



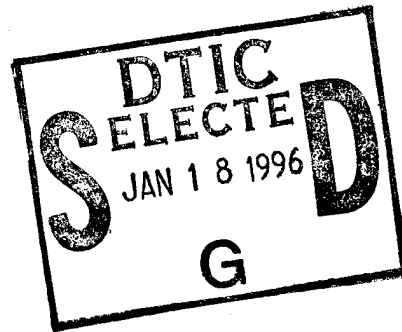
NAVAL FACILITIES ENGINEERING SERVICE CENTER
Port Hueneme, California 93043-4328

Technical Report TR-2046-ENV

USER DATA PACKAGE FOR IMPLEMENTATION OF ELECTROLYTIC RECOVERY TECHNOLOGY IN NAVY ELECTROPLATING SHOPS

by

K. Ford and J. Koff



October 1995

19960116 003

Sponsored by
Naval Facilities Engineering Command
Alexandria, VA 22332-2300

Approved for public release; distribution unlimited.

DTIC QUALITY ASSURANCE

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-018	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE October 1995		3. REPORT TYPE AND DATES COVERED Final; Mar 1993 through Jan 1995
4. TITLE AND SUBTITLE USER DATA PACKAGE FOR IMPLEMENTATION OF ELECTROLYTIC RECOVERY TECHNOLOGY IN NAVY ELECTROPLATING SHOPS			5. FUNDING NUMBERS PR - Y0817	
6. AUTHOR(S) K. Ford and J. Koff				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESSE(S) Naval Facilities Engineering Service Center 560 Center Drive Port Hueneme, CA 93043-4328			8. PERFORMING ORGANIZATION REPORT NUMBER TR-2046-ENV	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESSES Naval Facilities Engineering Command 200 Stovall Street Alexandria, VA 22332-2300			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) In FY94, the Naval Facilities Engineering Service Center (NFESC) completed tests on three electrolytic recovery systems used for the recovery of metals and destruction of cyanide from electroplating wastewaters. Field testing and evaluation was conducted at NSY Norfolk, NAWC Indianapolis, and NADEP Cherry Pt. for five metal recovery applications: silver cyanide, copper cyanide, acid copper, electroless nickel, and tin-lead fluoborate. Advanced design features for metal recovery, including enhanced fluidized circulation, specialized oxidizing anodes, and high porous surface area cathodes were evaluated to optimize performance. NFESC demonstrated that electrolytic recovery systems can be adapted for effective use in the Navy plating operations where production is often sporadic as contrasted to industrial plating processes. The electrolytic recovery units removed metal ions from the rinsewater to below 1 ppm for each application. Electrowinning, as an alternative technology, can reduce industrial waste treatment costs and hazardous sludge generated from conventional treatment. This User Data Package (UDP) covers the design, operational and maintenance requirements for these electrolytic systems. This UDP will be applicable to small Navy plating shops where closed-loop waste recycling and point source minimization is necessary for environmental compliance and cost competitiveness.				
14. SUBJECT TERMS Electrowinning, electrolytic recovery unit (ERU), wastewater treatment, metal recovery, cyanide oxidation			15. NUMBER OF PAGES 80	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	UL	

Disclaimer

This report has been reviewed by NFESC and approved for publication. The mention of trade names or commercial products does not constitute endorsement or recommendation for use.

EXECUTIVE SUMMARY

This User's Data Package (UDP) provides the necessary information to implement electrolytic recovery technology on Navy plating rinsewaters. Based on field test results from three Navy plating shops, this UDP was developed for five applications: silver cyanide, copper cyanide, acid copper, electroless nickel, and tin-lead fluoborate. This UDP instructs the user in selection of advanced designed Electrolytic Recovery Units (ERU). Key guidelines for sizing, installation, operation, maintenance, safety, and training are discussed in this UDP. A sample economic cost/savings analysis for an average plating shop is contained in Appendix B. This UDP also gives guidance for selecting applications that were not field tested, but potentially will be highly successful using advanced electrolytic recovery technology.

Electrowinning

Electrolytic recovery from plating rinsewaters, often called electrowinning, provides direct recovery of metal instead of the conventional end-of-pipe treatment. The electrolytic recovery unit (ERU) is connected in a closed loop to the first rinse tank or still rinse. After parts are plated, they are rinsed to remove any residue in the still rinse. A running rinse serves as a final rinse, with discharge to the industrial wastewater treatment plant (IWTP). The ERU has a cell with anodes and cathodes, a pump for circulation to and from the still rinse tank, and a rectifier. When a direct current is applied to the cell, the metal cations are reduced to elemental metal at the cathode, with simultaneous oxidation of organic anions, i.e., cyanide, at the anode.

Benefits of Advanced Design Electrolytic Recovery Units

Due to the Navy's varied plating applications, innovative designs in electrowinning can extend the operating range of this technology for metal recovery at low concentrations, continuous operation, ease of maintenance and cost effectiveness. Metal recovery can be enhanced at the cathode by increasing the cathodes' surface area and by greater agitation in the electrolytic cell through air sparging or a fluidized bed. In the rinsewaters tested, metal ions could be removed to below 3 ppm for each plating application. Using precious metal-coated anodes, cyanide destruction by oxidation to nontoxic substances enables this technology to have the potential of eliminating end-of-pipe treatment for cyanide laden wastewaters if applied to all the metal cyanide plating lines. For applications containing cyanide in the rinsewater, cyanide destruction at the anode resulted in concentrations less than 5 ppm in this anion.

Navy Pollution Prevention Program

Advanced electrolytic recovery technology supports the Navy's Pollution Prevention Program as outlined in OPNAVINST 5090.1B.

Technical Distribution and Use

The publication of this UDP completes the distribution of information on electrolytic recovery technology by NFESC Code 421, Pollution Prevention Technology Development Branch. NFESC Code 423 Information/Technology Transfer Branch, will continue to provide technical support and guidance to Navy activities that request information for the implementation of ERU at their facilities. The points of contact (POC) are listed in Appendix G. Supplemental guidance to this UDP will be issued if there is a significant enhancement to this technology for pollution prevention in Navy plating shops.

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification _____	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

CONTENTS

	Page
CHAPTER 1. INTRODUCTION	1-1
1.1 GENERAL	1-1
1.1.1 Scope	1-1
1.1.2 Navy Pollution Prevention Program	1-1
1.1.3 User's Data Package for Advanced Designed ERUs	1-1
1.2 BACKGROUND	1-2
1.2.1 Navy Electroplating Operations	1-2
1.2.2 Conventional Treatment of Electroplating Waste	1-2
1.2.3 Previous RDT&E Electrolytic Recovery Efforts for Cadmium Cyanide	1-3
1.2.4 1990 Survey of Navy Plating Shops for Metals Amenable to Advanced Design Electrolytic Recovery	1-3
CHAPTER 2. ELECTROLYTIC RECOVERY TECHNOLOGY	2-1
2.1 TYPICAL PROCESS FLOW IN METAL PLATING SHOPS	2-1
2.2 PROCESS FLOW WITH INSTALLED ELECTROLYTIC RECOVERY UNIT	2-1
2.3 THE BASIC ERU	2-1
2.4 ADVANCED DESIGN ERU COMPONENTS	2-4
2.4.1 Cathode Description	2-4
2.4.2 Enhanced Metal Recovery Rates Using Advanced High Surface Area Cathodes	2-4
2.4.3 Anodes of Corrosion Resistant Materials With Variable Oxidizing Properties	2-6
2.4.4 ERU Circulation Systems: Agitation, Sparging, and Fluidized Bed	2-6
2.5 ELECTROWINNING IN DILUTE PLATING RINSEWATERS	2-9
2.5.1 Electrowinning Theory	2-9
2.5.2 Optimizing Conditions at Reduced Current Efficiency	2-9
2.5.3 Current Density for Optimal Metal Recovery	2-11

