Electrowinning
in

Pollution Prevention and Control Technology for Plating Operations

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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.

Electrotwinning 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 tow&d 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 currentdensity 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 adrag-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 fiat 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.

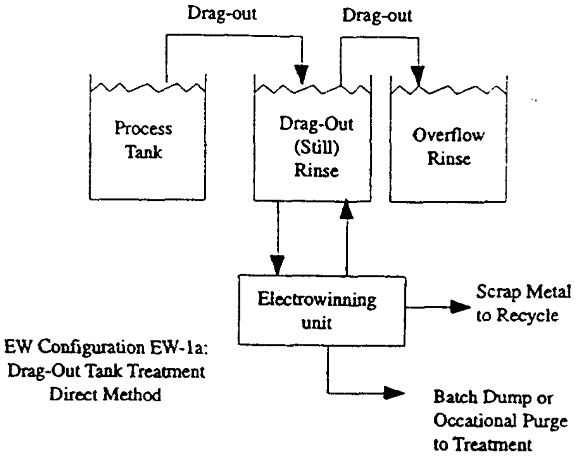
The second configuration (EW-2) is a combination of ion exchange and electrowinning. This configuration potentially has a much higher metal recovery efficiency than the first configuration. It addresses both of the factors that impact metal recovery efficiency. The ion exchange unit maintains a low metal 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.

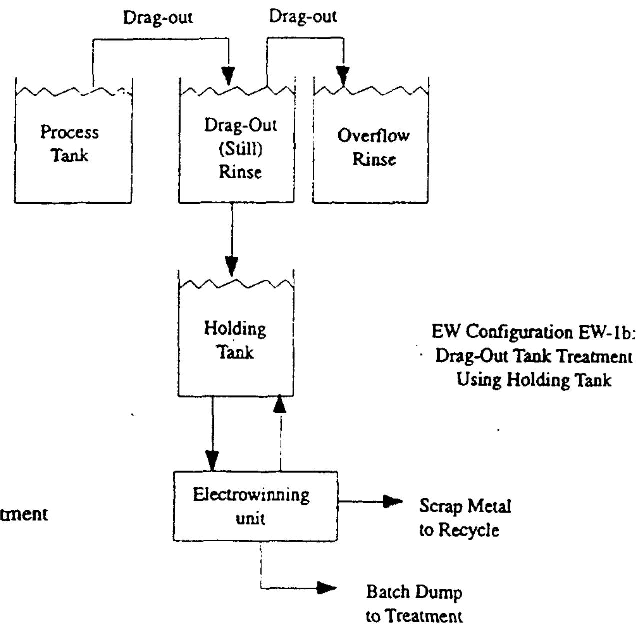
The third configuration shows the recovery of metal from a spent process solution. Either the flat plate or reticulate cathode type of unit can be used in this configuration. The reticulate cathode type will provide greater metal recovery efficiency because it can lower the metal concentration of the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

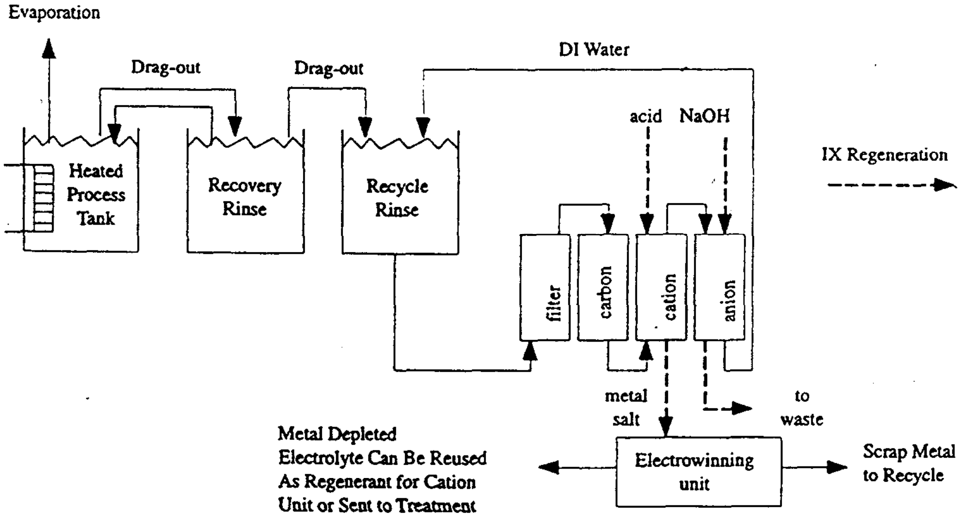
Electrowinning is applied to a wide variety of chemical solutions in the electroplating industry. The literature indicates that the metals that are most commonly recovered by electrolytic treatment are gold, silver, copper, cadmium, and zinc. The metal recovery applications identified from the Users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

