention:

Fact Sheet 21: Governor's Awards Recipient - Walbridge Coatings. Ohio EPA. Ohio EPA, Columbus, OH. May 1994.

Waste Minimization Assessment for a Manufacturer of Finished Metal Components. EPA/600/S-92/030. U.S. EPA. 1992.

Waste Minimization Assessment for a Manufacturer of Metal-Plated Display Racks. EPA/600/S-92/019. U.S. EPA. 1992.

Source Reduction and Metal Recovery Techniques for the Metal Finishing Industry

This is the twenty-fourth in a series of fact sheets Ohio EPA has prepared on pollution prevention. For more information call the Office of Pollution Prevention at (614) 644-3469.

The Office of Pollution Prevention was created to encourage multimedia pollution prevention activities within the state of Ohio, including source reduction and environmentally sound recycling practices. The office analyzes, develops, and publicizes information and data related to pollution prevention. Additionally, the section increases awareness of pollution prevention opportunities through education, outreach, and technical assistance programs directed toward business, government, and the public.

Ion Exchange
in

Pollution Prevention and Control Technology for Plating Operations

George C. Cushnie Jr.
CAI Engineering

A Project Sponsored by the
National Center for Manufacturing Sciences
and Conducted in Cooperation with the
National Association of Metal Finishers

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3.4 ION EXCHANGE

3.4.1 Overview

Ion exchange is a technology that is very familiar to the plating industry. Of the 318 plating shops responding to the Users Survey, at least 80 or (25%) have used ion exchange, including 34 applications for chemical recovery (the total number of ion exchange users is not known since not types of all applications were covered by the Users Survey). The five most common applications of this technology by the plating industry are: (1) treatment of raw water (e.g., city water) to produce high quality rinse water (includes both softening and deionization); (2) chemical recovery from rinse water; (3) treatment of plating baths to remove contaminants (e.g., tramp metals); (4) as a primary end-of-pipe treatment process; and (5) as a polishing end-of-pipe treatment process to comply with stringent effluent limitations. Chemical recovery applications of ion exchange are covered in this section. Bath maintenance and end-of-pipe treatment applications are covered in Sections 4 and 6, respectively. Raw water treatment is not covered by this project, although some respondents indicated in their survey responses that they use ion exchange for raw water treatment (e.g., PS 127, PS 196, PS 203).

Ion exchange is a chemical reaction wherein an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle (i.e., ion exchange resin). Ion exchange reactions are stoichiometric (i.e., predictable based on chemical relationships) and reversible. The resins are normally contained in vessels referred to as columns. Solutions are passed through the columns and the exchange occurs. Subsequently, when the capacity of the resins is reached, the ions of interest, which are attached to the resin, are removed during a regeneration step where a strong solution containing the ions originally attached to the resin is passed over the bed.

The strategy employed in using this technology is to exchange somewhat harmless ions (e.g., hydrogen and hydroxyl ions), located on the resin, for ions of interest in the solution (e.g., plating chemicals). In the most basic sense, ion exchange materials are classified as either cationic or anionic. Cation resins exchange hydrogen ions for positively charged ions such as nickel, copper and sodium. Anion resins exchange hydroxyl ions for negatively charged ions such as chromates, sulfates and cyanide.

Ion exchange resins are usually contained in vessels referred to as columns. The basic column consists of a resin bed which is retained in the column with inlet and outlet screens, and service and regeneration flow distributors. Piping and valves are required to direct flow and instrumentation is required to control regeneration timing. The systems are typically operated in cycles consisting of the following steps (ref. 39, 348):

1. **Service (exhaustion)** - Water solution containing ions is passed through the ion exchange column or bed until the exchange sites are exhausted.
2. **Backwash** - The bed is washed (generally with water) in the reverse direction of the service cycle in order to expand and resettle the resin bed.
3. **Regeneration** - The exchanger is regenerated by passing a concentrated solution of the ion originally associated with it through the resin bed; usually a strong mineral acid or base.
4. **Rinse** - Excess regenerant is removed from the exchanger; usually by passing water through it.

3.4.2 Development and Commercialization

Ion exchange is a versatile separation process with potential for broad application in the metal finishing industry. The ion exchange process has been commercially available for many years, but early use was primarily for water deionization or softening. Widespread interest in the process for metal finishing pollution prevention and control is a more recent application that has grown rapidly over the past 10 to 20 years.

Although the ion exchange process was first recognized in 1850, and defined as a reversible process in 1858, the first practical application of the process did not occur until 1905 when the inorganic sodium aluminosilicate cation exchanger was synthesized and used to soften water. In the early 1930's a cation material was developed from sulfonated coals, which extended the operable pH range of the process. In 1935, condensate polymers were first used as structural substrates for various functional groups, thereby creating both anion and cation exchange materials. The early anion product was not the strong base anion exchanger available today. Instead, it acted as an acid adsorbent capable of removing only free acids from the process stream. The cation and anion forms were used in series for the first time and deionization was accomplished; however it was limited in application. Strong base anion exchange materials were developed in the 1940's that extended the use of the process. In 1945 synthetic organic polymers were developed using styrene and divinylbenzene as the monomers. These were later prepared in bead form (earlier, only granular products were available). This gave rise to the modern "gel" type ion exchange materials. Improvements during the 1950's focused on reducing the fouling of resins by organic substances (ref. 383). One of the earliest applications of ion exchange to metal finishing mentioned in the literature was a hard chromium bath maintenance system operated by the Rock Island Arsenal in 1952 (ref. 368). The use of ion exchange as a pollution control and chemical recovery tool progressed steadily as pollution control regulations became more widespread and more stringent. As with many technologies, ion exchange use for pollution control in the metal finishing industry increased very rapidly in the late 1970's and early 1980's with the implementation of the Federal effluent guidelines. The most recent developments have focused on expanding the range of applications (e.g., cyanide plating and electroless plating baths) with new resins, equipment and techniques.

3.4.3 Applications and Restrictions

Ion exchange is used for a variety of purposes in the metal finishing shop, including: treatment of raw water; recovery of plating chemicals from rinse water; purification of plating solutions; wastewater treatment; and wastewater polishing. The following discussion of applications and restrictions focuses on use of this technology for chemical recovery from rinse water. The other applications, with the exception of raw water purification, are discussed in other interim reports.

Ion exchange is a useful technology for recovering plating chemicals from dilute rinse waters. Two common configurations are shown in Exhibit 3-22, application IX-1 is referred to as metal scavenging. It uses only one type of ion exchange resin, either anion or cation, depending on the charge of metal or metal complex being recovered. Because this system does not have both cation and anion resins, the rinse water will not be fully "deionized" and cannot be reused as rinse water for common rinsing purposes. In AE-2, both anion and cation resins are employed and the rinse water can be recirculated in a closed loop. With both of these configurations, rinse water containing a dilute concentration of plating chemicals is passed through an anion and/or cation column (or dual columns of the same type) and the metals are removed from the rinse water and held by the ion exchange resin. When the capacity of the unit is reached, the resin is regenerated and the metals are concentrated into a manageable volume of solution. Depending on the chemical nature of the process, the regenerant (eluate) solution can be returned directly to the plating tank for reuse, further processed and returned, or the metals can be recovered by another technology such as electrowinning (see Section 3.5). The most common applications for these configurations of ion exchange are with the recovery of copper, nickel, and precious metals.

Application IX-3 (Exhibit 3-23) is a bath maintenance configuration that is only applicable to chromic acid solutions. The chromium bearing rinse water is passed through a cation column to remove trivalent chromium, and tramp metals such as iron, nickel and aluminum and is then used as make-up for evaporation in the bath. This application prevents the build-up of contaminants in the bath, a process that is hastened by recovery rinsing. Since hexavalent chromium is an anion, it is not removed by the cation resin.

Drag-out recovery tanks (see Section 2) are used with ion exchange systems whenever feasible. In operation, the drag-out tanks return the bulk of the plating chemicals to the plating bath and an ion exchange column captures only the residual quantities of chemicals. The needed size of the ion exchange unit and its regeneration frequency are therefore reduced.

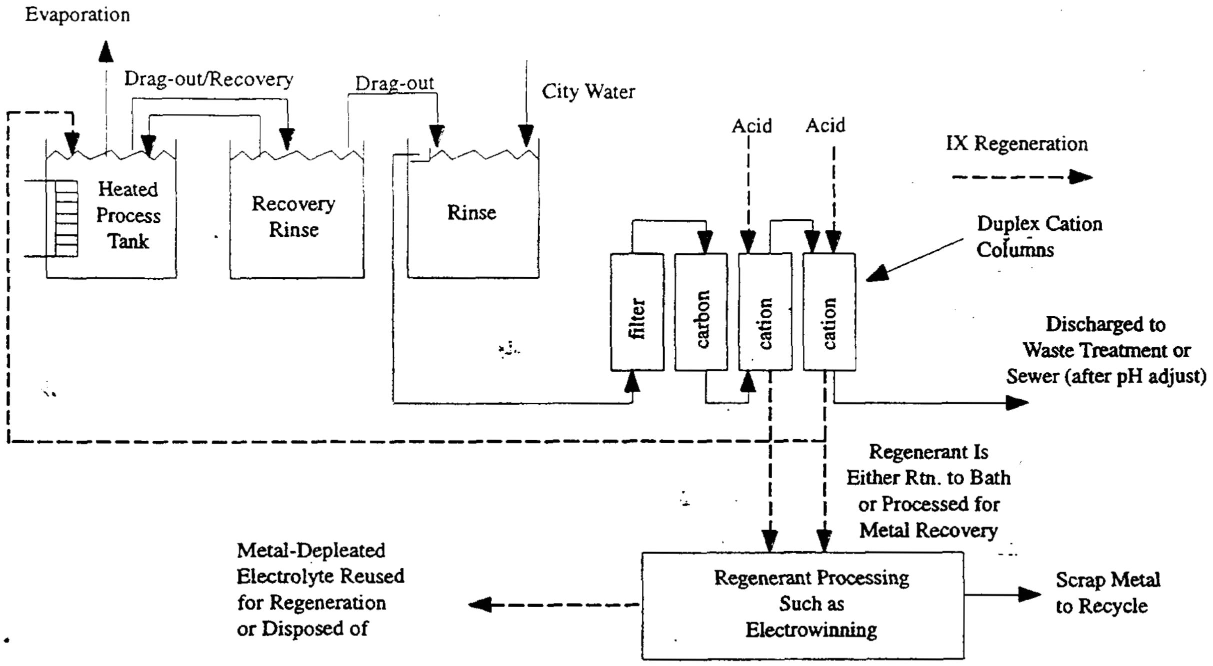
Some of the respondents to the Users Survey misapplied the ion exchange technology for chemical recovery. For example, PS 261, operates a Watts nickel plating line with a 140°F bath and a four stage counter flow rinse. This shop feeds the ion exchange system from the first rinse, which is the most concentrated, and returns the treated water to the last rinse. Instead, this shop should utilize the configuration shown in Exhibit 3-22. Application IX-1. The use of a recovery rinse will greatly reduce the nickel load on the ion exchange columns.

As a recovery technology, ion exchange should be applied to dilute rinse waters. It is not applicable to concentrated drag-out solutions or plating baths (although it can be used as a bath maintenance technology to remove tramp metals, see Section 4). A major limitation of this process is that many plating baths are more concentrated than the ion exchange regenerant. Therefore, it should not be used in a "bleed and feed" system, where spent bath is bled to the rinse water. The result in these cases is that the chemicals are diluted in the rinse water, collected by ion exchange, regenerated (using costly chemicals), and recovered in a lower concentration than they started (ref. 40).

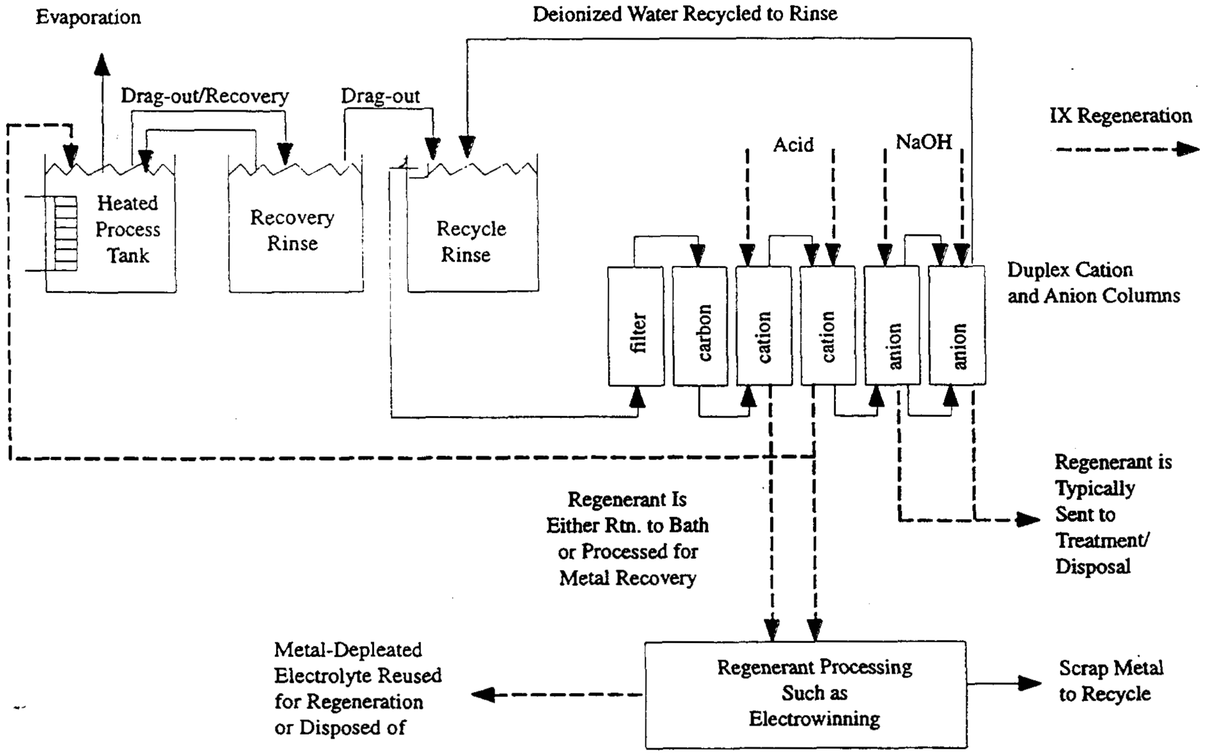
Ion exchange is applicable to a wide range of plating processes. Exhibit 3-24 shows the applications identified by the Users and Vendors Surveys.

Ion exchange is used much more frequently for metal recovery from non-cyanide solutions than for cyanide solutions (e.g., cadmium cyanide, copper cyanide, zinc cyanide), with the exception of gold cyanide. When applied to cyanide solutions, the task of recovery is more difficult due to the nature of the cyanide complex. As explained by Reinhard (ref. 342), when a cation followed by an anion column arrangement is used, the cyanide complex in the rinse water is decomposed into free metal cations and cyanide anions and these cations and anions are exchanged for H^+ and OH^- ions in the corresponding resin beds. When

Exhibit 3-22. Common Configurations for Application of Ion Exchange for Chemical Recovery

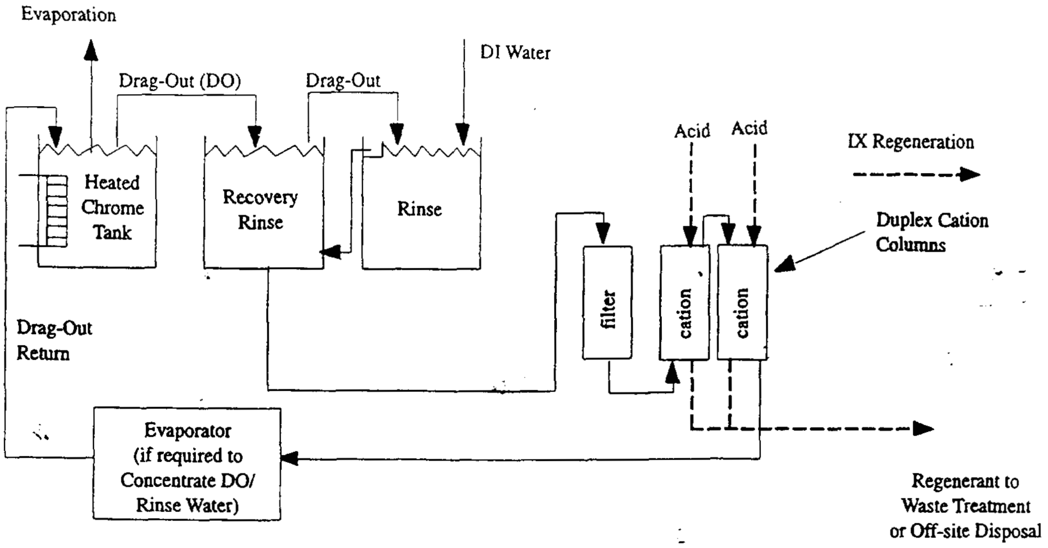


Application IX-1: Ion Exchange Recovery-Metal Scavenging Configuration



Application IX-2: Ion Exchange Recovery-Metal Recovery/Deionized Water Recycle

Exhibit 3-23. Additional Configuration for the Application of Ion Exchange for Chemical Recovery



Application IX-3: Ion Exchange Recovery-Chromium Drag-Out Return

Exhibit 3-24. Listing of Ion Exchange Applications Identified from the Users and Vendors Surveys

	Number of Applications Identified During Surveys[1]	
Application/Process Solution	**Users Survey**	**Vendors Survey**
Recovery Applications:		
Brass Plating, cyanide	0	1
Copper Plating, not specified	0	40
Copper Plating, acid	0	6
Copper Plating, cyanide	0	1
Copper Plating, electroless	0	2
Chromium, Cr^{+3}	0	1
Chromium, Cr^{+6}	5	6
Cadmium, cyanide	3	0
Gold, Cyanide	9	0
Gold, non-cyanide	1	0
Lead Plating	0	20
Nickel Plating, not specified	1	1
Nickel Plating, Watts	9	5
Nickel Plating, sulfamate	2	0
Nickel Plating, electroless	1	2
Tin Plating	0	10
Tin-Lead Plating	0	2
Zinc Plating, cyanide	0	0
Zinc, non-cyanide	3	1
Metal Scavenging, not specified	0	45
Solution Pruification[2]	9	25
Rinse Recirculation, no recovery[3]	10	75
End-of-Pipe Treatment, primary[3]	8	0
End-of-Pipe Treatment, polishing[3]	1	21

Notes:

[1] This exhibit compares the number of ion exchange applications identified during the Users and Vendors Surveys. The Users Survey data includes the responses from 318 plating shops. The Vendors Survey data includes responses from Kinetico Systems Engineering, Kinetic Recovery Corporation and Memtek Corporation.

[2] Details contained in Section 4.

[3] Details contained in Section 6.

the cation resin bed becomes exhausted there is insufficient acidity left to decompose the cyanide complex which is an anion and it will be exchanged for an OH^- ion in the anion resin bed. This presents a significant problem since the cyanide complex will accumulate in the anion resin and because of its high affinity to the resin matrix, regeneration will not remove it. If this occurs, the resin may require replacement. This problem is not a concern with gold cyanide applications because in most cases the resins are incinerated during the recovery process, rather than regenerated. Incineration of spent gold resin is an economically acceptable practice because of the relatively small quantity of resin used and its low cost in comparison to the gold contained on the resin.

Another operational problem with cyanide solutions can be caused by excessive free cyanide in the rinse water. If this condition exists, the free cyanide will remove the heavy metal from the cation resin and form a new metal-cyanide complex.

3.4.4 Technology/Equipment Description

The initial part of this section describes some of the more important design elements of ion exchange systems and the latter part presents a description of commercially available equipment.

3.4.4.1 Ion Exchange Resins and Columns

A wide range of ion exchange resins are manufactured, the choice of which depends mainly on the type of metal being recovered and the chemical composition and characteristics of the solution being treated. Properly matching the ion exchange resin and the process chemistry should result in efficient operation, quality byproducts and lower operating costs. Inappropriate selection of resin can result in total system failure.

Resins can be broadly classified as strong or weak acid cation exchangers or strong or weak base anion exchangers. Strong acid resins are so named because their chemical behavior is similar to that of a strong acid. The resins are highly ionized in both the acid and salt form. In a weak acid resin, the ionizable group is a carboxylic acid (COOH) rather than the sulfonic acid group (SO_3H) used in strong acid resins. These resins behave similarly to weak organic acids that are weakly dissociated. Because weak acid resins have an affinity for hydrogen ions, they have a limited exchange capacity when used to treat solutions with a pH below 6.0 (ref. 39).

Like strong acid resins, strong base resins are highly ionized and can be used over the entire pH range. Weak base resins are like weak acid resins, in that the degree of ionization is strongly influenced by pH. Consequently, weak base resins exhibit minimum exchange capacity above a pH of 7.0 (ref. 39).

A major advantage of both weak acid and weak base resins is that they can be regenerated much more efficiently than the strong acid and strong base resins. The weakly ionized resins can be regenerated using slightly greater than the stoichiometric reagent requirements, whereas the strongly ionized resins require significantly more regenerant (ref. 39).

Many specialty resins, such as chelating resins, are also in commercial use. Chelating resins that exhibit a high selectivity for heavy metal cations over other cations in solution have been commonly used in metal finishing, especially in the past ten years. Because of their selectivity, they are especially useful for end-of-pipe polishing following hydroxide precipitation. Chelating resins are also used in recovery with electroless copper and electroless nickel plating solutions. Generally, chelating resins cannot be used at low pH (<4) and a pH adjustment step is typically needed before the ion exchange process.

Exhibit 3-25 provides some general guidance on the types and capacities of resins used for common metal finishing chemical recovery applications, the chemicals used for regeneration and the method of recovery.

Most industrial applications of ion exchange used fixed-bed column systems, the basic component of which is the ion exchange column. The column must:

- Contain and support the ion exchange resin
- Uniformly distribute the service and regeneration flow through the resin bed
- Provide space to fluidize the resin during backwash
- Include the piping, valves, and instruments needed to regulate flow of feed, regenerant, and backwash solutions

After the feed solution is processed to the extent that the

Exhibit 3-25. Information and Data for Ion Exchange Resins Used for Metal Finishing Applications

Plating Solution	Resin Type	Capacity lbs. Metal/ft^3	Regenerant	Typical Recovery Method(s)
Watts Nickel	strong acid cation	1.8	H_2SO_4 or HCl	electrowin Ni or use nickel sulfamate in bath
Sulfamate Nickel	strong acid cation	1.8	sulfamic acid	nickel sulfamate used in bath
Acid Copper	strong acid cation	2.0	H_2SO4 or HCl	electrowinning
Acid Zinc	strong acid cation	1.8	HCl	zinc chloride used in bath
Cyanide Copper[1]	strong acid cation	1.5	H_2SO4	electrowinning
Cyanide Zinc[1]	strong acid cation	1.2	H_2SO4 or HCl	electrowinning
Cyanide Cadmium[1]	strong acid cation	1.3	H_2SO4	electrowinning
Cyanide[1]	medium base anion	1.6	NaOH	treatment
Tin/Lead Fluoroborate	strong acid cation	6.5	methyl-sulfamic acid	electrowinning
Chrome Plating Cation	strong acid cation	1.7	H_2SO4 or HCl	treatment
Chrome Plating Anion	medium base anion	3.1	NaOH	membrane electrolysis, or pass through cation resin, then use chromic acid in bath
Final Polishing	selective cation (chelating)	2.7	H_2SO4 or HCl/NaOH	treatment

[1] Cyanide metal solutions are treated first by a strong acid cation resin (cyanide complex destruction and metal recovery) followed by a medium base anion resin (cyanide recovery). This process is discussed in Section 3.4.3.

Source: Based on data provided by Dr. Fred Reinhard, Kinetic Recovery Corporation.

resin becomes exhausted and cannot accomplish any further ion exchange, the resin must be regenerated. Resin capacity is usually expressed in terms of equivalents per liter (eq/l) of resin. An equivalent is the molecular weight in grams of the compound divided by its electrical charge or valence. For example, a resin with an exchange capacity of 1 eq/l could remove 37.5 gram of divalent zinc (Zn^{+2}, molecular weight of 65) from solution (ref. 39).

The hydraulic loading of resins will vary considerably from application to application, depending on: column design; type of resin employed; concentration of metal in solution; other chemical characteristics of the feed solution (e.g., pH); and the allowable concentration of metal in the column effluent. Typical hydraulic loadings range from 2 to 3 gpm of rinse water per cubic foot of resin.

3.4.4.2 Integrated vs Modular Designs

An integrated ion exchange system design is one in which the various components needed to perform the ion exchange recovery and regeneration functions are connected within the one unit. Such systems may also have attached electrowinning units and/or chemical treatment systems for processing the regenerant. The modular or point source design separates the ion exchange column from the regeneration and regenerant processing equipment. With the modular design, the columns are transported to a central station for regeneration (in some cases the modules are hard piped). The regeneration station can be either in the plating shop or at an off-site location (i.e., centralized waste treatment facility). The modular ion exchange strategy can reduce capital costs for small to medium-sized applications where low to moderate regeneration frequency is required. Also, the modular units are considerably smaller and therefore do not occupy as much production area floor space as integrated units (i.e., if the regeneration station is remotely located to a non-production area). However, operating costs are usually higher for modular systems due to the labor needed for transporting the modules and connecting them to the regeneration station (or for changing operating modes and valve positions for hard piped modular systems) and initiating regeneration. Some commercial ion exchange modules have the appearance of large cans and are referred to as ion exchange canisters. With this type of unit, the canisters can be stacked upon one another to combine anion and cation types or to increase the resin bed volume. Standard column designs are also available.

3.4.4.3 Single vs Duplex Column Operation

Duplex column ion exchange systems are used in many chemical recovery operations, especially where a continuous feed flow is expected. Dual column configurations avoid downtime during regeneration. Two different duplex column arrangements are commonly used. In one arrangement, which is referred to as parallel/standby, the feed stream flows through either one column or the other, but never both. The off-line column is regenerated and then is held in reserve until the other column is ready for regeneration. This is a somewhat inefficient use of the two columns since column switching must take place before breakthrough occurs, which happens before the resin is completely loaded with ions of interest. In the second case, which is referred to as lead/lag, the two columns are placed in series flow. During operation, the majority of metal removal is accomplished in the first column (lead column) until it approaches capacity. The process can continue until the first column is essentially loaded to full capacity with ions of interest, since the second column (lag column) will remove the breakthrough of the first column. After breakthrough is reached, the first column is taken off-line for regeneration and then put back into service as the lag column. The roles of the two columns continue to be reversed following each regeneration. The switching of the columns, initiating of regeneration and other functions of modern ion exchange equipment is usually controlled by a microprocessor.

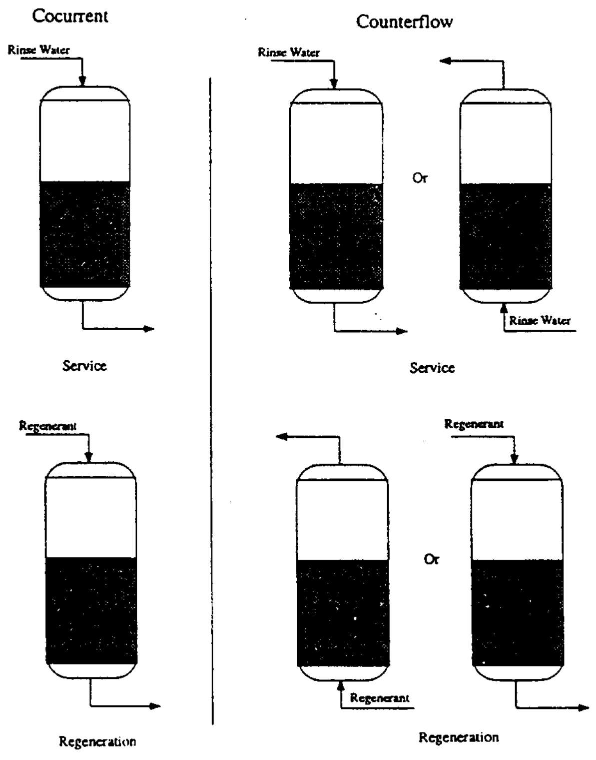
A special single column design that is widely used is referred to as reciprocating flow ion exchange (RFIE). A commercial application of this design is the Recoflo® (ref. 39, 349, 364, 365). The Recoflo® system is characterized by its short resin beds (6 to 24 in. as compared to 40 to 60 in. minimum for standard counterflow design) containing fine particle size resin beads. The Recoflo® process operates in a counterflow mode (see Section 3.4.1.4) with approximately a five minute cycle. During the cycle, the feed stream is fed for approximately 2.5 minutes, then regeneration occurs for approximately 2.5 minutes. The cycles are controlled by a microprocessor and are continuously repeated. The short cycle time, which is made possible by the short resin bed, emulates a continuous flow process.

3.4.4.4 Counterflow vs Cocurrent Flow/Regeneration

One method of categorizing the operation of different ion exchange systems is by the direction of the service flow (e.g., rinse water) vs the direction of the regeneration flow. The two configurations that can be used are shown schematically in Exhibit 3-26. With cocurrent operation, the service flow and the regeneration cycle flow in the same direction and with countercurrent flow, they flow in opposite directions (as shown, service flow can be either downward or upward). Countercurrent flow is considered by most sources to be the more efficient method (e.g., ref. 42).

With cocurrent flow the hydrogen ions displace metal ions from the top to the lower portion of the bed. Complete removal of these ions can only be accomplished by the use of excessive levels of acid regenerant. With normal regenerant usage, there is a "heel" left at the exit end of the column (i.e., undisplaced metal ions). On the following service cycle, the desired exchange reaction occurs in the upper portion of the bed. However, as the hydrogen ion concentration increases to-

Exhibit 3-26. Comparison of Cocurrent and Counterflow Regeneration



Source: ref. 43

ward the lower section of the bed, some reexchange with previously undisplaced metal ions leads to metal ion "leakage."

After regeneration of the counterflow system, the residual ions are in the top of the bed, with the bottom being fully converted to hydrogen. Thus, there are no residual metal ions present at the bottom of the bed to permit the leakage reaction to occur on the subsequent service cycle (ref. 43).

In addition to reduced ion leakage, counterflow regeneration can increase operating capacities, decrease the need for waste stream pH adjustment, and reduce water rinsing requirements (ref. 43).

3.4.4.5 Other Equipment/Design Considerations

In addition to the basic ion exchange column, auxiliary equipment is employed for various purposes, among which include: resin bed channeling and fouling prevention; pH adjustment of the feed stream; solution pump and flow control; need for regeneration identification; and regeneration cycle control.

Pretreatment of the feed stream is usually performed. Filtration is a basic requirement for nearly all ion exchange applications. If solids are permitted to enter the ion exchange bed, they will often create an uneven film on the top of the bed that acts as a plug. The solids will impede flow and cause channeling through the bed. Channeling of the feed solution will result in incomplete usage of the bed and inefficient processing (ref. 349). Most commonly, cartridge filtration is used for this purpose. Multimedia filters are sometimes used in high flow applications, where changing of the cartridge filters would be too time consuming (ref. 348). Other types of pretreatment include pH adjustment and carbon filtration. The adjustment of pH is used for certain applications where resin capacity can be enhanced by increasing or lowering the pH. Carbon filtration is used to remove certain organics such as oils that can become irreversibly sorbed by ion exchange resins and oxidants such as peroxide that can oxidize and ruin the resins (ref. 348).

The means for identifying the point at which regeneration should be initiated varies among commercially available equipment. The methods employed depend on the overall design of the system (e.g., a lead/lag unit may be able to tolerate some ion leakage from the first column whereas a single column may not), the tolerable leakage concentration, the variability of the feedstream, the ion(s) of concern, and the solution chemistry. Some equipment uses direct measurement methods to identify breakthrough. Examples of applicable methods and instruments include: conductivity meters, sometimes used in conjunction with pH meters; specific ion probes; and colorimetric analytical methods. A different strategy is to regenerate a column based on elapsed time or flow. These latter methods are applicable to feed streams with relatively constant parameters.

Other design features of ion exchange systems, such as controls, are discussed in Section 3.4.1.6.

3.4.4.6 Commercial Equipment

This subsection contains a description of commercially available ion exchange equipment that is manufactured and/or sold by vendor survey respondents. This is intended to provide the reader with information and data on a cross section of available equipment. Mention of trade names or commercial products is not intended to constitute endorsement for use.

Kinetico Engineered Systems, Inc. (Kinetico) manufactures various ion exchange equipment including that applicable to chemical recovery, bath maintenance, raw water treatment, and end-of-pipe polishing. Since 1980, they have sold more than 300 units. The Kinetico Complete Ion Exchange (CIX) series is applicable to metals recovery and water recycling with configurations similar to that shown in Exhibit 3-22 (applications IX-1 and IX-2). The CIX series are integrated packaged units with standard sizes ranging from 30 to 500 gpm. All units are dual column design for continuous operation (lead/lag configuration) with counterflow regeneration. Regeneration is initiated automatically by a patented control valve that monitors flow or by a manual override (push button). The control valve, which is non-electric, also directs the flow of solution for the regeneration cycle. Power for the valve comes from the flow and pressure of the water.

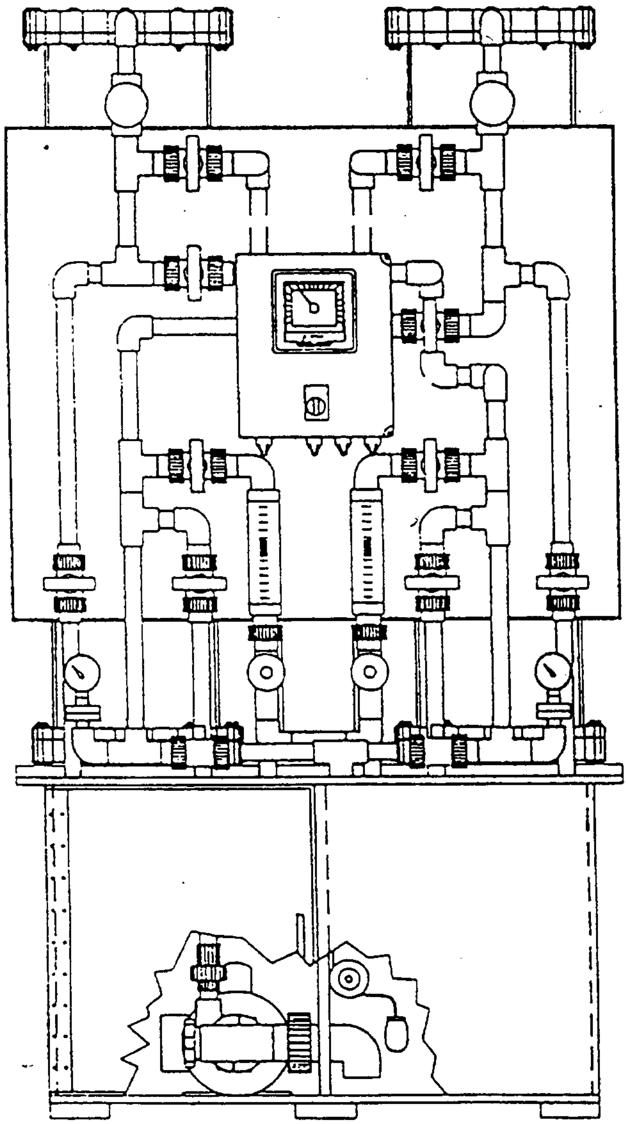
Kinetic Recovery Corporation offers modular ion exchange and regeneration systems for metals recovery and water recycling (see Exhibit 3-22, applications IX-1 and IX-2) as well as bath maintenance and end-of-pipe polishing. The modular ion exchange systems, which are dual column, are packaged with a cartridge filter system, flow meter, level sensor, feed pump, valve assembly, conductivity monitoring system and pump controls. The separate regeneration system (Exhibit 3-27) is capable

Exhibit 3-27. Modular Ion Exchange Equipment
(Courtesy of Kinetic Recovery Corporation)

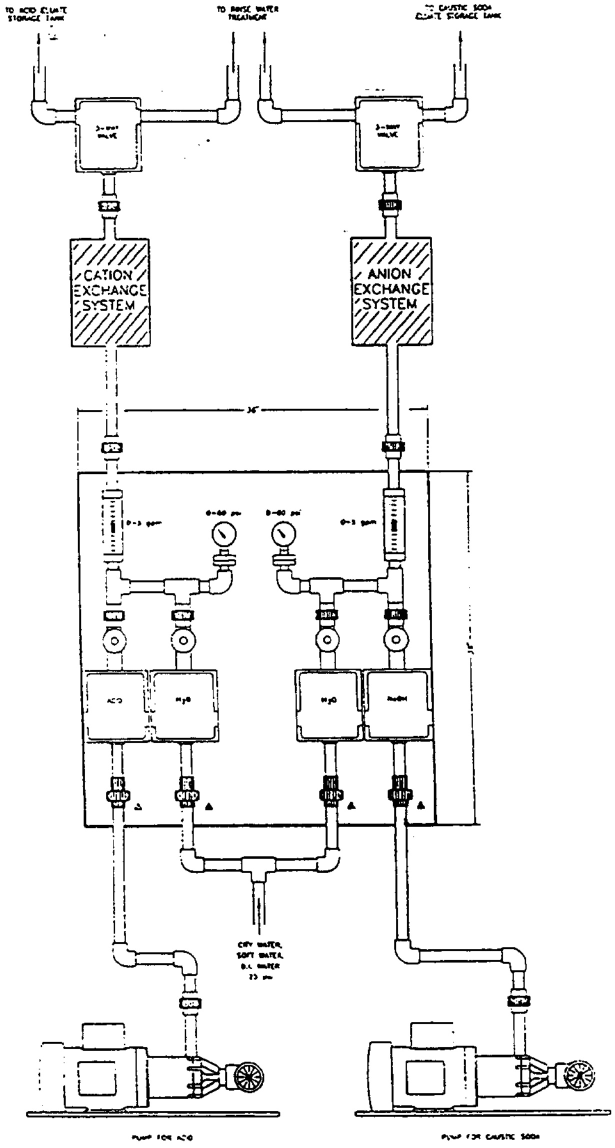
Cation/Anion Systems, including conductivity controls

Model	D200C	D300C
Resin Column	2 ft^3	3 ft^3
Column Dimensions:		
Height	50"	73"
Flange Diameter	14"	14"
Base Tank Dimensions:		
Length	40"	40"
Width	28"	28"
Height	23"	23"
Capacity	34"	34"

Total Height of System	73"	96"
Operating Flow Rate	6-8 gpm	8-10 gpm
Pump Motor	0.75 hp	2.0 hp
Maximum Operating Pressure	25 psi	25 psi
Maximum Operating Temperature	110°F	110°F

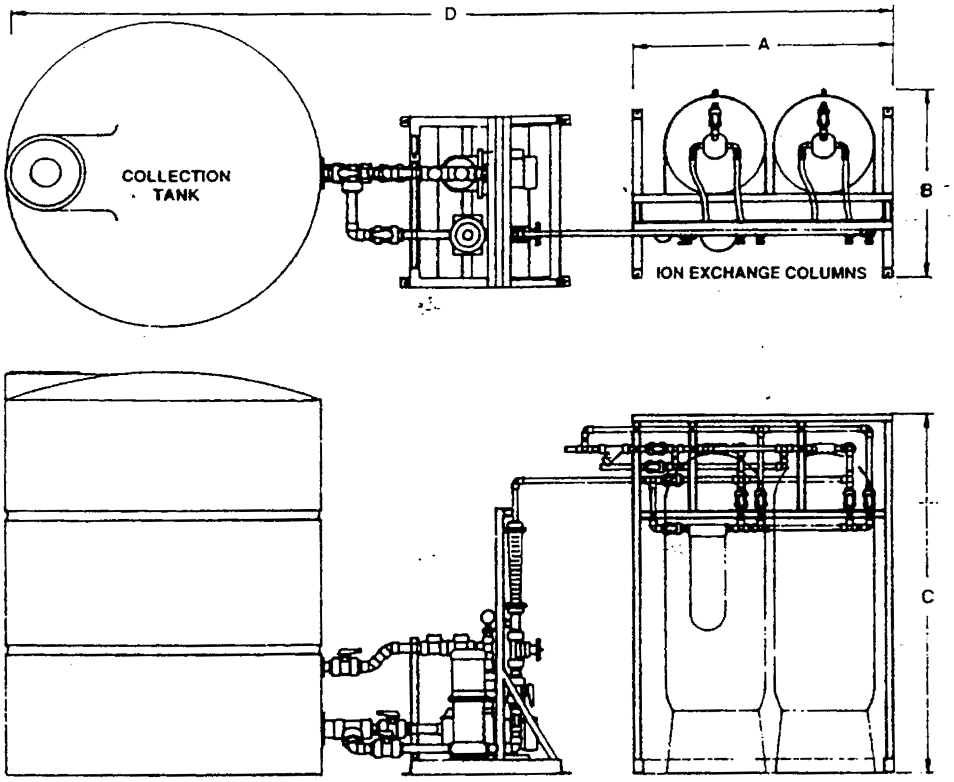


Modular Ion Exchange Unit



Dual Regeneration System

Exhibit 3-28. Ion Exchange Equipment for Lead-Bearing Rinse Waters (Courtesy of MemtekCorporation)



Pre-Conditioning Section

Ion Exchange Section

Specifications (Typical)*

System Designation		**PBX-10**	**PBX-12**	**PBX-16**	**PBX-24**
Flow (maximum)	gpm	2	4	7-10	15-20
Lead Capacity	lbs./column	3	6	10-16	22-30
Metal Removed (design)	lbs./week	0.75	1.5	2.5-4.0	5.5-7.5
Dimensions					
A. Length		55"	55"	61"	61"
B. Width		34"	34"	36"	44"
C. Height		65"	70"	83"	83"
D. Overall Length		12'	13'	13'	15'
Collection Tank Volume	gallons	220	500	750	1,000
Power Rating	volts/amps	460/5	460/5	460/7.5	460/10

Standard system components are pre-plumbed and pre-wired in the factory for easy on-site installation and include the following items:

- One (1) pre-conditioning HDPE tank
- One (1) pH monitor/controller
- One (1) level control probe with high level alarm
- Two (2) chemical feed pumps
- One (1) mixing pump
- One (1) lot Memtek proprietary ion exchange resin (PBX-R7)
- One (1) process pump
- One (1) cartridge filter
- Two (2) fiberglass ion exchange columns
- One (1) console for automatic pumps and pH control

*The specifications shown illustrate typical sizes, dimensions, and power requirements.

of regenerating cation and anion exchange resins simultaneously. It consists of two chemical feed pumps, a valve assembly/control board with electrically actuated ball valves, flow meter and globe valve and a regeneration controller with a PLC and an operator interface. The valve assembly board allows the adjustment of the ion exchange into several modes of operation (parallel, series) and regeneration. With the operator interface unit, the regeneration mode can be selected and all operating conditions (mode, time elapsed, alarm condition) are displayed.

Memtek Corporation manufactures integrated ion exchange equipment for metal recovery and water recycling and end-of-pipe treatment. Their metals recovery/water-recycle series (Rinse water Maintenance System or RMS™) is a dual column (lead/lag) packaged system with prefiltration, conductivity monitors and alarms, regenerant make-up tanks with level controls, and microprocessor controller. Memtek markets specific ion exchange systems for electroless copper and lead applications (see Exhibit 3-28). These two system include a preconditioning pH adjustment step.

Ionics International Ltd. (i^3) offers both a semi-automatic integrated ion exchange system and a modular system with separate ion exchange and regeneration stations. Both the integrated and modular ion exchange systems are dual column (lead/lag) systems used for metals recovery and water recycle. The integrated systems typically include two anion and two cation columns containing approximately 6 ft^3 of resin per column. Regeneration is manually initiated and automatically controlled. The modular systems are hard piped to the regeneration station rather than transported. The modular units typically permit a service flow rate of 10 gpm.

3.4.5 Costs

3.4.5.1 Capital Costs

Capital costs for modular and integrated ion exchange systems for metal recovery and water recycle (anion and cation columns) are presented in Exhibit 3-29. The modular ion exchange system costs are based on two responses to the Vendors Survey . The graphs show the costs for one and two modules of 2 ft^3 and 3 ft^3 capacities each. A single regeneration station is included in the cost for both the one and two module cases. Typically, one regeneration station can serve up to ten modules. Therefore, capital costs would be expected to increase in the step-wise manner shown in Exhibit 3-29 up to 20 ft^3/30 ft^3 resin capacities. The installed costs were estimated based on the projected costs for electrical and piping, including two components of electrical costs (service module and regeneration station) and three components of the piping costs (service module, regeneration module and service/regeneration module interface). The Vendor 1 system is hard piped to the regeneration station and the Vendor 2 system is transported (e.g., hand truck) to the regeneration station. Therefore, the vendor-2-installed cost includes only the first two piping components.

The integrated system capital costs include automated and semi-automated systems. The fundamental difference between the two types is that the regeneration cycle of the automated system is automatically initiated and the unit goes back into service automatically, whereas the semi-automatic system requires an operator to initiate regeneration and to put it back into service. Both systems operate automatically after regeneration or service is initiated. The installed cost for each system is the same, based on estimates for electrical and piping costs.

For small, manual applications, capacity is usually expressed in terms of resin volume, to which capital costs are directly related. Larger system capacities are more often expressed in terms of flow rate, but direct vendor-to-vendor pricing comparisons based only on capacity units such as gallons-per-minute can be quite misleading. Based only on flow rate specifications of four vendors, Exhibit 3-29 does not account for several cost factors including the amount of customization, the precise level of automation (which can vary considerably within the categories of "automatic" and "semi-automatic"), the type and quality of metering and monitoring instrumentation, and the general design strategies and criteria pursued by the manufacturer. These factors, in part, explain the wide range of prices quoted for similar flow rates.

Manual systems are often sized to provide an acceptable service period. Larger columns offer the benefit of fewer regenerations or replacements, less downtime and less labor expense. Automatic systems, on the other hand, are sized to handle the expected flow rate. While still a major design consideration, the service period has less impact on the user in terms of planning and labor. Thus, for highly automated systems, more frequent regenerations of smaller columns is a viable design strategy. An extreme example of this strategy is the reciprocation flow ion exchange, described in Section 3.4.4.3.

Exhibit 3-29(a). **Capital Costs for Fully Automatic, Water Recycle Ion Exchange Equipment**

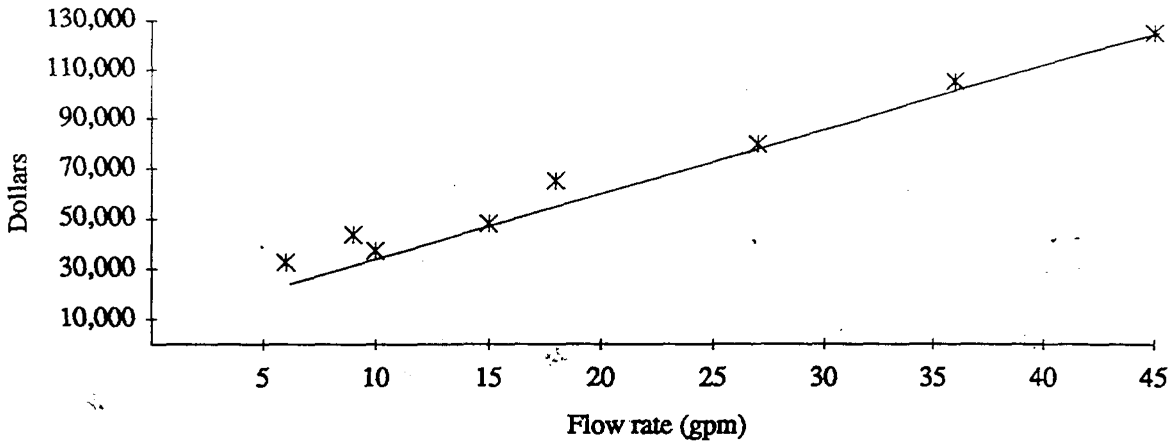
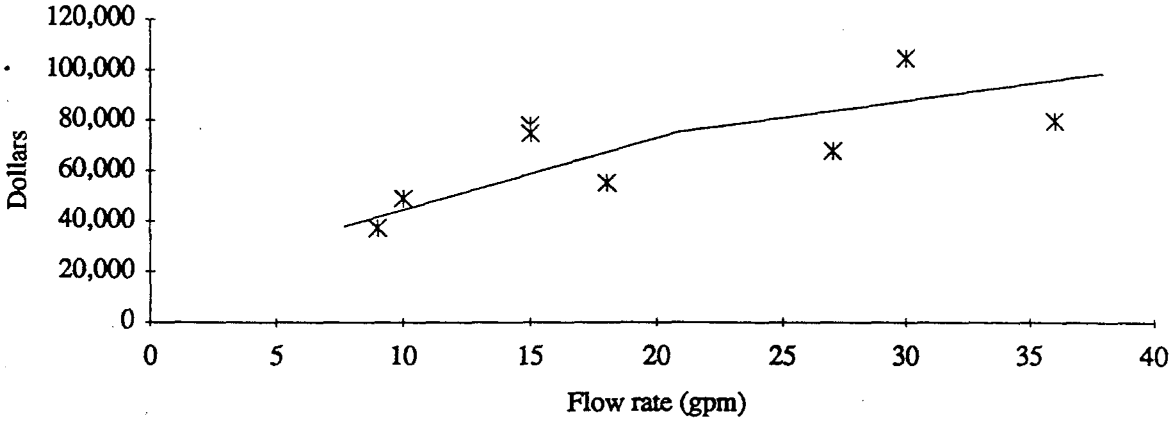


Exhibit 3-29(b). Capital Costs for Fully Automatic, Metal Scavenging Ion Exchange Equipment



Water recycling systems are, in general, more expensive than metal-scavenging units. These systems require both anion and cation columns, which alone roughly doubles the regenerations required, and the cation resin must remove all cations, including non-regulated common cations such as calcium, sodium and potassium. In most cases, these factors make automation highly desirable or an outright requirement.

Installation expenses are site-specific but can be significant typically 5 to 40 percent or more of basic equipment costs). Shops currently employing trenches may require extensive plumbing to segregate the ion exchange stream from other wastewater. On the other hand, modular systems with off-site regeneration may incur no significant installation costs at all. In general, water-recycle systems that service several sources will require the largest installation outlay.

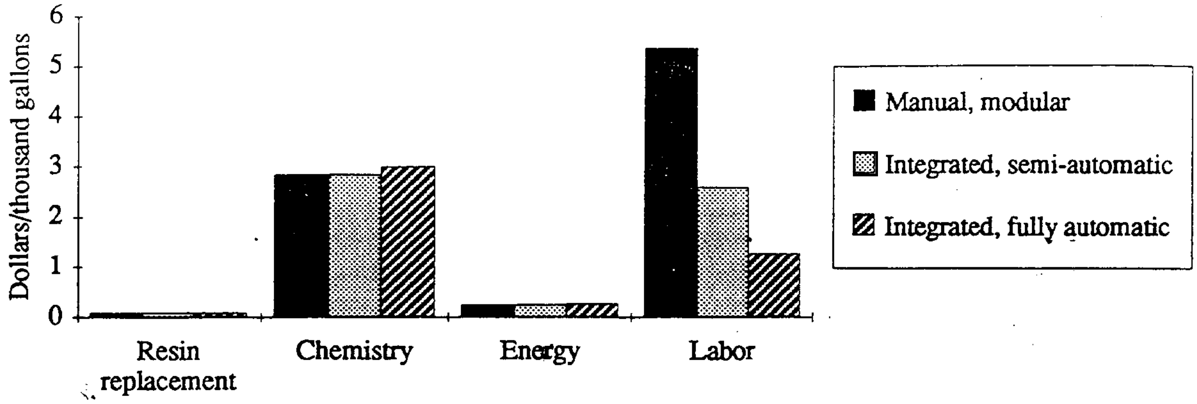
3.4.5.2 Operating Costs

Labor, regeneration chemistry, resin replacement, and energy are the major operating cost categories. Exhibit 3-30 presents operating costs for various operating modes of the ion exchange technology. This operating cost graph is based on a water-recycle application handling copper sulfate rinse water and is not necessarily representative of a wide range of applications.

Labor costs are significantly affected by the automation level of the system and automation capital costs are often quickly returned. Undersized or mis-applied equipment can greatly impact labor and other costs (see section 3.4.7).

Resin life is usually measured in years, but can be shortened by misuse and improper application. Resin fouling, mentioned by several respondents (see section 3.4.7),

Exhibit 3-30. Operating and Maintenance Costs for Ion Exchange Systems



is usually a result of a marginal application, misuse, or insufficient upstream filtration or pre-treatment. Instrumentation designed to halt ion exchange system operation when harmful levels of chemistries enter the feed stream can be cost-effective where spills and accidental dumps are possible.

The operating costs estimates are based on the following assumptions:

Feed Characteristics (rinse water)/Resin Capacity

- Copper sulfate plating process generating rinse water containing 50 mg/l Cu^{++}.
- Resin capacity of 38 eq. Cu^{++}/ft^3 (=12,900 gal between regenerations for 2 ft^3 column).
- Assume two anion regenerations for each cation regeneration (=1.79 days between regenerations for 2 ft^3 column).

Energy

- 1 hp-hr/300 gal
- $.10/kWh (= $0.25/1,000 gal)

Regeneration Chemicals

- Assume 4 bed volumes for cocurrent (Vendor 1-Modular) and 2 bed volumes for counterflow (all others).
- H_2SO_4 (Modular 1): 12 gal (conc.) @ $2/gal per 12,900 gal flow (= $1.9/1,000 gal)
- NaOH (Modular 1): 24 gal (conc.) @ $2/gal per 12,900 gal flow (= $3.8/1,000 gal)

Resin Replacement

- Assume 5 year life with 3% mechanical loss per year.
- Cation: $200/$ft^3$ (= $0.03/1,000 gal)
- Anion: $400/$ft^3$ (= $0.06/1,000 gal)

Labor

- $25.00/hr
- Modular 1: 1.0 hr/day (= $2.71/1,000 gal)
- Modular 2: 2.0 hr/day (requires transport) (= $5.43/1,000 gal)
- Semi-automatic: 1.0 hr/day (= $2.71/1,000 gal)
- Automatic: 0.5 hr/day (= $1.36/1,000 gal)

3.4.6 Performance Experience

A summary of the Users Survey data for ion exchange recovery applications is presented in Exhibit 3-31. Within this exhibit, the response data has been grouped by types of plating solution. These include: nickel, chromium, non-cyanide zinc, cadmium cyanide, and gold cyanide. A general discussion of the ion exchange data is presented, followed by specific information regarding each of the different types of applications.

The following information and data summarizes the performance experience of the survey respondents.

- The average satisfaction level for ion exchange recovery is 3.2 (on a scale of 1 to 5, with 5 being most satisfactory), which is lower than the average level rating for chemical recovery in general (weighted average for all chemical recovery applications is 3.4). Fifty-four percent of the shops indicated that this technology satisfied the need for which it was purchased and another 11% indicated that it partially satisfied their need. Thirty-five percent indicated that it did not satisfy the need for which it was purchased. The following is

Exhibit 3-31. Partial Summary of Users Survey Data for Ion Exchange Metals Recovery Applications

				Capital Costs			Operating Costs (Yr.)		Annual Savings								Satisfaction Levels (4)		
Shop Code	Application	Manf.	Year	Equipment Cost	Other Capital	Total	Non-labor	Labor Hrs.	Water	Process Chemicals	Treatment Chemicals	Sludge Disposal	Other	Total	Use Code (3)	Down Time %	Manf. Support	Tech-nology	(5) Future Decision
015	Nickel, Watts	NAPCO	1990	$50,000	$0	$50,000								ND	1			3	1
063	Nickel, Watts	Inviroserve Co.	1989	$150,000	$50,000	$200,000		1,200	√		√	√		√	1	5	4	4	1
105	Nickel, Sulfamate	Kinetico	1993	$12,000	$7,000	$19,000								ND	3			4	1
124	Nickel, Watts	Eco-Tec Inc.	1977	$60,849	$0	$60,849								ND	2	100		3	3
139	Nickel, Watts	Engineer/Consultant	1993	$60,000	$30,000	$90,000								ND	3				1
161	Nickel, Sulfamate	Dayton Water Systems	1991	$5,200	$5,000	$10,200	$7,500		$2,000	$1,000		$200		$3,200	1	3		5	1
163	Nickel	Bartix Eng. Systems	1987	$15,000	$0	$15,000	$2,477	1,000				$10,000		$10,000	1	1	5	5	1
196	Nickel, Electroless	Dayton Water Systems	ND	$100,000	$3,000	$103,000	$3,000	150			$1,000	$1,000		$2,000	1	2		3	3
212	Nickel, Watts	Technology, Inc.	1989	$12,000	$3,000	$15,000								ND	2				3
261	Nickel, Watts	Eco-Tec Inc.	1986	$60,974	$0	$60,974	$2,000	70						ND	1	1		4	1
263	Nickel	Kinetico	1988	ND	$500	$500	$500	250	$5,000					$5,000	2	10		2	4
317	Nickel, Electroless	Millipore	1989	$10,000	$2,500	$12,500	ND	ND	$0	$0	$0	$0	$0	ND	2	ND	1	1	ND
318	Nickel, Electroless	Tiree Ind. (DMR 20)	1985	$2,000	$700	$2,700	ND	100						ND	2	20	3	1	3
	Average-Nickel		*1988*	*$52,602*	*$8,955*	*$61,557*	*$3,095*	*534*								*17*		*3.7*	
														ND					
052	Chromium, Hard	Ionsep	1988	$56,000	$0	$56,000	$500	200						ND	3	2		3	1
080	Chromium, Hard	Burt Process Tech.	1984	$3,025	$500	$3,525	$1,000	250						ND	2	99		1	3
161	Cr, Decorative (+6)	Dayton Water Systems	1992	$500	$2,000	$2,500	$5,000	100	$1,000	$1,300		$200		$2,500	1	5	4	5	1
163	Chromate, Aluminum	Bartix Eng. Systems	1987	$15,000	$0	$15,000	$3,064	1,000				$10,000		$10,000	1	1	5	5	1
305	Cr, Decorative (+6)	Haz. Matls. Mangt. Team	1992	$22,000	$0	$22,000	$6,000	50	√	√			√	√	1	6	5	5	1
308	Cr, Decorative (+3)	Haz. Matls. Mangt. Team	1990	$17,500	$7,000	$24,500	$4,000	50	$10,000	$20,000				$30,000	1	ND	4	4	1
	Average-Chromium		*1988*	*$18,631*	*$625*	*$19,256*	*$2,391*	*388*								*27*		*3.5*	
														ND					
061	Zinc, Acid	Bio Recovery	1989	$123,000	$0	$123,000	$20,000	1,040						ND	2	75		1	3
126	Zinc, Acid		1992	$40,000	$0	$40,000								ND	1		3	4	1
130	Zinc, Non-Cyanide	Bio Recovery	1990	$100,000	$0	$100,000								ND	3	50		3	3
245	Zinc, Non-Cyanide	Memphis Mobile	1984	ND	ND	ND								ND				1	3
289	Zinc, Non-Cyanide	Quin-Tec	1992	ND	ND	ND								ND	1			4	1
	Average-Zinc		*1989*	*$87,667*	*$0*	*$87,667*	*$20,000*	*1,040*								*63*		*2.6*	
														ND					
025	Cadmium, Cyanide	Ebbco	1991	$4,000	$1,200	$5,200	$3,400	300						ND	1	1		3	1
229	Cadmium, Cyanide	Unk	1984	$400,000	$350,000	$750,000	$100,000	2,080	$10,000	$2,000	$10,000	$30,000		$52,000	1	2		3	3
245	Cadmium, Cyanide	Memphis Mobile	1984	ND	ND	ND								ND				1	
254	Cadmium, Cyanide	Illinois Water Treatment	1986	$54,000	$2,000	$56,000	$8,000							ND	2	20		1	4
	Average-Cd-CN		*1986*	*$152,667*	*$117,733*	*$270,400*	*$37,133*	*1,190*								*8*		*2.0*	
														ND					
064	Gold, Cyanide	In-House				$0	$1,300							ND	1	5		4	1
123	Gold, Cyanide		1975	$2,000	$1,500	$3,500	$20,000			$1,344,000				$1,344,000	1	10		5	1
179	Gold, Cyanide	Technic	1983	$2,000	ND	$2,000	$200			$2,000				$2,000	1	1		5.	1
283	Gold, Cyanide	RFE Industries	1979	ND	ND	ND				$1,320				$1,320	1	10		3	1
287	Gold, Cyanide	Pennfield	1979	ND	ND	ND								ND	1	1		3	1
	Average-Gold		*1979*	*$2,000*	*$1,500*	*$3,500*	*$7,167*							ND		*5*		*4.0*	
														ND					
	Average-All		*1979*	*$44,050*	*$4,714*	*$48,764*	*$11,529*	*553*						$11,802		*20*	*4.3*	*3.2*	

(1) MRS is the Metropolitian Recovery Systems, a CWT facility in Minnesota.

(2) Other capital costs include installation and ancillary equipment.

(3) Use Codes: 1-currently operating; 2-not currently operating and no intention for future use; 3-not currently in use, but intend to use in future.

(4) Satisfaction levels (manufacturer and technology) 1 to 5, with 1=lowest and 5=highest.

(5) Future decision codes: 1-purchase the same technology from the same vendor; 2-purchase the same technology from a different vendor; 3-purchase a different technology; 4-do nothing.

(6) "√" indicates that a savings was realized, but not quantified.

(7) Average total equipment cost is the sum of average equipment and other capital costs, excluding data from PS 229. Average annual operating cost is the sum of average non-labor and labor costs. Average savings is simply the average of reported savings, excluding PS 123. This method of calculation probable understates the average annual savings of the users.

(8) ND = no data

a breakdown of the reasons why shops purchased this technology (not all shops responded and some shops gave multiple reasons):

To meet or help meet effluent regulations:	21
To reduce plating chemical purchases:	8
(includes all four gold applications)	
To reduce the quantity of waste shipped off-site:	14
To reduce wastewater treatment costs:	13
To improve product quantity:	6
Other:	0

- The use of ion exchange generally did not impact production quality or the rate of production. The following responses were provided:

	Product Quality	Production Rate
Improved	5	1
No Change	16	18
Decreased	3	4

- The majority of plating shops indicated, that based on their experience with this technology, if given the chance they would purchase the same type of equipment from the same vendor. The following is a breakdown of their responses:

Purchase the same technology from the same vendor:	18
Purchase the same technology from a different vendor:	0
Purchase a different technology:	8
Do nothing:	2

- The major savings from the operation of ion exchange for non-gold applications was due to reduced water use and reduced sludge generation. For gold applications, the major savings was due to the recovered gold.

3.4.6.1 Nickel Plating Performance Experience

Thirteen respondents to the User Survey provided detailed data regarding their experience applying ion exchange to nickel rinse waters. Two of these responses cover systems that were being installed at the time of the survey and therefore, no performance data are available from these shops (PS 105, PS 139). Three shops used the process for a short time period, but abandoned their efforts due to disappointing results (PS 212, PS 317, PS 318). None of the remaining eight shops currently operate the traditional recovery configurations (Exhibit 3-22), where the cation regenerant is subsequently processed by electrowinning to recover the nickel or nickel sulfate is returned to the bath. At one time, PS 124 recycled nickel sulfate regenerant directly to the bath. However, this shop discontinued use of the process due to "continuous and repeated" equipment failure. PS 015 purchased an electrowinning unit for nickel recovery, but the unit did not work and therefore, they selected to treat the regenerant instead. Also, one of the two new installations plans to operate with metal recovery (PS 139). Three shops use off-site recycling for regeneration of their columns (PS 161, PS 196 and PS 063) and another shop regenerates on-site and sends the regenerant to an off-site metals recycling firm (Inmetco) (PS 261).

Although no on-site recovery is presently practiced, the configurations used by the respondents involve the recycle of water. These applications have been included in this recovery section because they process a segregated nickel rinse water with ion exchange. As such, that they most likely experienced many of the same performance and O&M problems as recovery operations.

The following performance details were provided by survey respondents:

- The two most successful installations among survey respondents are PS 161 and PS 261. PS 161 sends their used ion exchange columns to off-site services for regeneration, most recently using Dayton Water Systems for regeneration of both nickel and chromium columns. This shop has used this form of off-site recycling since 1972. Originally, their equipment was purchased from Pollutronics and the columns were regenerated in Cleveland (company name not specified). They used Culligan's service in the late 1970's until 1991, when they switched to Dayton Water Systems "because of their recycling ability." After contacting Dayton Water Systems, it was learned that they do not currently provide a regeneration service for heavy metals, but may resume this service in the near future. The ion exchange columns used by PS 161 contain 3.2 ft^3 of mixed (anion and cation) resin. During the past year, PS 161 sent 18 nickel columns and 8 chromium columns to Dayton Water Systems. The cost of the service was $336 per column for regeneration plus a $70 per month rental fee for the equipment (therefore, the total annual cost for most recent year is $6,888 for nickel and

$3,528 for chromium). According to PS 161, Dayton Water Systems sent the regenerant to Inmetco for recovery of the metal (see Section 7 for information on off-site recycling).

- Only one of the shops indicated that an ion exchange unit applied to nickel plating was the cause of an effluent compliance excursion (PS 196). This shop stated: "Excursions happen when the mixed bed of resin is saturated with copper and nickel and will no longer polish the water." This shop uses an off-site service for regeneration and is charged by the number of columns used. Therefore, the shop may tend to load the resin beds to their maximum or beyond their breakthrough point.

- PS 261 reported a satisfaction level of 4 for ion exchange applied to nickel rinse waters. Their configuration is unusual in that the ion exchange unit is connected to the first rinse tank (i.e., most concentrated). Rinse water from the first rinse is pumped through the ion exchange column and is recycled to the last rinse (four-stage counterflow system). With this configuration, the ion exchange column receives the most concentrated rinse water. The normal configuration (see Exhibit 3-22) makes use of drag-out recovery to reduce the chemical load on the ion exchange system and recycles the final rinse. Using their configuration, PS 261 probably experiences the need for frequent regeneration. Their regenerant is sent to Inmetco for off-site recycle.

- PS 317 and PS 318 applied ion exchange to rinse waters from electroless nickel plating. Both shops eventually abandoned their efforts to make the technology work. PS 317 described their use of the technology as a poor experience and indicated that their unit "required more water to restore the resin beads than water being processed." PS 318 indicated that the "process did not meet expectations or effluent guidelines."

3.4.6.2 Chromium Plating Performance Experience

Five respondents to the Users Survey provided some detailed data on their experience using ion exchange for chromium recovery. One of these shops uses an off-site regeneration/recycle service (PS 161) for regenerating columns applied to decorative chromium rinses (chromic acid, fluoride, barium carbonate). This shop also uses the off-site service for nickel recovery, details of which are provided in Section 3.4.6.1. Another respondent (PS 305) regenerates their unit on-site and sends the regenerant (sodium dichromate) to an off-site recycle company (Inmetco). One of the respondents recovers chromium from combined chromic acid anodizing and chromate conversion coating rinse waters and recycles the anion regenerant (dichromate) to the dichromate seal tank (PS 001). This system includes both anion and cation columns. The cation column removes contaminants such as aluminum and the anion column removes hexavalent chromium. Rinse water from the first rinse is filtered and passes through the columns and is returned to the final rinse. The cation column regenerant is treated and the anion column regenerant is transferred to the dichromate tank. Two of the four respondent's systems are not currently in use, but were previously used for chromium recovery from hard chrome plating rinse waters. One of these respondents intends to put their system back into use if the need arises (PS 052). Presently they have zero discharge, which is achieved through drag-out recovery rinsing. Bath contaminants are removed using membrane electrolysis and a porous pot. The other shop tried the ion exchange process for a short time period in 1984 and does not intend to reuse it in the future (PS 080).

The following information and data summarize the performance experience of the five survey respondents.

- In one case, performance was hampered by operational and maintenance problems. PS 080 indicated that: "Initial attempts to use ion exchange for removal of impurities from chromic acid rinse water failed. Resins became fouled and could not be regenerated and maintain plating production throughput requirements." It should be noted that this system was relatively inexpensive ($3,025) as compared to the other chromium recovery units. The respondent indicated that the supplier stated capacity was 200 gpd and that the actual capacity was 0 gpd. The respondent provided a diagram in the survey that seems to indicate they were processing rinse water from drag-out tanks. This solution may have been overly concentrated with chromic acid for the apparently small ion exchange unit, causing almost immediate total loading of the resin. Also, their low capital expenditure may indicate that prefiltration was not included with the purchased ion exchange equipment.

- PS 001 indicated that the supplier stated capacity and the actual capacity of their ion exchange system was 6 gpm at a feed concentration of 100 mg/l CrO_4. At this flow rate the system recovered 98% of the chromium.
- None of the shops indicated that an ion exchange unit applied to chromium recovery was the cause of an effluent compliance excursion.

3.4.6.3 Non-Cyanide Zinc Performance Experience

Five respondents to the Users Survey provided data on their experience with ion exchange used with non-cyanide zinc plating. Only two of these respondents provided sufficient detail to be considered useful for this report (PS 061 and PS 130). Both of these systems were manufactured by the same company and were purchased just one month apart. One ion exchange system was applied to acid zinc and the other to alkaline zinc. As will be discussed, the performance of the two systems was reportedly very different. The more successful of the two systems (PS 130) is a combination ion exchange and electrowinning system, similar in configuration to that shown in Exhibit 3-22. The other shop (PS 061) used ion exchange as an end-of-pipe treatment for "zinc bearing rinses and selected bath dumps," with the ion exchange regenerant going to an evaporator for concentration and the concentrated solution being hauled to an off-site recycle firm. The ion exchange processed wastewater was pH adjusted and discharged to a city sewer. This shop does not have a conventional hydroxide precipitation system following the ion exchange process. Originally this shop planned to return the zinc chloride concentrate from the evaporator to the zinc plating tank. As discussed later in this section, this plan did not work.

The following information and data summarize the performance experience of the two survey respondents.

- One of the two shops providing detailed data on zinc applications indicated that their ion exchange unit was not the cause of an effluent compliance excursion (PS 130). The other shop indicated that their overall treatment system, which included zinc and chromium ion exchange, evaporation and pH adjustment, caused an effluent limitation excursion. Their treatment system was put into operation in December, 1989. On July 4, 1990, they received a cease and desist order from their control authority.
- The performance of the ion exchange system operated by PS 061 was hampered by operational and maintenance problems. These are discussed in Section 3.4.6.3.2. The supplier stated capacity of this application was 18 gpm and the actual capacity was 10 to 12 gpm.
- PS 061 originally planned to recover the zinc chloride regenerant by concentrating it with evaporation and then reusing it in the zinc plating tank. This was not possible due to: (1) Chromium was present in the regenerant, and to remove the chromium would have required redesigning the ion exchange system. (2) The amount of zinc chloride generated by "false regenerations (a constant problem)" was much more volume than could be used in the plating tank, even after evaporation. (3) The low pH of the regenerant kept destroying the heaters in the evaporation unit and the steam from the system was so acidic that it corroded a hole in the shop roof. This shop also tried to recover the zinc using electrowinning. They found that it was too difficult to maintain a chemical balance during the process and that chlorine gas was liberated. Both problems made the process ineffective and the electrowinning unit was never put into full operation.
- Although PS 130 gave their system a satisfaction level rating of 3, they indicated that its downtime due to O&M problems was 50%.
- Both of the shops indicated, that based on their experience with this technology, they would purchase a different technology if given the opportunity to repeat the process.

3.4.6.4 Cadmium Cyanide Performance Experience

Four respondents indicated that they have used ion exchange for chemical recovery with a cyanide plating solution other than gold cyanide. These four shops included four applications to cadmium cyanide rinse waters and one for zinc cyanide rinse waters (one shop did both).

The shop using both applications (PS 229) installed their equipment in stages during the early to mid-1980's and it was integrated with an HSA electrolytic recovery system. The shop provided insufficient details to draw any conclusions, however, they offered the following as a summary of their experience with the combined system: "Costs in 11 years far outweigh benefits. Would have been much more practical to install conventional precipitation technology."

The other three respondents also provided sketchy information for their applications. One of the units was a pilot system purchased in 1991 that is still being used in 1993 (PS 025). The response from that shop indicate that they are relatively satisfied with the system. PS 245 used a rented ion exchange column for cadmium recovery and found that the resins "loaded very quickly and did not appear to be the right application." They intend to use the equipment following conventional precipitation for water reuse. Since these two applications require different types of resins, it appears that this respondent has not received sufficient technical support to utilize this technology. PS 254 purchased ion exchange equipment in 1985 for cadmium recovery. They later eliminated the ion exchange process because it was recycling ferrocyanides to the plating bath.

The following information and data summarizes the performance experience of the survey respondents.

- The major savings from the operation of ion exchange for this application was the result of water use reduction, treatment chemical reduction and sludge volume reduction.

- PS 229 reported that the capacities of their ion exchange columns were 50 percent of the supplier stated capacity (2 lb/column vs 4 lb/column). They also indicated that they were unable to reuse either their zinc chloride or cadmium chloride regenerant due to an excess volume problem in the plating tank (i.e., insufficient surface evaporation from the low temperature baths). They evaporate water from the zinc chloride regenerant (500 gpy) and send the concentrated solution to a landfill. They electrowin cadmium from that regenerant (1,000 gpy) and then send the metal-depleted regenerant to off-site disposal. A discussion of cyanide plating applications is presented in Section 3.4.3. Low cation capacity may be due to excess free cyanide. Methods for concentrating the solution and making headroom in the plating tank using evaporation are discussed in Sections 3.2 and 3.3. Electrowinning of the cadmium regenerant is an acceptable method of recovery. The recovered metal can often be used as anode material. It is possible to increase the recovery rate by reusing the cation regenerant following electrowinning (see Exhibit 3-22). PS 229 also indicated that the fact that their equipment manufacturer went out of business within two years of installing their ion exchange equipment hindered the performance of their application.

- None of the shops completing the survey indicated that an ion exchange unit applied to cyanide plating rinse waters was the cause of an effluent compliance excursion.

3.4.6.5 Gold Cyanide Performance Experience

Five user survey respondents provided some detailed data on their experience with ion exchange used for gold recovery. All but one of these shops send their used resins to their gold solution suppler for credit toward bath chemicals. The other shop regenerates the resin on-site and uses electrowinning to recover the metal (PS 123). The following information and data summarizes the performance experience of the survey respondents.

- The average satisfaction level for ion exchange applied to gold cyanide is 4.0 (on a scale of 1 to 5, with 5 being most satisfactory), which is higher than the average level rating for ion exchange chemical recovery in general. Also, all of the shops indicated that this technology satisfied the need for which it was purchased. In each case the need was identified as reducing plating chemical purchases or other (i.e., reclaim gold). The range of savings from gold recovery for these shops was $1,320 (PS 283) to $134,400 (PS 123) per year.

- Only one of the shops provided any capacity data. PS 179 indicated that they experience an average resin loading of 4 troy ounces per cubic foot of resin. They typically use 1 ft^3 of resin per year.

- In some cases, performance was hampered by operational and maintenance problems. These are discussed in Section 3.4.7.

3.4.7 Operational and Maintenance Experience

Of the 27 shops providing data, 17 (or 63%) were still operating their ion exchange equipment at the time of the survey. The average age of the operating systems was 7.0 years (only 4.2 years excluding gold plating applications). The average percentage of downtime experienced by the respondents was 20% (only 8.7% excluding PS 124, PS 080 and PS 061).

The following summarizes the respondents operating labor information. Details on O&M experiences are discussed for each type of application in Sections 3.4.7.1 through 3.4.7.5

- Fourteen shops provided operating labor data. For these shops, the average number of annual operating hours per ion exchange system were: 553 hrs/yr. The skill requirement commonly needed for operating this technology is a trained technician or a wastewater treatment plant operator. The following is a breakdown of the responses for skill requirements:

Environmental Engineer:	5
Process/Chemical Engineer:	5
Chemist:	4
Consultant:	3
Plumber/Pipe Fitter:	4
Electrician:	4
Vendor:	1
Senior-Level Plater:	6
Junior Level Plater:	4
Trained Technician:	14
Wastewater Treatment Plant Operator:	13
Common Labor:	3
Other:	0

3.4.7.1 Nickel Plating O&M Experiences

Reported O&M problems for nickel plating ion exchange applications relate to equipment failure and process chemistry concerns. Of the 11 shops providing data, six (or 63%) were still operating their ion exchange equipment at the time of the survey. The average age of the operating systems was 4.4 years. The average percentage of downtime experienced by the respondents was 17% (only 4% excluding PS 124).

The following O&M experiences were reported by respondents:

- PS 124 was the earliest installation (1977). Considering the cost ($60,849 total installation cost), this was apparently a major recycling project for the shop. The shop provided the following responses concerning the equipment and the process: "Continuous and repeated failure of cheap valves used in design caused unit to plug up". "Return of calcium sulfate to plating tank clogged pipes and anode bags."

- PS 212 reported that: "(The ion exchange system) was used for a short period of time. It never did the job it was intended to do."

- PS 263 reported that their equipment, which they refer to as "prototype", "worked well, but created plating problems." This was a 4 gpm unit that recycled rinse water from the final rinse of a muti-stage counterflow rinse system. The shop believes that their plating problem was caused by the water in the final rinse (i.e., that which is recycled to the ion exchange column) because it was too clean and resulted in passivation of the nickel plated parts before chrome plating (i.e., the subsequent process).

- PS 261 was the only shop that reported that they had no significant O&M problems.

- PS 063 reported O&M problems with probe indicators and the balancing of chemicals.

3.4.7.2 Chromium Solutions O&M Experiences

Reported O&M problems for chromium ion exchange applications relate to resin fouling and equipment failure. Of the four respondents providing data for this application, two were still in operation at the time of the survey. The average age of operating systems was 3.5 years. The percentage of downtime experienced by the respondents was 27% (only 3% excluding PS 080).

The following summarizes the respondent's O&M experiences:

- PS 080 indicated that their ion exchange system failed due to resin fouling. A discussion of this shop's system is presented in section 3.4.6.2.1.

- PS 052 indicated that their ion exchange regeneration process was very time consuming. They also indicated that only dilute rinse waters can be effectively processed by the unit and that their rinse waters are occasionally too concentrated for the unit.

- PS 001 indicated that their ion exchange system was also sensitive to the chromium concentration of the rinse water (i.e., feed to the ion exchange unit) and that to prevent overloading of the resin they initially rinse over the plating bath before using the rinse tanks.

- PS 305 indicated that they cannot process the contents of their drag-out tank with ion exchange, without oxidizing the resin. (Note: The recovery of chemicals from concentrated solutions is not a good application for ion exchange. This technology is best applied to dilute solutions.)

3.4.7.3 Non-Cyanide Zinc Plating O&M Experiences

Reported O&M problems for non-cyanide zinc plating ion exchange applications relate to equipment failure and resin contamination with oil. Of the two respondents providing data for this application, none were still in operation at the time of the survey. One was purchased in December, 1989 (PS 061) and the other in January, 1990 (PS 130). PS 130 indicated that they intend to use their system in the future, although no specific plans were discussed in their survey form.

The following summarizes the respondents O&M experiences:

- PS 061 provided the following information that relates to O&M problems: "Never believe an engineer again! This technology should be never used to treat zinc wastewater from a job shop. Way to touchy-system, must be simple-discontinued July 4, 1990." "Pump failure, resin fouled, computer failure, float switch failure, heater failure, and on and on and on-" "Nothing worked for this project." This same shop offered the following regarding technical restrictions of the technology that they have encountered: "Chemical concentration & flow rates are critical! Failure of any one part can shut down the whole system without warning-[sic]"

- PS 130 indicated that the reason they are no longer using their zinc ion exchange system was a problem with oil in the rinse water feed to the unit that fouled the resin. They indicated that they plan on using the system in the future, after making changes to their cleaning process. This shop indicated the ion exchange system was not working 50% of the time as a result of the oil problem.

3.4.7.4 Cadmium Cyanide Plating O&M Experiences

Reported O&M problems for cadmium cyanide plating ion exchange applications relate to equipment failure, frequency of regeneration, excess regenerant production and bath contamination. Of the four shops providing data, two systems were operational at the time of the survey. The average age of the operating systems was 5.5 years. The average percentage of downtime reported by the respondents was 8%.

The following summarizes the respondents O&M experiences:

- PS 229 reported that their ion exchange units were overloaded due to high drag-out rates and improper rinsing practices by their operators (discussed in Section 3.4.6.4.1). They also indicated that they felt their O&M problems were related to the manufacturer going out of business.

- PS 245 reported that their ion exchange columns loaded quickly and that the frequency of regeneration was very high.

- PS 254 eliminated their ion exchange process because it was returning ferrocyanides to the plating bath.

3.4.7.5 Gold Cyanide Plating O&M Experiences

Generally, the ion exchange units used for this purpose are small (< 0.5 ft^3 of resin) and are free of complex regeneration and control systems. As a result, the operational and maintenance problems are minimal and the units that are purchased remain in use. In fact, all of the gold cyanide ion exchange installations identified in the Users Survey were in operation at the time of the survey. The average age of the units was 14 years. The only specific problem identified by a respondent was flow blockage caused by algae growth. The average percentage of downtime experienced by the respondents was 5%.