	Page
2.6 POTENTIAL ERU APPLICATIONS	2-11
2.6.1 Technical Feasibility	2-11
CHAPTER-3. COST/BENEFITS OF ERU OPERATION	3-1
3.1 POLLUTION PREVENTION/COST SAVINGS BENEFITS	3-1
3.1.1 Pollution Prevention and Minimization	3-1
3.1.2 Benefits of Applying Advanced Electrowinning Technology	3-2
3.1.3 Cost Analysis	3-2
3.2 ACQUISITION	3-3
CHAPTER 4. ELECTROLYTIC RECOVERY UNIT SELECTION	4-1
4.1 BASIC ERU DESIGN CRITERIA	4-1
4.2 ERU ADVANCED DESIGN FEATURES FOR SPECIFIC SHOP APPLICATIONS	4-1
4.2.1 Potential Contaminants of Drag-out in Still Rinse Tank	4-2
4.2.2 Anode Selection Based on Known Plating Bath Chemistry	4-2
4.2.3 Fluctuating Metal Loading in the Still Rinse Tank	4-3
4.2.4 Cathode Selection Based on a Summary of Recycling or Reclamation	4-3
4.3 SIZING THE ERU FOR EFFICIENT METAL/CYANIDE MANAGEMENT ..	4-5
4.3.1 Drag-Out Concentration of Metal/Cyanide in Still Rinse Tank	4-6
4.3.2 ERU Rate of Metal Recovery in Dilute Plating Rinsewaters	4-6
4.3.3 Estimating ERU Capacity	4-6
4.3.4 Single Pass Recovery (SPR) Misconceptions	4-7
CHAPTER 5. ERU INSTALLATION	5-1
5.1 FACILITIES INSTALLATION	5-1
5.1.1 Location of ERU in Plating Process	5-1
5.1.2 ERU Installation to Still Rinse Tank	5-1
5.1.3 Tank and Piping Modifications	5-1
5.1.4 Connections to Utilities	5-2
5.1.5 Y-Strainer	5-2

	Page
CHAPTER 6. ELECTROLYTIC RECOVERY UNIT OPERATION AND MAINTENANCE	6-1
6.1 DETERMINING ERU INITIAL OPERATIONAL PARAMETERS	6-1
6.1.1 Determining ERU Initial Amperage	6-1
6.1.2 Relationship Between Cathode Surface Area and Amperage	6-1
6.1.3 Initial Off-Line Performance Curves With Varying Concentrations ..	6-2
6.2 ERU START-UP AND SHUT-DOWN PROCEDURES	6-6
6.2.1 Start-Up Procedures	6-6
6.2.2 ERU Shut-Down Procedures	6-7
6.2.3 Maintenance, Inspection, and Monitoring	6-7
6.2.4 Cathode and Anode Cleaning and/or Replacement	6-8
6.3 MAINTENANCE REQUIREMENTS FOR OPTIMAL PERFORMANCE OF ERUs	6-9
6.3.1 Determining Standby Amperage Setting for ERU	6-9
6.3.2 Optimal Conductivity for Electrowinning	6-9
6.3.3 Maintenance of Cathodes and Anodes for Long Lifetime	6-9
6.4 SPECIAL CHEMICAL FACTORS EFFECTING OPTIMAL ELECTROWINNING	6-10
6.4.1 Consequences of Proprietary Plating Bath Chemistry in Dilute Rinsewaters	6-10
6.4.2 pH Control to Prevent Hydroxide Ion Formation	6-10
6.4.3 Micro-Organisms Growth Preventive Steps	6-11
CHAPTER 7. ANALYTICAL LABORATORY SUPPORT	7-1
7.1 ANALYSIS OF METALS	7-1
7.2 ANALYSIS OF CYANIDE CONCENTRATION IN STILL RINSE TANK ..	7-1
7.3 METAL ASSAYS FOR RECYCLING METALS TO PLATING BATH	7-2
7.4 FIELD TEST KITS FOR METALS AND FREE CYANIDE	7-2

	Page
CHAPTER 8. TRAINING FOR OPERATION AND MAINTENANCE	8-1
8.1 TWO-HOUR ERU TRAINING	8-1
8.2 ERU INSTRUCTION MANUALS	8-1
CHAPTER 9. SAFETY	9-1
9.1 SAFETY CONSIDERATIONS	9-1
9.2 PRE-EXISTING HAZARDS	9-1
9.3 POSSIBLE NEW HAZARDS	9-1
9.4 MATERIAL SAFETY DATA SHEETS	9-2
9.5 APPROPRIATE PERSONNEL PROTECTIVE EQUIPMENT (PPE)	9-2
CHAPTER 10. REFERENCES	10-1
APPENDIXES	
A - Tables	A-1
B - Economic Benefits/Acquisition Costs	B-1
C - ERU Selection Worksheet	C-1
D - Concentration in Rinsing Tanks From Drag-Out	D-1
E - Calculations to Maintain Desired Metal Recovery Rate	E-1
F - List of Vendors	F-1
G - NFESC Points of Contact	G-1

CHAPTER 1 INTRODUCTION

1.1 GENERAL

1.1.1 Scope

This User Data Package (UDP) was developed by the Naval Facilities Engineering Service Center (NFESC) for implementation of electrolytic recovery technology in Navy electroplating shops that are a major source of hazardous waste and wastewaters. Electrolytic recovery, often called electrowinning, emulates the electroplating process. The basic unit of this electrowinning technology is the electrolytic cell containing electrodes (anodes and cathodes). When a direct current is applied to this cell containing plating rinsewaters, the metal cations are reduced to metal plate at the cathode and the anions (cyanides) are oxidized to carbon dioxide and nitrogen. NFESC's RDT&E efforts have developed electrowinning as a "point source recovery" technology for minimization and cost effect treatment of metal and cyanide laden rinsewaters. Application of advanced design electrolytic recovery units (ERUs) have been evaluated and demonstrated for copper cyanide, silver cyanide, acid copper, ten-lead fluoborate, and electroless nickel. NFESC's RDT&E results, which were completed at three host sites by August 1994, are published in a Technical Report entitled "Operational Test Report for Testing and Evaluation of Electrolytic Metal Recovery Units at Naval Aviation Depot Cherry Point, Naval Air Warfare Center, Indianapolis, and Norfolk Naval Shipyard" (Ref 1). This Technical Report incorporates data presented in 3 separate Technical Memorandums describing results obtained at each of these test sites (Refs 2, 3, and 4).

1.1.2 Navy Pollution Prevention Program

NFESC recommends electrowinning as a method of point source pollution prevention for Navy shore activities. This technology supports the Navy's Pollution Prevention Program as outlined in OPNAVIST 5090.1B. The Pollution Prevention Act of 1990 established the national policy that "pollution should be prevented or reduced at the source whenever feasible." To support these policies, Executive Order 1285 established a goal of 50 percent reduction in the release of off-site transfer of toxic chemicals and/or toxic pollutants by 31 December 1999, using quantities reported in 1994 as the baseline. The application of electrolytic recovery to plating shop rinsewaters will be instrumental in achieving these goals.

1.1.3 User's Data Package for Advanced Designed ERUs

Based on the field test results from three Navy plating shops, this User's Data Package has been developed for ERU selection, installation, operation and maintenance (O&M), and training for five plating wastewater applications. Due to the Navy's varied plating applications, innovative designs of electrowinning devices were chosen that extended the operating range of electrolytic recovery technology for metal recovery at low concentrations, continuous operation,

ease of maintenance, and cost effectiveness. NFESC demonstrated that electrowinning can be optimized for Navy plating rinsewater using the operational parameters that were developed through NFESC's RDT&E effort with three different electrolytic recovery units (Refs 1 through 4). In the rinsewaters tested, metal ions could be removed to below 3 ppm for each plating application, while simultaneously oxidizing cyanide to nontoxic substances. Efficient metal recovery at low concentration, which is usually difficult to achieve, was found to be feasible by enlarging the cathode surface area and by increasing the agitation in the electrolytic cell with air sparging or using a fluidized bed effect.

1.2 BACKGROUND

1.2.1 Navy Electroplating Operations

The Navy has approximately twenty electroplating shops supporting repair activities for aircraft, ships, weapons and communications systems. All combined, these shops represent the Navy's second largest generator of hazardous waste, only superseded by the combined HWs of industrial wastewater treatment plants. Plating metals include chromium, cadmium, copper, zinc, nickel, lead, silver, and gold. These Navy metal finishing processes, used for electroplating a variety of Navy parts and in printed circuit board manufacturing, annually generate over 235,000 tons of heavy metal-laden wastewater with an associated treatment and disposal cost of nearly \$1M annually (Ref 5).