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

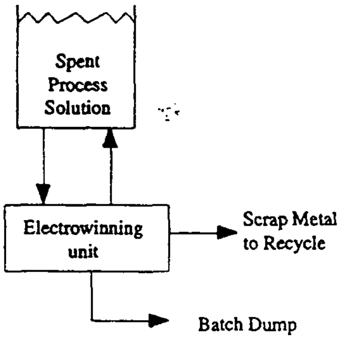


EW Configuration EW-1a: Drag-Out Tank Treatment





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 withcopper 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 tiles

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 over-potential 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 over-potential increases current efficiency; and (3) corrosion resistance provides higher durability and stability.

Most commonly, fiat 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-Tee 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 l/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. 10.5).

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)

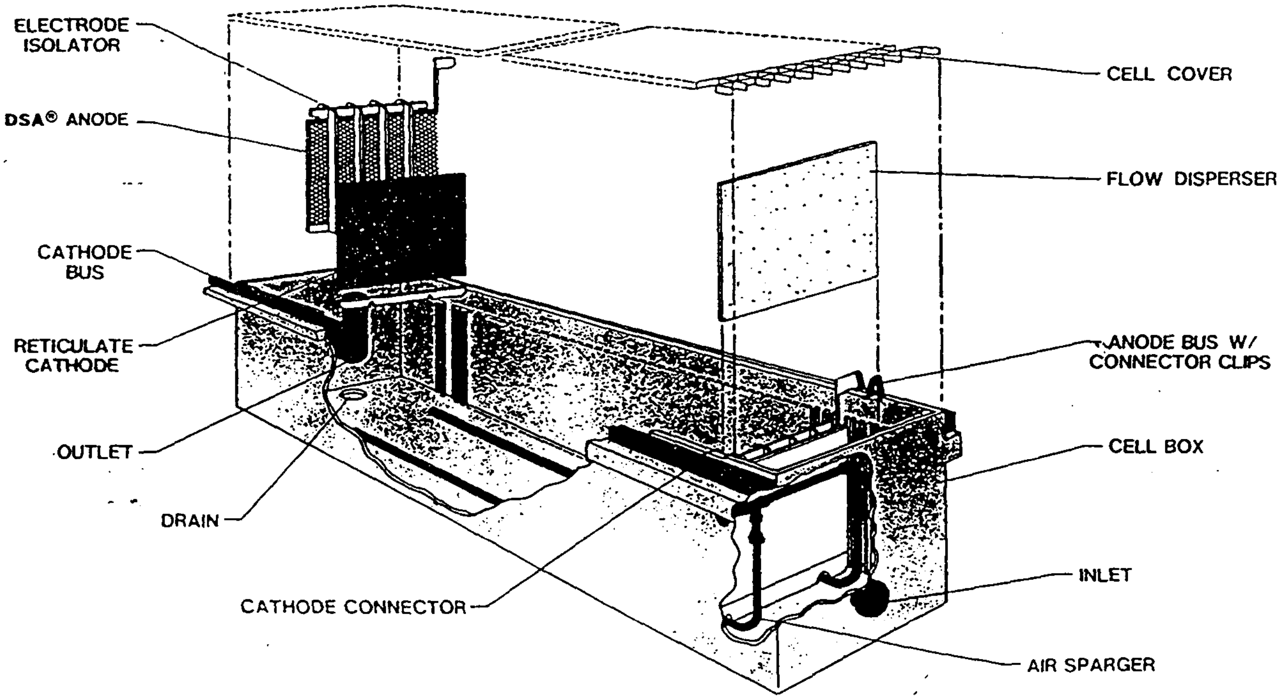
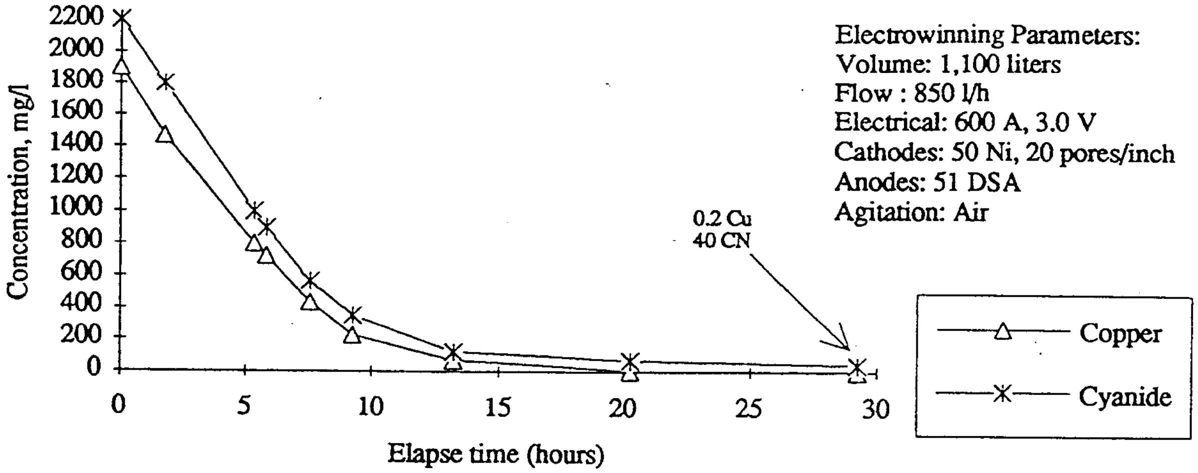