3.4.8 Residuals Generation

The primary residuals from ion exchange recovery processes are the regenerants (eluates) and backwash solutions. The regenerants are concentrated wastes and the backwash is dilute. Both solutions are either caustic or acidic, depending on the resin type and application. High metal bearing regenerates (typically cation resin) are: (1) sometimes reused directly in the bath; (2) further processed to recover the metal (e.g., electrowinning); (3) waste treated; or (4) sent to an off-site recovery facility. Low metal bearing regenerants (typically anion resin) and backwash solutions are typically treated on-site. Waste treatment processes generate sludge that is an EPA listed hazardous waste (F006).

The volume of regenerant produced will depend on the regeneration requirement (e.g., lbs of acid per ft^3 of resin) and the concentration of acid used (typically 1 to 5%). The regeneration requirement will depend on the resin type, application (metal or complex being recovered) and the configuration (cocurrent vs counterflow). Typical volumes of regenerant are 20 to 50 gal/ft^3 of resin. The volume of regenerant waste is sometimes reduced by reusing the last portion of the regenerant, which will be less contaminated with metal and contains free acid. Backwash volumes depend mostly on the equipment design and the application. Typically, backwashing generates 25 to 75 gal/ft^3. The backwash is partly reused by some equipment vendors as makeup water for regenerant, in an effort to reduce the total waste volume generated. Because backwash contains only dilute concentrations of pollutants it is typically not a major concern and is treated on-site and discharged. However, for shops working toward zero discharge, the backwash volume could present a significant problem. Both backwash and regenerant can processed by evaporation to reduce the volume requiring disposal. However, this increases the capital and operating costs of the system. Also, evaporation of hazardous wastes is sometimes regulated as a RCRA technology and may require a permit to operate.

Application of Ion Exchange Technology in Pollution Prevention

by Lisa F. Wilk and Robert S. Capaccio,
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With the increasing regulatory emphasis on waste minimization and pollution prevention, metal finishers are constantly evaluating new and existing technologies and techniques for achieving environmental as well as production goals. Ion exchange is an existing technology that is widely used for generating high purity process waters, and is now seeing greater application in pollution prevention and waste minimization, particularly for metal finishing and electroplating process operations.

This article will assist metal finishers in determining whether ion exchange technology fits into their pollution prevention and waste minimization programs by reviewing pollution prevention applications of ion exchange for the metal finisher; important considerations in the selection, design, and operation of an ion exchange system; and advantages and disadvantages of the technology.

REGULATORY BACKGROUND

In response to public concern about the increasing number of hazardous waste sites, Congress enacted the Resource Conservation and Recovery Act (RCRA) in 1976, which established the regulatory framework for management of hazardous waste. The initial laws and regulations focused on controlling the symptoms of hazardous waste generation; however, with reauthorization of RCRA in 1984, the focus switched to causes of waste generation and RCRA's primary objectives changed to minimization of waste generation.

As originally defined, the term "waste minimization" referred to source reduction, recycling and reuse, and some forms of alternative treatment. Source reduction (e.g., minimizing or eliminating waste at the point of generation via chemical substitution, process modification) was identified by the United States Environmental Protection Agency (US EPA) as the preferred means of achieving waste minimization. EPA guidance identified recycling and reusing the waste in the same process or another process operation as the next preferred method of achieving waste minimization after attempting to minimize or eliminate the wastestream at the source. Alternative treatment was identified as the least preferred means of achieving waste minimization because it is often just a transfer of pollutants from one environmental media to another (e.g., from land to air, land to water). In fact, alternative treatment is only acceptable as a means of achieving waste minimization if it facilitates recovery and reuse, or reduces the volume and toxicity of the wastestream without dilution.

Although the initial regulatory focus was on minimization of solid and hazardous waste, with the enactment of the Pollution Prevention Act (PPA) of 1990, the concept of waste minimization has been expanded to include all environmental media (land, air, water). In addition, the majority of states have created their own pollution prevention legislation, some prior to the Federal legislation.

The term *waste minimization* has been replaced with the term *pollution prevention* to emphasize the multimedia focus as well as source reduction as the most effective means of achieving the goals of the PPA. Some state legislation takes pollution prevention even one step further by focusing on "toxics use reduction."

USE OF ION EXCHANGE FOR POLLUTION PREVENTION

Due to its versatility and cost effectiveness, ion exchange technology is becoming widely used in pollution prevention applications. Ion exchange is considered to be advanced in the sense that it can achieve a much better effluent quality than conventional sludge-generating metal hydroxide precipitation technologies; however, from an operational standpoint, it is much less operator-intensive to achieve a consistent effluent.

Ion exchange can be used at end-of-pipe as a polish to enhance existing wastewater treatment equipment, and it can help ensure compliance with increasingly more stringent wastewater effluent limitations. Ion exchange can achieve a much better effluent quality than conventional (sludge-generating) metal precipitation technology.

With the addition of ion exchange columns for demineralization, the treated effluent may then be reused in process rinsing operations.

Application of ion exchange directly in the process area is more in line with the intent of EPA pollution prevention goals, which emphasize the reduction of generation of pollutants at the source (i.e., source reduction) via process modifications, chemical substitutions, etc. as the most effective means of achieving waste minimization. In many cases, by the very nature of the business, metal finishers will need to use certain chemicals (customer or military specifications may require use of the chemical or an acceptable alternatives may not be available due the limitation of existing technology); in these cases, recycling and reuse technologies can be applied as a means of pollution prevention and waste minimization.

For the metal finisher, ion exchange is a cost-effective technology for achieving pollution prevention. Ion exchange has been used successfully in a variety of metal finishing operations including treatment and recycling of mixed metal rinsewaters, chromium recovery, nickel recovery, copper recovery, silver recovery, and other applications.

BASIC PRINCIPLES OF OPERATION

Ion exchange uses a resin consisting of either positively or negatively charged ionic species (i.e., cations or anions) attached to an inert polymer. The typical treatment operation consists of four cycles: service, backwash, regeneration, and rinsing.

During the service cycle, the wastestream is passed through the resin (typically in a resin bed or column) and charged ions present in the wastestream with greater affinity for the resin are exchanged with similarly charged ions attached to the resin bed.

After the majority of the exchange sites have been used up, the resin is considered to be spent or exhausted. Although the resin could be discarded and replaced when it becomes exhausted, the resin would typically be regenerated at this point so that it can be reused due to the cost of the resin and the goals of pollution prevention.

Prior to regeneration, the resin bed is backwashed to remove any particulates and resuspend the bed. A regenerant solution is subsequently passed through the resin bed to return the original charged ion to the bed and replace the now concentrated ions (e.g., metals) that have been removed from the wastestream. The spent regenerant solution may be directly recycled or reused, or may require further treatment, such as electrolytic recovery prior to recycling, reuse or disposal. The ions from the wastestream are thus concentrated in the regenerant solution. This step is frequently followed by a rinsing step (using deionized water) to remove excess regenerant solution.

In typical metal-finishing applications, the ion exchange resin essentially concentrates the heavy metals from dilute rinsewater wastestreams, thereby reducing the volume of the wastestream and enhancing the opportunities for recovery and reuse of the heavy metals.

IMPORTANT CONSIDERATIONS IN ION EXCHANGE SYSTEM DESIGN

Typically, an ion exchange system consists of a particulate filter and/or a carbon filter followed by ion exchange vessels. The filters serve to protect the resin from fouling. The ion exchange vessels may be arranged in a series or parallel configuration. Additionally, tanks and associated pumps for pH adjustment and regeneration are typically included with the system design.

The components of an ion exchange system are relatively inexpensive with the exception of the resin itself, which, depending on the application, can range from $100 to $400 per cubic foot. With ion exchange technology, however, the resin can be regenerated and reused. Treatability testing will help ensure appropriate resin selection, regenerant solution selection, and system sizing.

Ion exchange is widely used for generating high purity process water via deionization and demineralization; however, the resins used in demineralization and deionization applications are not capable of efficiently treating the heavy metals typically found in metal finishing and electroplating operations.

It is important to conduct treatability testing of your specific wastestream to ensure proper resin selection and sizing of the system. Treatability testing will help ensure that the system is not undersized or oversized and that interferences are not present that will render the resin ineffective in your application.

For example, a common problem with mixed metal wastestreams containing lead is that lead sulfate precipitates out on the resin during regeneration. Treatability testing can ensure appropriate selection of resin as well as regenerant solution for this application.

Ion exchange treatability testing can be done simply and at a relatively low cost and will result in significant savings in the final system as well as help ensure that the proper resin is selected and that ion exchange will be an effective solution for your application.

OPTIMIZING ION EXCHANGE SYSTEM PERFORMANCE

OPERATIONAL CONSIDERATIONS

Regeneration Volume and Frequency

A properly designed system will minimize regeneration frequency and the volume of waste regenerant solution generated. Various methods for regeneration are available, including in-column batch or continuous and out-of-column batch techniques. From the operator's standpoint, in-column methods are generally preferred. The batch in-column method (also referred to as the flooded vessel method) involves filling the column with regenerant solution, allowing it to sit for a specified time period, and then repeating this step or proceeding with the deionized rinsing step. The continuous in-column technique involves passing a specified volume of regenerant solution through the resin bed in a continuous flow-through manner either in a downflow or an upflow configuration. Although some operators may prefer the ease of operation of the flooded vessel method, the continuous method generally requires a lower volume of regenerant solution. Regenerant solution concentrations and volumes are calculated based on the specific characteristics of the resin and treatability test data.

Determining Breakthrough

Breakthrough is defined as the point at which the resin has become exhausted or spent, and therefore must be regenerated for continued use in the service cycle. In some applications, the ion exchange columns must be regenerated just prior to breakthrough in order to meet required effluent quality. In other applications, the presence of a limited concentration of the parameter(s) being treated is acceptable in the ion exchange system effluent stream.

Various methods are available for determining breakthrough and regeneration points, including timed-interval regeneration, on-line monitoring of ions and flow to identify appropriate regeneration, and periodic off-line sampling to monitor effluent quality. Selection of the appropriate method depends on the effluent requirements of the specific application.

Series versus Parallel Configuration

Ion exchange systems may be configured in a series or a parallel configuration. Parallel configurations are generally selected for higher flow rates. In applications where final effluent quality is critical, the series configuration has the advantage of allowing the operator to observe breakthrough in the initial column(s) of the series prior to breakthrough at the end-of-pipe (i.e., final effluent quality).

Charging and Recharging Vessels with Resin

Adding or replacing (i.e., charging and recharging) resin in the vessels must be performed appropriately to prevent premature loss in capacity due to flow restrictions or increased resin deterioration. Prior to charging the vessels, clean and inspect the resin vessel and internal distribution systems. It is important to accurately measure resin volume added to the vessel to ensure sufficient capacity within the vessel for bed expansion during backwashing. Fill half the vessel with deionized water, and pour the resin beads into the vessel being careful to avoid splashing so as to reduce resin loss. If the liquid level becomes too high during the recharging process it may be necessary to drain off some of the water. After filling the vessel with the appropriate volume of resin, the bed should be backwashed to remove any packing materials, resin fines or broken resin particles. After backwashing the bed depth and volume should be rechecked; if adjustments to the bed depth are necessary, then backwashing and measurement of the bed should be repeated after these adjustments are made.

Storage of Resins

Resins should not be allowed to dry out during storage (upon re-wetting, cracking and deterioration of the resin will occur). Additionally, resin vessels should be backwashed prior to shutdown to prevent fouling or cementing of particulates within the resin bed. Prior to long-term shutdown, anion resins should be rinsed with brine solution to ensure conversion to the more stable chloride form (versus the hydroxide form).

TROUBLESHOOTING

Sampling

Periodic sampling of the effluent from the ion exchange system is recommended to monitor the system performance. Often, in a series configuration, sampling ports are installed between each column to identify breakthrough in the initial columns of the series prior to breakthrough occurring in the final effluent.

When troubleshooting an ion exchange system, it may be necessary to collect samples of the resin for evaluation.

Short or Reduced Capacity

When an ion exchange system operates below its design capacity, potential causes that should be investigated include:

1. *Design Throughput*: Verify accuracy of the flow throughput measurement and recording device.
2. *Resin Loss*: Check resin volume. Resin loss typically occurs during backwashing, particularly if flow is not carefully controlled. Also check distribution and screening systems for potential damage.
3. *Inefficient Regeneration*: Due to operational and cost considerations, the resin will typically not be regenerated to 100% of its original capacity during actual operating conditions; however, the regeneration procedure should be designed and operated to ensure consistently adequate capacity. Appropriate amount, concentration, and contact time of the regenerant solution are important to achieve sufficient conversion of the resin to the proper form.
4. *Influent Loading Variation*: An apparent reduction in capacity may be observed if there is a significant change in the characteristics of the influent to the ion exchange system. The ion exchange system is typically designed to handle a specific loading. Should the loadings to the system increase significantly above design capacity, more frequent regeneration will be required.
5. *Service Flow*: The optimal service flow rate is specified by the system design. A significant increase above the optimum design flow rate will impact capacity.
6. *Resin Deterioration*: Resins have a limited service life, which is dependent on the specific type of resin and operating conditions. Resin deterioration can occur due to physical breakdown over time, loss of functional groups, or fouling. Physical breakdown of the resin can reduce the capacity of ion exchange systems through loss of broken resin during backwashing, poor flow distribution due to accumulation of resin debris, and blockage of internal distributors and screens. Depending on the stability of the functional groups of the particular resin, there may be some loss of functional exchange capacity during the first few months of operation; typically this is negligible for cation resins, but strong-base anion resins can lose 10–15% of total capacity in the first few months before slowing to a 1–2% per year. Resin fouling occurs via formation of precipitates, scaling, or films on the surface of the resin; or through internal fouling of the resin structure.

Poor Effluent Quality

If after regeneration, the effluent quality during the service cycle is inadequate, areas that should be investigated include: change in characteristics of the influent wastestream to the ion exchange system, change in the regenerant solution type or concentration or volume, potential resin fouling, or mechanical equipment component failure.

Flow Reduction and High Pressure Drop

Flow reduction (or increase in pressure loss across the resin bed) can be caused by a buildup of debris on the surface of the resin bed, broken or fine resin beads blocking the internal distributors and screens, or accumulation of precipitates within or on top of the resin bed or distribution system.

Cleaning Fouled Resins

Should the resin become fouled, various methods are available for cleaning the resin including air scouring, air agitation and abrasion backwashing, brine treatment, and acid or alkali soaking. It is important that the cause of the fouling be identified and remedied prior to returning to the service cycle. Generally, it is more time- and cost-efficient to evaluate cleaning methods on a laboratory scale prior to implementing them on the full-scale system.

PROS AND CONS OF ION EXCHANGE IN POLLUTION PREVENTION

Ion exchange is designed for application in treating dilute wastestreams such as the running rinses from plating operations. More concentrated wastestreams, such as dragout recovery or still rinses are more efficiently treated via alternate technologies such as electrolytic recovery or evaporation.

Ion exchange is a proven technology that can be applied as an effective means of achieving pollution prevention for metal finishing operations. It can achieve a high quality effluent with minimal operator attention. Although it generates a concentrated wastestream requiring further treatment or disposal, the volume of waste generated is significantly reduced and the technology facilitates recycling and reuse of rinsewaters and plating solutions. Depending on the application, the initial capital equipment costs may be moderate to high, but operating costs are relatively low compared with conventional treatment technologies.

MF

Biographies

Lisa F. Wilk is a registered professional engineer and has completed the course requirements for a Certified Toxics Use Reduction Planner. She is an Associate with Capaccio Environmental Engineering Inc. where she is responsible for environmental engineering design and consulting. She has extensive experience in the application of pollution-prevention and source-reduction technologies, and in the design, troubleshooting and evaluation of in-process and end-of-pipe industrial wastewater pretreatment systems.

Robert S. Capaccio is a registered professional engineer in over twenty states, a Certified Chemical Engineer and a Diplomate of the American Academy of Environmental Engineers. He serves as President of Capaccio Environmental Engineering Inc. and is involved in all levels of design and consulting for industrial facilities in the U.S. and abroad. He has extensive experience in the areas of waste minimization/pollution prevention, air and water pollution control and site remediation, and environmental auditing.

Using Your Ion Exchange Wastewater Treatment Equipment

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Ion exchange (IX) has become one of the most widely used technologies for wastewater treatment. There are many reasons for this widespread use, foremost of which is the ability to recover and reuse metals and wastewater. Not only is the generator's liability greatly reduced, but costs of disposal are reduced or eliminated. The waste is often converted into a product that can be sold to a reclaimer.

Given the widespread use of ion exchange, it is surprising that little has been written on proper operation of the equipment used in the process. The generally poor quality of documentation provided by some equipment vendors compounds this problem. Since failure to operate a system properly can result in failure to meet effluent limits and waste of money, some guidelines on operating ion exchange wastewater treatment equipment are outlined for metal-finishing facilities; however, most topics are relevant for other ion exchange users as well.

The suggestions made in this report are general guidelines and should not be considered an alternative to following the specific recommendations in an operation and maintenance manual. If this article supplies information that disagrees with specific information supplied by your vendor, the vendor's information should generally be used, since they may be using an unusual design.

There are two major considerations to be made in proper operation of the IX system: one is proper operation of the IX system and the other is proper operation of the plating facility. These will ensure both reliable operation at startup and reliable long-term performance.

DRAGOUT REDUCTION

The largest single factor in reducing the cost of operating an ion exchange system is reducing the amount of dragout. Many equipment vendors will work with the end user on dragout reduction before installing a system. Even if earlier attempts were made to reduce dragout, continued work is essential. A 10% reduction in dragout will result in a similar reduction in ion exchange operating costs.

In addition to reducing the cost of operating an ion exchange system, reducing dragout will improve the performance of the system. Unlike precipitation systems that may require some minimum amount of metal for proper performance, ion exchange will work better as the metal concentration is reduced. It will also reduce wear and tear on the system by reducing the frequency of regenerations.

There are many inexpensive options for reducing dragout, including spray rinses, drip trays, dragout rinses, and many more. Companies selling this equipment and consulting firms specializing in the metal-finishing industries may be able to help with dragout reduction. Some gains in dragout reduction will occur at no cost simply by draining parts for a few more seconds before transferring them to the rinse tank.

FLOW REDUCTION

Properly designed ion exchange systems have enough of a safety factor that they are relatively insensitive to the flow rate within the range stated by the vendor; however, an ion exchange system should not be operated at flow rates exceeding the design. They may sometimes work at high flow rates, but will not be able to remove surges in metal concentration.

It may be desirable to reduce flow rates, especially when the flow rate through the column is at the high end of the acceptable range (i.e., over about 2.5 gpm per cubic foot of resin—consult the equipment vendor for information on the most efficient flow rates). For systems that are approaching their limits, significant gains in performance will be obtained by reducing the flow rate. For systems with adequate safety factors, the gains on reducing the flow rate will be small. This is one of the things you get by buying a high-quality system—additional flexibility because of a large safety margin in design.

Ion exchange has a minimum acceptable flow rate determined by the equipment design. Operation at flow rates below the design recommendations can cause poor performance. If your shop regularly operates at flow rates lower than suggested by the equipment vendor, consider installing a collection tank to hold the rinse water. The water can then be collected and periodically pumped through the ion exchange unit at proper flow rates rather than trickling the rinses through the unit constantly. If the vendor has not provided information on minimum flows, ask about them. Typically, flows less than about 1/2 gpm per cubic foot of resin can cause problems.

BATH DUMPS

An ion exchange system treating the rinse water from a plating bath will generally be capable of treating the diluted bath as well. This is why many "bleed and feed" systems are installed; spent baths are bled into the rinse water before ion exchange treatment. This process is viable, but has its limits.

The major limitation to this process is that many plating baths are more concentrated than the ion exchange regenerant. The result in these cases is that the chemicals are diluted in the rinse water, collected on ion exchange, regenerated (using costly chemicals), and recovered in a lower concentration than they started. If the plating bath or bail out contains metal concentrations greater than the ion exchange regenerant (typically no more than a few percent for most systems), bleeding the bath into the rinse is probably wasteful. Only if the bath is much more diluted than the ion exchange regenerant will this process be practical.

When the bath is added to the rinse water, care must be taken to ensure that it is added slowly enough not to disrupt the ion exchange system's performance. A rapid change in pH or operation outside recommended pH limits must be avoided.

DEIONIZED OR SOFTENED WATER

Several articles have been written on the use of deionized and softened water for rinsing and bath makeup. There are substantial advantages gained in plant operations to using softened water instead of tap water, including improved rinsing quality, reduced bath replacement, and fewer plating problems. There can be substantial waste treatment cost savings, as well.

In systems where the wastewater is treated and discharged, hardness is the biggest problem for ion exchange. If hardness is very high, the resin's capacity for heavy metals will be reduced. With high hardness levels, a resin's ability to perform can be greatly degraded, especially if conventional (non-chelating) resins are used.

Even if hardness is low, some calcium will be retained on the resin. If sulfuric acid is to be used for regeneration, calcium sulfate can precipitate, fouling the resin. Even chelating resins have this problem. While common chelating resins have a much higher selectivity for heavy metals than for calcium, they still retain some calcium. The high price of cleaning or replacing ion exchange resins makes the use of softened water attractive. Industrial softeners are inexpensive and will generally pay for themselves very quickly. Deionization equipment for pretreating rinse water is more expensive, but often will pay for itself relatively quickly.

In systems where the rinse water is deionized and reused, there is always some amount of makeup water. If this makeup water contains high levels of hardness, the same problems as mentioned above will occur, and a softener should be used. Even if the hardness level is negligible, a significant amount of the resin's capacity will be used removing sodium and other salts from the water. Since the regenerant from the ion exchange system must be further processed (usually an expensive process), it is desirable to reduce the volume as much as possible. Therefore, it may be worthwhile to add a small deionization system to purify incoming water to be used for makeup. This will reduce the load on the waste treatment system.

CHEMISTRY CHANGES

Precipitation systems are not especially sensitive to changes in chemistry (as long as chelating agents are not present). Ion exchange systems can be very sensitive to the process chemistry (every advance in technology has its price). In many cases, there is no problem with simple replacement of one vendor's chemistry with a competitive product. In others, a slight change in ion exchange operating conditions will be enough. In a very few cases, the change will not be recommended because of ion exchange performance problems. As with precipitation, electroless plating baths are especially prone to problems.

The user should never change process chemistry without consulting the ion exchange equipment vendor. If the equipment vendor is unfamiliar with the proposed new chemistry, the chemical supplier may be familiar with its ion exchange properties. It is especially important for chemical suppliers to provide as much information as possible about their plating baths to allow the evaluation of ion exchange processes.

pH CONTROL

Ion exchange systems (especially those using chelating resins, weak acidic resins, or weak basic resins) will be sensitive to the pH of the feed water. In a plant where the water is very consistent and rarely fluctuates, it may be possible to install an ion exchange system without pH control. Usually, there needs to be some control over pH. This problem is especially severe in job shops because of their rapidly changing wastewater composition. Operation of an ion exchange system at its optimum pH will be much less expensive than operating a system outside the optimum range. The ideal range can be wide for some systems, but others will have major problems if the pH changes by as little as 0.5 units.

pH control is not as important in systems that recycle the water. These systems usually use strong acid and strong base resins that are not very sensitive to pH.

OXIDATION

Ion exchange resins are organic polymers and are sensitive to oxidation. Care should be taken to remove oxidizing materials before treating the wastewater. If these materials are present in significant amounts, resin destruction can occur very quickly.

In many plants, oxidation concerns will merely mean that baths containing oxidants cannot be bled through the ion exchange system. In others, a pretreatment system with oxidation-reduction potential control will be needed.

FILTRATION

Ion exchange is a process designed to remove ionic species from solution. If contaminants are present in particulate form, they may pass through the bed, causing the shop to be out of compliance. Careful filtration before ion exchange will reduce or eliminate this problem. Besides failure to meet effluent limits, improper filtration will lead to plugging of the resin bed, frequent resin replacement, and reductions in flow through the bed. Proper filter maintenance and operation will usually eliminate these problems.

MAINTENANCE

It hardly needs to be mentioned that an ion exchange system contains pumps, valves, controllers, and other components that require regular maintenance. Follow the maintenance schedule supplied by the equipment vendor. A periodic maintenance review of the system should be performed, even if not specifically recommended by the equipment vendor.

DATA COLLECTION

The only way to know whether an ion exchange system is performing properly is to regularly monitor the influent and effluent water quality. This statement seems glaringly obvious, but there have been numerous cases where a customer has claimed that a system was not working (or that it was working well) without ever verifying the performance.

Proper maintenance and troubleshooting requires a regular analysis of the water both entering and leaving the unit, a schedule of when regeneration took place, and, where applicable, a listing of what processes were in use at the time that sampling took place. This practice will reduce problems in the long run and is the first step in getting the most from your system.

CONCLUSION

Ion exchange is a highly efficient process that can result in high effluent quality, low costs, and reliable reuse of rinse water and waste metals. Like all technologies, it has its limitations. Installation of an ion exchange system should be accompanied by training that covers all the factors mentioned here.

With proper operation, an ion exchange system will effectively and reliably treat a plant's wastewater for many years. Failure to operate the system properly will cause continual problems and will increase operating costs significantly. MF

Biography

Joseph M. Ragosta received his B.S. degree in chemistry from Pennsylvania State University and his M.S. and Ph.D. degrees in inorganic chemistry from Cornell University. He joined Rohm and Haas in 1985 as a research chemist in the concrete modifiers group. Early in 1987, he transferred to the ion exchange group at Rohm and Haas where he had marketing, sales support, and technical support responsibilities for non-traditional ion exchange applications, including chemical processing and wastewater treatment. In January, 1990, he joined Bio-Recovery Systems as vice president of marketing and technical services. He left Bio-Recovery and started Ionex Consulting Services in August, 1990 to provide marketing and technical consulting services for industries using ion exchange technology.

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Ion Exchange for Metal Recovery: A Discussion of Trade-Offs

By S. Karrs, D.M. Buckley and F.A. Steward

Ion exchange for metal salt recovery has advantages and disadvantages, as do other recovery systems. However, its flexibility makes it especially attractive for some purposes. In particular, the combination of ion exchange and electrolytic metal recovery is effective for wastes containing complexing or chelating agents.

Ion exchange (IX) has been a useful process in metal finishing for several decades. The earliest, and still the most common, application in the U.S. is for the production of high-purity water. To minimize discharges and reduce the consumption of limited water supplies, the metal finishing industry in W. Germany began recycling treated wastewaters through IX systems in the 1950s and it is still the predominant method for handling those wastes in that country. In view of its extensive application, IX for water recycle can be considered a mature technology whose use is well documented.[1,2]

A somewhat younger field of application uses either weak acid or chelating cation-exchange resins for the removal of trace objectionable heavy metals from effluent prior to discharge to the environment.[1,3] This procedure has been used commercially mainly in Germany and Japan. In those countries, the treated effluent—often the regenerant waste from the main deionization and recycle systems—is given a final treatment through such metal-capture systems to give extremely low concentrations of regulated heavy metals in the discharge.

Finally, there has been considerable worldwide interest in IX resins as a medium to transport pollutants from a metal finishing operation to a centralized treatment facility.[4,5] This approach has been attracting increased interest in the U.S. in connection with the centralized treatment concept. However, none of these approaches is specifically aimed at the recovery of metal values or the avoidance of sludge generation.

For at least 20 years, there has been interest in using IX to capture metals from wastewater so they could be recycled or recovered, thus avoiding the generation of sludge.[1,4-6] However, a number of other technologies compete for such applications, and the trade-offs among them are frequently far from obvious. Regulations on sludge disposal have been intensifying dramatically in the U.S. due to the Resource Conservation and Recovery Act of 1976 and amendments to same issued in 1984. Metal finishers have found that it is becoming progressively more important to evaluate their alternatives and choose the most efficient way to minimize sludge generation.

Materials capable of accomplishing IX come in a variety of forms. Defined in the broadest sense, these could range from naturally occurring clays and zeolites to specially prepared natural materials (e.g., cellulose, peat moss, biomass) and, finally, to an array of synthetic materials manufactured specifically for the purpose. Comments regarding the applicability of IX in this paper will focus on the traditional form of the synthetic polymeric materials—beads of a co-polymer consisting of styrene and divinylbenzene. These beads are the familiar IX resin known to most metal finishers. Some of the less familiar or newer forms include liquid IX compounds (e.g., IX materials dissolved in an organic carrier fluid that is immiscible with water), fibrous polymers such as polypropylene that can be fabricated into cloth or felt, and hydrophobic plastic membrane materials that can be used to immobilize a liquid IX material.

IX can be used in a variety of modes to reduce sludge generation. For example, IX beads are frequently employed to remove cations from chromic acid, purifying it for recycle to a chromium plating operation. In a totally different approach, the beads can be used for a sorption process known as acid retardation[7] to capture and recycle free acid to a process such as aluminum anodizing, avoiding the need to discard and treat the process waste. For gold recovery, anion-exchange resins are used to capture the gold cyanide complex, and, most often, the resins are burned so that the gold can be removed from the ash by a refiner. However, the most widespread commerci

Table 1
Alternative Recovery Systems

	Evaporation	RO	Electrodialysis	IX
Feed conc.	High	Low	Medium	Very low
Product conc.	Very high	Low	High	Medium
Capture efficiency	Low	High	Medium	Very high
Energy	High	Medium	Low	Very low

application, and the focus of this paper, is the use of cation-exchange resins to capture metal ions from a waste stream to allow their recycle or recovery.

Sorption of metal cations on a resin can be an important step in metal recovery or recycle. The process can be used to transfer the metal ions from one chemical matrix to a different one that is more favorable for recovery. For this purpose, sorption can be applied to either dilute or concentrated waste materials. The process can also be used to collect the metal ions from dilute wastewater and transfer them to a relatively concentrated solution of metal salts from which the metal can be recovered, or the metal salts can be recycled to an originating process bath. Most of the commercial applications in the metal finishing industry are of the latter type.

Recovery of Metal Salts

At first glance, returning the metal salts carried out of a process bath may seem like the best way to avoid waste treatment and sludge disposal. To the extent that the metal salts *can* be returned, it is the most desirable route because t avoids the need to find a market for a byproduct and because the salt form of the metal, as purchased by the metal finisher, is invariably more valuable than the metal tself.

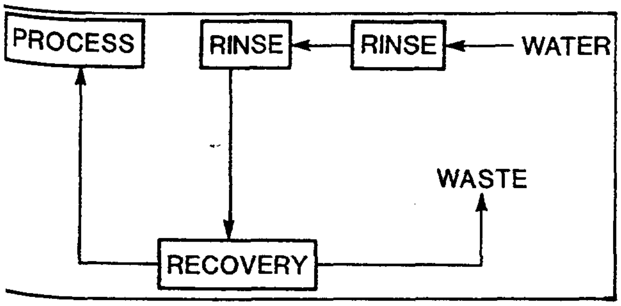
Unfortunately, there are two important reasons for the return of metal salts not being a cure-all approach.[8-10] First, many plating baths containing high concentrations of dissolved metals are discarded on a regular basis because hey steadily gain metal content during use. Unless a egeneration process is used on such a bath, return of the metal salt in the dragout will simply accelerate the need for discarding it. Examples are pickles, bright dips, etches, chemical milling solutions, and chromate conversion coating baths. Secondly, the major baths that use soluble anodes can accept some return of the metal salt lost to dragout but recycle of 100 percent is not practical because the anodes tend to dissolve more rapidly than the metal deposits at the cathodes. Therefore, without the purging effect of dragout, the concentration of metal would tend to steadily climb.

These points notwithstanding, direct recycling of metal salts will continue to play an important role in reducing waste and sludge production from metal finishing shops. In those cases in which it is applicable, the optimum approach will be to directly recycle as much as possible, and either discard, sell, or electrolytically recover that portion of the metal that cannot be recycled to the originating process.

Alternative Technologies

IX is one of a group of technologies that have found commercial application in recycling metal salts. The others having fairly extensive commercial application are evaporation, reverse osmosis (RO), and electrodialysis. A brief discussion of each will assist in evaluating trade-offs. For the purpose of this discussion, it is assumed that the process solution to be recovered is followed by two rinse tanks. As will be seen later, the availability of multiple rinse tanks can have an important bearing on the applicability of certain technologies, but the two-rinse model is being used here to allow each technology to be evaluated on a comparable basis. In some cases, the two rinse tanks might be piped as a counterflow arrangement and connected to the recovery equipment (Fig. 1). In other cases, it might be more desirable to use the first rinse step as a recovery rinse—often flowing at a relatively slow rate—and the second tank as a free-flowing water rinse (Fig. 2).

- *Evaporation:* Salts are recovered from the rinsewater by heating it to drive off the water as vapor. Because the water is being moved away from the salts by an energy-intensive phase change, it is imperative to minimize the flow of water. Typically, this approach is characterized by an arrangement like that shown in Fig. 2, operating at a relatively low flow rate. Therefore, the valuable salts are



g. 1—Counterflow rinse model.

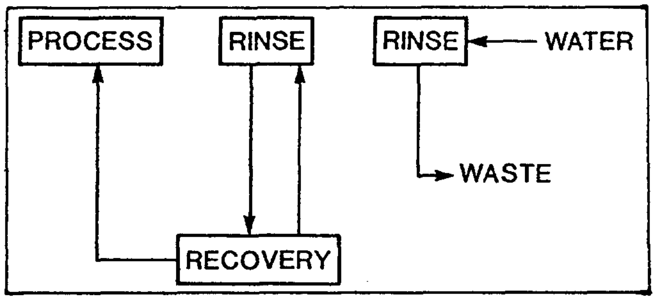


Fig. 2—Recovery rinse model.

rather concentrated in the recovery rinse, and losses to waste are relatively high. On the other hand, the concentration of the product is almost unlimited.

- *Reverse Osmosis:* Because it is less energy intensive, higher flow rates are typically used to give better capture efficiency for the metal. Unfortunately, the RO product cannot be highly concentrated because of inherent limitations of the technology. This can be a serious restriction on its applicability unless supplemental evaporation is provided. It is noteworthy that both evaporation and RO return essentially all of the constituents in the dragout to the originating process. This can be either an advantage or a liability, depending on the circumstances of the particular case.[9]
- *Electrodialysis:* In this case, ionized salts are moved out of the recovery rinsewater through IX membranes under the influence of an electromotive field. Because the conductivity of the recovery rinse must be reasonably high, the losses to subsequent rinsing would typically be higher than those associated with RO or IX but lower than evaporation. The concentration of the product is quite high, being limited only by the volume of water transported through the membranes with the ions. Thus, the volume of the product is seldom a limitation in its capability of being returned.
- *Ion Exchange:* Unlike the other methods, IX is almost totally unaffected by the dilution of the water being fed to the recovery unit. Rinsing with relatively high flow rates can be used effectively (Fig. 1). An extremely high capture efficiency is typical because metal discharge from the IX column can be less than 0.1 mg/L. Product concentration is rather low compared with that of evaporation and electrodialysis but is typically higher than that of RO.

The major characteristics of these four technologies are summarized in Table 1.

Pros and Cons

Without question, a very important advantage of IX is its capability of extracting essentially all of the metal from a relatively dilute feed stream. This makes it the only candidate for certain applications. It also means that it is the only one of the four aforementioned technologies that can produce an effluent stream suitable for discharge without further treatment. Finally, IX has rather low capital and operating costs by comparison with other methods at a given loading rate (i.e., lb of metal/hr).

The two primary disadvantages of IX are the dilute product that results and the fact that it is a chemically driven process. The dilute product is a consequence of the relatively high water content of the styrene/divinylbenzene resin, which is subject to osmotic pressure differentials that develop when a solution outside the resin bead has a much higher concentration than that inside. This limits the acid concentration that can be used to regenerate the cation-exchange resin, thus restricting the metal salt concentration that can be obtained from the process. Under ideal conditions, metal concentrations as high as 50 g/L can be obtained, but in practice the product is more likely to contain 15 to 30 g/L. To obtain higher concentrations, engineering innovations are needed for the process equipment. However, such innovations tend to add complexity, control problems, and labor requirements for operation and maintenance.

Because IX is chemically driven, it increases the consumption of chemicals by the plant and the quantity of salt in the water being discharged. Of more immediate concern is the virtually inevitable excess acid. In many cases, fre acid in the product will prevent recycle to the originatin process, and schemes to separate it from the desired met salt add cost, complexity, and operating and contr requirements.

Control is an important factor in using IX becaus breakthrough of the metal being captured occurs rathe abruptly once the resin bed is saturated. Compared with th other technologies, this means that metal loss will go u very sharply once breakthrough is exceeded. Conversel metal loss with the other technologies would be increase only slightly if control and operator attention were sub optimal. Because of this, most commercial installation avoid using the resin bed to exhaustion. Unfortunately, thi makes it impossible to pace the regenerant acid to th requirement, inevitably resulting in even more excess aci in the product. This problem could be eliminated with a instrument that would reliably detect breakthrough c metal ions.

There has been steady progress in developing rugged reliable instruments for this purpose, but even the best ar too delicate and sophisticated for many metal finishin shops. Obviously, if IX is being used to produce a high quality effluent for discharge, detecting breakthrough i even more important than if used simply as a recovery tool In addition, close control over pH of the feed to th exchanger is necessary. Lower pH tends to reduce capacit and performance, and slightly higher values cause meta precipitation and plugging of the exchanger or its filter.

IX for Waste Treatment

The capability of IX to produce high-quality discharge water has led to extensive consideration of the technolog for combined treatment and recovery. As our selec example will soon illustrate, this happy circumstance can occur under the right conditions. Unfortunately, they are relatively rare.

Most metal finishing shops have a combination of metals in the discharge water. This situation all but eliminates the possibility of economical metal recovery. In addition, the regulated heavy metals are quite often found in a variety o process baths at varying concentrations, so that segregation of one or a few rinse tanks will not bring a plant into compliance. Examples include: zinc and cadmium in an alkaline cleaner, acid or chromate dip on a zinc or cadmium plating line; chromium and/or nickel in an alkaline cleaner, acid dip, parts or rack stripper in a decorative plating plant; and copper in numerous process baths in a printed circuit shop.

Clearly, the installation of an IX system on the rinse following the main plating process will not assure that the total plant effluent will meet regulations. Conversely, installation of a metal-capture system on the total plant effluent will essentially rule out recycle of metal salts to the main plating process.

Attractive Applications

When multiple rinses following a process are simply out of the question, IX may be a very attractive way to capture metal ions before the water goes to treatment. In rare cases, it might be attractive to fully deionize the water and recycle it back to the tank, but this will seldom be optimal because (1) a single rinse tank cannot remove sufficiently the dragout film to justify the use of ultrapure water, and (2) the production of high-quality water requires strong cationic resins that need excess acid for regeneration. If metal recovery is the aim, a single column containing chelating cation-exchange resin will minimize the amount of excess acid needed for regeneration.

In some cases, a single rinse tank and capture by IX may be the best choice for metal recovery. One example is the existing finishing shop in an urban location where space for additional rinse steps cannot be obtained. Another is the shop handling very large pieces in large rinse tanks but relatively light loadings. The expense and space required for additional rinse steps cannot be justified.

A different situation exists when rinsing requirements are extremely critical. Such situations frequently occur when the cost of a product or its reliability are overriding considerations and rule out normal economic trade-offs. In such cases, manufacturing engineers may insist upon extremely high rinsewater flow rates and/or may prohibit any use of recycled water. As in the case mentioned earlier, these situations may favor the use of IX even if it is not the most efficient and economical approach.

Electrolytic Recovery

If return of metal salts to the originating process tank does not look attractive, IX can be linked with electrolytic metal recovery (EMR), sometimes referred to as electrowinning. The two primary IX disadvantages discussed earlier (dilute product and excess acid) are of no concern in this scheme. Figure 3 is a simplified depiction of the arrangement.

The metal-depleted wastewater would require pH adjustment prior to discharge. Control would be critical to minimize discharge of metal because the breakthrough is rapid once the resin is exhausted. Sulfuric acid would be used to regenerate the exchanger and the product from the exchanger would go to EMR, where the metal would be deposited as a slab for sale as a byproduct, and the acid content would be re-formed. The excess acid in the depleted liquor from the electrolytic cell can be used for the first stage of regeneration on subsequent cycles of the exchanger. Because this liquor still contains some metal, fresh acid is needed to complete the regeneration cycle. The excess acid leaves the system by being neutralized with the incoming raw waste and passed through the ion exchanger so that the metal content is not lost.

The inefficiency in this scheme is that a portion of the metal being recovered is constantly recycled, requiring oversized exchange equipment. A more efficient scheme would use electrolytic recovery for about 80 to 90 percent of the loading and IX to capture the small amount remaining in a subsequent rinse. Such an approach is illustrated in Fig. 4.

In this scheme, only a tiny fraction of the total amount of metal being recovered gets recycled through the exchanger. Figures 3 and 4 are simplified diagrams; holding tanks and control instruments are needed to make a practical system. Obviously, the extra cost and complication is undesirable if one of the more straightforward approaches discussed earlier can give acceptable results.

The scheme depicted in Fig. 3 can be especially attractive for complexed or chelated metal if the IX material will remove metal from the waste. In this case, expensive waste-treatment methods normally used for such difficult-to-treat streams can be avoided.

Laboratory testing is highly recommended for any application of IX that has not been done on a commercial scale with exactly the same process chemicals. The entire chemical matrix of a waste stream can influence exchange rates, capacities of the IX resin, and volume of regenerant acid needed.

Centralized Recovery

Combining portable ion exchangers with EMR at a centralized recovery facility can provide an attractive option where the geographic location of a number of small sources of a recoverable metal makes it logistically feasible. The capacity of the resin for metal can be case specific, and, in many instances, lower than the average values published in the literature. A range of 0.5 to 2.5 lb of copper/ft^3 of resin is not unusual, depending on both the pH control of the feed stream and the entire chemical matrix involved.

When at the lower end of this range, the trucking costs can become a significant factor unless the distances are short. This arrangement is likely to be feasible only for the more valuable and recoverable metals and then only when they are in a segregated condition. As discussed earlier, this approach is very different from that of using portable IX canisters to attempt to bring an entire metal finishing shop into compliance with effluent discharge requirements.

Case History: Electroless Nickel

A client had approximately 500 gal/day of discarded electroless nickel plating solution. In addition, there were smaller volumes (less than 10 gal/day on the average) of electroless cobalt plating solution. A treatment system was needed to produce an effluent with less than 1 mg/L of nickel. Treatment of the concentrated waste by conventional means was problematic because of the presence of high concentrations of complexing agents for nickel. Laboratory and pilot-scale tests indicated that an elec-

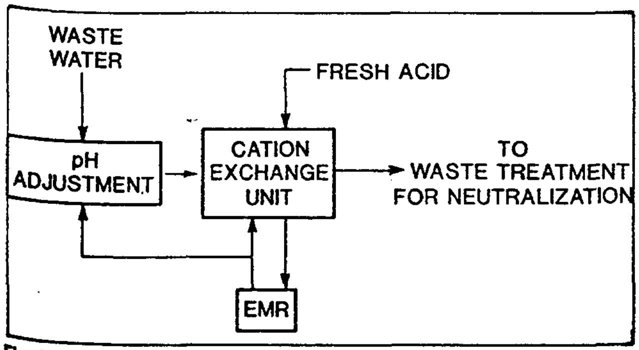


Fig. 3—Ion exchange linked with EMR.

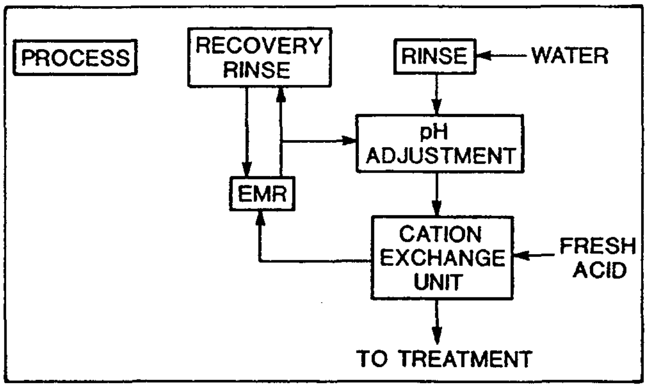


Fig. 4—Optimum combination of IX and EMR.

Table 2
Treatability Tests on Electroless Nickel Dump*

Method	Effluent conc.,* mg/L
Electrolytic recovery	140
Hot lime/hydrosulfite	25
Sorption filter	8.0
Excess sulfide and sorption filter	3.1
Sodium borohydride treatment	32.0
Chelating IX resin	<0.25

*Initial Ni concentration was 3.9 g/L.

Table 3
Influence of Bed Depth on Loading Capacity

	Ni conc., mg/L	
Bed volumes	0.5-ft column	2-ft column
10	0.10	0.05
20	0.50	0.10
30	0.10	<0.05
40	0.20	<0.05
50	0.10	<0.05
60	1.00	<0.05
70	2.10	<0.05
80	8.00	<0.05
90	—	<0.05
100	—	0.30
110	—	5.00

trolytic cell* would decrease the nickel concentration from the initial 5 to 7 g/L to approximately 150 mg/L. Table 2 indicates the results of several attempts to further treat the depleted liquor from the electrolytic cell.

The chelating IX resin showed considerable promise as the most effective approach, particularly since the loadings were relatively light and the nickel could be recycled to the electrolytic cell after regeneration of the ion exchanger.

Numerous tests were conducted during a period of several years on many different proprietary electroless plating baths. Some of the results illustrate key factors to be considered in applying the technology. Guidelines provided by resin manufacturers fôr conventional applications may not apply for difficult-to-treat or concentrated waste streams. In the case of electroless nickel bath dumps, the high concentration of soluble complexing agent in the waste provides competition for the nickel ions and alters the sorption kinetics from that which would be typically experienced in rinsewater.

Most applications of IX resin use the material in a continuous reactor that takes the form of a relatively tal column. As waste moves downward through such a column the upper layers become saturated first and a moving zone which can be considered the actual reaction zone or wave front for the adsorption process, is produced. The length of this reaction zone is dependent on the kinetics of the actua sorption process as well as the flux rate or throughput of waste (often expressed as gal/min/ft^2). The test results in Table 3 illustrate the significance of column configuration on both removal performance and the capacity of a given quantity of resin to hold metal.

For this test, a proprietary bath was diluted to approximately 150 mg/L of nickel. The pH was adjusted to 9 and the adsorption tests were conducted at 1 gal/min/ft^3 of resin, so that the total contact time between waste and resin was the same in both tests. The short column had an internal diameter of ⅞ in. and a resin bed height of 6 in. The long column had an internal diameter of ⅜ in. and a bed depth of 24 in. Each column had the same quantity of IX resin. Using 1.5 mg/L as the unacceptable discharge level

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*Lancy International, Inc., Zellenople, PA (patent pending).

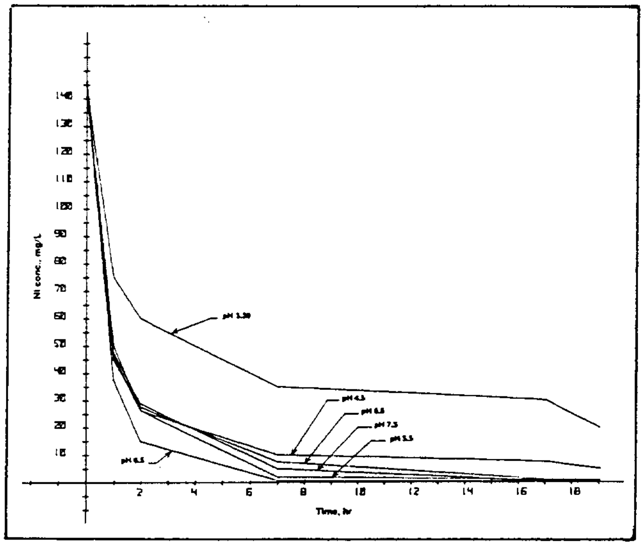

Fig. 5—Nickel concentration in discharge from a resin column (Rohm and Haas Amberlite IRC-718) as a function of time and pH of electroless nickel solution initially containing 146 mg/L nickel and 16 mg/L cobalt.

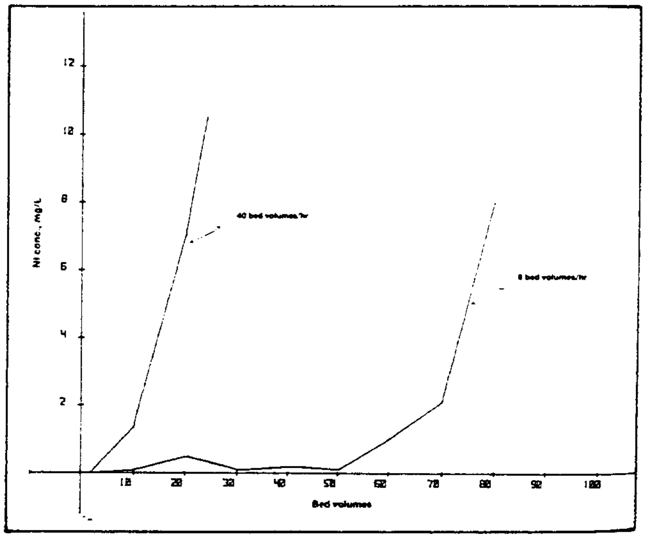

Fig. 6—Influence of flow rate on loading capacity. Feed solution contained 150 mg/L nickel and had a pH of 5.28.

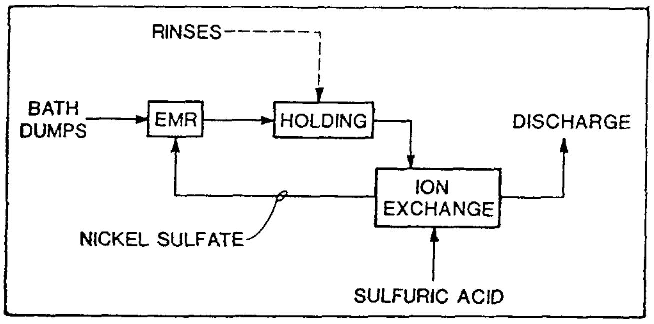

Fig. 7—System devised for electroless nickel bath dumps.

indicated that the same quantity of resin in a taller column had the capacity for about 70 percent more metal than the shorter column. In a full-scale system, the bed depth would normally be considerably greater, reducing the significance of the capacity effect, but this test clearly illustrates the presence of the reaction zone and the importance of using proper laboratory techniques and interpreting the results for engineering purposes.

The significance of pH control is illustrated by another series of tests using the liquor from the electrolytic cell mentioned earlier. These tests were isotherms in which a measured quantity of resin, calculated to be approximately the amount needed to totally sorb the nickel contained in a measured quantity of waste, was stirred for hours. The resin was previously put in the sodium form, and the pH of each test sample was adjusted with sodium hydroxide. Figure 5 plots the adsorption of nickel over time at the various pH levels.

The plots illustrate the significance of pH, both on the capacity of the resin to hold metal and on the rates at which adsorption occurs. For this application, pH 6.5 is optimum and is fortunately a practical value because the complexing agent keeps the nickel soluble. Unfortunately, in many applications the metal will be insoluble at an optimum pH, so the waste must be kept acidic (typically pH 4.0 to 4.5), thus reducing both resin capacity and adsorption kinetics.

The flow rate at which waste can be applied is dependent on the adsorption kinetics. Resin manufacturers give guidelines for typical applications, and the range of hydraulic loadings is normally 8 to 40 bed volumes/hr. Figure 6 illustrates the significance of this factor.

A proprietary electroless nickel bath was diluted to 150 mg/L and run at the resulting pH of 5.2. The column for these tests was 24 in. deep. As can be seen in Fig. 6, only the lower end of the typical hydraulic loading range is practical under these conditions, and the effect is even more pronounced if the bath is used full strength (without dilution).

The end result of the treatability study for this company was a compact treatment system illustrated as a simplified flow diagram in Fig. 7. Rinsewater was not included in this particular case because it was adequately handled by an existing treatment system. Because relatively constant bath volumes with the same composition would be dumped, metal detection in the exchanger effluent was considered unnecessary. Although rinsewater could be incorporated, its variable composition would necessitate a metal detector to avoid a resin breakthrough and optimize the loading cycle. The system consisted of an electrolytic cell with 100 ft^2 of cathode surface area and a pair of IX reactors, each containing about 1.6 ft^3 of chelating resin.

Table 4
Regeneration of Ion Exchanger

Cycle	Bed volumes throughput	Copper, g/L
Backwash	1.0	0.3
Regeneration 10% by wt H_2SO_4	0.2	7.2
	0.2	24.3
	0.2	15.1
	0.2	6.0
	0.2	5.3
Rinse	1.0	0.01
	1.0	0.003

One column would be held on standby while the other was used on stream.

Case History: PC Board Waste

A circuit board manufacturing facility, originally set up as a prototype rather than as a production shop, had a waste-treatment system that added ferrous sulfate, sodium hydrosulfite, and lime on a continuous and batch basis. Production rates increased over the years, and chemical consumption, sludge disposal and loading to the treatment system became prohibitive.

Laboratory tests were made to identify an IX/EMR system capable of handling waste containing complexed copper from alkaline rinse dumps, electroless copper dumps and rinses, etchant rinses, and solder strip rinsewater. Samples of each were blended to provide a fairly wide range of ratios of electroless copper dump to rinsewater. The copper concentration in the blends ranged from < 2 to 65 mg/L. Figure 8 shows the results of running three different wastes through a 24-in.-deep column of chelating IX resin at 1 gal/min/ft^3. In these tests, the resin was in the sodium form, but subsequent testing showed essentially the same loading rates and capacities with the resin in the hydrogen form.

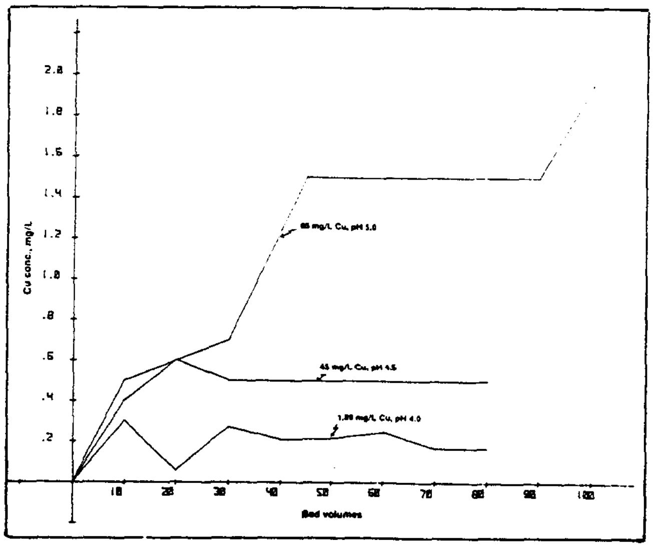

Fig. 8—Dependence of copper concentration in discharge from resin column on the influent copper concentration.

The scheme contemplated for handling these wastes would route all of the complexed or chelated wastes through the IX system, and the regenerant waste from the exchanger would be processed in an electrolytic recovery cell. The same cell would also remove copper from high-strength, non-chelated copper sulfate wastes. To illustrate the manner in which the regenerant waste from the exchanger can be split into high- and low-strength streams, Table 4 lists the g/L of copper leaving the column. Approximately 80 percent of the copper is eluted in the first 60 percent of the volume of acidic waste from regeneration. This quantity would be recycled to the electrolytic metal recovery cell, and the remainder would be neutralized and recycled back through the ion exchanger.

Figure 9 is a simplified block flow diagram of the contemplated treatment system. In this case, a metal detector is mandatory because of the relatively high variability of the feed stock to the exchanger. The net result of employing this scheme is that approximately 65 lb/week of copper will be recovered from the wastewater as high-grade byproduct slabs. The cost of the recovery system cannot be justified on the basis of copper recovery, but when savings for treatment chemicals and sludge disposal are included, the overall picture is an attractive return on investment.

Summary

Ion exchange is a flexible process that can be useful in recovering metals from metal finishing wastewaters under certain conditions. The outstanding advantage of the process is its capability of capturing essentially all of the metal fed to it even when the feed stream has a very low metal concentration. On the other hand, the two major disadvantages are that the product has a relatively low metal concentration and contains appreciable free acid. Also of importance in certain cases is the increase in total dissolved salts that must be discharged from the plant when using IX.

The two chief drawbacks can be troublesome when attempting to recycle metal salts from rinsewater to an originating process bath, but are of little consequence when the process is linked with electrolytic metal recovery. Although joining two technologies adds cost and complexity, the trade-off can be favorable in special situations such as those in which complexing agents interfere with metal removal by traditional waste treatment and where the IX process can serve the dual function of capturing the metal for recovery and producing effluent suitable for discharge.

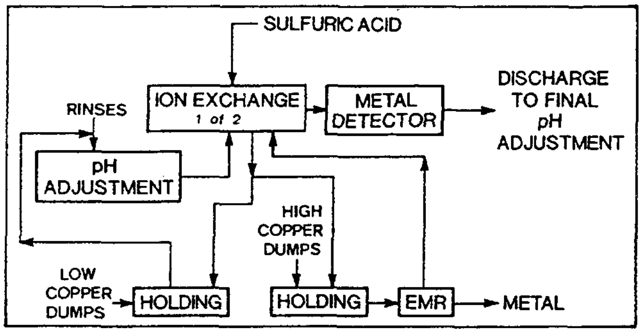

Fig. 9—System planned for printed circuit shop.

Acknowledgment

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Project Summary

Cadmium and Chromium Recovery from Electroplating Rinsewaters

Arun R. Gavaskar, Robert F. Olfenbuttel, and Jody A. Jones

This evaluation addresses the product quality, pollution prevention potential, and economic factors involved in the use of ion exchange to recover cadmium and chromium from electroplating rinsewaters and to remove contaminants for reuse of rinsewater. Cadmium, chromium, and cyanide (which is part of the cadmium bath) are on EPA's 33/50 list of target chemicals. Test results showed that the water returned to the rinse after ion exchange was of acceptable quality for both the cadmium and chromium processes. The ion exchange resins are regenerated with sodium hydroxide (NaOH). On the cadmium line, the regenerant was subjected to electrolytic metal recovery (EMR) to recover cadmium for reuse in the plating bath. On the chromium line, the regenerant was passed through a cation exchange resin in an effort to recover chromic acid. Although the recovery results were good on the cadmium line, chromic acid could not be recovered in this test. The pollution prevention potential of ion exchange on the cadmium and chromium rinsewater is good; however, further testing is needed to establish good recovery of chromium as chromic acid from the regenerant. The ion-exchange processes also proved economically viable.

This Project Summary was developed by the U.S. EPA's Risk Reduction Engineering Laboratory (RREL), 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

This study, performed under the U.S. EPA Waste Reduction and Innovative Technology Evaluation (WRITE) Program, was a cooperative effort among EPA's RREL, the Connecticut Hazardous Waste Management Service, and the Torrington Company. The objective of the WRITE Program is to evaluate, in a typical workplace environment, examples of prototype or innovative commercial technologies that have potential for reducing waste. The ion exchange system used in this study was manufactured by CTEO Tek, Inc.* and supplied by Plating Services, Inc. Other ion exchange units and technologies applicable to the same wastestream (electroplating rinsewaters) are also commercially available.

The objectives of this study were to evaluate (1) the effectiveness of the ion exchange unit in cleaning the rinsewater for reuse in the rinse tanks, (2) the pollution prevention potential of this technology, and (3) the cost of ion exchange versus the cost of the former practice (disposal).

Figure 1 shows the cadmium ion exchange system configuration. The water from Rinse 1 tank is first passed through a filter to prevent suspended solids from contacting the resin in the ion exchange column. The anionic resin captures the cadmium-cyanide complex, and the water

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* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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is returned to the Rinse 2 tank. An emergency bypass valve allows this water to be discharged to waste in case cadmium or cyanide levels are found to be too high.

The resin is periodically regenerated with a 15 to 20% NaOH solution, and the regenerant is taken to the electrolytic metal recovery (EMR) unit, where cadmium is recovered on the cathode and returned to the plating tank. Some cyanide is destroyed by decomposition during the EMR process.

Figure 2 shows the chromium system configuration. The primary ion exchange resin is anionic to remove hexavalent chrome. In the future, a cationic resin component will be added to the primary resin to remove any trivalent chrome that may be present in the rinsewater. The anionic resin is also regenerated with a 15 to 20% NaOH solution. The resulting solution (sodium chromate) is run through a secondary (cationic) exchange unit that should convert the regenerant back to chromic acid and return it to the plating tank.

Product Quality Evaluation

The objective of this part of the evaluation was to show that water processed through the ion exchange system is clean enough for use as rinsewater in the cadmium or chromium plating lines. Contaminant-free rinsewater ensures a good workpiece finish. The approach was to collect three samples each of the rinsewater, before and after passing through the ion exchange system. These samples were analyzed in the laboratory to evaluate the removal of contaminants. In addition, batches of rinsewater (one batch for cadmium and one for chromium) were spiked with plating bath solution to elevate contaminant levels (cadmium or chromium), and the spiked rinsewater was run through the ion exchange to test the limits of the unit. Because rinsewater was continuously circulated through the ion exchange system during the day, three samples of the rinsewater — at the beginning, middle, and end of a shift — were taken to ensure that water quality remained relatively steady over time.

Table 1 presents the results of the laboratory analysis of the cadmium rinsewater

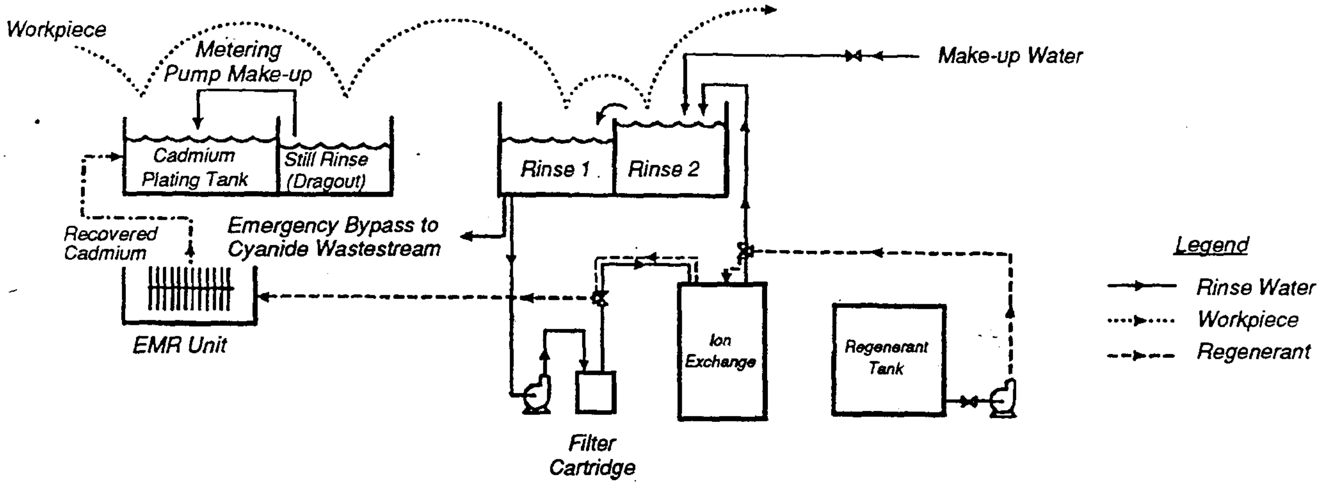

Figure 1. *Ion exchange recovery of cadmium from plating rinsewater.*

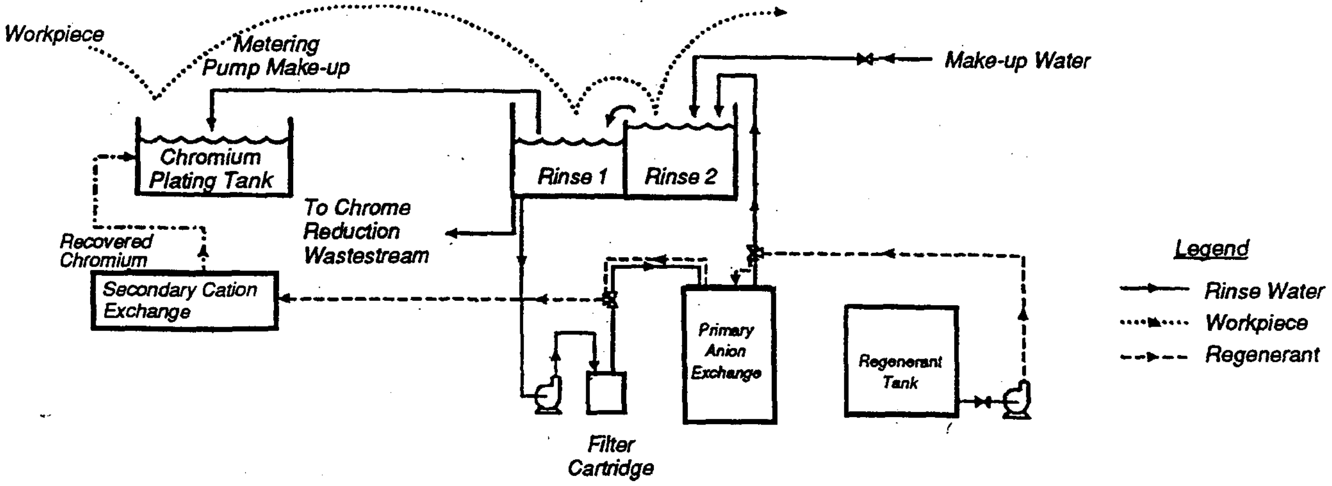

Figure 2. *Ion exchange recovery of chromium from plating rinsewater.*

Table 1. Cadmium Rinsewater Analysis

Sample No.	Sample Description	pH	Conductivity (umhos/cm)	Cadmium (mg/L)	Cyanide (mg/L)	Iron (mg/L)	Dissolved Solids (mg/L)	Suspended Solids (mg/L)
CD-X1-B1	Before ion-x, Run 1	11.26	783	7.28	35.60	0.57	226	1
CD-X1-B2	Before ion-x, Run 2	11.41	864	2.23	9.26	0.22	196	< 1
CD-X1-B3	Before ion-x, Run 3	11.48	936	2.58	13.80	0.31	205	< 1
CD-X1-A1	After ion-x, Run 1	11.45	867	0.015	0.037	0.06	147	< 1
CD-X1-A2	After ion-x, Run 2	11.51	845	<0.01	0.047	0.06	161	2
CD-X1-A3	After ion-x, Run 3	11.51	885	0.01	0.041	0.02	163	< 1
CD-XS-B1	Spike, before ion-x	NA(a)	NA	38.7	117	NA	NA	NA
CD-XS-A1	Spike, after ion-x	NA	NA	3.69	14.6	NA	NA	NA
CD-R1-B1	Rinse 1, 9:00 am	10.72	278	1.80	8.55	0.28	90	1
CD-R1-B2	Rinse 1, 12:30 pm	11.37	823	3.55	15.60	0.34	190	< 1
CD-R1-B3	Rinse 1, 4:00 pm	11.40	985	4.71	24.70	0.41	225	10
CD-R2-B1	Rinse 2, 9:00 am	11.07	360	0.067	0.28	0.11	80	2
CD-R2-B2	Rinse 2, 12:30 pm	11.50	860	0.105	0.62	0.07	164	3
CD-R2-B3	Rinse 2, 4:00 pm	11.47	970	0.269	1.23	0.09	191	< 1
CD-X30-B1	Rinse 1, 30-min	11.35	760	4.31	17.60	0.33	189	3
CD-FB-1	Field blank	7.50	65.3	<0.01	<0.01	0.21	50	1

(a) NA = not analyzed.

samples. Most of the cadmium and cyanide were removed by ion exchange — in some cases, to below detection levels. The pH of the rinsewater remained steady at alkaline levels throughout the testing.

A statistical t-test (95% significance level) was performed based on the averages and standard deviations of the 1-min "before" and "after" (CD-X1-) data. Suspended solids levels were very low in both "before" and "after" samples. After ion exchange, concentrations of cadmium, cyanide, and iron in the rinsewater decreased significantly. Overall dissolved solids levels also showed a significant decrease after ion exchange; this indicated a decline in dissolved mass levels. Interestingly, conductivity did not show any significant change after ion exchange, indicating that the current-carrying capacity of the rinsewater did not change. During ion exchange, heavier ions (cadmium, iron, etc.) transfer to the resin and lighter sodium ions are transferred to the water. Thus, dissolved mass in the water decreases but conductivity remains relatively constant. Small amounts of fresh makeup water were added to the rinsewater loop from time to time to compensate for the water lost to evaporation and dragout with the parts; this also helped control conductivity.

Table 2 describes the results of the laboratory analysis of the chromium rinsewater samples. After ion exchange, the rinsewater pH levels were slightly alkaline (9.31 to 9.45) because chromate ions (and any other contaminant anions) had been substituted with hydroxide ions. The alkaline pH was neutralized in the rinse tanks by the chromic acid residue on the parts (workpiece).

Similar statistical analyses were performed on the chromium data as have been described for the cadmium data. Suspended solids levels were significantly reduced by the cartridge filter ahead of the resin. Chromium (total chromium) and iron levels decreased significantly after ion exchange. Iron removal may be due either to removal of ferrous suspended particles on the cartridge filter or to deposition of complexed iron on the resin. As in the cadmium tests, dissolved solids mass decreased significantly, but conductivity (current-carrying strength) remained constant after ion exchange. This is because heavier chromates in the rinsewater were replaced with lighter hydroxide ions.

Pollution Prevention Evaluation

The pollution prevention potential of the ion exchange technology was assessed in terms of waste volume reduction and pollutant reduction. Waste volume reduction addresses the gross wastestream (e.g., lb of wastewater treatment sludge) and affects environmental resources (e.g., landfill space) expended through disposal. Pollutant reduction addresses the specific pollutants in the wastestream (e.g., chromium in the sludge).

Table 3 summarizes the waste volume reduction. By using ion exchange, large volumes of water are saved from going to waste. This water (an important resource) can be reused as a rinse on the cadmium and chromium lines. Without ion exchange, Torrington must maintain high rinsewater flow rates (8 gpm for the cadmium line and 2 gpm for the chromium line). These continuous flows generate large amounts of wastewater that have to be treated on site. With the ion exchange system on the cadmium line, Torrington requires only 50 gal/day to make up for dragout losses. A similar makeup rate is expected on the chromium line. Therefore, with the addition of the ion-exchange system, the amount of wastewater that must be treated is reduced. Virtually eliminating the wastewater stream also eliminates the hazardous sludge (containing cadmium or chromium) that has to be handled, transported, and disposed.

In terms of pollutant reduction on the cadmium line, the pollutants of interest are cadmium and cyanide. Before ion exchange, cadmium in the rinsewater was lost to wastewater, which was sent to an on-site wastewater treatment plant. The wastewater was treated in a steel cyanide

Table 2. Chromium Rinsewater Analysis

Sample No.	Sample Description	pH	Conductivity (umhos/cm)	Total Chromium (mg/L)	Iron (mg/L)	Dissolved Solids (mg/L)	Suspended Solids (mg/L)
CR-X1-B1	Before ion-x, Run 1	4.83	103	20.0	0.90	93	9
CR-X1-B2	Before ion-x, Run 2	4.67	104	18.2	0.85	99	8
CR-X1-B3	Before ion-x, Run 3	4.41	106	21.3	0.87	106	6
CR-X1-A1	After ion-x, Run 1	9.38	198	0.048	0.15	96	< 1
CR-X1-A2	After ion-x, Run 2	9.31	126	0.111	0.20	70	< 1
CR-X1-A3	After ion-x, Run 3	9.45	115	0.271	0.26	71	< 1
CR-XS-B1	Spike, before ion-x	NA(a)	NA	33.6	NA	NA	NA
CR-XS-A2	Spike, after ion-x	NA	NA	0.294	NA	NA	NA
CR-X2-B1	Rinse 1, 30-min	4.68	105	19.9	0.73	87	2
CR-FB-1	Field blank	7.50	65.3	0.04	0.21	50	1

(a) NA = Not analyzed.

Table 3. Waste Volume Reduction

Without Ion Exchange		With Ion Exchange	
Waste Description	Amount Generated per Year[a]	Waste Description	Amount Generated per Year[b]
Cadmium System Wastewater	1,920,000 gal	Wastewater	0 gal
		Regenerant	660 gal
		Filter cartridges	6
Chromium System Wastewater	480,000 gal	Wastewater	0 gal
		Regenerant	840 gal
		Filter cartridges	12

(a) Based on values of 16 hr/day, 5 days/wk, 50 wk/yr.
(b) Based on pilot tests conducted by the Torrington Company and resin capacity.

treatment tank using chlorine gas, sodium hypochlorite, calcium hypochlorite, and NaOH to oxidize the cyanide. The cadmium and other metals formed hydroxides that settled in the clarifier as sludge, which was then hauled off site for disposal. The treated water was discharged to the municipal sewer under a permit.

At Torrington, prior to ion exchange, approximately 69 lb of cadmium and 281 lb of cyanide were discharged annually. Now, because most of the cadmium can be recovered and reused, this pollutant is virtually eliminated from the wastestream. Some cyanide is also destroyed in the cadmium recovery process.

On the chromium line, without ion exchange, approximately 80 lb of chromium is discharged annually. With ion exchange, most of the chromium will be captured on the resin, which will be regenerated with NaOH. The regenerant then will pass through a cation exchange resin for conversion of sodium chromate to chromic acid. However, when this recovery was performed during the pilot unit testing, the final regenerant liquid still showed a pH of 13.08. This indicates that sodium chromate had not been converted to chromic acid; if it had been, the pH would have been much lower. This may be because (a) an excess of NaOH was used to regenerate the resin and/or (b) insufficient resin was available to exchange all the sodium in the regenerant. Further testing is needed to determine the feasibility of the chromic acid recovery process.

Economic Evaluation

The economic evaluation involves comparing the costs of the ion exchange operation with those of the former practice (counterflow rinse). These comparisons are summarized in Tables 4 and 5. Operating costs for ion exchange recovery are much lower than those for counterflow rinse alone. The main cost saving is the reduction in wastewater treatment costs.

In addition to operating cost savings, the recovered cadmium has value because it is reused in the plating bath as a cadmium anode. The cost of cadmium anodes is approximately $15/lb. The resulting value of the 69 lb/yr of recovered cadmium is approximately $1,036/yr.

The chromium deposited on the ion exchange resin also has value if it can be successfully recovered as chromic acid. The cost of chromic acid is approximately $2.50/lb. Approximately 80 lb/yr of chromium metal is deposited on the ion exchange resin. This corresponds to about 154 lb of chromic acid (CrO_3). However, further testing is needed to establish the feasibility of chromic acid recovery from the chromium in the regenerant.

The purchase price of the cadmium ion exchange system was $8,100 (including ion exchange resin column, pumps, and collection tanks). The EMR equipment price was $4,125 (including rectifier, pump, anodes, cathodes, and solution tank). Installation cost at Torrington, including materials (piping, etc.) and labor, was approximately $3,500, to which $5,000 was added to approximate the cost of in-house pilot testing to determine specifications for the individual plant.

The purchase price of the chromium ion exchange system is estimated to be $8,200 (including ion exchange resin column, pumps, and tanks). Installation cost at Torrington is expected to be $3,500, including materials (piping, etc.) and labor.

Table 4. Operating Costs Comparison for Cadmium System

Item	Amount Used per Year	Unit Cost	Total Annual Cost
Without Ion Exchange			
Freshwater	1,920,000 gal	$ 0.70/1000 gal	$ 1,344
Wastewater treatment	1,920,000 gal	$ 22/1000 gal	$ 42,240
		Total	$ 43,584
With Ion Exchange			
Freshwater	12,500 gal	$ 0.70/1000 gal	$ 9
Chemicals (50% NaOH)	96 gal	$ 1.50/gal	$ 144
Energy	1564 kW hr	$ 0.075/kW hr	$ 117
Labor	173 hr	$ 7/hr	$ 1,211
Routine maintenance			
- filter cartridges	6	$ 5	$ 30
- EMR anode plates	1	$ 30	$ 30
- EMR cathode plates	12	$ 30	$ 360
- labor	24 hr	$ 7/hr	$ 168
Waste Disposal			
- regenerant	660 gal	$ 22/1000 gal	$ 15
- filters	6	$ 400/36 units	$ 67
		Total	$ 2,151

Table 5. Operating Costs Comparison for Chromium System

Item	Amount Used per Year	Unit Cost	Total Annual Cost
Without Ion Exchange			
Freshwater	480,000 gal	$ 0.70/1000 gal	$ 336
Wastewater treatment	480,000 gal	$ 15/1000 gal	$7,200
		Total	$7,536
With Ion Exchange			
Freshwater	12,500 gal	$ 0.70/1000 gal	$ 9
Chemicals (50% NaOH)	240 gal	$ 1.50/gal	$ 360
Energy	1492 kW hr	0.075/kW hr	$ 112
Labor	149 hr	$ 7/hr	$ 1,043
Routine maintenance			
- filters	12	$ 5	$ 60
- labor	24	$ 7/hr	$ 168
Waste Disposal			
- regenerant	840 gal	$ 15/1000 gal	$ 13
- filters	6	$ 400/36 units	$ 67
		Total	$ 1,832

The approximate cost of $5,000 for in-house testing was also added for this unit.

A rough estimate of the payback period can be obtained by the following formula:

$$\text{Payback, years} = \frac{\text{capital costs}}{\text{operating cost savings} + \text{recovery value}}$$

Therefore, the payback period for the cadmium ion exchange system is less than 1 year. For the chromium system, the payback period is approximately 3 years. Because chromic acid recovery from the regenerant is yet to be established, no recycled chromium value is assumed.

The above payback period estimation is a simple calculation that does not take into account such factors as taxes, depreciation, inflation, etc. A more detailed economic evaluation, based on the worksheets provided in the Facility Pollution Prevention Guide (EPA 600/R-92/088), was performed that took these factors into account. The results showed that, for the cadmium process, the return on investment (with cost of capital equal to 15%) was still less than 1 year. For the chromium process, the return on investment (with cost of capital equal to 15%) was over 5 years. This includes capital costs of engineering and installation as well as increased overhead costs due to addition of the units.

Conclusions and Discussion

The evaluation showed that rinsewater on both cadmium and chromium lines at Torrington Company can be reused after subjecting it to filtration and ion exchange to remove impurities. Large volumes of water are thus saved, and large amounts of hazardous metals sludge are kept from the environment. The sidestreams from ion exchange are negligible compared with the wastewater and sludge wastestreams that are generated in the absence of ion exchange. The ion exchange resin can be regenerated with NaOH. On the cadmium line, the regenerant can be subjected to EMR and the cadmium recovered on the cathode. This electrode, with the deposited cadmium, is then inserted in the plating tank as a cadmium anode. Thus, a hazardous pollutant, cadmium, is reused. On the chromium line, further testing is needed to establish the feasibility of recovering chromium as chromic acid for reuse in the bath.

Without ion exchange, the rinsewater must undergo an expensive wastewater treatment process. The cost of operating the ion exchange unit is more than offset by the savings in wastewater treatment costs and by the value of the recovered product. In addition to the direct economic benefits, the ion exchange system also reduces Torrington Company's potential liability by virtually eliminating the risks involved during off-site transport and disposal of hazardous sludge.

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The complete report, entitled "Cadmium and Chromium Recovery from Electroplating Rinsewaters," (Order No. PB94-156395; Cost: $19.50, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
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The EPA Project Officer can be contacted at:

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Electrowinning
in

Pollution Prevention and Control Technology for Plating Operations

George C. Cushnie Jr.
CAI Engineering

A Project Sponsored by the
National Center for Manufacturing Sciences
and Conducted in Cooperation with the
National Association of Metal Finishers

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3.5 ELECTROWINNING

3.5.1 Overview

Electrowinning is one of the two most widely used methods of metal recovery in the plating industry, the other being atmospheric evaporation (Section 3.2). Of the 318 plating shops responding to the Users Survey, 61 (or 19%) have employed this technology. Some shops have purchased or fabricated two or more units for different applications, resulting in a total number of 80 electrowinning units used by the 318 survey respondents.

Electrowinning is most frequently used to: (1) reduce the mass of inexpensive regulated metals (e.g., zinc, copper, lead) and cyanide being discharged to treatment and thereby reduce the quantity of treatment reagents used and the quantity of sludge generated and/or (2) recover expensive common metals (e.g., nickel and cadmium) or precious metals (e.g., silver and gold) for recovery/recycle and thereby reduce overall operating costs. In either case, electrowinning is most often applied for gross metal recovery from concentrated solutions such as drag-out rinses or ion exchange regenerant. Used in this manner, it is not sufficient as a stand-alone technology to meet discharge standards. Reticulate cathode, high surface area (HSA) or high mass transfer (HMT) cathode designs also make this technology applicable to some dilute metal bearing solutions (e.g., overflow rinses). The reticulate cathode units have been proven to be effective in maintaining the metal concentration of recirculated rinses to less than 1 mg/l. The HSA units have been advertised as a method of compliance (ref. 98) and in the late 1970's and early 1980's attempts were made to use the electrowinning technology in this manner. However, none of Users Survey respondents are currently discharging an effluent from an HSA or HMT unit without further treatment for metals removal. Some non-continuous discharges of batch-treated solutions are found. However, for these cases, the volume of the discharge is insignificant compared to total wastewater flow.