1.2.2 Conventional Treatment of Electroplating Waste

Navy electroplating wastewaters are treated at industrial wastewater treatment plants (IWTPs) prior to discharge. The IWTPs process the plating shop effluents from chrome electroplating, cyanide rinsewaters and dips, and acid/alkali cleaning rinsewaters. Conventional treatment of these waste streams involve a series of unit processes including cyanide oxidation by alkaline chlorination, chromium reduction, heavy metals precipitation, flocculation/clarification, and sludge dewatering.

The IWTP's preliminary step in the treatment of cyanide wastewater is the destruction of the free cyanide by alkaline chlorination. This method destroys cyanides by adding either sodium hypochlorite or chlorine gas and sodium hydroxide. However, there are several disadvantages to alkaline chlorination, such as:

1. Difficulty in storing and handling chlorine gas and caustic sodium hydroxide
2. Inability to treat strongly complexed metal cyanide species
3. Creation of chlorinated hydrocarbons
4. High potential for generating poisonous hydrogen cyanide gas or toxic cyanogen chloride

Following the alkaline chlorination, the highly caustic wastewater is mixed with acidic wastewater in which the hexavalent chromium has been reduced to the trivalent form. The pH of this mixture is adjusted to between 7.5 and 9.5 promoting the precipitation of heavy metals as hydroxides. The metal hydroxides are removed by gravity settling, which is enhanced by using a flocculating agent. The precipitated metal hydroxide sludge is then dewatered and disposed of in a hazardous waste landfill. Over 2,000 tons per year of hazardous sludge is generated from Navy IWTPs.

1.2.3 Previous RDT&E Electrolytic Recovery Efforts for Cadmium Cyanide

In FY88, electrolytic technology was successfully tested by NCEL (now realigned within NFESC) for the recovery of cadmium at NADEP Norfolk. The electrolytic recovery system featured flat-plate stainless steel bipolar cathodes and anodes. The electrolytic recovery unit (ERU) resulted in 99 percent cadmium recovery and 82 percent reduction in plating wastewater volume. Annual cadmium cost savings at NADEP Norfolk was \$25,977, a savings to investment ratio of 13.8, and simple payback period of 5.3 months (Ref 6). This technology was implemented by NEESA (also realigned within NFESC) at four more Navy plating shops.

The cadmium electrolytic recovery units are operated in batch mode. A minimum start-up metal concentration of 400 ppm in the still rinse tank is needed to obtain an adherent plate. The cadmium ERU is typically operated for 3 to 5 days, or until the metal concentration reaches approximately 50 ppm. Continued operation at low metal concentrations may cause corrosion of the anodes (Ref 7). In order to extend the range of electrolytic recovery technology to lower concentrations that may be found in other metal plating applications, advanced design anodes, coated with precious metal or precious metal oxides over titanium, were tested in a subsequent RDT&E effort by NFESC in FY93-94. These advanced design anodes were found to mitigate corrosion problems, enabling the ERUs to be operated continuously to low metal concentrations of less than 50 ppm.

1.2.4 1990 Survey of Navy Plating Shops for Metals Amenable to Advanced Design Electrolytic Recovery

A survey of Navy plating shops (Ref 8) recommended RDT&E effort with advanced design electrolytic recovery units. Those applications chosen for testing and evaluation were based on the volume of rinsewaters generated, as shown in Table 1-1 and technical feasibility. Silver cyanide, copper cyanide, electroless nickel, copper sulfate, and tin-lead fluoborate rinsewaters were selected for testing at three host sites.

Table 1-1
Navy Plating and Printed Circuit Board Shops Survey Summary (Ref 3)

Plating Process	Heavy*	Medium	Light	Total
Silver cyanide	5	5	6	16
Copper cyanide	2	1	12	15
Copper sulfate	1	0	4	5
Copper pyrophosphate	0	0	1	1
Electroless copper	1	0	0	1
Acid copper etch	1	0	0	1
Nickel sulfamate	2	6	5	13
Electroless nickel	1	5	3	9
Tin-lead fluoborate	2	0	6	8
Gold	1	1	5	7
Zinc cyanide	1	0	3	4
Acid zinc	2	1	1	4

*Concentration classified as Light, Moderate, Heavy usage by the following scale:

- Very Light: < 50 ppm per day
- Light: > 50 ppm but < 250 ppm
- Moderate: > 250 ppm but < 500 ppm
- Heavy: > 500 ppm
- Very heavy: > 1,000 ppm

CHAPTER 2 ELECTROLYTIC RECOVERY TECHNOLOGY

2.1 TYPICAL PROCESS FLOW IN METAL PLATING SHOPS

A general process flow diagram for metal plating is shown in Figure 2-1 (A) for a countercurrent rinse system. Parts are plated and then must be rinsed in a tank that has a continuous flow of fresh water to remove any residual film (drag-out). The flow of fresh water is in the range of 3 to 12 gpm. The rinse tank overflow, which contains dilute concentrations of metal and cyanide, is discharged to the on-site IWTP. Since rinse tanks are used sporadically, the overflow rinses are costly in terms of water consumption and wastewater treatment of large volumes of dilute contaminated rinsewaters.

2.2 PROCESS FLOW WITH INSTALLED ELECTROLYTIC RECOVERY UNIT

Since the ERU provides point source metal recovery from plating rinsewaters, the ERU will be installed and operated as an integral part of the plating process in the shop. If the shop has countercurrent rinsing tanks, they must be modified to a still rinse and running rinse, as shown in Figure 2-1. Plated parts are first immersed in a still rinse tank where the drag-out is treated in the still rinse using an electrolytic recovery unit (ERU). A final rinse is performed of the plated part in a running rinse with a fresh water supply. The electrolytic unit is designed to operate continuously on the still rinse tank and maintains the concentrations of metal and cyanide in the still rinse at low ppm levels (commonly < 5 ppm). Consequently, transfer of contaminants into the following running rinse is greatly minimized. A flow restrictor on the running rinse may also decrease the volume of wastewater going to the IWTP.

The metal recovered from the still rinse can only be recycled if it is of sufficient purity. The ERU is not used for treatment of general discharges of wastewater, as the ERU cannot differentiate between various types of metals for selective recovery. Thus, the electrolytic process is most applicable to a single metal rinsewater to permit recycling or selling to a reclaimer.

2.3 THE BASIC ERU

The primary ERU components consist of an electrolytic chamber, power supply (with rectifier), and pumps necessary for the intake, circulation, and output of electroplating rinsewater are shown in Figure 2-2. Input power is converted from alternating current (AC) to direct current (DC) by the rectifier, which is regulated by a rheostat. Depending on the manufacturer, the rectifier may be associated with other ERU components (2-2A) or as a separate component (2-2B). When the rectifier is separated as 2-2B, the plating shop may use their own rectifier. The electrolytic chamber contains the anodes and cathodes, which are connected to the rectifier in parallel.