Exhibit 3-38. Example of the Performance of a Reticulate Cathode Electrowinning Unit Treating a Copper Cyanide Bath



Source: ref. 103

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

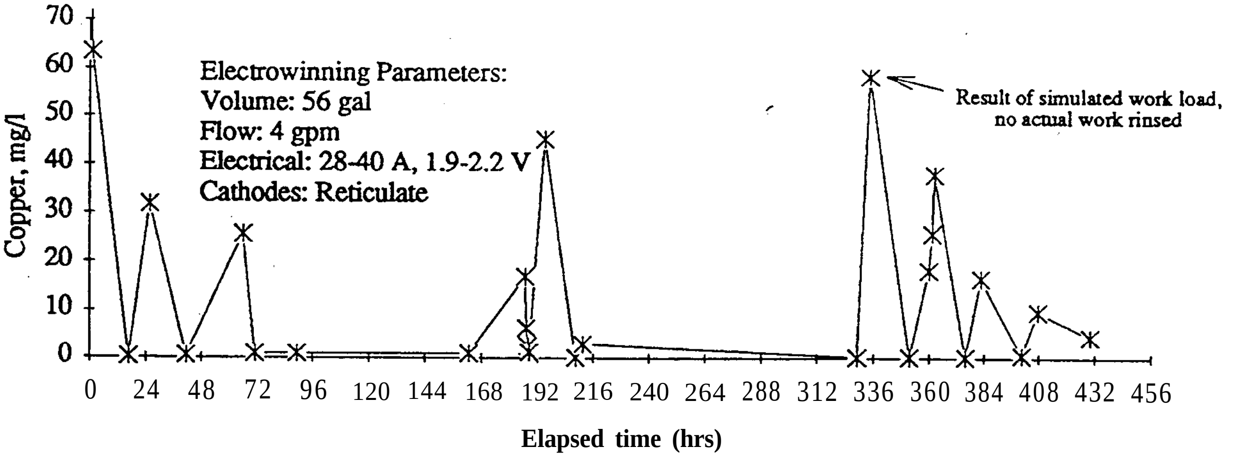
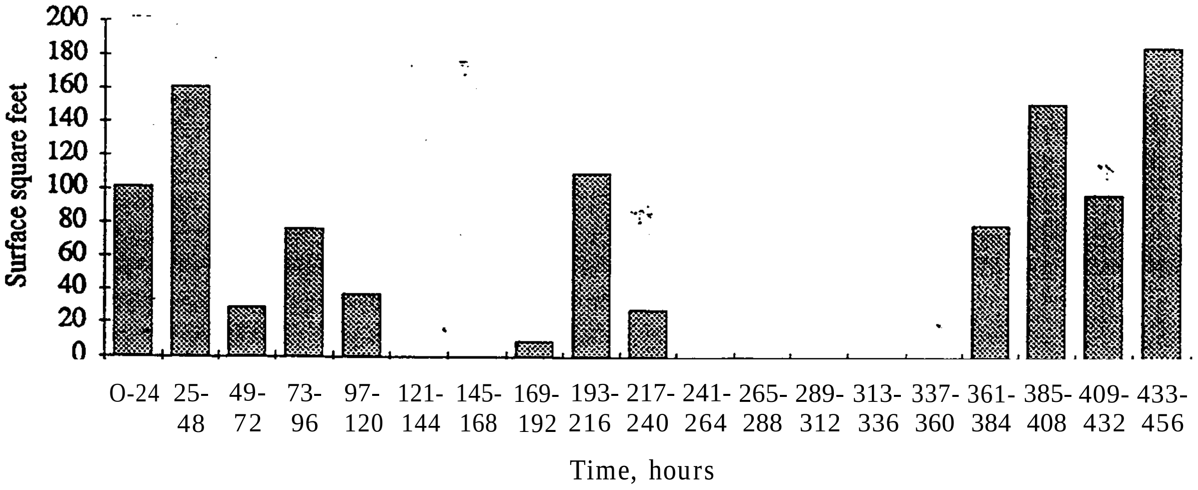


Exhibit 3-39(b). Work Load Through Copper Sulfate Static Rinse



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

set-up as EW configuration EW-la, 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.

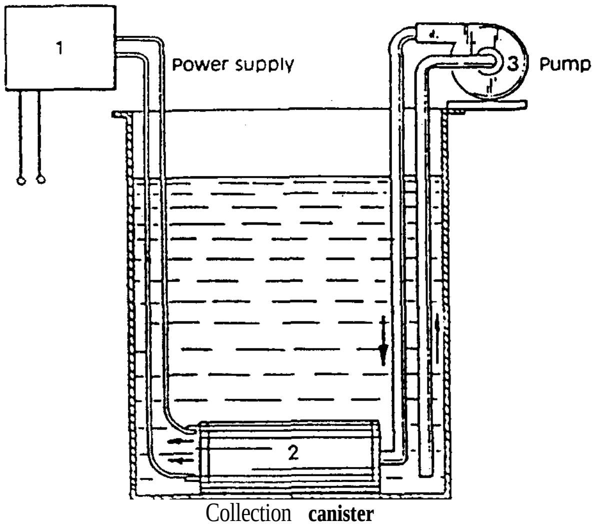
A reticulate and disposable cathode is often used for gold electrowinning. A small commercial unit, operating with only 25 amps output, is shown in Exhibit 3-40. The cathode of this unit is placed directly into a small drag-out tank. This unit is applicable to the recovery of most precious metals. It 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 equip** ment to achieve agitation and reduce the impact of concentration polarization. One manufacturer (ref. Eco-Tee 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 tile). 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 3-4 1. 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):