The basic unit of the electrowinning technology is the electrolytic cell: two electrodes (anode and cathode) are placed in a solution containing ions, where there occurs a movement of ions toward the charged electrodes. Dissolved metals in the electrolyte are reduced and deposited on the cathode. The deposited metal is removed by mechanical (e.g. scraping) or chemical means and either reused as anode material or sent off-site for refining/reuse or disposal.

The types of cathodes used in electrowinning can be grouped into three categories. These include, in order of increasing surface area: (1) flat plate, (2) expanded metal, wire mesh or reticulate plate, and (3) porous or woven carbon and graphite types. The flat plate cathodes are used for applications of gross metal recovery from concentrated solutions (e.g., >1 g/l of metal). The expanded metal, wire mesh, or reticulate plate and the porous or woven types are used for recovering metals from solutions with lower metal concentrations, with the latter group effective in some cases in the low mg/l range. Reticulate cathodes, which permit flow-through of the electrolyte, have an effective surface area of approximately 10 times the face or apparent area of the cathode. Porous or woven cathodes have internal pores that also permit flow-through of the electrolyte and have a surface area up to 13,000 times greater than the apparent area.

There are several common terms used in describing the equipment and processes relative to electrowinning. The basic electrolytic cell is composed of two electrodes, one anode (positive charge) and one cathode (negative charge). The chemical reactions that take place at the anode are oxidations and the reactions at the cathode are reductions. The solution is referred to as an electrolyte. When a direct current (D.C.) is applied to the cell, the anions present in the electrolyte migrate toward the anode and the cations migrate toward the cathode. An important controlling factor in the process is the amount of current flowing through the cell. The level of current is measured in amperes per unit area of electrode (typically, amperes per square foot) and is referred to as the current density. Current density affects the nature of the electroplated deposit, the distribution of the deposit, the current efficiency, and to some extent whether a deposit forms at all. In electrowinning, the theoretical quantity of metal that is deposited onto the cathode is described by Faraday's Law. This law states that the amount of chemical change produced by an electric current is proportional to the quantity of electricity used (ref. 350). Some of the electric current is used for reactions other than metal deposit. Electroplaters refer to the ratio of desired chemical change (deposit) to the total chemical change as the current efficiency, usually expressed as a percentage of current applied.

As indicated previously, the current density has a substantial impact on the rate of metal deposit. It is desirable to operate electrowinning processes at the maximum current density where good deposition still takes place. The current density should, however, not exceed that which deposits metal faster than ions can diffuse through the electrolyte. When the thin film of electrolyte surrounding the cathode is depleted of metal ions, a condition referred to as concentration polarization occurs. This results in an adverse effect on the current efficiency as well as the quality of the deposit due to excessive hydrogen evolution at the cathode and oxygen evolution at the anode. The allowable or critical current density is determined by the concentration of metal ions in the electrolyte and the thickness of the film surrounding the cathode. Innovations in the design of electrowinning devices have generally focused on extending the operating range of the process by: (1) increasing the surface of the cathode (i.e., high surface area), or (2) reducing the thickness of the film using agitation or heating (ref. 349, 351).

For most applications, the primary use of electrowinning is the recovery of metal. However, when performed with an electrolyte containing cyanide, the process also oxidizes some of the cyanide at the anode (alternatively CN can be oxidized with hypochlorite ions which result from the electrochemical oxidation of chloride ion in a basic medium). Although the anodic reactions are given less consideration in most applications, they can play an important role in the economic viability of the process by reducing the treatment reagent requirements for end-of-pipe treatment. Anodic reactions including cyanide destruction and organic complexing agent destruction (e.g., treatment of an electroless copper bath) were examined in detail by Waiux and Nguyen (ref. 123).

3.5.2 Development and Commercialization

Electrowinning is presumed to be one of the earliest methods of metal recovery used in the plating industry, although no specific reference to its use prior to the 1960's was found (ref. 128). One of the reasons for its presumed early development and current widespread use is the fact that this process emulates the electroplating process. As such, it is readily accepted and understood by the plating industry. Further, for these same reasons, there are fewer system failures caused by misapplications or operational errors than with other recovery technologies such as ion exchange or membrane technologies. The electrowinning technology also has technical roots and contemporary applications in other industries, including electrorefining of copper, extraction of metallic aluminum from bauxite, and recovery of silver from photographic film manufacturing and developing operations.

Electrowinning can be performed using very simple equipment. As such, many plating shops have constructed units in-house. The effectiveness of these home-made units varies from shop to shop. Commercial units for plating applications are manufactured/sold by at least 40 companies (ref. 421). Many of these units, like the home-made models are also relatively simple in design. As discussed in Section 3.5.1, the efficiency of the electrowinning process is impacted by several electrochemical factors. Some commercial units, through the incorporation of more sophisticated design elements, minimize the impact of the electrochemical forces that reduce plating efficiency. Typically, these design elements are limited to the commercial units and are not found to any significant extent with the home-made versions.

3.5.3 Applications and Restrictions

Exhibit 3-32 shows the three basic configurations in which electrowinning was successfully applied by the shops responding to the survey.

The most common configuration (EW-1) employs an electrowinning unit connected directly to a drag-out tank. Alternatively, the solution from the drag-out tank can be periodically transferred to a holding tank that is connected to the electrowinning unit. Either of these arrangements can be used with flat plate or reticulate cathode units. The reticulate cathode types will maintain the rinse system at a lower metal concentration (in some cases below 1 mg/l) but, because the cathodes are not reusable, the operating costs will be higher. The operation of the flat plate cathode types are more significantly affected by fluctuations in the metal concentration of the electrolyte. Therefore, if the plating operation causes sharp fluctuations in the drag-out tank concentration, the user should consider the use of a side tank or a reticulate type of cathode. The HSA cathode units should be directly connected to the drag-out tank. This will permit them to maintain a low steady state concentration of metal in the drag-out tank.

Electrowinning removes metal from the drag-out solution, but does not remove all dissolved solids. For this reason, the drag-out solution must be occasionally discarded or purged to prevent the build-up of dissolved solids (e.g., acid). When this occurs, any residual metal in the drag-out solution will be lost.

The metal recovery efficiency (i.e., the percentage of metal recovered from drag-out) of the first configuration depends on two key factors: (1) the average concentration of metal in the drag-out tank and (2) the mass of metal in the purge. The concentration of metal in the drag-out tank is important because it determines the mass of metal that will be carried over by drag-out to the next rinse, which is treated. This factor points out the weakness of the flat plate cathode types. These units operate efficiently only when the metal concentration is high (usually 1 to 5 g/l of metal). Therefore, the drag-out tank must be operated until this level is achieved, which in turn increases the loss of metal to the free running rinse. The higher surface area of the reticulate and HSA units allow the user to operate the drag-out tank at a lower metal concentration and therefore reduce metal losses. Further, these types of electrowinning units generate a purge with a lower metal concentration.

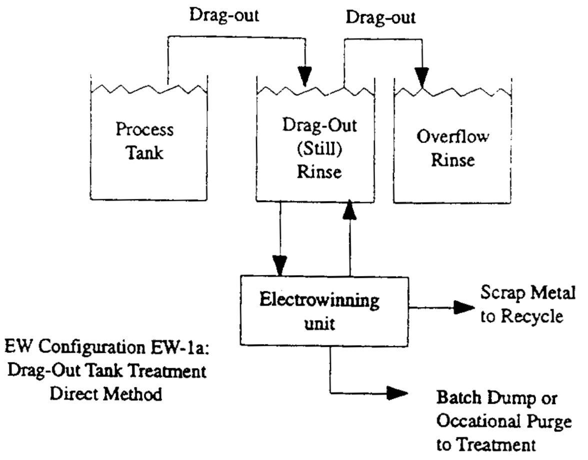
The second configuration (EW-2) is a combination of ion exchange and electrowinning. This configuration potentially has a much higher metal recovery efficiency than the first configuration. It addresses both of the factors that impact metal recovery efficiency. The ion exchange unit maintains a low metal concentration in the final rinse, thereby almost eliminating drag-out losses. The ion exchange unit concentrates the metal into a regenerant stream and the electrowinning unit removes the metal. Residual metal in the regenerant is of less concern than the first configuration since it can be reconcentrated by the ion exchange unit. For the same reason, a flat plate cathode will suffice for this second configuration.

In some cases, the reticulate cathode units can be substituted for the second type of configuration. When such a unit maintains the drag-out rinse in the low mg/l range, the metal recovery efficiency of the process would approach that of the ion exchange/electrowinning combination. Some recent operating data for a copper recovery application using this configuration are presented in Section 3.5.4.3.

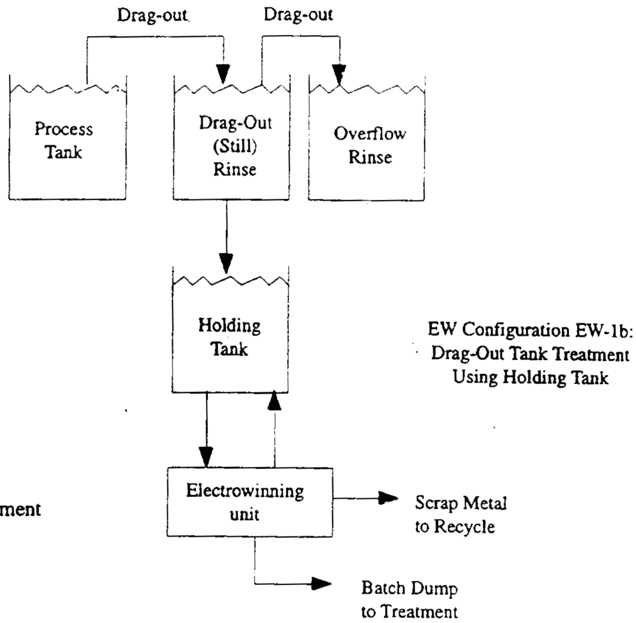
The third configuration shows the recovery of metal from a spent process solution. Either the flat plate or reticulate cathode type of unit can be used in this configuration. The reticulate cathode type will provide greater metal recovery efficiency because it can lower the metal concentration of the spent bath below that of the flat plate. Because the reticulate cathodes are not reusable, its higher recovery efficiency comes at an increased operating cost.

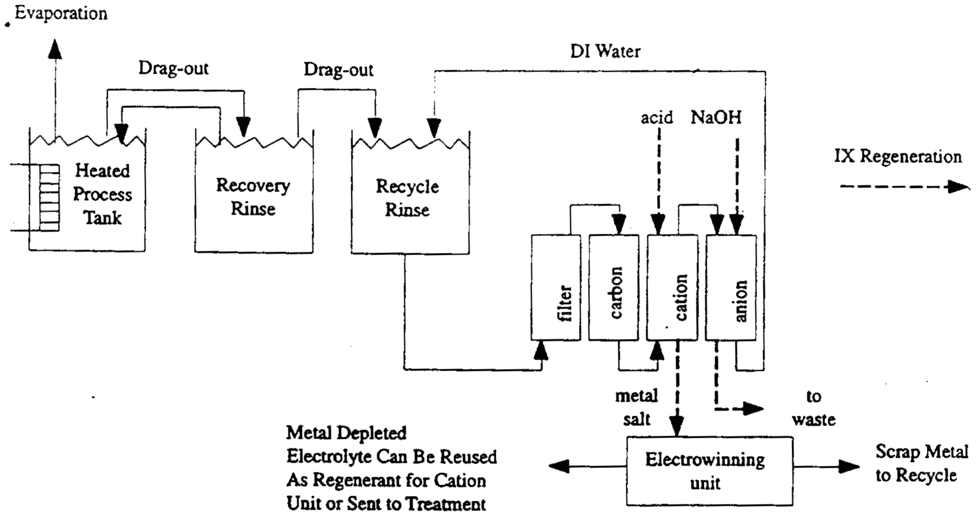
Electrowinning is applied to a wide variety of chemical solutions in the electroplating industry. The literature indicates that the metals that are most commonly recovered by electrolytic treatment are gold, silver, copper, cadmium, and zinc. The metal recovery applications identified from the Users Survey are shown in Exhibit 3-33.

Exhibit 3-32. Three Primary Configurations for the Application of Electrowinning for Metal Recovery

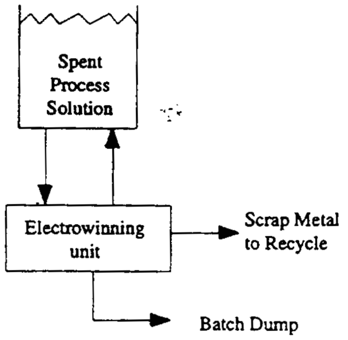


EW Configuration EW-1a: Drag-Out Tank Treatment





EW Configuration EW-2: Ion Exchange/Electrowinning Combination



EW Configuration EW-3: Spent Process Solution

This exhibit indicates the number of survey respondents that applied electrowinning to each of the processes and the average satisfaction level of the technology for that application, based on a scale of 1 to 5 (1 equals the lowest satisfaction level and 5 equals the highest).

For practical purposes, the degree to which a metal can be recovered by electrowinning can be determined by its position in the Electromotive Series (see Exhibit 3-34). Metals that have more positive standard electrode potentials plate more easily than the ones with less positive potentials. As an illustration, the more noble metals, such as silver and gold, can be removed from solution to less than 1 mg/l using flat plate cathodes whereas with copper and tin, a concentration in the range of 0.5 to 1 g/l or more is required for a homogeneous metal deposit. Equations for accurately estimating the potential for a given application were presented by Brown (ref. 349) and Bailey and Chan (ref. 128).

It is interesting to compare the satisfaction levels in Exhibit 3-33 to the position of the metal in the electromotive series. The satisfaction levels for silver, copper, cadmium and zinc cyanide plating (the most common applications of the respondents) fall into nearly the exact order as the metal's position in the electromotive series.

Although copper, cadmium and zinc have a lower position in the electromotive series than precious metals and they received only moderate to low satisfaction levels from survey respondents, this is not to say that these applications cannot be successfully performed. With the application of proper engineering and good equipment selection these electrowinning applications can be highly successful, as indicated by some of the respondents. For additional data, Exhibit 3-35 groups potential electrowinning applications based on their frequency of use and success in industry and the general difficulty of the application. These rankings are based on input from electrowinning vendors and information from the literature. Included in this exhibit are a much broader range of metals than those identified in the Users Survey.

Although there are limitations for electrowinning nearly every metal, chromium is the only commonly electroplated metal that is not recoverable using electrowinning. Nickel recovery is possible, but it requires close control of pH and therefore is less frequently performed than, for example, cadmium or copper. Also, Altmayer suggests that nickel recovery is hampered by the absence of inexpensive suitable inert anodes that do not give off chlorine gas and disintegrate (ref. 482).

Solutions such as electroless plating solutions containing chelated metals, reducing agents and stabilizers are more difficult for the direct application of electrolytic recovery.

Exhibit 3-33. Electrowinning Applications Identified from the Users Survey

Process Solution	Number of Applications	Average Satisfaction Level
Anodize, hardcoat	1	2.0
Brass plate, cyanide	2	3.5
Cadmium, strip	1	ND
Cadmium plate, cyanide	26	2.8
Copper plate, cyanide	8	2.8
Copper plate, sulfate	5	3.0
Copper strike, cyanide	1	4.0
Gold plate, cyanide	2	ND
Gold plate, non-cyanide	2	4.0
Nickel strip	1	4.0
Nickel plate, sulfamate	2	4.0
Nickel plate, watts	2	ND
Nickel plate, woods	1	ND
Nickel plate, electroless	1	ND
Passivation, nitric	1	1.0
Silver strip	1	4.0
Silver plate, cyanide	11	4.4
Zinc plate, cyanide	6	1.3
Zinc plate, non-cyanide	5	2.0
Total/Average	57	3.1

ND = no data

Exhibit 3-34. Electromotive Series

Electrode Reaction			E°, Volts at 25°C
$S_2O8^= + 2e^-$	---------- >	$2SO4^=$	+2.01
$H_2O2 + 2H^+ + 2e^-$	---------- >	$2H_2O$	+1.78
$Au^+ + e^-$	---------- >	Au_m	+1.69
$2Cl + 2e^-$	---------- >	$2Cl^-$	+1.36
$1/2O_2 + 2H^+ + 2e^-$	---------- >	H_2O	+1.23
$Pd^{++} + 2e^-$	---------- >	Pd	+0.99
$Ag^+ + e^-$	---------- >	Ag	+0.80
$Fe^{+++} + e^-$	---------- >	Fe^{++}	+0.77
$Cu^+ + e^-$	---------- >	Cu	+0.52
$Cu^{++} + 2e^-$	---------- >	Cu	+0.34
$2H^+ + 2e^-$	---------- >	H_2	+0.00
$Pb^{++} + 2e^-$	---------- >	Pb	-0.13
$Sn^{++} + 2e^-$	---------- >	Sn	-0.14
$Mo^{++} + 2e^-$	---------- >	Mo	-0.20
$Ni^{++} + 2e^-$	---------- >	Ni	-0.25
$Co^{++} + 2e^-$	---------- >	Co	-0.28
$Cd^{++} + 2e^-$	---------- >	Cd	-0.40
$Fe^{++} + 2e^-$	---------- >	Fe	-0.44
$Zn^{++} + 2e^-$	---------- >	Zn	-0.76
$Mn^{++} + 2e^-$	---------- >	Mn	-1.19
$Al^{++} + 3e^-$	---------- >	Al	-1.66
$Mg^{++} + 2e^-$	---------- >	Mg	-2.36
$Na^{++} + e^-$	---------- >	Na	-2.71

Source: ref. 349

Exhibit 3-35. Potential Applications for Electrowinning of Metals Identified from the Vendors Survey and Literature

Group	Metals (electrolyte)
Group 1 Includes metals with a high potential for successful application. All metals listed in this group are commonly recovered using electrowinning.	brass (cyanide), cadmium (cyanide), copper (acid, cyanide), gold (cyanide), silver (cyanide), zinc (cyanide)
Group 2 Includes metals with a high potential for successful application, however, metals listed in this group are less commonly recovered using electrowinning than those in Group 1.	antimony, cadmium (ammonium sulfate), iridium, lead (acid), palladium, ruthenium, rhodium, selenium, tin (acid, alkaline)
Group 3 Includes metals with a moderate potential for successful application. May require chemical adjustment of the electrolyte or special equipment (e.g., unusual anodes).	cobalt, copper (electroless, strong acid, ammononical etches), gold (strip), indium, lead (fluoborate), nickel (Watts, woods, sulfamate, electroless), silver (thiosulfate), tin-lead (fluoborate), zinc (acid)
Group 4 Low potential for success. No known instances of use.	aluminum, barium, beryillium, boron, calcium, cadmium (strip), chromium, iron, magniesium, manganese, mercury, molybdenum, silicon, tantalum, titanium, tungsten, vandium

Sources: ref. 99, vendor files

However, there was one survey respondent that indicated they were successfully electrowinning nickel from a spent electroless solution (PS 188). Another shop (PS 164) is in the process of starting up a unit for the same purpose. One vendor (ref. 349) indicated that these baths can be processed by electrowinning after undergoing pretreatment (e.g., selective ion exchange) to break the metal-chelate bond. Another reference suggests that reducing and oxidizing agents can be combined to neutralize their effects; e.g., a printed circuit board shop can mix spent micro-etch and electroless copper baths and with proper pH adjustment create a solution that can be treated by electrowinning (ref. I^3 file). Another reference indicates that electroless copper can be processed using electrowinning, but that anode life will be short (ref. 99).

Fluoborate solutions (e.g., tin, tin-lead) are not commonly treated using electrowinning due to their attack upon anode materials including iridium oxide coated titanium and niobium. However, one source (ref. 287) indicates that titania ceramic anodes coated with iridium can provide a successful application. This material and its application have been recently commercialized (ref. Kinetico file).

Certain corrosive solutions (e.g., certain etchants) may also pose problems for electrowinning because metal that is plated on the cathode may be etched off as quickly as it is plated (ref. 348). One reference suggests that increasing the current density will partially overcome the etching action of ammonomical etches when electrowinning copper from these solutions, but that complete removal is difficult to achieve (ref. 99).

3.5.4 Technology/Equipment Description

This subsection contains names and/or descriptions of commercially available electrowinning equipment that is manufactured and/or sold by vendor survey respondents or discussed in the literature. This is intended to provide the reader with information and data on a cross section of available equipment. Mention of trade names or commercial products is not intended to constitute endorsement for use.

3.5.4.1 General

The typical electrowinning system consists of a tank that holds the electrolyte, sets of anodes and cathodes, a pump for transferring solutions from a feed tank to the electrolyte tank, rectifier, and controls.

Most electrolyte tanks are manufactured from polypropylene, although one of the surveyed manufacturers (ref. Eco-Tec file) also used lined steel tanks. The tanks range in size from approximately 10 to 1,500 gal. Rectifier output amperage ranges from approximately 25 to 5,000 amps (ref. vendor files), with the smallest units used primarily for precious metals (e.g., Au, Ag, Rh) recovery (ref. vendor files and 111).

The three most common types of electrolytic metal recovery equipment use either: (1) parallel flat plate cathodes, (2) reticulate cathodes; and (3) fibrous or high surface area cathodes. Generally, the parallel flat plate cathode units are used with concentrated metal solutions, the reticulate cathode units work over a wide range of concentrations, and high surface area cathode units are used exclusively with solutions containing dilute metal concentrations.

Various materials are used in the fabrication of anodes and cathodes. Until the 1960's, graphite and lead alloys were the most preferred anode materials. However, their high overpotential requirement and degradable nature presented significant drawbacks. More recently, anodes are commonly being manufactured of titanium and niobium and coated using the solid phase roll bonding method with precious metals, metallic oxides and/or their alloys and fluoride resistant metal composites (ref. 128). These types of electrodes are generically referred to as dimensionally stable anodes. The advantages of the newer anodes over the lead alloy anodes include: (1) produce higher purity product (deposit); (2) low oxygen overpotential increases current efficiency; and (3) corrosion resistance provides higher durability and stability.

Most commonly, flat plate, wire mesh and expanded metal cathodes are fabricated from stainless steel, reticulate cathodes are metal coated foam and high surface area cathodes are fabricated from carbon fibers. Additional details of cathode design are discussed in Sections 3.5.4.2 through 3.5.4.4.

Exhibit 3-36 indicates the different materials used for electrode fabrication by the four manufacturers that responded to the Vendors Survey for their most common applications. It also includes other types of materials identified in the literature and known to be in common use.

3.5.4.2 Flat Plate Cathode Units

The flat plate design is often referred to as the conventional method of electrowinning because of its long stand-

Exhibit 3-36. Materials of Construction for Electrodes Used for Common Electrowinning Applications

Electrolyte	Cathode Material	Anode Material
Cadmium Cyanide	2, 3, 4	3, 6, 9
Cadmium Sulfate	3, 4	6, 9
Copper Cyanide	4	10
Copper Persulfate Microetch	14	14
Copper Peroxide Microetch	14	14
Copper Pyrophosphate	14	14
Copper Sulfate	2, 3, 4	1, 7, 10, 11
Gold Cyanide	2, 3, 4	7, 11
Lead Fluoborate	4	12
Lead Sulfamate	4	7
Nickel Sulfate	1, 2, 3, 5	7, 10, 11
Silver Cyanide	2, 3, 4	3, 7, 11
Tin Alkaline	2, 3	8, 11
Tin-Lead Fluoborate	2, 3	8, 11
Zinc Alkaline	13	7
Zinc Cyanide	1	10
Zinc Unspecified	1	10

Legend

1 Proprietary
2 Stainless steel mesh
3 Stainless steel sheet
4 Reticulated copper coated
5 Reticulated nickel
6 Carbon fiber
7 Dimensionally stable anodes (DSA®)
8 Ebonex®
9 Ebonex® iridium oxide or platinum coated
10 Lead alloy
11 Platinum clad titanium, niobium, tantalum
12 Graphite
13 Zinc mesh
14 Unknown

Sources: Data provided by Eltech International Corporation, Kinetico Engineered Systems, Eco-Tec Inc., and Memtek Corporation. These companies manufacture electrowinning equipment that employ either flat plate or reticulate cathodes. Also, the data are based on common material usage as identified from the literature.

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ing role in the plating industry and as well as other industries. Conventional electrowinning equipment is found in a variety of configurations. The basic design consists of a tank containing alternating flat sheets of cathodes and anodes. Commercially available electrolytic recovery units, used for waste treatment and recovery, have total cathode surface areas ranging from 1 ft^2 to 200 ft^2. Such units are extremely small in comparison to those used for primary copper production. An average copper refinery producing 500 tons per day of copper utilizes approximately 2.6 million square feet of total electrode area (ref. 349). A packaged recovery unit generally is supplied with a reactor tank or cell, copper bussing, cathodes, anodes, rectifier, current controller, recirculation pump, internal piping, and valves.

With the parallel flat plate electrode units, the recovered metal is removed in strips or slabs and can be sold to a refiner or used in-house by electroplaters as an anode material. Several variations of the conventional electrowinning process are used. Variations in design are typically aimed at overcoming electrode polarization and low ion diffusion rates which reduce recovery rates in low concentration solutions. This is typically achieved by reducing the thickness of the diffusion layer through agitation of the solution or movement of the cathode.

Flat plate electrowinning units are usually operated on a batch basis, although continuous configurations are also in use. With a batch operation, a solution containing metal ions is added to the electrowinning cell tank or continuously circulated from a side tank and a D.C. electrical current is applied. As the recovery process proceeds, metal ions are plated onto the cathode and the solution becomes depleted. Typically this process is halted when the deposition rate drops below a given point or when the metal deposit thickness reaches approximately 1/4 to 3/8 inch. The plated metal sheets can then be pealed from the cathode and reused or sold. It is possible for the plated deposit to envelop the cathode, making removal nearly impossible. This problem can be overcome by employing a technique termed current shadowing that gradually reduces the current density at the outer edges of the cathode plate. Another method is to use non-conductive edge strips. However this may result in the production of dendrites at the juncture of the edge-strips (ref. 349).

3.5.4.3 Wire Mesh, Expanded Metal and Reticulate Cathode Units

The wire mesh, expanded metal and reticulate cathode designs are aimed at increasing the surface area of the cathode. The wire mesh and expanded metal (appearance of floor grating) types are usually fabricated from stainless steel. Reticulate is a term used by at least one manufacturer of electrowinning units to describe their cathodes (ref. Eltech file). The term reticulate, which means having veins arranged like the threads of a net, accurately describes the appearance of this type of the cathode. The manufacturer also describes the reticulate cathode as a "foam metal cathode" (ref. 105).

The metalized surface of the reticulate cathode is rough and therefore has a greater actual surface area than its geometric surface. The manufacturer indicates that the surface area is 10 times greater than the apparent area. The higher surface area permits use of the units at lower metal concentrations than possible with conventional flat plate cathodes of the same size. One user of this technology (PS 196) indicated that it treats cadmium to below 5 mg/l, but that a significant concentration of residual cyanide remains. A diagram of a reticulate cathode electrowinning system used by nine survey respondents is shown in Exhibit 3-37.

The wire mesh and expanded metal types are used as anodes in a plating bath after they have been plated with metal in the electrowinning unit (ref. 130). The reticulate cathodes are not reusable. When they are fully coated with metal, they are either sent off-site for sale as scrap or are discarded, depending on the type and purity of the deposit and the ability of a reclaim site to deal with the non-metallic core of the cathode. Operations where the cathodes are discarded are referred to as extractive methods of electrowinning (ref. 421).

Vendor provided data for the electrowinning treatment of a copper cyanide bath using a reticulate cathode design is shown in Exhibit 3-38. Operating data for a reticulate cathode unit provided by the Naval Facilities Engineering Service Center (Port Hueneme, CA) are graphically displayed in Exhibit 3-39. These tests were performed on a printed circuit board line over a time period of 432 hours (18 days). The electrowinning unit is a Retec Model 6 (21 ft^2 of reticulate cathode surface area). Exhibit 3-39 (a) shows the copper concentration in the drag-out rinse tank (56 gal) during the test period (same

Exhibit 3-37. Diagram of an Electrowinning Unit Employing Reticulate Cathodes (Courtesy of ELTECH Systems Corportation)

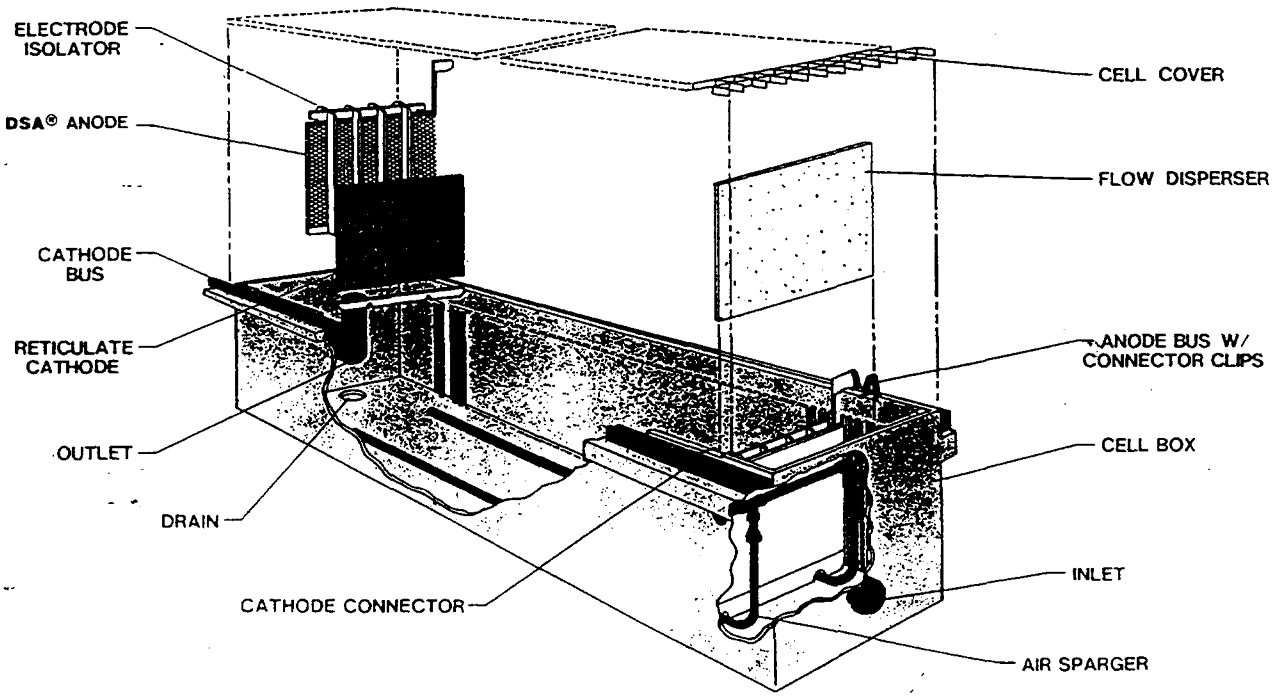
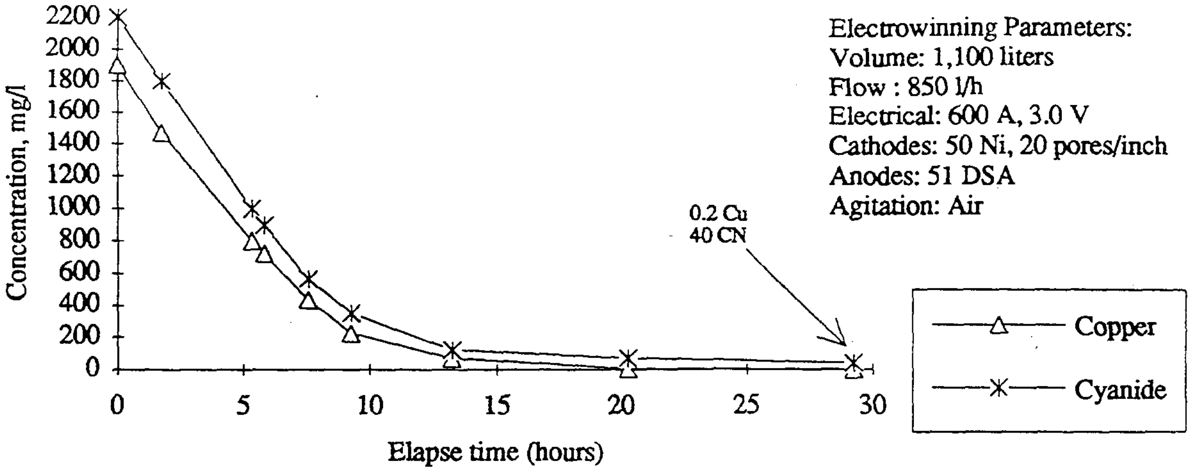
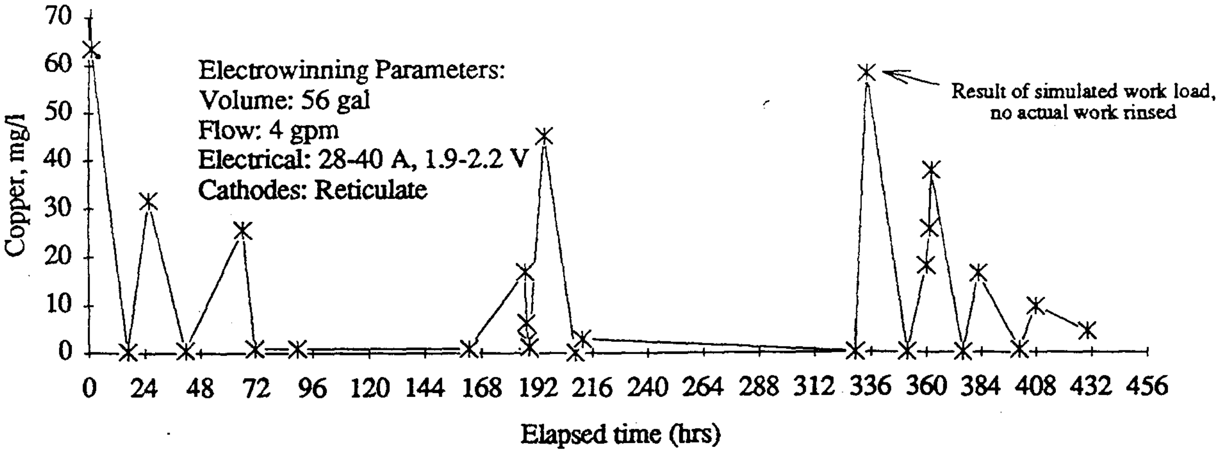


Exhibit 3-38. Example of the Performance of a Reticulate Cathode Electrowinning Unit Treating a Copper Cyanide Bath


Electrowinning Parameters:
Volume: 1,100 liters
Flow : 850 l/h
Electrical: 600 A, 3.0 V
Cathodes: 50 Ni, 20 pores/inch
Anodes: 51 DSA
Agitation: Air

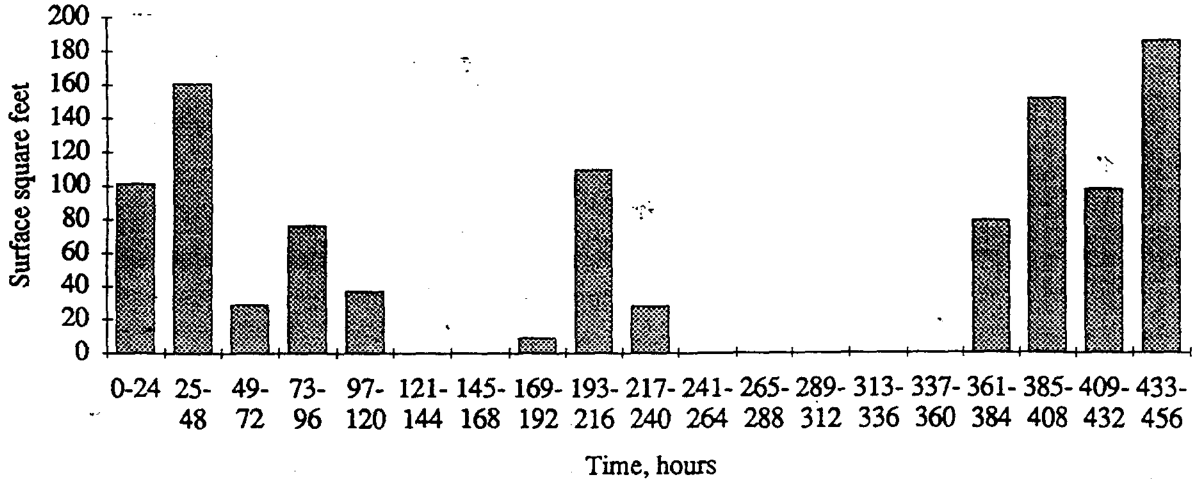
Source: ref. 103

Exhibit 3-39(a). Example of the Electrowinning Performance on Copper Sulfate Static Rinse


Electrowinning Parameters:
Volume: 56 gal
Flow: 4 gpm
Electrical: 28-40 A, 1.9-2.2 V
Cathodes: Reticulate

Result of simulated work load, no actual work rinsed

Exhibit 3-39(b). Work Load Through Copper Sulfate Static Rinse



Data provided by Jennie Koff, Naval Facilities Engineering Service Center, Port Hueneme, CA.

set-up as EW configuration EW-1a, Exhibit 3-32). The highest concentration measured in the drag-out rinse during the test was 64 mg/l Cu. The copper concentration invariably fell to less than 1 mg/l overnight and during any idle period of a few hours duration. During one segment of the test, the copper concentration fell from 16 mg/l to 1.5 mg/l in 2 hours; during another segment, the copper concentration fell from 25.7 mg/l to less then 1 mg/l in 5 hours. The data suggest that for the conditions present at this facility, the copper concentrations will generally remain below 60 mg/l in the drag-out rinse and will reach 1 mg/l or less within approximately 5 hours or less after plating has ceased.

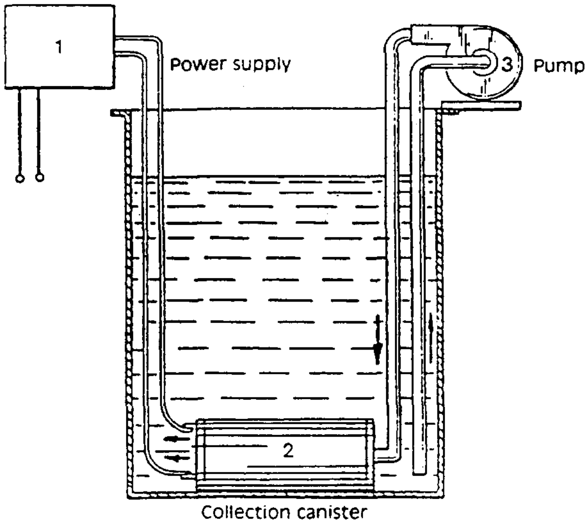
A reticulate and disposable cathode is often used for gold electrowinning. A small commercial unit, operating with only 25 amps output, is shown in Exhibit 3-40. The cathode of this unit is placed directly into a small drag-out tank. This unit is applicable to the recovery of most precious metals. It was used by four respondents to the Users Survey. The metal deposited onto the cathode is recovered chemically and/or thermally (dissolved in acid from cathode, precipitated, then melted or simply melted from the cathode) (ref. Gold Bug File).

3.5.4.4 High Surface Area Cathode Units

High surface area units are used in rinsing operations, where low concentrations of metals are desired. The advantage of maintaining a lower equilibrium concentration is two fold; first, the percentage of material recovered is increased and second, the free rinse after the recovery rinse may be sufficiently dilute to be sewered without treatment. High surface area units extract the metal onto cathodes made of fibrous material such as carbon. The high surface area allows for metal removal at solution concentrations much lower than flat plate cathode types and even the reticulate types. The fiber cathode is regenerated by passage of a strip solution through the unit and reversal of the current. Plating solutions can sometimes be used as the strip solution and returned to the bath for reuse. More commonly, the concentrated metals in the strip solution are removed by a second electrolytic unit, employing conventional electrowinning.

One commercially available carbon-fiber cathode system employs a three dimensional flow-through type assembly, consisting of carbon fibers woven into layers of fabric secured to the electrical distribution feeder sheets in a plastic coated frame (ref. 128 and Baker Brothers file).

Exhibit 3-40. Diagram of a Precious Metal Electrowinning In-Tank Unit (Courtesy of Precious Metals Processing Consultants, Inc.)



The high surface area units have been mostly applied to recovery of metals from the rinses of cyanide based plating processes (e.g., cadmium, copper, zinc, gold and silver). These units remove metal ions to low concentrations and also oxidize the cyanide in the rinse water. Other applications noted in the literature include: copper etch, electroless copper, acid gold, acid silver, tin-lead fluoborate and tin-lead sulfate solutions.

Cyanide oxidation with HSA units can be performed with the addition of sodium chloride electrolyte to the rinse, although the practicality of the process is not widely accepted. With this method, the chloride ions are oxidized to chlorine at the anode and react with cyanide in the rinse (ref. 39).

3.5.4.5 Other Equipment/Operational Considerations

Various design methods are used in commercial equipment to achieve agitation and reduce the impact of concentration polarization. One manufacturer (ref. Eco-Tec file) advertises the use of convection air agitation that directs a uniform curtain of fine air bubbles across the face of the cathode and thereby bringing a constant supply of fresh solution to the cathode surface. According to the manufacturer, the improved agitation permits close anode to cathode spacing (1 in.) which reduces the IR (ohmic) resistive voltage drop across the cell, resulting in lower energy consumption. It also reduces the overall size of the electrowinning unit for a given cathode area requirement. Another manufacturer uses a fluidized bed design to achieve agitation (ref. BEWT file). With this design, mesh metal electrodes sit in a bed of inert glass beads, which is fluidized by the action of the pumped electrolyte. The scouring action of the beads against the mesh electrodes unit provides agitation to reduce concentration polarization and improves the quality of the deposit. Due to the mesh design, the deposit cannot be mechanically removed from the cathodes. Rather they are placed into specially designed anode bags and put into plating tanks, where they function as anodes. This equipment is advertised for recovery of nickel, nickel-iron, zinc, cadmium, silver and gold. Most of the electrowinning units manufactured for silver recovery for use in the photographic industry employ a rotating cylindrical cathode. Rotating the cathode provides the needed agitation at the interface between the cathode and the solution.

Several types of controls are available with electrowinning units. Inexpensive units usually have just an on/off switch as the only means of current control. Such equipment may be satisfactory if the solution variables remain relatively constant. Many units have variable current control and a meter to indicate current flow in the solution. Sensor probes are available on some units which will automatically adjust the current to the metal concentration. Microprocessor controls are also offered by many manufacturers.

Nickel, although it is one of the most frequently plated metals, has traditionally not been recovered by electrowinning. This is partially due to the fact that alternative technologies exist for nickel recovery, but is also due to the difficulty of the nickel electrowinning process. The recovery of nickel using electrowinning has become more common in recent years owing to research and development. The reason for the difficulty with nickel is that the pH of the electrolyte (typically a sulfate media) will drop as the electrowinning process proceeds due to the electrode reaction (electrolysis) that produces hydrogen ions. As this occurs, the metal deposition rate will decrease and hydrogen production will continue to increase. For this reason, it is necessary to control the pH of the electrolyte. A nickel recovery system employing ion exchange and electrowinning is shown in Exhibit 3-41. With this process, the electrolyte is continuously circulating from the cell to an adjustment tank where the critical operating parameters are controlled. This includes caustic addition for pH control. Another reference suggests the use of ammonia for adjusting the pH of Watts, Woods and sulfamate nickel baths. Note that the overall recovery system in Exhibit 3-41 includes the recovery of metal from both electroplating and electroless plating processes. A selective ion exchange column is used prior to electrowinning to separate the nickel from the chelates contained in the electroless bath and rinses.

3.5.5 Costs

3.5.5.1 Capital Costs

The capacity requirement for conventional electrowinning depends most heavily on the amount of metal to be recovered and the rate of metal deposition. Factors that influence the rate of metal deposition are (ref. 39 and 128):

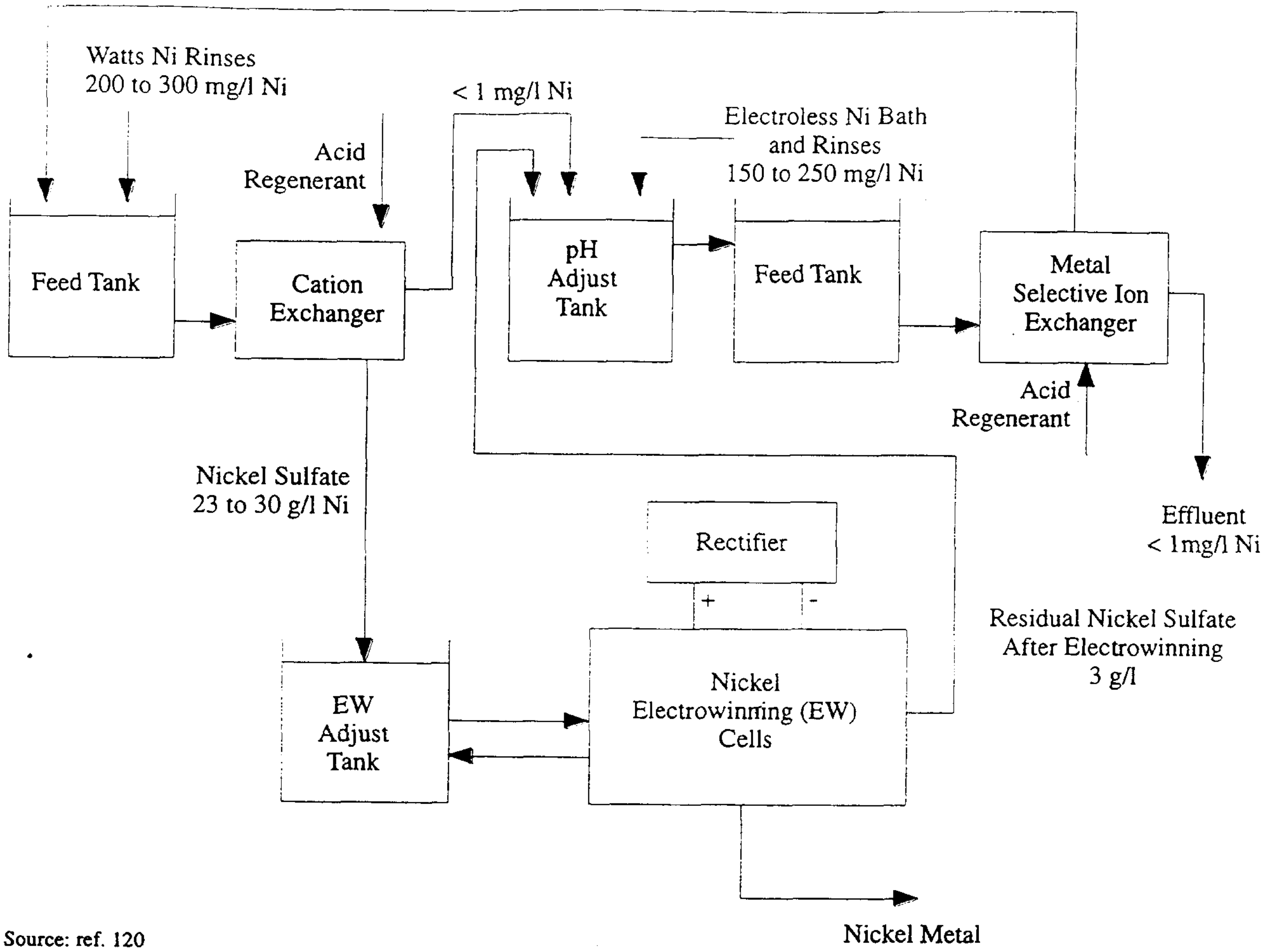
- Electrode type and area
- Agitation rate (or in general, mass transfer)
- Solution chemistry
- Electrical variables
- Temperature

The cathode surface area depends on the size and number of the cathodes employed in the unit. The agitation rate, average metal concentration in the rinse solution, solution conductivity and temperature all influence the current density that can be maintained and still result in an even, homogeneous metal deposit on the cathode. The higher the current density allowed, the higher the rate of metal deposition per unit area of cathode (ref. 39). Exhibits 3-42 and 3-43 present useful data for cathode sizing exercises.

A nearly linear relationship between cost and capacity is displayed in Exhibit 3-44. Capital costs, therefore, can be estimated once capacity requirements are determined. Most vendors refer to capacity in terms of amperage; more precisely, the maximum amperage setting on a unit's rectifier. Less commonly, capacity is expressed in terms of total cathode area. The rectifier and electrodes comprise the majority of the cost for most units; other contributing components are the fluid containment tank, pumps, filters and optional metering devices.

The strategy for determining the appropriate capacity of an electrowinning unit for a specific application is straightforward in theory: match the expected plate-out rate of the unit with the application's waste metal generation rate. For drag-out tank applications, such as those diagrammed in Exhibit 3-32, the rate at which metal is

Exhibit 3-41. Electrowinning System Applicable to Nickel and Electroless Nickel Plating Operations



Source: ref. 120

Exhibit 3-42. Faraday Table for Common Metals

Element	Symbol	Density g/cc	Gram Atomic Weight	Valence	Gram Equivalent Weight	Deposition Rate g/amp-hr	Current Required amp-hr/g
Cadmium	Cd	8.65	112	2	56	2.10	0.476
Copper	Cu	8.96	63.5	1	63.5	2.37	0.422
Copper	Cu	8.96	63.5	2	31.8	1.19	0.840
Gold	Au	19.3	197	1	197	7.35	0.136
Gold	Au	19.3	197	3	65.7	2.45	0.408
Lead	Pb	11.3	207	2	104	3.87	0.258
Platinum	Pt	21.5	195	4	48.8	1.82	0.550
Nickel	Ni	8.90	58.7	2	29.4	1.10	0.909
Rhodium	Rh	12.4	103	3	34.3	1.28	0.781
Silver	Ag	10.5	108	1	108	4.03	0.248
Tin	Sn	7.30	119	2	59.5	2.21	0.452
Tin	Sn	7.30	119	4	29.8	1.11	0.901
Zinc	Zn	7.13	65.4	2	32.7	1.18	0.847

Conversions:
1 Faraday = 96,500 coulombs = 26.8 ampere-hours
gram equivalent weight/26.8 = grams/ampere-hour
density X 2.36 = gram/mil-square feet

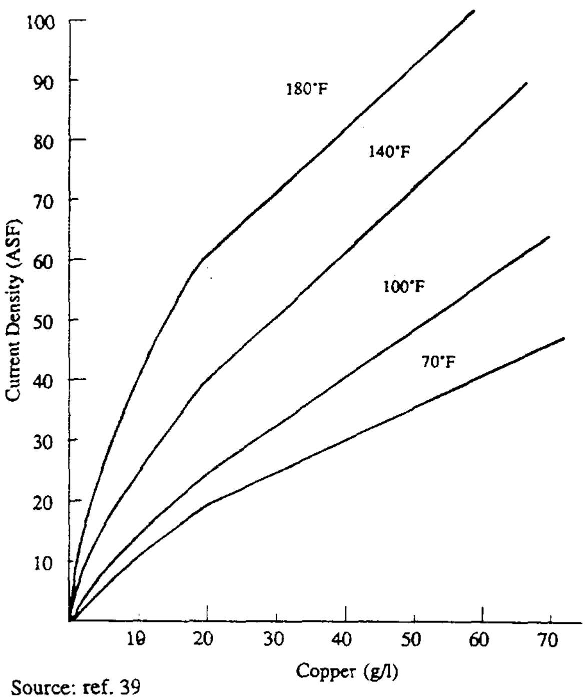
introduced into the tank is determined either by direct analysis, or by a method such as that proposed in Section 2.5.3.1. The plating rate of the metallic species in question is obtained from the Faraday Table presented in Exhibit 3-42. Capacity requirement in amperes, therefore, is the introduction rate in g/hr divided by the plating rate in g/amp-hr. This quotient requires an adjustment for expected current efficiency (that portion of current available to the cell that actually is employed reducing the target metal on the cathode) before serving as a reliable guide for required capacity. Current efficiency for electrolytes with high metallic concentrations will approach theoretical levels, but it may range down below < 10% of the theoretical rate for electrolytes concentrations of metal below 100 mg/l.

Other application configurations lend themselves to similar analysis. For units employed to electrowin metal from ion-exchange regenerant, the volume and concentration of the regenerant is required for capacity sizing. These quantities will be known from the analyses required for ion exchange sizing. The time available for electrowinning is limited by the time between regenerations. Spent regenerant may be contaminated by several species of metallic ions; this will make the calculation of appropriate cell amperage less accurate. For batch dumps, concentration of metal in the spent bath and the dump period are usually available data. The following formula applies to regenerant or process batches alike.

amps = [g/batch]/[g/amp-hr]/[hours/batch or cycle]

Cell amperage is not likely to approach the maximum rectifier output. It is limited by the maximum practical cathode current density for the metallic species being electrowinned which, in turn, is a function of metallic concentration. Thus, in practice, it is the total cathode area and the concentration of metal in the electrolyte that best determines the practical amperage capacity of a unit. Exhibit 3-43 demonstrates the considerable effect of concentration (and temperature) on maximum current density for copper electrowinning; similar curves are to be expected for other metals.

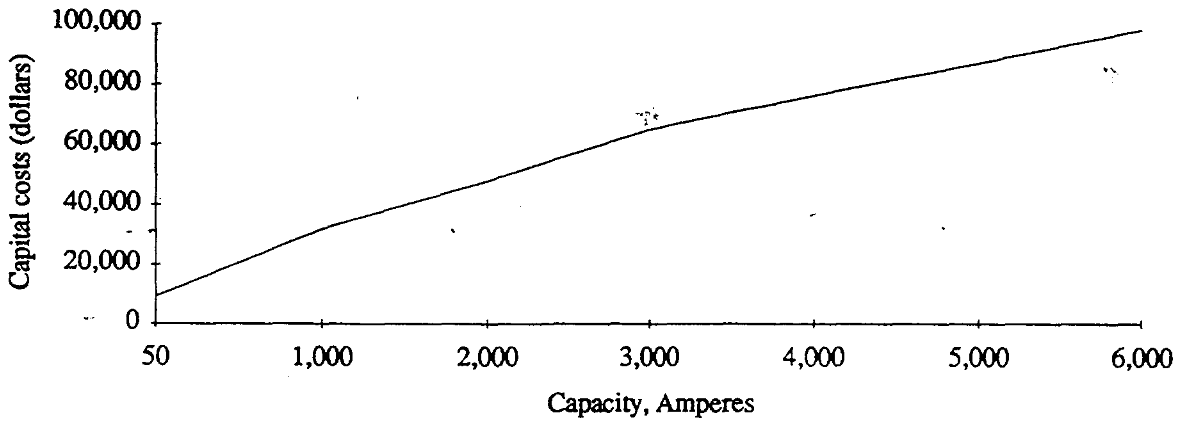
Exhibit 3-43. Maximum Current Density for Copper Electrowinning



Source: ref. 39

Low concentration electrolytes present significant sizing implications. Plating proceeds at a fraction of high concentration current densities and efficiency is lost as current is wasted reducing hydrogen at the cathodes.

Exhibit 3-44. Capital Costs for Electrowinning Units



Units lacking design features aimed at reducing the thickness of the polarization depletion layer and not equipped with high surface area cathodes will be least efficient in these environments. At concentrations of <100 mg/l, a reasonable current efficiency estimate may be 10% or less. These factors must be offset with larger capacity units. Success at low concentrations will also depend on the metallic species being electrowinned, the presence of multi-valent cations in the electrolyte (such as tin and iron, which further lower efficiency by oxidizing to higher valence at the anode and reducing to lower valence at the cathode, thereby wasting current and yet staying in solution) and the time available for electrowinning (eventually, units so designed can reduce concentrations of certain metals to below compliance levels).

Anode and cathode construction will significantly impact the cost of an electrowinning unit. A list of cathode and anode materials is displayed in Exhibit 3-36. Materials options for a specific application are limited by the peculiarities of the electrolyte being electrowinned and by the manufacturer of the unit. Cost differences can be significant; e.g., ELTECH Systems Corporation offers it's units with either graphite or DSA® (proprietary rare earth coating) anodes. The graphite anodes were quoted in 1993 at $80, while the DSA were $335. For a Retec 25 (26 anodes) this represents a cost difference of $6,630.

3.5.5.2 Operating Costs

Typical operating costs for this technology are shown in Exhibit 3-45. Respondents employing this technology reported their annual operating costs to be only $4,100/yr on average, roughly split between the labor and non-labor categories. This technology is not labor-intensive nor expensive to run. Operating costs components are labor, electrode replacement, maintenance and energy.

Labor costs are largely installation- and application-specific. Units used in batch configurations may require considerable solution transport, pre-adjustment of the electrolyte, cleaning of salt deposits and adjustment of batch releases from the unit. On the other hand, dedicated drag-out rinse units treating fluids with lower total dissolved solids may require only occasional cleaning and rare maintenance of any kind. In all, little scheduled maintenance beyond cleaning and replacement of corroded connectors is to be expected.

Energy costs will comprise only a small percentage of total operating costs for most applications. For large units, however, energy costs may more significant in relation to total operating costs as other expenses benefit from economies of scale. Predicting energy costs for a given application is complicated by the fact that several variables affecting total power consumption are difficult or impossible to know prior to actually running the unit. Conductivity, required voltage, rectifier efficiency, and current efficiency are either unknown or will vary with time or batch to batch. Once the unit is operating, energy costs will become easy to assess. In the example given in Exhibit 3-46, electrical costs were $0.4198/lb of Cu; these costs reflect metal removal to <5 mg/l and should be typical of similar applications.

Electrode replacement costs depend on their construction and life expectancy. Stainless steel cathodes are usually peeled or scraped free of plating deposits and reused. Reticulated cathodes must be replaced after they accumulate sufficient metal to lower their effectiveness, roughly 5-10 pounds/sq. ft. of cathode area. Anodes may, as in the case of DSA® and other proprietary materials, be semi-permanent and last in excess of 5 years. Graph-

Exhibit 3-45. Operating and Maintenance Costs for Electrowinning Equipment

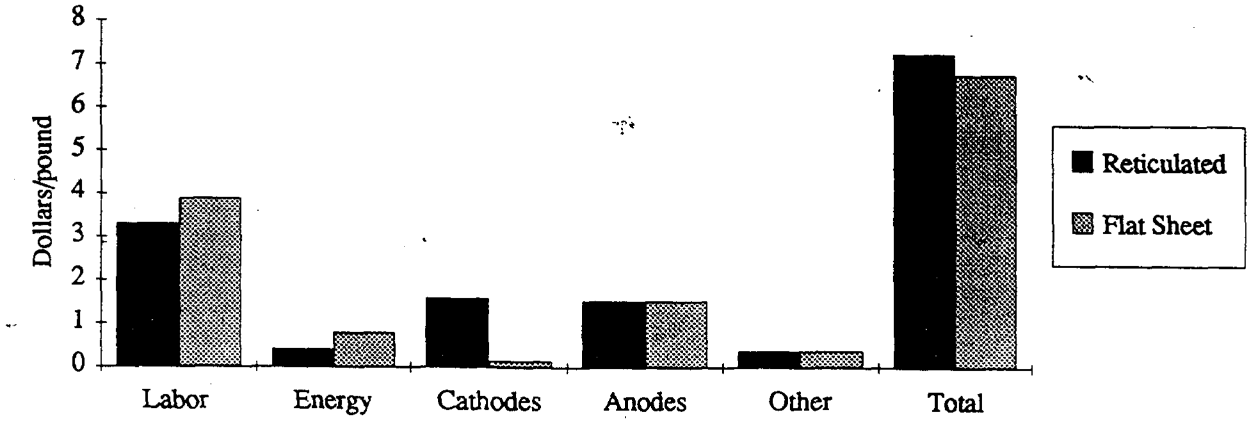


Exhibit 3-46. An Example of Calulating Operating Costs for an Electrowinning Application

Application: Batch treatment of copper-containing spent process and dragout solution, including acid copper sulfate and potassium persulfate.

Capital Costs:	
Cost of Unit	$ 22,000
Installation[a]	5,100
Total	$ 27,100
Operating Costs/Year:	
Energy	$ 450
Labor	3,900
Cathodes[b]	895
Anodes[c]	1,650
Parts	300
Chemistry[d]	750
Scrap metal value[e]	(643)
Total	$ 7,302
Savings/Year:	
Waste treatment savings[f]	$ 2,700
Metal recovered	1,072 lb

[a] Unit required a fume hood and exhaust system due to the generation of SO_2 gas during reduction of persulfate, and cost figure includes a pH adjust tank with mixer.
[b] Reticulated, cathode held approximately 10 lbs of Cu before replacement.
[c] Annualized, assuming 5 year life. No anodes were actually procured.
[d] Sodium hydroxide and sodium meta-bisulfite.
[e] Received average of $0.60/lb. Metal price averaged $1.00 during year.
[f] Labor-intensive batch precipitation method.

ite anodes are well-known to "melt" or gradually exfoliate carbon particles into the electrolyte; this obviously shortens their operating life.

The example offered in Exhibit 3-46 has total operating costs at $6.81/lb of Cu. Unlike a drag-out rinse application, considerable labor was involved transporting and adjusting spent process baths prior to electrowinning. Labor, at $3.64/lb, was by far the largest operating cost component.

3.5.6 Performance Experience

A partial summary of the User Survey data relative to electrowinning is presented in Exhibit 3-47. There are a number of general observations that can be made from these data and other data contained in the Users Survey database and literature:

- The average satisfaction level for the electrowinning technology is 3.1 (on a scale of 1 to 5, with 5 being most satisfactory), which is lower than the average level rating for all recovery technologies. Fifty-six percent of the shops indicated that this technology satisfied the need for which it was purchased and another 15% indicated that it partially satisfied the purchase need. The following is a breakdown of the reasons why shops purchased this technology:

To meet of help meet effluent regulations:	38
To reduce plating chemical purchases:	9
To reduce the quantity of waste shipped off-site:	20
To reduce wastewater treatment costs:	20
To improve product quantity:	1
Other (mostly to recovery valuable metals):	8

- The use of electrowinning for metal recovery generally did not impact production quality or the rate of production. The following responses were provided:

	Product Quality	Production Rate
Improved	0	1
No Change	55	50
Decreased	1	5

(Where product or production impacts occurred, the respondents did not provide any details of the impacts.)

Exhibit 3-47. Summary of Users Survey Data for Electrowinning

Shop Code	Application	Vendor	Year Purchased	Equipment Costs			Annual Operating Costs				Annual Savings					Use Code	Sat. Level	Future Decision	Shop Code
				Equip.	Other Cap.	Total	Non-Labor	Hrs	Labor	Total	Bath Chem.	Treat. Chem.	Disposal	Other	Total				
008	Cadmium, Cyanide	BBWT	1989	$25,000	$8,000	$33,000	ND	500	$6,000	$6,000	ND	ND	ND	ND	ND	2	1	4	008
008	Zinc, Non-Cyanide	BBWT	1989	$25,000	$8,000	$33,000	ND	500	$6,000	$6,000	ND	ND	ND	ND	ND	2	1	3	008
009	Cadmium, Cyanide	In-House	ND	$5,000	$1,000	$6,000	ND	50	$750	$750	ND	ND	ND	ND	ND	1	3	3	009
012	Cadmium, Cyanide	HSA	1981	$80,000	$20,000	$100,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	2	ND	3	012
023	Cadmium, Cyanide	Eltech	1992	$19,000	ND	$19,000	$700	20	$260	$960	ND	$5,330	$1,000	$4,290	$10,620	1	4	1	023
025	Cadmium, Cyanide	In-house	1986	$15,000	ND	$15,000	$7,000	120	$1,080	$8,080	ND	ND	ND	ND	ND	1	4	1	025
036	Copper, Cyanide	In-House	1984	$4,000	ND	$4,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	2	1	3	036
039	Cadmium, Cyanide	HSA Reactors	1983	$32,500	$44,000	$76,500	$20,000	1000	$18,000	$38,000	ND	$250	$500	ND	$750	3	2	3	039
041	Copper, Sulfate	In-House	1990	$4,000	$6,000	$10,000	$2,000	100	$1,500	$3,500	$144	$250	$4,500	ND	$4,894	1	3	1	041
043	Z inc, Cyanide	In-House	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	ND	4	043
053	Cadmium,Cyanide	Covofinish Co.	1989	ND	ND	ND	ND	100	$1,400	$1,400	ND	ND	ND	ND	ND	3	2	3	053
061	Zinc,Acid	not given	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	ND	3	061
081	Cadmium,Cyanide	Precious Metals Pr	1991	$10,000	$2,000	$12,000	$2,900	24	$240	$3,140	ND	ND	ND	ND	ND	1	4	1	081
086	Cadmium,Cyanide	HSA	1982	$90,000	$60,000	$150,000	$7,000	250	$2,750	$9,750	ND	ND	ND	ND	ND	2	1	4	086
086	Zinc,Cyanide	HSA	1982	$90,000	$60,000	$150,000	$7,000	250	$2,750	$9,750	ND	ND	ND	ND	ND	1	ND	2	086
090	Cadmium,Cyanide	Eltech	1984	$15,000	$1,000	$16,000	$1,900	250	$6,000	$7,900	ND	ND	ND	ND	ND	2	1	3	090
091	Cadmium,Cyanide	Eltech	1986	$10,000	$16,000	$26,000	$1,050	150	$2,250	$3,300	ND	$1,000	$3,000	ND	$4,000	1	3	1	091
107	Zinc, Non-Cyanide	Eltech	1988	$6,500	$1,100	$7,600	ND	160	$12,800	$12,800	ND	$500	ND	ND	$500	3	3	1	107
114	Silver Cyanide	In-House	1983	$1,000	$100	$1,100	ND	60	$5,400	$5,400	$800	ND	ND	ND	$800	1	4	1	114
119	Gold, Non-Cyanide	Precious Metals Pr	1990	$2,600	$300	$2,900	$300	24	$288	$588	ND	ND	ND	$15,900	$15,900	1	4	1	119
123	Silver, Cyanide	In-House	1980	$1,000	$500	$1,500	$100	200	$2,400	$2,500	ND	ND	ND	ND	ND	1	4	1	123
124	Cadmium, Cyanide	HSA Reactors	1981	$64,692	ND	$64,692	ND	ND	ND	ND	ND	ND	ND	ND	ND	2	2	3	124
124	Z inc, Cyanide	HSA Reactors	1982	$37,000	$28,000	$65,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	2	1	3	124
128	Passivation, Nitric	Serfilco	1988	$3,500	$1,500	$5,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	2	1	3	128
139	Brass	Technic Inc.	1985	$2,500	$625	$3,125	$125	15	$240	$365	ND	ND	ND	ND	ND	1	4	1	139
139	Cadmium, Cyanide	Technic Inc.	1985	$2,500	$625	$3,125	$125	15	$240	$365	ND	ND	ND	ND	ND	1	4	1	139
139	Copper, Cyanide	Technic Inc.	1985	$2,500	$625	$3,125	$125	15	$240	$365	ND	ND	ND	ND	ND	1	4	1	139
139	Silver, Cyanide	Technic Inc.	1985	$2,500	$625	$3,125	$125	15	$240	$365	ND	ND	ND	ND	ND	1	4	1	139
146	Nickel	In-House	1992	$2,000	$1,000	$3,000	$2,000	300	$2,400	$4,400	ND	$1,000	$5,000	$1,000	$7,000	1	4	1	146
146	Zinc,Cyanide	In-House	1989	$1,000	$400	$1,400	$3,000	ND	ND	$3,000	ND	ND	ND	ND	ND	3	2	1	146
164	Nickel, Electroless Plate	Eltech	1993	$8,000	$3,000	$11,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	3	ND	1	164
167	Anodize, Hardcoat	Eltech	1990	$7,500	$1,000	$8,500	$100	50	$400	$500	ND	ND	ND	ND	ND	2	2	3	167
174	Cadmium, Cyanide	In-House	1992	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	4	1	174
176	Copper, Strike (CN)	Clinton	1988	$2,000	$300	$2,300	ND	60	$600	$600	ND	ND	ND	ND	ND	1	4	1	176
176	Silver, Cyanide	Precious Metals Pr	1991	$1,500	ND	$1,500	ND	50	ND	ND	$1,500	ND	ND	ND	$1,500	3	4	1	176
179	Silver, Cyanide	RPB Industries Inc	1987	$6,000	ND	$6,000	$2,000	24	$192	$2,192	ND	ND	ND	$18,000	$18,000	1	5	1	179
184	Cadmium, Cyanide	Eltech	ND	$14,000	$31,000	$45,000	ND	250	$2,500	$2,500	ND	ND	ND	ND	ND	2	2	1	184
188	Cadmium, Cyanide	MRT	1985	$3,000	ND	$3,000	ND	30	$450	$450	ND	ND	ND	ND	ND	1	4	1	188
188	Nickel, Sulfamate	MRT	1985	$3,000	ND	$3,000	ND	20	$300	$300	ND	ND	ND	ND	ND	1	4	1	188
189	Copper, Cyanide	ND	1989	$2,000	$700	$2,700	$750	80	$1,600	$2,350	ND	ND	ND	$200	$200	1	3	1	189
196	Cadmium, Cyanide	Eltech	1989	$5,000	$2,000	$7,000	$500	50	$500	$1,000	ND	$1,500	$200	$2,100	$3,800	1	4	1	196
213	Copper, Sulfate	Napco	1988	$4,731	ND	$4,731	ND	ND	ND	ND	ND	ND	ND	ND	ND	3	3	2	213
221	Silver, Cyanide	Jaynor	1988	$2,300	ND	$2,300	$50	52	$520	570	ND	$500	$200	$200	$900	1	5	1	221
223	Brass	ND	1991	$10,000	$10,000	$20,000	$5,000	150	$4,500	9500	ND	$40,000	$20,000	$8,000	$68,000	3	3	2	223
245	Silver, Cyanide	Jaynor	1989	$1,500	$500	$2,000	$500	15	$195	695	ND	ND	ND	$3,000	$3,000	1	4	1	245
252	Copper, Cyanide	Serfilco	1986	$5,000	$200	$5,200	$1,000	40	$3,600	4600	ND	ND	ND	$200	$200	1	3	2	252
254	Cadmium, Cyanide	Eltech	1988	$14,000	$2,000	$16,000	$2,400	ND	ND	2400	ND	ND	ND	ND	ND	2	4	1	254
262	Cadmium, Cyanide	Serfilco Ltd.	1990	$2,500	$500	$3,000	$50	20	$300	350	ND	$300	$400	ND	$700	1	4	1	262
273	In-House	In-House	1950	$3,000	$5,264	$8,264	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	4	1	273
276	Cadmium, Cyanide	HSA	1979	$40,000	ND	$40,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	2	ND	4	276
285	Silver, Cyanide	Jaynor	1985	$2,500	ND	$2,500	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	5	1	285
288	Copper, Sulfate	In-House	1990	$5,000	$2,000	$7,000	$1,000	150	$2,250	3250	$1,000	$7,200	$7,500	ND	$15,700	1	3	1	288
288	Zinc, Non-Cyanide	In-House	1982	$1,000	$200	$1,200	$600	300	$6,000	6600	ND	ND	ND	ND	ND	2	ND	1	288
290	Nickel, Sulfamate	In-House	1992	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	4	1	290
295	Gold, Non-Cyanide	Precious Metals Pr	1991	$3,000	$300	$3,300	$1,200	5	$250	1450	ND	ND	ND	ND	ND	1	4	1	295
300	Cadmium, Cyanide	HSA	1983	$96,710	$48,000	$144,710	$3,000	ND	ND	3000	ND	ND	ND	ND	ND	2	1	3	300
308	Copper, Sulfate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	ND	1	308
316	Zinc, Cyanide	Clev. Fluid	1990	$35,000	$3,000	$38,000	$2,500	100	$2,000	4500	$4,000	$6,000	$19,000	$7,200	$36,200	1	4	1	316
318	Cadmium, Cyanide	HSA	1980	$20,000	$2,500	$22,500	ND	ND	ND	ND	ND	ND	ND	ND	ND	2	1	3	318
	Average		1986	$16,076	$9,119	$25,195	$2,378	139	$2,548	$4,178	$1,489	$5,319	$5,573	$5,463	$10,140		3.1		
	Average (excluding HSA)		1987	$6,717	$2,480	$9,198	$1,396	117	$2,142	$3,353	$1,489	$5,780	$6,105	$5,463	$10,690		3.4		

(1) Other capital costs include installation and ancillary equipment. (2) Use Codes: 1-currently operating; 2-not currently operating and no intension for future use; 3-not currently in use, but intend to use in future.

(3) Satisfaction levels (manufacturer and technology) 1 to 5, with 1=lowest and 5=highest.

(4) Future decision codes: 1-purchase the same technology from the same vendor; 2-purchase the same technology from a different vendor; 3-purchase a different technology; 4-do nothing.

(5) Average total equipment cost is the sum of average equipment and other capital costs. Average annual operating cost is the sum of average non-labor and labor costs. Average savings is simply the average of reported savings. This method of calculation probable understates the average annual savings of the users. (6) ND = No data

- Most plating shops indicated that based on their experience with this technology, if given the chance, they would purchase the same type of equipment from the same vendor. The following is a breakdown of their responses:

Purchase the same technology from the same vendor:	35
Purchase the same technology from a different vendor:	4
Purchase a different technology:	13
Do nothing:	4

- The major savings from the operation of electrowinning were reduced treatment chemical use, reduced sludge generation and the value of the recovered metal (especially precious metals and to a lesser extent, cadmium).

- Most of the respondents use electrowinning to recover metal from rinse water and incorporate drag-out (or drag-in/drag-out) tanks to concentrate the metals prior to electrowinning. The electrowinning system is either connected directly to the drag-out tank or the drag-out is periodically pumped to a side tank for electrowinning. Other configurations from the survey forms include: (1) an electrowinning unit recovered metal from a spray rinse (PS 184); (2) metal was recovered from a spent process solution (PS 039, PS 128, PS 164); (3) metal was recovered from a copper sulfate bath purge (i.e., used to control a build-up of metal concentration in bath) (PS 041).

- Nearly 50 percent of the respondents' applications of electrowinning were used for cadmium recovery.

- The most successful application of electrowinning appears to be precious metals recovery (based on the number of applications, the percentage of applications still in use, and the satisfaction level of the users). This includes the use of both commercial and home-made units. This is most likely due to the fact that noble metals are more easily recovered by electrowinning than common plated metals.

- All the HSA units purchased between 1979 and 1983 were purchased from a single manufacturer (HSA Reactors Ltd.). The average cost of these units was $66,360. The high capital cost was probably tolerated at the time because these units were advertised as compliance technologies rather than simple recovery methods (PS 276). As such, they were intended to fulfill a portion of a plant's conventional treatment requirements. These units received an average technology satisfaction level of 1.4. Asked what they would do if given the opportunity to repeat the technology selection process, the eight users of this technology indicated:

Purchase the same technology from the same vendor:	0
Purchase the same technology from a different vendor:	1
Purchase a different technology:	5
Do nothing:	2

Only one of these early HSA units is currently operating (PS 086) and that unit was extensively modified by the user by replacing the carbon cathodes with corrugated steel panels and by removing the heat exchanger and the cyanide destruct module. Some shops indicated that the performance of the HSA system was good, when it was operating (PS 012, PS 124, PS 276). Other shops reported complete dissatisfaction, e.g., "it has been a major expense and headache...too much downtime" (PS 086). Another problem cited with this equipment was the competing nature of the cyanide destruction and metal removal processes. As reported by PS 039, the cyanide destruction process reduced the technology's ability to remove cadmium. PS 086 also cited this problem and reported that they abandoned this portion of the technology.

Of the various "black box" technologies utilized during the late 1970's and early 1980's, a period when plating shops were installing equipment to meet the new Federal effluent standards, the high surface area units probably had a negative impact on the utilization of advanced technology. Following this time period, the plating industry moved in the direction of conventional treatment with sludge dewatering and dehydration and off-site metals reclamation.

- Two HSA type units were purchased from a manufacturer other than HSA Reactors Ltd. in 1985 (PS 188). These are much lower cost units ($3,000) that are still in use and received higher than average satisfaction ratings.

- Eltech International Corporation, a producer of reticulated cathode units, manufactured more of the electrowinning units reported in the survey forms than any other manufacturer.

The average technology satisfaction level for these units was 2.9, slightly less than average. However, asked what they would do if given the opportunity to repeat the technology selection process, the users of this technology indicated:

Purchase the same technology from the same vendor:	8
Purchase the same technology from a different vendor:	0
Purchase a different technology:	1
Do nothing:	0

- Some performance failures of the electrowinning technology can be attributed to misapplications by the user. This is especially true with the use of home-made units and units purchased from manufacturers' representatives rather than the manufacturer. For example, PS 128 purchased an electrowinning unit from a manufacturer's representative to recover copper, nickel and chromium (chromium cannot be recovered using electrowinning because very high concentrations of chromium are required for a deposit to form) from a spent nitric acid solution (inappropriate electrolyte). The user indicated that he intended to recover the metals and reuse the nitric acid. The supplier-stated capacity of the unit, according to the user, was 8 gpm (flow-through is an inappropriate application). The result was that "it did not work" and "it fumed." Another shop (PS 146) that modified an old commercial unit indicated that they could not determine the proper electrical settings for its use. They were using the unit with a 5 gpm flow-through of zinc cyanide rinse water (flow-through is an inappropriate application because it does not permit sufficient time for the metal to be plated-out). That same shop indicated in their survey form that they are planning to use their electrowinning unit in the future for chromium recovery.

- Approximately 26% of the electrowinning units used by respondents were constructed in-house (where the manufacturer was not given, those data were not used in the percentage calculation). These units received a higher average satisfaction level than the commercial units (3.6 vs 3.1), although plating shops with home-made electrowinning units gave mixed performance reviews. The capacity and quality of the components that went into these units probably had a significant bearing on performance. Also, the lack of technical support available led to misapplications and unsolvable problems. For example, PS 025 spent $15,000 on their equipment in 1986. This unit was still running at the time of the survey (1993) and the shop gave the unit a satisfaction level of 4. On the other hand, PS 036 constructed a unit in 1984 using components available in-house and purchased iridium coated anodes ($4,000) from an anode supplier. The unit had a 60 to 70 percent downtime, reportedly was labor-intensive and their efforts were abandoned in four months. This unit was applied to treatment of drag-out and spent bath (copper cyanide). PS 041 constructed a unit for $4,000 in 1990. Although this unit is still operating, it has a downtime of 20% and is ineffective in removing copper unless the copper sulfate concentration is 75 g/l or higher (unit used to treat bath purge, lower copper concentration and electrowinning discharge is returned to bath). PS 043 abandoned their home-made unit because of problems with conductivity and sluffing off of metal (zinc) from the cathode.

3.5.7 Operational and Maintenance Experience

The following summarizes the respondents O&M experiences and provides operating labor information.

- The average number of annual operating hours per electrowinning unit were: 140 hrs/yr. The labor categories commonly used for operating this technology are wastewater treatment plant operator and trained technician. The following is a breakdown of the responses for skill requirements (based on data from 39 respondents):

Environmental Engineer:	4
Process/Chemical Engineer:	5
Chemist:	12
Consultant:	2
Plumber/Pipe Fitter:	13
Electrician:	11
Vendor:	3
Senior-Level Plater:	10

Junior Level Plater:	14
Wastewater Treatment Plant Operator:	20
Trained Technician:	17
Common Labor:	10

- The average percentage of downtime for this technology experienced by the respondents was 20 percent.

- The most frequent and significant operational and maintenance problems identified with electrowinning include: labor intensive to clean (e.g., anode cleaning, electrode contact cleaning) (PS 025, PS 053,); high level of fuming or gassing (PS 036, PS 053, PS 128); sluffing off of deposit from cathode (PS 043); temperature build-up (PS 036); salting of the electrolyte (PS 036); anodes polarize at high current density and deteriorate or are attacked by chemicals (PS 213); anodes passivate (PS 239); and deterioration of fiber cathodes (PS 086).

- Approximately 40% of the total number of electrowinning units reported in the survey forms are no longer in use.

- Some shops reported that poor support from the manufacturer was partially the cause of their system failure. PS 008 indicated that their zinc recovery unit was removed after 4 to 5 months of operation because they could not get help with system problems ("everything went wrong...like pulling teeth to get help").

- Two of the shops that purchased equipment from HSA Reactors Ltd. indicated that the fact the company went out of business led to the failure of their systems (PS 012, PS 276). The carbon cathodes and other equipment components used in their products were too unique to find elsewhere. Also, users cited numerous mechanical problems (e.g., pump failures-PS 086) with these units and they complained about the fragile nature, short life and high cost of electrodes (PS 039, PS 086). The labor costs for HSA systems appear to be higher than the average electrowinning system, which points to the complexity of the systems. Further, the operation of the equipment required a moderate level of expertise. As one shop (PS 276) indicated, it was "too technical for our people." Generally, it is observed that this technology was probably sound from a theoretical standpoint, but lacked good engineering design and components. A similar conclusion is presented in a report sponsored by the Canadian Branch of the AESF (ref. 351). That report concluded that such a system could be operated in a manual mode, but that more developmental work was needed before an adequate automated system could be marketed.

- Some facilities have added sodium chloride to the electrolyte to increase the efficiency of cyanide destruction (PS 036). One shop reported unsatisfactory results, because the solution temperature increased and gassing occurred and the residual cyanide level was too high for sewering (PS 036).

- Shops that reported difficulty with the electrowinning process cited two possible technical causes, including: (1) contamination in electrolyte (PS 036, PS 090) and (2) build-up of carbonates (PS 036).