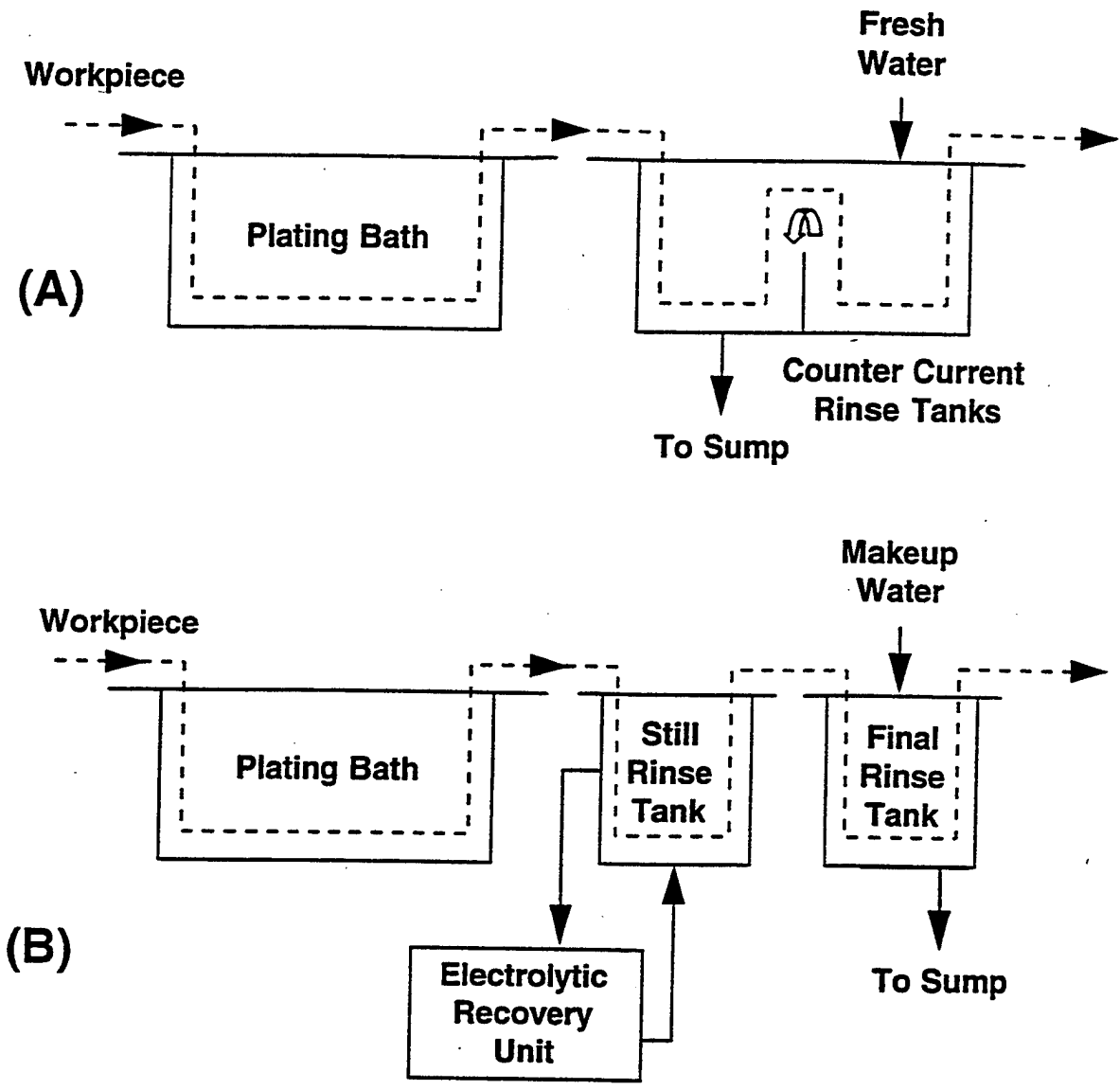
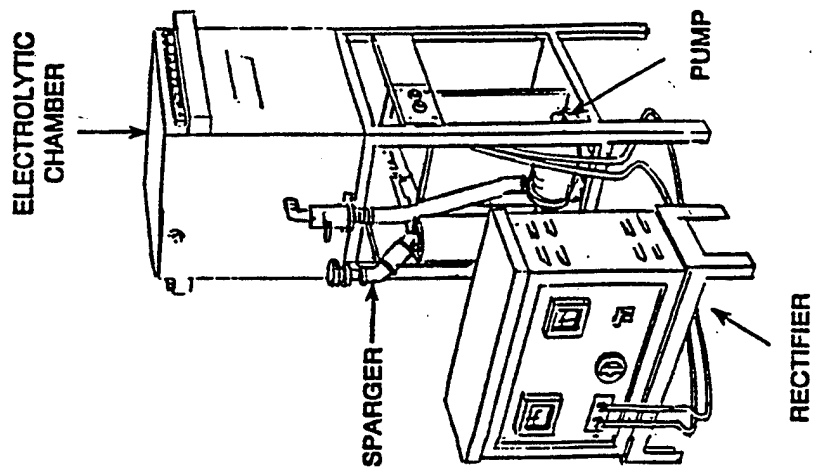
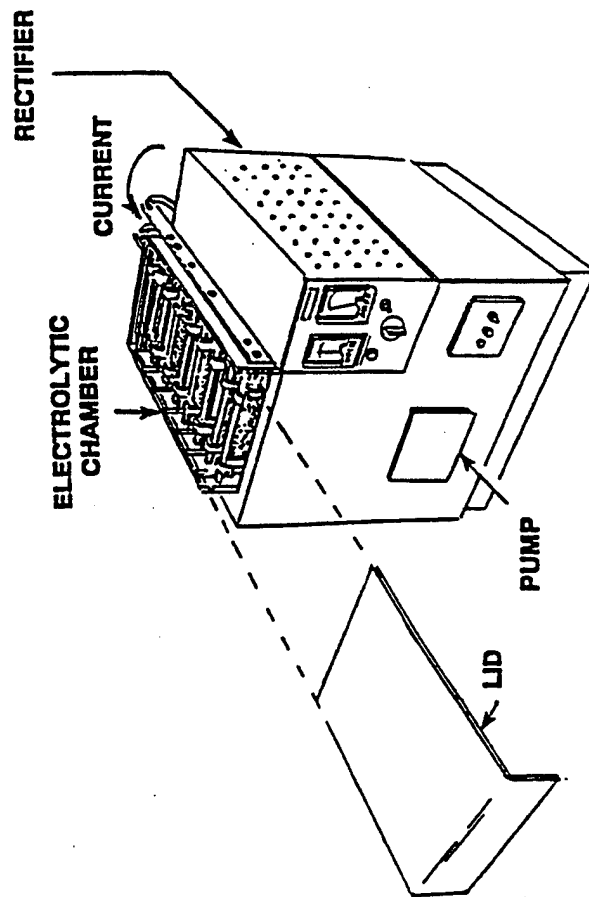


Figure 2-1
 Process flow in metal plating with (A) countercurrent rinsing
 and (B) in-line electrolytic treatment in process metal plating.



(B)



(A)

Figure 2-2
 Electrolytic Recovery Unit system components with, (A) rectifier part of the unit and (B) rectifier separate from the unit.

2.4 ADVANCED DESIGN ERU COMPONENTS

For many years commercial electrolytic recovery systems have been available to the plating industry having high metal concentrations ($> 1,000$ g/L) to treat. However, recent innovations in design of electrowinning equipment extend the operating range of the process to include wastewaters that are more dilute (< 500 mg/L) in terms of the metal and cyanide concentrations that are typically found in Navy plating shops. Advanced ERU design features may be selected to optimize electrolytic recovery for specific rinsewater applications (Ref 9).

2.4.1 Cathode Description

Stainless steel flat plate cathodes - are most frequently used for applications of metal recovery from rinsewaters with starting concentrations of 1 g/L of metals. With stainless steel flat plate cathodes, metal plate is removed in strips and can be reutilized as an anode in the plating bath or alternatively sold to a reclaimer. The stainless steel flat plate cathodes are less effective in rinsewaters where there is a large fluctuation in metal concentration. Tests have shown that start-up concentrations for flat plate cathodes should not be less than 50 mg/L.

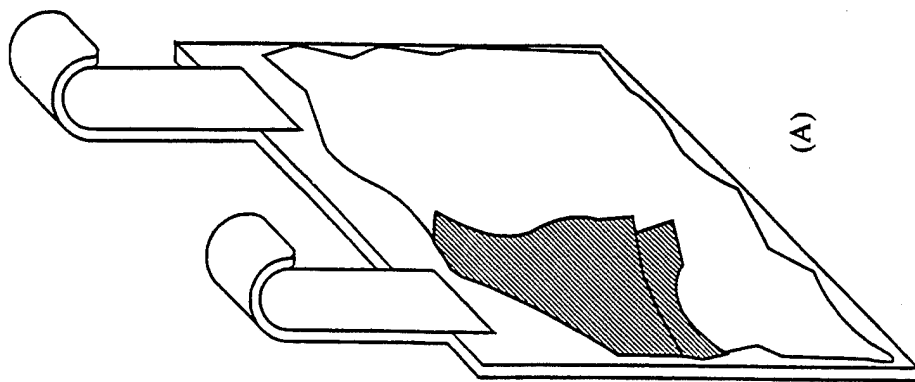
The expanded metal/wire mesh cathodes - are designed to increase the surface area over the stainless steel flat plate. Although the actual surface area is 40 percent less than the stainless steel flat plate cathode of similar dimensions, the area for metal deposition is larger due to its geometric shape. The expanded metal/wire mesh cathodes may be reutilized as plating bath anodes. The expanded metal/wire mesh cathodes are manufactured in either copper or titanium.