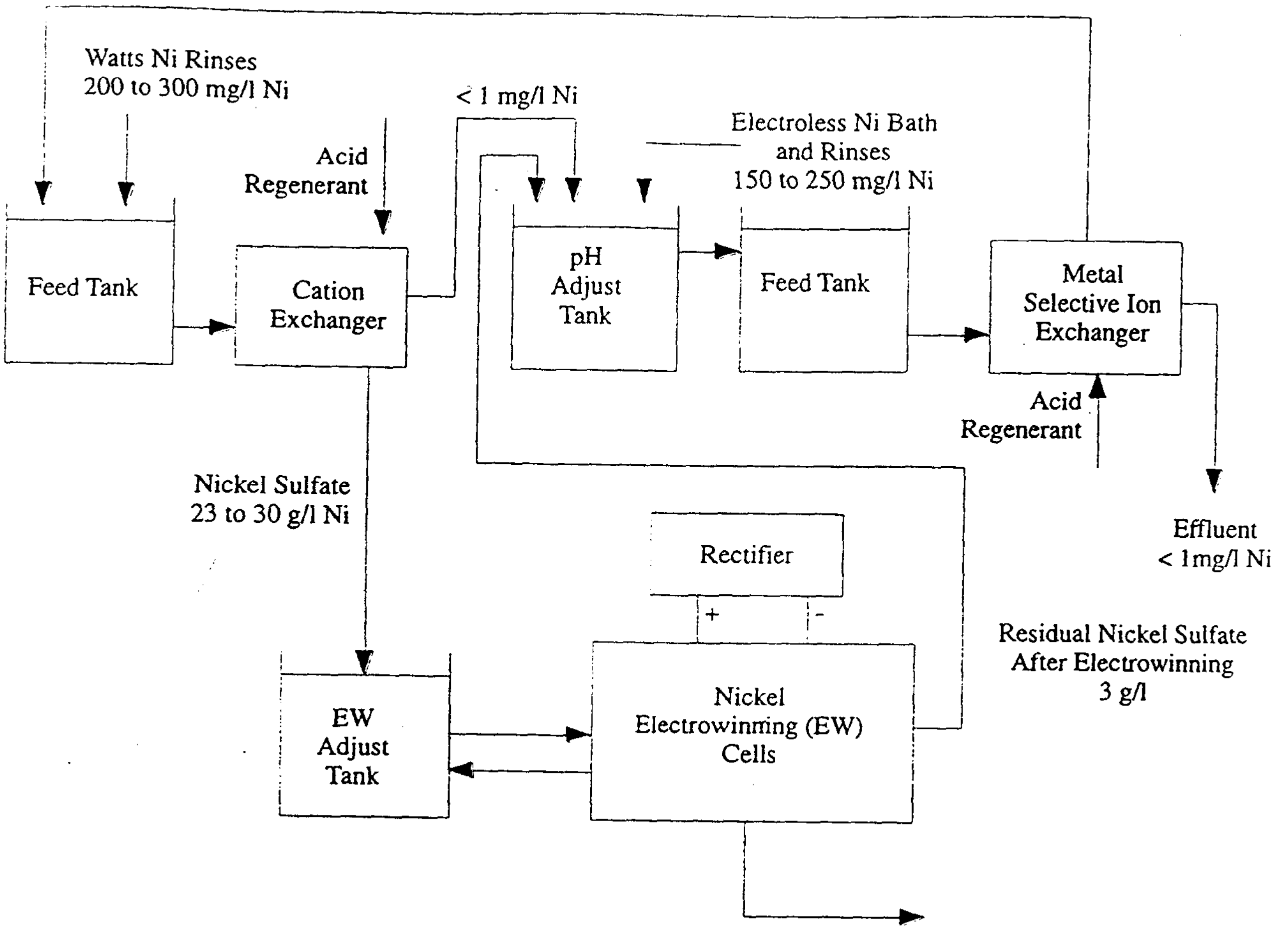
- Electrode type and area
- Agitation rate (or in general, mass transfer)
- Solution chemistry
- Electrical variables
- Temperature