- Shops using the small precious metals recovery units (both commercial and in-house) reported none or very few operational and maintenance problems.

3.5.8 Residuals Generation

The standard, flat plate cathode unit recovers metals in the form of metal sheets 1/8 to 3/8 inch thick. Some shops (e.g., PS 053) described their deposit as a metal sponge rather than a metal sheet. Depending on the purity of the deposit, which in turn will depend on the purity of the solution being recovered, these residuals can be either used as anodes, sold to a scrap dealer or refiner for recycle, or disposed of in a landfill. When sold as scrap, the plater receives approximately 50 to 90% of the commodity price for the material, depending mostly on quantity and purity. Some electrowinning cathodes are specifically designed to be hung in plating tanks after they are coated with metal and serve as anodes. This eliminates the need to mechanically remove the deposit.

The reticulate cathodes cannot be used as anodes. They must be either sent off-site for recovery or disposed of. Most of the shops responding to the survey that use reticulate cathodes send them to a scrap dealer. They receive approximately the same price as for flat plate cathode material.

The high surface area electrolytic units generate a strip solution that can be recycled to a plating bath, or more frequently, is recovered using conventional flat plate electrowinning.

Electrolytic Effluent Treatment for Acid or Cyanide Zinc Plating Baths

by I. Ehmann,
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Ehrmmann, I. 1993. *Electrolytic Effluent Treatment for Acid or Cyanide Zinc Plating Baths.* Metal Finishing 91(5): 36-37. Reprinted with permission from Elsevier Science Inc.

The purification of metal-containing effluents from plating shops and the simultaneous recovery of reusable materials must be given special priority when considering the shortage of such natural resources as water and metal. The objective must be to restore dissolved metals to metallic form and re-incorporate them into the cycle of materials as well as to reduce rinsewater requirements through closed-loop operation. These conditions are achieved through electrolytic deposition of dissolved metals, which offers an alternative or supplement to hydroxide precipitation. This concept is also appropriate for the purpose of following technical procedures for waste treatment, because it specifies draining, reduction and reuse of waste material before waste treatment. Because of its simple structure, equipment can be engineered in such a way that installation costs represent only a marginal increase in capital outlay and small installations operate cost-effectively as well. Operating expenses are essentially the cost of energy and cathode replacement, which is almost totally offset by the returns from metal recovery. The costs of investment are saved in the shortest time through a significant reduction in the volume of metal-containing sludge, and are clearly among the costs of the ion-exchange, ultrafiltration, reverse-osmosis, and vacuum-evaporation equipment.

AREAS FOR IMPLEMENTATION IN ELECTROPLATING

For applications where zinc concentrations for rinsewater are between 0.1 and 50 g/L, undivided electrolytic cells are employed. These cells act as plating cells that cause dissolved metal to be deposited onto sheet-cathodes (Fig. 1). These cells are designed for high plating efficiency, and they reduce the metal load to a fraction of the original concentration. Cyanide-containing effluents are especially well-suited for electrolytic treatment because the metal concentration can be cathodically reduced while the cyanide complex is anodically destroyed. Using available water treatment equipment, the amount of metal-containing sludge or the level of metal concentration in the subsequent recovery systems is substantially reduced; combined with exceptional water savings and with the returns from metal recovery, this type of cell is a good value that yields significant cost savings.

TREATMENT OF ZINC-CONTAINING RINSEWATERS

Electroplated zinc deposits constitute the most common and widespread surface treatment for corrosion-endangered components. This results in a large quantity of rinsewater that must be reconditioned. Zinc baths in particular produce an arduous wastewater problem, because the use of sodium hypochlorite detoxification is no longer permissible due to the formation of chlorinated organic compounds. With the application of electrolytic cells, the zinc-cyanide complex can be chemically transformed. The zinc is deposited onto the cathode and at the same time, the cyanide is oxidatively destroyed at the anode. This happens over a series of intermediate steps; the gross reaction is described in the following equation:

$$2CN^- + 6OH^- - 10e^- \rightarrow 2CO_2 + N_2 + 2H_2O + 2H^+$$

Furthermore, negligible amounts of ammonia emerge. In most cases, a single-stage cell is sufficient to reduce the metal and cyanide concentrations.

Fig. 1. Sheet cathode laden with zinc (deposited from rinsewater) after an acid sulfate zinc bath.

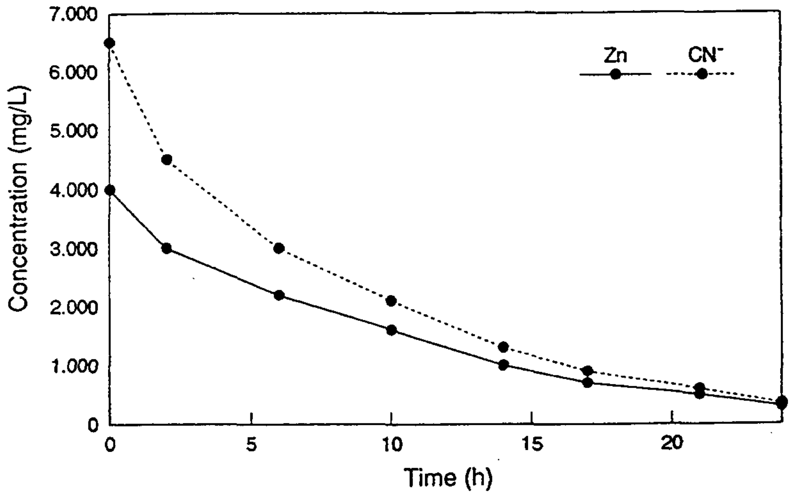

Fig. 2. Discontinuous reduction of metal concentration from a standing rinsewater in a plating line after a cyanide zinc bath.

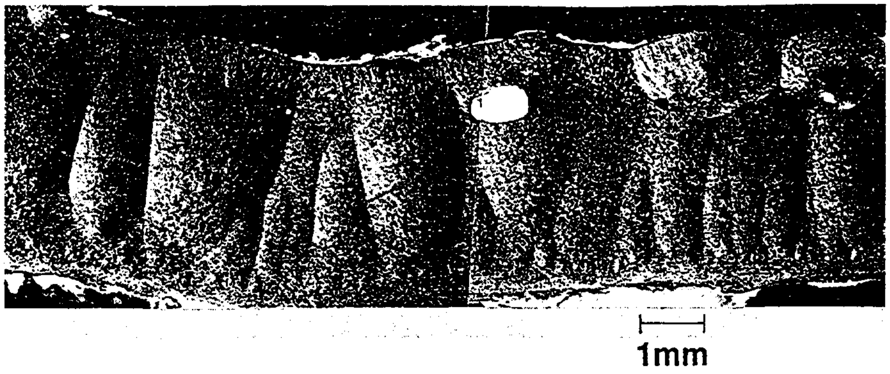

Fig. 3. A layer of zinc deposited out of a rinsewater.

In baths with especially high portions of cyanide, an electrolytic cell with a higher current density can be integrated into the process to reduce cyanide contents to levels that are under the legally permissible limits. In Figure 2, decreases in zinc and cyanide concentrations are plotted in relation to the cell operating time with a constant cell current. The reduction of zinc loads in sulfating bath rinsewaters initially caused problems due to a heavy buildup of dendrites, which was later avoided by controlling the current density in the cells. A cross-section of the zinc layer shows a thick layer that can be removed from the sheet anode by bending it (Fig. 3). The reduction of heavy-metal loads is likewise possible from zinc-nickel baths. The nickel complex is anodically destroyed and the free nickel, together with the zinc, is deposited onto the cathode (Fig. 4). Using this method, the problem-ridden detoxification process for wastewater that these nickel complexes entail can be avoided.

APPLICATIONS

In principle, the electrolytic cells can be used for applications in a continuous arrangement or in a discontinuous arrangement for batch treatment of the solution. The cells described here are equally suitable for both types of operation. The continuous output of heavy metals arrives efficiently at a still rinse in the bypass operation. The unit's size is determined by the average concentration of heavy metals in the rinsewater, the amount of metal to be eliminated per unit of time and the type of heavy metal. For placement of the cells, there are many possibilities that depend on whether the plating facility is equipped with still or save rinses. The most cost-effective solution is reduction of metal concentrations after the still rinse, because the threshold values for introducing effluent into the public water system often fall short due to counterflow rinsing. Figure 5 shows a schematic for the layout of an electrolytic cell. Similar results are obtained with cascading rinse systems.

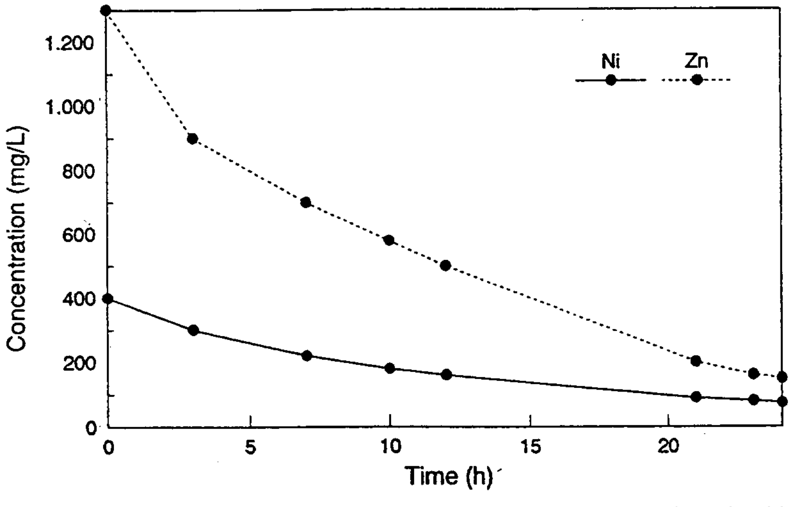

Fig. 4. Discontinuous reduction of metal concentration from a rinsewater in a plating line after a zinc-nickel bath.

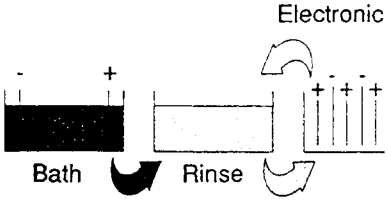

Fig. 5. Flow chart of the cyclical process
electrolytic rinsewater.

In this case as well, the greatest po
of metal should be removed at the
rinse. With the help of an electro
cell integrated after the still ri
almost 90% of the metal contents
deposited. Bearing in mind the ef
of evaporation and the resulting
tion from freshwater replenish
superior rinsing ensues with consid
bly reduced amounts of water. Wit
help of a reservoir-tank, the units
space and are also able to op
below the normal water level of
rinse.

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Recovered Value from Electroplating Industry Waste*

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INTRODUCTION

The metal finishing industry's growing concern with protection of the environment is causing it to reconsider the management of its waste. During the past 10 years, many changes have been made which are influencing a change in attitude. These include:

- The progressive increase in cost relative to the production of rejects and concentrated toxic wastes such as heavy metal hydroxide sludges.
- The progressive increase in the cost of destroying toxic wastes.
- More stringent regulations regarding materials classified as hazardous and the increased expense of transporting these materials.
- A decrease in the number of disposal sites for heavy metal sludges and other toxic wastes (controlled waste disposal).
- A progressive enforcement of laws pertaining to the quality of industrial wastewater and of its application.

The environmental protection branches of the government favor recycling waste materials in a manner which will reduce the volume of toxic waste.[1]

Industry finds itself confronted with selecting the best method and the best technique for appropriately resolving the problems associated with production of wastes whether they be solids, liquids, or gases. This paper examines the recycling alternatives for an industry where the consumption of material and production are exclusively concentrated around one metal such as nickel. In spite of the limits imposed by the choice of such an example, it is interesting to consider a general approach to this problem. It permits consideration of maximum internal recycle of the material and also of working with existing companies which are engaged in closing the recycle loop.

Table I. Material Balance Sheet for a Nickel Electroplating Shop

Average deposit thickness	20 microns	
Nickel weight	0.56 oz/20 microns/ft^2	
Annual surface plated	235 x 10^4 ft^2, or 10,760 ft^2 per day	
Annual nickel consumption	40 MT	
• Lost as solid waste	2%	0.8 MT
• Lost by entrainment in the rinse	5%	2.0 MT
• Lost in the flowing rinse	0.5%	0.2 MT
• Total	7.5%	3.0 MT
Nickel hydroxide sludge produced	about 20 tons	
Recyclable metallic production waste	6,600 lbs per year	
Nickel contained in the liquid waste	4800 lbs	

THE MATERIAL BALANCE SHEET

The case studied considers that part of the metal finishing industry which electroplates nickel. This industry is facing several different types of waste (see Fig. 1):

- Solid nickel wastes from the production process and from the fabricated articles. S.W.
- Gaseous waste: G.W.
- Liquid wastes: L.W.

The liquid wastes come from sources such as the flowing water from the cascade rinses, the static rinsewater, water from the floor, eluants from the regeneration of the pretreatment system, filter water from the precipitation process, and spent stripping/plating baths.

Today, industry is optimizing procedures to eliminate production waste associated with low efficiencies or fabrication problems. Good shop management minimizes material losses by optimizing the material balances and the fabrication costs.

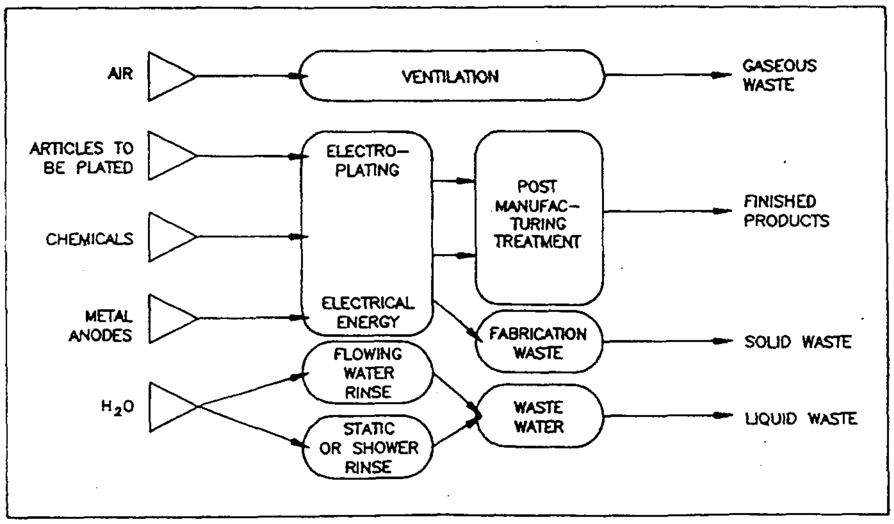

Fig. 1. Electroplating shop material balance.

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*This paper was translated from French by J.J. Dietrich, Eltech Systems Corp., Chardon, OH. The article originally appeared during 1989 in the European publication *Oberflache Surface*.

As shown in Table I, a shop using 40 tons of nickel per year can have 3 tons of waste nickel. This can be distributed as 0.8 tons of solid metal waste, which can be directly recycled, and 2.2 tons of metal dissolved in wastewater.

Where scrubbers are used, it is assumed that the metals entrained in the gas streams will be found in the liquid effluents.

Fabrication losses are generally scrap items which can be directly recycled and include metal foil, nickel pieces, plated pieces, and other rejected parts. The scrap can be sold to companies which customarily handle metal residues in the metallurgical industry.

It is difficult to consider direct reuse of the metal waste in the water effluents. These metal wastes must be pretreated before their value can be realized.

EFFLUENT PRETREATMENT

"Effluent treatment from an electroplating factory is generally based on the removal of metal from water by chemical procedures which precipitate the metal as hydroxide, sulfide or sulfate sludges. It is, however, possible to recover the dissolved metal ions as metal by electrolysis.

Reselling salts of common metals is not practical because of the cost involved in purification. The only example seen of metal salt recycling is with precious metals. For the common metals, the most practical solution until recently has been disposal. There exists, nevertheless, modern technology which permits the recycling of common metal salts where recycling is desirable and where the purity of the production is guaranteed.[2]

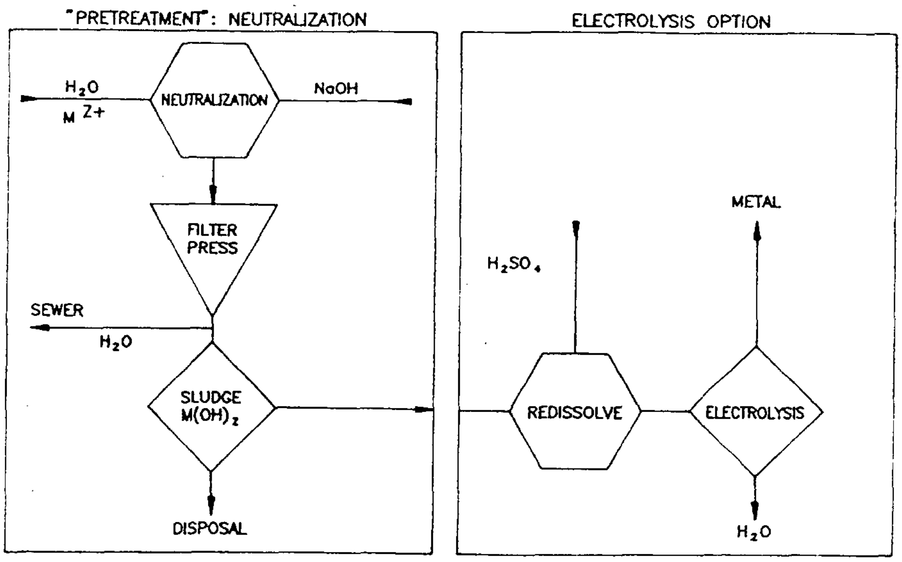

Fig. 2. Schematic for neutralization pretreatment.

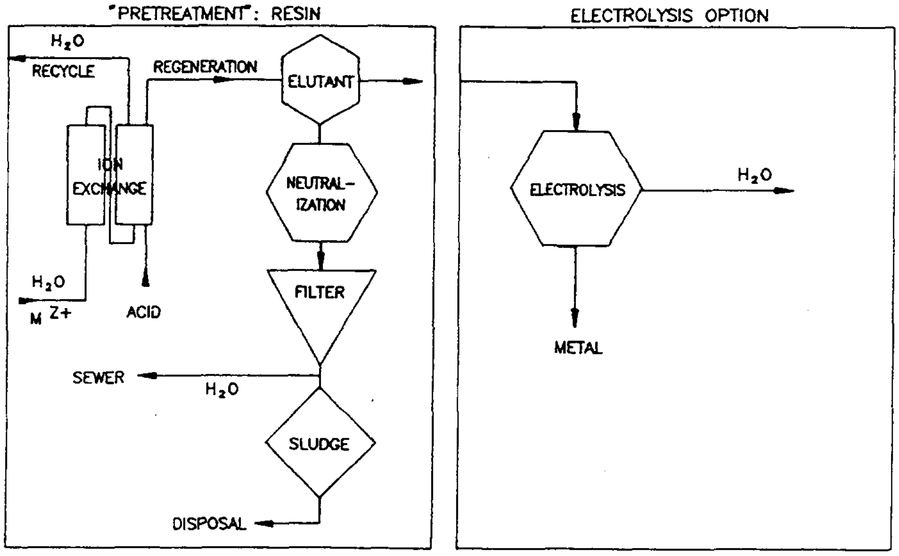

Fig. 3. Schematic for ion exchange pretreatment.

Pretreatment stations, which have been installed in electroplating shops for more than 20 years, are generally based on the concept of effluent neutralization (Fig. 2). The normal operation involves precipitation of the metal as the hydroxide. Theory predicts that the common metals are extremely insoluble at a pH around neutral.

Since metal plating baths contain a series of important organic and inorganic additives, the theoretical laws very seldom apply. As a consequence, the metal precipitation equilibriums are displaced and the metal content found in the wastewater after precipitation is higher than the legal limits. For this reason a second generation of treatments has appeared. One of these involves the treatment of effluents with ion exchange resins (Fig. 3). The ion exchange resins play a three-fold role.

- Metallic ions are concentrated on the resin.
- Treated wastewater can be recycled.
- Ion exchange resins can be regenerated when they are saturated with metal.

The general use of these resin systems is due in part to the ability to easily fit into the available space by virtue of their modular character. Nevertheless, when the ion exchange resins are regenerated, the effluent contains concentrated metallic ions which must be neutralized and which produces a sizeable quantity of heavy metal hydroxides.

The presence of organic additives (brighteners, surfactants, complexing agents) can lead to a loss of resin capacity or, in extreme cases, blockage of the resin. The evolution of pretreatment techniques which were made attractive by the utilization of ion exchange resins and neutralization continues with the appearance of a new generation of techniques on the market which are generally complementary to existing technologies. These include evaporation, electrolysis, and electrodialysis.

These techniques deal with two basic concepts: concentration and recycling. Evaporation is particularly well suited where the working temperature is above 50°C. A minimum volume static rinse associated with a spray rinse enhances bath economies.[3] The rinse water is evaporated for reconcentration and recycling to the bath; however, when using this process it must be recognized that the plating additives are not in the same ratio or in the same condition as those in the working bath. This operation requires close chemical control of the bath. Modern shops are normally equipped to handle the necessary analyses.

Certain plating techniques are not compatible with the above concept. This is particularly the case in the production of thick deposits where the chemical composition of the baths is strictly controlled.

Evaporation is equally applicable for concentrating the metal bearing eluants from ion exchange resins. The volume of the eluant is reduced and the concentration of the heavy metals is increased. This concentrated liquid solution can be transported to a treatment station before neutralization and production of the heavy metal sludge.

Electrodialysis can be utilized to regenerate spent baths by eliminating impurities such as oxidation products from the treated pieces. Recycling is possible when electrodialysis is combined with evaporation to concentrate the bath. An electrolysis scheme for a hard chrome bath has already been described.[4,5] In this technique, it is necessary to use a selective ion exchange membrane which permits recycling the entire bath while eliminating impurities which are formed during the course of the operation. The best known example is the elimination of iron and copper from hard chrome baths. This is a technology which requires knowledgeable management of chrome baths and the contained impurities. This technology is expected to develop rapidly in the near future.

The simplest electrochemical technique is direct electrolysis which addresses the two criteria of recycling and concentration of the waste. The principal advantage of electrolysis is the removal of the metal at its source in the most concentrated form. The recovered metal is easily disposed of through the metal service industries.

Finally, the electrolysis operating conditions allow for the treatment of the organic additives at the anode while recovering the metal at the cathode. The best known examples are the destruction of cyanide, the oxidation of metal complexing agents such as quadrol, or in general, a reduction in the oxygen demand of the electrolytically treated effluent.[6-8]

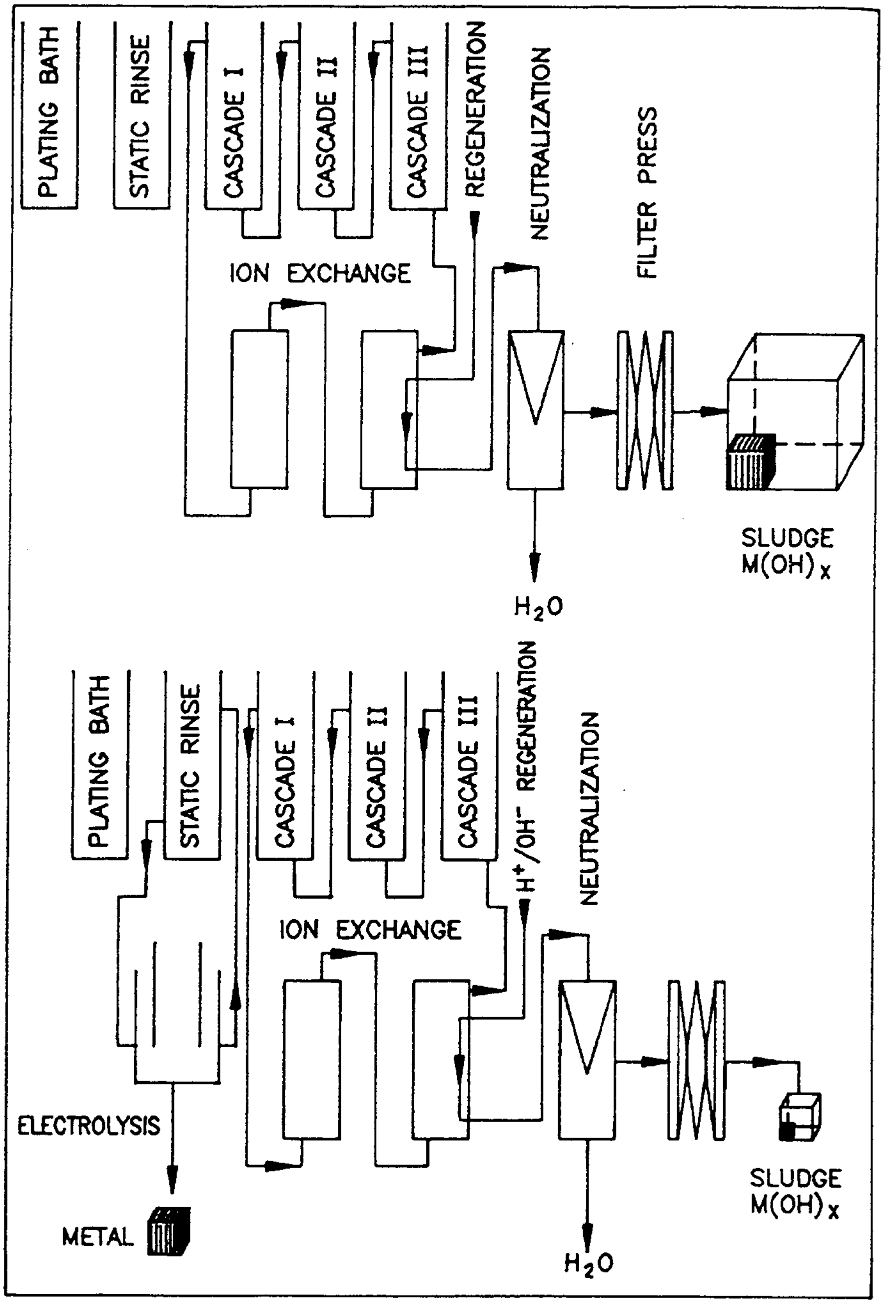

Fig. 4. Schematic illustrating the influence of electrolysis on the production of sludge.

ELECTROLYSIS AS A COMPLEMENT TO WATER TREATMENT TECHNIQUES

One of the first electrolysis applications, that can be visualized for the electroplating shop which has a neutralization station, is shown in Fig. 2 (Electrolysis Option). The metal hydroxide sludge is dissolved in sulfuric acid before electrolysis. The recovered metal can be recycled and the discharge of toxic products is eliminated.

When the pretreatment station is equipped with an ion exchange resin system, electrolysis can play a roll as one of the techniques for treatment of the ion exchange eluant. In the case of ion exchange alone, the metal is concentrated and the shop must either send the metal to an outside treatment facility or neutralize on site. In both instances, the production of sludge is inevitable as is shown in Fig. 3 - Electrolysis Option. But there is an advantage in combining electrolysis with ion exchange to electrolytically treat the eluant to recover the metal and to avoid the production of heavy metal hydroxides.

Electrolysis can be applied in close proximity to the source of the metal emission. It is here that electrolysis is most efficient. Placed, for example, on a static rinse bath in an electroplating line, it can remove more than 95% of the metal from this dilute stream as shown in Fig. 4. It can be used in association with ion exchange systems. This treatment will remove the last traces of metal while oxidizing materials at the anode. Finally, the eluant from the ion exchange resin can be electrochemically treated to minimize or eliminate production of metallic hydroxide sludges.

The principal advantage of electrolysis is to offer an important reduction in the volume of toxic waste. As shown in Fig. 4, electrolysis places a new value on existing pretreatment stations such as simple neutralization or ion exchange. By installing electrolysis at the head of a station, more than 95% of the metal is recovered before it reaches the treatment station. This leads to sizable savings by reducing the amount of chemicals needed to treat the water. Also, the utilization of electrolysis eliminates problems caused by the dilution of the many streams. Table II lists a series of practical advantages associated with the continuous treatment of a static rinse bath.

Table II. Effects of Electrolytic Recovery

Operation	*Impact*
Static rinse	• Electrolytic recovery of the metal at its source • improve rinse quality and life • reduce water use and maintenance
Cascade rinse	• improve efficiency • reduced quantity to the ion exchange resin • less frequent regeneration • reduce chemical and labor cost
Pretreatment station	• reduced handling and transportation • reduction of associated costs • reduction of sludge volume

ECONOMIC CONSIDERATIONS

The shop example described in the introduction is examined here. Electrolysis can be applied to different stages of the pretreatment of the wastewater. In the first case, an existing sludge can be put into solution with sulfuric acid and then electrolyzed (an installation scheme is proposed in Fig. 5). In the second example, the eluant from ion exchange regeneration can be electrolyzed under controlled pH conditions. In both cases, the total amount of metal is identical. The neutralization operations for both are about the same. The economic aspects of these processes are now considered.

CHEMICAL DATA:

The dissolution of nickel hydroxide using sulfuric acid takes place with an excess of acid maintained at a pH between 4 and 5. This provides ideal conditions for nickel electrolysis. At this pH, the deposit is very adherent to the cathode over the limits of concentration which range down to 0.01 g/L. The reactions which govern the stages of dissolution (reaction [1]) and the electrolytic treatment [4] and [5] are the following:

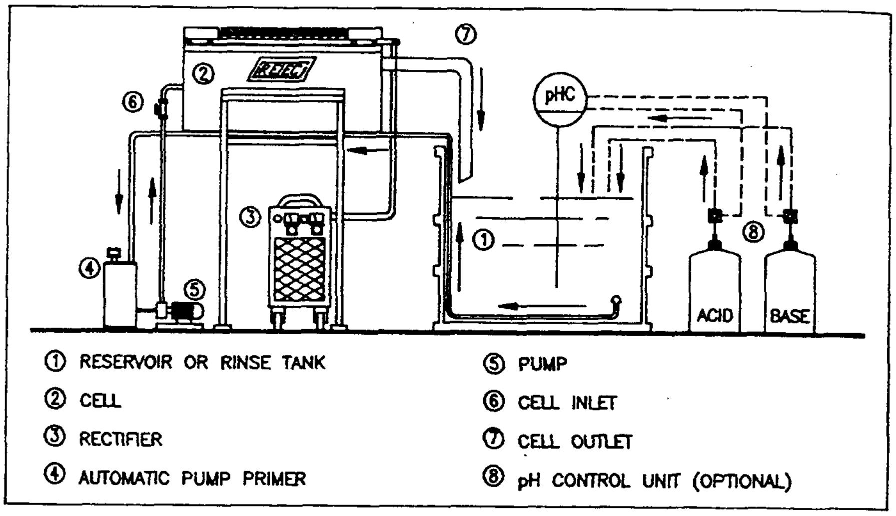

Fig. 5. Installation layout for electrolytic treatment of sludge and eluants.

Dissolution:

$$\mathrm{Ni(OH)_2 + H_2SO_4 = NiSO_4 + H_2O} \qquad (1)$$

Electrolysis:

$$\mathrm{NiSO_4 + 2\,e^- = Ni + SO_4^{=}} \qquad (2)$$

$$\mathrm{H_2O = 1/2\,O_2 + 2\,H^+ + 2\,e^-} \qquad (3)$$

$$\mathrm{NiSO_4 + H_2O = 1/2\,O_2 + Ni + H_2SO_4} \qquad (4)$$

A parallel reaction is:

$$\mathrm{H_2O + e^- = 1/2\,H_2 + OH^-} \qquad (5)$$

When a solution of nickel is electrolyzed in a cell, the yield of the electrolysis declines as the concentration decreases below 500 ppm. For this reason the most advanced electrolysis systems on the market contain high surface area or reticulated cathodes which offer the advantage of increasing the electrolytic yield at low metal concentrations.[4]

When analyzing the recovery of metal from the dissolution of sludge or from the ion exchange eluant, the average electrolysis efficiency obtained at high concentration must be considered. In the example given this is greater than 50%. The electrolysis results for this type of application are presented in Fig. 6. In the case presented, the parallel electrolytic reaction of water (reaction [5]) produces hydroxide at the cathode. This reaction reduces the acidity produced at the anode (reaction [3]).

ECONOMIC DATA:

The basis for the economic calculations are described in Table III. The detailed economic calculations of Table IV show that the recovery of nickel is expected to cost about $6.25 per pound of metal recovered taking into account only expenses. In the case where the regeneration eluant is treated, the production of sludge and its disposal is avoided and thus there is value associated with this eliminated operation. In the treatment of the sludge, only its disposal was avoided. These operations can be counted as valuable items in the economic calculations. They are reported in Table IV. The balance sheet shows the economic viability of electrolysis under the conditions described.

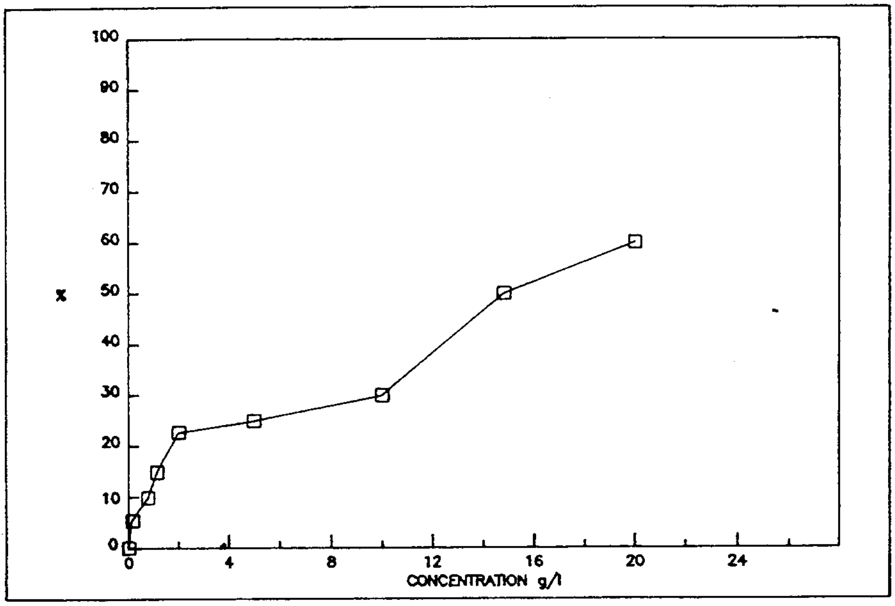

Fig. 6. Nickel electrolysis efficiency.

Table III. Economic Calculations

Operating parameters	*Cost*	
Metal recovery	4,800 lbs/yr	
Electrolytic cell capacity	26 lbs/day—132 lbs/wk	
Cathode capacity	6-9 lbs/cathode	
Cathode requirement	700/yr	
Maintenance	4 hrs/wk—$31/hr	
Cathode cost	700 x $ 9.40 = $ 6,580	
Cost of electric power	1000 A x 5 V = 5 kW/h 5 kW x 24 h x 250 days = 30,000 kWh/yr at $ 0.06/kWh = $ 1,800	
Investment		
	530 gallon tank	= $ 940
	Mixing	= $ 940
	Control	= $ 1,560
	Cell	= $ 22,500
	Ventilation	= $ 1,880
	Rectifier, 10 V — 1000 A	= $ 7,800
	Rinse & store cathodes	= $ 625
	Total	$ 36,245

Table IV. Economics of Nickel Recovery

Expense Items		*Cost In $/Yr.*
Investment: Amortized over 3 years		$ 12,250
Interest		2,250
Cathodes		6,560
Electricity		1,875
Labor		6,250
Neutralization chemicals		625
Total		$ 29,810
Recovered nickel	4800 lbs @ $ 4.25	$ 20,400
Reduced sludge	22 T @ $310	6,800
Reduced sludge handling & transportation		1,250
Precipitation chemicals		1,250
Total		$ 29,700

ELECTROLYTIC TREATMENT OF STATIC RINSES

In the example chosen, it is assumed that several nickel plating lines were utilized. After each electroplating bath a static rinse was installed in order to collect entrained bath liquid (drag out). Next, the cascade rinse utilized recycled water which has been treated by ion exchange resin to eliminate waste carried through by entrainment. Fig. 7 shows the principal calculations which were used to justify the installation of an electrolysis cell on the first static rinse bath.

Each static rinse bath receives a charge of 2.1 ounces of metal per hour. Considering 2,000 hours of work per year, the annual entrainment is 265 lbs of metal per plating line.

The electrolysis cells will recover more than 90% of the total metal charge which is removed from the electroplating bath. The metal is recovered directly on the electrolytic cell's cathodes and, therefore, does not go to a pretreatment station. It is recovered at the source as metal.

Two cases were presented in Fig. 7 to demonstrate the advantage of electrolysis. First, in the framework of an existing pretreatment station, electrolysis removes a significant quantity of heavy metals which normally go to the purification station (chemical neutralization or ion exchange treatment). This gives added value to existing installations which would be under capacity for increased plant production. Second, when a new station must be built, electrolytic treatment of the static rinse bath permits the installation of a much smaller system for neutralization or ion exchange treatment. The capital investment for electrolysis is compensated by a reduced investment for the pretreatment station; moreover, the production of a large volume of toxic waste is avoided along with the problems associated with its disposal.

In the example given, one can size the electrolysis unit based on four principal parameters.

- The hourly entrainment of metal from the plating bath to the static rinse bath.
- The volume of the static rinse tank.
- The daily plating line operating hours.

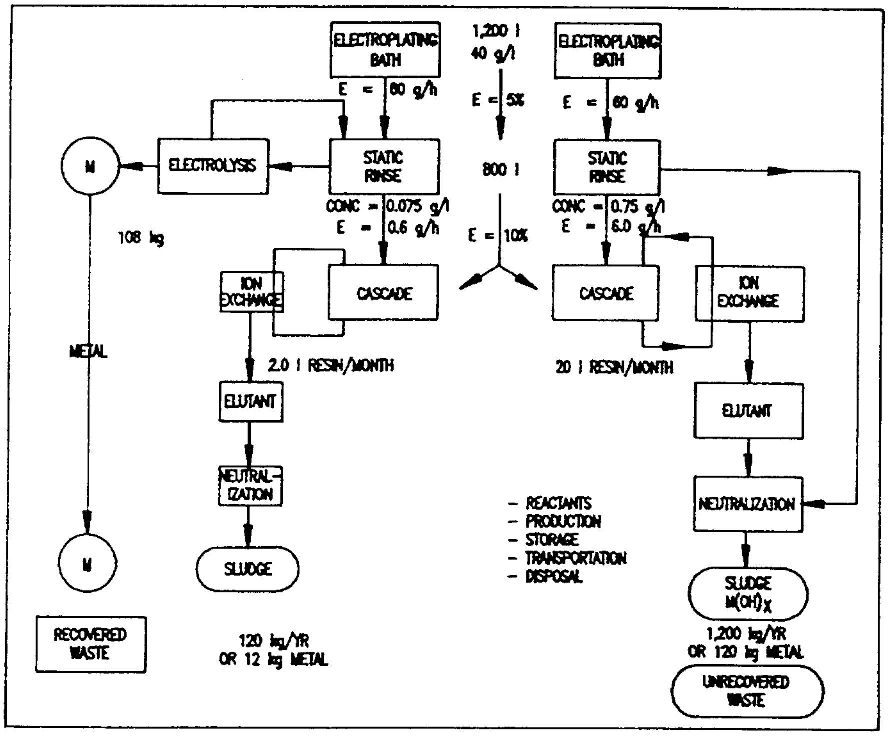

Fig. 7. Material balance sheet for electrolytic recovery on a static rinse.

- The electrolysis time necessary to treat a certain amount of metal.

The utilization of electrolysis on combined waste streams as they near the pretreatment station cannot be excluded. It is recommended, nevertheless, that the metal be captured as close to its source as possible. The installation of an electrolysis system on a static rinse tank which is in essence a diluted plating bath (ideal conditions for electrolysis), will always be preferred to treating a mixture of rinse baths which are quite different and usually quite dilute in metal (poor conditions for electrolysis). It is sufficient to study the electrolysis yield curve with metal concentration (Fig. 6) to understand that the most advantageous economics are associated with treatment of the individual static rinses.

CONCLUSIONS

Modern techniques for recycling and reconcentrating metal bearing effluents offer the advantage of minimizing pretreatment costs for electroplating shop wastes. Concentration by evaporation reduces the transportation costs of toxic materials and permits the recycling of a portion of the entrained materials.

Electrodialysis permits treatment of strong oxidizing and very concentrated metal baths. It is a recycling technique which can be applied to baths that are particularly difficult to treat by the classic methods.

Electrolysis allows for treatment of the entrained metal at its point source without modifying the shop production scheme. It is also possible to treat effluents at other points on their way to the pretreatment station.

Effluent treatment will be analyzed in the future with the objective of maximizing recycling in the form most acceptable not only from the economic viewpoint, but also from the standpoint of minimizing the necessity to handle, produce, stock and transport a minimum of toxic waste. The various aspects of the problem must be considered according to a principle relatively new in the area of environmental protection: risk minimization. **MF**

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Biographies

J.P. Wiaux is a PhD electrochemist who is the owner of Titalyse S.A., Meyrin/Geneva, Switzerland. The company specializes in electroplating of precious metals and the application of electrochemical treatments to waste purification.

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Cadmium Compliance Achieved With Electrowinning

By Joseph Shaulys, CEF, and Bob Rovinelli

For two years, a medium-sized job plating shop in Bridgeport, CT, had difficulty staying in compliance with cadmium discharge limits, using its existing waste-treatment system. A low-cost method of recovering cadmium from wastewater was devised, using electrowinning technology and high-surface-area cathodes. Cadmium and cyanide levels have been lowered significantly, and the shop now operates in compliance with environmental regulations.

At Specifications Plating, Inc., in Bridgepot, CT, all plating is done by manual racks. The shop normally operates one, eight-hour shift daily, five days per week. A variety of finishes are offered by the facility, including nickel, hard chromium, decorative chromium, electroless nickel, copper (cyanide), zinc and cadmium (cyanide), tin, black oxide, manganese and zinc phosphate.

With the exception of cadmium, all wastewater discharge limits had been met, using a conventional waste-treatment system. It was obvious that, after two years of being in non-compliance, the existing waste-treatment system couldn't routinely achieve the discharge limit for cadmium. Because products for the military comprise a major portion of the shop's work load, elimination of cadmium plating was not an option. A solution to the problem of cadmium discharge limits had to be found.

The cadmimium tank is 800 gal, with 350-gal, single-stage, air-agitated rinses on each side of the plating tank. The flow rate to each rinse is 3 gpm. To meet these limits, a low-cost method of recovering cadmium from wastewater has been developed, using electrowinning technology and high-surface-area cathodes. Data collected shows that cadmium and cyanide levels in the wastewater have been lowered significantly, and the shop is able to operate in compliance with environmental regulations.

All cyanide rinses from the plant are sent to a two-stage, cyanide-destruct system that oxidizes the cyanide with sodium hypochlorite. The effluent from the cyanide-destruct system flows by gravity to a precipitation tank, where the pH is adjusted with lime, to 9.5. Flocculating agents and an anionic polymer are added, and the solution is transferred to a clarifier. All metals are easily precipitated, with the exception of cadmium, which constitutes the bulk of the cyanide-bearing waste. Because the stringent 0.10 mg/L discharge limit for cadmium was not being met, it was necessary to look for alternative methods to the existing waste-treatment system.

Approach

Ion exchange was evaluated, but because this is one of a number of concentrating techniques, the resulting regenerant solution containing cadmium would still have to be processed. Evaporation was another option, but high energy costs and a build-up of cyanide were negative factors that suggested other methods. Several alternative techniques were considered but, by a process of elimination, electrolytic recovery was selected. A system that used high-surface-area cathodes was chosen, because of its operating efficiency and ability to recover metals at very low concentrations.

A pilot test was conducted,[*] using an electrolytic heavy metal recovery system.[**] A sample of the rinse water was taken and the flow of water to the rinse tanks was then turned off, making the rinse tanks stagnant, dragout tanks. After 24 hrs, a second sample was taken. The two samples were analyzed, and the cadmium was found to have increased from 15.1 mg/L to 36.3 mg/L.

Ten gallons of this solution were collected and processed by continuous recirculation, at 5 gpm, through the small electrolytic cell. The current on the cell was maintained at 30 A, and the voltage held constant at 4 V. Figure 1 shows the results, with the cadmium concentration reduced to below 1 mg/L in less than six hrs. A little more than 97 percent of the cadmium was recovered in that period of time.

System Design

Based on the results of the pilot test, it was determined that an electrowinning cell, with a working volume of 38 gal and equipped with 16 precious-metal-oxide-coated, titanium-mesh anodes and 15 high-surface-area-reticulated cathodes, would be installed on the cadmium plating line. Taking into consideration the highly porous nature of the cathodes, their total surface area—measuring 14" x 18" x 0.25"—is almost 300 square feet. These cathodes permit operation at low current density, which enhances metal recovery at low-metal concentrations. The large electrode surface area, per unit cell volume, also minimizes cell size and cost. The electrolytic cell is operated with a 300 A, 9 V rectifier.

Because of the unit's compact size (32" x 23" x 21"), it was located in front of the cadmium plating tank. The legs of the cell stand were adjusted, so that the cell inlet would be three in. lower than the overflow outlet of the rinse tanks. This allowed the rinse water to flow to the cell by gravity, eliminating the need for a feed pump. The treated

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[*] In cooperation with Tridon Chemical Corporation, Plainview, NY

[**] RETEC. ELTECH International, Fairport Harbor, OH

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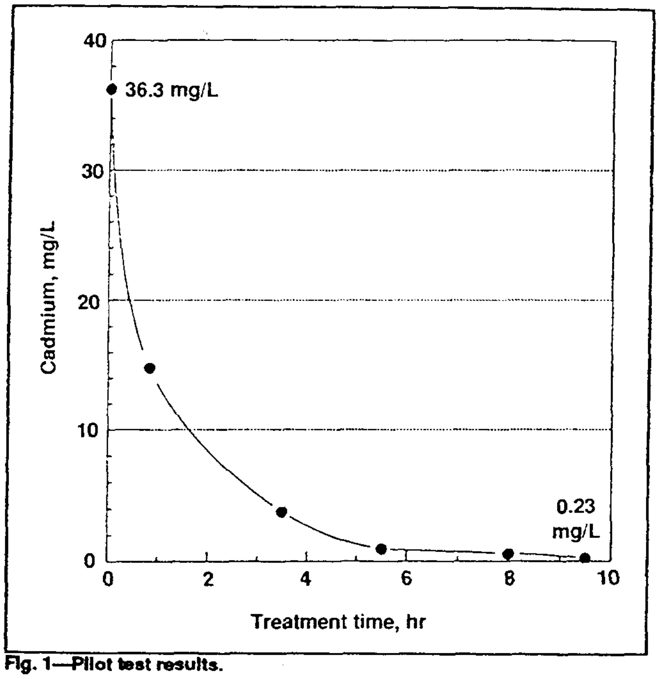

Fig. 1—Pilot test results.

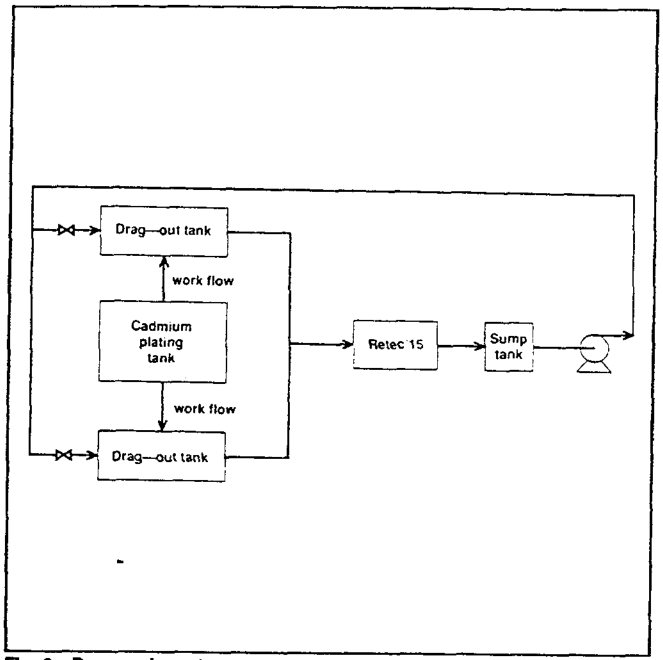

Fig. 2—Process layout.

liquid from the cell flows by gravity to a 20-gal polypropylene collection sump. A 10 gpm magnetic-drive pump transfers water from the sump and returns it to the rinse tanks to close the loop. The flow rate to each leg of the manifold is regulated by ball valves. A schematic drawing of the process is shown in Fig. 2. The system has run constantly, 24 hrs/day, at 250 A and 6 V, since its Oct. 1989 start-up.

Operating Results

After the first two months of operation, a test was conducted to evaluate the system's performance. The rinse water tanks were replenished with clean water and were operated as stagnant dragout tanks, without electrowinning. Over a two-day period, samples were taken and analyzed for cadmium, to determine the rate of metal accumulation in the tanks. Results are shown in Fig. 3. At the end of the two, eight-hour operating days, cadmium had reached a value of 24.7 mg/L. This represented a drag-in rate of cadmium to the rinse tanks of about 4.1 g/hr. The cyanide level in the tanks reached 20.9 mg/L.

On the following day, rinse-water circulation through the electrowinning cell was initiated and power was applied. During a three-day period thereafter, samples were periodically taken and analyzed. During the first day of testing, the rinse water reached a maximum value of only 3.88 mg/L cadmium and 12.5 mg/L (total) cyanide. System operation continued overnight, and by the start of the following day, the cadmium level was less than 1 mg/L. The pattern of results shown in Fig. 4 was similar during the three-day test period.

Cadmium levels were 1 mg/L or less at the start of plating operations in the morning, and increased to less than 6 mg/L during the course of the day. During the 16 hrs of the day that the plating line was not operating, the cadmium levels were reduced to less than 1 mg/L. Because the third day of testing was a Friday, system operation was continued over the weekend, during which time the electroplating bath did not run. At the start of the follow-

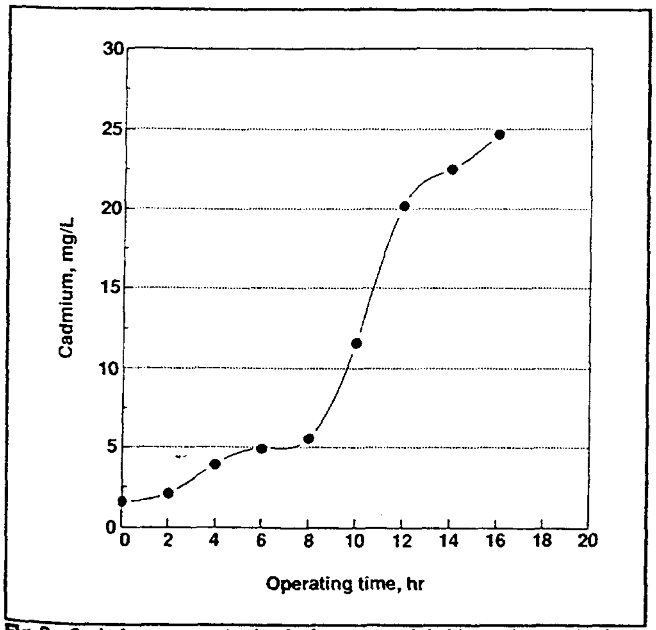

Fig. 3—Cadmium concentration in drag-out tank (without electrowinning).

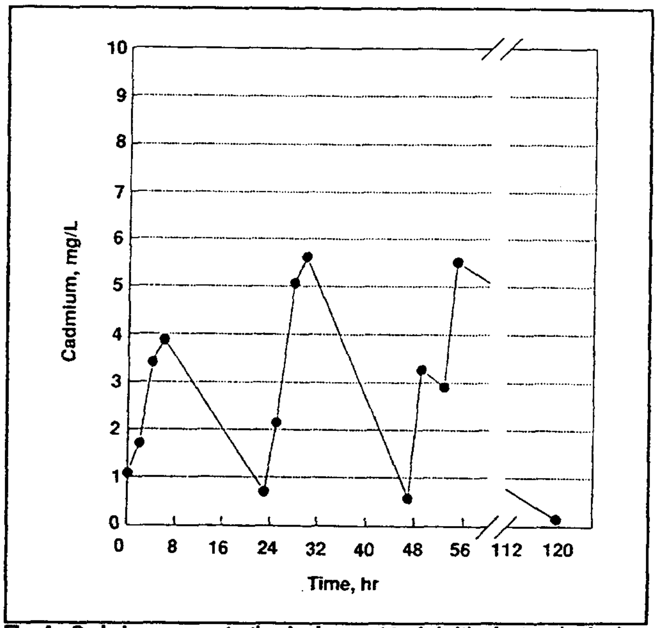

Fig. 4—Cadmium concentration in drag-out tank (with electrowinning).

ing week, the cadmium level was less than 0.2 mg/L. While the rinse water was not clean enough to discharge, it was more than adequate for rinsing plated parts.

The cadmium dragout tanks have been in continuous use and have not been dumped in more than 20 months. The performance of this system far surpassed expectations. Since the system's start-up, there have been no cadmium discharge violations, and for all of 1990, the average level of cadmium in the wastewater effluent was 0.04 mg/L.

The rinse water was allowed to recirculate without electrowinning, to determine the increase of cyanide. In eight hours, the level of cyanide increased from 3.6 mg/L to 20.3 mg/L. We therefore had a concern about closing the loop caused by build-up of cyanide in the rinse water. While it was known that a certain amount of cyanide would be oxidized at the anode, it was found that close to 90 percent was destroyed with the system operating 24 hrs/day. The operating benefits of the system included:

- a reduced metal-loading on the plant wastewater-treatment system;
- a saving in the amount of water used; and
- no cyanide to be destroyed.

Metal-loading on the cathodes was monitored by visual inspection of both the cathodes and rinse water. It was hoped that the cathodes would have a three-month useful life, before they had to be replaced. Operating results, however, indicated that a useful life of six months could be expected.

There was some anxiety about the possibility of autocatalytic oxidation of the cadmium on the cathodes after removal from the solution in the electrolytic cell. Although not completely understood, an exothermic reaction can occur with certain metals, which may be the result of surface morphology. The heat generated could be enough to cause ignition and, therefore, presented a potential fire hazard. In fact, when the cathodes were removed from the cell and stacked to dry, an immediate build-up of heat was detected. But, when the cathodes were arranged so that they did not touch, they could be air-dried without generating heat. An alternative precaution involved soaking the cathodes for a few minutes in a solution of sodium hypochlorite, immediately upon their removal from the cell. When removed from this solution, rinsed with water and allowed to air-dry, the cadmium-laden cathodes exhibited neither short- nor long-term heat build-up, and they could be safely stored for disposal or sale.

Economics

Although operating cost figures are not available at this time, the initial capital cost of the electrowinning cell and related equipment (rectifier, sump pump, etc.), as well as installation costs, were relatively low. Maintenance consists of a visual inspection of the system and the addition of 5 gpd of water, to replace loss from evaporation.

Cathodes are easily removed from the cell. A wing nut at the cathode bus bar, where the cathode wire connector is secured, is first loosened. The cathode is then slid out of the cell and is replaced. The cathode wire is slipped into the cathode bus connector, and the wing nut is tightened. The total time for a complete cathode exchange—including soaking the cathodes in sodium hypochlorite, followed by rinsing—is about one man-hr.

Because the rinse water from the cadmium plating operation is no longer sent to the conventional waste-treatment system, there is a reduction of chemical and labor costs, as well as of the disposal cost for the sludge that would have been generated. There is also a cost savings of 150,000 gpy of water and accompanying sewage fees. The cathodes containing the cadmium are no longer a hazardous waste, and can be sold to a scrap-metal dealer. Most important, however, is the fact that total compliance for cadmium in the waste effluent has been achieved routinely, efficiently and cost-effectively.

As the discharge limit for cadmium becomes more stringent, surface finishers are finding it more difficult and increasingly expensive to comply with regulations. Electrowinning, using high-surface-area cathodes, has been demonstrated to be very effective in recovering cadmium ions, as the metal, from process waters. In addition, cyanide is destroyed during electrowinning. □


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Project Summary

Recovery of Metals from Sludges and Wastewaters

This report presents information on the state-of-the-art of metals recovery technologies to assist in identifying waste-management options for metal-bearing sludges and wastewaters that may be regulated under the Resource Conservation and Recovery Act (RCRA). Only a few of the technologies addressed in this report (e.g., electrowinning, high-temperature metals recovery [HTMR]) are directly applicable to the recovery of metals from wastes; other technologies treat the wastes to a physical form that may be amenable to eventual metals recovery.

Wastewaters can be treated effectively by several methods. Precipitation processes have been widely used to remove arsenic, cadmium, chromium (+3), copper, iron, manganese, nickel, lead, and zinc from metal-bearing wastewaters. For economic reasons, electrowinning is a commercial technology that has normally been restricted to the treatment of wastewaters containing noble metals such as gold and silver.

After appropriate pretreatment, sludges can be effectively treated by HTMR processes. These processes allow for the direct recovery of metals from sludges. The economic feasibility depends on the amount of sludges treated and the amount of metals contained in the sludges. Membrane separation processes such as microfiltration (MF) and ultrafiltration (UF) can be used in combination with chemical treatment for the physical separation of metal sludges. Leaching may be used to extract cadmium, chromium, copper, lead, nickel, and zinc directly from sludges by using various process trains.

This Project Summary was developed by EPA's Risk Reduction Engineering 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

Section 3004 of the Resource Conservation and Recovery Act (RCRA), as amended by the Hazardous and Solid Waste Amendments of 1984, prohibits placing untreated RCRA-regulated hazardous wastes in or on the land. Waste management options are needed to help recyclers comply with these regulations. In the full report, summarized here, we address the following processes that are amenable for recovery of metals from hazardous wastes: chemical precipitation, electrolytic recovery, HTMR, membrane separation, leaching, ion exchange and evaporation. For each of these technologies, the following parameters are summarized: (1) design specifications of applicable processes, (2) waste characteristics affecting performance, (3) pretreatment/posttreatment requirements, (4) available performance data, and (5) availability of the technology and feasibility for treating various hazardous waste categories.

Waste Chacterization

This report covers nine major metal-waste-producing industries:

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(1) metal coatings; (2) smelting and refining of nonferrous metals; (3) paint, ink, and associated products; (4) petroleum refining; (5) iron and steel manufacturing; (6) photographic industry; (7) leather tanning; (8) wood preserving; and (9) battery manufacturing. Waste streams from each of these industries have unique characteristics; however, the wastes also contain common metals, such as aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), silver (Ag), and zinc (Zn).

Table 1 presents the number of metal-waste generators (as of 1983) by Standard Industrial Classification (SIC) code for the major industry categories discussed in the report.

Table 2 indicates the amount and number of generators of metal-bearing wastes by D (wastes which are hazardous because they exhibit a particular hazardous characteristic), F (wastes from non-specific sources), and K (wastes from specific sources) EPA hazardous waste codes. Until very recently, only about half of the industries that generate metal-bearing wastes recovered the metals from wastewaters and sludges.

Table 3 presents brief descriptions of the hazardous wastes generated from the major industry categories included in the report.

Table 1. *Number of Major Metal-Waste Generators, by SIC Code, in 1983*

SIC Code No.	*SIC Description*	*No. of Facilities*
3471	*Plating and surface finishing*	*4,287*
2851	*Paints and allied products*	*2,145*
3479	*Metal coating and allied products*	*2,902*
3714	*Motor vehicle parts and accessories*	*4,151*
2819	*Industrial inorganic chemicals*	*2,183*
3341	*Metals, nonferrous, secondary*	*876*
3400	*Fabricated metal products*	*55,380*
9711	*National security*	*393*
3721	*Motors and generators*	*966*
3900	*Miscellaneous manufacturing industries*	*32,867*
3356	*Metal, nonferrous, rolling, drawing*	*384*
2893	*Printing ink*	*609*
3312	*Blast furnaces, steel mills*	*1,229*
3321	*Foundries, gray iron*	*1,229*
4911	*Electric services*	*2,614*
2869	*Industrial organic chemicals*	*1,160*
2821	*Plastics material*	*1,529*
3662	*Radio and TV communication equipment*	*4,656*
3679	*Electronic components*	*5,392*
3711	*Motor vehicle bodies*	*1,040*
3545	*Machine tool accessories*	*3,432*

Table 2. *Nationwide Metal-Waste-Generation Data by Waste Group*

	Waste Volume, 10^6 gal/yr	*Percent of Total Metals*	*Number of Generators*
D Wastes	*3685*	*46.9*	*3860*
F Wastes	*3920*	*49.9*	*2091*
K Wastes	*219*	*2.8*	*402*

Metals Recovery Technologies

Chemical Precipitation

Precipitation of metal-laden wastewaters involves adding chemicals to alter the physical state of the dissolved or suspended metals and to facilitate their removal through sedimentation. These precipitates may then be processed further for metals recovery. Chemicals used to effect precipitation include: caustic soda, lime, ferrous and sodium sulfide, soda ash, sodium borohydride, and sodium phosphate. Some wastewater constituents, e.g., hexavalent chromium, cannot be effectively precipitated without first chemically reducing the metal to a more favorable form for precipitation. Reducing agents typically used by industry include sulfur dioxide, sodium bisulfite, sodium metabisulfite, and ferrous sulfate. Coagulation chemicals may be needed to enhance settling times of the precipitated metal particles. Examples of coagulants currently used by industry include lime, alum, and synthetic polyelectrolytes.

Chemical precipitation is commonly used to treat metal-bearing wastewaters from electroplating, pigment manufacture, the photographic industry, leather tanning, wood preserving, the electronics industry, battery manufacture, and nonferrous metal production. Approximately 75% of all electroplating facilities use precipitation in the treatment of their wastewaters. The process is several decades old, and chemical feed reagents are being improved to yield better metal removals from the aqueous phase.

Specific waste characteristics that affect the performance of chemical precipitation systems include (1) the concentration and type of metals, (2) the concentration of total dissolved solids, (3) the concentration of complexing agents, and (4) the concentration of oil and grease.

Pretreatment of wastewaters before metals precipitation can involve segregation, removal of large solids, flow equalization, cyanide destruction (if applicable), chrome reduction, oil separation, neutralization, and/or waste treatment of the individual process streams.

Sand filtration is a common post-precipitation/sedimentation effluent treatment technique. If concentrations in the effluent do not meet discharge standards, additional metal treatment technologies (e.g., ion exchange, reverse osmosis) may be needed.

Electrolytic Recovery

Electrolytic processes are used extensively to recover metals from industrial wastewaters. The electrolytic cell is the basic device used in electrolytic recovery operations. The cell consists of an anode and a cathode immersed in an electrolyte. When current is applied, dissolved metals in the electrolyte are reduced and deposited on the cathode. Because the metal(s) removed from solution can be reused, the technology, termed "electrowinning," is con-

Table 3. Metal-Bearing Hazardous Wastes From Major Industry Categories

EPA Hazardous Waste No.	Hazardous Waste Description	Listed Constituent(s)
F006	Wastewater treatment sludges from electroplating operations except the following: (1) sulfuric acid anodizing of aluminum; (2) tin plating on carbon steel; (3) zinc plating (segregated basis) on carbon steel; (4) aluminum or zinc-aluminum plating on carbon steel; (5) cleaning/stripping associated with tin, zinc, and aluminum plating on carbon steel; and (6) chemical etching and milling of aluminum.	Cadmium, hexavalent chromium, nickel, cyanide (complexed)
F007	Spent cyanide plating bath solutions from electroplating operations.	Cyanide/salts
F008	Plating sludges from the bottom of plating baths from electroplating operations where cyanides are used in the process.	Cyanide/salts
F009	Spent stripping and cleaning bath solutions from electroplating operations where cyanides are used in the process.	Cyanide/salts
F019	Wastewater treatment sludges from the chemical conversion coating of aluminum.	Cadmium, hexavalent chromium, cyanide (complexed)
K002	Wastewater treatment sludge from the production of chrome yellow and orange pigments.	Hexavalent chromium, lead
K003	Wastewater treatment sludge from the production of molybdate orange pigments.	Hexavalent chromium, lead
K004	Wastewater treatment sludge from the production of zinc yellow pigments.	Hexavalent chromium
K005	Wastewater treatment sludge from the production of chrome green pigments.	Hexavalent chromium, lead
K006	Wastewater treatment sludge from the production of chrome oxide green pigments (anhydrous and hydrated).	Hexavalent chromium
K007	Wastewater treatment sludge from the production of iron blue pigments.	Cyanide (complex), hexavalent chromium
K008	Oven residue from the production of chrome oxide green pigments.	Hexavalent chromium
K048	Dissolved air flotation (DAF) float from the petroleum refining industry.	Hexavalent chromium, lead
K049	Slop oil emulsion solids from the petroleum refining industry.	Hexavalent chromium, lead
K050	Heat exchanger bundle-cleaning sludge from the petroleum refining industry.	Hexavalent chromium
K051	API separator sludge from the petroleum refining industry.	Hexavalent chromium, lead
K052	Tank bottoms (leaded) from the petroleum refining industry.	Lead
K060	Ammonia still lime sludge from coking operations.	Arsenic
K061	Emission control dust/sludge from the primary production of steel in electric furnaces.	Hexavalent chromium, lead, cadmium
K062	Spent pickle liquor generated by steel-finishing operations of facilities within the iron and steel industry.	Hexavalent chromium, lead
K064	Acid plant blowdown slurry/sludge resulting from the thickening of blowdown slurry from primary copper production.	Lead, cadmium

(continued on p.4)

sidered a recovery process. If a membrane is used between the cathode and the anode for the selective transport of some ions, the process is called electrodialysis. Electrowinning is most effective for recovery of noble metals such as gold and silver. These metals have high electrode potentials and are easily reduced and deposited on the cathode. Metals such as cadmium, copper, chromium, lead, tin, and zinc can be removed, but a greater amount of current is required. Electrowinning is very effective for plating solutions used in printed circuit boards; these contain chelated metals that are difficult to remove by other means.

Electrowinning of metals is a particularly attractive process because it completely eliminates the generation of a metal-bearing sludge. Its applicability, however, is limited to waste streams containing metals in solution such as cadmium, copper, chromium, gold, lead, silver, tin, or zinc. For dilute solutions, electrowinning can be difficult because of the low mass-transfer rates; however, mass transfer rates can be enhanced both by agitating the solution and by increasing the effective surface area of the cathode.

The principal area of application of electrodialysis is the recovery of metals from electroplating bath rinse waters.

In many cases, the wastewater must be filtered before it is fed through the electrolytic reactor. Adjustment of pH is a necessary pretreatment measure because the waste pH affects metal speciation.

Metal recoveries of up to 98% from plating rinse waters have been demonstrated with the use of high-surface area (HSA) electrodes.

Several vendors are currently manufacturing electrodialysis systems for treatment of wastes from gold, chromium, silver, and zinc cyanide plating operations and from nickel plating operations. Other successful electrodialysis applications include recovery of metals from tin and trivalent chromium baths and the recovery of chromic acid and sulfuric acid from spent brass etchants. Electrowinning and electrodialysis systems have both been used extensively in industrial applications.

High-Temperature Metals Recovery (HTMR)

Several types of HTMR processes are currently available or under development for the recovery of metals from sludges generated either directly by industrial processes or from the treatment of industrial wastewaters. These HTMR processes may involve plasma-based or high-temperature fluid-wall reactor systems (which use elec-

(continued on p.4)

Table 3. (Continued)

EPA Hazardous Waste No.	*Hazardous Waste Description*	*Listed Constituent(s)*
K065	*Surface impoundment solids contained in and dredged from surface impoundments at primary lead smelting facilities.*	*Lead, cadmium*
K066	*Sludge from treatment of process wastewater and/or acid plant blowdown from primary zinc production.*	*Lead, cadmium*
K069	*Emission control dust/sludge from secondary lead smelting.*	*Hexavalent chromium, lead, cadmium*
K086	*Solvent washes and sludges, caustic washes, and sludges from cleaning tubs and equipment used in the formulation of ink from pigments, driers, soaps, and stabilizers containing chromium and lead.*	*Lead, hexavalent chromium*
K090	*Emission control dust or sludge from ferro chromium silicon production.*	*Chromium*
K100	*Waste leaching solution from acid leaching of emission control dust/sludge from secondary lead smelting.*	*Hexavalent chromium, lead, cadmium*
D004	*Characteristic waste based on concentrations.*	*Arsenic*
D006	*Characteristic waste based on concentrations.*	*Cadmium*
D007	*Characteristic waste based on concentrations.*	*Chromium*
D008	*Characteristic waste based on concentrations.*	*Lead*
D009	*Characteristic waste based on concentrations.*	*Mercury*
D011	*Characteristic waste based on concentrations.*	*Silver*

tricity as the energy source) or coal/natural- gas-based technologies.

HTMR processes are applicable only for the processing of sludges, not for wastewaters. One significant advantage of the HTMR processes is that other toxic constituents in the wastes, such as complexed cyanides/organics, would also be destroyed at the high temperatures (>1100°C) prevailing in the furnaces.

Important waste characteristics affecting the performance of HTMR processes include: (1) concentrations of undesirable volatile metals, (2) boiling points of the metal constituents, and (3) thermal conductivity of the waste. Pretreatment requirements for HTMR processes vary with the type of process. This may include operations such as drying of feed sludges or pelletizing with special additives. The crude metallic oxides produced in certain HTMR processes must be further treated for separation and recovery of metals. Gases from the high temperature furnaces must be treated before atmospheric release.

The INMETCO Plant in Ellwood City, PA (which utilizes a rotary hearth/electric furnace) and the Horsehead Waelz Kiln in Palmerton, PA, have processed hazardous wastes (sludges) under an Interim Permit status. The INMETCO Plant has processed the following waste codes: F006, K061, K062, D006, D007, and D008. The Horsehead Waelz kiln has processed F006, F019, K061, D006, and D008.

Horsehead has two operating Waelz plants in the United States—one at Palmerton, PA, and one at Calumet City, IL. The Palmerton plant has three Waelz kilns with a total capacity of 270,000 tons/yr; the Calumet plant has one kiln with a capacity of 80,000 tons/yr. The INMETCO plant is capable of treating 50,000 tons of wastes per year. Both of the Horsehead Waelz plants as well as the INMETCO plant are operated primarily to treat steelmaking electric arc furnace dust (K061); however, as previously mentioned, they are capable of treating other sludges. A third Horsehead Waelz plant with a capacity of 60,000 tons/yr is planned for Rockwood, TN.

Membrane Separation

The commercially available membrane processes for removal of metals from industrial wastewaters are microfiltration, ultrafiltration, reverse osmosis, and electrodialysis. Microfiltration (MF) and ultrafiltration (UF) are used in combination with chemical treatment for the physical separation of metal sludges. Reverse osmosis (RO) and electrodialysis (ED) are used to recover plating compounds from rinse water and to enable reuse of rinse waters.

MF and UF membranes cannot be applied directly to recover metals present as dissolved solids in wastewaters. UF, however, can be used as a pretreatment method for RO units to avoid fouling of the RO membranes.

When applied to heavy metal wastes with appropriate pretreatment chemistry, the metal content of the effluent can be extremely low. Each application requires treatability studies to integrate the chemical pretreatment and the MF/UF membrane system.

If oil and grease are present, additional pretreatment of the waste stream will be required. Well-run precipitation/UF and MF systems can achieve metal removals greater than 99%. Over 150 full-scale industrial systems, ranging in size up to 400 gal/min, have been installed in the electroplating, printed circuit board manufacturing, battery manufacturing, and photographic processing industries.

RO systems consist of several modules connected in series, or parallel, or a combination of both. The application of RO to the treatment of metal-containing wastes is limited by the pH range in which the membrane can operate. Cellulose acetate membranes cannot be used on waste streams where the pH is much above 7. The amide or polysulfone membranes, however, have a pH range of 1 to 12. Collodial matter, low-solubility salts, and dissolved organics can seriously inhibit the effectiveness of RO. Pretreatment steps such as pH adjustment, carbon adsorption, chemical precipitation, or filtration are therefore recommended to ensure extended service life of RO systems. Systems are being used commercially to recover brass, hexavalent chromium, copper, nickel, and zinc from metal-finishing solutions.

Leaching

Leaching is a process in which a solid material is contacted with a liquid solvent for selectively dissolving some components of the solid into the liquid phase. Leaching can sometimes be used to extract various metals from sludges. The goals of this process are: (1) to dissolve the metals in a liquid phase to produce a solution that can be reused directly in a process or from which the metal can be recovered by other techniques, such as electrowinning; and (2) to produce a secondary sludge that is nonhazardous or from which additional metals can be reclaimed by other processes. Several leaching agents can potentially be used, including sulfuric acid, ferric sulfate, ammonia or ammonium carbonate, hydrochloric acid, sulfur dioxide, ferric chloride, nitric acid, or a caustic solution. Selection of a suitable solvent and unit process depends on the chemical state and physical environment of the metals.

Sludges that contain only one metal often can be sent directly to a refiner for reclamation; however, in some operations (e.g., electroplating), all metals are precipitated from solution in the same wastewater treatment plant, usually as hydroxides. A process train with numerous unit operations, therefore, is necessary to separate each metal. Complete recovery of the metals typically includes electrowinning of the leachate.

At the Recontek waste recycling facility in Newman, IL, zinc-bearing solutions are leached with alkaline solutions, whereas non-zinc sludges are treated with acidic solutions. Zinc-bearing sludges are digested at approximately 80°C with sodium hydroxide for a sufficient period of time, cooled, and filtered. The filtrate is processed in a zinc cementation tank to precipitate metals more electronegative than zinc (e.g., lead, cadmium) and then pumped to a zinc electrowinning system. The non-zinc sludge waste from the digester (primarily copper and nickel) is digested with sulfuric acid and filtered to produce a residue containing precious metals (e.g., gold, silver). The filtrate is then sent to the copper electrowinning system for production of copper cathodes.

Ion Exchange

Ion exchange is a treatment technology applicable to (1) metals in wastewaters where the metals are present as soluble ionic species (e.g., Cr^{+3} and CrO_4^{-2}); (2) nonmetallic anions such as halides, sulfates, nitrates, and cyanides; and (3) water-soluble, ionic organic compounds including (a) acids such as carboxylics, sulfonics, and some phenols, at a pH sufficiently alkaline to yield ionic species, (b) amines, when the solution acidity is sufficiently acid to form the corresponding acid salt, and (c) quaternary amines and aklylsulfates.

Ion exchange is a reversible chemical reaction in which an ion from solution is substituted for a similarly charged ion attached to an immobile solid particle. The use of this process is practical only on wastewaters and sludge leachates. In conventional ion exchange, metal ions from dilute wastewater solutions are exchanged for ions electrostatically held on the surface of the exchange medium. Ion exchange systems have proven to be effective in the removal of barium, cadmium, chromium (VI), copper, lead, mercury, nickel, selenium, silver, uranium, and zinc.

Evaporation

Evaporation is a simplified recovery system for the separation of substances based on volatility differences. Although the technology is established, recent advancements have made mechanical evaporation a more viable cost-efficient method for metals recovery. The four basic types of evaporators used in the electroplating industry today are rising-film, flash, submerged-tube, and atmospheric.

Conclusions

Only a few of the technologies addressed in this report (e.g., electrowinning, HTMR) are directly applicable to recovering metals from wastes; other technologies treat the wastes to a physical form that may be amenable to eventual metals recovery.

Commercial waste recycling facilities render services that are important if metals are to be recovered as opposed to being treated and disposed. Technologies used at the metals recovery facilities include chemical precipitation, leaching, electrowinning, and evaporation.

Current information on metals recovery technologies show that combinations of technologies may often be required to recover metals from wastewaters and sludges. Additional studies are needed to determine the specific combinations of methods that will most effectively recover metals from different types of wastes.

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This Project Summary was prepared by the staff of IT Corporation, Cincinnati, OH 45246.

Ronald J. Turner *is the EPA Work Assignment Manager (see below).*

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Electrolytic Metal Recovery **Comes of Age**

By C A Bennati and W J McLay

Electrolytic metal recovery is one of a growing number of tools available to the metal finisher for recovering dragout from plating tanks. Stringent restrictions on the disposal of finishing wastes, along with increasing costs, combine to make recovery of dragout a very attractive proposition.

The most commonly used technologies are evaporation, reverse osmosis, electrodialysis, ion exchange, and electrolytic recovery. Each of these has its niche in the field and two or more sometimes are combined in practice. For example, ion exchange can be used to concentrate a metal ion from a very dilute rinse stream and the metal then recovered electrolytically from the concentrated regenerant.

The first four of the above-named recovery methods are concentrative in nature. Basically, they remove water and varying amounts of impurities from the dragout and produce a concentrate available for return to the plating bath. However, two problems are inherent in concentrative methods: (1) the growth of bath volume and (2) solution contamination. These are the consequences when the efficiency of a soluble anode is higher than that of the cathode. The resultant metal buildup is usually more than compensated for by dragout. But when dragout return is employed, the increase in metal concentration can become a significant problem. Plating baths are normally purged of trace impurities by dragout; however, when dragout is artificially reduced, trace impurities can increase to significant levels. The buildup of impurities can be controlled to some extent by incorporating purification steps in the recovery system and by using high-purity water for rinses and bath makeup.

Electrolytic recovery differs from other methods in that it is selective, removing only the metal and thus decoupling the production and recovery processes. Because electrolytic metal recovery doesn't concentrate the dragout and return it to the bath, a properly functioning

Metals can be salvaged from dragout solutions and plated onto sheets for recovery purposes.

ı will continue to give satisfactory ıance. Electrolytic techniques re- he most valuable constituent of the t—the metal—which is also the nent that generates sludge.

tive vs. Concentrative

hoice between electrolytic metal ry and one of the concentrative ɔs is fundamentally an economic ıe metal is the most valuable con- t of the dragout from many plating whereas the cost of replacing the ɔomponents is not high enough to ıt the cost of recovering them. In instances, the metal is relatively ːnsive and recovery of the entire ɹt stream makes more economic . Capital expenditures and operat- sts for the recovery equipment must nsidered along with the recovery of the dragout. The complexity of quipment and the skill and time ɘd of the operator also are important s in the decision.

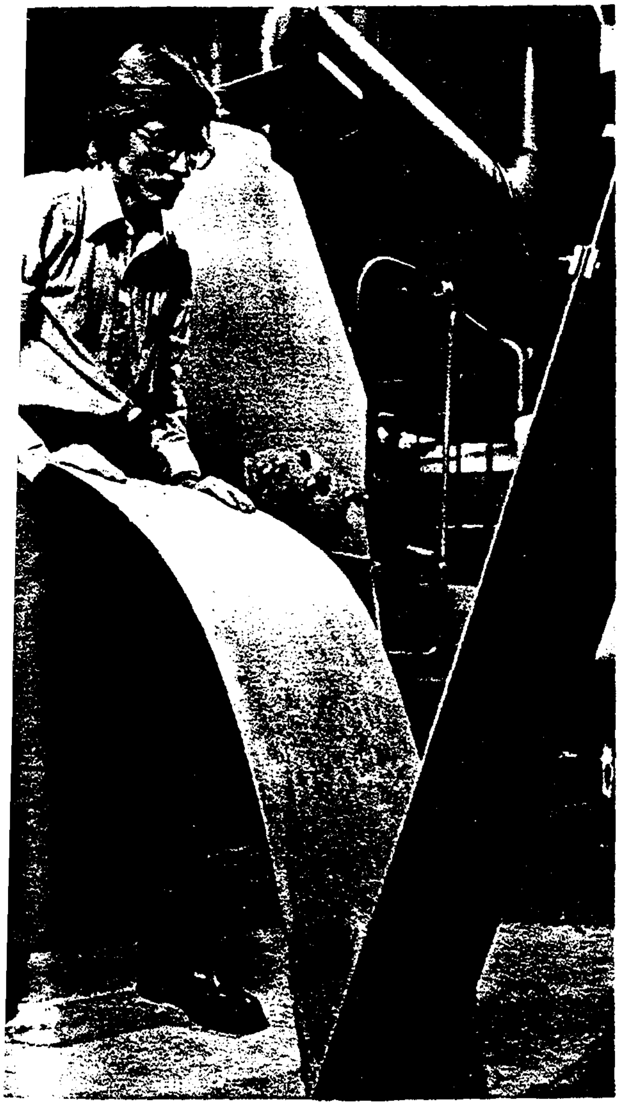
ɔtrolytic metal recovery is not a new ɔlogy. The mining industry has used olytic means of refining ores for many years, and copper has been recovered from pickling solutions for a significant period of time. In recent years, there has been considerable and increasing interest in the use of electrolysis for the recovery of metals from dilute rinsewater.

Dilute rinsewater poses a special problem in electroplating. Cathode polarization, a concern for all platers, is much more acute when the solution under consideration is very dilute. In general, as plating proceeds, the area of solution next to the cathode becomes depleted in metal ions, forming a polarized layer. The ions must diffuse into and across this layer before they can be plated out. There are fewer ions in dilute solutions, so the rate of diffusion into the polarized layer is much lower, and the layer becomes thicker and more depleted. Severe cathode polarization can lead to poor-quality deposits: the formation of dark, powdery, burned areas and trees that can grow across to the anodes and short-out the cell. The efficiency at the cathode can be greatly reduced because the electricity is used to decompose water and form hydrogen gas instead of plating out the metal. There are a number of ways that the problems associated with cathode polarization can be minimized. These include adopting a lower current density, adjusting the chemistry and temperature of the solution, and providing for agitation.