The reticulate cathode - is used over a wide range of metal concentrations and is effective at low metal concentration, particularly for less than 50 mg/L. The reticulate cathode is a carbon based foam or spongy material that has been impregnated with either copper or nickel to provide a conducting surface. The apparent area of the reticulate cathode is about ten times the surface area of a stainless steel flat plate cathode of the same dimensions. Once laden with recovered metal, the reticulate cathode can be sold to reclaimer.

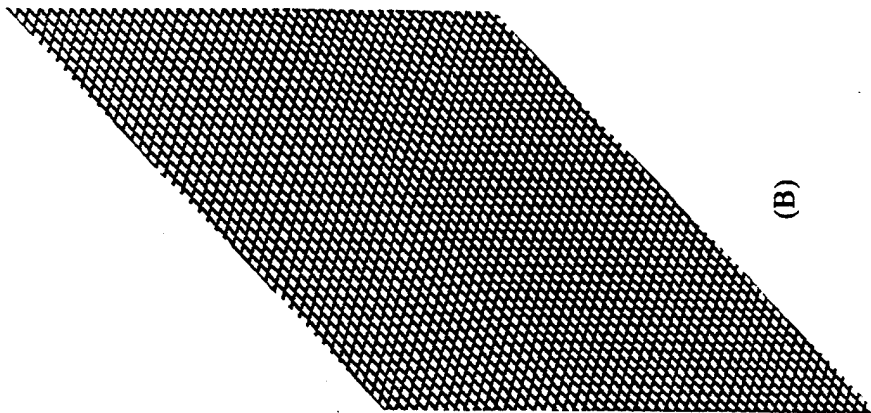
2.4.2 Enhanced Metal Recovery Rates Using Advanced High Surface Area Cathodes

The geometry and surface characteristics of any given cathode must be taken into consideration before predicting the rate of metal recovery from the rinsewater. For example, the expanded metal/wire mesh cathodes may show a greater rate of metal recovery than the stainless steel flat plate cathode. The surface area of the stainless steel flat plate cathode can be easily measured as shown in Figure 2-3. In an identical ERU, the expanded metal/wire mesh cathodes area appears to be 40 percent less than the surface area of the stainless steel flat plate cathode (Ref 1). The expanded metal/wire mesh cathode's geometry allows plating to take place on two sides simultaneously and on a third edge (Ref 10). Due to this three dimensional effect, the recovery rate of the metal will be increased over the stainless steel flat plate. The surface area of the reticulate cathode is estimated to be 10 times greater than that of the expanded metal/wire mesh cathode.

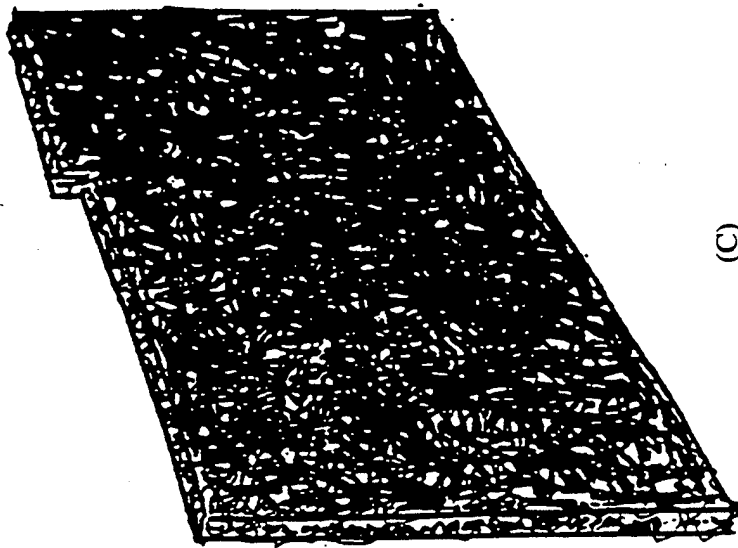
Thus, the types of cathodes can be grouped in order of increasing surface areas: (1) flat plate, (2) expanded metal/wire mesh, and (3) reticulate carbon. As shown in Figure 2-3, the expected metal recovery rate should increase in the same order.



(A)



(B)



(C)

Figure 2-3
Flat plate: (A) expanded metal/wire mesh, (B) reticulate, and (C) cathodes.

2.4.3 Anodes of Corrosion Resistant Materials With Variable Oxidizing Properties

The electrolytic recovery units can be operated continuously even at concentrations below 50 ppm if corrosion-resistant, insoluble anodes are used. Dimensionally stable anode (DSA) is a generic term for insoluble anodes where base metal (titanium, niobium, or tantalum) is coated with a precious metal or precious metal oxide usually selected from the platinum group of metals (ruthenium, osmium, rhodium, iridium, palladium and platinum). DSA anodes are also called catalytic anodes. The metal oxide coating (iridium dioxide) is successful for electrolyzing solutions containing chloride (Ref 11). Other anodes may be manufactured with a coating of precious metal (usually platinum) on a base metal such as titanium. Platinum clad niobium anodes are recommended for more severe environments (Ref 12).

Anode construction materials vary from chemically inert to highly oxidizing with regard to organics, such as cyanides. Anode materials listed with increasing oxidizing properties are: graphite, lead alloy, stainless steel, titanium, and rare earth metal coatings (platinum, ruthenium, iridium) over other base metals (titanium, niobium and tantalum). Anodes are selected based on the chemistry of the electrolyte or drag-out constituents. The most oxidizing anodes are selected for cyanide bearing wastewaters.

2.4.4 ERU Circulation Systems: Agitation, Sparging, and Fluidized Bed

It is desirable to operate electrowinning processes at the maximum current density (highest amperage per cathode surface area) where good metal deposition still takes place. Current density should not exceed the diffusion of ions (metal cations or cyanide anions) migrating through the electrolyte. If the current density exceeds ion diffusion, a muddy, non-adherent plate will be formed at the cathode. In "dilute" rinsewater solutions, diffusion is the controlling factor for metal ion reduction ($M^+ \rightarrow M^0$) at the cathode unless other physical devices are employed for greater metal ion contact with the cathode. There are three physical methods for achieving higher yields of metal plate: (1) increasing circulation of the rinsewater passing through the electrolytic cell, (2) changing the geometry of the cathode, and (3) rotating the cathode in the electrolytic cell. The rotating cathode was not tested by NFESC because commercial units did not meet basic criteria.

In the simplest circulation system of the electrolyte is limited to agitation provided by the inlet flow (or inlet dispersion) of solution between the cathodes and anodes, leaving the electrolytic cell by an overflow weir, and returning by gravity to the still rinse tank. Air agitation or air sparging can enhance circulation for the flow-through ERU design, as seen in Figure 2-4. The fluidized-bed electrolytic cell in Figure 2-5 uses inert glass beads to enhance circulation and create a scouring action by the beads against the electrodes, which increases adhesion of the metal deposited on the cathode.