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

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

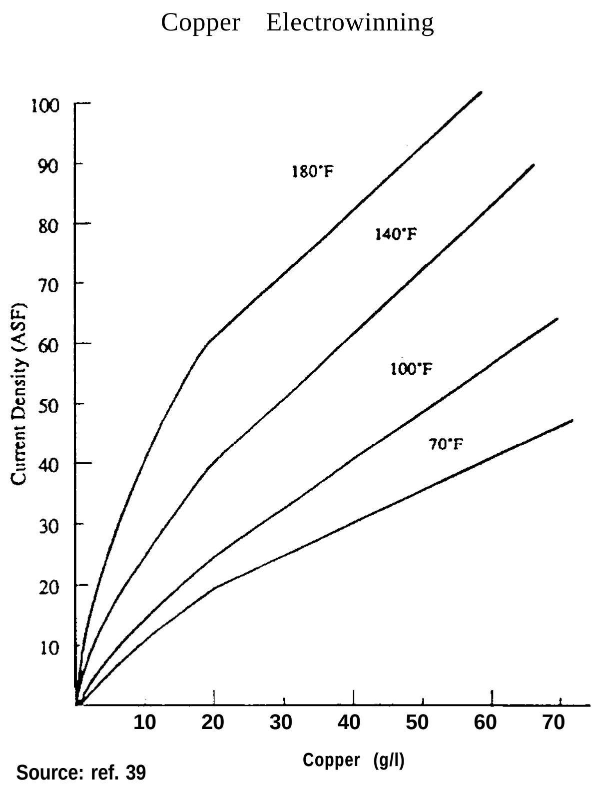
introduced into the tank is determined either by direct analysis, or by a method such as that proposed in Section 2.5.3.1. The plating rate of the metallic species in question is obtained from the Faraday Table presented in Exhibit 3-42. Capacity requirementin amperes, therefore, is the introduction 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/batchl]/[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

concentration. Thus, in practice, it is the total cathode



Source: ref. 39

area and the concentration of metal in the electrolyte that

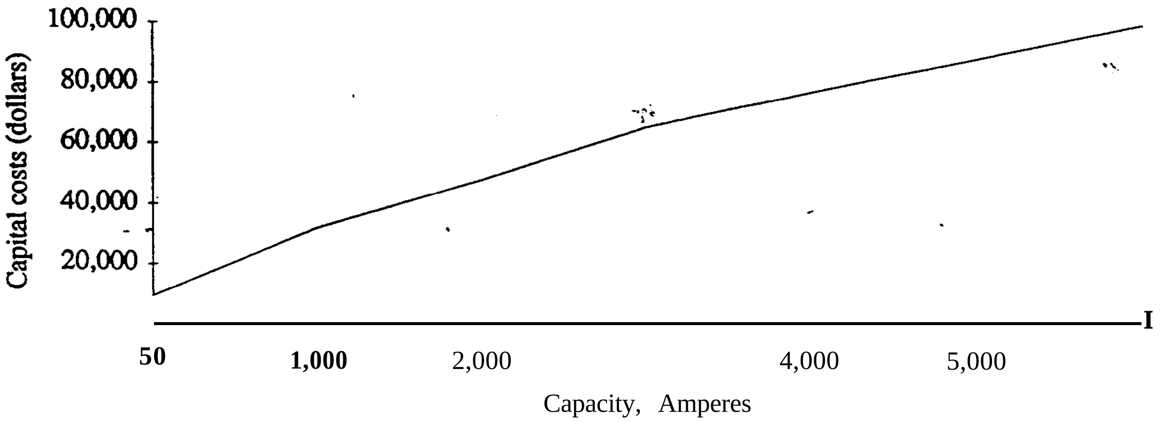
Exhibit 3-43 demonstrates the considerable effect of con-

sity for copper electrowinning; similar curves are to be

Low concentration electrolytes present significant siz-

concentration current densities and efficiency is lost as

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 re-

on average, roughly split between the labor and non-labor categories. This technology is not labor-intensive nor electrode replacement, maintenance and energy.