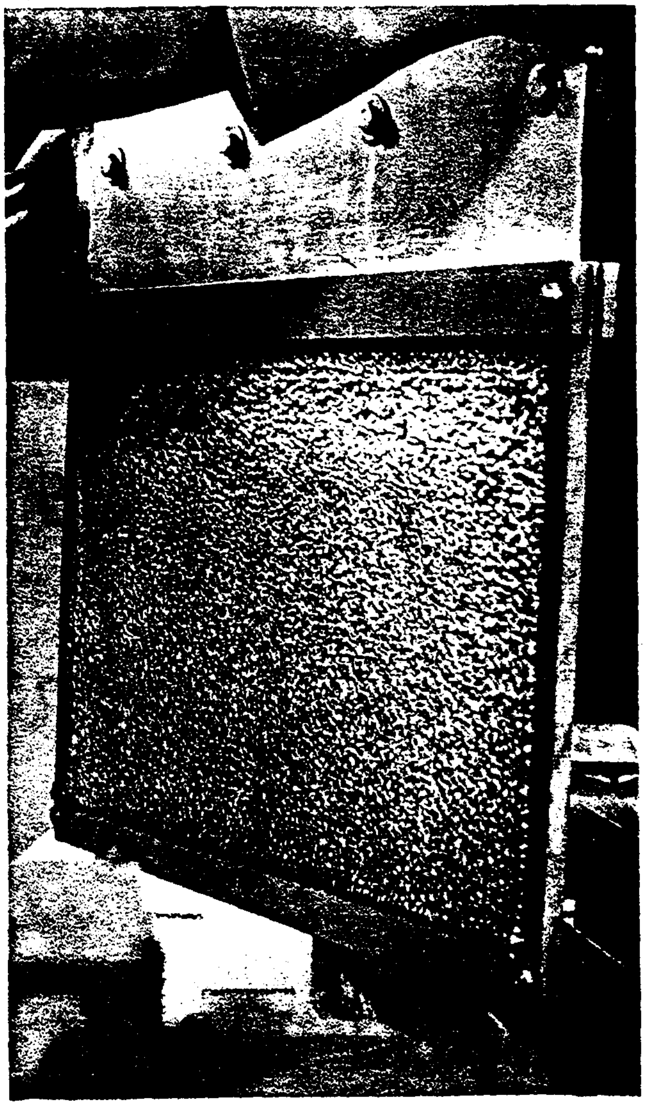
Overcoming Polarization

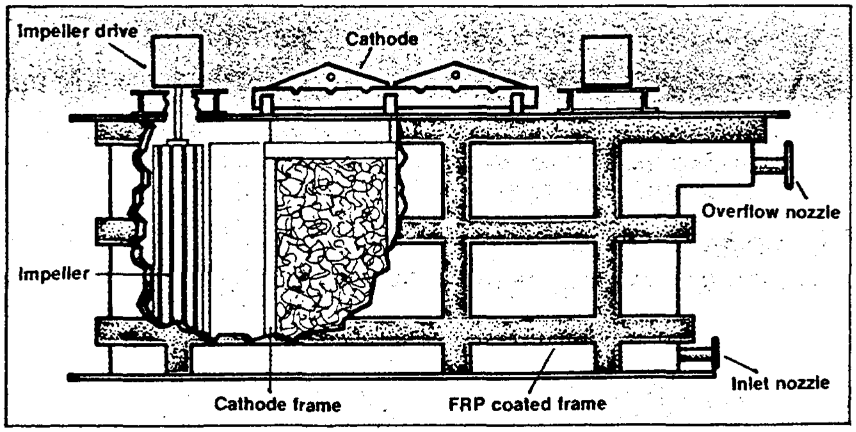
When plating is carried out at low current density, the polarized layer is relatively thin and metal ions can diffuse across it at a low enough rate to minimize hydrogen formation. For a given amount of metal, the larger the cathode surface area the lower the current density necessary to plate out the metal. One way of increasing the cathode surface area is to use a large tank with many rows of cathodes and anodes. This approach is cumbersome at best, and dozens of parts would be needed for recovery from low-concentration rinsewater. A more practical way to achieve a large surface area, in a small volume, is by using stainless-steel wool or porous carbon as a cathode. There are companies working on both of these approaches. It is easy to remove the metal from dilute solutions in this

peels copper from cathode. Up to 99.5% pure metal can be recovered agout solutions and either sold or reused as soluble anode



Stainless-steel cathode in frame has edge guards to aid in removing metal deposit





Rapid agitation with impeller system is a key to good electrolytic recovery with copper sulfate, gold cyanide, silver cyanide, tin-lead fluoborate and many other solutions.

manner, but the metal can't be recovered until it is dissolved from all cathode surfaces in a concentrated solution, then plated out by conventional methods.

The characteristics of a plating solution can be chemically altered in a number of ways. The concentration of metal ions in solution can be increased and chemical additions can be made. For example, electrolytes can be added to improve solution conductivity and grain refiners to improve deposit quality. In addition, when the temperature of a plating bath is elevated, the metal ions in solution become much more mobile and can diffuse far more rapidly through the polarized layer.

Every plater knows that if he agitates his solution or cathodes he can either plate at a higher current density or lower the concentration of metal in the bath. Metal has been electrolytically recovered from wastewater containing as little as 100 mg/L of metal with the aid of rapidly rotating cathodes.

Many of the potentially favorable adjustments that can be made to an electrolytic recovery system are impractical for a single-pass system, but can be taken advantage of if a closed loop is utilized. The first rinse after the plating tank can be isolated and continually recirculated through an electrolytic recovery cell. Since the basic recovery solution is being reused, it can be heated, the concentration of metal ions can be allowed to build up to a reasonable level, and other adjustments can be made to the bath chemistry.

Metal Sheets

One electrolytic system utilizing rapid agitation of the recovery solution has been used to reclaim up to 99.5 percent pure metal from dragout solutions. The solution is recirculated past the electrodes by impellers located at each end of the cathode compartment. Impeller design has been optimized to provide a uniform flow of recovery solution past the surface of the cathodes. The reusable stainless-steel cathodes are manufactured with edge guards to aid in removing the metal deposit. The metal produced with this electrolytic recovery cell is of high quality and can be either reused as the soluble anode in the plating tank or sold. The system basically is simple to operate, and once the startup period is over, requires a minimum of operator time.

Although recovery can be achieved from solutions containing metal concentrations as low as 30 mg/L, the range of 3 to 6 g/L is usually recommended for economic reasons. When recovering precious metals such as gold and silver, it makes sense to use the extra capacity necessary to maintain the metal concentration on the order of 30 to 200 mg/L in the recovery rinse. Furthermore, when an electrolytic cell is used to recover metal from a spent plating bath, the initial metal concentration is high enough that it is often economically feasible to reduce the concentration to levels below 1 mg/L.

Commercial Applications

The electrolytic metal recovery system has been successfully operated on copper sulfate, gold cyanide, silver cyanide, tin-lead fluoborate, and many other solutions. Moreover, laboratory work recently was completed on the recovery of copper from a cyanide solution used in high-speed barrel plating. Because of the large difference in cathode and anode plating efficiencies and the large volume of dragout associated with barrel plating, a growth in the volume of the plating bath was anticipated if dragout return were practiced, and it was felt that an electrolytic cell placed on the rinse immediately following the plating bath would be a useful adjunct. During a five-week plating test, dragout to the rinse was simulated by periodically adding small quantities of used copper cyanide plating bath to the solution in the recovery cell. The copper concentration was maintained at an average of 5 g/L, and 1,365 g of copper was recovered during 852 A-hr of plating. The cathode efficiency was 67 percent, and 82 percent of the cyanide added to the system was destroyed.

One of the most common applications of the electrolytic system is the recovery of copper from sulfuric acid solutions. At a GTE/Automatic Electric facility, copper is being recovered from the rinse following a pre-etch solution. Data were collected over a five-week period during which 536 lb (243 kg) of copper was recovered. The average copper concentration was approximately 5 g/L and the cathode efficiency 90 percent.

The electrolytic cell also can be used to recover metal from crystals and sludge, and to regenerate process solutions. Data were collected from the same GTE facility utilizing an electrolytic cell to regenerate a sulfuric acid leach solution. The copper concentration in the leach was maintained at an average of 2 g/L, and 86 lb of copper was recovered in a week at a cathode efficiency of 96 percent.

Summary

Electrolytic metal recovery is one of the most versatile and valuable tools available to the plater. It has minimal impact on the production line when used for the recovery of dragout and can be applied from other areas of the plating shop.

Electrolytic recovery is particularly suited to metals such as gold, silver, copper and tin, whose values are higher than those of other bath components. When the costs of capital equipment and operation are considered, payback periods for the electrolytic systems are generally less than two years. For metals such as copper and tin, the system will pay for itself in three to 21 months by virtue of recovered metal values and reduced costs for chemical treatment and sludge hauling. A system recovering gold can pay for itself in less than a week. ☐

McLay

About the Authors

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Reverse Osmosis
in

Pollution Prevention and Control Technology for Plating Operations

George C. Cushnie Jr.
CAI Engineering

A Project Sponsored by the
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National Association of Metal Finishers

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3.7 REVERSE OSMOSIS

3.7.1 Overview

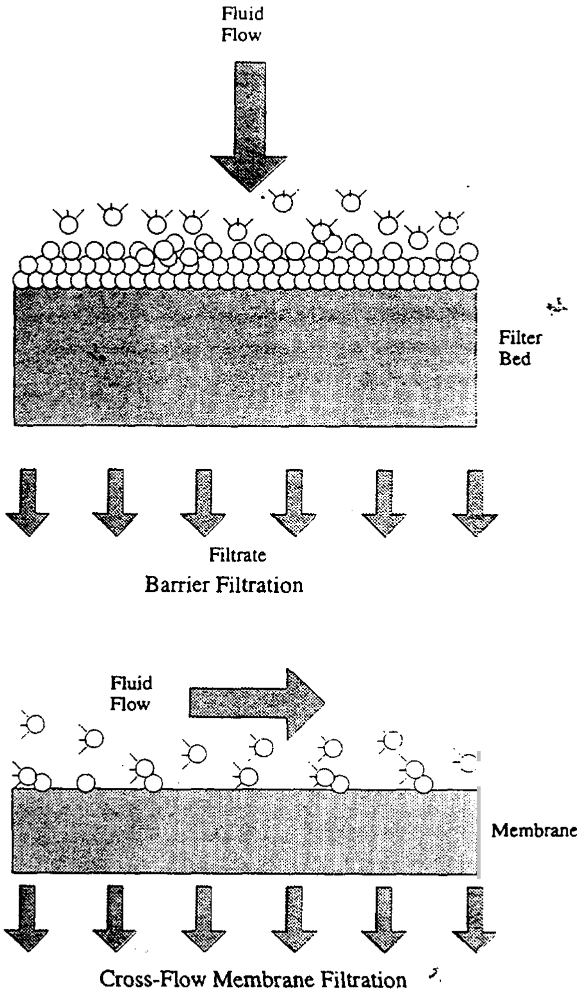
Reverse osmosis (RO) is a separation process that has been employed in the metal finishing industry to purify raw water (e.g., city water) before use as rinse water, recover plating chemicals from rinse water, and polish wastewater treatment effluents (usually for reuse as rinse water). Of particular interest in this section of the report is the application of RO for chemical recovery, however; end-of-pipe applications are also covered. Use of this technology as a raw water treatment technology is not covered in this report.

As a recovery technology, RO has been applied to a range of processes, including: brass, chromium, copper, nickel, tin and zinc plating solutions (ref. 269, 348), with nickel recovery being the most frequent and successful (ref. 39). Of the 318 plating shops responding to the Users Survey, only six applications of RO chemical recovery were identified. The survey also included one application for end-of-pipe treatment and several applications of raw water purification. The infrequent use of RO for chemical recovery may be due to the limited number of baths to which it has been successfully applied and the availability of competing technologies (especially for nickel plating). Further, one of the competing technologies frequently used for nickel recovery is atmospheric evaporation, which has a very low capital cost.

Reverse osmosis is often referred to as a "crossflow filtration" process. This term, which also describes most ultrafiltration and microfiltration equipment used by the metal finishing industry, distinguishes these processes from surface barrier filtration, which operates in dead-end flow. As shown in Exhibit 3-53, in dead-end filtration, all of the feed solution is forced through the membrane by an applied pressure. With crossflow filtration, the fluid to be filtered is pumped across the membrane, parallel to its surface. Because the feed and concentrate of RO flows parallel to the membrane instead of perpendicular to it (i.e., dead-end flow), the process is termed crossflow. The pressure required to drive the process is determined by the specific nature of the feed solution and the membrane pore size (ref. 380, Osmonics file).

There are several key differences between RO and ultra-

Exhibit 3-53. Diagram of Barrier vs Cross-Flow Filtration



filtration/microfiltration: (1) only RO has the ability to concentrate dissolved salts (e.g., plating chemicals); (2) RO cannot tolerate significant concentrations of suspended solids, whereas the other two processes can, especially microfiltration; and (3) RO operates at higher pressures and usually requires a heavy gage stainless steel housing, whereas the other two lower pressure processes can be housed in plastic or lightweight stainless steel. It should be noted, that whereas RO is a distinctly unique filtration process, ultrafiltration and microfiltration are similar to one another and have overlapping definitions (ref. 380). Microfiltration, which has the largest pore size of the three technologies, is discussed in Section 4, as a method of alkaline cleaner maintenance. Also, both microfiltration and ultrafiltration are discussed in Section 6, as end-of-pipe polishing technologies. Ultrafiltration is also used by several survey respondents for the recovery of electrocoat (paint), an application not covered by this project. It is also used in the machining industry for the recovery of cutting oils.

RO theory is based on two physical processes: osmosis and ionic repulsion. Osmosis is related to diffusion, which describes the tendency of molecules in solution to move about until they are uniformly distributed. Osmosis is the tendency for diffusion to take place across a semipermeable membrane. It occurs when a water permeable membrane separates two solutions of different concentrations of dissolved solids. Pure water will flow into the concentrated solution until an equilibrium energy state is achieved. By applying pressure to the more concentrated solution, the normal osmotic flow is reversed and pure water is forced through the semipermeable membrane into the less concentrated solution. Suspended solids are blocked by mechanical exclusion and dissolved solids are chemically repulsed by the membrane surface. Multi-charged ions are rejected at rates exceeding 99 percent and single-charged ions have rejection rates in the range of 90 to 96 percent. RO will also reject neutral solutes, although no general efficiency data are available. Besides ionic charge, rejection efficiency is also affected by the concentration gradient. As the concentration gradient increases, the rejection efficiency decreases. The flow of water through an RO membrane (flux) is determined by the pressure differential across the membrane. Higher pressure differentials generally result in higher flow rates.

The RO process is designed to operate continuously. The RO membrane is enclosed in a pressure vessel and the feed stream is pumped through the vessel under pressure, 400 to 1,000 psig, where it is separated into a clean water permeate stream and a concentrated chemical stream by selective permeation. Three important parameters describe the performance of the RO process: recovery, flux, and rejection.

Recovery is defined as the percentage of the feed that is converted to permeate and it is usually expressed as percent. Flux is the rate at which the permeate passes through the membrane per unit of membrane surface area. Rejection is the ability of the membrane to restrict the passage of dissolved salts into the permeate, and is related to particular salt species (ref. 39).

There are different types of RO membranes used (tubular, spiral wound and hollow fiber), the selection of which depends mostly on the applications and in particular the plating bath chemistry. The most common RO membranes are the hollow fiber and spiral wound configurations.

Most reverse osmosis systems are designed with a single filtration stage operating below 700 psig. With a single stage system operating in this pressure range, the practical limit for concentrating plating chemicals in rinse waters is 15 to 20 g/l. Because this concentration is below that of most plating baths, a "solution volume" problem is sometimes created with an RO recovery application, in that there is insufficient head-room in the process tank for the return of the recovered chemical solution. This problem occurs especially with ambient to low temperature baths, where the surface evaporation rate is low. This condition limits the direct reuse of the RO concentrate stream in the plating tank. An evaporator can be used to further concentrate the solution or to supplement tank surface evaporation. However, the added capital and operating costs of an evaporator often make this approach less attractive than using an alternative recovery method.

Newer reverse osmosis technology includes multiple stage systems and higher operating pressures (800 to 1,000 psig). With the multiple stage design, the concentrate stream from the first stage is passed through a second stage to further concentrate the chemicals. This permits the direct reuse of some solutions that could not be directly recovered with the less effective single pass units.

The key attributes of RO as a recovery technology are: (1) it is an ambient temperature, low energy process; (2) it generates a permeate stream that is usually of sufficient quality that it can be reused for rinse water; and (3) for some applications, it has relatively low capital and operating costs as compared to other recovery technologies. The negative aspects of this technology are: (1) RO membranes can be fouled by precipitation products and/or suspended solids; (2) membranes have a fairly limited life-span; (3) this technology does not sufficiently concentrate the chemicals for direct return in some applications; and (4) similar to most other recovery technologies, RO returns both essential plating chemicals and unwanted impurities to the bath, unless some post-treatment is performed.

3.7.2 Development and Commercialization

Reverse osmosis is a relatively mature technology, having the distinction of being the first membrane-based separation technology to be widely commercialized (ref. 380). Much of the early developmental work for this technology took place in the late 1950's and the 1960's and focused on desalination for drinking water supplies. This work was sponsored by the U.S. Department of the Interior, Office of Saline Water (ref. 380). The spiral-wound element, which is the building block of modern recovery units was developed in 1963 (ref. 380). The first large industrial application of RO occurred in 1970 when a 100,000 gpd system was placed into operation at Texas Instruments' (TI) electronic manufacturing facility in Dallas, TX. The application at TI was the purification of municipal water for use in manufacturing. Now, essentially all electronics plants in the U.S. use RO for this purpose (ref. 65). The first RO metal finishing application for chemical recovery that was identified in the literature occurred in 1974, which was applied to copper cyanide (ref. 382). Other applications during the 1970's and 1980's included: bright nickel, Watts nickel, acid copper, acid zinc, and end-of-pipe effluent polishing. In 1976 the USEPA sponsored a series of experiments to evaluate the application of RO to plating chemical recovery. These experiments evaluated the performance and life-spans of membranes that were commercially available at the time (ref. 382).

Metal finishing applications of RO are very limited in comparison to those of desalination and other industrial applications. Worldwide, there are approximately 1,500 RO desalinating plants with a total capacity of more than 750 million gallons per day. Estimated RO membrane sales were approximately $118 million in 1988. Of these sales, Osmonics, one of the largest U.S. manufacturer's of RO equipment for the plating industry, accounted for $3 million (ref. 380). Osmonic's sales figures include not only the metal finishing industry applications, but also a range of other industries, including: food, beverage, dairy, chemical processing, and textile manufacturing. There are approximately 20 companies that manufacture and/or sell RO and ultrafiltration equipment to the U.S. plating industry (ref. 421). Of these companies, five responded to the NCMS vendors survey, but only four provided data on the number of systems they have sold within the metal finishing industry. The total number of systems sold by these four companies is 15, with nine units applied to chemical recovery, five applied to reuse of wastewater and one applied to raw water treatment. These numbers significantly understate the total number of RO units in use in the metal finishing industry because two major manufacturers (Osmonics and Ionics) did not provide data.

3.7.3 Applications and Restrictions

Exhibit 3-54 shows an example of applying reverse osmosis as a chemical recovery technology. In this example, nickel salts are recovered from rinse water and returned to the bath. A three stage counterflow rinse system is used in order to concentrate and reduce the flow rate of the feed to the RO unit. The 100 gph feed rate is typical for this application. The feed is pumped (high pressure feed pump) through a cartridge filter (typically 5 micron) and through the RO system. The reject passes through a carbon filter to remove bath impurities and is returned to the plating bath. In this example, the surface evaporation of the bath is sufficient to create the necessary headroom. The permeate is returned to the counterflow rinse system.

The primary plating chemical recovery application for RO is nickel plating. This includes Watts nickel and bright nickel plating (ref. 382). A wide range of other successful applications are identified in the literature (mainly articles written by RO equipment manufacturers). Some of the more frequently discussed applications include: brass cyanide, cadmium cyanide, copper cyanide, non-cyanide alkaline zinc, and zinc cyanide (ref. 156, 157, 263). From the Users Survey, there were only two successful application of RO for chemical recovery. These involved recovery of nickel acetate seal and acid zinc drag-out (PS 010, 230). Another shop successfully operates an RO unit on a cadmium cyanide process, but does not return the concentrate to the bath due to their concern over bath contamination (PS 131). This shop indicated that they operate under stringent aircraft manufacturer's specifications.

Reverse osmosis is applicable to the recycle of effluent from an end-of-pipe treatment system. End-of-pipe systems that employ hydroxide precipitation generate an effluent that is relatively free of toxic metals; however, it contains a high concentration of total dissolved solids (TDS). A typical effluent contains between 500 to 4,000 mg/l of TDS (ref. Memtek file). Although approximately 1.2% of the shops responding to the Users Survey indicated that they directly reuse this effluent (see Section 2.6), most sources indicate that it is of insufficient quality for rinsing, especially in critical rinse situations. Typically, rinse quality criteria for functional and bright plating is in the range of 100 to 700 mg/l and 5 to 40 mg/l TDS, respectively (Exhibit 2-16). Most end-of-pipe RO wastewater recycle applications consists of: preconditioning to prevent the precipitation of salts in the membrane; prefiltration; RO filtration and storage. One survey respondent used RO and other recycling technologies in place of an end-of-pipe treatment system (PS 233). Their system is described in Exhibit 3-55, where RO is incorporated into a complex, zero discharge configuration. In this application, RO is employed to upgrade the quality of the ultrafiltration permeate so that it can be reused as rinse water. Because this plant operates at zero discharge, the concentrated stream from the RO unit is hauled off-site for treatment/disposal; ordinarily, it would be treated on-site.

RO is generally not considered applicable to highly concentrated, oxidative solutions, like chromic acid, nitric acid and peroxy-sulfuric etchant. Process chemicals in these solutions can be recovered using RO; however, membrane life-span is a concern (ref. 157). The membrane life-span for these applications was demonstrated on a bench scale to be only 15 to 35% of that for nickel plating applications (ref. 157). However, one supplier advertises use of their equipment for chromate conversion coating (ref. KRC file). That company agrees that membrane life is shortened by this application, but indicated that RO is still cost effective. For this application, the primary competing technology is vacuum evaporation.

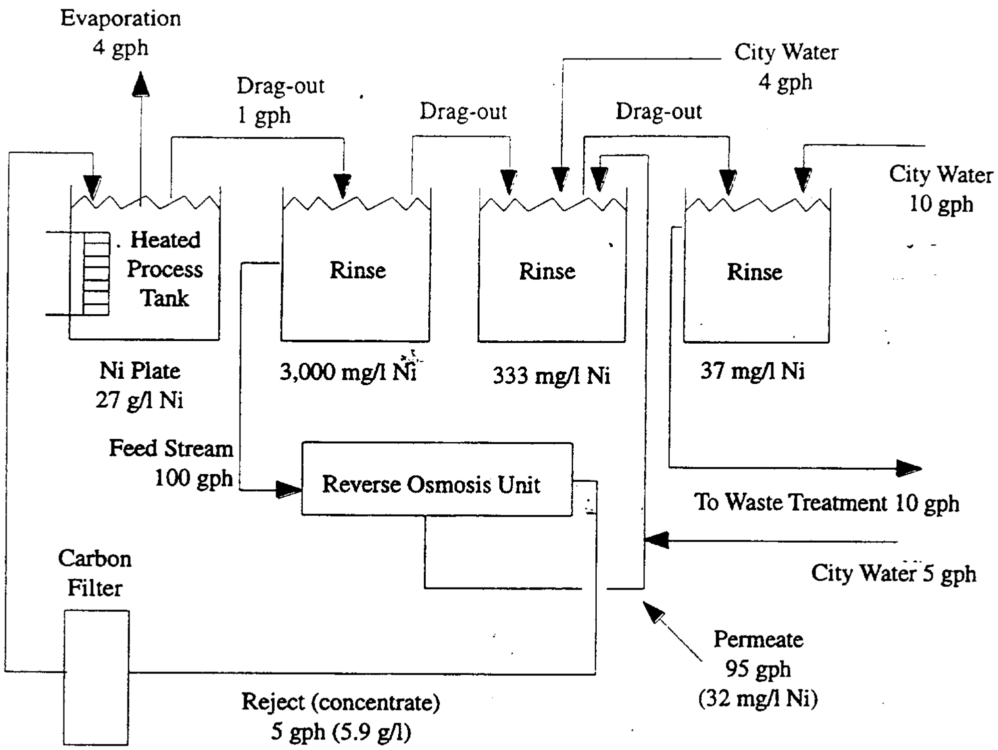
The unsuccessful chemical recovery applications from the Users Survey included: Watts nickel (PS 172), zinc cyanide (PS 008), acid zinc (PS 010), and copper cyanide (PS 089). The reasons for failure of these systems relate mostly to fouling, and are discussed in subsection 3.7.7.

3.7.4 Technology/Equipment Description

This subsection contains names and/or descriptions of commercially available reverse osmosis equipment that is manufactured and/or sold by vendor survey respondents or discussed in the literature. This is intended to provide the reader with information and data on a cross section of available equipment. Mention of trade names or commercial products is not intended to constitute endorsement for use.

Kinetic Recovery Corporation supplies an advanced reverse osmosis ("ARO") packaged system for chemical recovery from rinse waters. The system consists of: membrane modules (usually two, maximum of three); prefiltration (5 to 10 micron); conductivity controls for rinse water and concentrate quality test; miscellaneous controls (flow, pressure, level) for system automation; recycle and boost pumps for liquid transfer; pressure pumps for liquid/solids separation; internal tanks for

Exhibit 3-54. Common Configuration for a Reverse Osmosis Nickel Recovery Application

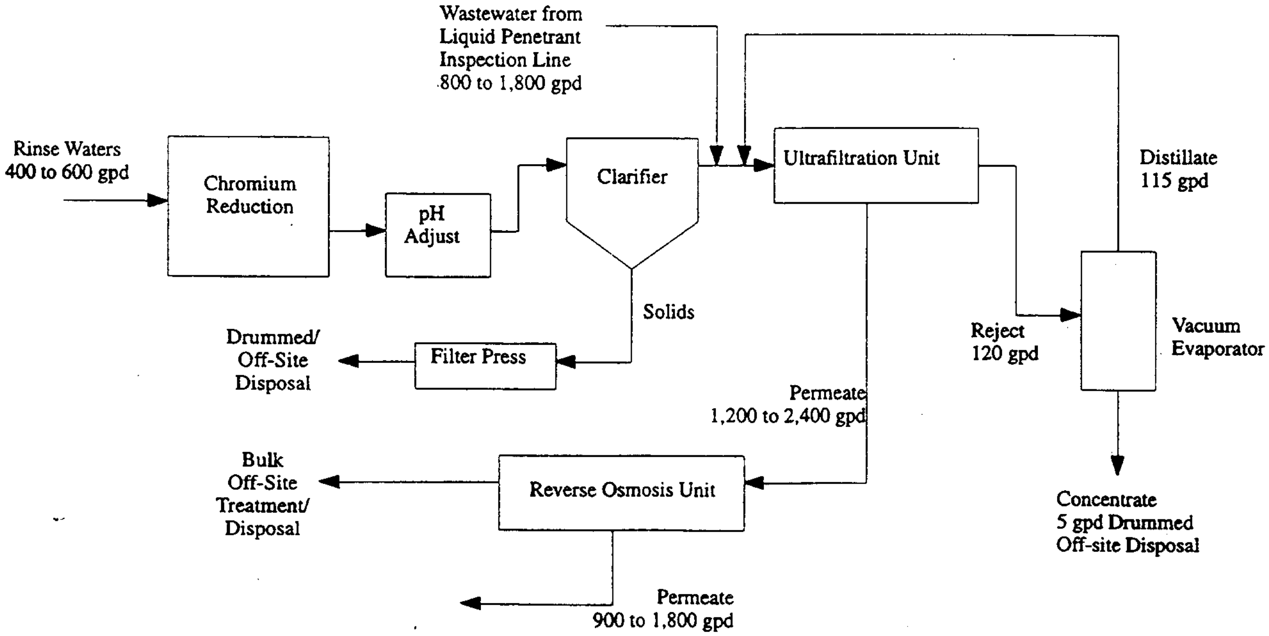


Note: drag-in is assumed to equal drag-out (1 gph).

Note: Drag-in is assumed to equal drag-out (1 gph).

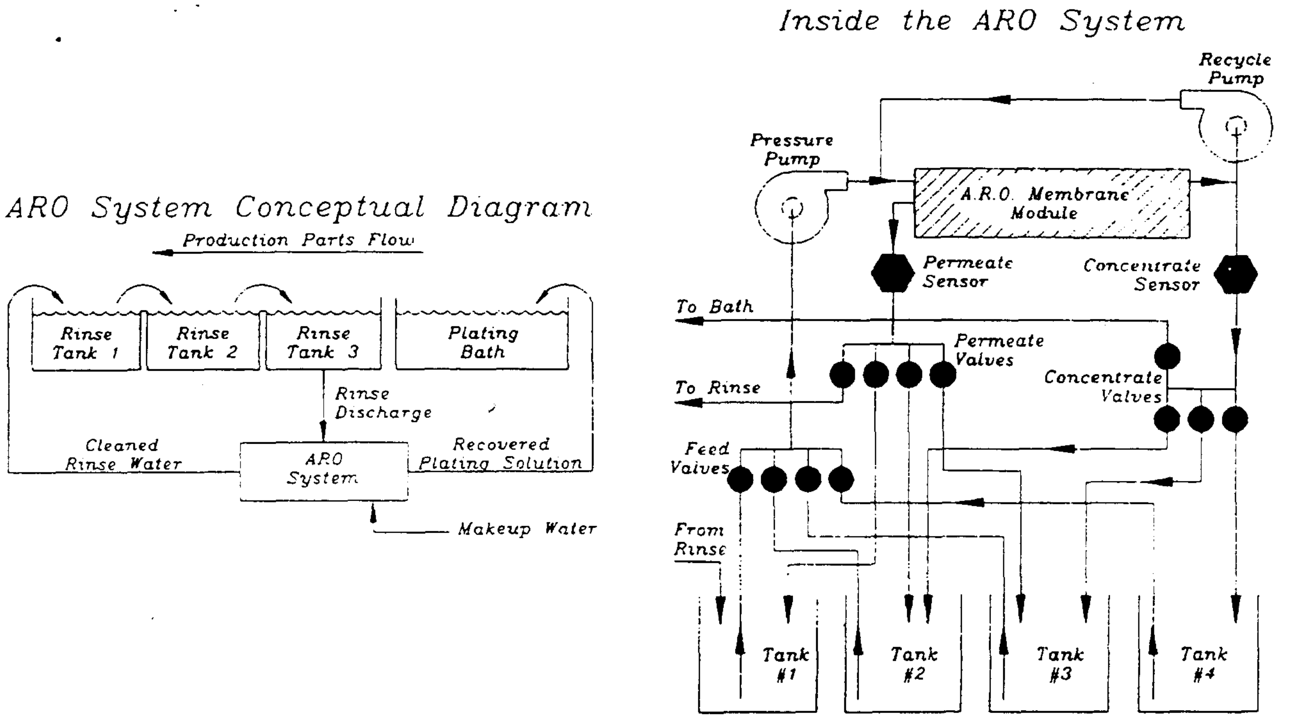
Source: ref. 65

Exhibit 3-55. End-of-Pipe Reverse Osmosis Configuration Used by PS 233



concentrate storage; and an electrical control system, including PLC and operator's interface unit. A diagram and system specifications for the ARO system is shown in Exhibit 3-56. A diagram showing a typical layout for chromate conversion coating recovery is shown in Exhibit 3-57. The ARO typically has two membrane modules. The first membrane module is dedicated to the initial feed stream (rinse water) and the second is dedicated to increasing the concentration of the concentrate stream through successive passes. From the first module, the permeate is returned to plating rinses while the concentrate is held in the first internal storage tank. The concentrate is then passed through the second module for further concentrating. The permeate from the second module, depending on its conductivity, is returned to the rinse tank or directed to one of the internal storage tanks. The concentrate moves sequentially through the series of tanks to tank 3, where it is most concentrated, and then is pumped to the bath. The ARO's internal microprocessor changes operating parameters for each pass of concentrate through the second membrane. Pressures and process times are controlled in order to achieve higher concentrated solutions and improve membrane life (ref. 157, Kinetic Recovery Corporation file). The ARO operates in a pressure range of 900 to 1,000 psig, whereas most RO chemical recovery systems operate below 700 psig. According to the manufacturer, an ARO system can concentrate dilute solutions to at or near bath strength without any evaporation or additional concentration technology (however, for most applications a concentration of 40% to 70% of bath strength is targeted) (ref. 157). Results of bench scale tests on various plating and finishing solutions are shown in Exhibit 3-58.

Exhibit 3-56. Operational Diagram and System Specifications for Advanced Reverse Osmosis (ARO) (Courtesy of Kinetic Recovery Corporation)



Specifications of Standard Systems

System Type	500	1500	3000	4500
Membrane Surface (ft^2)	597	1,494	2,390	3,585
Max. Operating Pressure (psi)	1,000	1,000	1,000	1,000
Avg. Operating Pressure (psi)	950	950	950	950
Process Water Feed (gpm)	5	15	30	45
Concentrate (gph)	0.75	2.3	4.5	6.75
Temperature (°F)	100	100	100	100
pH Range	0.5 to 13	0.5 to 13	0.5 to 13	0.5 to 13
Number of Modules	2	5	8	12

Exhibit 3-57. Advanced Reverse Osmosis (ARO) Application to Chromate Conversion Coating Recovery (Courtesy of Kinetic Recovery Corporation)

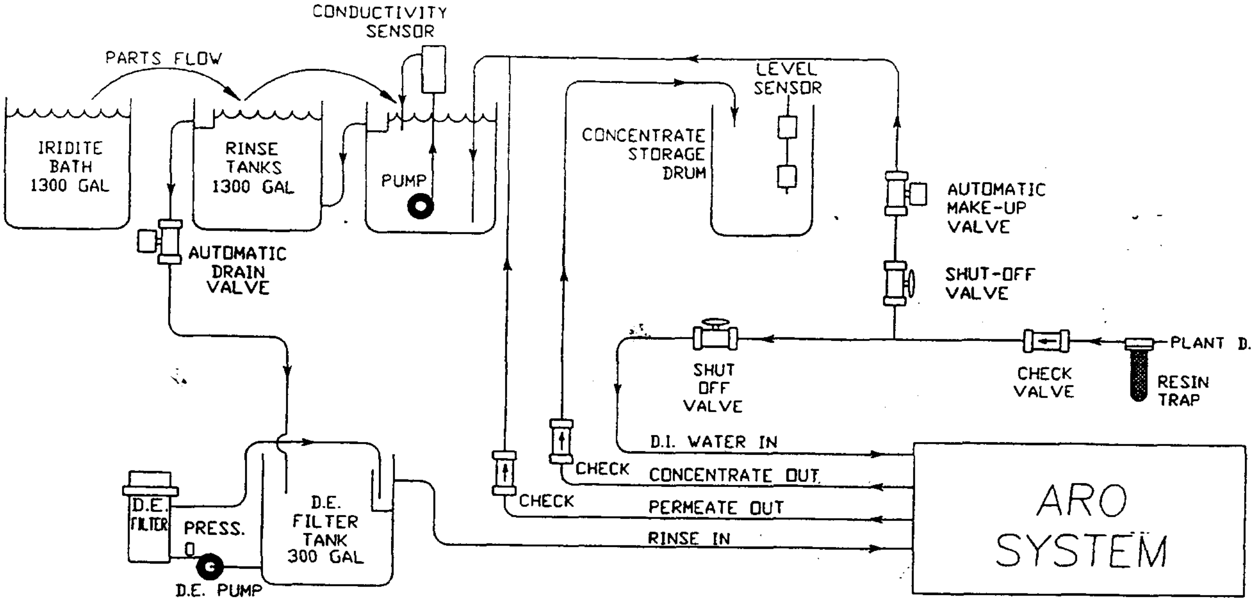


Exhibit 3-58. Reverse Osmosis Bench-Scale Test Results for Various Applications

Process Solution	Bath pH	Concentration Ratios	Passes to Reach Required Strength	Membrane Life Years
Plating Solutions:				
Copper Sulfate	0	40	3	6+
Copper Pyrophosphate	8	200	2 to 3	6+
Tin/Lead Fluoborate	0	10	4	6+
Tin and Tin/Lead Methane Sulfonic	3.6	10	4	6+
Electroless Copper	12	1,000*	1*	6+
Electroless Nickel	10	250	2	6+
Bright Nickel	4.3	110	2 to 3	6+
Nickel Sulfamate	4	250	2 to 3	6+
Watts Nickel	4.4	100	2 to 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 to 4	6+
Hexavalent Chromium	-0.14	100	2 to 3	1
Etchants:				
Peroxy-Sulfuric	0	30	4	1 to 2
Ammonium Chloride	8.0	60	3	6+
Chromic-Sulfuric Acid	-0.5	70	2 to 3	1
Sulfuric Acid	0	40	3 to 4	6+
Hydrochloric Acid	0.5	20	4	6+
Cotings/Sealers/Passivators/Cleaners				
Chelated Lead Brightener	13.5	80	2	4+
Chrome Iridite	2.0	11	2 to 3	1+
Nickel acetate	5.5	150	2	6+
Nitric Acid	1.0	30	4	1
Sodium Hydroxide	13.5	20	4	3+

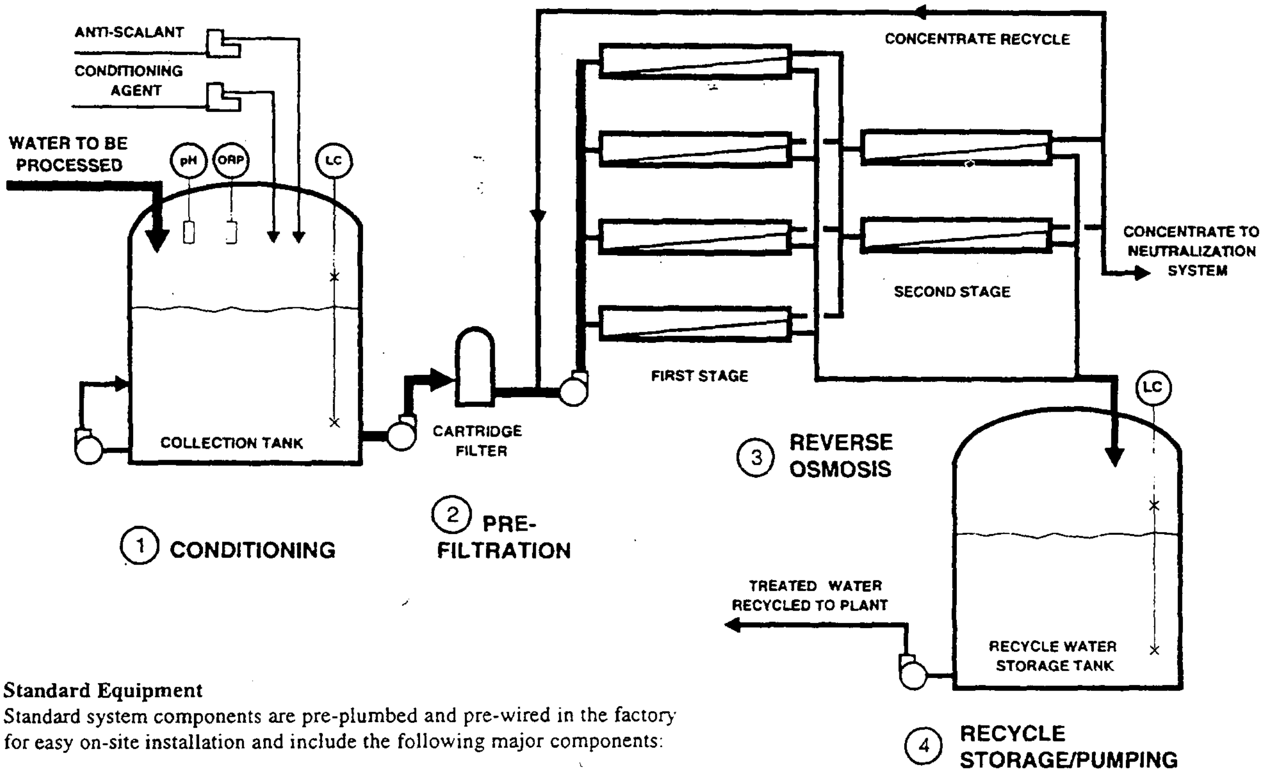
*Special membrane, selective separation.

Source: ref. 157

The ARO is the only unit that was advertised for recovery of chromate conversion coating (it is also sold for traditional applications such as nickel plating). These conversion coating baths, which contain chromic acid, are usually operated at low temperatures and therefore, there is little surface evaporation to provide head room for recovered solution. According to the vendor, the multi-pass design and higher operating pressure of the ARO permit this application. Because the first membrane module of the ARO unit contains more dilute rinse waters and the second membrane module contains more concentrated solution, the life-spans of the two module sets are very different. The first module has a life-span of 1 to 2 years and the second module, 4 to 6 months.

Memtek Corporation manufactures an RO wastewater recycle system (Exhibit 3-59). This system is used to upgrade wastewaters from hydroxide precipitation systems for use as rinse water. There are four stages in the system. The first stage is a pre-RO conditioning step where, as

Exhibit 3-59. Diagram and Equipment List for Commercial Reverse Osmosis Filtration and Related Equipment
(Courtesy of Memtek Corporation)



Standard Equipment

Standard system components are pre-plumbed and pre-wired in the factory for easy on-site installation and include the following major components:

- Preconditioning System
  - One HDPE tank
  - On pH monitor/controller
  - Up to three PCP-50 chemical metering injection systems (optional)
  - One all-plastic mixing pump
  - One ORP monitor/controller
  - One level control for RO pump on/off and high level alarm
  - One RO low pressure feed pump
- Reverse Osmosis Filtration
  - One epoxy coated carbon steel frame
  - One set of 5 micron filter cartridges
  - Three flow-indicator-totalizers for monitoring feed, product, and concentrate flow
  - One electrical panel for automatic control
  - One 304 stainless steel cartridge filter housing
  - One high-pressure multistage RO process pump
  - One temperature monitor
  - Temperature and pressure alarms
  - Cleaning skid (optional)
- Product Water Recycle Station
  - One product water collection tank
  - One level control for RO pump on/off and high level alarm
  - One diverter valve and piping for recycle to preconditioning tank (optional)
  - One duplex recycle water pump station rated at 60 psig
  - One recycle water pressure tank

necessary, pH adjustment is performed, an anti-scalant chemical is added to prevent precipitation of salts in the membrane elements, reducing agents are added to destroy residual oxidizers, and carbon filtration (optional) removes oxidizers and organics. The second stage is prefiltration, which is achieved by a cartridge filter unit (5 micron). Optional multimedia filtration can be purchased for wastewaters with high suspended solids loadings, where cartridge filters would require frequent replacement. The third step is reverse osmosis filtration. The wastewater is pumped through the unit at 200 to 600 psig, depending on the selection of RO elements. Cellulose acetate or thin film composite elements are used for rejection of dissolved salts. The choice of a membrane element is determined by the chemical characteristics of the wastestream and by the percent recycle desired. The permeate from the RO unit is collected in a storage tank equipped with water recycle pumping equipment. The RO unit is equipped with conductivity monitors to monitor product quality. Optional membrane cleaning systems are available.

3.7. 5 Costs

3.7.5.1 Capital Costs

The capital costs of reverse osmosis units are best expressed in terms of membrane surface area, where the required area for a given chemical recovery application will depend on the flux rate and the percent rejection. Flux is the volume flow of permeate per unit of membrane area, usually expressed as gal/ft^2/day or gfd. The percent rejection is defined as follows (ref. 348):

% Rejection = [(feed concentration - permeate concentration)/(feed concentration)] x 100%

Higher percent rejections will result in better quality (i.e., higher purity) permeate and a higher concentration of the plating chemicals. The permeate is typically reused for rinsing and the concentrated chemicals are typically returned to the bath.

In turn, these two factors are affected by the design of the RO equipment and the operating conditions of the system. More specifically, this includes: the type of membrane used, the applied pressure of the RO unit, the number of RO stages, the flow rate of the feed stream, the chemical concentration of the feed stream, and the required concentration of the product returned to the bath.

The feed stream flow to the RO unit is the rinse water, as shown in Exhibit 3-54. The flow rate of this stream and its chemical concentration will depend on the bath concentration, the drag-out rate, the required quality of rinse water in the final rinse and the rinsing configuration employed. For example, if drag-out recovery rinsing is practiced, the RO membrane surface area will be proportionally reduced by the percentage of drag-out returned to the bath by the recovery rinse.

Unfortunately, there are insufficient data available to account for the various parameters that impact RO system sizing and cost. Articles and conference papers that describe this technology fail to provide all of the needed data on system components such as membrane area, flux rates, drag-out rates, etc. Therefore, at this time, capital costs are simply presented in terms of the feed stream rate (Exhibit 3-60). The multi-pass data include systems with feed stream rates of 5 and 10 gpm and corresponding membrane surface areas of 597 ft^2 and 1,194 ft^2. The single pass data include systems with feed stream flows of 5 and 200 gpm. These units are applicable to end-of-pipe polishing. No corresponding membrane surface area data were provided for the single pass units.

Most RO units are sold as packaged systems that include a set of membrane modules, feed and recirculation pumps, prefilters, controls, and internal tanks.

3.7.5.2 Operating Costs

The most significant operating costs include O&M labor, energy, chemicals (cleaning) and membrane replacement. Estimates of RO operating costs for single and multi-pass systems are shown in Exhibit 3-61.

3.7.6 Performance Experience

A partial summary of the user data relative to reverse osmosis is presented in Exhibit 3-62. There are a number of observations that can be made from these data and other data contained in the database and literature:

- The average satisfaction level for chemical recovery applications is 3.2 (on a scale of 1 to 5, with 5 being most satisfactory), which is slightly less than the average rating for all recovery technologies (3.4). Only 33% of the shops using RO for chemical recovery indicated that this technology satisfied the need for which it was purchased. The following is

Exhibit 3-60(a). Capital Costs for Single Pass Reverse Osmosis Systems

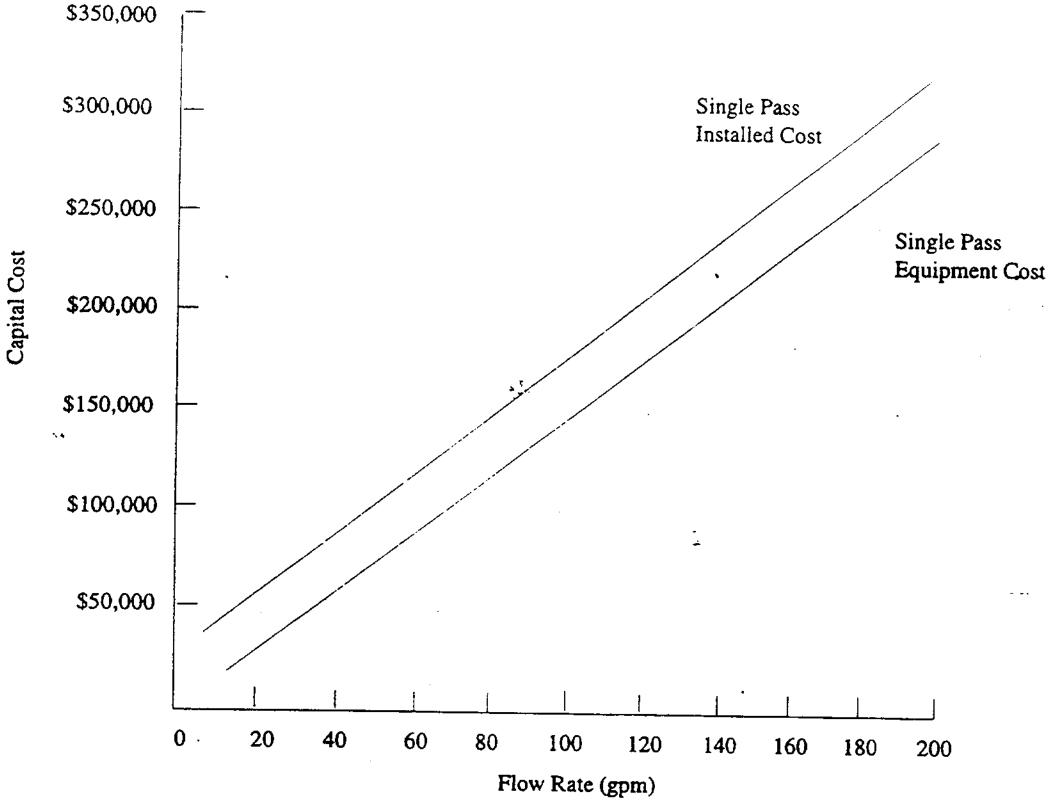


Exhibit 3-60(b). Capital Costs for Multi-Pass Reverse Osmosis Systems

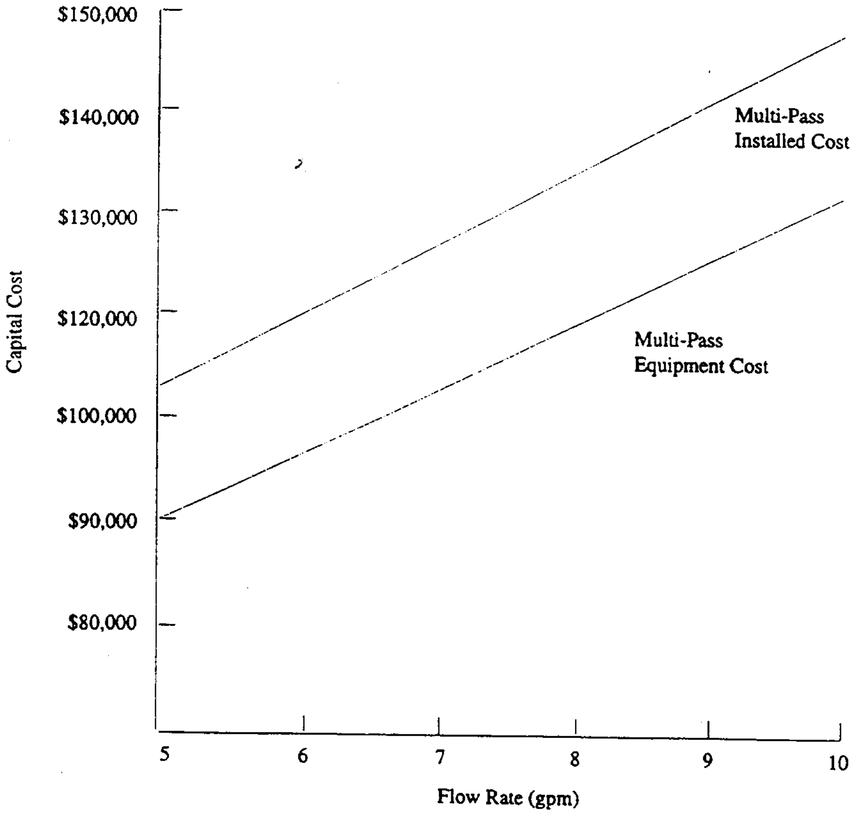
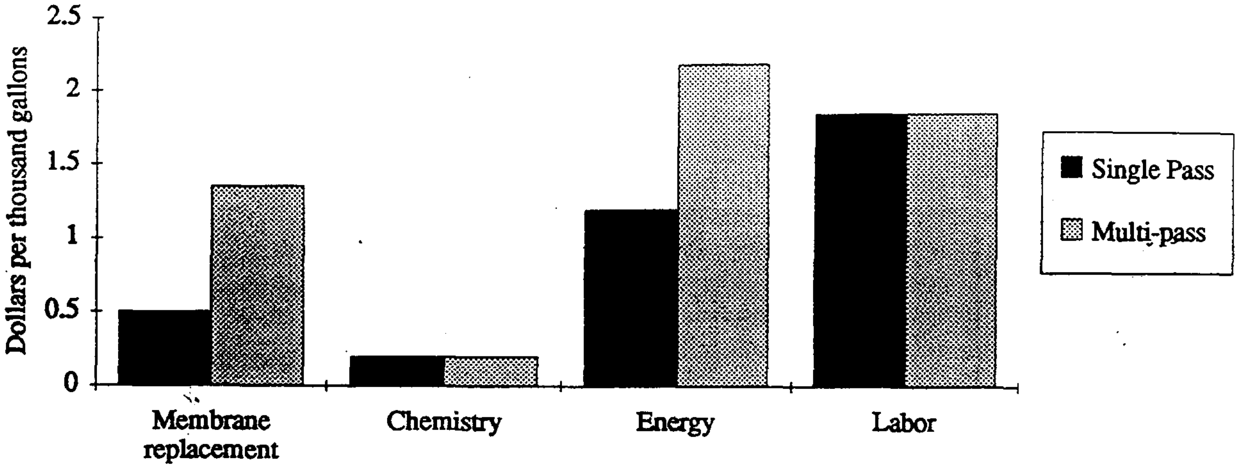


Exhibit 3-61. Operating and Maintenance Costs for Reverse Osmosis Equipment



a breakdown of the reasons why shops purchased this technology:

To meet of help meet effluent regulations:	4
To reduce plating chemical purchases:	4
To reduce water usage:	2
To reduce the quantity of waste shipped off-site:	2
To reduce wastewater treatment costs:	3
To improve product quantity:	0

- The only recovery applications that were fully successful for survey respondents were: nickel acetate and zinc, acid.

- The use of reverse osmosis as a recovery technology did not impact production quality or the rate of production for the survey respondents. The following responses were provided:

	Product Quality	Production Rate
Improved	0	0
No Change	5	5
Decreased	0	0

- The respondents indicated that, based on their experience with this technology and, if given the opportunity, they would:

Purchase the same technology from the same vendor:	2
Purchase the same technology from a different vendor:	1
Purchase a different technology:	3
Do nothing:	0

- None of the respondents indicated that their reverse osmosis system was the cause of an effluent compliance excursion.

- Although RO application to Watts nickel is a well established application, one of the survey respondents found it to be unsuccessful (PS 172). The supplier stated capacity of their unit was 120 gph and the actual capacity was 50 to 80 gph. PS 172 indicated that their unit did not concentrate the product sufficiently for return to the plating bath.

3.7.7 Operational and Maintenance Experience

The message from the Users Survey respondents with respect to operational and maintenance problems is very clear: RO membranes are highly susceptible to fouling and have relatively short life-spans. As stated by one respondent: "Membrane problems, not enough filtration with (original) unit. Had to add much, much extra filtration ahead of (the RO) unit" (PS 008). The shop using RO as an end-of pipe technology also had membrane fouling problems and frequent membrane replacement (every 3 mth.) (PS 233). They also indicated that their efforts to clean the membrane have been unsuccessful. Short membrane life was identified as a problem by another respondent (PS 172). Membrane fouling by algae was identified as a problem by one respondent (PS 172). Another identified high caustic and carbonate levels as the cause of fouling (PS 089). This shop suggested that carbonate levels must be below 45 g/l or "some kind of caustic membrane washing must be applied."

RO membranes are susceptible to fouling by suspended

Exhibit 3-62. Partial Summary of Users Data for Reverse Osmosis Recovery Applications

Code	Application	Manf.	Year	Capital Costs			Operating Costs (Yr.)		Savings							Use	Down	Satisfaction Levels		Future
				Equip. Cost	Other	Total	Non-labor	Labor Hrs.	Water	Process Chem	Treat. Chem	Sludge Disp	Energy	Other	Total	Code	Time %	Manf. Support	Technology	Decision
008	Zinc, CN	Water Technologies	1988	$11,355	$2,000	$13,355		550	$0	$0	$0	$0	$0	$0	$0	2		3	1	3
010 (1)	Zinc, acid	Unk.	1987	$65,000	$30,000	$95,000	$3,000	250	$2,500	$8,300	$5,000	$3,000	$10,000	$0	$28,300	1		4	5	1
089	Copper, CN	Water Technologies	1988	$29,650	$2,000	$31,650	$4,000	100		√	$600				$600	3	30	2	2	3
131 (2)	Cadmium, CN	Osmonics (1)	1988	$16,000	ND	$16,000	ND	ND	√							1	<1	5	5	2
172	Nickel, Watts	Osmonics	1978	$15,000	$3,000	$18,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	2	10	3	1	3
230 (3)	Ni acetate seal	Ecosystems (2)	1992	ND	ND	ND	ND	ND		$624					$624	1	<1	4	4	1
Average for Recovery Applications			1985	$27,401	$9,250	$36,651	$3,500	300	$1,250	$4,150	$1,867	$1,500	$5,000	$0	$8,987		10	3.5	3.0	
233 (4)	EOP	Aboor/Koch	1984	$46,000	$10,000		$800	200	√	$0	$0	$0	$0	$0	$0	1	30	3	3	1

(1) Other capital costs include an atmospheric evaporator used to make head-room in the zinc plating tank.
(2) Equipment purchased used, original manufacture date is not known.
(3) Equipment leased for $500/mth. Nickel acetate use reduced by 3 lbs/week.
(4) End-of-pipe application.
(5) Use Codes: 1-currently operating; 2-not currently operating and no intension for future use; 3-not currently in use, but intend to use in future.
(6) Satisfaction levels (manufacturer and technology) 1 to 5, with 1=lowest and 5=highest.
(7) Future decision codes: 1-purchase the same technology from the same vendor; 2-purchase the same technology from a different vendor; 3-purchase a different technology; 4-do nothing.
(8) "√" indicates that a savings was realized, but not quantified.
(9) ND = No data

solids in the feed stream or materials that precipitate during processing. Solids in the feed stream can be controlled by installing prefilters that are properly selected for the solids encountered and sized for the loading. Precipitation is inhibited by changing operational parameters such as pH. Because pH adjustment of plating chemicals is not usually possible, applications where precipitation may occur should be investigated through bench and/or pilot testing before purchasing equipment.

Two respondents reported no operational or maintenance problems and a percentage downtime of less than 1% (PS 131, PS 230).

A respondent that has eliminated use of their RO unit, indicated that the process "increased solution purification requirements with attendant solution losses, yielding questionable benefits from the technology" (PS 172). It should be noted that any recovery technology that returns both bath chemicals and contaminants to the process tank will cause this problem. However, when contaminants can be removed from the process bath (e.g., carbonates), the benefits of recovery will often outweigh any losses.

3.7.8 Residuals Generation

As discussed in Section 3.7.1, RO separates the feed stream into two components: (1) the permeate which passes through the membrane and (2) the concentrate which retains the dissolved and suspended solids. In typical chemical recovery applications the permeate is used as rinse water and the concentrate is used in the bath. In typical wastewater recycle applications, the permeate is used as rinse water and the concentrate is treated on-site by the end-of-pipe treatment system. In such cases, the quantity of residuals from RO is low, and mostly restricted to used cartridge filters and RO membranes.

The experience of the respondents to the Users Survey was generally the same as described above. One respondent indicated that quantity of used filters generated was 0.3 drums per year. That same shop sent 60 to 300 gpy of unspecified "overflow" to off-site treatment (PS 089). The wastes from all other respondents were treated on-site, except for the end-of-pipe, zero discharge application (PS 233). That shop indicated that the reject stream from their RO unit (300 to 600 gpd of concentrated waste with 2.5% total dissolved solids) is hauled off-site for treatment/disposal.

United States
Environmental Protection
Agency

Research and Development

Risk Reduction
Engineering Laboratory
Cincinnati, OH 45268

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EPA

Project Summary

Recycling Nickel Electroplating Rinse Waters by Low Temperature Evaporation and Reverse Osmosis

Timothy C. Lindsey

Low temperature evaporation and reverse osmosis systems were each evaluated (on a pilot scale) on their respective ability to process rinse water collected from a nickel electroplating operation. Each system offered advantages under specific operating conditions. The low temperature evaporation system was best suited to processing solutions with relatively high (greater than 4,000 to 5,000 mg/L) nickel concentrations. The reverse osmosis system was best adapted to conditions where the feed solution had a relatively low (less than 4,000 to 5,000 mg/L) nickel concentration. In electroplating operations where relatively dilute rinse water solutions must be concentrated to levels acceptable for replacement in the plating bath, a combination of the two technologies might provide the best process alternative. Initially, the reverse osmosis system could be used to concentrate the feed solution. This could be followed by low temperature evaporation processing to concentrate the solution to levels acceptable for replacement in the plating bath.

This Project Summary was developed by EPA's Risk Reduction Engineering 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

This project was a joint effort of Graham Plating, Chicago, IL, an electroplating firm; the Hazardous Waste Research and Information Center (HWRIC), a division of the Illinois Department of Energy and Natural Resources, Champaign, IL; and the Pollution Prevention Research Branch of the U.S. Environmental Protection Agency's Risk Reduction Engineering Laboratory, Office of Research and Development, Cincinnati, OH.

Graham Plating is a large "job-shop" that has been located for many years on the northwest side of Chicago. A new modern building has recently been completed in Arlington Heights, IL, and Graham Plating currently plans to relocate the plating operations to the new facility. This new facility has been designed and constructed such that special features have been installed to promote waste reduction. Large underground rinse water collection tanks have been installed to facilitate accumulation, segregation, and storage of rinse waters by principal metal component. This water can subsequently be treated through a reverse osmosis system, a low temperature evaporation unit, or both.

This project was performed to evaluate, compare, and document the effectiveness of low temperature evaporation and reverse osmosis technologies for recovery and reuse of water and plating bath chemicals associated with electroplating rinse waters. These technologies were examined on a pilot scale at the HWRIC pilot laboratory facility by using actual rinse water samples collected from a Graham Plating nickel electroplating line. Economic assessments conducted for these technologies assumed that 7,200 gal of nickel electroplating rinse water would have to be processed per day at this facility on a 5-day week and 80% availability basis.

Technology Descriptions

Low temperature evaporators (Licon, Inc., Pensacola, FL)* heat water under a vacuum to produce steam at relatively low temperatures (150 to 160° F). The steam rises into a condenser where distilled water results. The plating bath chemicals do not rise with the steam and become a concentrated slurry or solution of chemicals. The evaporation unit is a model C-3, single effect, pilot-scale evaporator especially designed for conducting pilot-scale tests on a variety of feed solutions. Figure 1 provides a schematic of material flow through a low temperature evaporation system.

Reverse osmosis is a pressure-driven membrane separation process in which a feed stream under pressure (200 to 800 psi) is separated into a purified "permeate" stream and a "concentrate" stream by selective permeation of solution through a semi-permeable membrane. The pressure required to force the permeate through the membrane is dictated by the osmotic pressure of the feed stream. Membranes are constructed of a variety of materials such as aromatic polyamide, cellulose acetate, and polyether/amide. The reverse osmosis unit used in this project was an Osmonics Model PES/OSMO-19T-80SSXXC reverse osmosis machine for

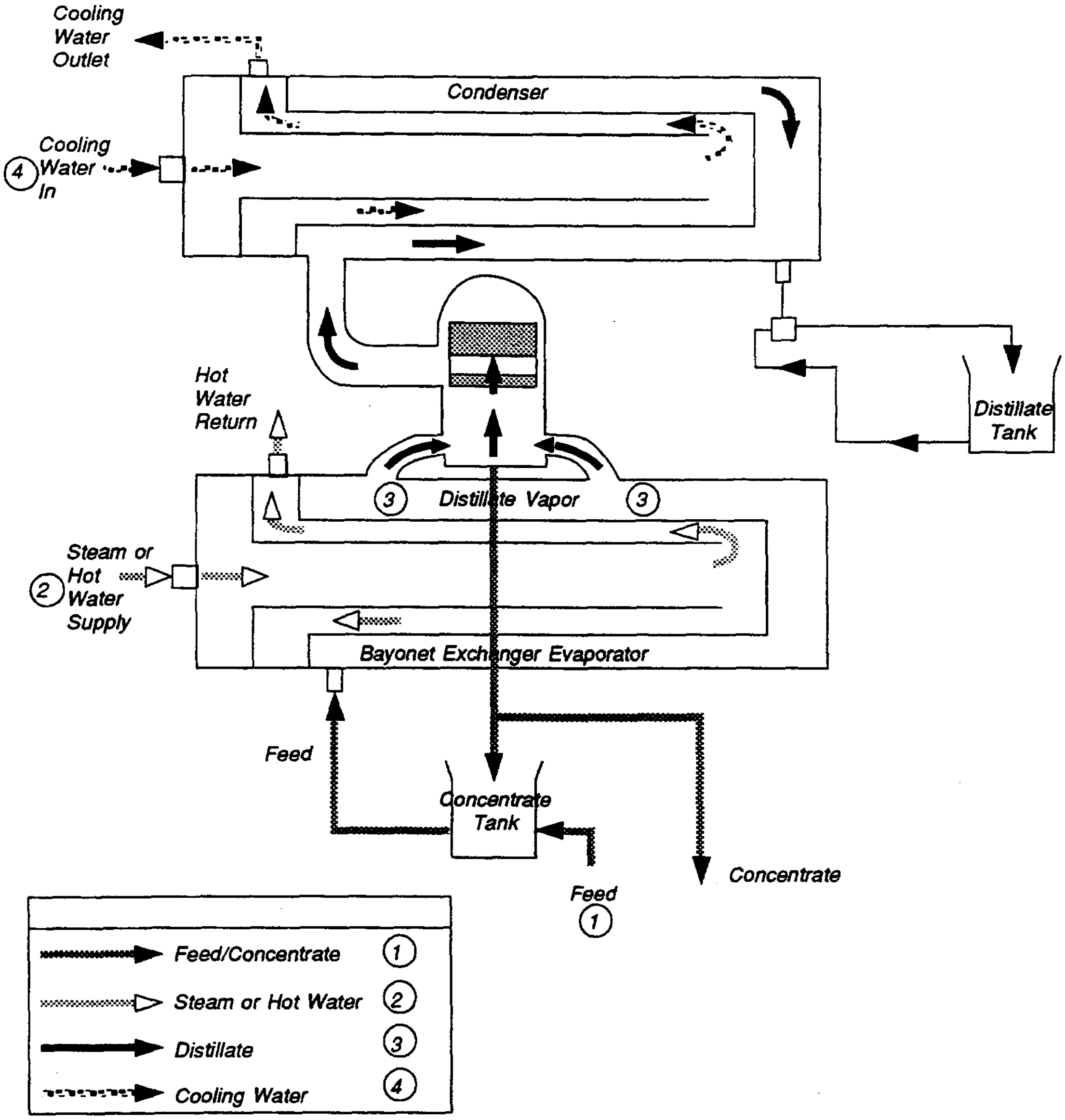

Figure 1. Basic flow diagram for single effect evaporator.

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* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

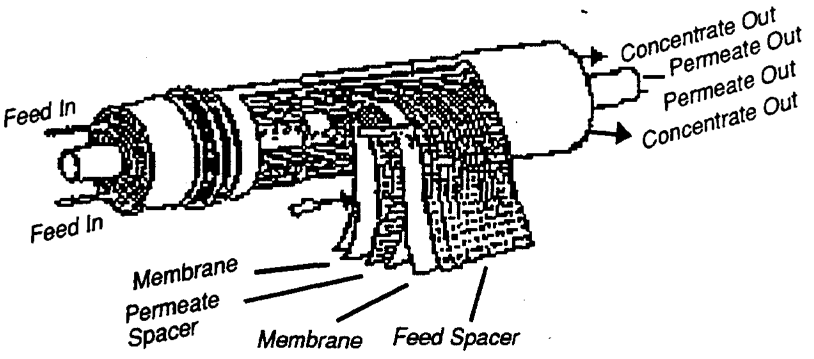

Figure 2. *Components of a spiral-wound membrane.*

process evaluation. It was equipped with one Osmonics Model Number 192T-MSO5 thin-film, composite, spiral-wound membrane cartridge. Figure 2 provides a view of the components that comprise a spiral wound membrane. The solution was prefiltered through a 5 µ cartridge filter for the reverse osmosis testing.

Four, 55-gal drums of nickel electroplating rinse water were collected from the Graham Plating facility and processed through the low temperature evaporation (Drums A and B) and the reverse osmosis (Drums C and D) systems. The reverse osmosis tests were conducted at two different operating pressures: Drum C at pressures of 250 to 300 psi and Drum D at 350 to 380 psi. Samples of the concentrated feed solution as well as the distillate (low temperature evaporation system) and permeate (reverse osmosis system) were collected at regular intervals throughout the tests as the rinse water was processed. Nickel analyses were done to determine how efficiently the systems removed nickel from the rinse water and concentrated it for potential recycling. Analyses for total organic carbon (TOC) were done to indicate the fate of organic constituents (e.g., brighteners) in the rinse water. Immediately after samples were collected, electrical conductivity measurements were made to indicate the soluble salts present in the samples.

Low Temperature Evaporation System Efficiency

The low temperature evaporation system exhibited consistent productivity throughout the tests. This performance feature was unfailing regardless of the chemical concentrations of the feed solution provided to the system. The evaporation system concentrated the rinse water, which had exhibited initial nickel concentrations of 2,540 to 4,140 mg/L to nickel levels as high as 13% to 18%. These levels are well above the 8% required for placement into the plating bath. The concentrate, permeate, and distillate nickel concentrations exhibited in samples collected throughout the tests have been summarized (Table 1). Figure 3 shows how nickel levels changed in the feed solution during the course of the low temperature evaporation tests. Nickel concentrations increased at a steady rate until concentrations of approximately 25,000 to 30,000 mg/L were reached. This level corresponds to a point where approximately 80% to 85% of the rinse water volume had been processed. Beyond this point, nickel concentrations increased dramatically until the final concentrations of 13% and 18% were achieved. The rinse water feed solution volume was reduced by over 98% as a result of this process. The evaporation system concentrated the organic constituents of the rinse water from initial TOC levels of 550 to 990 mg/L to final levels of 25,000 to 26,000 mg/L. TOC levels in the Graham Plating nickle baths are normally maintained at approximately 14,000 mg/L. The concentration rate of the organic components paralleled the nickel concentration rate suggesting that little of the organic material was lost to volatization. As shown in Table 2, distillate produced by the low temperature evaporation system was very low in nickel concentration (average 0.37 to 0.71 mg/L). Additionally, TOC concentrations in the distillate were very low (average 3.04 to 3.50 mg/L).

Disadvantages of the low temperature evaporation system include its relatively high ($140,000) capital cost and high energy requirements ($20/1,000 gal processed). The implied rate of return of 10.6% and payback period of 6.9 yr determined in the economic assessment for this system suggest that it is a marginal investment opportunity by today's standards. These estimates do not, however, consider the reduced future liabilities brought about by drastically decreasing the hazardous waste discharges from the facility.

Reverse Osmosis System Efficiency

The feed solution processed through the reverse osmosis system contained initial nickel concentrations of 1,425 to 2,580 mg/L (Table 1). Figure 4 depicts how nickel concentrations in the feed solution changed as the solutions were processed. Nickel concentrations increased steadily until about 60% of the rinse water volume was processed. At this point, nickel concentrations were about 4,000 to 5,000 mg/L in the two drums. Beyond this point, nickel concentrations increased more rapidly until final concentrations of 12,560 mg/L (Drum C) and 17,900 mg/L (Drum D) were reached. The reverse osmosis system exhibited superior productivity at the beginning of the tests, and productivity dropped off dramatically after about 60% of the feed solution had been processed. Beyond these levels, the productivity of the reverse osmosis equipment decreased dramatically as solids began to precipitate and foul the membrane. The final concentrations achieved with the reverse osmosis process were 12,560 to 18,200 mg/L (1.256% to 1.82%) and are well below the 8% nickel concentration required for the plating bath. Some of this solution could be used to replace water losses in the electroplating process. The reverse osmosis system, however, would probably produce excess volumes of concentrated rinse water composed of 1.2% to 1.8% nickel. This material would have to be further processed with the use of an alternative technology such as low temperature evaporation or be shipped to a facility that could extract the nickel for use in other industrial processes.

The reverse osmosis system concentrated the organic constituents present in the rinse water feed solution from initial TOC levels of 340 to 540 mg/L to levels of 2,800 to 3,500 mg/L. These concentrations suggest that the organic bath constituents are concentrated by the reverse osmosis equipment at rates that parallel the nickel concentration rates.

The quality of the cleaned rinse water permeate produced by the reverse osmosis equipment was directly related to the

Table 1. Comparison of Nickel Concentrations in Concentrate, Distillate, and Permeate

	Low Temp. Evap.		*Reverse Osmosis*	
Product	*Drum A*	*Drum B*	*Drum C*	*Drum D*
Concentrations at beginning of test (mg/L):				
Concentrate	*4,140*	*2,540*	*2,580*	*1,425*
Distillate	*2.5*	*2.2*	—	—
Permeate	—	—	*44.5*	*14.5*
Concentrations at end of test:				
Concentrate	*179,000*	*128,000*	*12,560*	*18,200*
Distillate	*1*	*0.3*	—	—
Permeate	—	—	*210*	*790*
Ratio of distillate permeate to concentrate:				
Distillate	*0.02%*	*0.01%*	—	—
Permeate	—	—	*1.49%*	*1.54%*

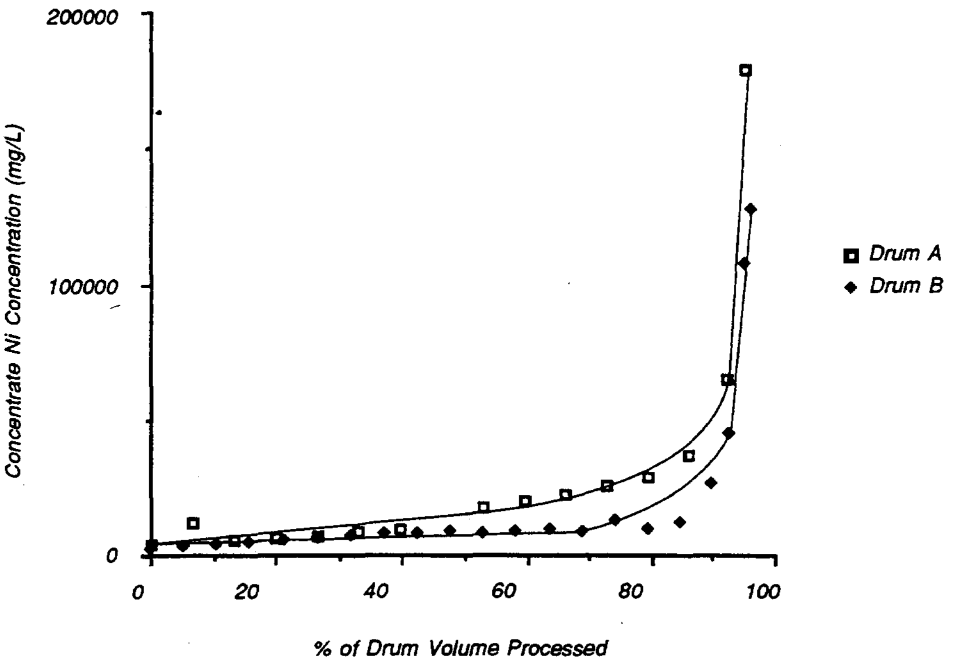

Figure 3. ***Concentrate nickel concentration versus percent of drum volume processed; low temperature evaporation tests.***

quality of the feed solution pumped into the unit. Permeate produced by the reverse osmosis system averaged 89 to 134 mg/L nickel (Table 2). These levels are about 98.5% lower than the nickel concentrations present in the concentrated solution. This solution would not, however, be acceptable for discharge to publicly owned treatment works. The nickel levels present in this solution could be further reduced by passing this solution through the reverse osmosis equipment again. TOC concentrations averaged 19.46 to 21.98 mg/L in the permeate solution which suggests that some of the organic compounds were able to permeate the membrane. The reverse osmosis equipment condensed the feed solution to final volumes that were 88% to 94% less than the original volumes of the two tested drums. Differences between the two tests can be attributed to the difference in operating pressures used during the tests.

Advantages of the reverse osmosis system include its relatively high production rates with respect to low concentration feed solutions. Additionally, it would require lower capital investment (about $50,000) than a comparably sized low temperature evaporation system. Energy costs required to operate a reverse osmosis system would be only about $2.50/1,000 gal processed. Disadvantages associated with a reverse osmosis system include its inability to concentrate the feed solution to levels beyond the 12,560 to 18,200 mg/L levels revealed in this study. This factor alone would prevent use of a stand-alone reverse osmosis system at the Graham Plating facility because of the economic impracticalities associated with the concentrate produced by the system. Another disadvantage associated with the reverse osmosis system is the lower quality permeate produced by the system. This solution would probably have to be reused within the plant or further processed through the reverse osmosis system before discharge to the POTW.

Combined Use

Both the low temperature evaporation and reverse osmosis systems appear to offer advantages under specific operating conditions. Based on this factor, the potential for utilizing these technologies in tandem was examined. The reverse osmosis system is best adapted to conditions where the feed solution has a relatively low nickel concentration. It can process the low concentration feed solution with relatively high efficiency to a level of 4,000 to 5,000 mg/L. At this point, the solution could be transferred to a low temperature evaporator for further concentration. The low temperature evaporation system appears to be best adapted to processing solutions with relatively high nickel concentrations. It can process these solutions so that a concentrate solution composed of 8% or more nickel is produced along with a very high-quality distillate solution. Using the equipment within its optimum operating ranges would augment the ability of the systems to process the rinse water with maximum efficiency while supplying the electroplating operation with high-quality concentrate, distillate, and permeate solutions for reuse. Since the equipment would always be functioning within optimum concentration ranges, smaller reverse osmosis and low temperature evaporation units could be implemented than if the individual units were used alone. If this type of combined system were installed at the Graham Plating facility, it would require a capital investment of $115,000, which would be paid back in 2.8 yr through a 27.6% implied rate of return.

Electrical Conductivity

Electrical conductivity measurements taken during operation of both the low temperature evaporation and reverse osmosis systems could be of great value during actual plant operating conditions. The electrical conductivity data obtained in this project were well correlated with nickel concentration, TOC concentration, and membrane flux characteristics. Accurate assumptions regarding concentrate, permeate, and distillate quality could be based on electrical conductivity measurements taken throughout the work day. Further, the equipment could be automated to accumulate and discharge the various solutions based on in-process electrical conductivity measurements that could activate pumps, valves, and/or switches when preset levels were attained.

Additional Research Needs

Additional tests need to be conducted with rinse water from other electroplating lines involving other metals. These tests would aid in determining the usefulness of these technologies with respect to processing the entire spectrum of rinse water streams that would be produced at a full-scale electroplating operation. Detailed analysis of all organic and inorganic rinse water components (organic brighteners, sulfate, chloride, etc.) would be useful to determine the effects of low temperature evaporation and reverse osmosis processing on the relative quality and quantity of these constituents. Onsite testing should be done at an electroplating facility to allow comparison of full-scale systems with the pilot-scale tests performed in this study. This onsite testing would include detailed study of the performance of the concentrated rinse water that is returned to the plating bath.

The full report was submitted in fulfillment of Contract CR-815829 by Hazardous Waste Research and Information Center under the sponsorship of the U.S. Environmental Protection Agency.