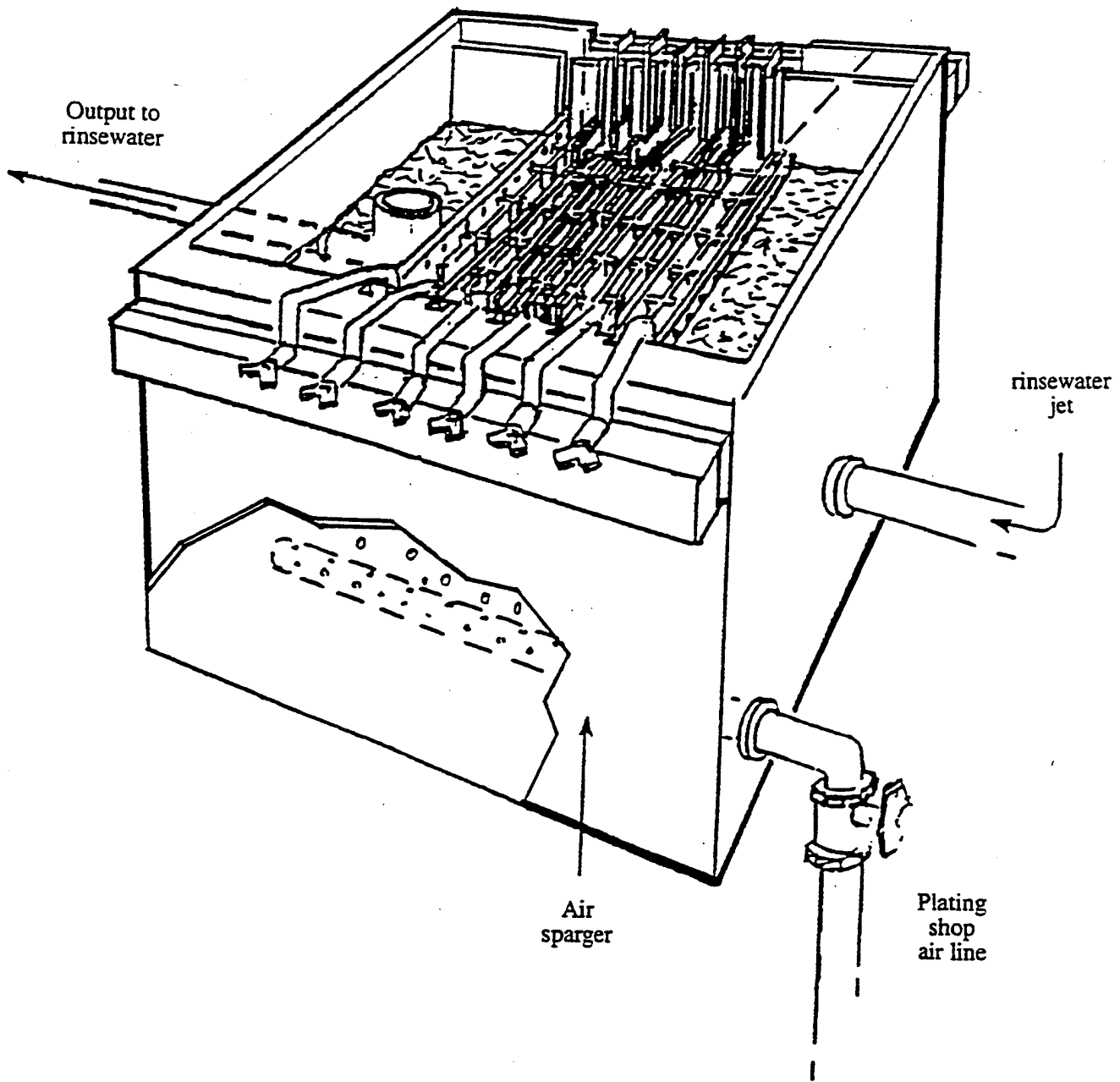
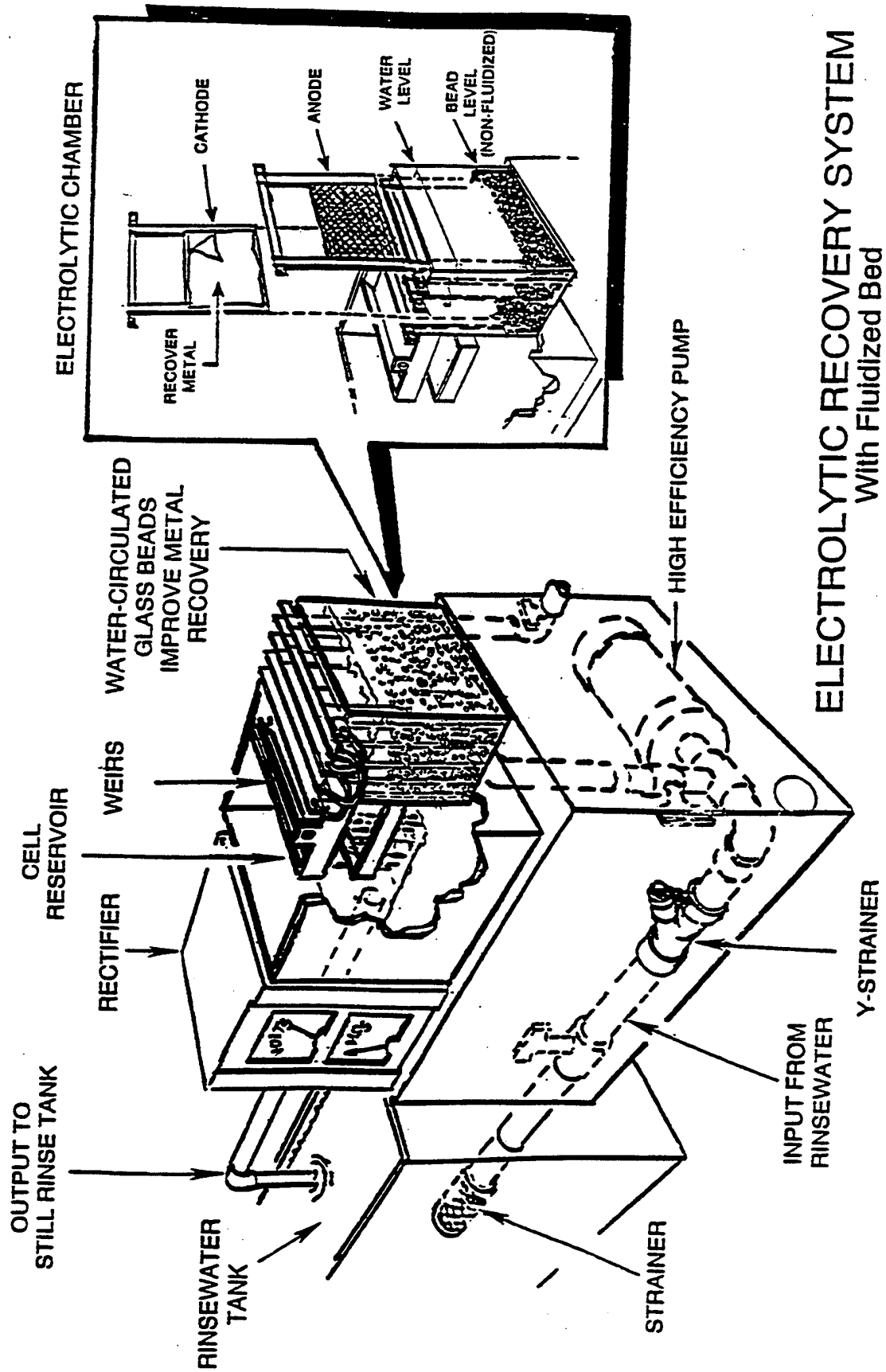


Figure 2-4
Air sparged enhanced circulation for flow-through design.



ELECTROLYTIC RECOVERY SYSTEM With Fluidized Bed

Figure 2-5
Enhanced electrolytic cell circulation with fluidized glass bead bed.