Labor costs are largely installation- and application-spe-

considerable solution transport, pre-adjustment of the electrolyte, cleaning of salt deposits and adjustment of

cated drag-out rinse units treating fluids with lower total dissolved solids may require only occasional cleaning

maintenance beyond cleaning and replacement of corroded connectors is to be expected.

total operating costs for most applications. For large units, however, energy costs may more significant in re-

from economies of scale. Predicting energy costs for a given application is complicated by the fact that several

or impossible to know prior to actually running the unit. Conductivity, required voltage, rectifier efficiency, and

time or batch to batch. Once the unit is operating, energy costs will become easy to assess. In the example

of Cu; these costs reflect metal removal to <5 mg/l and should be typical of similar applications.

tion and life expectancy. Stainless steel cathodes are usually peeled or scraped free of plating deposits and

accumulate sufficient metal to lower their effectiveness, roughly 5-10 pounds/sq. ft. of cathode area. Anodes may,

be semi-permanent and last in excess of 5 years. Graph-

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

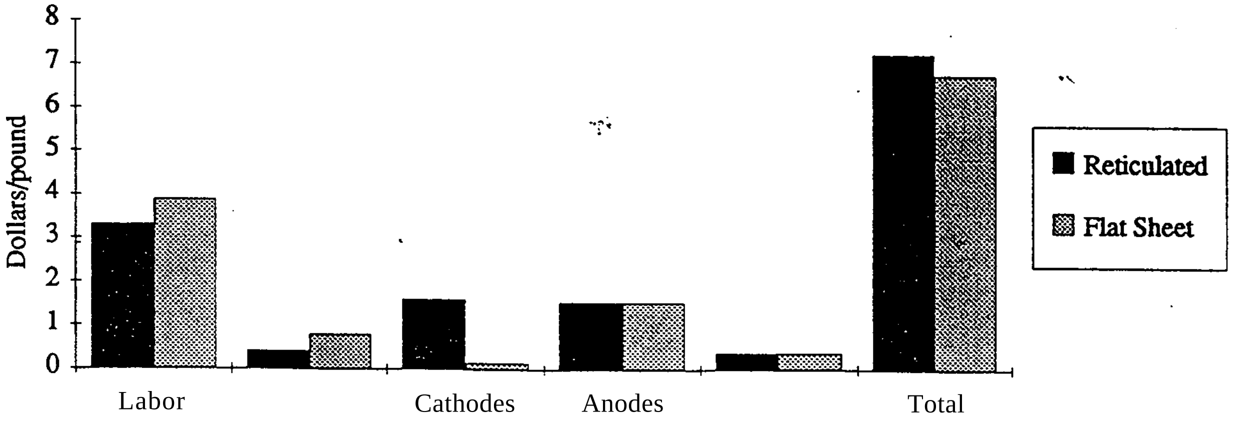


Exhibit 3-46. An Example of Calulating Operating Costs for an Electrowinning Application

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
Installations	5,100
Total	$ 27,100
Operating Costs/Year:	
Energy	$450
Labor	3,900
Cathodes[b]	895
Anodes’	1,650
Parts	300
Chemistry“	750
Scrap metal value’	(643)
Total	$7,302
Savings/Year	
Waste treatment savings’	$7,700
Metal recovered	

Unit required a fume hood and exhaust system due to the generation of SO, 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.

[c] Received average of $0.60/ilb. Metal **price** averaged $1.00 during year.

[r] Labor-intensive batch precipitation method.

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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	I
No Change	55	50
Decreased	1	5

(Where product or production impacts occurred. the respondents did not provide any details of thc 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	BEWT	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	BEWT	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	Zinc, 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	Zinc, 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 Phos	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	RPH 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 techoology; 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 bf 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 present&d 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 l/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.