Table 2. *Average Nickel Concentrations in Distillate and Permeate*

	Distillate Ni Concentration		*Permeate Ni Concentration*	
	Mean (mg/L)	*Standard Deviation (mg/L)*	*Mean (mg/L)*	*Standard Deviation (mg/L)*
A (n=13)	*0.71*	*0.63*	—	—
B (n=16)	*0.37*	*0.52*	—	—
C (n=22)	—	—	*89.55*	*49.22*
D (n=17)	—	—	*134.38*	*202.19*

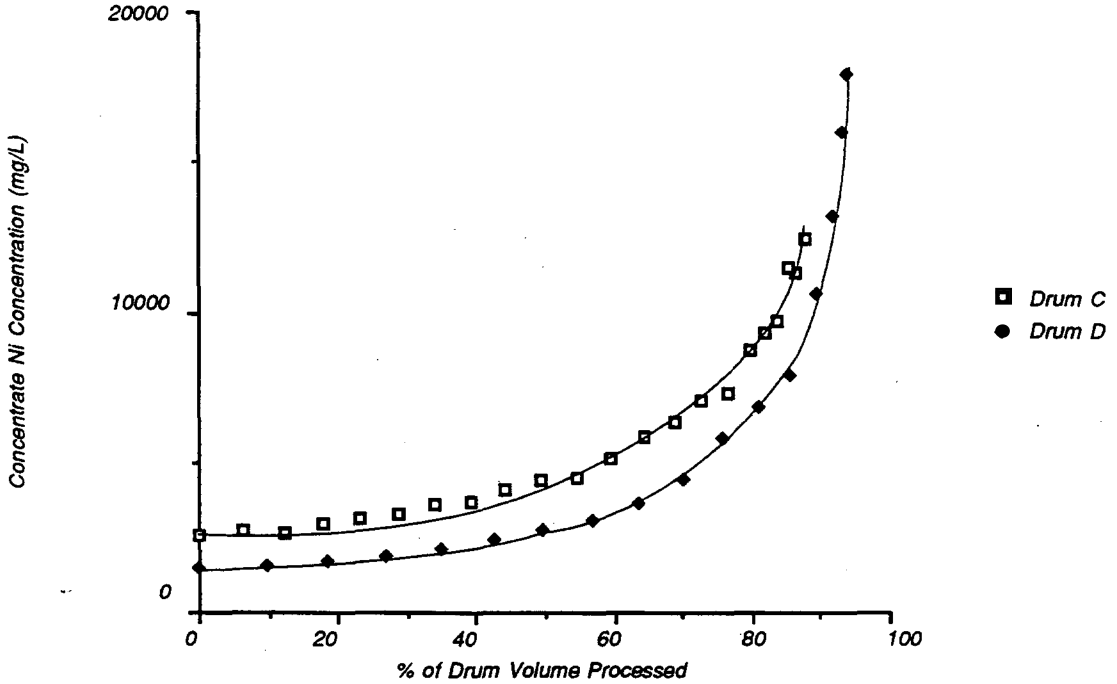

Figure 4. *Concentrate nickel concentration versus percent of drum volume processed; reverse osmosis tests.*

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***Paul Randall** is the EPA Project Officer (see below).*

The complete report, entitled "Recycling Nickel Electroplating Rinse Waters by Low Temperature Evaporation and Reverse Osmosis," (Order No. PB93-218865; Cost: $19.50, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

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Atmospheric Evaporators
in

Pollution Prevention and Control Technology for Plating Operations

George C. Cushnie Jr.
CAI Engineering

A Project Sponsored by the
National Center for Manufacturing Sciences
and Conducted in Cooperation with the
National Association of Metal Finishers

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3.2 ATMOSPHERIC EVAPORATORS

3.2.1 Overview

Atmospheric evaporators are the most widely used method of chemical recovery in the plating industry. Of the 318 plating shops responding to the Users Survey, 71 (or 22.3%) have employed atmospheric evaporators for chemical recovery. Some shops have purchased or built two or more units for different recovery applications, resulting in a total number of 91 units used by survey respondents. The literature cites an extreme case, where a Virginia shop employs 14 atmospheric evaporators and has achieved zero discharge of wastewater effluent (ref. 33). Most of the atmospheric evaporators used by survey respondents were commercial units although approximately 5% were built in-house. By comparison, 26% of the electrowinning units were built in-house. The low percentage of home-made atmospheric evaporation units is most likely due to the low capital cost and successful track record of the commercial units.

Atmospheric evaporators are also used by some shops to concentrate liquid plating wastes prior to hauling them off-site for treatment/disposal, thereby reducing transportation costs and in some cases treatment/disposal costs. A total of 3 shops responding to the survey used atmospheric evaporators for this purpose.

An atmospheric evaporator is a device that evaporates water to the atmosphere. The commercial atmospheric evaporator used for recovery in the plating shop consists of a pump to move the solution, a blower to move the air, a heat source, an evaporation chamber in which the solution and air can be mixed, and a mist eliminator to remove any entrained liquid from the exit air stream (see Exhibit 3-3). The evaporation chamber is usually filled with packing material or finned panels to increase the air to water interface. In operation, the temperature of the solution being evaporated is elevated and the heated so-

Exhibit 3-2. Reasons Why Respondents Purchased Chemical Recovery Technologies

Why the Technology Was Purchased[b]	Recovery Technologies[a] ED	EW	ATM EV	VAC EV	IX	ME	RO	Totals
To meet or help meet effluent regulations	1	38	42	14	18	4	4	121
To reduce plating chemical purchases	0	14	42	12	8	5	4	85
To reduce the quantity of waste shipped off-site	0	20	34	12	13	2	2	83
To reduce wastewater treatment costs	1	20	39	11	12	2	2	87
To improve product quality	0	1	9	0	5	1	3	19
Other	0	3	6	1	0	3	0	13

[a] Technology key: ED=electrodialysis, EW=electrowinning, ATM EV=atmospheric evaporation, VAC EV=vacuum evaporation, IX=ion exchange, ME=meshpad mist eliminator, RO=reverse osmosis.

[b] Multiple reasons for purchasing technologies were often given by a respondent for the same technology/application.

lution is introduced into the evaporation compartment. Air from the plating room is then blown through the compartment where it accepts the water vapor, and is then vented out of the chamber.

Commercial units are advertised to have evaporation rates of 10 to 90 gph, depending on the size of the unit and operating conditions (e.g. solution temperature). Often actual evaporation rates are considerably less because the atmospheric conditions within most plating shops do not match the ideal conditions under which the manufacturers rate their systems. To meet higher evaporative requirements, it is feasible to utilize multiple atmospheric evaporators in series. However, the use of atmospheric evaporators is generally limited by energy costs to applications where the required evaporation rate is 50 gph or less. Beyond this point, vacuum evaporators (Section 3.3) are more cost effective, considering both capital and operating costs.

The key attributes of atmospheric evaporators include: (1) low capital cost; (2) simple operation and low maintenance; (3) very high recovery rates can be achieved (usually 90% to nearly 100%); (4) no additional reagents are needed; and (5) no sludges or only small quantities of sludges are generated (when used in recovery application). The major negative aspects of this technology are: (1) high energy requirement (i.e., requires constant solution heating and during the winter months there is a heat loss due to venting the exhaust to the outside); (2) the air that is vented by these devices must be discharged to the outside (due to contaminants present and its high humidity) and may be a regulated source of air pollution; (3) because moisture is exhausted to the atmosphere it cannot be reused as rinse water as with vacuum evaporators[1]; (4) evaporators return contaminants to the bath and may reduce bath life; and (5) spray/fog rinsing over the bath or fume suppressants (floating chemical type or plastic balls) are not compatible with atmospheric evaporators since they reduce the head room in the plating tank and limit the return of rinse water/drag-out.

Most commercial atmospheric evaporator units have the same principals of operation. To achieve chemical recovery, solution from a heated plating tank is fed to and concentrated by the evaporator and returned to the plating tank. This approach reduces the volume of solution in the plating tank, thereby "making room" for the recovery rinse water/drag-out to be added to the plating bath. Often two or more recovery rinse stations are used to minimize the overall rinse water requirements of the process and increase the recovery rate of plating chemicals. Less frequently, atmospheric evaporation is applied to ambient or low temperature baths. In this case, the recovery rinse water may be fed to the evaporator from a heated transfer tank, which increases the overall evaporative capacity of the system. The latter application is often restricted by the maximum temperature that can be applied to the solution, since heat sensitive components of the bath could be destroyed.

Although some commercial atmospheric evaporators have their own heat source, nearly all units employed for plating chemical recovery in use today use the heat in the plating tank (and/or heated transfer tank) as the energy source for evaporation. Any solution above room temperature that is pumped to the evaporator will be returned at a lower temperature. The temperature difference is primarily due to the heat that goes into evaporation, which is (ref. 358):

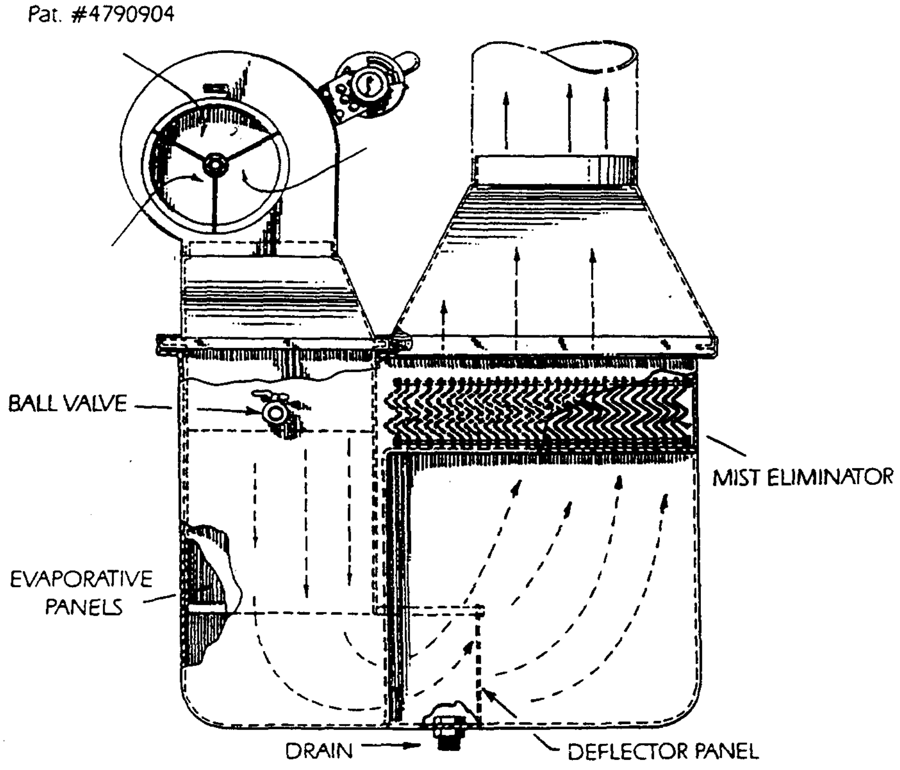
- 540 calories/g of water evaporated, or
- 2,137 Btu/l (8,090 Btu/gal), or
- 626 watts/l (2,371 watts/gal), or
- 0.02137 "gas company" therms/l (0.08090 therms/gal), or
- 0.0637 boiler hp/gal

The heat taken from the plating bath must be replaced by the tank heating system (e.g., immersion heaters or steam system).in order to maintain the operating temperature of the bath. During winter months, when a plating shop is heated, the room's ambient air that is exhausted by the evaporator (typically 300 to 3,000 cfm) must be replaced. These two elements make up the bulk of the non-labor operating costs for atmospheric evaporation.

The humidity and temperature of a plating shop will significantly affect the evaporative capacity of an atmospheric evaporator, especially for low to moderate solution temperature applications. If the air in the plating shop is very humid (e.g., 90% relative humidity) before entering the evaporation chamber, it will hold a limited amount of additional water and the evaporation rate will be affected. From thermodynamic tables, it is known that warmer air holds more moisture than cooler air. For example, one pound of air will hold 0.015 pounds of water at 70°F. By comparison, that same pound of air will hold 0.220 pounds of water at 120°F. In all cases, the air entering the evaporation chamber is heated to a maximum temperature equal to a point less than the solution temperature (the closeness of the air and solution temperatures will depend on the evaporator design and resultant heat transfer efficiency). With high temperature solutions, the air temperature will reach 100°F or more. At this temperature level, the original moisture content of the air is relatively small in comparison to the new capacity of the air, hence relative humidity plays a lesser role.

The above example also indicates that preheating of the plating shop air before introducing it to the evaporation chamber would improve performance. Although air heating systems are discussed in the literature (e.g., ref. 299), no commercial units designed for plating shops were identified with this feature. The strategy of manufacturers of commercial units is to maximize air flow and increase

Exhibit 3-3. Common Commercial Atmospheric Evaporator Used for Chemical Recovery (Courtesy of Poly Products Corporation)



the water/air contact area rather than increase air temperature.

Platers may be tempted to use outside air for make-up to their atmospheric evaporator, especially during winter months in colder climates, to reduce the loss of heated indoor air. This strategy generally does not work. Although the outside air may be dryer than the inside air, its low temperature will have an overriding impact on the evaporation process. The low temperature of the air will prevent it from reaching a sufficiently high temperature in the evaporation chamber to attain a reasonable water holding capacity.

In many cases, the types of commercial units used for concentrating wastes before off-site disposal are the same types of units used for recovery. However, there are also available specially designed waste concentration units. These devices usually have a direct heat source and operate at much higher temperatures than the recovery units. Higher temperatures can be used with wastes since there is no concern for the integrity of the chemical components. Because higher temperatures are used, the materials of construction for these units differ from the recovery units. Evaporation of water from wastes may be viewed by regulatory agencies as thermal treatment and they may require a RCRA permit for the operation of these units, depending on the interpretation of the application. Regulatory aspects of evaporators are not discussed in this report, but should be closely investigated before purchasing and operating evaporation equipment.

3.2.2 Development and Commercialization

Atmospheric evaporators are essentially adjuncts to plating tank evaporation. They increase the head room in the plating tank, thereby increasing the quantity of rinse water/drag-out that can be recovered using recovery rinsing. The use of recovery rinsing in the plating industry was documented more than 50 years ago. The use of evaporators for chemical recovery extends back more than 40 years (see reference list in ref. 1). Most of the early evaporators used by the plating industry were the vacuum type, which was basically a technology transfer from the chemical processing industry. These were large units, often with capacities of 400 to 600 gph (1,500 to 2,300 l/hr). Large units were used because water conservation and pollution control were less important at that time, resulting in higher flow rates. Also, energy was much less expensive at that time and therefore there was less incentive to minimize flows prior to evaporation. In 1974, with the advent of rapidly rising energy costs, there began a movement to down-size recovery systems (ref. 300). Coupled with the Federal pollution control standards, first promulgated in 1979, plating shops turned to the small and inexpensive atmospheric evaporators for chemical recovery. Based on the results of the Users Survey, it is apparent that purchases of this technology have continued into the 1990's.

There are approximately 25 companies that manufacture evaporative recovery equipment applicable to the plating industry. This includes vacuum and atmospheric evaporators for both chemical recovery and waste concentration (ref. 421). The firms most often mentioned in the Users Survey were Poly Products Corporation, Techmatic Inc. and NAPCO.

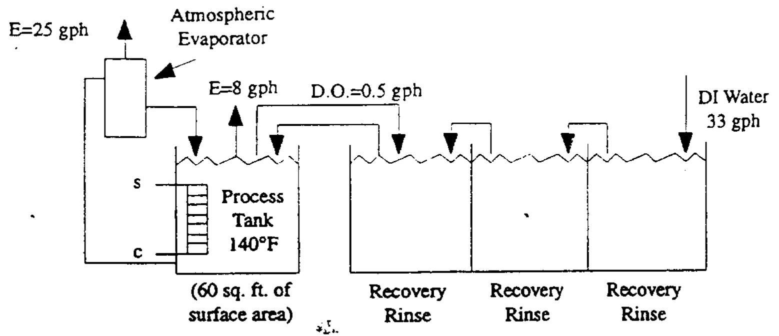
Vend [illegible]

3.2.3 Applications and Restrictions

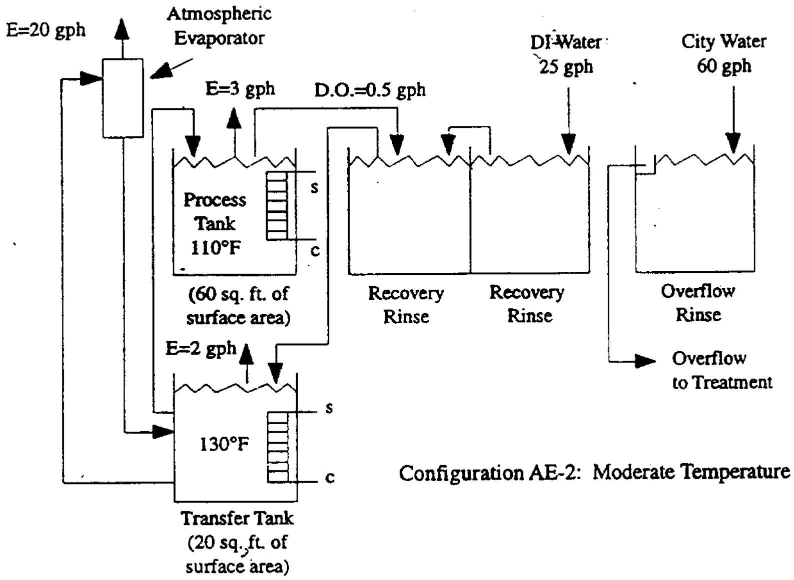
Exhibit 3-4 shows the three basic configurations used for application of atmospheric evaporators for chemical recovery. Application AE-1 is used mostly for elevated process baths (>120°F), AE-2 for moderate temperature baths (100 to 120°F) and AE-3 for ambient or low temperature baths (ambient to 100°F). In each case, an important aspect to the implementation of this technology is the incorporation of recovery rinsing. The quantity of recovery rinse solution that can be added into a bath equals the sum of the evaporation from the tank's surface and the evaporation caused by the atmospheric evaporator (i.e., ignoring any differences in drag-in and drag-out). For some processes, where the operating temperature is high and drag-out is sufficiently low, a closed-loop configuration can be employed. Several of the respondents to the Users Survey indicated that have they achieved a closed-loop (e.g., PS 003 for nickel, PS 213 for nickel and chrome). Generally, these shops used either a three or four stage recovery rinse. Lower temperature processes and those with high drag-out rates will usually require a free running rinse (or countercurrent arrangement) following the recovery rinse tank in order to maintain sufficiently clean water in the final rinse. The effects of rinsing configurations on recovery and plating quality are discussed in detail in Section 2.

The strategy with moderate temperature baths is to connect the atmospheric evaporator to a heated transfer tank with the idea that the solution in the transfer tank can be heated to a higher temperature than the maximum operating temperature of the plating process. For example, a transfer tank used with acid zinc can be heated to 140°F,

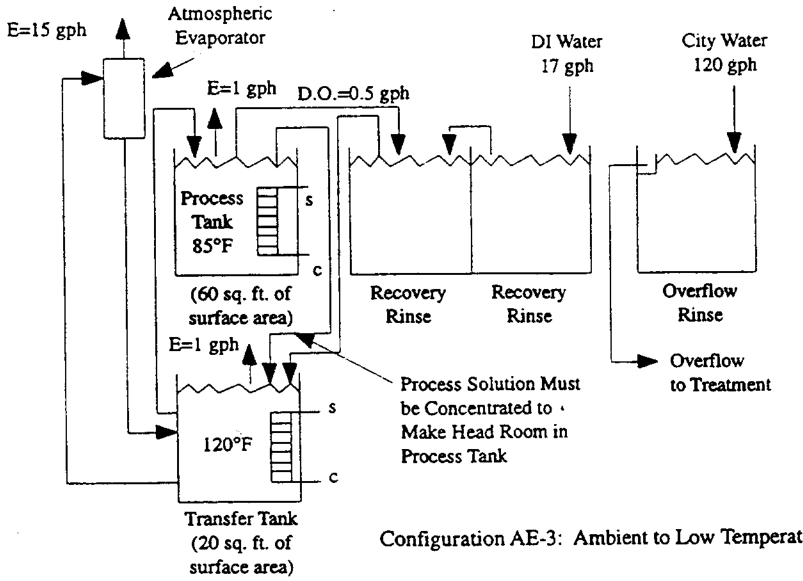
Exhibit 3-4. Three Primary Configurations for the Application of Atmospheric Evaporation to Chemical Recovery



Configuration AE-1: High Temperature Process



Configuration AE-2: Moderate Temperature Process



Configuration AE-3: Ambient to Low Temperature Process

Exhibit 3-5. Atmospheric Evaporation/Process Matrix

Process Solution	Percentage of Atmospheric Evaporator Applications (%)	Percent of Process Solutions for which there is an Atmospheric Evaporator Application*
Brass	3.2	3.7
Cadmium, cyanide	6.6	3.3
Chromium, decorative (Cr+3)	3.2	8.7
Chromium, decorative (Cr+6)	18.0	11.8
Chromium, hard	6.6	5.1
Copper, cyanide	8.2	2.6
Nickel, not specified	3.2	11.7
Nickel, sulfate	3.2	11.8
Nickel, Watts	18.0	8.9
Zinc, acid	9.8	18.2
Zinc, cyanide	3.2	4.4
Zinc, non-cyanide	4.9	2.4
Other	11.5	—

*For example, there were 54 brass plating processes identified during the Users Survey. Of these, two processes had an associated atmospheric evaporation/chemical recovery unit (2/54 = 3.7%).

whereas the maximum operating temperature of the process bath is about 90°F. By connecting the evaporator to the transfer tank, the evaporation rate will be approximately tripled. A number of shops responding to the Users Survey indicated that they were using heated transfer tanks (e.g., PS 098, PS 252 and PS 278).

With low or ambient temperature baths, where there is no appreciable surface evaporation from the process bath, a bleed from the process bath to the transfer bath is used to make the needed headroom. Alternatively, a second evaporator could be used. For some ambient baths that contain wetting agents, drag-in may exceed drag-out. The design capacity of the atmospheric evaporator must account for this difference plus the desired recovery rinse rate. In some cases, an atmospheric evaporator may be used simply to create the headroom needed to prevent discarding "extra" plating solution created by these conditions (ref. 355). One such application was found in the Users Survey (PS 214).

The Users Survey also showed that many shops were incorrectly using their atmospheric evaporators. Approximately 20% of the shops connected either an unheated recovery rinse or an unheated plating tank to the evaporator. Generally, these facilities experienced below average results. Performance experience is discussed in Section 3.2.6.

With all applications of atmospheric evaporators, the user should install water treatment in the form of ion exchange and/or reverse osmosis to remove the hardness and other impurities in the raw water that would otherwise accumulate in the process tank.

Recovery applications that were identified during the Users Survey are presented in Exhibit 3-5. The most common recovery application for atmospheric evaporators is nickel plating. On a combined basis, the nickel applications accounted for nearly 30% of all applications (includes bright nickel and electroless nickel applications).

When used in conjunction with hard chrome plating or other processes that have solution heating and cooling requirements and ventilation requirements, the atmospheric evaporator can serve as a recovery unit, cooling device and an air scrubber (ref. 299). Because the unit would be using waste heat from the tank for evaporating excess water, the evaporation process operates essentially free. The appropriate tank configuration is basically the same as shown in Exhibit 3-4, application AE-1. The plating tank's exhaust air would serve as the inlet air to the evaporator, which would remove its chromic acid mist. In such cases, the exhaust of the evaporator is usually connected to the existing ventilation system and the evaporator's blower is eliminated. Because of anticipated regulations for hard chrome plating air emissions, it is questionable that the evaporator's mist eliminator would adequately substitute for a future emission control device. At this time there are insufficient data to evaluate this application.

Atmospheric evaporators are not applicable in cases where the solution temperature cannot be raised above approximately 85°F, either in the process tank itself or in a heated transfer tank. Generally, these are solutions that either contain highly heat sensitive components or fume excessively when heated or aerated. Also, atmospheric evaporators should not be applied to any process solution which cannot be maintained through use of methods and/or technologies that replenish active bath ingredients or remove the contaminants that build-up as a result of recovery rinsing. When applied in these cases, the atmospheric evaporator hastens the disposal rate of the bath resulting in essentially the same mass of chemicals discarded as if recovery were not practiced. Methods of bath maintenance for process solutions are covered in Section 4.

Atmospheric evaporators should not be applied to solutions that foam significantly when air agitated (e.g., high cyanide baths and still nickels). Such solutions will foam in the evaporation chamber and render the system inoperable. A simple jar test is recommended by one manufacturer to determine if foaming is a potential problem. This test is accomplished by placing a sample of the solution in a jar, vigorously shaking it and then observing to see if the foam quickly disappears (ref. Poly Products file).

3.2.4 Technology/Equipment Description

The equipment described in this section is manufactured by four firms that responded to the Vendors Survey. Three of these companies represent approximately 90% of the total number of atmospheric evaporators purchased by the respondents of the Users Survey (not counting home-made units or in cases where the manufacturer was not given).

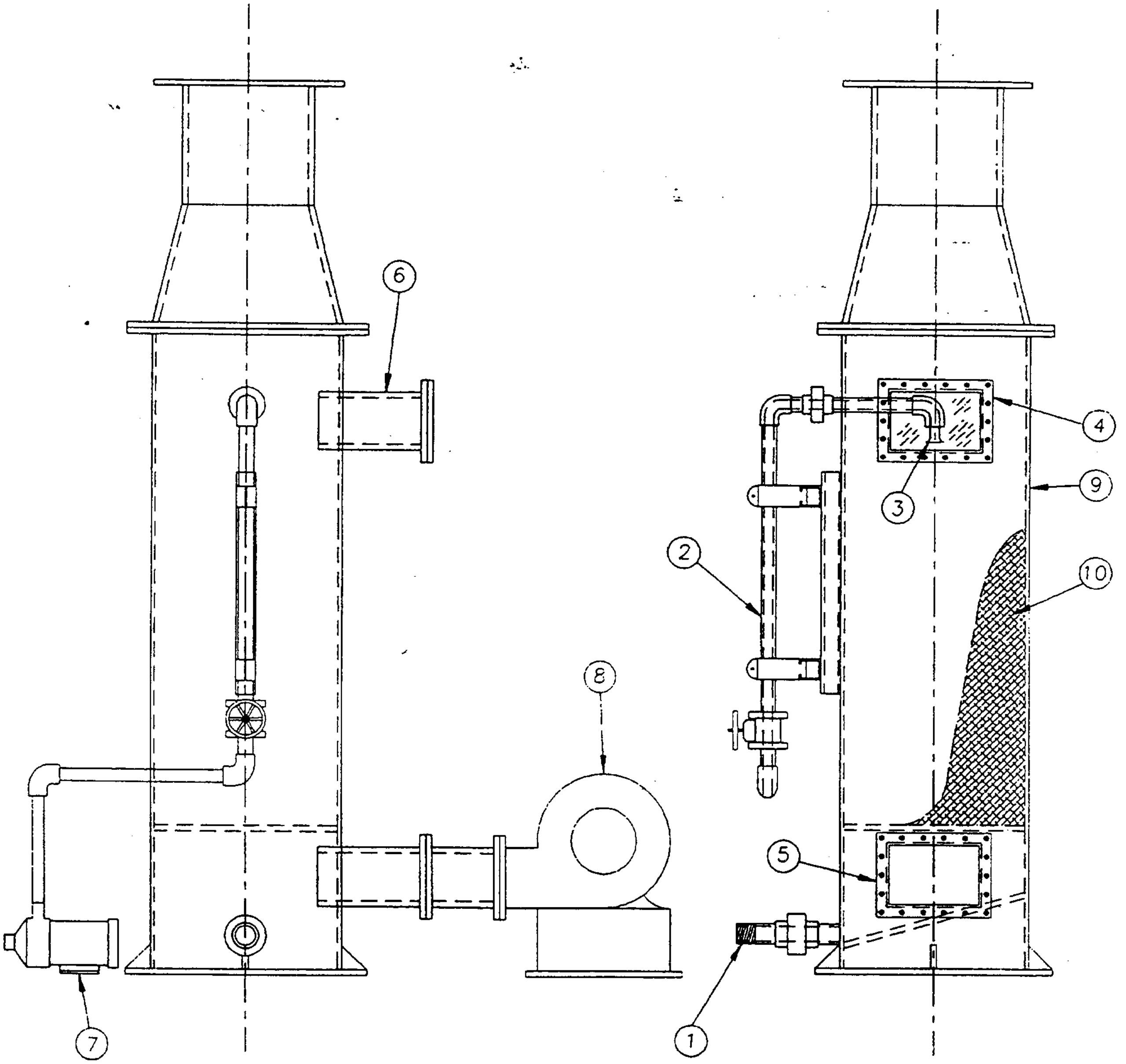
The manufacture of atmospheric evaporators most often found in the Users Survey data is Poly Products Corporation. They manufacture four different models: ET-II Junior, ET-II, ET-III and ET-III-W. The ET-II Junior, ET-II, and ET-III are progressively larger units of the same design. The ET-III-W has a modified design, intended for use with solutions that have a high solids content. Each model has the same basic appearance and operating principles (refer back to Exhibit 3-3). During operation, pumped solution is circulated at approximately 10 to 45 gpm from the process tank or transfer tank to the unit and is gravity drained back to the tank. In the evaporator, solution is sprayed onto 700 to 1,000 ft^2 of evaporative panels to humidify the blower air that is forced through these panels. The air is provided by a blower sized from 1/2 to 1-1/2 hp, depending on the model. The humid air then passes through a chevron mist eliminator to remove entrapped chemical solution droplets and is ducted to the outdoors. Poly Products offers an optional mesh pad mist eliminator to further decrease chemical emissions. The ET units are manufactured of molded polyethylene. The largest ET unit occupies a floor space of 48 in. x 34 in. All models have maximum air temperature limits of 104°F and solution limits of 160°F (ref. Poly Products file).

Techmatic Inc. manufactures the MAX-EVAP™. There are four models available: MAX-EVAP, Super MAX-EVAP, MAX-EVAP Cr and Super MAX-EVAP Cr. The MAX-EVAP and Super MAX-EVAP are general purpose units with advertised evaporation rates of 50 to 60 gph and 80 to 90 gph, respectively. The bodies of these units are manufactured from polyethylene. The MAX-EVAP Cr and Super MAX-EVAP Cr are designed specifically for hexavalent chromium plating solutions. These two models are manufactured from steel and are lined with Koroseal (PVC). As with the operation of the Poly Products line, solution is circulated from the process tank or transfer tank to the unit and is gravity drained back to that tank. In the evaporator, solution is sprayed onto 5 to 10 ft^3 of polyethylene packing. Air is drawn through the unit by the shop's existing ventilation system or air movement is provided by an optional blower. The exhaust air passes through a "vertical extruded mist eliminator" (not defined by manufacturer) to remove chemical mists. The MAX-EVAP unit occupies a floor space of 63 in. x 21 in. and has a height of 31 in. (blower option measures 55 in. high) (ref. Techmatic file).

Kinetic Recovery manufactures a unit with a somewhat different design than the two previously discussed units. With the Kinetic Recovery unit (Exhibit 3-6) the process solution is pumped from its tank up to the liquid distributor of the evaporator which is located at the top of the cylinder. The liquid trickles over a tower packing down to the bottom drain of the cylinder and returns to the process tank. A blower, located at the bottom of the cylinder, blows air (300 cfm) upward through the packing to the top of the evaporator. When the air goes through the packing (pressure drop 0.3 in. of superfacial vapor velocity of 1.5 fps) it becomes saturated with vapor from the process solution. The cylindrical design improves air flow distribution by reducing dead space. On the top of the cylinder there is a vent transition which contains a mist eliminator (12 in. flexi-chevron). There are two view ports located on the unit, one at the liquid distributor and another below the packing. The basic Kinetic Recovery unit is manufactured from polypropylene and they offer construction in PVDF. The PVDF unit operates with a maximum solution temperature of 180°F.

NAPCO manufactures atmospheric evaporators with two basic designs: (1) cross-flow air pattern and (2) vertical air flow pattern. Both types of units are normally constructed of polyethylene, but a variety of plastics are also available, depending on the customers needs. The basic NAPCO unit consists of a blower, recirculation pump, high surface area packing and demister baffling. Numerous options are available, including heating coils, temperature controls, level controls and make-up solenoids and pumps. Their stan-

Exhibit 3-6. Commercial Atmospheric Evaporator with Cylindrical Design (Courtesy of Kinetic Recovery Corporation)



Description:

1 - Discharge
2 - Deed Pipe
3 - Spray Nozzle
4 - Sight Glass
5 - Duct Inlet
6 - View Port
7 - Pump
8 - Blower
9 - Main Cylinder
10 - Tower Packing

dard size units range from 10 gpm process feed/1,200 cfm air flow (NAPVAP Jr) to 30 gpm process feed/4,000 cfm air flow (NAPVAP Sr). NAPCO has been marketing their equipment to the plating industry since 1985 and have sold approximately 160 units to 100 different plating shops.

For each of these four commercial evaporators, the heat used for evaporation comes from the plating or transfer tank (unless a heating coil option is specified). Heat taken from the plating bath must be replaced by the tank heating system (e.g., immersion heaters or steam system) in order to maintain the operating temperature of the bath. Most tank heating systems are designed to provide a quick heat-up and are underutilized after the operating temperature is maintained. Therefore, auxiliary tank heating equipment is usually not necessary when an atmospheric evaporator is installed (unless a transfer tank is also installed). However, each potential installation should be evaluated before purchasing evaporative equipment. Nomographs and methods of calculating tank heating requirements are available in electroplating engineering references (e.g., ref. 341).

The atmospheric evaporators previously discussed are used primarily for chemical recovery, but are occasionally applied to waste concentration. Some evaporators are designed specifically for waste concentration. Two such units include the Technotreat Wastewater Evaporator and the Samsco Water Evaporator.

The Technotreat unit consists of an enclosed carbon steel (stainless steel available) tank equipped with electric immersion heaters (stainless steel or titanium). Liquid waste is fed into the evaporator by a feed pump from a drum or storage tank. The solution level in the evaporator is maintained by a level switch which activates the feed pump. The steam is vented by an assisting electric blower. As water is evaporated, the waste is concentrated. Oil floats to the top and is drawn off periodically. Sludge and viscous materials are removed through a bottom drain. The Technotreat unit comes in 100 and 200 gpd capacities. The range of costs is approximately $10,000 to $15,000 for the standard materials of construction (ref. 360).

The SAMCO Water Evaporator combines direct heating and air flow. The unit consists of an enclosed tank (carbon steel or 304 or 316 stainless steel) that contains a serpentine gas-fired heat exchanger and blower (530 cfm to 2,000 cfm) that draws air in through both the burner and an opening in the top of the tank. In operation, solution is fed to the tank in either a batch or continuous mode. The solution is heated to boiling (approximately 212°F) by the heat exchanger. The action of the blower draws air across the surface of the heated liquid, sweeping away water vapor as it breaks to the surface. The moisture-saturated air and the flue gases leave the tank via separate passages and are joined together at the blower entrance. The two air streams are mixed in the blower and released up a stack. Free oils that float on the surface of the liquid overflow a trough into an external waste receptacle. Solids that settle onto the sloping bottom of the tank are removed via a clean-out port. The SAMCO Water Evaporator comes in three capacities: 15 gph, 33 gph and 63 gph. The area dimensions of the largest unit are 65 in. x 68 in.

Installation of an atmospheric evaporator is a relatively easy task with the exception of the ventilation ducting. The basic units are shipped pre-piped and preassembled. For ventilation, ductwork is usually routed directly to the outdoors through a roof penetration. Alternatively, the exhaust of the evaporator can be connected by ductwork to an existing ventilation system. In this case, an evaporation system blower is unnecessary and the air would be drawn through the evaporation chamber rather than being pushed or blown through. As discussed in Section 3.2.3, this configuration is occasionally used with hard chromium plating.

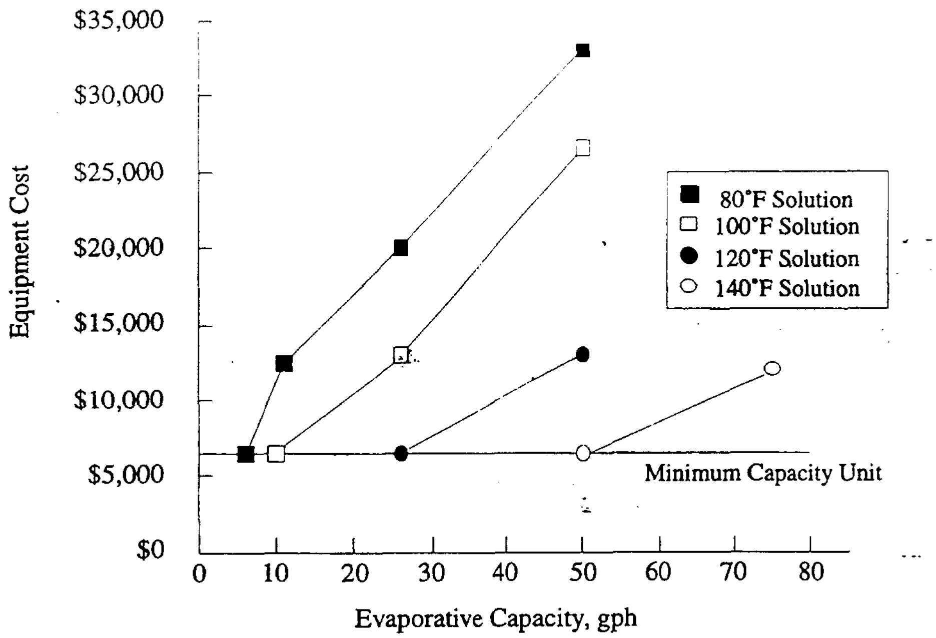
Installation and operation of an atmospheric evaporator may require a new air permit or revisions to an existing air permit.

3.2.5 Costs

3.2.5.1 Capital Costs

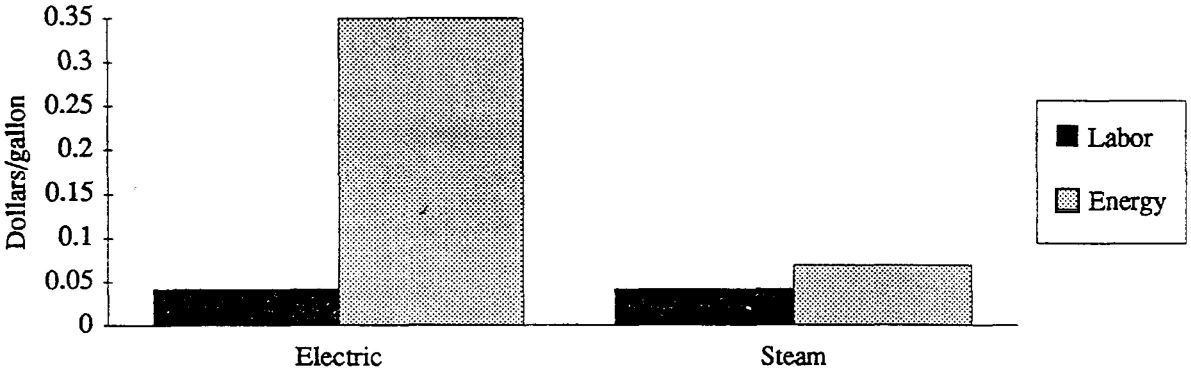
The basic equipment cost for atmospheric evaporators is relatively low. However, all installations will experience some installation costs and most installations will require auxiliary equipment. The most common and significant installation cost is for exhausting the air exiting the evaporator. Ductwork must be run to either to an existing ventilation duct or, more frequently, through a roof penetration. Other installation work includes connecting power and water to the evaporator, rearranging of other equipment or tanks, installation of controls and installation of a transfer tank. Auxiliary equipment may include, for example, a transfer tank, additional recovery rinse tanks, an additional heat exchanger or a DI water system.

Exhibit 3-7. Equipment Costs for Atmospheric Evaporators as a Function of Solution Temperature



Note: Total installed costs (includes basic equipment, auxillary equipment and installation) are approximately 180% of equipment costs.

Exhibit 3-8. Operating and Maintenance Costs for Atmospheric Evaporators



Capital cost estimates for atmospheric evaporators are shown in Exhibit 3-7. These costs are presented as a function of evaporative capacity (gph) over a range of process solution temperatures (either the process tank or transfer tank, whichever is fed to the evaporator). Exhibit 3-7 shows the basic equipment costs, which were derived by taking the median costs from the three vendor survey respondents (where a single evaporator is unable to provide the desired evaporation capacity, multiple units were assumed). The installed capital costs are approximately 180% of the basic equipment costs (based on Users Survey data).

3.2.5.2 Operating Costs

The major operating costs for atmospheric evaporators include O&M labor and energy. Estimates of these operating cost components are shown in Exhibit 3-8. From the Users Survey, the average O&M labor is 157 hrs/yr. In constructing the operating cost graph, it was assumed that this level of labor is adequate for a unit evaporating 15 gph, 24 hrs/day for 260 day/yr. The energy cost shown in Exhibit 3-8 is for replacement heat in the process tank and for operating a pump. The energy cost does not account for energy loss due to ventilation of shop air during winter months.

3.2.6 Performance Experience

A partial summary of the NCMS Users Survey data relative to atmospheric evaporators is presented in Exhibit 3-9. There are a number of observations that can be made from these data and other data contained in the database and literature:

- The majority of shops that have used atmospheric evaporators have found them to perform adequately. The average satisfaction level for this technology is 3.8 (on a scale of 1 to 5, with 5 being most satisfactory), which is the highest level rating for any of the chemical recovery technologies, except for meshpad mist eliminators. Also, 81 percent of the shops indicated that this technology satisfied the need for which it was purchased. The following is a breakdown of the reasons why shops purchased this technology:

To meet or help meet effluent regulations:	46
To reduce plating chemical purchases:	45
To reduce the quantity of waste shipped off-site:	35
To reduce wastewater treatment costs:	39
To improve product quantity:	9
Other:	6

- The use of atmospheric evaporators generally did not impact production quality or the rate of production. The following responses were provided:

	Product Quality	Production Rate
Improved	7	3
No Change	52	53
Decreased	6	9

- Where the product quality was impacted (PS 098, PS 118, PS 139 and PS 306), PS 098 and PS 139 indicated that contaminant build-up occurred in their chromium plating and nickel plating baths and PS 118 indicated that product quality is only impacted occasionally due to low rinse water flows.

- Where the production rate was impacted (PS 098, PS 139, PS 252, PS 262 and PS 306), PS 098 and PS 252 attributed work slowdowns to bath contamination.

- Most plating shops indicated, that based on their experience with this technology, they would purchase the same type of equipment from the same vendor. The following is a breakdown of their responses:

Purchase the same technology from the same vendor:	73%
Purchase the same technology from a different vendor:	12%
Purchase a different technology:	12%
Do nothing:	3%

- The reported savings from use of atmospheric evaporators was mostly due to reduced purchases of plating chemicals. The average annual savings per shop were slightly less than the sum of the average capital costs plus annual operating costs. This indicates, that on the average, shops experienced a payback period of approximately one year.

- Very few survey respondents reported the evaporation rate they were achieving with their atmospheric evaporator. Presumably, this is because such data are not routinely collected. The highest evaporation rate reported by a respondent was 60 to 75 gph (PS 183). Oddly, with this particular application, the shop connected the evaporator to a heated, 150°F cadmium cyanide transfer tank. (This is not a recommended application because heating of the cadmium solution will destroy cyanide and create carbonates.) PS 183 indicated in their survey form that they would have achieved a closed-loop "if it were not for the carbonate problem." For more traditional applications (nickel and chrome operated at 130 to 140°F), the highest reported evaporation rates were in the range of 20 to 50 gph (e.g., PS 228, PS 213).

- Some of the plating shops that gave atmospheric evaporation a lower rating may have misapplied the technology. The most frequent misapplication is the use of this technology for the concentration of ambient temperature process solutions or drag-out. The commercial units do not have a direct heat source, but rather use heat from the process or transfer tank to evaporate water (see complete explanation in Section 3.2.1). When applied to an

Exhibit 3-9. Summary of Users Survey Data for Atmospheric Evaporators

Shop			Year	Equipment Costs			Annual Operating Costs				Annual Savings					Use	Sat.	Future	Shop
Code	Application	Vendor	Purchased	Equip.	Other Cap.	Total	Non-Labor	hrs	Labor	Total	Bath Chem.	Treat. Chem.	Disposal	Other	Total	Code	Level	Decision	Code
003	Nickel, Watts	Poly Products Corp.	1988	$3,985	$5,000	$8,985	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	3	1	003
015	Nickel, Watts	NAPCO	1988	$5,000	$500	$5,500	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	5	1	015
015	Zinc, Non-Cyanide	NAPCO	1988	$5,000	$500	$5,500	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	5	1	015
018	Cr+6, Decorative	In-House	1986	$500	$2,000	$2,500	$250	25	$375	$625	$10,000	$500	$500	$0	$11,000	1	0	1	018
018	Nickel, Sulfate	In-House	1986	$500	$2,000	$2,500	$1,000	100	$1,500	$2,500	$30,000	$1,500	$1,500	$0	$33,000	1	4	1	018
020	Nickel, Watts	Poly Products Corp.	1991	$5,000	$500	$5,500	$500	ND	ND	$500	$6,000	$0	$775	$1,000	$7,775	1	5	1	020
029	Chromate on Aluminum	Gumm Chemical	1989	$5,000	$1,000	$6,000	$1,000	500	$5,000	$6,000	$1,000	$1,000	$12,000	$1,000	$15,000	1	5	1	029
038	Nickel, Watts	Brucer	1985	$3,000	$2,000	$5,000	ND	20	$200	$200	ND	ND	ND	ND	ND	1	3	3	038
040	Cadmium, Cyanide	Poly Products Corp	1985	$5,000	$1,000	$6,000	$100	20	$120	$220	ND	ND	ND	ND	ND	3	1	4	040
045	Nickel, Watts	Max-Evap (2 units)	1989	$5,000	$1,200	$6,200	$400	ND	ND	$400	$20,000	$20,000	$0	$0	$40,000	1	4	2	045
053	Cadmium, Non-Cyanide	Poly Products Corp.	1985	$5,000	ND	$5,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	2	4	1	053
053	Cr+6, Decorative	Poly Products Corp.	1985	$5,000	ND	$5,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	4	1	053
053	Copper, Cyanide	Poly Products Corp.	1985	$5,000	ND	$5,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	4	1	053
053	Nickel, Watts	Poly Products Corp.	1985	$5,000	ND	$5,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	4	1	053
054	Zinc, Acid	Not Given	1989	$10,000	$2,500	$12,500	$100	1	$10	$110	$40,000	$0	$0	$0	$40,000	1	5	1	054
071	Chromium, Hard	In-House	1975	ND	ND	ND	ND	ND	ND	ND	$10,000	$0	$0	$0	$10,000	1	4	2	071
077	Chromium, Hard	Poly Products Corp.	1991	$2,500	$500	$3,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	5	1	077
081	Zinc, Cyanide	Techmatic	1989	$4,300	$1,000	$5,300	$400	20	$200	$600	$1,100	$0	$0	$0	$1,100	1		1	081
089	Brass	Poly Products Corp.	1988	$4,300	$3,000	$7,300	$400	10	$150	$550	$0	$300	$0	$0	$300	1	4	2	089
098	Cr+6, Decorative	Techmatic Inc	1985	$3,000	$6,500	$9,500	$1,000	50	$500	$1,500	$0	$0	$0	$0	$0	1	2	3	098
101	Silver, Cyanide	Not Given	1987	$3,500	$350	$3,850	$2,400	260	$3,900	$6,300	$0	$0	$0	$0	$0	2	2	3	101
105	Nickel	Corrotec (OH)	1992	$6,000	$2,700	$8,700	$1,200	250	$11,875	$13,075	$1,400	$1,800	$700	$1,500	$5,400	1	5	1	105
118	Nickel, Watts	In-House	1989	$110,000	$30,000	$140,000	$15,000	ND	ND	$15,000	$20,000	$2,715	$6,000	$1,300	$30,015	1	5	1	118
139	Nickel, Watts	Napco Inc.	1987	$10,000	$3,500	$13,500	ND	ND	ND	ND	$5,000	$0	$0	$0	$5,000	2	1	4	139
160	Zinc, Acid	Not Given	1988	$4,000	$1,000	$5,000	ND	100	ND	ND	$0	$0	$0	$0	ND	1	5	1	160
172	Cr+6, Decorative	Poly Products Corp	1989	$1,800	$3,000	$4,800	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	3	1	172
175	Nickel, Watts	Poly Products Corp.	1990	$4,500	$2,500	$7,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	4	1	175
181	Chromium, Hard	Kontek Ecology Sys.	1992	$3,200	$1,050	$4,250	ND	ND	$576	$576	$0	$0	$0	$0	ND	1		1	181
183	Copper, Cyanide	Poly Products Corp.	1986	$5,000	$5,500	$10,500	$6,000	ND	ND	$6,000	$4,800	$6,000	$3,000	$2,400	$16,200	1	4	1	183
191	Cr+3, Decorative	Poly Products Corp.	1985	$2,830	$2,494	$5,324	$150	50	$1,000	$1,150	ND	ND	ND	ND	ND	1	5	1	191
193	Cr+3, Decorative	Techmatic Inc.	1982	$12,000	$5,700	$17,700	$3,500	150	$2,250	$5,750	$28,500	$10,000	$0	$16,500	$55,000	1	5	1	193
193	Nickel, Watts	Techmatic Inc.	1982	$12,000	$8,600	$20,600	$3,500	150	$2,250	$5,750	$28,500	$10,000	$0	$16,500	$55,000	1	5	1	193
209	Zinc, Acid	Maxi Vap	1991	$4,000	$500	$4,500	$800	100	ND	$800	$2,600	$2,600	$500	$633	$6,333	1	4	1	209
213	Cr+6, Decorative	Napco Inc.	1988	$7,400	ND	$7,400	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	4	2	213
213	Nickel, Brite	Napco Inc.	1988	$6,500	ND	$6,500	ND	12	$300	$300	$0	$0	$0	$0	ND	1	5	1	213
214	Cadmium, Cyanide	Not Given	1988	$5,000	$2,000	$7,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	2	2	3	214
214	Zinc, Acid	Not Given	1988	$5,000	$2,000	$7,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	2	3	214
224	Nickel, Woods	Maxi-Vap	1986	$4,500	$1,500	$6,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	4	1	224
228	Nickel, Watts	Techmatic	1990	$3,500	$2,000	$5,500	$1,000	ND	ND	$1,000	$30,000	$5,000	$7,500	$0	$42,500	1	4	1	228
239	Cadmium, Cyanide	Not Given	1989	$3,000	$500	$3,500	ND	400	$4,000	$4,000	$2,500	$2,500	$2,500	$2,500	$10,000	1	5	1	239
241	Cr+6, Decorative	Techmatic	1988	$4,000	ND	$4,000	ND	ND	ND	ND	$5,000	$0	$0	$0	$5,000	1	4	1	241
245	Chromium, Hard	In-House	1984	$2,000	$6,000	$8,000	$2,000	15	$195	$2,195	$2,000	$2,000	$2,000	$0	$6,000	1	4	1	245

Exhibit 3-9 (continued). Summary of Users Survey Data for Atmospheric Evaporators

Shop			Year	Equipment Costs			Annual Operating Costs				Annual Savings					Use	Sat.	Future	Shop
Code	Application	Vendor	Purchased	Equip.	Other Cap.	Total	Non-Labor	hrs	Labor	Total	Bath Chem.	Treat. Chem.	Disposal	Other	Total	Code	Level	Decision	Code
247	Zinc, Acid	Poly Products Corp.	1991	$4,700	$2,000	$6,700	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	3	1	247
252	Cr+6, Decorative	Not Given	1987	$7,000	$5,500	$12,500	$3,000	200	$2,000	$5,000	$2,500	$0	$0	$350	$2,850	1	3	2	252
252	Copper, Cyanide	Techmatic Inc.	1987	$7,000	$5,500	$12,500	$3,000	200	$2,000	$5,000	$2,000	$0	$0	$300	$2,300	1	3	2	252
252	Nickel, Watts	Techmatic Inc.	1987	$7,000	$5,500	$12,500	$3,000	200	$2,000	$5,000	$2,000	$0	$0	$350	$2,350	1	3	2	252
254	Z inc, Acid	Not Given	1984	$1,400	$1,000	$2,400	ND	ND	ND	ND	$3,200	$1,600	$5,600	$0	$10,400	1	4	1	254
255	Brass	Poly Products Corp.	1990	$4,600	$1,000	$5,600	$2,000	100	$1,000	$3,000	$2,000	$5,000	$1,000	$0	$8,000	1	4	1	255
255	Cr+6, Decorative	Poly Products Corp	1991	$5,000	$1,000	$6,000	$2,000	100	$1,000	$3,000	$4,000	$5,000	$2,000	$0	$11,000	1	4	1	255
258	Cadmium, Cyanide	Poly Products Corp.	1989	$5,467	$1,200	$6,667	$1,600	12	$180	$1,780	ND	ND	ND	ND	ND	1	4	1	258
261	Alkaline, Ultrasonic	Poly Products Corp.	1992	$6,685	$500	$7,185	$1,000	ND	ND	$1,000	ND	ND	ND	ND	ND	1	4	3	261
262	Cr+6, Decorative	Techmatic Inc.	1985	$5,000	$1,200	$6,200	$500	20	$300	$800	$500	$1,000	$1,000	$0	$2,500	1	3	3	262
278	Dye	Poly Products Corp.	1988	$9,000	$7,000	$16,000	$2,000	120	$1,200	$3,200	ND	ND	ND	ND	ND	3		1	278
279	Zinc, Non-Cyanide	Technic Inc.	1991	$3,500	$1,000	$4,500	ND	ND	ND	ND	$2,500	$0	$500	$0	$3,000	1	3	1	279
282	Cr+6, Decorative	Water Technology	1989	$13,000	$10,000	$23,000	$12,000	1,000	$10,000	$22,000	$0	$0	$0	$0	$0	1	1	3	282
286	Nickel	Napco Inc.	1988	$14,000	$11,600	$25,600	$2,000	5	$250	$2,250	$5,000	$2,000	$750	$750	$8,500	1	4	1	286
293	Zincate	Not Given	1985	$3,000	$500	$3,500	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	4	1	293
298	Zinc, Cyanide	Poly Products Corp.	1992	$5,000	$4,000	$9,000	$500	520	$7,800	$8,300	ND	ND	ND	ND	ND	1	3	1	298
300	Cr+6, Decorative	Poly Products Corp.	1990	$4,985	$2,000	$6,985	$250	ND	ND	$250	ND	ND	ND	ND	ND	1	4	1	300
300	Nickel, Sulfate	Techmatic Inc.	1988	$17,680	$7,600	$25,280	$1,000	ND	ND	$1,000	ND	ND	ND	ND	ND	2	4	2	300
306	Cr+6, Decorative	Not Given	1985	$5,000	$50,000	$55,000	ND	200	$4,000	$4,000	$30,000	$0	$0	$5,000	$35,000	1	5	1	306
306	Nickel, Brite	Not Given	1985	$5,000	$50,000	$55,000	ND	200	$4,000	$4,000	$40,000	$0	$0	$5,000	$45,000	1	5	1	306
306	Nickel, Semi-Brite	Not Given	1985	$5,000	$50,000	$55,000	ND	200	$4,000	$4,000	$40,000	$0	$0	$5,000	$45,000	1	5	1	306
308	Copper, Cyanide	Not Given	unk	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1		1	308
308	Ni, Electroless,Other	Not Given	unk	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1		1	308
314	Zinc, Non-Cyanide	Not Given	unk	ND	ND	ND	ND	ND	ND	ND	$25,000	$0	$0	$0	$25,000	1		1	314
317	Ni,Electroless,Phosph	Napco	1989	$5,000	$4,000	$9,000	$1,000	24	$240	$1,240	$0	$0	$5,000	$0	$5,000	1	3	1	317
	Averages (5)		1987	$7,077	$5,932	$13,009	$2,159	157	$2,254	$4,412	$10,178	$2,013	$1,321	$1,502	$16,230		3.8		

Notes:

(1) Other capital costs include installation and ancillary equipment.

(2) Use Codes: 1-currently operating; 2-not currently operating and no intension for future use; 3-not currently in use, but intend to use in future.

(3) Satisfaction levels (manufacturer and technology) 1 to 5, with 1=lowest and 5=highest.

(4) Future decision codes: 1-purchase the same technology from the same vendor; 2-purchase the same technology from a different vendor; 3-purchase a different technology; 4-do nothing.

(5) Average total equipment cost is the sum of average equipment and other capital costs. Average annual operating cost is the sum of average non-labor and labor costs. Average savings is simply the average of reported savings. This method of calculation probable understates the average annual savings of the users.

(6) ND = no data

ambient solution, very little evaporation will take place. For example, PS 081 attains an evaporation rate of only 3 gph from a unit connected to a zinc cyanide bath that is operated at 85 °F. PS 279 attains a rate of 2 to 5 gph for an ambient acid zinc application. Other plating shops that may have misapplied the technology include (based on a review of supplied schematics): PS 040, PS 045, PS 101, and PS 143.

- The high incidence of misapplication for this technology may be due in part to the fact that 54% of the commercial atmospheric evaporators purchased by survey respondents were sold to them by manufacturer's representatives rather than direct purchases. The manufacturer's representatives may not have had sufficient knowledge of the technology to recommend proper installation.

- In some cases, performance was hampered by operational and maintenance problems. These are discussed in Section 3.2.7.

3.2.7 Operational and Maintenance Experience

The following summarizes the respondents O&M experiences and provides operating labor information relative to atmospheric evaporators.

- The quantity of labor required for the operation of this technology is relatively low compared to other recovery technologies. For shops providing data, the average number of annual operating hours per evaporator were: 157 hours per year. The skill requirement commonly needed for operating this technology is a trained technician, a wastewater treatment system operator, a plumber/pipe fitter or common labor. The following is a breakdown of the responses for skill requirements:

Environmental Engineer:	0
Process/Chemical Engineer:	3
Chemist:	5
Consultant:	0
Plumber/Pipe Fitter:	15
Electrician:	9
Vendor:	1
Senior-Level Plater:	8
Junior Level Plater:	11
Trained Technician:	24
Wastewater Treatment Plant Operator:	16
Common Labor:	16

- Approximately 90 percent of the atmospheric evaporator installations identified in the Users Survey were in operation at the time of the survey. The following is a breakdown of the responses for current operating status:

Currently in use:	89.6%
Not currently in use and have no intention of future use:	7.5%
Not currently in use, but intend to use in the future:	3.0%

- The average percent of downtime experienced with this technology was 7%. Only 15 percent of the respondents indicated that their downtime was greater than 5% (those with greater than 5% downtime included: PS 045, PS 101, PS 105, PS 139, PS 213, PS 239, PS 282, PS 298, PS 300 and PS 317).

- Generally, this technology is free of complex mechanical operational and maintenance problems because of the simple design and limited number of moving parts. There are however, some common maintenance requirements, most of which relate to cleaning. A list of the most frequently reported maintenance requirements follows (the percentage of all respondents identifying the problem is given in parenthesis):

Cleaning of evaporation chamber packing or evaporative panels:	11%
Cleaning of nozzles that spray solution over packing or evaporative panels:	4.7%
Maintaining pumps:	4.7%
Unplugging of pipes:	1.6%
Maintaining timers:	1.6%

- Fifty-seven percent of the plating shops that reported cleaning as a maintenance item have purchased the units equipped with evaporative panels rather than the plastic packing. The company that manufactures the panel-type unit has recently introduced a model that is designed better handle high solids conditions (see 3.2.4). In some cases, the cleaning requirement was blamed on carbonates that precipitated from aerating cyanide containing [redacted] [redacted]

solutions in the evaporator (PS 089, PS 101, PS 239, PS 258). In two other cases, crystals that formed from the drying of plating chemicals were blamed (PS 045, PS 172).

- According to the literature, plating chemical crystals can be removed from the packing and nozzles by a weekly recirculation of hot water through the evaporator with the fan shutoff. Salts that have formed on the nozzles and packing will dissolve (ref. 355). Carbonate deposits present a more significant problem and most likely will require mechanical (e.g., scraping) removal.

- One shop indicated that operation of their atmospheric evaporator for chromium plating solution recovery resulted in degrading of the unit and piping and that the manufacturer has replaced their evaporator twice in the past five years (PS 252). This shop also operates units for cyanide copper and nickel plating and has not experienced any problems with these other units. A leaking problem around welds was reported by another shop (PS 300). Eventually, PS 300 discontinued use of three of their atmospheric evaporation units because of leaking.

- Many shops indicated that use of an atmospheric evaporator has caused a build-up of contaminants in the plating bath. The most frequently identified problem was carbonate build-up in cyanide containing baths such as zinc, cadmium and copper (ref. PS 081, PS 089, PS 183). Respondents also indicated problems with contaminant build-up in chromium baths (PS 089, PS 172, PS 252 and PS 255), and nickel baths (PS 038, PS 105 and PS 139). PS 139 reported a build-up of brightner and iron in their nickel bath. Twice PS 139 has tried evaporative recovery for nickel and abandoned their efforts.

- Other bath problems attributed to use of an atmospheric evaporator include a breakdown of nickel bath chemicals (PS 039) and increased bath chemistry maintenance for trivalent chromium plating (PS 191).

- Several shops reported that climatic conditions effect the evaporative capacity of their atmospheric evaporator (PS 160, PS 183 and PS 224). These three shops are located in different regions (survey regions SE, FW and MW).

3.2.8 Residuals Generation

Most shops using atmospheric evaporators did not report the generation of any residuals. Presumably, this is because most residuals that would form in the evaporator (e.g., carbonates) will, for the most part, gravity drain back to the process tank. Two shops that reported residuals from the evaporator were PS 089 and PS 113. PS 089 uses a home-made evaporator for chromium solution recovery and generates a "minimal" quantity of sludge. PS 089 generates 30 gal/mth of sludge from evaporative recovery of cadmium solution.

Several other shops listed the carbonates removed from their cyanide containing plating solutions as a residual generated by evaporation. Presumably, they feel that the evaporator created this waste product. The most significant quantity is generated by PS 183 (80 lbs/week).

Vacuum Evaporators
in

Pollution Prevention and Control Technology for Plating Operations

George C. Cushnie Jr.
CAI Engineering

A Project Sponsored by the
National Center for Manufacturing Sciences
and Conducted in Cooperation with the
National Association of Metal Finishers

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3.3 VACUUM EVAPORATORS

3.3.1 Overview

Vacuum evaporators are one of the earliest technologies used in the plating industry for chemical recovery. However, vacuum evaporators are currently used less frequently than some other recovery technologies, such as atmospheric evaporators (see Section 3.2). This is primarily due to the fact that the average vacuum evaporation unit costs approximately ten times more than the average atmospheric unit. Also, the vacuum units have more sophisticated and expensive operational and maintenance requirements. Of the 318 plating shops responding to the Users Survey, 23 shops (or 7.2%) have employed vacuum evaporators (30 total units of which approximately 80% were still in operation at the time of the survey) for chemical recovery, whereas, 71 shops (or 22.3%) have used atmospheric evaporators (86 total units). Another six shops (or 1.9%) use vacuum evaporators as end-of-pipe technologies to concentrate their wastes prior to off-site hauling and disposal. This section discusses recovery applications of this technology and Section 6.4.4 addresses end-of-pipe applications.

A vacuum evaporator is a distilling device that vaporizes water at low temperatures when placed under a vacuum.

The following explanation of the kinetic theory of liquids and in particular vapor pressure helps in understanding this phenomena.

Liquids as well as gases are in constant motion in varying degrees, depending upon the chemical composition of that matter and the temperature and pressure applied to it. Molecules near the surface have a tendency to escape into the surrounding atmosphere. In open systems, most of these molecules do not return to the liquid and the substance is said to vaporize. In a closed system, molecules return to the liquid in proportion to their concentration in the gaseous phase. Eventually a steady state is reached where the quantities of molecules leaving and returning to the liquid are equal. The vapor is then said to be saturated and the pressure exerted by these escaping molecules is referred to as vapor pressure (ref. 361). Since the kinetic energy of all molecules increases with increasing temperature, so does the vapor pressure. When a liquid reaches the temperature at which its vapor pressure becomes equal to that of the atmosphere above it, boiling occurs. This is the rapid evaporation from all parts of the liquid mass, with bubbles of vapor forming in the interior and rising to the surface. Liquids with appreciable vapor pressure may be caused to boil over a wide range of temperatures by decreasing or increasing the pressure of the atmosphere above it (ref. 362). For example, water boils at 212°F at sea level, but will boil at room temperature if the pressure above it is reduced to about 0.4 psia (ref. 361).

Vacuum evaporators depend on the fact that water, when introduced into a vacuum, tends to boil off, or vaporize. The rate of vaporization is directly related to the level of the vacuum and the temperature of the solution. In operation, heated solution is introduced into the vacuum chamber, the boiling point of the solution is reduced by the vacuum and the resultant vapor (distilled water) is removed from the chamber. The vapor can be either discharged or can be condensed for return to the process (e.g., as rinse water).

Vacuum evaporation systems are relatively complex and are therefore more expensive to construct and maintain than the more simple atmospheric systems discussed in Section 3.2. There are several types of vacuum evaporators used in the plating industry: rising film, flash type, and submerged tube. Generally, each consists of a boiling chamber which is under a vacuum, a liquid/vapor separator and a condensing system. Site-specific conditions and the mode of operation influence the selection of one system over another.

Two techniques have been applied successfully to reduce steam demand for evaporation; both involve reusing the heat value contained in the vapor from the separator. The most common technique is to use a multiple-effect evaporator. Essentially, these are vacuum evaporators in series with different boiling points, made possible by varying the pressure between effects (subsequent effects have lower pressures). The driving force of a multiple effect system is the pressure drop from the first to the last effect. The solution to be concentrated is fed into the boiling chamber of the first effect and external heat is introduced to volatilize the water. The water vapor is then condensed at a different vacuum level and the energy is used to heat the subsequent vacuum chamber. Therefore, the same energy is used several times in multiple stages.

The second technique is to use a mechanical compressor. With this equipment, the water vapor from the separator enters the suction of the compressor where its temperature and pressure are increased. The vapor is then desuperheated and enters the reboiler. Thus the latent heat of evaporation, normally lost to the condenser is recycled by the compressor, providing a temperature difference across the heat exchanger. The needed energy then comprises only the power for the pressure increase to provide the temperature difference.

There are a number of advantages accruing to vacuum systems. Among them are the fact that they are essentially independent of the requirement to heat and move large volumes of air, thus reducing the air pollution problem, at least when compared to atmospheric systems. Further, they are operated at relatively low temperatures, which could be of considerable importance in systems that handle temperature-sensitive products. Additionally, vacuum systems are advantageous with alkaline cyanide solutions which would build up carbonates more rapidly with atmospheric evaporators because the latter type aerates the solution.

3.3.2 Development and Commercialization

Evaporation has been used for centuries for food and beverage processing. Modern vacuum evaporator design for industrial use dates back to the early 1900's with the development of the rising film evaporator. Plating applications for vacuum evaporators began in approximately 1949, when systems were used to recover chromic acid (ref. 300). The early plating applications were purchased primarily to reduce operating costs through chemical conservation. Subsequently, evaporation was sporadically implemented as a pollution control method in response to local discharge standards. In some cases, this was a sufficient method of meeting the local standards for targeted pollutants such as cyanide and chromium. The early evaporators used for plating applications were the same types of units used by other industry segments (e.g., chemical processing, dairy, food and beverage industries). These units had large capacities, due in part because water conservation and pollution control were less important at the time, resulting in higher flow rates. Also, energy was much less expensive. In 1974, with the advent of rapidly rising energy costs, there began a movement to down-size recovery systems. Coupled with the Federal pollution control standards, first promulgated in 1979, plating shops turned to smaller and more energy efficient vacuum evaporators and the less expensive atmospheric evaporators for chemical recovery. Energy efficiency was achieved by the employment of multi-effect vacuum units and mechanical vapor compression. During the 1980's and early 1990's firms have sought methods of low or zero effluent discharge to reduce their regulatory requirements. As a result, the newer energy efficient vacuum evaporators were applied as end-of-pipe technologies (ref. 300, 375).

There are approximately 25 companies that manufacture and/or supply evaporative recovery equipment applicable to the plating industry. This includes vacuum and atmospheric evaporators for both chemical recovery and waste concentration (ref. 421). Of these companies, three firms have responded to the vendors survey (LICON, Inc., Calfran Int., and QPS Inc.).

3.3.3 Applications and Restrictions

Two common configurations for the application of vacuum evaporators to chemical recovery are shown in Exhibit 3-10. In configuration VE-1, a closed-loop process is achieved using a four stage rinse system with the feed from the first rinse being concentrated by the evaporator and directed to the plating bath. A solution purification step is shown, which removes bath contaminants that would buildup in the bath due to the closed-loop process. Typical solution purification technologies used for this purpose include ion exchange and/or carbon filtration. PS 125 employs this configuration using a cation exchange unit to remove contaminants from its decorative chromium plating rinse water/drag-out. PS 124 has a similar arrangement. PS 082 installed a cation exchange unit and electrolytic purification unit that are connected to a storage tank. The use of multiple-stage rinsing is nearly always required with evaporator applications in order to minimize the quantity of water to be evaporated. The survey respondents used a minimum of two and a maximum of four rinsing stations. The second configuration (VE-2) shows an open process, where a small portion of the drag-out is not recovered. Also shown in VE-2, is a direct bleed from the bath to the evaporator. This may be required for ambient or low temperature baths, where there is a limited surface evaporation rate and insufficient "head-room" in the plating tank to return the concentrated drag-out/rinse water.

Vacuum evaporators are applied to the recovery of a wide range of plating solutions. They are especially applicable in situations where atmospheric evaporators are either technically or economically impractical. This includes: (1) the recovery of heat sensitive chemicals (e.g., cyanide plating baths); (2) the recovery of chemicals that are sensitive to air oxidation (e.g., cyanide plating baths or the stannous tin bath); (3) low or ambient temperature plating solutions where there is no appreciable surface evaporation; (4) the recovery of solutions that contain volatile components; and/or (5) where high evaporation rates (e.g., >20 to 40 gph) are necessary to achieve recovery and atmospheric evaporators become too expensive (i.e., energy cost) to operate (ref. 299).

The results of the Users Survey and Vendors Survey showed that vacuum evaporators are applied to a range of plating and finishing solutions. These identified applications are shown in Exhibit 3-11.

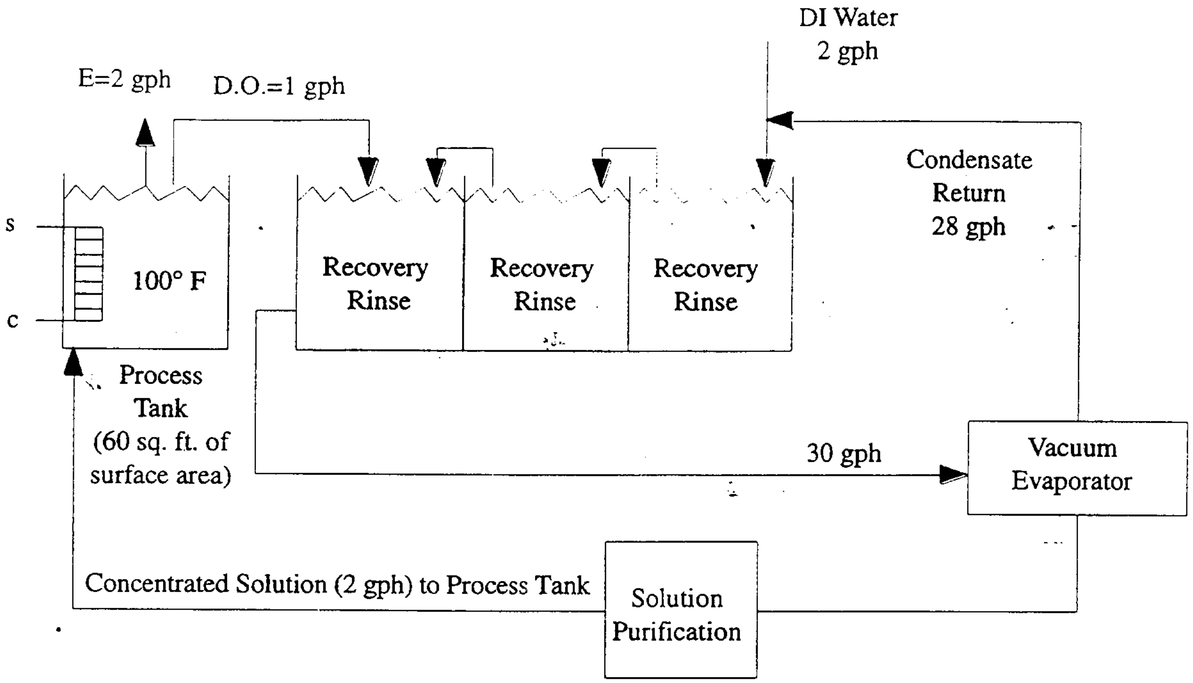
Although vacuum evaporators may provide an energy savings over the atmospheric types of evaporators, neither one is economically practical to purchase or operate where large volumes of low concentration solutions are involved. In those cases, ion exchange or reverse osmosis are the more cost effective methods of recovery (ref. 299).

3.3.4 Technology/Equipment Description

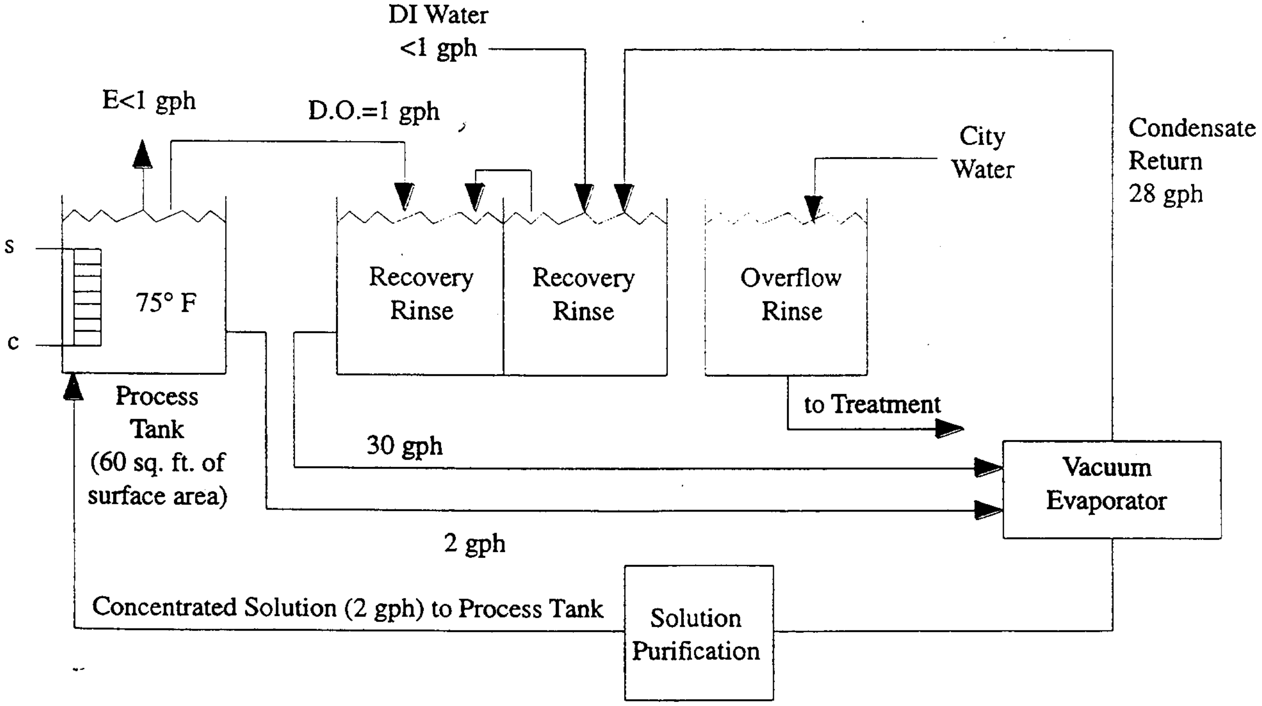
3.3.4.1 General

This subsection discusses commercially available vacuum evaporation equipment that is manufactured and/or sold by vendor survey respondents. This is intended to provide the reader with information and data on a cross section of available equipment. Mention of trade names or commercial products is not intended to constitute endorsement for use.

Exhibit 3-10. Two Configurations for the Application of Vacuum Evaporatrs for Chemical Recovery



Vacuum Evaporation Configuration VE-1: Closed-Loop System



Vacuum Evaporation Configuration VE-2: Open Rinse System

Exhibit 3-11. Applications of Vacuum Evaporation Identified During the Users and Vendors Surveys

	Number of Users Survey Applications[1]	Number of Vendors Survey Applications
Alkaline Cleaners	0	30
Brass, cyanide	0	25
Bronze	0	2
Cadmium, cyanide	3	8
Chromium, decorative (Cr^{+3})	1	0
Chromium, all Cr^{+6}	7	51
Copper, acid	0	11
Copper, cyanide	1	0
Gold	0	20
Lead-tin	1	20
Nickel, electroplating	3	58
Nickel, electroless	0	3
Phosphate	0	8
Silver, cyanide	0	10
Sulfuric acid	0	6
Zinc, acid	0	3
Zinc, alkaline (non-CN)	0	1
Zinc, cyanide	3	65
End-of-pipe concentration	5	80

[1] not all uses of vacuum evaporators by the Users Survey respondents were determined.

There is a wide range in design of vacuum evaporators, although the majority of these devices work on the principles described in Section 3.3.1. Vacuum evaporators are built by various manufacturers for different applications. Exhibit 3-12 classifies vacuum evaporators according to the way water is vaporized. This design element helps to differentiate between some of the commercial equipment available to the electroplater. It should be noted that not all manufacturers of plating evaporation equipment are represented in this exhibit.

As with any technology group, the vacuum evaporation industry has developed their own terminology for their equipment and its components. Some of their commonly used terms are defined in Exhibit 3-13.

The following subsections describe the types of vacuum evaporators that are applicable to the plating industry. Where information is available, specific commercial units are briefly described.

3.3.4.2 Submerged Tube Evaporators

The submerged tube evaporators, which includes the short and long tube vertical (LTV) types and the horizontal tube type, are termed natural circulation evaporators, because no pump or other recirculation device is employed. These units, which are older, but still widely used types of vacuum evaporators, are sometimes referred to as calandria type evaporators. With the basic design (short tube type), a vertical tube bundle is placed inside a vertical cylindrical evaporator shell. The tubes or tube sheets, usually two to six feet in length, span the body diameter. The liquid level in the body is typically maintained such that 50% of the tube sheets are immersed. Liquid circulates through the tubes at a rate many times greater than the feed rate. The liquor travels up through the tubes and down a central pipe called a "downcomer." Steam or water vapor condenses on the outside surface of the tubes and the liquor is heated and boiled inside the tubes. The circulation of the liquid is achieved because of the difference in specific gravity between the liquor and vapor in the tubes plus a vapor lift effect. This combined phenomenon is known as the thermosyphon effect and it is the design basis for all natural circulation evaporators, which includes the falling film types (ref. 376, 422, 423). In some cases, an agitator, located inside or beneath the downcomer, is used to increase circulation in salting-type applications.

Generally, the submerged tube evaporators are less expensive to purchase than rinsing film or flash units of equal capacity. Steam or thermal demand is the same as for rising film (ref. 376). The evaporators find application for processing mildly scaling liquors and relatively viscous solutions (ref. 422).

Exhibit 3-12. Classification of Commercially Available Evaporators for Plating Applications According to the Way Water is Vaporized

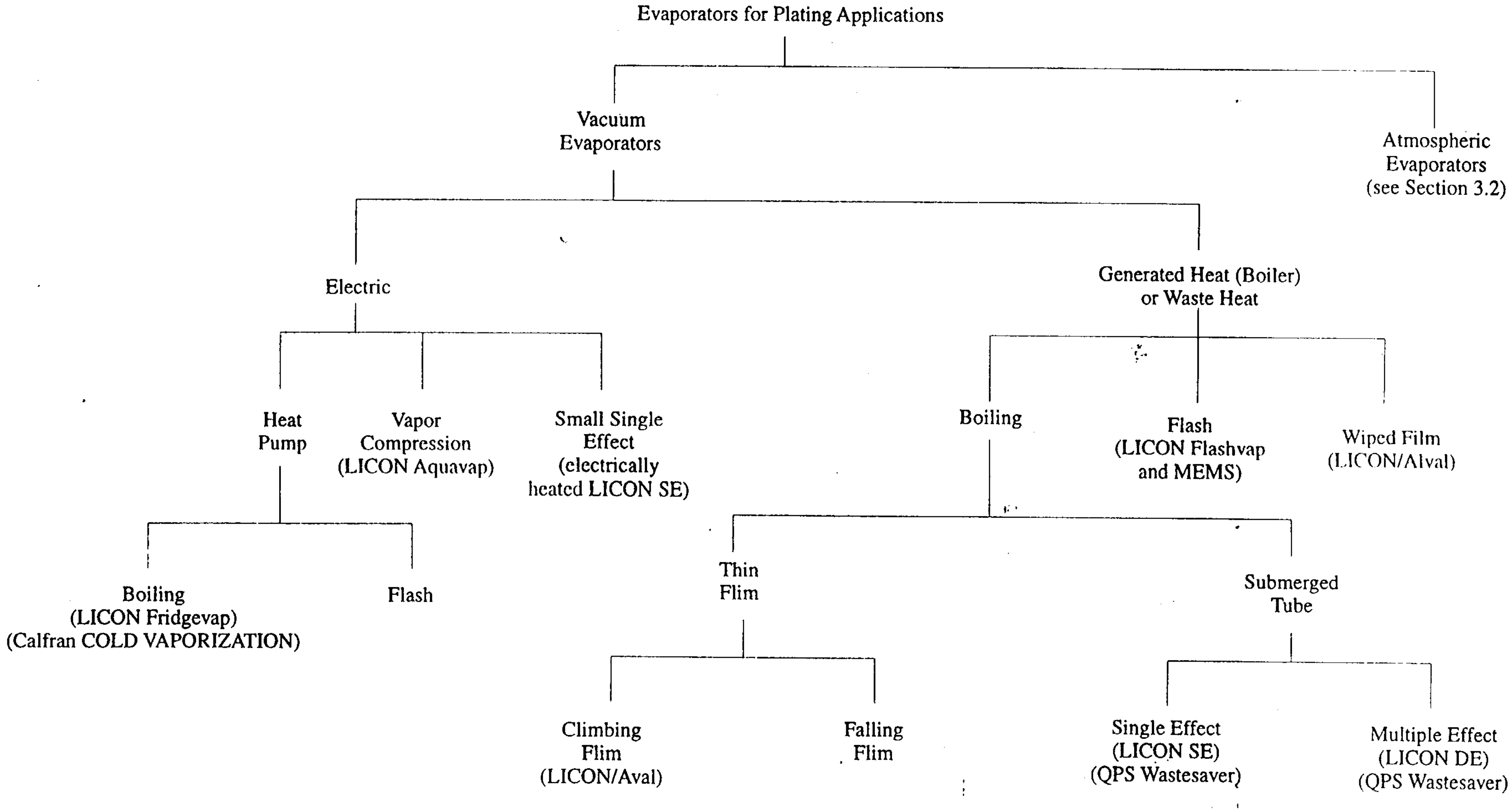


Exhibit 3-13. Common Vacuum Evaporator Terminology

Bodies	Also called vapor heads or flash chambers; the unit where vapor-liquid separation takes place. Also a label given to the basic module of an evaporator, comprising one heating element and one flash chamber.
Calandria	The unit in which heat transfer takes place.
Compression Evaporation	A process in which evaporated vapor is compressed to a higher pressure level and then condensed. The compressed vapor provides heat required for evaporation. Energy economy obtained by multi-effect evaporation can often be equalled in a compression evaporation system.
Condenser	Evaporator equipment used to condense the vapor from the last effect or used as an intercondenser in multi-stage vacuum producing systems.
Cooling Water	Water used in the condenser of an evaporator to condense the vapor phase that exists in the separator. Cooling water can come from cooling towers or reservoirs, or once-through process water can used.
Direct Contact Condenser	Condenses vapors as they are contacted with the cooling medium. There are no heat transfer surfaces and therefore the vapor pressure drop is low. Due to contact with the process solution, the cooling water will require waste treatment.
Effect	One or more bodies boiling at the same time.
Evaporator	The entire system of effects, not necessarily one body or one effect.
Fouling	Formation of deposits other than salt or scale.
Heat Pump	A device in which a refrigerant fluid is continuously circulated through a closed cycle. The gaseous refrigerant is first compressed and then allowed to condense by giving out heat to a cooler environment. The liquid refrigerant is then throttled to low pressure, by means of an expansion valve and allowed to evaporate in another heat exchanger, drawing in heat. The vapor is then circulated to the compressor to begin another cycle.
Intercondenser	A condenser within a multistage system that condenses some of the steam between stages and reduces steam consumption.
Mechanical Compression	Uses a compressor driven by a mechanical drive to compress all the overhead vapors.
Mechanical Pumps	One of two devices (see steam jet ejectors) used to produce a vacuum. More energy efficient than steam jet ejectors but less reliable due to the number of moving parts involved.
Precondenser	A condenser that removes process vapors and permits the use of smaller vacuum pumps.
Refrigeration	Systems that absorb heat not wanted or needed and reject it elsewhere. Heat is removed from the system by evaporation of a liquid refrigerant and is rejected by condensation of the refrigerant vapor.
Scaling	Growth or deposition on heating surfaces of a material that is either insoluble or has a solubility that decreases with an increasing temperature.
Staging	Two or more sections of a single effect evaporator operating at different concentrations.
Steam Jet Ejectors	One of two devices (see mechanical pump) used to produce a vacuum. Jet ejectors usually have lower initial costs, lower maintenance costs (fewer moving parts) but higher operating costs (less energy efficient) than mechanical systems. Multistage jet ejectors (connected in series) improve thermodynamic efficiency.
Surface Condenser	A condenser with a heat transfer surface on which condensing occurs. The heat transfer surface is subject to fouling, corrosion and plugging. Generally more expensive than direct contact condensers. Cooling water is not contaminated with the process solution.
Thermal Compression	Uses a steam jet to compress a fraction of the overhead vapors with high pressure steam.
Thin Film	Thin films of solution are created in evaporators to maximize the liquid surface area per unit volume of flow and therefore facilitate rapid evaporation.