2.5 ELECTROWINNING IN DILUTE PLATING RINSEWATERS

2.5.1 Electrowinning Theory

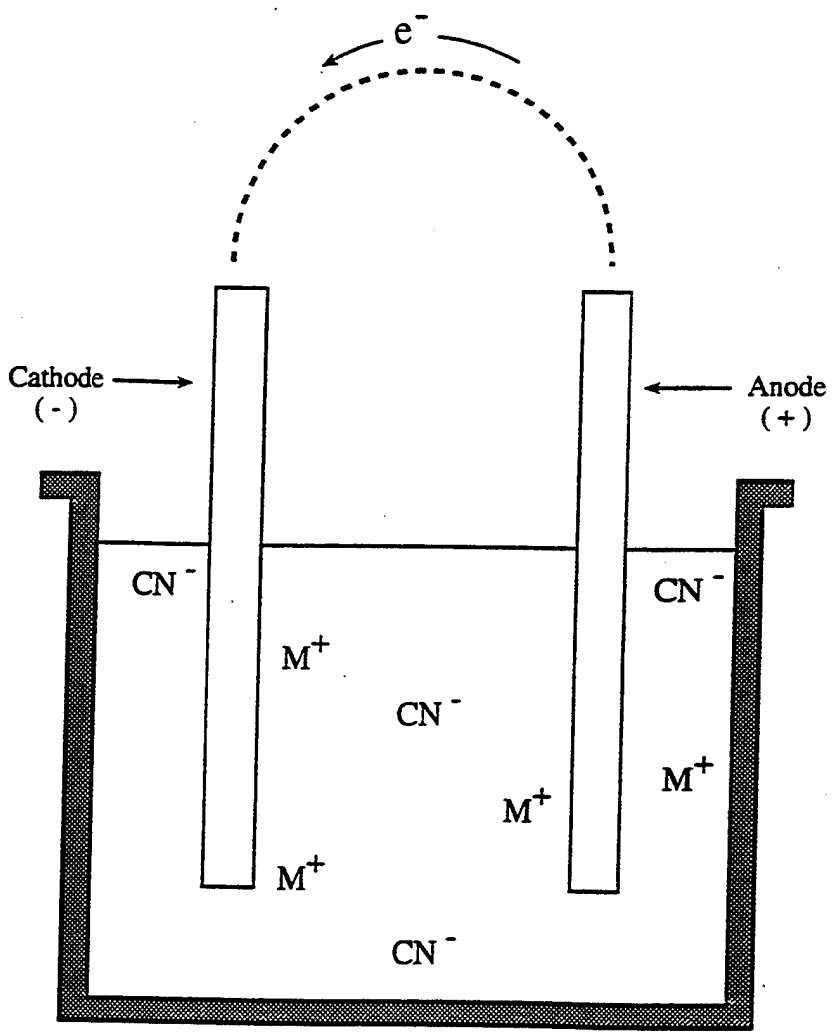
Figure 2-6 shows the electrochemical reactions that occur in an electrolytic cell. When direct current (DC) is applied to the electrolytic cell, the chemical reactions that take place at the anode are oxidations ($CN^- \rightarrow CO_2 + N_2$) and reductions at the cathode ($M^+ \rightarrow M^0$) where M^+ is the particle metal ion, i.e., Cu^{++} , Cd^{++} , etc. These electrochemical reactions are governed by Faraday's law which states that one faraday of charge will reduce an electrochemical gram equivalent of metal from a metal-bearing solution at 100 percent current efficiency. For each metal, Table 2-1 shows the number of grams that can be plated on the cathode per hour, assuming 100 percent current efficiency (Ref 10).

Table 2-1
Theoretical Maximum Metal Deposit For 1 Amp-Hr

Metal	Atomic Weight	Ion Form and Metal Deposited	Deposit (g)
CuCN	63.57	Cuprous (Cu^+)	2.372
CuSO4	63.57	Cupric (Cu^{++})	1.185
Pb	207.22	Lead salt (Pb^{++})	3.864
Cd	112.41	Cadmium (Cd^{++})	2.097
Ni	58.69	Nickel (Ni^{++})	1.095
Ag	107.88	Silver (Ag^+)	4.025
Sn	118.70	Stannous (Sn^{++})	2.213

2.5.2 Optimizing Conditions at Reduced Current Efficiency

In Navy plating shops, the ERU will be operating at metal concentrations less than the required concentration for 100 percent current efficiency as shown in Table 2-1. When operating at less than 100 percent current efficiency, some of the electric current is lost to side reactions. Due to these side reactions, theoretical maximum deposition for any particular metal is rarely achieved. RDT&E testing with Navy plating rinsewaters showed that the current plating efficiency averaged about 10 percent for all metal concentrations less than 500 ppm. For metal concentrations greater than 2,000 ppm, current efficiency rose to 37 percent (Ref 1). For ERU operation, this low current efficiency associated with dilute rinsewaters can be optimized by: (1) increasing the cathode surface area, (2) reducing the applied amperage to the electrolytic cell to nearly one half that recommended for concentrated solutions, (3) maintaining conductivity at or greater than 8.5 mmhos, and (4) increasing the circulation within the electrolytic cell.



Cathode Reactions



Anode Reactions

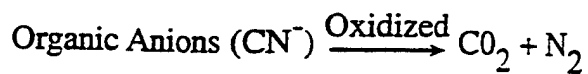


Figure 2-6
Electrolytic cell reactions at the anode and cathode.

2.5.3 Current Density for Optimal Metal Recovery

A highly controlling factor in the type deposition of metal at the cathode is the amount of current flowing through the cell or current density (CD), measured in amperes per unit area of cathode. Since current density affects the quantity and nature of the electroplated deposit, it is desirable to operate the electrowinning process at the maximum current density where good metal deposition still takes place on the cathode. At low current efficiencies as previously mentioned, current density is restricted to less than 30 A/m² (Ref 1). Since current density is a function of cathode surface, any change in cathode surface area, i.e., change either in the number or geometric shape of the cathode, will require an adjustment in the current flowing through the cell to maintain the current density for the formation of adherent metal plate on the cathode.

2.6 POTENTIAL ERU APPLICATIONS

2.6.1 Technical Feasibility

Electrowinning can be applied to a variety of plating rinsewaters but must be technically feasible for the plating application under consideration. Table 2-2 lists the potential applications from those that are highly successful to those where there is no known instance of electrolytic recovery of the metal (Ref 13). Gold, silver, copper, cadmium and zinc are the most common metal recovered in industry and are the most likely to be successful in Navy plating shops. The electropotential series closely resembles Table A-1 in Appendix A.

Table 2-2
Potential Applications for Electrowinning of Plating Rinsewaters (Ref 16)

Group	Metal (electrolyte)
<p>Group 1</p> <p>Includes metals with a high potential for successful application. All metals (electrolyte) listed in this group are commonly recovered using electrowinning.</p>	<p>Cadmium (cyanide)* Copper (acid, cyanide) Silver (cyanide) Gold (cyanide) Zinc (cyanide) Brass (cyanide)</p>
<p>Group 2</p> <p>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, when cyanide is the complexing anion.</p>	<p>Antimony, Cadmium (ammonium, sulfate), Iridium, Lead (acid), Palladium, Ruthenium, Rhodium, Selenium, Tin (acid, alkaline)</p>
<p>Group 3</p> <p>Includes metal with a moderate potential for successful application. May require chemical adjustment of the electrolyte (pH monitoring) or special equipment (e.g., unusual anodes), addition of antioxidant.</p>	<p>Cobalt, Gold strip copper (electroless strong acid, ammoniacal etches), Indium, Lead (fluoborate), Nickel (watts, woods, sulfamate, electroless), Silver (thiosulfate), Tin-lead (fluoborate), Zinc (acid)</p>
<p>Group 4</p> <p>Low potential for success. No known instances of use.</p>	<p>Aluminum, Barium, Beryllium, Boron, Calcium, Cadmium (strip), Chromium, Iron, Magnesium, Manganese, Mercury, Molybdenum, Silicon, Tantalum, Titanium, Tungsten, Vanadium</p>

*Cyanide baths have better macrothrowing power than, for example, acid baths that are found in Group 2 (Ref 10). Therefore, electrowinning is most successful for those plating rinsewaters containing the cyanide anion.

CHAPTER 3 COST/BENEFITS OF ERU OPERATION

3.1 POLLUTION PREVENTION/COST SAVINGS BENEFITS

The economic savings potential of the electrowinning system will depend on the economics of the existing treatment system (IWTP), the value of the metal, and need for additional treatment following electrolytic recovery. The capital investment is small and includes the ERU and associated PVC piping. The installation of the ERU may require minor modification to the existing rinse tanks. The O&M costs may be absorbed by personnel during periods of inactivity in the plating shop as the ERU maintenance is not a daily requirement. The efficiency with which the ERU will recover the metal at low concentration is dependent on proper selection of advanced design features.