Sources: ref. 373, 374, 423.

LICON Inc., a manufacturer of electroplating evaporation equipment and a Vendors Survey respondent, manufactures single effect and double effect submerged tube evaporators. These devices have been applied to the concentration of chromium (Cr^{+3} and Cr^{+6}), zinc chloride, nickel chloride, nitric acid, and sulfuric acid bearing waters as well as mixed wastestreams (ref. LICON file).

QPS manufactures the Wastesaver® submerged tube evaporator, which is available with either single, double or triple effects. Their newer units have a pumpless liquid transfer system that reportedly eliminates problems commonly associated with mechanical liquid transfer equipment (e.g., pumps, seals, impellers, etc.). These units are manufactured with capacities ranging from 25 gph to 1,500 gph. The basic units are manufactured from stainless steel with titanium offered as an option.

3.3.4.3 Rising Film (Climbing Film)

The basic rising film evaporator consists of an evaporator body, separator and condenser. The evaporator body is a shell-and-tube heat exchanger. Liquid feed enters the bottom of the heat exchanger, it is preheated until it reaches the boiling point and it then moves up the tube. The vapor generated occupies the center of the tube and the liquid is forced to the tube wall. As the fluid travels up the tube, more vapor is formed resulting in a higher central core velocity. The upward velocity of the vapor forces any remaining liquid to the tube wall and continues to provide an upward motion. As the process continues, the higher vapor velocities result in thinner and more rapidly moving liquid films. This design provides a high heat transfer coefficient and relatively short residence time (ref. 373, 375, 376).

Evaporation is typically accomplished at pressures of 1.3 to 7.5 psia (67 to 388 mm Hg absolute), thereby lowering the boiling point to 110° to 180°F (43° to 82°C). The wastewater leaves the body and enters the separator where the water vapor is separated from the heavier plating solution. The plating solution is either returned directly to the bath or held in an integral reservoir. The vapor leaving the separator is condensed in a shell-and-tube heat exchanger and the distillate is directed to the rinse tanks (ref. 376).

Commercially available rinsing film evaporators used in the plating industry are manufactured by LICON/Aval and Corning. Several existing plating applications of rinsing film evaporators identified in the Users Survey were manufactured by the Pfaudler Company.

3.3.4.4 Falling Film

Liquid enters the top of the evaporator and a liquid film is formed by gravity, which then flows down the heat transfer surface. During evaporation, vapor fills the center of the channel and as the momentum of the vapor accelerates, the film becomes thinner. Also, the solution accelerates in velocity as it descends inside the tubes because of gravity and the drag of the vapor. Since the vapor is working with gravity, a falling film evaporator produces thinner films than a rising film evaporator for any given set of conditions. This gives rise to shorter residence times and a further improvement over the rising film types in heat transfer. With these devices, liquid is usually separated from the vapor in the bottom liquid chamber of the body.

The falling-film evaporator is particularly useful in applications involving heat sensitive chemical solutions. This is due to a low "driving force" or temperature difference between the heat-transfer medium and the liquid (ΔT's less than 15°F compared to 25°F or more for the rising film) (ref. 375, 377).

No commercial electroplating applications of the falling film evaporator were identified during the Users or Vendors Surveys, although they presumably exist due to the widespread commercialization of these devices (ref. 373, 377).

3.3.4.5 Wiped Film Evaporator

Feed is introduced at the top of the evaporator and is spread by wiper blades on to the vertical cylindrical surface inside the unit. Evaporation takes place as the thin film moves down the evaporator wall. The heating medium is usually high pressure steam. Use of the wiped film evaporator is limited primarily to highly viscous liquids and the stripping of solvents. The high number of moving parts, such as the rotor and wiper blades, may result in higher maintenance costs than other types of evaporators (ref. 375).

LICON Inc. manufactures a wiped film evaporator (Stratavap) with capacities from 5 to 700 gph, but no plating shop applications were identified in the Users or Vendors Surveys for this device or other wiped film evaporators.

3.3.4.6 Flash Evaporators

Unlike with thin film types (e.g., falling film or wiped film), with flash evaporators, vaporization does not occur on the heat exchanger surfaces. Instead, liquor flashes as it enters a separator, crystallization takes place, and a suspended slurry results. Since evaporation does not take place on a heat transfer surface, the tendency for scale to deposit is significantly reduced. The flash evaporation system can be used in single or multiple effects.

The LICON Inc. Flashvap is sold as an end-of-pipe industrial waste concentrator.

3.3.4.7 Thermal Compressor Evaporators

The thermal compressor evaporators are not, by themselves, a separate category of evaporator. Rather, they are evaporators, such as a rising film type, that uses a steam jet ejector or thermocompressor in order to increase steam economy. They can be designed with either single or multiple effects, although the thermocompressor is normally used on a single effect evaporator or only on the first effect of a multiple effect evaporator. Typically, the addition of a thermocompressor will provide an improved steam economy equal to the addition of another effect, but at lower cost. They should be considered only when high pressure steam is available. Because of their smaller size in comparison to an additional effect, they are favored in applications where space limitations exist. A disadvantage of these units is that the condensate is sometimes contaminated with product traces and may have to be treated, rather than reused as rinse water.

No applications of thermal compression evaporators were identified during the Users Survey or Vendors Survey.

3.3.4.8 Heat Pump Evaporator

A heat pump is a device that upgrades a heat source to a higher temperature, thus rendering it more useful. With conventional evaporator/heat pump operation, a refrigerant, upon boiling, absorbs the heat that would otherwise be rejected in a condenser. The refrigerant vapor is compressed to a pressure adequate to permit the vapor to be condensed in the calandria, thereby providing the heat needed for evaporation. The condensate from the calandria is flashed into the condenser, thereby completing the cycle (ref. 373). The heat pump eliminates the waste of single and double effect designs, but does cost electrical power to operate the heat pump. Therefore, it is not applicable to plating shops where waste heat is available. Also, it is generally confined to small flows (≤ 100 gph) due to the range of heat pumps available.

LICON Inc. manufactures the Fridgevap (3 to 100 gph) heat pump evaporator, in which the solution is evaporated at around 100°F (40°C). This unit finds application where heat sensitive chemicals are involved.

Calfran, Int. manufactures a line of heat pump evaporators that they term COLD VAPORIZATION™. These include the PTU series (immersion coil design) and STU series (reaction vessel type) for applications of 1,000 gpd or less and greater than 1,000 gpd, respectively and the VTU series designed for low solids feed streams (75 to 1,000 gpd). Their basic materials of construction include 316 stainless steel heat exchangers and PVC shells. Their units are also available in all stainless steel design and heat exchangers are available in titanium and Hastelloy.

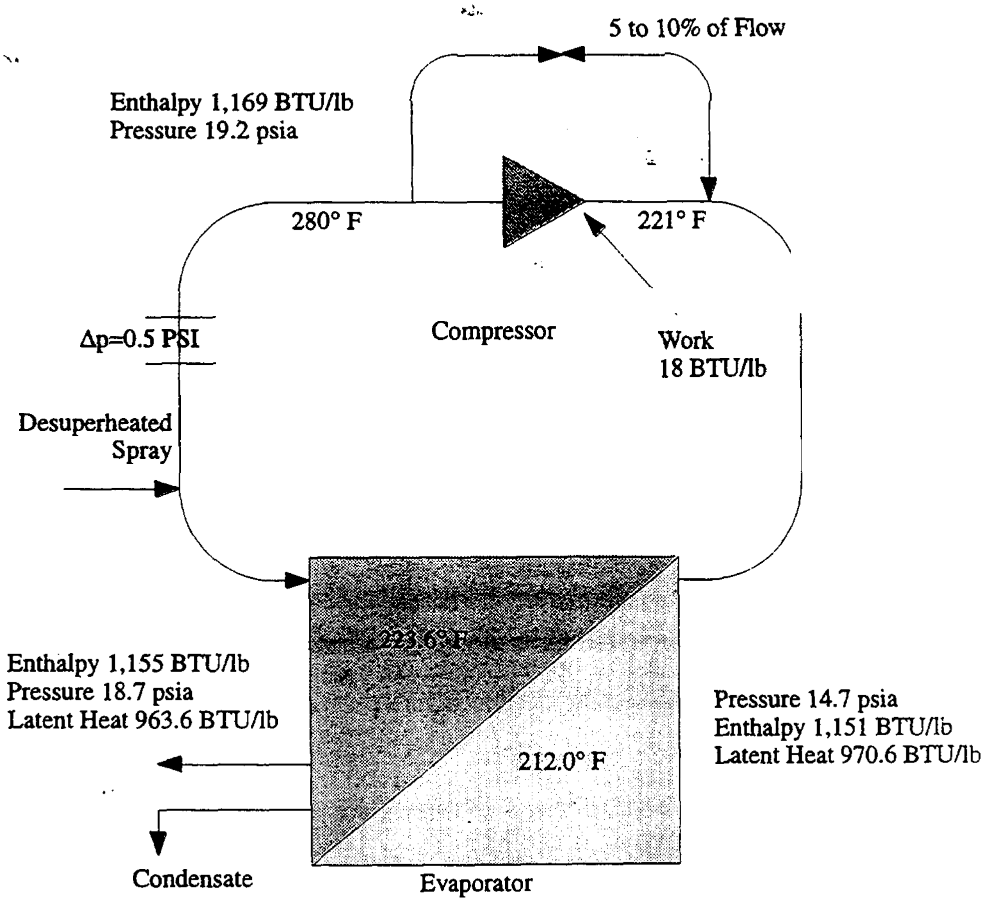
3.3.4.9 Mechanical Vapor Recompression (MVR)

The MVR evaporator is the highest priced evaporator type used in the electroplating industry and it is also the most energy efficient. The MVR evaporator is similar to a conventional single-effect evaporator, except the vapor released from the boiling solution is compressed (adds energy) in a mechanical compressor. This compressed water vapor condenses and gives up its latent heat, which is used to vaporize more water from the liquid that is being concentrated. The following example from the literature shows the potential operating cost savings from using the MVR evaporator (ref. 375).

Exhibit 3-14 shows an evaporator with a liquid boiling point of 212°F (atmospheric pressure). All of the water vapor that is boiled off passes to a compressor. In order to keep the energy input to the system as low as possible, the pressure boost across the compressor is limited. In the majority of cases, this pressure boost will correspond to a saturated temperature rise in the region of 15°F or less. In this example, there is a pressure boost of 4.5 psi across the compressor. Assuming that there is a pressure loss of 0.5 psi in the system, the effective pressure on the steam side of the evaporator is 18.7 psia. This compressed water vapor condenses and gives up its latent heat, which is used to vaporize more water from the liquid that is being concentrated. The latent heat of vaporization of water at atmospheric pressure is 970 Btu/lb. Note that it only requires a theoretical energy input of 18 Btu/lb to raise the water vapor from 14.7 to 19.2 psia. The theoretical steam economy, therefore, is 970/18 = 54. When compressor efficiency is taken into account, this figure is brought down to between 32 and 35 which is another way of saying that the MVR system is equivalent to an evaporator with 32-35 effects (see definitions in Exhibit 3-13). However, when the electricity cost for the compressor drive is taken into account, the MVR system then becomes the economic equivalent of just under a 19 effect evaporator.

The MVR has another definite advantage over steam. The condensate is available at high temperature and is ideal for evaporator feed preheating, particularly if the condensate rate is as high as 90% of the feed rate, i.e., a 10:1 concentration ratio within the evaporator. There are many such evaporators in operation where the sole energy input to the system is through the compressor-with steam

Exhibit 3-14. Mechanical Vapor Recompression Evaporator/Condensor Schematic



Effective Steam Economy:	970 +18 = 54
Efficiency of Drive & Compressor:	65 ---> 72%
Inefficiency due to By-Pass:	5 ---> 10%
Actual Effective Steam Economy:	32 ---> 35 Effects

Effective Steam Economy:	970 + 18 = 54
Efficiency of Drive and Compressor:	65 → 72%
Inefficiency due to By-Pass:	5 → 10%
Actual Effective Steam Economy:	32 → 35 Effects

Source: ref. 375

requirements limited to approximately 15 minutes during start up (ref. 375).

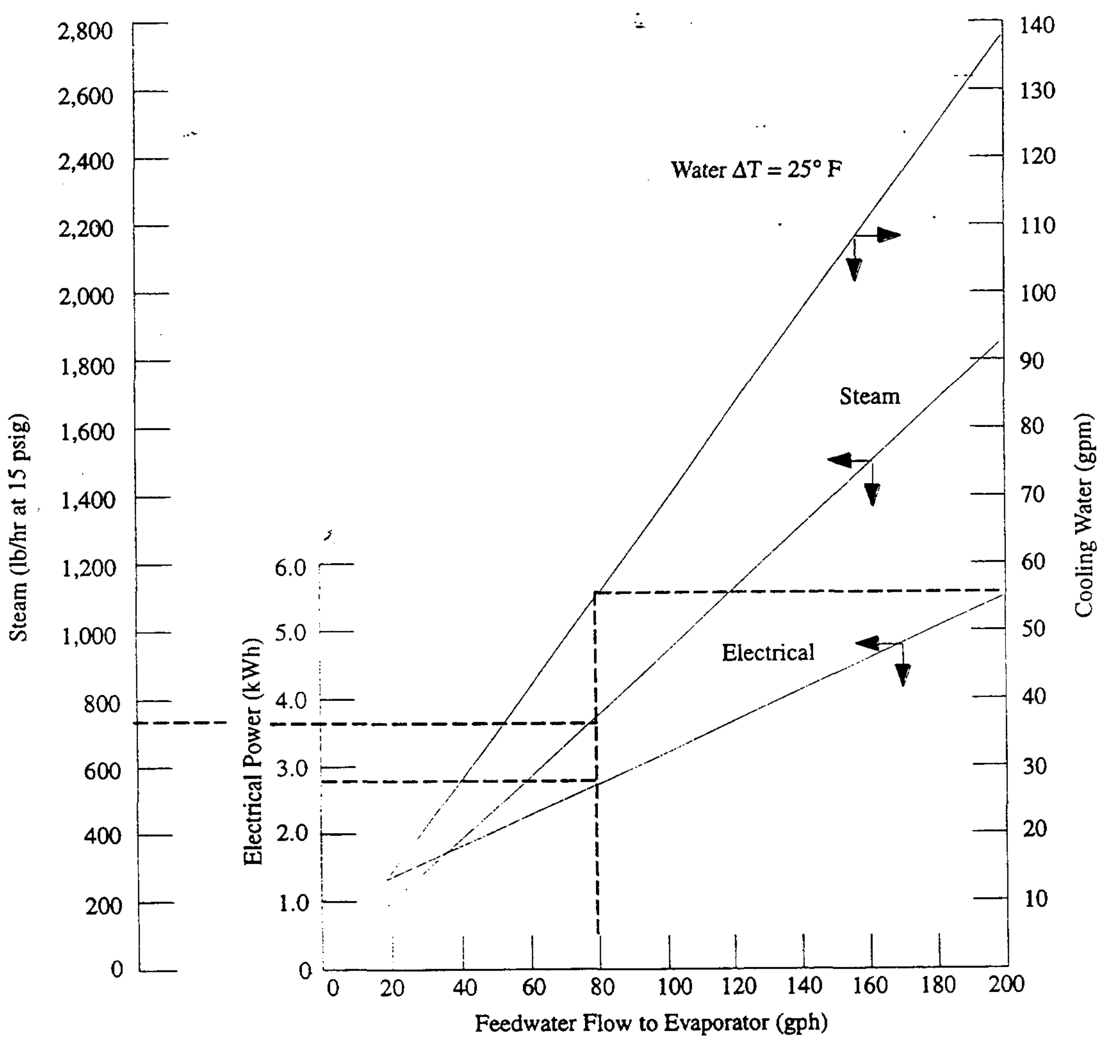
An example of a commercial MVR evaporator used by the plating industry is the LICON Inc. Aquavap. This evaporator has an auxiliary flash stage and is capable of achieving concentrations of 500,000 mg/l or more. Evaporative capacities for the Aquavap range from 50 to 600 gph. Existing plating applications include: concentrations of zinc phosphate rinses (multiple units totaling 1,800 gph), concentration of RO reject (300 gph), and end-of-pipe wastewater concentration (50 to 600 gph) (ref. LICON Inc. file).

3.3.4.10 Multiple Effect Evaporators

Multiple effect evaporators are not a specific type of evaporator, but rather a design element employed to improve the energy efficiency of the evaporation process.

Most evaporators used in the plating industry are single-effect units. Single-effect evaporators operate with one boiler or evaporator section. The water vapor is condensed or exhausted to the atmosphere. Approximately 1.1 pounds (0.5 kg) of steam is consumed in evaporating each pound of water from the plating solution (ref. 376).

Exhibit 3-15. Utility Requirements for Single-Effect Evaporators



Notes: Evaporation at 1.3 psia. Wastewater feed at 100°F. Cooling water supply at 70°F. Steam at 15 psig. Rising film or submerged tube. Example: A single effect evaporator boiling 80 gph of wastewater at 1.3 psia pressure has the following requirments – steam (15 psig), 730 lb/hr; electric power, 2.9 kWh; cooling water at ΔT = 25°F, 56 gpm.

Source: ref. 376

Exhibit 3-15 shows the utility requirements for single-effect evaporators as a function of liquid flow rates to the evaporator. The electrical demand is associated with power requirements of the vacuum pump, recirculation pump, and feed pump. As a rule, the cooling water rates are based on a temperature rise of 25°F (14°C) across the condenser (ref. 376). For example, from Exhibit 3-14, if the wastewater flow rate to the evaporator is 80 gal/hr (303 l/hr), the steam rate is 730 lb/hr (331 kg/hr) for 15 lb/in^2 gauge (1,536 mm Hg absolute) steam. The electrical demand is 2.9 kWh and the cooling water rate is 56 gal/min (212 l/min). For atmospheric evaporators where no cooling water is used, the steam rate would be at least 20 percent higher (ref. 376).

A general application of a double-effect evaporator, is shown in Exhibit 3-16. The basic principle is to use the heat given up by condensation in one effect to provide the reboiler heat for another effect. In the system shown in Exhibit 3-16, approximately 50 percent of the wastewater is concentrated in the first effect using steam. The vapor from the separator of the first effect enters the second-effect reboiler and condenses to provide the thermal energy required to reach the final concentration of the plating solution.

The steam and cooling water rates for the double-effect unit in Exhibit 3-17 are approximately 50 percent of those required for the single-effect unit.

Some platers using double-effect units achieve an additional benefit by recovering two different plating baths simultaneously. However, care should be taken in employing this arrangement however, because there is a possibility of cross-contaminating baths (ref. 376).

Multiple effect evaporation, when used in the plating industry, is most often applied to submerged tube evaporators, rinsing film and flash types (ref. 376). An alternative method for reusing the heat value contained in the vapor from the separator is to employ a mechanical compressor (see Section 3.4.2.9).

3.3.5 Costs

3.3.5.1 Capital Costs

The basic equipment costs and installed costs for vacuum evaporators are indicated in Exhibits 3-18 and 3-19 for heat generated (steam) and electric types. Equipment costs will vary depending on the materials of construction; costs shown are for the basic materials offered by the manufacturer. Evaporators are currently marketed with a wide range of construction materials to resist the corrosiveness of various plating chemicals. The more popular materials include titanium, tantalum, borosilicate glass, stainless steel and carbon steel. Most evaporators are supplied as package units and only require the hook-up of utilities before start-up. However, some ancillary equipment is required (e.g., tanks), which are reflected in the installed costs. The installed cost estimate (140% of basic equipment cost) is based on Users Survey data.

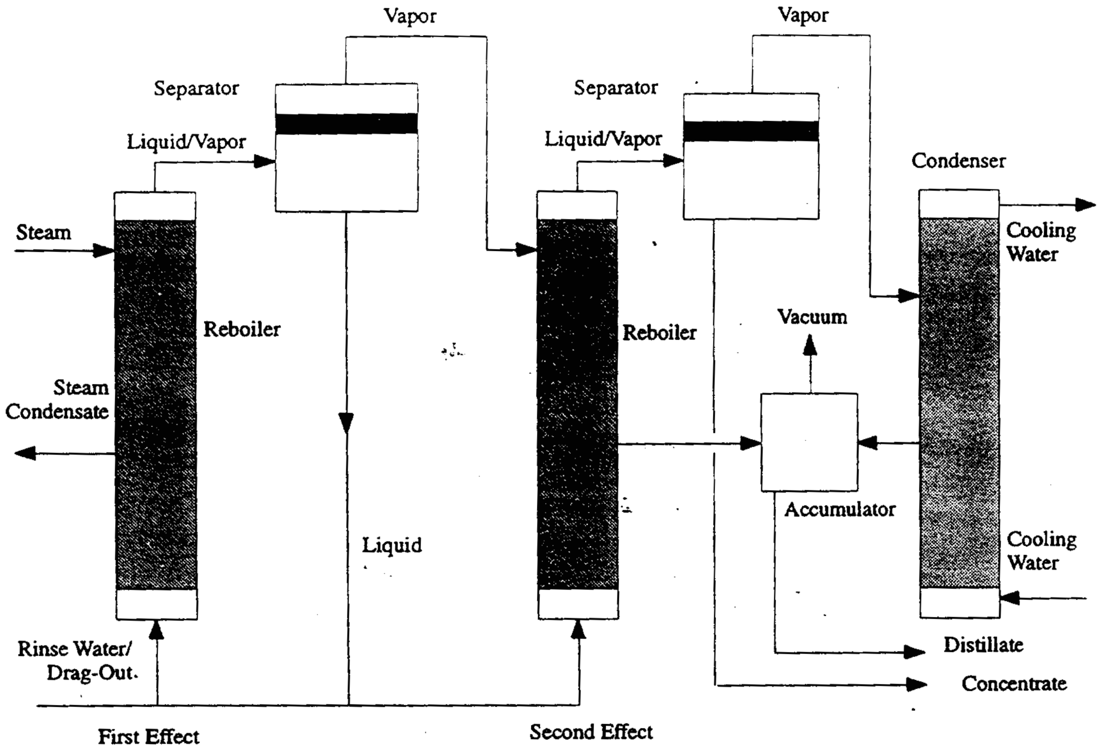
Due to the capital intensive nature of this technology, it is prudent that the buyer make every effort to reduce the flow rate of the feed stream by employing pollution prevention measures. Methods of flow reduction are discussed in Section 2.

When selecting a vacuum evaporator, the plater should consider, in addition to costs, the following: (1) availability, quantity and quality of steam, hot water or waste heat (i.e., if unavailable or insufficient, then choose one of the electric units); (2) cooling water requirements; (3) electrical power requirements; (4) maximum temperature that can be applied to the feed stream (i.e., concern for heat sensitive chemicals); (5) expected feed rate; (6) required solids concentration of product (i.e., how concentrated must the plating solution be before it can be returned to the bath); (7) anticipated use of distillate; (8) materials of construction (depends on both the type and maximum concentration of chemicals); (9) controls (most units have microprocessor controls for automatic operation and manual override); (10) auxiliary equipment requirements (e.g., bath maintenance technologies for removal of contaminants that will be returned to the bath by the evaporator); and (11) O & M requirements (level of expertise required and number of man-hours per year).

3.3.5.2 Operating Costs

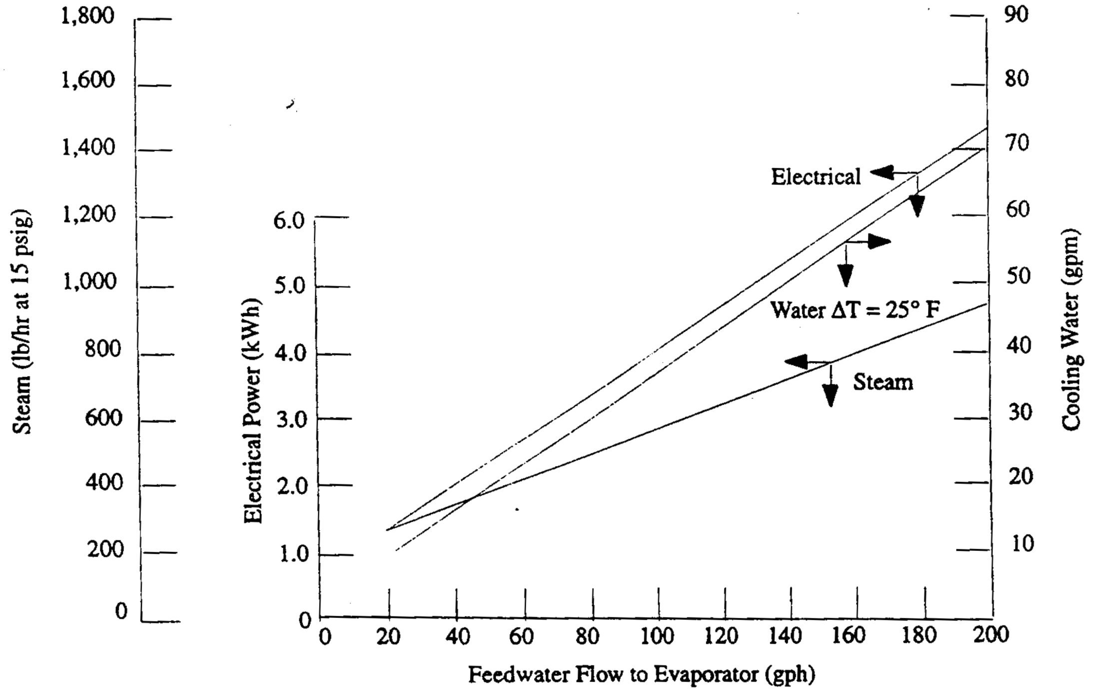
The primary operating costs for vacuum evaporators are labor, energy and cooling water. Energy and operating labor costs per gallon evaporated are shown in Exhibit 3-20. In this exhibit, a distinction is made between operating costs for segregated recovery and the concentration of mixed waste streams (e.g., end-of-pipe). Higher O&M costs can be expected for end-of-pipe applications because the solutions are evaporated to higher solids levels, which increases fouling and scaling.

Exhibit 3-16. Double-Effect Evaporation for Chemical Recovery



Source: ref. 376

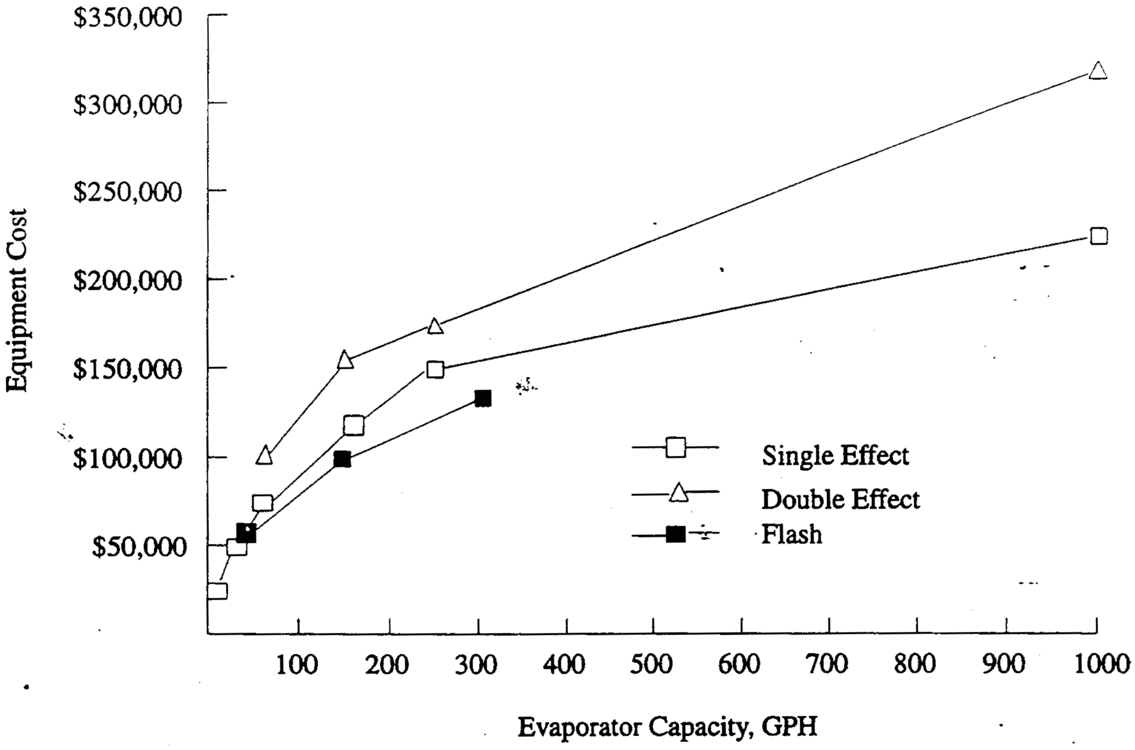
Exhibit 3-17. Utility Requirements for a Double-Effect Evaporator



Notes: Wastewater feed at 100°F; cooling water supply at 70°F; and steam supply at 15 psig.

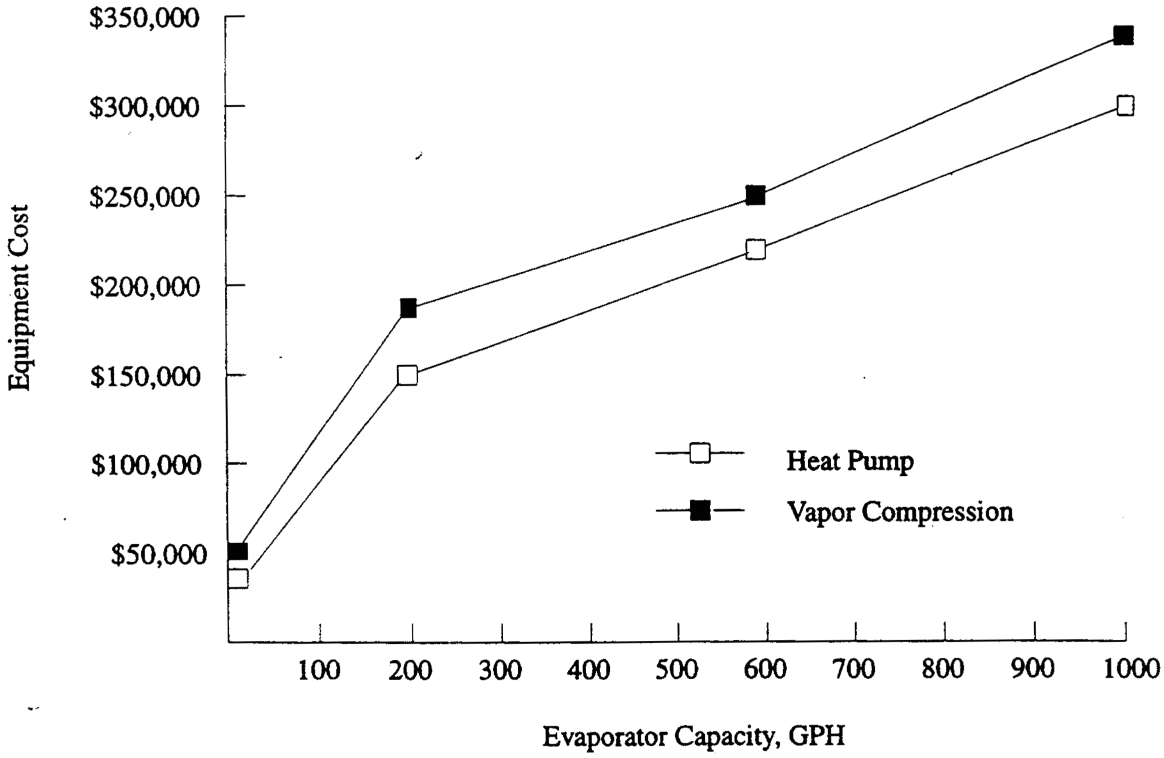
Source: ref. 376

Exhibit 3-18. Equipment Costs for Steam Type Vacuum Evaporators



Note: Total installed costs (includes basic equipment, auxillary equipment and installation costs) are approximately 140% of equipment costs.

Exhibit 3-19. Equipment Costs for Electric Type Vacuum Evaporators



Note: Total installed costs (includes basic equipment, auxillary equipment and installation costs) are approximately 140% of equipment costs.

Exhibit 3-20(a). Operating and Maintenance Costs for Vacuum Evaporators (Segregated Recovery)

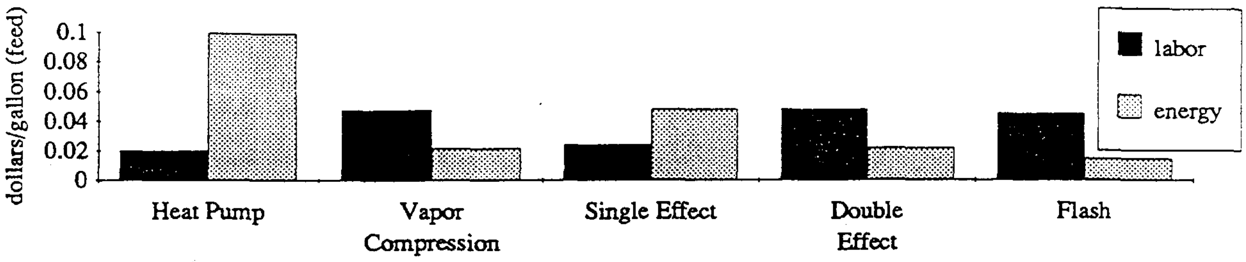
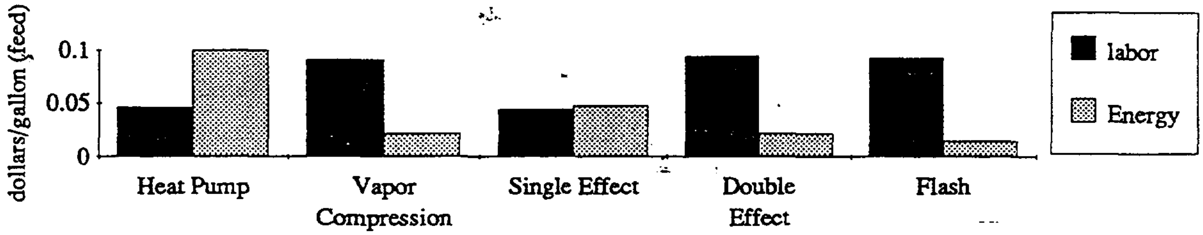


Exhibit 3-20(b). Operating and Maintenance Costs for Vacuum Evaporators (Mixed Waste Concentration)



3.3.6 Performance Experience

A partial summary of the user data relative to vacuum evaporation is presented in Exhibit 3-21. There are a number of observations that can be made from these data and other data contained in the database and literature:

- The average satisfaction level for chemical recovery applications is 3.5 (on a scale of 1 to 5, with 5 being most satisfactory), which higher than the average rating for all recovery technologies. Seventy-five percent of the shops using vacuum evaporation for chemical recovery indicated that this technology satisfied the need for which it was purchased. The following is a breakdown of the reasons why shops purchased this technology:

To meet of help meet effluent regulations: 14
To reduce plating chemical purchases: 12
To reduce the quantity of waste shipped off-site: 12
To reduce wastewater treatment costs: 11
To improve product quantity: 0
To close-loop a particular process: 1

- Vacuum evaporators were successful for most applications identified in the Users Survey except for zinc-cyanide plating solution recovery. The average annual savings from using vacuum evaporators exceeded the sum of the average capital cost plus the average annual operating cost. The most significant savings were derived from reductions of bath chemical and treatment chemical usage.

- The use of vacuum evaporation as a recovery technology generally did not impact production quality or the rate of production for the survey respondents. The following responses were provided:

	Product Quality	Production Rate
Improved	1	1
No Change	13	13
Decreased	2	0

- PS 298 indicated that use of their evaporator decreases product quality because their distillate is contaminated and not adequate for good rinsing. PS 102 also indicated that their unit decreases product quality.

- The respondents indicated, that based on their experience with this technology and, if given the opportunity, they would:

Purchase the same technology from the same vendor: 12
Purchase the same technology from a different vendor: 4
Purchase a different technology: 3
Do nothing: 0

- Two of the respondents indicated that their vacuum evaporation system was the cause of an effluent compliance excursion (PS 039 and PS 088). PS 280 did not respond to the ques-

Exhibit 3-21. Summary of Users Survey Data for Vacuum Evaporators

Shop			Year	Equipment Costs			Annual Operating Costs				Annual Savings					Use	Sat.	Future	Shop
Code	Application	Vendor	Purchased	Equip.	Other Cap.	Total	Non-Labor	Hrs	Labor	Total *	Bath Chem.	Treat. Chem.	Disposal	Other	Total	Code	Level	Decision	Code
034	Zinc, Cyanide	McDermit	1980	$35,000	$8,000	$43,000	ND	250	$5,000	$5,000	$500	$200	$1,000	$2,500	$4,200	3	2	2	034
039	Zinc, Cyanide	Waste Saver	1975	$50,000	$4,000	$54,000	$9,000	400	$2,400	$11,400	$5,000	$0	$0	$0	$5,000	2	1	2	039
082	Cr+6, Decorative	Pfaudler	ND	$150,000	$25,000	$175,000	$50,000	1,000	$15,000	$65,000	$130,000	$115,000	$30,000	$0	$275,000	1	4	1	082
088	Cadmium, Cyanide	Pfaudler	1982	$23,000	$2,050	$25,050	$10,000	500	$6,000	$16,000	$9,900	$15,000	$5,000	$0	$29,900	1	4	1	088
102	Copper, Cyanide	McDermid	1972	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2	4	3	102
123	Lead-Tin	Calfran	1991	$60,000	$2,000	$62,000	$6,912	2,080	$14,560	$21,472	$214,700	$0	$34,260	$0	$248,960	1	4	1	123
124	Cr+6, Decorative	Coming	1980	$108,210	$0	$108,210	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	4	1	124
125	Cr+6, Decorative	In-House	1985	$35,000	$10,000	$45,000	ND	200	$2,600	$2,600	$18,500	$0	$0	$0	$18,500	1	4	1	125
125	Nickel, Watts	In-House	1985	$70,000	$210,000	$280,000	$15,000	200	$2,600	$17,600	$38,000	$0	$0	$0	$38,000	1	4	1	125
132	Cadmium, Cyanide	Coming	1981	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2	1	3	132
143	Cadmium, Cyanide	Water Vap	1992	$10,000	$500	$10,500	$3,000	ND	ND	$3,000	$0	$0	$500	$1,000	$1,500	1	4	1	143
196	Cr+3, Decorative	Coming	ND	$240,000	$25,000	$265,000	$10,000	200	$2,000	$12,000	$450,000	$15,000	$12,000	$18,000	$495,000	1	4	1	196
197	Cr+6, Decorative	Macdermid Inc.	1979	$44,646	$56,890	$101,536	$28,565	2,920	ND	$28,565	ND	ND	ND	ND	ND	1	4	1	197
197	Nickel, Watts	Macdermid Inc.	1978	$41,521	$56,950	$98,471	$40,017	2,920	ND	$40,017	ND	ND	ND	ND	ND	1	4	1	197
197	Nickel, Watts	Macdermid Inc.	1979	$54,172	$56,960	$111,132	$40,016	2,920	ND	$40,016	ND	ND	ND	ND	ND	1	4	1	197
213	Chromium Etch	Coming	1988	$80,557	ND	$80,557	ND	ND	ND	ND	ND	ND	ND	ND	ND	2	5	1	213
275	Cr+6, Decorative	Coming	1984	$75,000	$6,500	$81,500	$10,000	250	$4,250	$14,250	$200,000	$200,000	$38,000	$0	$438,000	1	4	2	275
280	Chromium Etch	Coming	1990	$90,000	$8,000	$98,000	ND	ND	ND	ND	$16,400	$80,700	$10,000	$0	$107,100	1	4	3	280
298	Zinc, Cyanide	Wastesaver Corp	1991	$43,000	$29,000	$72,000	$15,600	780	$7,800	$23,400	$31,000	$13,000	$0	$3,000	$47,000	1	2	2	298
	Average		1983	$71,183	$31,303	$100,644	$19,843	1,125	$6,221	$21,451	$92,833	$36,575	$10,897	$2,042	$142,347		3.5		

PS 082 purchased their unit used.

PS 088 purchased their unit second hand, but unused.

Notes:

(1) Other capital costs include installation and ancillary equipment.

(2) Use Codes: 1-currently operating; 2-not currently operating and no intension for future use; 3-not currently in use, but intend to use in future.

(3) Satisfaction levels (manufacturer and technology) 1 to 5, with 1=lowest and 5=highest.

(4) Future decision codes: 1-purchase the same technology from the same vendor; 2-purchase the same technology from a different vendor; 3-purchase a different technology; 4-do nothing.

(5) "√" indicates that a savings was realized, but not quantified.

(6) ND = no data

tion. All other respondents indicated that their vacuum evaporation system was not the cause of an effluent compliance excursion.

- Several respondents provided the following quantitative performance data:
    - PS 082 indicated that the supplier stated capacity of their unit is 300 gph and that the actual capacity is 175 gph.
    - PS 123 has an evaporation rate of only 6 gph. It is used to make head-room in their tin-lead plating tank so that recovery rinsing can be used. The feed to their unit (tin-lead plating solution), has a concentration of 16 to 18 oz/gal and the concentrated return has a concentration of 32 to 36 oz/gal.
    - PS 088 indicated that the capacity of their unit is 60 gph and that they are able to operate their cadmium plating process on a closed-loop basis. Their drag-out rate is 1.5 gph and they have a three stage counterflow rinse system feeding the evaporator. The cadmium bath is operated at 75°F and there is essentially no surface evaporation.
    - PS 124 indicated that their unit has a capacity of 90 gph.
    - PS 125 indicated that their unit has a capacity of 100 gph.
    - PS 196 indicated that both the supplier stated capacities and actual capacities of their units (3) were 90, 75 and 50 gph.
    - PS 213 indicated that both the supplier stated capacity and actual capacity of their unit was 75 gph.
    - PS 298 indicated that their "unit does not meet levels stated in promotional" and that the "quality of distilled water is poor." The supplier stated capacity of their unit is 100 gph and the actual capacity is 70 to 80 gph.
- PS 132 indicated that their evaporator "never performed as sold." No details of their problems were provided.
- PS 034 expressed their feelings about their unit as follows: "Poor design, good technology."

3.3.7 Operational and Maintenance Experience

The following summarizes the respondent's O&M experiences and provides operating labor information relative to vacuum evaporators.

- The average number of annual man-hours spent for operating and maintaining a vacuum evaporation unit were: 657 hrs/yr. The skill requirement commonly needed for operating this technology is trained technician or a wastewater treatment plant operator. The following is a breakdown of the responses for skill requirements:

Environmental Engineer:	1
Process/Chemical Engineer:	1
Chemist:	1
Consultant:	1
Plumber/Pipe Fitter:	4
Electrician:	4
Vendor:	1
Senior-Level Plater:	4
Junior Level Plater:	1
Wastewater Treatment Plant Operator:	8
Trained Technician:	9
Common Labor:	1
Other:	0

- The most frequent and significant operational and maintenance problems identified with vacuum evaporation include: (1) mechanical problems with pumps; (2) damage to components by aggressive plating chemicals; and (3) contamination build-up in the plating bath.
- Approximately 26% of the total number of vacuum evaporation units reported in the survey forms are no longer in use. On the average, these units were purchased 16 years ago. Of those units still in use, the average age is 6 years. The oldest working unit was 14 years old.
- PS 034 indicated that they have weekly problems with their pump and vacuum system.

They attribute the pump problems to improper design. PS 039 also indicated that they problems with the vacuum pump. On a second unit, PS 039 had problems with the eductors. They have abandoned use of both of these units.

- Although they have installed both ion exchange and electrolytic purification, PS 082 indicated that they have trouble keeping their chromium bath free of contaminants because of the closed-loop recovery process. PS 102 used their unit for 4 years and then abandoned its use because of plating bath (copper, cyanide) contamination. PS 125 is experiencing a build-up of sodium and chloride in their nickel bath.

- PS 088 reported that their cooling water was too warm in the summer to effectively condense the vapors and operate their system.

- PS 088, which employs a four stage counterflow rinse prior to evaporation, indicated that users of this technology should concentrate on reducing rinse water flow and the resultant feed to the evaporator.

- PS 124 indicated that they need to clean the condenser of their unit approximately twice per year.

- PS 124 indicated that the maximum feed concentration to their unit is 1 oz/gal CrO_3 (presumably because higher concentrations will etch the glass of their Corning evaporation unit.) PS 196 reported some etching of their glass unit. PS 280, which operates a Corning unit with a fluoride bath, indicated that this application results in a shorter than average equipment life-span and higher maintenance costs. Their unit is three years old.

- PS 125 indicated that they must operate one of their units at <150°F because of nickel brightener considerations (nickel plating) and the other unit at ≤140°F due to fluoride considerations (decorative chromium plating).

- PS 196 indicated that they must operate their unit at >150°F to boil the chromium solution.

- PS 298 indicated that their distillate is sometimes contaminated beyond the limit for good rinsing. When this occurs, they recycle the distillate to the first rinse rather than the final rinse of their 3 stage counterflow rinse system. This results in a need to blow down rinse water to the treatment system.

3.3.8 Residuals Generation

Vacuum evaporators used for the recovery of plating chemicals create three streams: (1) the concentrate, which is reused in the plating bath; (2) the distillate, which is reused in the rinse system; and (3) cooling water, which is recycled using a cooling tower, reused as rinse water or discharged to the sewer. Cooling water requirements were previously described in Exhibit 3-145and 3-17.

Only two respondents indicated that they generate any residual wastes other than the three streams mentioned. PS 143 indicated that they generate approximately 30 gal/mth of sludge, which they mix with their other F006 sludge and sent to off-site recycle. This sludge is generated from the treatment of the distillate (cyanide oxidation, precipitation, filter press and sludge dryer), which they do not send to the rinse tanks. PS 298 reported that carbonates collect at the bottom of the evaporation chamber forcing periodic removal. They remove approximately 100 lbs/mth of this material and treat it on-site.

The Evaporator—A Great Tool, but No Free Lunch

by Peter L. Veit
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Veit, P.L. 1989. *The Evaporative Recovery Applied to a Nickel Plating Operation.* Metal Finishing 87(11): 31-34.
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One of the most effective tools in the area of resource recovery and waste treatment is the evaporator. These devices come in various sizes and degrees of complexity. They have been used in the chemical manufacturing industry, for sea water purification, and in the metal finishing industry for recovery for many years. They are devices for concentrating significant volumes of solution to smaller volumes by means of evaporating the solvent. In the metal finishing industry, that solvent is water. The product of the evaporator is always a concentrate. A byproduct of some types of evaporators may also be distilled water.

When applied to the area of metal finishing waste treatment, evaporators have a number of advantages and disadvantages as compared to other technologies. Some of these are self-evident, while others are frequently misunderstood, both by the prospective user and frequently even by the vendor selling the equipment. It is the purpose of this paper to identify some of these advantages and disadvantages in general, and to provide some of the basic information required for better understanding of this concept. There will be special emphasis on the total energy costs.

This paper will limit its consideration to the metal finishing or plating operations, and generally disregard the chemical manufacturing industry, even though the latter has had greater use of this technology and on a much larger scale.

EVAPORATORS—HOW AND WHERE APPLIED

The evaporator serves to concentrate the drag-out from various process solutions and allows the subsequent return of that drag-out to the process tank. This can be done without the addition of other chemicals or the formation of intermediate products or sludges.

There are two primary types of evaporators. Both serve to either concentrate the collected drag-out from static or counterflowing rinses, or they are used to evaporate a portion of the actual process solution in order to make tank room for the return of the concentrated drag-out. The latter frequently becomes necessary where the process solution is operated at or near room temperature with little or no inherent evaporation.

Evaporators, by their very nature, are generally relatively high energy intensive mechanisms. Therefore, where the intent is waste treatment or resource recovery, those rinses or drag-out solutions intended for evaporation must at the outset have a reasonably high product concentration. Evaporators are not practical where large volumes of very low concentration waters are involved. In those cases, ion exchange, reverse osmosis, or electrodialysis are by far the more cost effective and practical means of concentrating the effluent. In some of the high volume cases, even precipitating, settling, and resolubilizing may be the more expedient procedure.

Evaporators should also not be confused with drying devices, which produce a solid or semisolid product. While both evaporators and dryers apply the principle of volatilization of the water, the latter are specifically designed to address the problems inherent with handling the resultant solids from the drying process. By contrast, the evaporators considered here are employed to reduce the waste stream volume to a lesser amount, but not to one with a greater concentration than ½ to ¾ of the product solubility (i.e., a material which at room temperature has a solubility of 1 lb/gal should never be concentrated in an evaporator to greater than 8 to 12 oz/gal).

In order to achieve a high initial starting concentration and the low required volume for cost effective evaporator utilization, the use of counterflow rinsing or stagnant rinsing is almost always a must. The principles of counterflow rinsing, and the dramatic water flow rate reduction achievable through this technology, is well known and has been described in the literature by such authors as Joseph Kuschner and George Herrmann, and date back to the late 1940s. Therefore, counterflow rinsing will not be discussed in detail here, other than to present two formulas frequently employed to determine the required water flow rates. These rates are based on drag-out volumes, drag-out concentrations, time, and the desired rinse water quality in the last or final rinse. Similar mathematical formulas have been regularly published in the *Metal Finishing Guidebook*.

Flow Rate:

$$Q = \frac{D}{M}\left(\frac{C_o}{C_n}\right)^{1/n}$$

Concentration last rinse:

$$C_n = C_o\left(\frac{QM}{D}\right)^{-n}$$

C_n = Conc. of contaminant in nth countercurrent rinse tank
C_o = Conc. of contaminant in drag-out
D = Drag-out (gal or liters)
M = Time over which drag-out is measured (min)
Q = Flow rate (gal/min or liters/min)
n = Number of countercurrent rinse tanks

TYPES OF EVAPORATORS

Evaporators fall into two general categories, namely:

1. Vacuum evaporators—both single and multistage (or multieffect).
2. Atmospheric evaporators.

The basic difference between vacuum and atmospheric evaporators is the fact that the first is essentially a vacuum distilling device operating almost independently of air flow, while the atmospheric evaporator is entirely governed by air flow and temperatures.

The actual design of evaporators can

vary from the very simple to the very complex and sophisticated, with the latter having many control devices. The design selection depends upon the specific requirements which need to be addressed. Even a simple, open top, heated, and exhausted process tank (such as an air agitated nickel solution) may be considered to be a very basic atmospheric evaporator.

The vacuum systems depend on the fact that under various levels of vacuum conditions, there is a direct boiling off, or vaporization, of the liquid. Rates depend entirely on the severity of vacuum, the vapor pressure, the heat input, and the boiling point of the water resulting at those vacuum levels.

Vacuum evaporators themselves further fall into two categories, single effect and multiple effect; however, all vacuum types, whether single or multiple effect, still should be considered as devices for distillation. Climbing film or other techniques to enhance the surface areas and interface are largely system refinements which do not change the basic principle.

Atmospheric evaporators, on the other hand, depend upon the amount of air at specific temperatures which can be brought into contact with the water at specific temperatures. The air is saturated and then discharged from the evaporator to the atmosphere outside the plant. Discharging an atmospheric evaporator inside the plant will raise havoc with the plant's humidity, and is therefore not acceptable.

Please note that theoretical physicists might violently object to these descriptions as oversimplifications; however, for all practical purposes, especially with respect to selecting a unit, these concepts are valid.

Both systems are governed by the basic laws of physics:

1. The first of these is that it requires approximately 1,000 BTU of energy to convert one pound of water (at its boiling point) to one pound of water vapor at that boiling point. This is true no matter what that boiling point may be, and whether evaporation takes place under vacuum or under pressure.

2. The second law is based on vapor pressure and vacuum. The fact is that as the atmospheric pressure in a vessel is reduced (i.e. as a vacuum is created), the boiling point is reduced. The stronger the vacuum, the lower the boiling point. For example, even a nickel plating tank at 140°F, with the necessary replacement energy input, at Denver's elevation will have a considerably higher evaporation rate than that same nickel tank at sea level in New York City. In commercial vacuum process equipment, naturally higher vacuums than Denver's are formed, and thus much lower boiling points are achieved. Double effect devices make use of the higher differential.

VACUUM EVAPORATORS

Basically, vacuum evaporators provide one or more vacuum chambers in which the boiling point of the water is reduced to encourage volatilization. These units do not require air volumes of any significance, and generally produce distilled water as a byproduct. Units built by various companies will differ in design primarily in such areas as vacuum pumps, liquid entry, vapor removal and recondensation, agitation, heat source, concentrate removal, and surface area enhancement methods. Some also require cooling water to condense the vapor phase. Others use chillers and condensers, and thus preserve a major portion of the energy using power mainly to drive the compressors. The chiller's hot side heats the liquid, the cold side condenses the vapor, and then recovers a large portion of the heat of vaporization.

The primary advantages of vacuum evaporators are:

1. They have the ability to operate at comparatively low temperatures which prevents the deterioration of temperature sensitive products. This can be very critical in certain chemical manufacturing operations. In metal finishing, conceivably there could be less thermal cyanide decomposition and resultant carbonate build-up by using vacuum evaporators operating at or near ambient temperatures.

2. Vacuum evaporators are relatively safe on products which are sensitive to air oxidation because the solution is not exposed to large aeration effects. A typical case in point would be the recovery of stannous tin plating solution, which might be oxidized in an atmospheric evaporator to the stannic state. That in turn, could create solubility problems. Similarly, products which could absorb impurities such as carbon or sulfur dioxide or sulfides from the air stream, would be less exposed in a closed vacuum system.

3. Since vacuum evaporators are essentially independent of air movement, there is little possibility of their inadvertently acting as air stripping devices of any volatile components found in the product stream. This minimizes possible air pollution problems.

4. Multi-effect evaporators are vacuum evaporators in series. Because of the differing boiling points made possible by varying the levels of the vacuum, multiple energy utilization is possible. The product stream to be concentrated is introduced into the first chamber at one level of vacuum. External heat is introduced to volatilize the water. The water vapor is then condensed at a different vacuum level and the energy is used to heat the subsequent vacuum chamber. By this means, the same BTUs are used several times in multiple stages. In addition, multiple effect vacuum techniques are also used with chillers and condensers to provide a broader temperature gradient. Chillers, by acting as the heat source and the condensing medium, often produce surprisingly high energy efficiencies; however, there is a direct relationship between the complexity of a multistage evaporator system and its energy efficiency.

In order to achieve the multiple effect (or even a single effect using compressor/condenser heat sources) a rather sophisticated, well designed and well built piece of equipment is required. One must then be prepared to deal with vacuum pumps, vapor seals, tight temperature gradients, pressure regulators, and similar automated components. Thus, not everyone can design and build such a unit, and not every maintenance department can keep one running successfully.

Complex, multi-stage evaporators are primarily found in the chemical manufacturing industries where the chemical process is the controlling factor for the volume of water to be evaporated, and where that volume cannot be reduced by such plating expediencies as counterflow rinsing. After the initial equipment costs, energy costs are the primary expense for evaporators. Thus, when significant volumes of water need to be evaporated, multi-effect evaporators become the only economically viable methodology.

ATMOSPHERIC EVAPORATORS

Atmospheric evaporators are basically simple, both from the conceptual design and from the standpoint of maintenance of the various components.

Such devices basically consist of a tank, a spray compartment with packing to assure maximum liquid-air interface, a blower, a pump, a heat source, and some controls. Once properly designed and built of the correct materials of construction, maintenance of the unit should be possible for any maintenance department that can keep a pump and a blower running.

Originally, atmospheric evaporators were developed from modified fume scrubbers. To these, somewhat sophisticated temperature, level, and electrical control systems were added, as was an external heat exchanger to raise the spray temperatures. On today's market there are a number of very simplistic devices, often made from molded PVC or polyethylene components, which are shipped in prepiped and preassembled form. In the field, they are put both on process tanks to make room for the return of static drag-out rinses, or they are applied to counterflow rinses. Different plating processes require separate evaporators. Recovery is usually not possible if differing solutions are mixed.

ENERGY CONSIDERATIONS:

Because of their very simplicity, atmospheric evaporators are also subject to a great deal of misunderstanding, especially with respect to their energy consumption. There is a very high level of "sex appeal" for any prospective purchaser when all he needs to do is add a number of units at less than $6,000 each to the plant, get back all his solution, and generate no sludge. After all, each unit only requires a 1 hp blower, a ⅓ hp pump, and a little ductwork.

Since multiple effect is not possible, the rules of 1,000 BTU/lb of water is the controlling operating factor and energy cost must be considered. One gallon of water weighs 8.3 pounds. Thus each gallon of water to be evaporated requires 8,300 BTU of energy (assuming 100% efficiency). Furthermore, the air passing through the evaporator must also be heated to be able to hold a sufficient amount of water vapor to achieve the desired volume reduction.

Usually the source of heat is steam, although electric and/or gas can also be utilized. To fully appreciate the energy usage, one must realize that unless the plant is located in the Arizona desert on a 120°F day, with 5% relative humidity, the plant must provide all the BTU or energy input to:

1. Evaporate the required amount of water @ 1,000 BTU per pound (8300 BTU per gallon).
2. Heat the outgoing air from ambient (or incoming) to discharge temperatures sufficient to hold the water.
3. Allow for the boiler efficiency to convert oil or gas to steam.
4. Allow for the heat exchanger efficiency (whether the latter is internal or external).
5. Allow for the heat lost in the steam condensate (unless the latter is returned to the boiler).

There is no free lunch!

It must also be clearly understood that the evaporator will take the heat from somewhere, or it will simply not evaporate the required volume of water.

There are a number of available heat sources from which to draw:

1. The plating solution, which in turn must be reheated.
2. The air from the room, which must then be reheated (visit Chicago in January at −10°F and exhaust some 3,000 to 5,000 cfm of air). Room make-up air must be heated; it is not free.
3. From direct heat input into the evaporator. (Steam, electric, or gas).

AIR MINIMIZATION:

Since heating the make-up air is often a major factor in the actual cost of operating an atmospheric evaporator, good design calls for the minimizing of the air volume required. This can be achieved by evaporating at as high a spray temperature as feasible. The data below was extrapolated from the psychrometric chart published by The General Electric Co. This shows that one pound of air will hold 0.015 pounds of water at 70°F. By comparison, that same one pound of air will hold 0.22 pounds of water at 150°F. The curve relating pounds of air moved to pounds of water held to temperature rises significantly at 120°F, and goes up from there. Below 100°F, the curve is rather flat.

Another reinforcing factor for higher spray temperature operation is the capacity of the air on very humid days to hold additional quantities of water. If 90°F air at 90% relative humidity is heated to 150°F, it will hold an additional 0.193 pounds of water per pound of air. Therefore the humidity factor of incoming air plays a much lesser role, than were one to try to evaporate at room temperature on humid days.

THE EXCEPTION THAT MAKES THE RULE

Sometimes, on very rare occasions, the nonexistent "free lunch" does make an appearance. Some years ago the writer was involved in the design of several fairly large evaporator systems to be used on automatic hard chromium plating systems. In one of these cases:

1. The chromium solution needed cooling to the extent of removing 6 million BTU/hour. (The energy source)
2. The chromium tank needed exhausting. (The air source)
3. Waste treatment was required. (The recovery opportunity)

The available 6 million BTUs provided the energy for an evaporation rate in the order of 10 to 12 gpm. By using direct solution cooling, we achieved that evaporation rate. Make-up water, in turn, was fed into the system through four counterflow rinses. Accordingly the system cooled the plating solution, provided four countercurrent rinses at 10 to 12 gpm, and utilized and scrubbed the exhaust air from the chrome plating tanks which provided the air for the evaporator.

The system was rather complicated and costly, but the energy to run it was free.

SUMMARY

The principal advantages and disadvantages can be summarized:

ADVANTAGES OF EVAPORATORS:

1. Very high recovery rates, in the order of 90 to 99%, can generally be achieved with basically simple systems.
2. No additional reagents, which might impact on the total dissolved solid content of the plant discharge are required.
3. No sludges are generated.
4. Frequently, the drag-out can be reused directly in the process from whence it came.
5. Evaporators can usually be operated on a dedicated basis, one for nickel, another chrome, etc.

DISADVANTAGES OF EVAPORATORS:

1. The primary disadvantages are

high initial costs in capital equipment for the sophisticated, energy efficient vacuum or multiple effect units. A high quality, 1,000 gal/day evaporator can cost in the order of $60,000 and will require competent maintenance to keep it running.

2. The high total energy operating costs are the main drawback for the atmospheric evaporators.

3. Rinses from cleaners, acid pickles, chromating, and phosphating solutions generally do not lend themselves to evaporative recovery. Thus, additional waste treatment equipment is also needed.

4. It is necessary that the amount of water requiring evaporation be kept to an absolute minimum by such technology as intermittent fog rinses, counterflow rinsing, good drainage practice, air blow offs, etc. If this cannot be done, as in an older plant or on an existing automatic plating machine, evaporators may not represent an economical approach.

The purpose of this paper is not t discourage the use of a very valuabl and useful tool for waste treatment ar resource recovery. Rather, we encou age its use. It is suggested, howeve that a thorough and knowledgeable re view be made of evaporative tech niques as compared to other waste trea ment or recovery methods. M

Biography

Peter L. Veit i president and prin cipal engineer o TSR Engineerin Co. of Broadview IL, and holds a BS degree in metallurgical engineering from the Polytechnic Institute o Brooklyn.

For further information on this article, contact the author at TSR Engineering Co., 2600 Lexington St. Broadview, IL 60153. Tel: 312/345-8877.

ATMOSPHERIC EVAPORATIVE RECOVERY APPLIED TO A NICKEL PLATING OPERATION

POLLUTION PREVENTION PROGRAM
NORTH CAROLINA DEPARTMENT OF ENVIRONMENT, HEALTH, AND NATURAL RESOURCES

James G. Martin
Governor

William W. Cobey, Jr.
Secretary, EHNR

FEASIBILITY STUDY OF AN ATMOSPHERIC EVAPORATIVE RECOVERY APPLICATION TO A NICKEL PLATING OPERATION

BRIAN E. WELLS
PLANT ENGINEER

AUGUST 20, 1987

PREPARED FOR
DEPARTMENT OF NATURAL RESOURCES
AND COMMUNITY DEVELOPMENT
RALEIGH, NORTH CAROLINA
UNDER CONTRACT C-1615

ILCO UNICAN CORP.
400 JEFFRIES ROAD
ROCKY MOUNT, NORTH CAROLINA 27801

THE POLLUTION PREVENTION PROGRAM

The Pollution Prevention Program provides free technical assistance to North Carolina industries and municipalities on ways to reduce, recycle and prevent wastes before they become pollutants. This non-regulatory program addresses water and air quality, toxic materials, and solid and hazardous waste. Designated as the lead agency in waste reduction, the Program works in cooperation with the Solid Waste Management Division and the Governor's Waste Management Board. The services and assistance available fall into the following categories:

Information Clearinghouse. An information data base provides access to literature sources, contacts, and case studies on waste reduction techniques for specific industries or waste streams. Information is also available through customized computer literature searches. Waste reduction reports published by the Program are also available.

Specific Information Packages. The staff can prepare facility or waste-stream-specific waste reduction reports for industries and communities. Information provided by the facility is used to identify cost-effective waste reduction options. A short report detailing these options is provided along with references, case studies, and contacts.

On-site Technical Assistance. The staff can provide comprehensive technical assistance through facility visits. During an on-site visit, detailed process and waste stream information is collected. The information is analyzed, and a series of waste reduction options are identified. A report is prepared detailing these options and includes literature, contacts, case studies, and vendor information.

Outreach. The staff can give presentations on pollution prevention to industries, trade associations, professional organizations, and citizen groups. Depending on the audience, these programs range from an overview of the State's Pollution Prevention Program to in-depth discussions of technologies for specific industries.

Challenge Grants. A matching grant program provides finds for the cost of personnel, materials, or consultants needed to undertake pollution prevention projects. Projects eligible for grant funds range from characterizing waste streams in order to identify pollution reduction techniques to conducting in-plant and pilot-scale studies of reduction technologies.

For information or technical assistance contact:

Pollution Prevention Program
N.C. Department of Environment, Health, and Natural Resources
Post Office Box 27687
Raleigh, North Carolina 27611-7687

Telephone: (919) 571-4100

TABLE OF CONTENTS

ACKNOWLEDGEMENTS

We gratefully acknowledge the Department of Natural Resources and Community Development, for providing Ilco Unican Corp. the opportunity to perform this feasibility study.

I would personally like to thank David Ellis for his technical assistance in test preparation, test operations, and data collection.

Tom Maude, Dick Kriesel and their respective staff assisted in providing high quality engineering and maintenance services to the program.

Also, Paul Singelyn, Vice President of Techmatic, Inc., Nashville Tennessee, manufacturers of the MAX-EVAP $^{\text{T.M.}}$ Atmospheric Evaporator for his guidance during installation and technical assistance provided.

SUMMARY

A process feasibility study was successfully performed on an Atmospheric Evaporator System for the Department of Natural Resources. The study was made to determine the feasibility of a closed-loop rinse system on an electroplating line. Atmospheric evaporation is a process that converts liquid into a vapor and is discharged to the atmosphere.

Results indicate that an atmospheric evaporator system successfully reduced head-space in the electroplating tanks sufficient to provide use of the rinse water to replace the evaporated water. Reuse of the rinse water effectively contained constituents of the electroplating bath that are normally discharged to the pretreatment system and subsequently disposed. These favorable results indicate that an adequately designed low-cost atmospheric evaporator system could be utilized to close the loop. The closed loop would eliminate any pretreatment of rinse water and disposal of sludge. Also recovery of the valuable constituents is achieved.

INTRODUCTION

Ilco Unican Corp., the world's largest key blank and security product manufacturer operates a plant in Rocky Mount, North Carolina. The facility in Rocky Mount primarily produces key blanks. Approximately 80% of the key blanks produced are nickel plated. The nickel plating process like many other plating processes produce rinse waters containing inorganics which are hazardous wastes under current EPA regulations.

In recent years Ilco Unican Corp. has processed the rinse waters by several methods. The most recent method has been neutralization by adjusting the pH, clarification by floculation, settling, filtration and compaction of the sludge generated, and then disposal of the sludge to a hazardous waste landfill. Considerable costs and liability are incurred using this method.

Ilco Unican Corp. presently nickel plates approximately 800,000 keys daily. The pretreated rinse waters generate approximately 12,500 pounds of compacted sludge every 90 days. Although the pretreatment system is virtually automated, considerable labor costs are incurred in handling the sludge. The filter press requires dumping two times weekly. Approximately six man-hours are required to make each dump. The annual labor costs including overhead is estimated at $14,480.00. A monthly roll-off container is rented to hold the sludge at a cost of $3,000.00 annually. Transportation of the container to the landfill in 1986 was $3,351.00, and disposal cost $4,300.00.

A study performed by North Carolina State University (Reference 1) in 1984, based on a total of 115,910 pounds/year indicated the approximate value of the metal was $9,220.00. Since this study Ilco Unican Corp. has reduced the amount of sludge generated annually through waste minimization efforts by decreasing the percent of water. Based on the 1983-84 approximate dollar value of metal, approximately $4,000.00 annually of metals are discarded.

When you add this all up, $29,131.00 annually is either spent or destined in handling the sludge. This does not take into consideration liability associated with the waste and compliance costs associated with the EPA regulations. As EPA regulations become more stringent with regards to landfilling hazardous waste, EPA required waste minimization programs and the costs associated with hazardous waste, Ilco Unican Corp. must attempt to research all feasible recovery means.

Electrodialysis and Electrolytic Recovery are certainly means that can be used. However, both systems are very expensive and maintenance costs are high. The objective of this study was to demonstrate the feasbility of applying an Atmospheric Evaporation System to Ilco Unican's specific electroplating operation, a method that was virtually maintenance free, inexpensive, and a system that could close-the-loop and recover the costly chemicals presently discarded. The evaluation of test results has successfully indicated feasibility of the process to both close-the-loop and recover all constituents of the electroplating normally disposed.

PROCESS DESCRIPTION

The atmospheric evaporation process as applied to an electroplating process involves the installation of evaporators in close proximity to the electroplating or nickel plating baths. Consideration should be given to locating the evaporator close to a source of clean and dry air. A continuous flow of air which is humidified by the electroplating bath is drawn off and expelled to the atmosphere.

Unsaturated air absorbs moisture from a wet surface. Therefore, as the relative humidity drops, the evaporation rate increases. Head space or room is created in the plating tanks by taking advantage of the air's ability to absorb water while leaving the valuable constituents of the bath behind. The water evaporated is replaced by water from the rinse cycle.

Figure 1 illustrates the process sequence. The electroplating bath solution is pumped to the evaporator utilizing a magnetic drive March pump with a 1" suction and 3/4" discharge through the feed line to the two spray nozzles on top and one spray nozzle in the middle front of the evaporator. Latent heat of vaporization occurs upon passing through the spray nozzles and packing while coming into contact with forced air from a Dayton blower. The humidified air is expelled to the atmosphere through a 16", 20 gauge galvanized duct, with a ½" drain for condensation. The bath which is not evaporated returns to its original bath through a 1½" drain by gravity.

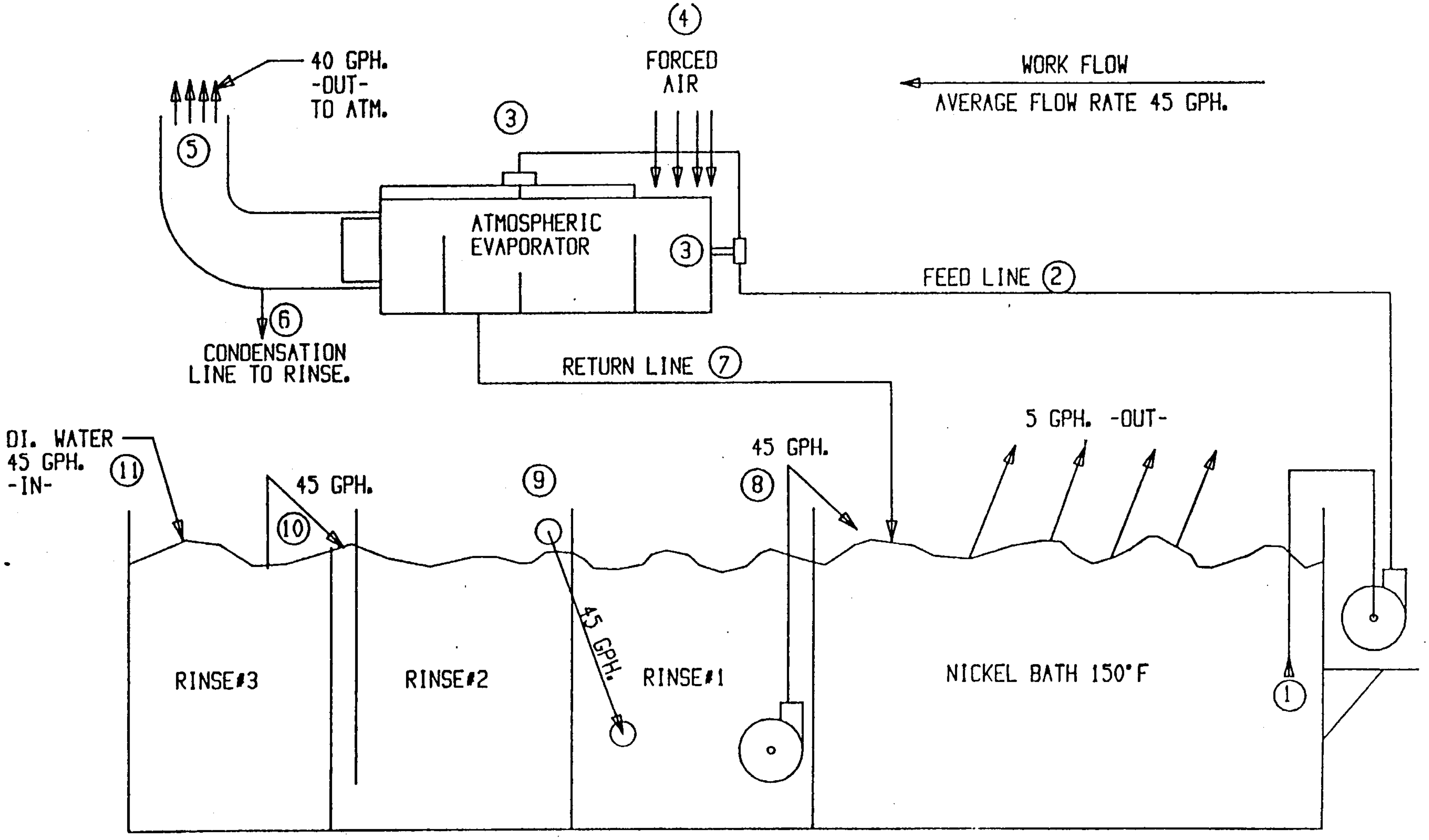


FIGURE 1: OPERATING SEQUENCE FOR ATMOSPHERIC EVAPORATOR SYSTEM

ILCO/UNICAN CORP.

The replacement of evaporated water in the nickel bath is accomplished by pumping from the Rinse #1. The amount of replacement is determined by the evaporation rate via a level control in the nickel bath. Simultaneously counterflow from Rinse #2 and Rinse #3 occurs as the level in Rinse #1 drops. As the level is dropping in Rinse #1 a solenoid valve is opened allowing for dionized water to enter Rinse #3.

Evaporation rates are variable and are determined by the surrounding air, temperature of the solution and flow of air. Conditions which favor evaporation are hot air, dry air, hot solution and high air flow. Figure 2 shows the manufacturers average actual and theoretical rate of evaporation. Actual, according to the manufacturer are results reported by users of the systems.

RATE OF EVAPORATION
NICKEL PLATE LINE

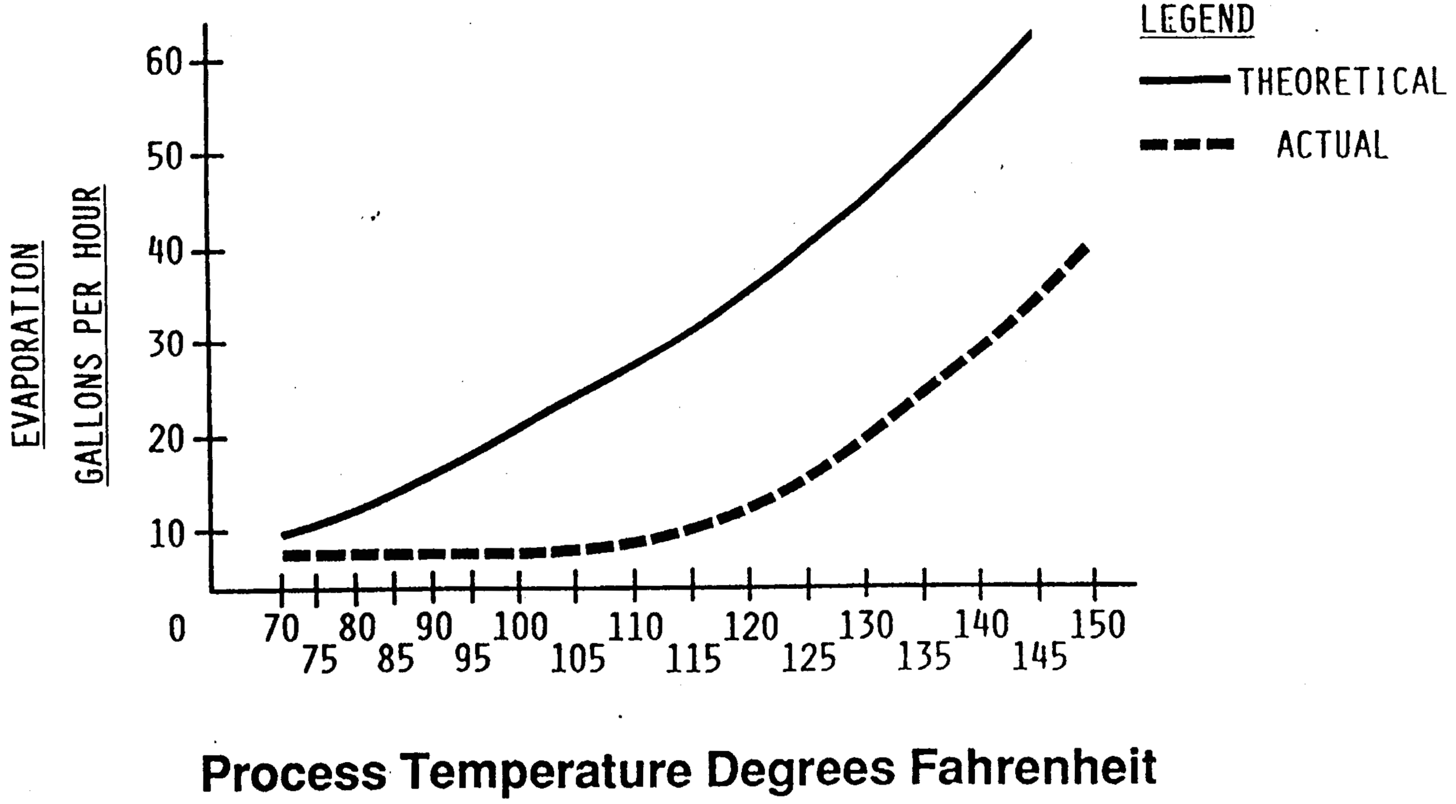


FIGURE 2

TEST DESCRIPTIONS

This section describes the pre-installation engineering tests, equipment, the specific test set-up and operations.

PRE-INSTALLATION TEST

Initial testing was performed to determine a worst case ot unacceptable rinse water by using a Serfilco Controller (see Figure 3) to measure the µmho of the rinse water. Upon obtaining an inadequate plating on the products, testing would be discontinued. Inadequate was defined as a reduction in the brightness due to staining, or an off-color deposit or coating on the surface of the product.

Preparation for testing was accomplished by insuring the plating bath was optimal in composition and conductivity. Next all rinse tanks were drained, cleaned and replenished with clean water. A reading of 250 µmhos was obtained from the clean rinse water.

During the testing period no clean water was introduced to simulate a closed-loop system. µmho readings were taken every five barrels to simulate an accountable pattern of increased µmhos to a worst case or unacceptable rinse water. All readings were taken in the final rinse.

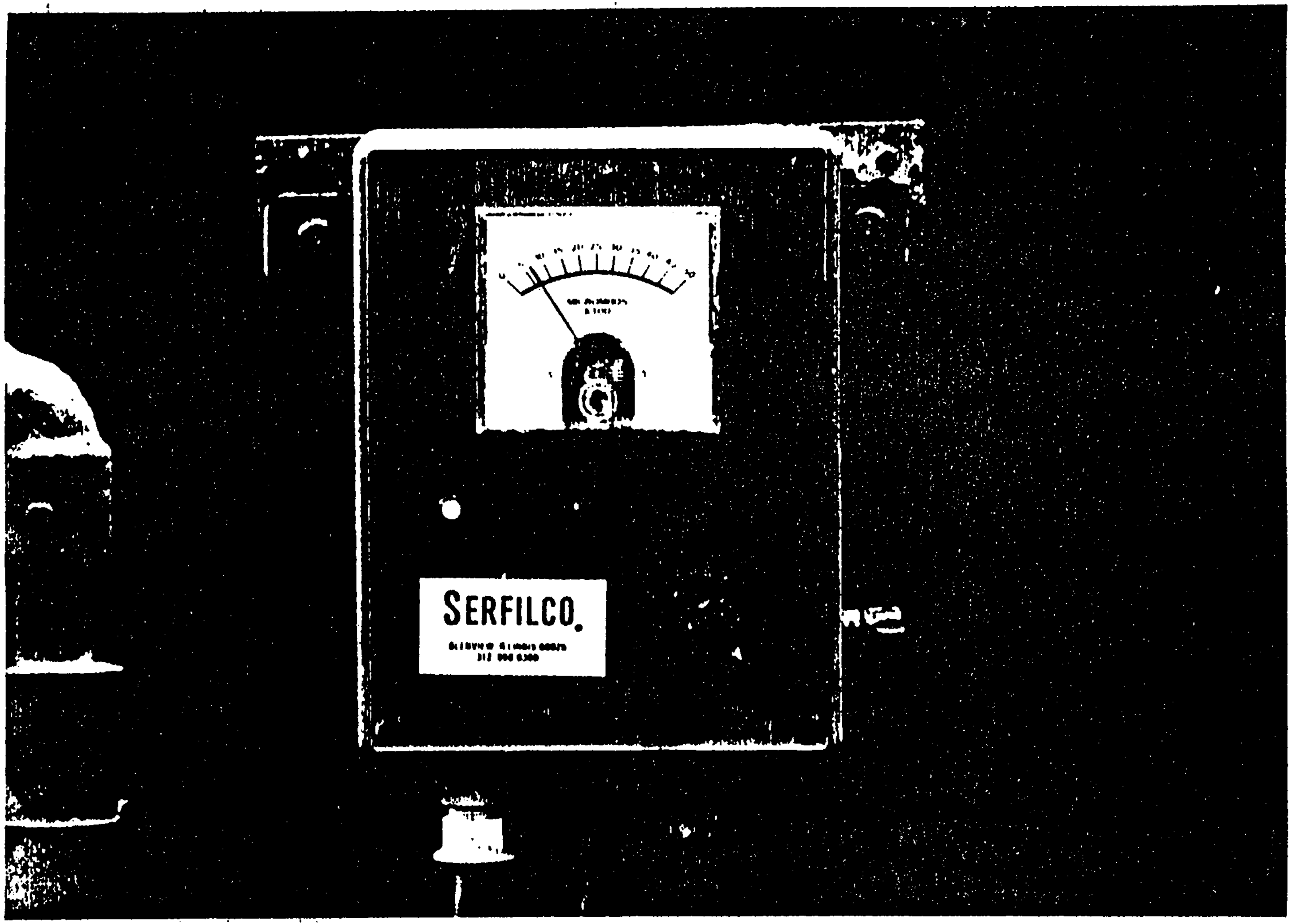


FIGURE 3 - SERFILCO CONTROLLER

Figure 4 shows the starting point at 8:25 AM and the progression of increased conductivity. After 65 barrels the µmhos increased to 2100. At this point a surface coating or haze appeared on the product and testing was discontinued.

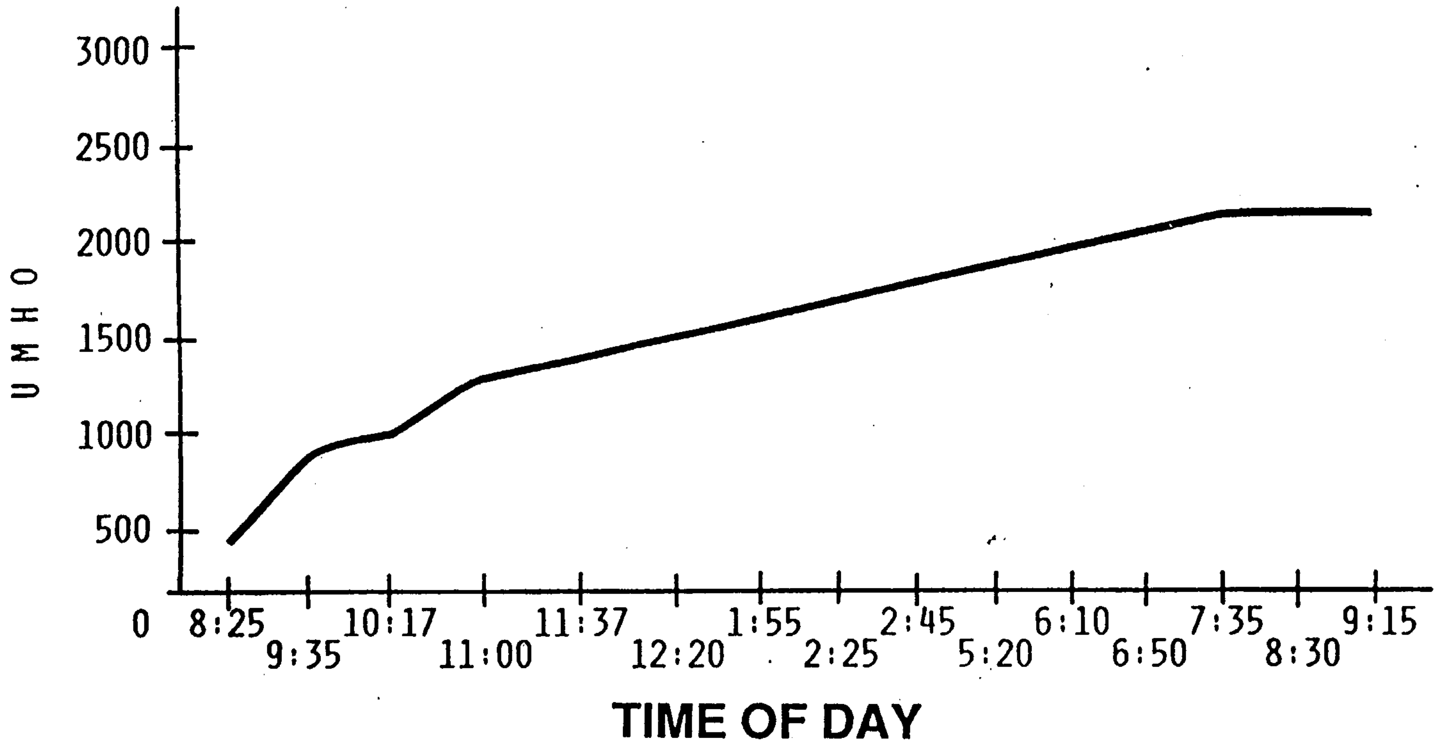
The next phase of testing required drainage and cleansing of all rinse tanks again. The controller was now relocated to the first rinse tank following the bath. A temporary water supply and counterflow was installed. Water was flowed at a rate of 45 gallons per hour to simulate a 45 gallon per hour evaporation rate. A safety factor of 600 µmhos was preconceived as a reduction in the factored 2100 µmho set point. Therefore at 1500 µmhos testing would again be discontinued at which time an increased flow of water would begin, if required.

The objective was to determine at what flow rate clean water could be introduced and keep the conductivity below 1500 µmhos. At 7:30 AM a reading of 250 µmhos was obtained on the clean rinse water. Over a 13 hour period µmhos never exceeded 1000. At 8:30 PM plating was discontinued due to a lack of production. Table 1 reflects the hourly readings. µmhos did stabilize one hour prior to the completion of production requirements.

EQUIPMENT

Two MAX-EVAP T.M. Atmospheric Evaporators manufactured by Techmatic, Inc., Nashville, Tennessee (See Figure 5) were installed following the engineering tests. Although the testing indicated

FIGURE 4 - MAXIMUM CONDUCTIVITY TEST



5 BARRELS / TIME BLOCK

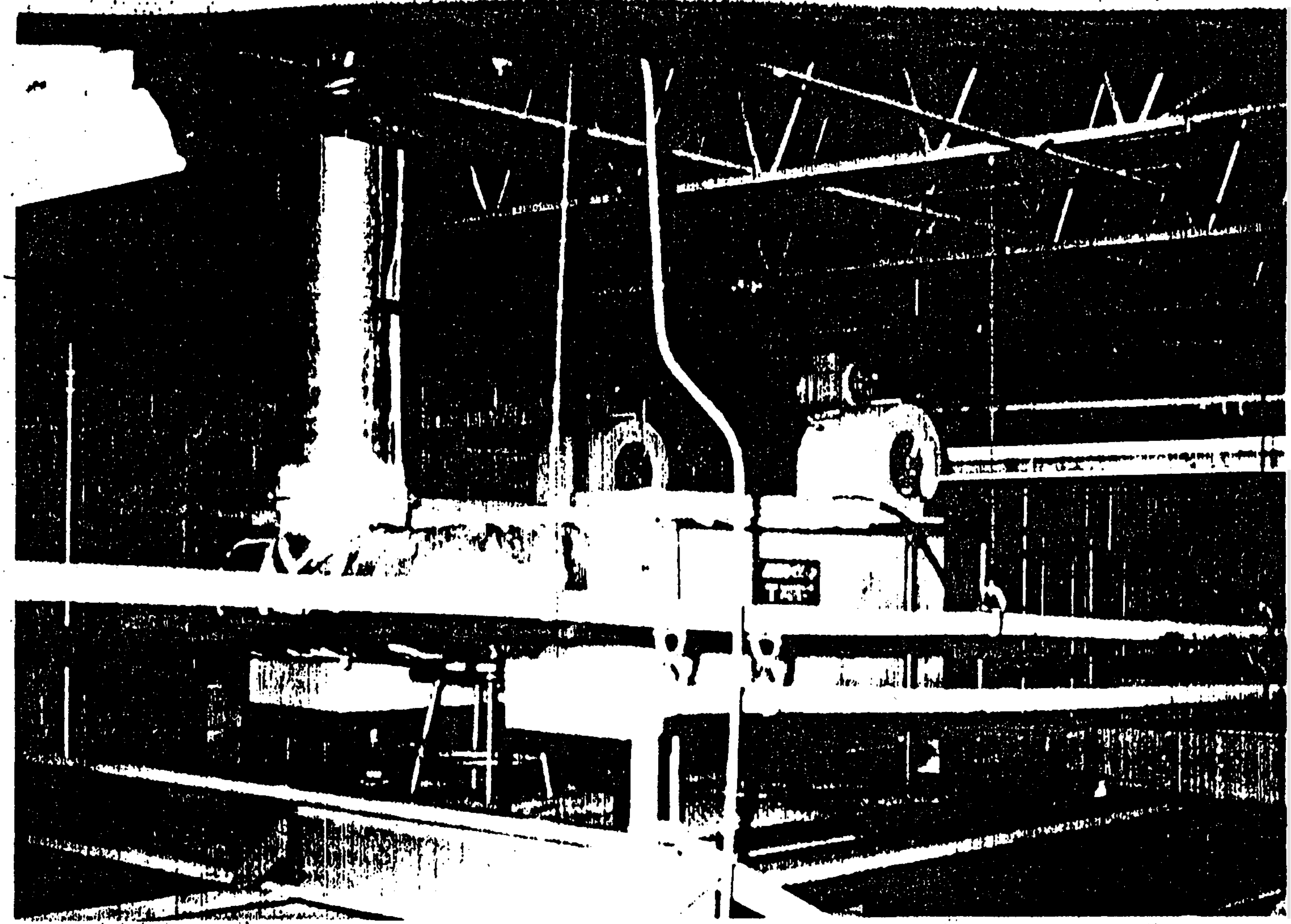


FIGURE 5 - INSTALLED ATMOSPHERIC EVAPORATORS

TABLE 1 - CONDUCTIVITY AT 45 GAL/HR FLOW RATE

TIME	µMHO
7:30	250
8:30	300
9:30	400
10:30	475
11:30	550
12:30	600
1:30	675
2:30	750
3:30	800
5:30	900
6:30	975
7:30	1000
8:30	1000

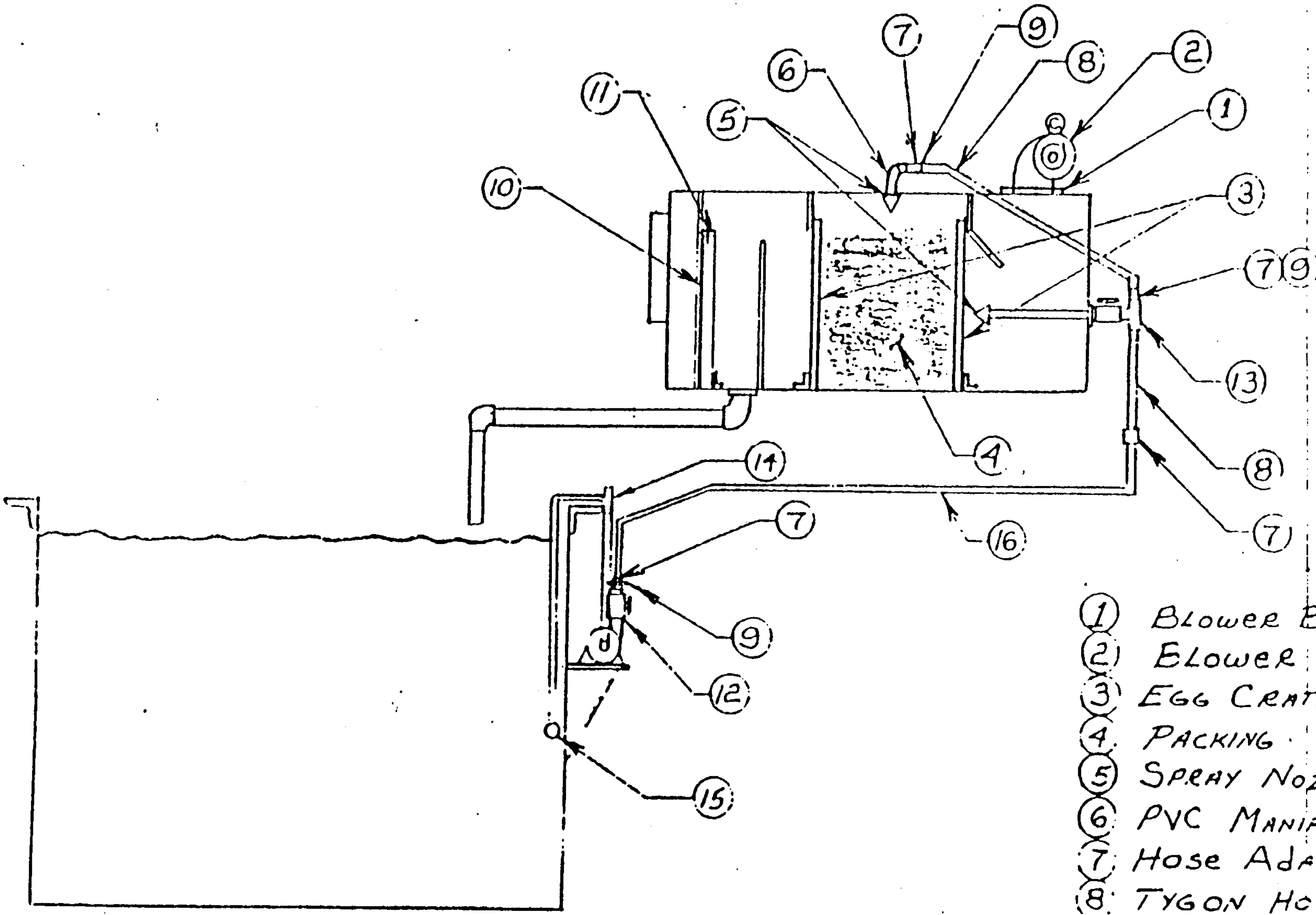
a 45 gallon per hour flow rate was adequate to subside the conductivity to an acceptable limit. There was the probability that the 45 gallon per hour evaporation rate would occur only under favorable conditions, therefore two evaporators were utilized.

An 8' x 8' platform with guardrail was installed over the automatic hoist directly above both plating tanks. Assembly of the evaporators was relatively simple, (See Figure 6) Packing retainers (3), a packing material for atomization (4), spray nozzles (5), flush assembly (13), dryer (10), holding pin (11), and blower (2) were assembled to the evaporator. These parts were all assembled on the ground prior to placement of the evaporators on the platform.

Support stands were then fabricated for the March pump. Three (3) March pumps with stands were installed. One dedicated to each evaporator and one to transfer the rinse water to the plating tanks.

Following installation of the March pumps, the feed lines and return lines to the atmospheric evaporators were installed (See Figure 6) from the pump servicing the evaporators.

Rinse tank piping to the plating tanks required the placement of solenoid valves in-line to each plating tank. Solenoid valves would open as described below.



① Blower Brackets
② Blower
③ Egg Crate
④ Packing
⑤ Spray Nozzle
⑥ PVC Manifold
⑦ Hose Adapter
⑧ Tygon Hose
⑨ Hose Clamp
⑩ Chevron Dryer
⑪ Holding Pin
⑫ PVC Valve
⑬ Flush Assembly
⑭ Priming Tee
⑮ Footvalve-Strainer
⑯ 3/4" PVC Pipe

FIGURE 6

ASSEMBLY OF MAX — EVAP

TECHMATIC, INC.

An electrical control system design and control circuit was required. The circuitry designed is shown in Figure 7 and 8. When #1 Start Button is pushed or closed, the #1 Circulation Pump becomes energized allowing the pump to transfer the #1 Plating Tank bath to #1 Atmospheric Evaporator. This process continues until the #1 Stop Button is pushed.

When #2 Start Button is pushed or closed, #1 Dayton Blower becomes energized flowing air through the evaporator. The forced air stimulates the vaporization process and forces the atomized particulate through the evaporator and exhaust system to the atmosphere.

Start buttons #3 and #4 perform the same functions as #1 and #2 above, but, apply to #2 Plating bath and evaporator.

Pump #3, which supplies makeup water for plating baths #1 and #3 is energized when liquid level floats in the plating baths reach a set low limit. The liquid level floats activate and open the appropriate solenoid valve. Each plating tank has its own float and dedicated solenoid valve. This pump is controlled by either an automatic or manual selector switch. In the manual mode a bypass of the liquid level controller takes place.

A third liquid level controller was installed in the 1st Rinse Tank following the plating bath. This liquid level controller opens the solenoid valve at the fresh water supply to the 3rd Rinse Tank as the level is reduced in the makeup process.

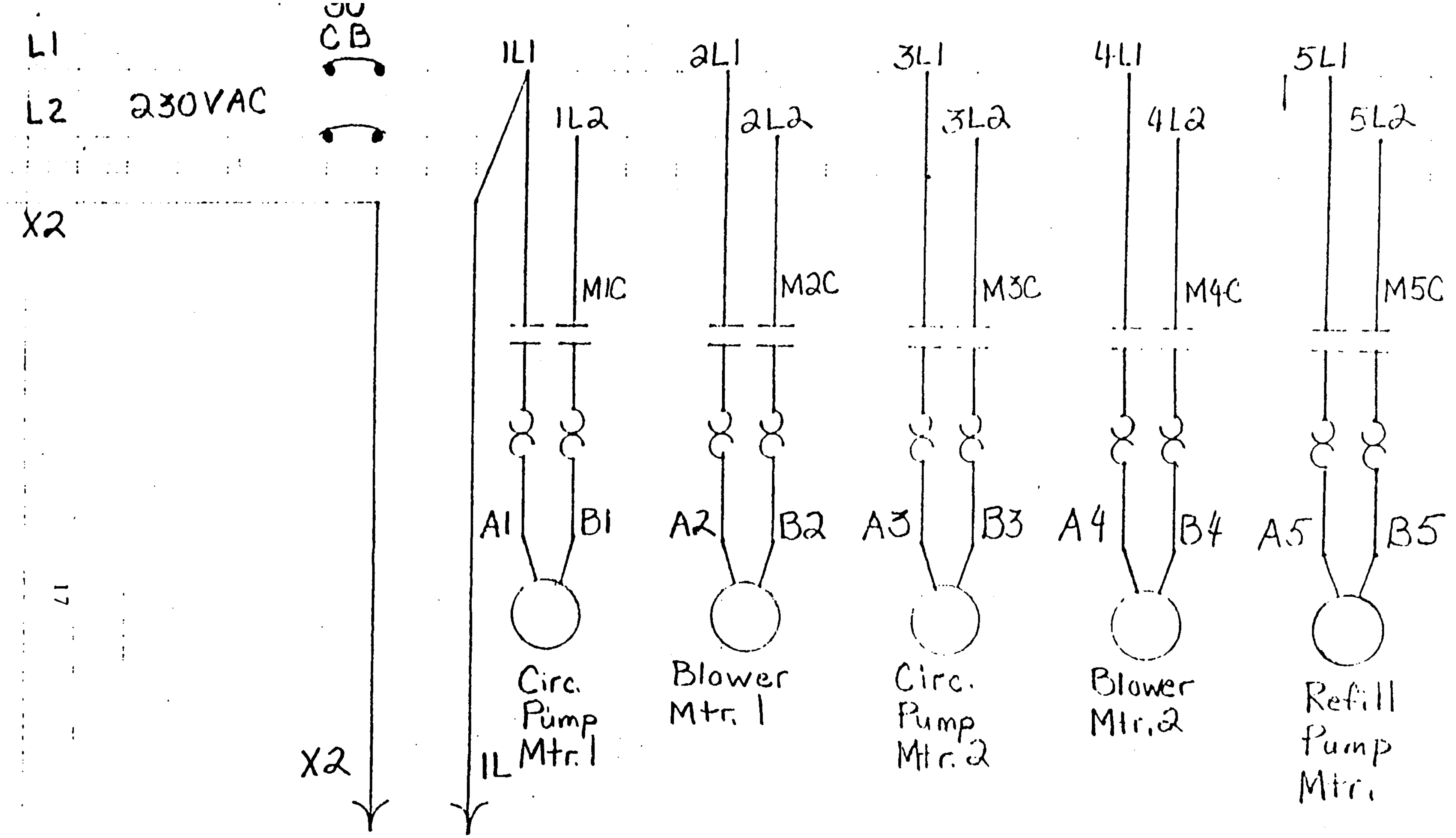


FIGURE 7 - ATMOSPHERIC EVAPORATOR CONTROL CIRCUIT

JOHN MESSER
ILCO UNICAN CORP

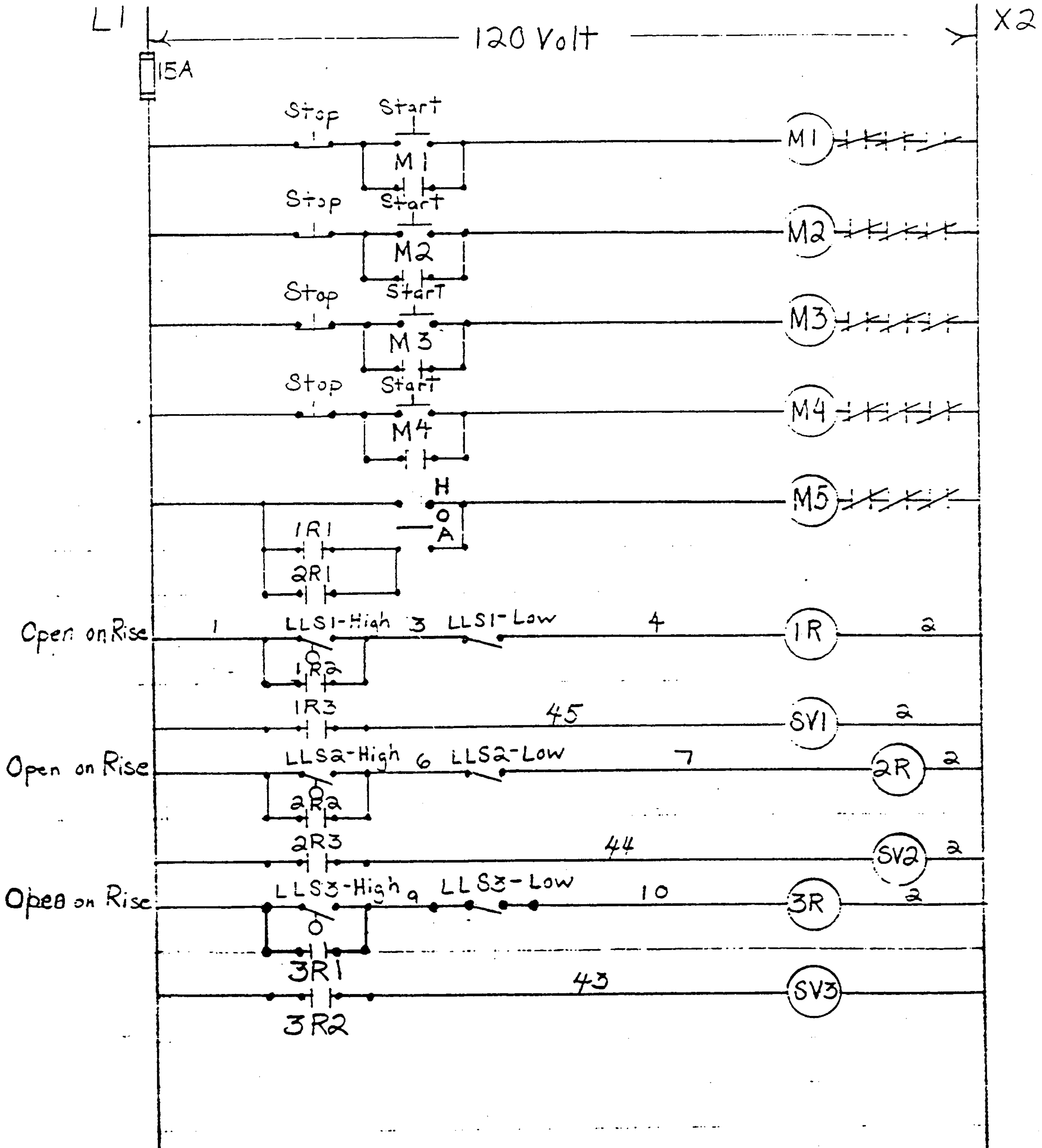


FIGURE 8 - ATMOSPHERIC EVAPORATOR CONTROL CIRCUIT

Following the above installation process a tee-exhaust consisting of a 16", 20 gauge galvanized duct with a ½" drain for condensation was installed. The duct was emplaced through the facility roof and capped.

TEST SET-UP AND OPERATIONS

All valves were checked to insure proper positioning to draw from and return to the process tank. The pumps required a prime. Doors were removed to check the spray manifold for proper spray flow, and the return line was checked for flow back to the plating bath.

With blower in the off position, the Flush Assembly Valve required a partial opening, enough for a good flow without causing any splash to the blower. At this time the blower was energized to allow air to pass through the evaporator.

The dragout tank was cleaned and drummed for reuse. All, other rinse tanks were released and pretreated. Clean water was emplaced in all rinse tanks.

Plating operations were resumed, at which time tests were made to determine the actual rate of evaporation in each plating tank and the actual maximum µmho during a normal production working day.

TEST RESULTS AND ANALYSIS

The test results clearly indicate that evaporative recovery is a feasible solution to closing the loop. All engineering technical data indicated the feasibility of this process as applied to an electroplating operation.

TEST RESULTS

It was determined in the pre-installation testing that an unacceptable conductivity occurred at 2100 µmhos to obtain an acceptable product and finish. Also a flow rate of fresh water at 45 gallons per hour would stabilize the rinse water in an automatic electroplating operation at 1000 µmhos.

Testing following installation showed the conductivity varied from 600 - 1100 µmhos in the third rinse tank. This was well below the unacceptable range of 1500 - 2100 µmhos.

The total actual evaporation rate has averaged between 60 - 70 gallons per hour, from the 500 and 750 gallon electroplating baths. Bath temperature ranges from 145°F - 150°F. This decrease in evaporation from the manufacturers actual is primarily due to climatic conditions surrounding the evaporators.

COST ANALYSIS

As derived from the heat of vaporization 970 Btu per pound of water are required to change the state. Therefore,

970 Btu per lb. x 8.34 gal. = 8,089.8 Btu per/gal.

8,090 Btu per gallon of evaporation are required.

With the evaporation rate averaging between 60 - 70 gallons per hour 485,400 - 566,300 Btu or 4.85 - 5.66 therm per hour are used. Inasmuch as this electroplating operation runs 24 hours per day/6 days per week; 36,346 - 42,382 therms are required annually to operate the system. The cost per therm of natural gas at this facility is 47¢ per therm. Therefore energy costs at $17,082.00 - $19,920.00 can be expected annually.

nickel salts

S~~od~~ium would continue to buildup at a rate of 3% due to anode/cathode efficiency and recovery, eliminating any future costs of nickel sulfate and nickel chloride. Table 2 shows breakdown and assessment of cost, payback period and annual cost savings associated with this system.

TABLE 2 - COST AND PAYBACK ANALYSIS

	COST	SAVINGS
1. Plating chemicals		
Nickel Chloride		
$\frac{6400\#}{\text{ANNUALLY}} \text{ X } \frac{\$1.45}{\#} \text{ X } \frac{100\%}{\text{RECOVERY}} =$		\$ 9,280.00
Nickel Sulfate		
$\frac{22{,}000\#}{\text{ANNUALLY}} \text{ X } \frac{\$0.88}{\#} \text{ X } \frac{100\%}{\text{RECOVERY}} =$		\$19,360.00
Boric Acid		
$\frac{8800\#}{\text{ANNUALLY}} \text{ X } \frac{\$0.46}{\#} \text{ X } \frac{80\%}{\text{RECOVERY}} =$		\$ 3,238.40
2. Two (2) evaporator systems =	\$ 7,200.00	
Valves, switches, piping, Labor for installation, Ductwork for venting =	\$ 5,000.00	
3. Disposal Costs		
Roll-off rental		
$\frac{\$250.00}{\text{MO}} \text{ X } \frac{12}{\text{MO}} =$		\$ 3,000.00
Quarterly Transportation		
$\frac{837.76}{\text{QUARTERLY}} \text{ X } \frac{4}{\text{YR}} =$		\$ 3,351.04
Landfill Costs =		\$ 4,300.00
Labor to handle waste =		\$14,480.00
4. Maintenance on Evaporator		
$\frac{1 \text{ Hr}}{\text{DAY}} \text{ X } \frac{312}{\text{DAY}} \text{ X } \frac{\$20.00}{\text{HR (OH)}} =$	\$ 6,240.00	

	COST	SAVINGS
5. Annual Water		
$\frac{20\text{ Gal}}{\text{MIN}}$ to $\frac{60\text{ Gal}}{\text{HR}}$ =		$ 2,636.93
6. Sewer usage =		$ 1,318.00
7. Energy usage =	$18,501.00	
	$36,941.00	$60,964.37
1st year projected savings....................		$24,023.37
Subsequent annual savings.....................		$36,223.37
Projected payback.........................		7.3 Months

Note:

- Annual savings does not include an undertermined long-term liability savings.

CONCLUSIONS

Feasibility testing of the Atmospheric Evaporation system was successfully performed on the electroplating process from the Ilco Unican Corporation, Rocky Mount, North Carolina plant. In addition, analysis of the data from the tests provided the following conclusions regarding performance of the Atmoshperic Evaporation process.

- Processing parameters (bath composition, temperature, climatic conditions, energy efficiencies for the Rocky Mount process demonstrated the feasibility of using Atmospheric Evaporation to process plating bath composition and effectively use the rinse water as recovery source, therefore closing-the-loop.

- Salt ~~Sodium~~ buildup has been a problem in the evaporator and the problem has been resolved by operating the pump approximately 30 minutes every 24 hours without the blower.

- Recovery of all salts, acid and brighteners normally disposed of, in addition to a generation of salts based on anode/cathode efficiency has occurred. Additionally a decrease of 50 - 80% in waste has occurred.

- Conclusions about the continual buildup of contaminants to the plating bath cannot be derived from the available test data. However, the plating industry is well aware of various treatments involving carbon filtration, hydrogen peroxide, electrolytic dummy plating, which allows removal of most contaminants should they build to a detrimental level.

- A off-line continuous dummy plate and treatment tank will be designed to decrease downtime associated with this process and any additional buildup of contaminants from the evaporator process.
- Atmospheric Evaporation is a cost-effective means.

Initial testing indicates the potential for the Atmospheric Evaporator to close-the-loop at the Rocky Mount plant. Based on the results of this feasibility test, adequate technical bases are available to design a system that is cost effective, efficient and act as a baseline for resolving problems associated with Atmospheric Evaporation in electroplating process.

REFERENCE 1

STUDY - VALUE OF METALS

North Carolina State University
School of Engineering

Department of Nuclear Engineering
Box 5636 Zip 27650

March 15, 1984

Mr. Brian Wells, Plant Engineer
ILCO UNICAN
400 Fawn Drive
Rocky Mount, NC 27801

Dear Mr. Wells:

Please ignore the first letter of this nature which we sent to you last week. Due to a misunderstanding, the letter was mailed without the calculations which are present below.

Thank you very much for responding to our letter of October 24, 1983. Below you will find a summary of our calculations based upon a total of 115,910 lbs./yr. of wet sludge containing 20.4 wt% solid and metal contents given as ppm or wt% values in the dry sludge.

		NCSU CALCULATIONS		
Component	Wt%, ppm	lb/yr of metal	Approximate $ Value of Metal	Comments or Corrections
Cd	<0.5 ppm	0.01	1.00	
Cu	1540 ppm	0.04	1.00	
Pb	11 ppm	0.26	~~0.30~~	
Ni	12 wt%	2,837.5	9,194.00	
Zn	2100 ppm	49.66	20.00	
Cr	2.2 ppm	0.05	4.00	
Fe	770 ppm	18.21	---	
Al	---	---	---	
Sn	<0.2 ppm	---	---	
Ag	<0.2 ppm	---	---	
Ti	<5 ppm	0.118	---	
TOTALS		2,905 lbs/yr	$9,220.00/yr	

We are aware of uncertainty in sludge composition and we would appreciate your feedback on the following questions concerning the correctness of the above values.

(1) Did we assume the analysis on a basis of wet or dry sludge correctly? If not, please indicate what fraction of your wet sludge was analyzed.

(2) Do our numbers for lbs. metal per year (as is or adjusted by your corrections in (1) above) appear at all reasonable considering the amounts of those metals you added to your plating baths in 1982? If the values for lbs. metal per year also reflect the metal resulting from acid etching, do they make sense or have you any basis for telling?

We have scheduled the Spring 1984 electroplaters' programs for Wednesday, May 30, 1984 in Raleigh at the NCSU McKimmon Center and for Thursday, May 31, 1984 in the Charlotte Area (Ft. Mill, S.C., Holiday Inn Carowinds). The attached sheet contains our program ideas. We will send you a flyer on these programs as soon as they are available.

Enclosed you will find an extra copy of this letter. We would appreciate your returning this letter with your comments by March 30, 1984 to:

J. Kohl, Sr. Extension Specialist, NCSU, P. O. Box 7909, Raleigh, NC 27695-7909

We are convinced that we must find alternatives to the land burial of our metal containing wastes. Your help on this study can help us look at other options.

Sincerely,

Jerry Kohl (BT)

J. Kohl, Sr. Extension Specialist
(919) 737-2303

JK:sh

Reducing Metal Losses and Sludge Production in the Electroplating Industry
May 30, Raleigh, McKimmon Center - May 31, Charlotte Area, Holiday Inn, Carowinds
Program Ideas from Advisory Committee Meeting of February 22, 1984

A. Closing The Cycle

1. Zero Water Discharge, Harry DeSoi, Manager, Pioneer Metal Finishing: Describe his system, changes since last year, disposition and metal content of boiler solids, plans for sludge disposal.

B. Reducing the Treating Load

1. Good Housekeeping, Reducing Dragout, Rack Design, Recycling, Managing Off-Spec. Plating Baths, George McRae, Stanadyne, Sanford
2. Innovative Spray Rinsing, Jim Adams, NCR
3. Ni Recovery by Ion Exchange, Terry Parsons, Lufkin
4. Electrodialysis for Metal Recovery, Brian Wells, Ilco Unicam
5. Using Tri-Chrome, Terry Parsons, Lufkin
6. Using an Evaporator, Scott Wallace, Stratford (?)
   Roger Woods, Eastern Plating (OK)

C. Sludge Handling and Disposal

1. Drying Sludge, John Gouldin, Techmatic Corp., Nashville, TN(?)
2. Delisting Sludge, Barry Nelson, Moore Gardner and Assoc. (OK)
3. Selling or Recycling Sludges and Solutions, Stan Taylor, Data General, possibly Chris Hord, Surtronics, and Dikkran Kabbendjian, ITT

D. Regulations and Pollution Prevention Pays

1. RCRA - Changes in Reauthorization Act, Is Drying Sludge Waste Treating? How are Zero Discharge-Recycle Operations Treated? Status of Delisting Electroplating Sludge.
2. Pretreatment Requirements, Representatives from one or more public waste water treatment facilities.
3. The NRCD - P.P.P. Program as it Applies to Platers, Roger Schecter (OK)

F. Other Possible Subjects and Speakers (not all discussed at the meeting)

1. Lab Analysis of Sludges - speaker(?)
2. Reverse Osmosis - David Birkhead, Acme United (?)
3. State of the Art in Metal Recovery or Other Subject - F. Steward, Lancy Intl. (?)
4. Experience with Evaporators - Roger Woods, Eastern Plating (confirmed)
5. Electroplating sludge quantity and composition - J. Kohl or B. Triplett
6. Water pollution regulations affecting direct dischargers (?)

G. Evening Session

An Exchange of Experiences in Operating Waste Treatment Facilities:
Leader, Dikkran Kabbendjian

Electrodialysis
in

Pollution Prevention and Control Technology for Plating Operations

George C. Cushnie Jr.
CAI Engineering

A Project Sponsored by the
National Center for Manufacturing Sciences
and Conducted in Cooperation with the
National Association of Metal Finishers

Cushnie Jr., G.C. 1994. *Pollution Prevention and Control Technology for Plating Operations*. Reproduced with permission from the National Center for Manufacturing Sciences (NCMS), Ann Arbor, Michigan.

Effort sponsored by the Manufacturing Technology Directorate, Wright Laboratory (WL/MTX), Air Force Materiel Command, USAF, under Cooperative Agreement number F33615-94-2-4423.

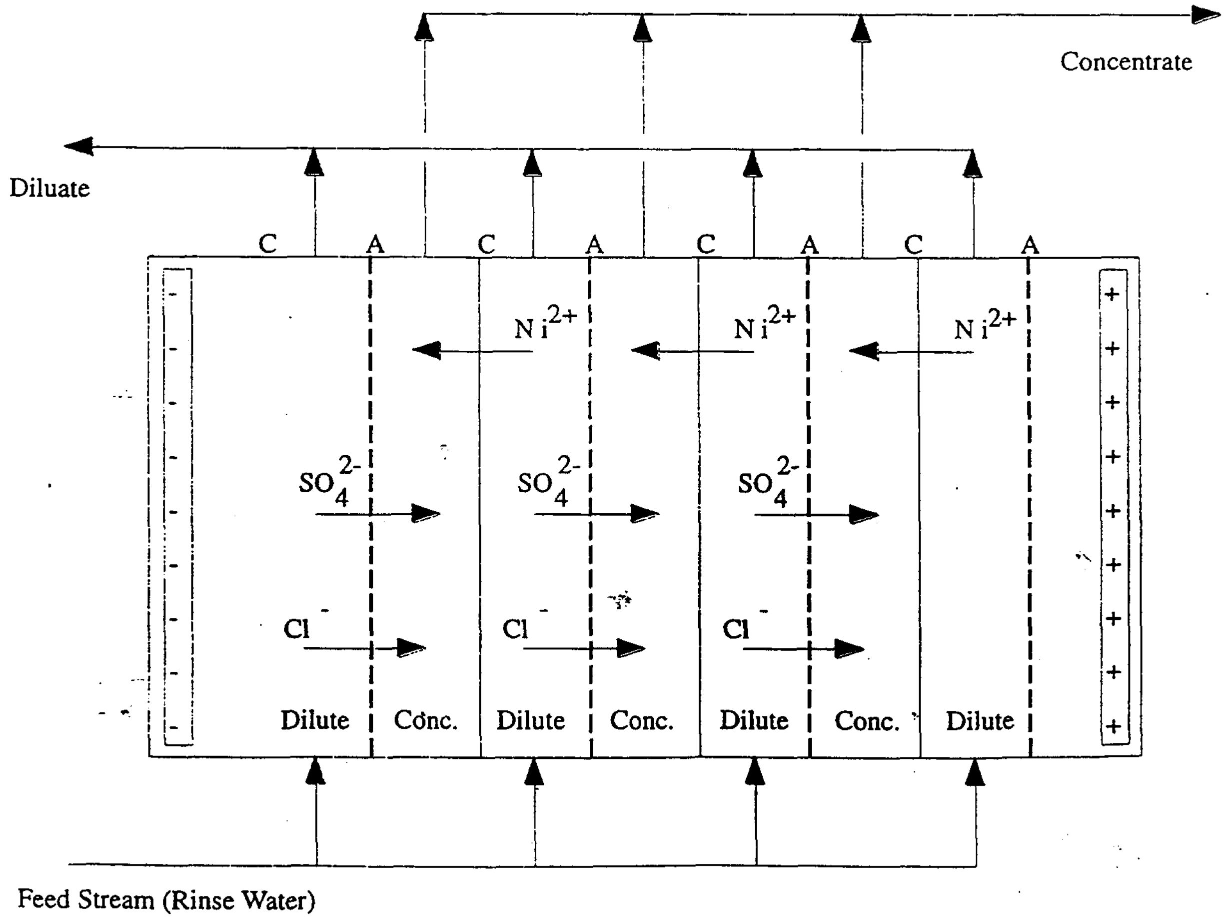
3.6 ELECTRODIALYSIS

3.6.1 Overview

The electrodialysis technology employs ion-permeable and selective membranes under an applied d.c. potential difference to separate ionic species from an aqueous solution. Its primary application for chemical recovery is nickel plating, where it competes with recovery rinsing (drag-out tanks), evaporation technologies and ion exchange. As such, it has not seen widespread use, despite being commercialized for this application for nearly fifteen years. The results of the Users Survey indicate that only three respondents (less than one percent) have employed electrodialysis for recovery. All of these units, which were used for nickel recovery, are no longer in operation

When used for nickel recovery, a concentrated rinse solution is pumped into an electrodialysis unit that is comprised of a stack of alternating cation- and anion-selective membranes, each separated by a spacer through which the solutions are allowed to flow (Exhibit 3-48). Due to the electrical potential applied across the stack, cations (Ni^{2+}) in solution migrate toward the cathode, and anions (SO_4^{2-} and Cl^-) toward the anode. When a cation encounters a cation-selective membrane, it passes through. As it continues to migrate, it will subsequently encounter an anion-selective membrane through which it cannot pass and will remain in that compartment. Similarly anions migrate toward the anode, pass through anion selective membranes and their travel is halted when they encounter a cation-selective membrane. This process results in alternating compartments between con-

Exhibit 3-48. Diagram of an Electrodialysis Process for Nickel Recovery



secutive membranes becoming increasingly enriched (concentrate) and increasingly depleted (diluate) in ion concentration (ref. 399). Based on data presented in the literature, the feed stream (typically from a drag-out tank) usually contains 2 to 5 g/l Ni, the concentrated return stream contains 30 to 60 g/l Ni and the depleted stream contains less then 200 mg/l Ni (ref. 32). The return stream is less concentrated than the bath (typically 70 to 90 g/l Ni). However, surface evaporation from the plating bath tank is generally sufficient to volumetrically accommodate complete assimilation. The percentage of nickel recovered from the feed stream is typically 90 to 95%.

A potential advantage of electrodialysis over other concentrating and return methods of nickel recovery (e.g., evaporation and reverse osmosis) is its ability to selectively retard the recovery of certain organic materials that tends to buildup in nickel plating baths, while more freely permitting the transport of a desirable organic bath constituent (saccharin) and nickel salts. This aspect of the process could reduce the frequency of bath purification as compared to other recovery schemes. Bath purification causes the loss of 10 to 15% of the bath per cycle, which significantly reduces the pollution prevention benefits of recovery (ref. 28).

3.6.2 Development and Commercialization

Although the phenomenon of electrodialysis was observed in the 1800's, it did not achieve any commercial application until durable, ion-selective membranes were developed in the 1950's (ref. 39). The two early applications of this technology, desalination and recovery of edible salt from sea water, still constitute the bulk of membrane utilization. The largest electrodialysis installations are salt recovery systems located in Japan. These systems replaced solar ponds that once occupied large tracts of land (ref. 400).

Large-scale industrial usage of electrodialysis began in the early 1970's with applications in chemical processing, biotechnology and water pollution control. In 1972, the first attempts were made to use electrodialysis to reclaim plating chemicals from rinse solutions (ref. 32). This early work was performed with unidirectional systems, where the transfer of ions is in one direction only. These efforts were plagued by membrane fouling with scale, slime and undesirable organics (ref. 32). Subsequently, the electrodialysis reversal (EDR) process was utilized, where there is a periodic reversal of direct current flow through the membrane stack and a simultaneous interchange of diluting and concentrating streams. This improvement greatly reduced the occurrence of membrane fouling. By 1984, there were more than 100 recovery units operating in the U.S. on a variety of plating solutions. The major area of application was nickel plating, with most other applications restricted to cyanide baths (e.g., gold, cadmium, silver and zinc). Additional applications at that time, mentioned in the literature, include tin and tin-lead fluoroborate and trivalent chromium (ref. 39). Since approximately 1985, there have not been any major changes to electrodialysis as applied to chemical recovery from rinse waters. However, similar technology applications for bath maintenance have significantly increased. Presently, membrane electrolysis, a related technology, is applied to the maintenance and reformulation of solutions containing chromic acid, nitric acid, sulfuric acid or sodium hydroxide (Section 4).

3.6.3 Applications and Restrictions

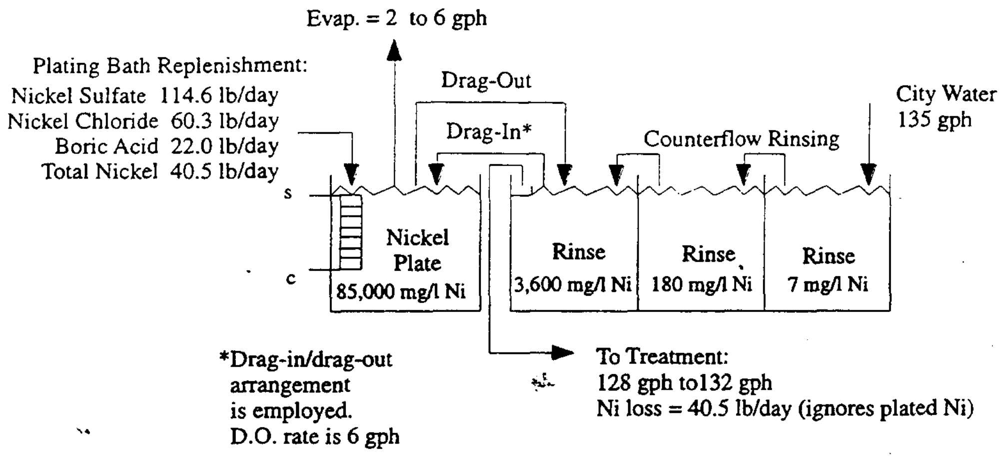
The application of electrodialysis for recovery of nickel plating chemicals is shown in Exhibit 3-49. This application, which includes a material balance, was taken from the literature (ref. 32), and is based on an actual case study performed by an electrodialysis equipment manufacturer. The work for this application was performed at a job shop with an automatic nickel barrel plating operation. The plating and rinsing configuration used prior to the implementation of electrodialysis is also shown. Based on a comparison of the two diagrams, the electrodialysis system recovered approximately 38 lbs of nickel per day more than the existing drag-out/drag-in recovery rinsing system. The difference in plating tank evaporation rates between the original and revised systems was not discussed in the article, but presumably was due to a change in the operating temperature of the bath.

Most applications for this technology have involved nickel recovery including Watts, sulfamate and bright nickel plating solutions and nickel galvanizing. Other applications identified by vendors include: gold, copper, cadmium, platinum, silver and zinc cyanide; tin-lead, palladium, zinc phosphating and zinc galvanizing (ref. 134, Kinetic Recovery Corporation file, Graver Co. file).

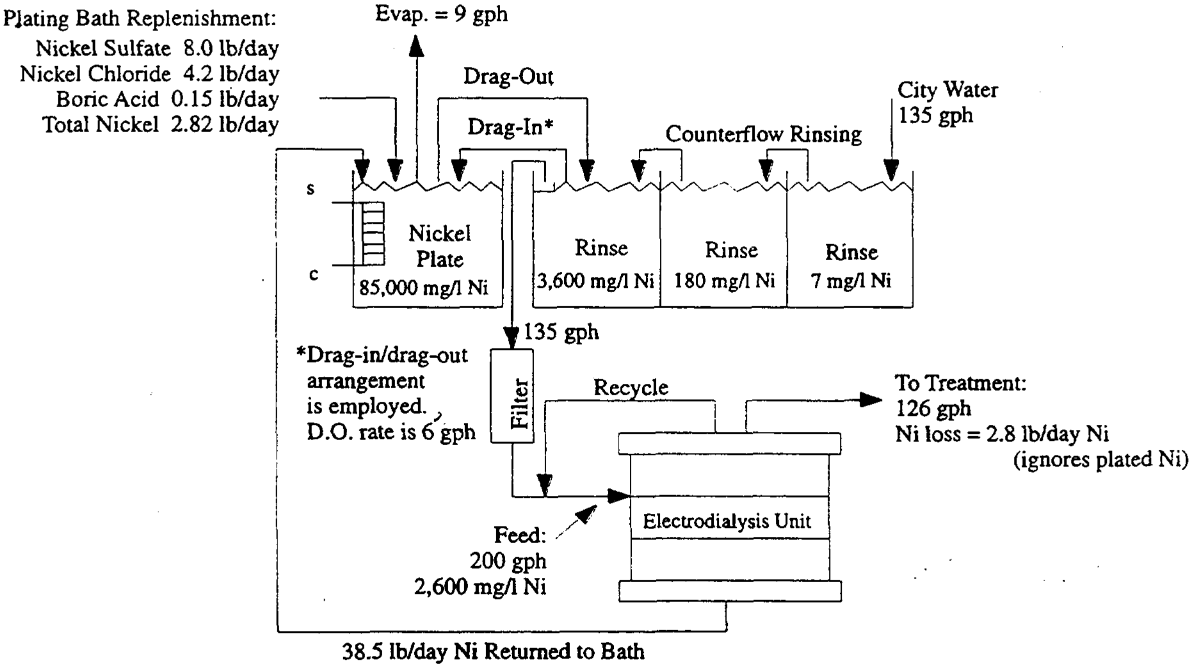
3.6.4 Technology/Equipment Description

This subsection contains names of commercially available electrodialysis equipment that is manufactured and/or sold by vendor survey respondents. This is intended

Exhibit 3-49. Flow Schematics of a Nickel Plating Line Before and After Installing Electrodialysis



Nickel Plating Line Prior to Installing Electrodialysis



Source: ref. 32

Nickel Plating Line After Installing Electrodialysis

to provide the reader with information and data on a cross section of available equipment. Mention of trade names or commercial products is not intended to constitute endorsement for use.

Graver Water, a division of The Graver Company, markets electrodialysis units manufactured by Tokuyama Soda, a world leader in the membrane technology. Their target industries are food, photograph finishing, pulp processing, waste control and metal finishing. Their key metal finishing applications include nickel and zinc recovery from galvanizing and acid or alkali recovery.

Kinetic Recovery Corporation markets electrodialysis equipment for various applications, including: Watts nickel, copper cyanide, cadmium cyanide, and zinc phosphates. Their typical units have membrane surface areas ranging from approximately 35 ft^2 to 190 ft^2, although all units are custom designed to meet individual process needs. Their systems are skid mounted and include: membrane stack, holding tank for concentrate, holding tank for diluate, holding tank for electrode rinse, three sets of level controls, three pumps for liquid transfer, plumbing, automated valves, flow meter, pressure gauges, cartridge filters and control panel.

3.6.5 Costs

3.6.5.1 Capital Costs

The capital cost of an electrodialysis unit is related primarily to the stack size, which can be expressed in terms of membrane area. Exhibit 3-50 shows typical membrane area requirements for Watts nickel solution and other applications in terms of the drag-out rate (gph). Exhibit 3-51 shows capital costs, based on feed stream flow rate (typical feed stream concentration of 2 to 5 g/l dissolved metal.

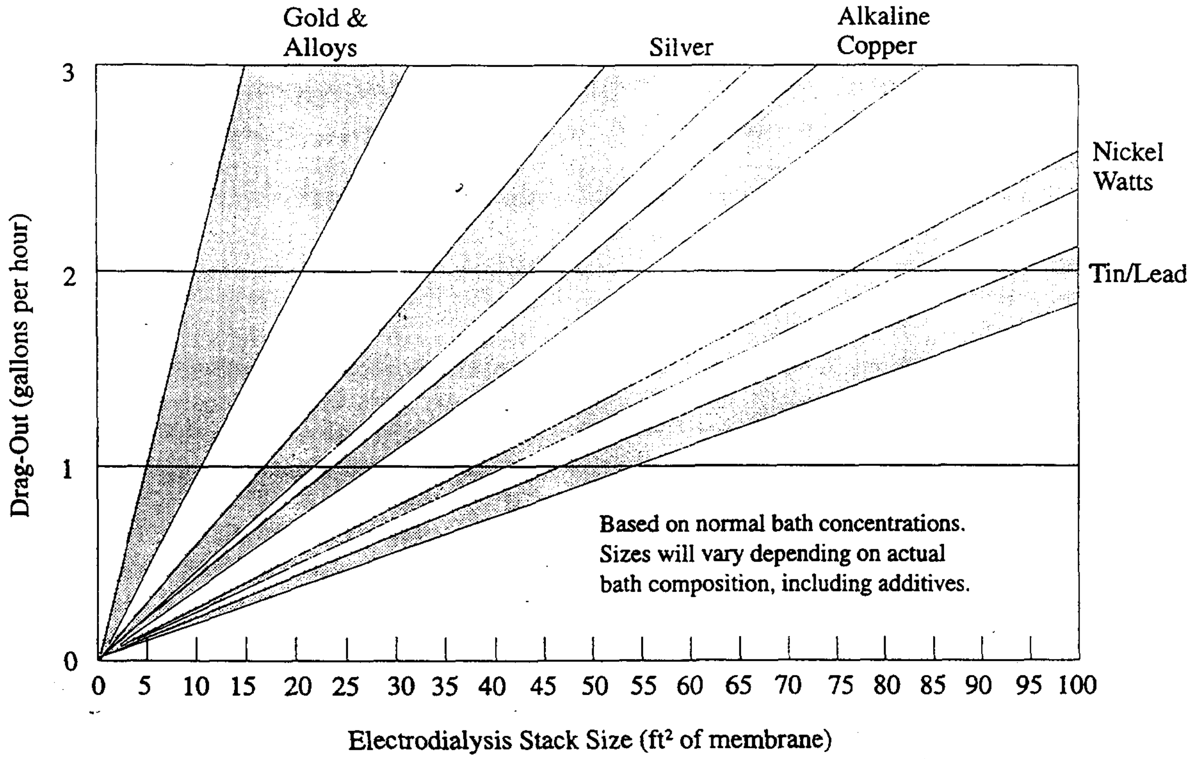
3.6.5.2 Operating Costs

Electrodialysis operating costs include O&M labor, electricity and replacement costs for membranes. Estimated operating costs are 15 to 30 percent of investment costs.

3.6.6 Performance Experience

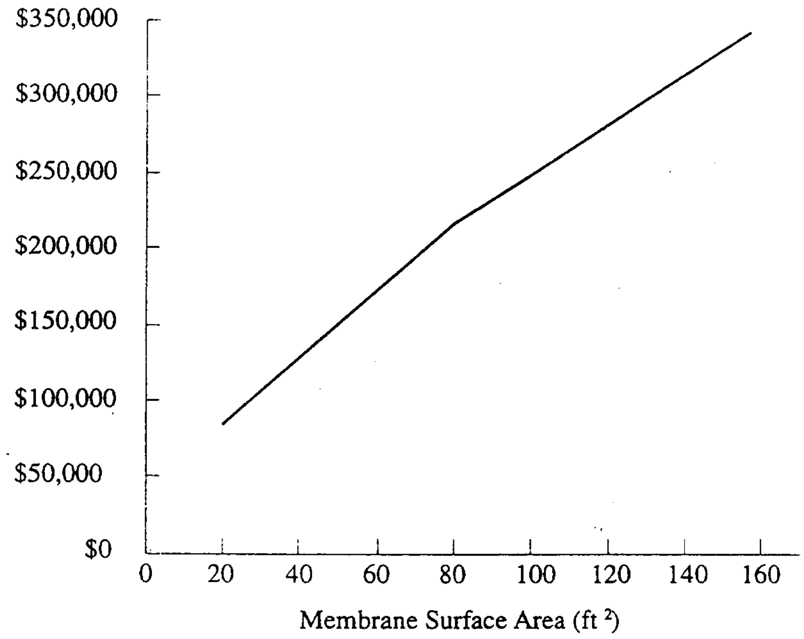
Only two of the user survey respondents indicated that they have used electrodialysis as a recovery technology (PS 012 and PS 125). PS 012 purchased a system from LEA in 1982 and PS 125 purchased a system from Baker Brothers in 1986. A summary of the data provided by these respondents is shown in Exhibit 3-52. Neither of these applications was successful. Failure of the technology at PS 012 was attributed to maintenance problems with the membrane and associated repair and parts replacement costs. Their system was removed from service in 1987 after 5 years of service (non-continuous due to O&M problems). They indicated that the technology did not satisfy the purpose for which they purchased it (i.e., to help meet effluent regulations and reduce operating costs). PS 125 did not provide many details on their

Exhibit 3-50. Electrodialysis Membrane Requirements Based on Drag-Out Rate for Common Plating Baths



Source: Lancy International, Inc. File

Exhibit 3-51. Capital Costs for Electrodialysis Recovery Units Applied to Metals Recovery from Rinse Waters



system's performance. They simply stated: "machine returned after threatened law suit because it never worked." Presently PS 125 uses a vacuum evaporator for nickel recovery that has been relatively successful (only reported problem was a build-up of sodium chloride in the nickel bath, see Section 3.3).

3.6.7 Operational and Maintenance Problems

Only one of the two survey respondents who used this technology provided any information on O&M problems. PS 012 provided the following statement:

> *"Lack of availability of replacement membranes and long repair time by factory after membrane failure (1 year and up to 6 months down) coupled with high repair cost for each failure ($6,000) made this a non-viable technology, was abandoned circa 1987."*

As with most membrane technologies, the life span of the membrane is a key concern to the system owner. One vendor provided estimates of membrane life span during the Vendors Survey. Kinetic Recovery Corporation estimated that their membranes (OS-FD/FS types) last three to seven years for all recovery applications. The Graver Company provided the following estimates for membranes, gaskets and electrodes for acid and alkali recovery (i.e., from concentrated baths, not rinse water).

	Acid Recovery	Alkali Recovery
Membranes	0.5 to 1.0 yr	0.3 to 1.0 yr
Gaskets	1 to 2 yr	1 to 2 years
Electrodes	2 to 4 yr	2 to 4 years

The Graver Company further indicated that the longevity of membrane life was dependent largely on the level of contaminants present.

3.6.8 Residuals Generation

When applied as a chemical recovery technology to plating rinse waters, electrodialysis produces two effluents from the unit: a concentrated stream that is recycled to the bath and a dilute stream that is either reused as rinse water or discharged to treatment.

Typically, electrodialysis recovers up to 95% of the plating chemicals in the drag-out. The remaining 5% are lost when discharged from the rinsing system or directly from the recovery unit. This waste is typically treated on-site which generates a hazardous sludge (RCRA hazardous waste code F006).

Other miscellaneous wastes generated by this technology include spent pre-filtration cartridge filters and worn

Exhibit 3-52. Partial Summary of Users Data for Electrodialysis Recovery Applications

Shop				Capital Costs			Operating Costs (Yr.)		Savings (Yr.)							Use	Down	Satisfaction Levels		Future
Code	Application	Manf.	Year	Equip. Cost	Other	Total	Non-labor	Labor Hrs.	Water	Process Chem.	Treat. Chem.	Sludge Disp.	Energy	Other	Total	Code	Time %	Manf. Support	Technology	Decision
012	Nickel, Watts	LEA (Lancy)	1982	$23,000	$4,000	$27,000	ND	125	√	√	√	√	$0	$0	√	2	ND	2	1	4
125	Nickel, Watts	Baker Bros.	1986	$44,000	$2,000	$46,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	2	ND			3
Average for ED Recovery Applications			1984	$33,500	$3,000	$36,500		125					$0	$0				2.0	1.0	

Notes:

(1) Use Codes: 1-currently operating; 2-not currently operating and no intension for future use; 3-not currently in use, but intend to use in future.

(2) Satisfaction levels (manufacturer and technology) 1 to 5, with 1=lowest and 5=highest.

(3) Future decision codes: 1-purchase the same technology from the same vendor; 2-purchase the same technology from a different vendor; 3-purchase a different technology; 4-do nothing.

(4) "√" indicates that a savings was realized, but not quantified.

(5) Blank spaces indicate that no data were provided.

(6) ND = no data.

United States
Environmental Protection
Agency
Research and Development

Risk Reduction
Engineering Laboratory
Cincinnati, OH 45268
EPA/600/SR-94/071 July 1994

EPA

Project Summary

Evaluation of an Electrodialytic Process for Purification of Hexavalent Chromium Solutions

Dale W. Folsom, Jody A. Jones, and Robert F. Olfenbuttel

The evaluation summarized here addresses the waste reduction and economics of an electrodialytic process that can be used to selectively remove impurities that build up in chromic acid solutions with use. The removal of impurities extends the useful life of the chromic acid solution and reduces periodic replacement of the solution. The electrodialytic units tested in this evaluation were manufactured by Ionsep™*. The units were tested at SL Modern Hard Chrome in Camden, NJ, (a hard chromium plating solution) and at Paramax in St. Paul, MN, (a chromic acid solution etching copper from printed wire boards).

The electrodialytic process was found to effectively remove the impurities that build up in chromic acid solutions. The rate of return on investment was not cost effective for the hard chromium plating bath but was cost effective for the chromic acid etch bath, which had a payback of less than 5 yr. In these two examples, the payback was related to the rate of contaminant buildup in the solution — the more frequently a solution was replaced when contaminants were not removed, the shorter the payback after an electrodialytic process had been installed. The chromium plating operation annually reduced chromium needing disposal by 73 kg (161 lb), and the copper etching operation projected an annual reduction of 4,410 kg (9,700 lb).

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

Introduction

This study, performed under the U.S. Environmental Protection Agency's (EPA) Waste Reduction and Innovative Technology Evaluation (WRITE) Program, was a cooperative effort among EPA's Risk Reduction Engineering Laboratory (RREL), SL Modern Hard Chrome, and Paramax. The goal of the WRITE Program is to evaluate, in a typical workplace environment, examples of prototype or innovative commercial technologies that have potential for reducing wastes and then to provide this information to potential users. The objectives of the electrodialytic technology study were to evaluate (1) the waste reduction potential of the technology, (2) the economic feasibility of the technology, and (3) the impact on product quality.

SL Modern Hard Chrome was the site for testing the electrodialytic process on a hard chromium plating solution. SL Modern Hard Chrome has specialized in industrial hard chrome plating for over 35 years and plates a full spectrum of materials, ranging from aluminum through the copper, ferrous, and nickel base alloys to zinc. The chromium thickness varies from 0.0001 in. to 0.030 in. or more on parts ranging in size from a few ounces to sev-

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* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

eral tons. Paramax (a Unisys company) was the site for testing the electrodialytic process on a chromic acid etching solution. Paramax manufactures multilayer printed wire boards at this facility.

At SL Modern Hard Chrome, contamination builds up in the chromium plating solution. The contaminants typically are in the form of cations, including iron, trivalent chromium, and lead. As the contaminants build up, the plating solution fails to produce the required product quality and must be replaced. The Ionsep™ electrodialytic process removes the cations from the chromium plating solution and allows it to be used longer. At SL Modern Hard Chrome, it has been more than 3 yr since a chromium plating bath was replaced.

Paramax uses a chromic acid solution to etch copper from printed wire boards (PWB). As copper builds up in the etching solution, the etching rate becomes unacceptably slow. Before Ionsep™ installation, the chromic acid solution was replaced with fresh solution from once a day to once a week at the operator's discretion. The Ionsep™ electrodialytic process extends the usefulness of the etching solution by removing copper from the etching solution and converting some of the trivalent chromium back to hexavalent chromium electrolytically.

Ionsep™ Electrodialytic Process

The aim of this technology is to reduce wastes by removing metals other than chromium from the process solution. This improves plating and etching product quality and extends process solution life.

Figure 1 shows a two-compartment cell used for the purification of a chromium plating solution. The Ionsep™ electrodialytic process uses a voltage gradient to separate salt in a solution into cations and anions. Chromium is present in the anionic chromate form in the plating and etching solutions. Metal contaminants (cations) migrate across a semipermeable membrane, under the influence of the electric field. Conversion of the electroplatable metal cations to insoluble hydroxides occurs when the cations migrate through the membrane; this migration eliminates the buildup of metals on the cathode. Membranes in the electrodialytic cells serve to physically separate the acidic, basic, and other process solutions.

Materials and Methods

One test site uses a chromium plating solution and one a chromic acid for etching copper. At each site, metal analyses were performed on the chromium solution and the catholyte solution to determine contaminant levels in the process solution and the rate of metals buildup in the catholyte solution. From the analyses, the rate of metals buildup in the catholyte solution was determined. This corresponded with metals removal from the process solution, which in turn was used to determine the bath life-extending capabilities of the Ionsep™ process and the waste reduction potential. Operating costs with and without the Ionsep™ process were used along with installation costs to determine the economics of the process.

Results and Discussion

The results from the two sites are discussed separately for each site because the bath process and the Ionsep™ process used at the two sites were very different. For each site, the discussion is divided into the three project objectives: waste reduction potential, economic evaluation, and product quality evaluation.

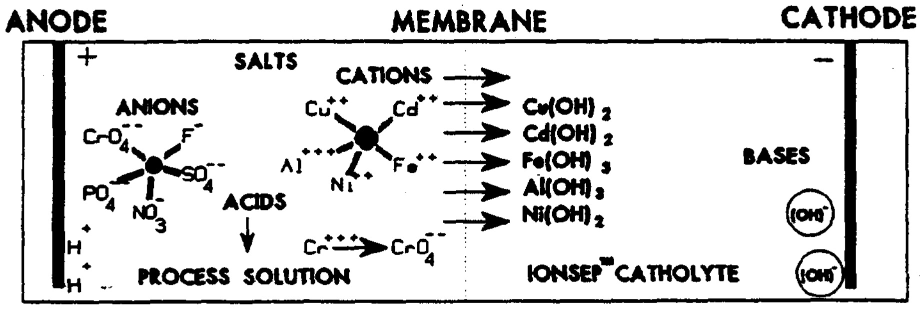

Figure 1. Ionsep™ electrodialytic process.
(Source: Ionsep™ Corporation, 1989)

Chromium Plating

At SL Modern Hard Chrome's 1,400-gal hard chromium plating bath, the chromium plating solution was recovered continuously by placing the Ionsep™ unit (cell) directly into the bath. The catholyte solution is contained in a plastic 55-gal drum outside the bath and is circulated through the Ionsep™ cell.

Waste Reduction Potential

SL Modern Hard Chrome purchased the Ionsep™ system as part of its plan to eliminate all industrial liquid waste discharges to the city. To achieve zero liquid discharge, SL Modern Hard Chrome initially rinses parts over the bath; the final rinse is totally collected in a sump, filtered, and then returned to the bath to make up water lost to evaporation.

Impurities build up in the plating bath because all rinse water is returned to it; the Ionsep™ system was purchased to reduce this buildup. With use of Ionsep™, the only resulting waste discharge is the sludge from the Ionsep™ catholyte solution. This catholyte sludge contains levels of chromium at 2000 to 3200 mg/L total chromium and 760 to 1050 mg/L hexavalent chromium and therefore must be handled as a hazardous waste. With the catholyte solution replaced monthly, the annual discharge of total chromium is 6.5 kg (14.2 lb).

The catholyte solution was analyzed after the solution had been in use for 1 to 2 months and immediately before disposal. The metals in the catholyte solution were removed from the plating bath. Analysis indicates a removal rate of approximately 25 g total contaminants/day for a 250-amp Ionsep™ unit. If the contaminants were not removed, levels would eventually reach the limit of 52 g/L in the plating bath. The time estimated from these data for a 1,400-gal bath to reach that limit is 52 g/L x 3.79 L/gal x 1,400 gal/25 g/day, or 11,036 days. Therefore, the use of Ionsep™ extends bath life beyond 40 years, which results in approximately 35 gal of solution saved/yr (that would otherwise be disposed of), based on an operation schedule of 250 days/yr (1,400-gal bath/40 yr).

Hexavalent chromium is significantly reduced with the use of the Ionsep™ unit — from 165 lb to 14.2 lb. The 14.2 lb of chromium is the small amount lost to the catholyte solution. The reduction is the result of not having to replace the bath periodically and of having all rinse water returned to the plating bath to make up evaporative water losses.

Chromium is saved not only through reduced replacement of plating solution, but also through the reduced number of rejects. For every reject, the company must strip and replate the part. The reject data are based on estimates of plant personnel, because no records were maintained. The 5% decrease in rejects experienced by SL Modern Hard Chrome corresponds to approximately 237 lb chromium/yr that is not disposed of with the stripper and that need not be purchased for addition to the plating solution. The 237 lb of chromium oxide is calculated from the company's plating rate from this bath of 42,900 ft^2/yr, at a plating amount of 1.77 oz CrO_3 per ft^2, and a 5% savings (0.05 x 42,900 ft^2/yr x 1.77 oz/ft^2 x 1/16 oz/lb).

Table 1 summarizes the waste reduction potential of the new technology. The top part of Table 1 (without Ionsep™) lists the wastes from infrequent bath replacement and the estimated amount of chromium stripped from rejected parts. The bottom part of Table 1 (with Ionsep™) lists the chemicals used to make the Ionsep™ catholytic solution and the additional barium carbonate used to adjust the sulfate levels of the chromium plating bath. Barium carbonate is used to precipitate the sulfate as barium sulfate. The use of barium carbonate increased when the Ionsep™ was installed.

The total waste without the use of Ionsep™ amounts to 317 lb of CrO_3 (165 lb Cr). The total waste with the use of Ionsep™ increases to 451 lb. This increase is the result of the catholyte salts and sludge and the increased use of barium carbonate to reduce sulfate in the bath. The sulfate concentration builds up faster in the bath because rinse water is reused in the bath when the Ionsep™ unit is used. In a 1-yr period, 36 lb of barium carbonate was used to form barium sulfate, which precipitates out in the bath. The precipitate is either filtered out or allowed to collect at the bottom of the plating bath. The 36 lb of barium carbonate would react to form 43 lb of barium sulfate.

Economic Evaluation

SL Modern Hard Chrome provided economic information for most aspects of its operations. The annual operating costs with and without the Ionsep™ unit are itemized in Table 2. Without the Ionsep™ system, the operation of a 1,400-gal bath costs \$3,684/yr. The cost for the same bath with an electrodialytic unit is \$3,578/yr.

According to SL Modern Hard Chrome personnel, a major incentive for installing the equipment was to improve product quality by reducing contaminant buildup in the plating bath. Fewer rejects result in economic savings (e.g., faster turnaround time, decreased need for stripping solution, and ease of operation). The costs for rejects and additional plating are included in the operation without Ionsep™.

The capital cost of a 250-amp Ionsep™ unit in the fall of 1991 was \$20,000. Because there is a savings of \$106 in annual costs using the Ionsep™ unit, there is a payback on the unit of 189 yr.

Although economic considerations are important, they are not the only justification for installing waste reduction equipment. SL Modern Hard Chrome has zero discharge from its plating operations to the city water treatment system because all rinsewater is returned to the plating baths.

Table 1. Waste Reduction of the Chromium Plating Line

Waste	*Annual Generation*
Without Ionsep™	
CrO_3 in bath solution	*80 lb (41.6 lb Cr)*
CrO_3 due to rejects	*237 lb (123 lb Cr)*
Total CrO_3	*317 lb (165 lb Cr)*
*With Ionsep™**	
Catholyte solution	
Sodium sulfate	*120 lb*
Sodium carbonate	*288 lb*
Additional barium sulfate from sulfate reduction w/$BaCO_3$	*43 lb*
Total†	*451 lb (14.2 lb Cr^{+6})*

* *Sludge from Ionsep™ not included because it should equal the amount of metal contaminants disposed of with the chromium plating solution without Ionsep™.*

† *The sludge for 1 yr would contain 14.2 lb Cr^{+6}.*

Product Quality Evaluation

Chemical analyses of the chromium plating solution were conducted to verify that the solution met operational specifications for hard chromium plating solutions. Analysis of the bath showed it was within specifications — the contaminant level was below the maximum of 52 g/L and the chromium level was above the minimum of 140 g/L.

The products, chromium-plated parts, are inspected for pits, blisters, other deformities, and chromium thickness. The product quality is the plated part quality, which correlates with the plating bath quality (specifications). Since installation of the Ionsep™ unit, the number of rejects has decreased by about 5%, a key factor in its continued use. The improved chromium plating quality has produced more uniform chromium deposit and fewer pits.

Chromium Etching

At the second company, Paramax, chromium-based etchant was tested as a batch process. Eight of the six cells in the process line were used, and over a 2-day period, 200-gal etchant baths were removed from the process line to a treatment tank and pumped through the Ionsep™ unit. The unit ran continuously for 3 days. Paramax has since established that the recovered etchant meets its stringent requirements for etching solutions. The company is currently using 12 cells to keep up with the buildup of copper and has successfully recycled the etchant during production.

Waste Reduction Potential

Calculation of the waste reduction potential was based on the difference between the amount of chromic acid etch solution disposed without Ionsep™ treatment and the amount of chromic acid etch that can be reused after treatment with the Ionsep™ unit.

Experience at Paramax indicates that use of the Ionsep™ unit prevents disposal of approximately 7.5 baths/wk. Paramax currently disposes of 8.5 baths/wk and estimates that, with the Ionsep™ unit, disposal will be reduced to one bath/wk. Each bath contains 110 gal (the Ionsep™ unit can treat up to 500 gal, or about four baths in 4 days), which means that 41,250 gal of etchant bath solution would not be disposed of per year (7.5 bath/wk x 110 gal/bath x 50 wk/yr). The etchant concentrate is diluted 50% to make up the bath. Therefore, the Ionsep™ unit could reduce 20,625 gal of etchant concentrate per year

Table 2. *Economics of the Chromium Plating Line**

Description	*Annual Use*	*Rate ($)*	*Annual Cost ($)*
Without Ionsep™			
Cr bath	*35 gal*	*$11.30/gal*	*$396*
Bath disposal	*35 gal*	*2/gal*	*70*
CrO_3 due to rejects	*237 lb*	*1.13/lb*	*268*
Labor due to rejects	*140 hr*	*20/hr*	*2,800*
Strip solution replacement and disposal	*100 gal*	*1.50/gal*	*150*
Total without Ionsep™			*$3,684*
With Ionsep™			
Catholyte solution			
Sodium sulfate	*120 lb*	*18/100 lb*	*$22*
Sodium carbonate	*288 lb*	*18/100 lb*	*52*
Water	*660 gal*	*2.66/1000 gal*	*2*
Barium carbonate	*36 lb*	*1.22/lb*	*44*
Sludge disposal	*4 drums*	*205/drum*	*820*
Labor	*41 hr*	*20/hr*	*827*
Maintenance	*—*	*—*	*1,080*
Power	*8,100 kWh*	*.0902/kWh*	*731*
Total with Ionsep™			*$3,578*
Annual savings			*$106*

* *Wastewater discharge costs are not applicable. Analytical costs are assumed to be the same for both cases.*

needing disposal. This amount of etchant contains approximately 7,154 lb of chromium that would otherwise have gone to waste (80 g/L CrO_3 in etchant x 52 g Cr/100 g CrO_3 x 20,625 gal x 3.785 L/gal). Table 3 summarizes the items evaluated in the waste reduction analysis.

To recover the etched copper, Paramax acidifies the cake filtered from the catholyte solution. Water use at Paramax is increased to make up the catholyte solution. After acidification and copper recovery, the resulting solution is nonhazardous.

Economic Evaluation

Paramax provided economic information for its etching operations. Because the Ionsep™ unit at Paramax is still undergoing testing, most of the cost analysis was based on Paramax estimates derived from economic information in plant records and experience of Paramax personnel. These estimates indicate that the unit can prevent disposal of approximately seven etchant baths/wk and, thus, save disposal and replacement chemical costs.

Operating cost factors involved in the economic analysis for Paramax include labor, maintenance, chemicals, utilities (water and electricity), and waste treatment/disposal. Table 4 compares costs with and without the Ionsep™ unit.

Without the unit, costs of approximately $198,000 are incurred for replacement and disposal of the etchant baths. Estimates for operating the unit are approximately $72,000/yr, mostly for added labor and maintenance on the unit. Thus, with the Ionsep™ system, an approximate annual savings of $126,000 would be realized. The capital cost of the unit (specific to Paramax), including installation and modifications, was $563,000. Dividing this by the estimated annual savings results in a payback period of 4.5 yr.

Table 3. *Waste Reduction of the Etching Line*

Description	*Amount Discarded Per Year*
Without Ionsep™	
Etchant	*20,625 gal*
Water	*20,625 gal*
Chromium	*7,100 lb*
With Ionsep™	
Catholyte solution	
Sodium chloride	*10,000 lb*
Sodium sulfate	*5,000 lb*
Soda ash	*1,000 lb*
Water	*25,000 gal*
Chromium	*42 lb**

* *Estimated.*

Product Quality Evaluation

The Ionsep™ unit at Paramax was in the initial testing phases during this study. The etchant was sampled and analyzed for both chromium and contaminants at the end of the 3-day treatment/recovery process. These analyses were used to determine whether the renovated bath was within specifications and whether bath quality was an indication of product quality. Although total chromium in the etchant remained constant, hexavalent chromium increased. The hexavalent chromium started at approximately 74% of the total and increased to about 99%. It is believed that oxidation of the trivalent chromium back to the hexavalent form caused the increase in hexavalent chromium concentration. The resulting hexavalent chromium concentration of 30.3 g/L in the etchant over the 3-day sampling period approached the minimum specification level of 31 g/L. This could be increased further by longer treatment or by adding etchant concentrate. At the time this study was conducted, the etchant had not been reused and the effect of recovered solution on in-house printed wire board product quality had not been evaluated.

The cationic contaminants were within specification. The 10.8 g/L (mostly copper) was below the maximum level of 25 g/L. Because the chromium and the contaminant levels are both near specification levels, the etchant should be acceptable.

The full report was submitted in partial fulfillment of Contract Number 68-CO-0003, Work Assignment 3-36, by Battelle (Columbus) under the sponsorship of the U.S. Environmental Protection Agency.

Table 4. Economics of the Etching Line

Description	*Annual Use*	*Rate ($)*	*Annual Cost ($)*
Without Ionsep™			
Etchant (concentrate)	*20,625 gal*	*$ 4.85/gal*	*$100,031*
Etchant disposal	*41,250 gal*	*2.31/gal*	*95,288*
Labor for disposal	*150 hr*	*20.00/hr*	*3,000*
*Water**	*20,625 gal*	*2.66/1000 gal*	*55*
Total			*$198,374*
With Ionsep™			
Catholyte solution			
Sodium chloride	*10,000 lb*	*3.50/50 lb*	*700*
Sodium sulfate	*5,000 lb*	*17.50/100 lb*	*875*
Soda ash	*1,000 lb*	*0.23/lb*	*230*
*Water**	*25,000 gal*	*2.66/1000 gal*	*66*
Labor	*2,000 hr*	*20.00/hr*	*40,000*
Maintenance	—	—	*30,000*
Power	*1,430 kWh*	*0.045/kWh*	*65*
Total			*$ 71,936*

** Water costs include sewage fee.*

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The complete report, entitled "Evaluation of an Electrodialytic Process for Purification of Hexavalent Chromium Solutions," (Order No. PB94-165214; Cost: $17.50, subject to change) will be available only from:

National Technical Information Service
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September 1995

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