3.1.1 Pollution Prevention and Minimization

3.1.1.1 Compliance With Federal, State, and County Regulations. Navy activities are required to reduce the release of toxic pollutants into the environment by Executive Order (EO) 12856 and OPNAV Instruction 5090.1B. OPNAV Instruction 5090.1B has established the Navy's Pollution Prevention (P2) Program to meet and exceed the P2 compliance requirements provided in the Emergency Planning and Community Right-to-Know Act (EPCRA) of 1986, the Pollution Prevention Act of 1990, and EO 12856. A goal of 50 percent reduction in toxic pollutant generation by the CY 1999, using CY 1994 as the base year, has been established. Each naval facility also has to develop a Pollution Prevention Plan by December 1995 that will outline specific steps the activity will take to achieve the reduction goals.

The discharge from plating rinsewaters where ERUs have been installed may or may not meet the pretreatment standards set by federal, state, or county regulations that the end user must comply. However, very low levels in the ppm range can be obtained as shown in Table 3-1.

3.1.1.2 Cyanide Destruction. In most shop applications, the primary use of electrowinning is the recovery of metal. However, when electrowinning is performed with an electrolyte containing cyanide and the proper anode material, the cyanide can be oxidized at the anode and thus can play an important role in the economic viability of the process by reducing the overall treatment reagent requirements at the end-of-pipe treatment. For example, at Norfolk Naval Shipyard the plating shop generates approximately 43,000 gal/yr of cyanide wastewater. This wastewater includes discharges from rinse tanks and washdown water. The cost of hauling/treatment for cyanide wastewater is \$2.90/gal. Based on discussions with plating shop personnel, it was estimated that use of the ERU technology would reduce rinse water discharge volume by 50 percent. The annual saving from avoiding hauling/treatment of cyanide wastewater is \$15,225 (based on 260 days/yr). A contingent benefit of cyanide destruction at the anode is the elimination of potential problems with cyanide streams mixing with acid streams in the plating shop, causing toxic hazardous gases.

Table 3-1
Industrial Pretreatment Discharge Standards for Metal/Cyanides

Metal/Organic	Pretreatment Discharge Standards (ppm)	NFESC Typical Results After ERU Treatment (ppm)
Copper	3.38	< 1.0
Silver	0.43	< 2.0
Lead	0.69	< 1.0
Nickel	3.98	< 3.0
Cyanide	1.2	4.0

3.1.2 Benefits of Applying Advanced Electrowinning Technology

When electrowinning technology is applied directly to dilute plating shop rinsewaters, the benefits of reducing metal hydroxide sludges produced by the following treatment at the IWIP will be to: (1) reduce the discharge of inexpensive regulated metals, e.g., zinc, copper, lead, and (2) recover expensive common metals, e.g., nickel and cadmium, or precious metals, e.g., silver and gold, for recovery/recycle. Some additional advantages are summarized below:

- Under single plating bath rinsewater installation, metals can be recycled to the plating bath
- Reduction of wastewater by 80 percent from electroplating operations
- Reduction of treatment chemicals at Industrial Wastewater Treatment Plants (IWTP)
- Selectively deposit a pure metal from a mixed waste stream, i.e., selective recovery of copper from a palladium bath (Ref 8)
- Coupling the recovery of metal with a useful anode reaction (destruction of cyanide) with ruthenized titanium or platinized titanium coated anode
- Treating complex metal cyanide, such as nickel cyanide, that resist conventional chemical oxidation methods

3.1.3 Cost Analysis

Appendix B is a cost analysis of the capital investment and annual operating costs for installing a typical ERU to handle non-cyanide plating rinsewaters. The yearly cost savings was calculated to be \$27,605, based on "average" cost data obtained from Navy installations (Ref 5). Additional cost savings may be gained if hauling/treatment of cyanide rinsewater is added to this cost analysis. As disposal and treatment costs increase, particularly if costs exceed

\$25,000/year, installation of an ERU is economically feasible. Appendix B shows a savings-to-investment ratio of 12.1 and a payback period of 6.1 months for installation of an electrowinning system. The annual operating costs are less than \$4,000/year. ERU technology is not labor-intensive nor expensive to run if properly selected and appropriate training is supplied for O&M procedures. The above estimated savings do not include the value of the metal recovered because these figures vary widely.

3.1.3.1 Power Consumption Costs at Low Current Efficiency. The efficiency with which the ERU will recover the metal at low concentration is dependent on proper selection of advanced design features. RDT&E results indicate that power consumption will increase at low concentration particularly below 20 ppm. This higher power consumption may not be a significant cost factor relative to the other cost/savings benefits.

During the initial ERU testing of the reticulate cathodes, on-line performance was monitored for a month. Analytical samples were taken to establish the lowest concentration achievable with the ERU after each plating episode. Figure 3-1 shows that after each plating activity for acid copper and electroless nickel, the ERU removes metal to 5 ppm in 24 hours or less in the rinsewater. As the concentration of copper ion reached low levels in the rinsewater, current efficiency dropped and power consumption increased; data are shown in Table A-3, Appendix A.

3.1.3.2 Estimated Value of the Metal Recovered. The estimated value of the metal recovered is represented by the cost of anode replacement.

If a pound of metal is returned to the plating bath as is the case for silver recovered from a silver cyanide rinsewater, then the savings are:

\$0.15 per gram or \$4.00/oz (28 grams/oz, 16 oz/lb)
 $28 \text{ grams/oz} \times 16 \text{ oz/lb} \times \$0.15/\text{gram} = \$67/\text{lb}$

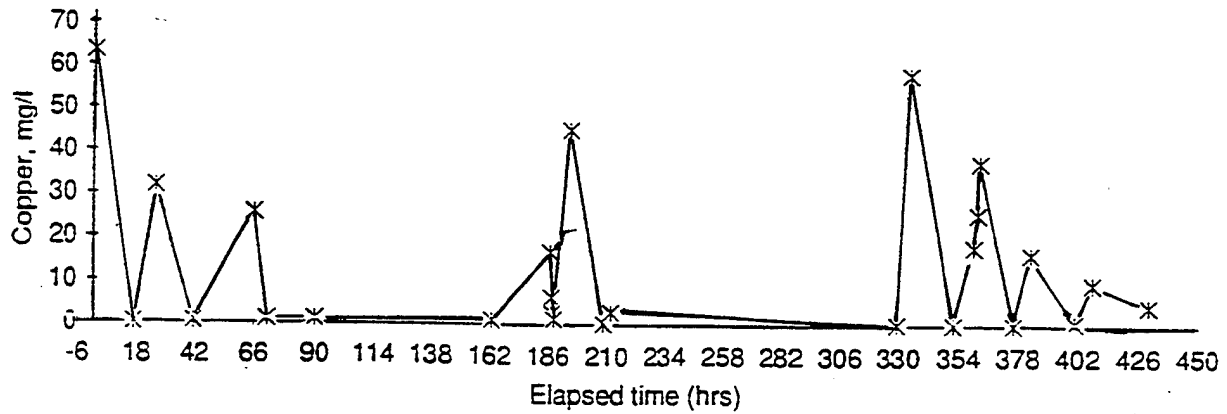
Alternatively, metals can be sold to a reclaimer. Scrap metal recycling programs are established at most Navy industrial activities or through DRMO. Cost savings will depend on the program specifics.

3.2 ACQUISITION

Electrolytic Recovery Units (ERU) are commercially available systems. Appendix F contains a list of potential vendors for ERUs. One of the benefits of implementing electrolytic recovery technology is the relatively low cost (less than \$20,000) for procurement of the unit and relatively easy installation requirements. Due to the 1995 Base Closure and Realignment (BRAC) process, the number of potential Navy customers for this pollution prevention (P2) technology is now limited to three Naval Aviation Depots (NADEPs) and three Naval Shipyards (NSYs). As the plating work load shifts to these remaining facilities, additional implementation of ERU technology will be considered for those applications where pollution prevention/cost savings benefits are warranted.

NFESC's Navy-wide implementation of ERUs will concentrate on the above six customers. Since these activities are Defense Base Operating Fund (DBOF) organizations, there is no centralized Navy P2 funding that can be used for this effort. These activities do have funded accounts for capital equipment purchases that can be used for the procurement and installation of ERUs. Acquisition costs are detailed in Appendix B. Site visits by requesting facilities will be made by NFESC personnel and the appropriate ERU for each application will be determined using the selection procedures discussed in Appendix C.

(A) Copper Removal During Online Test



(B) Nickel Removal During Online Test

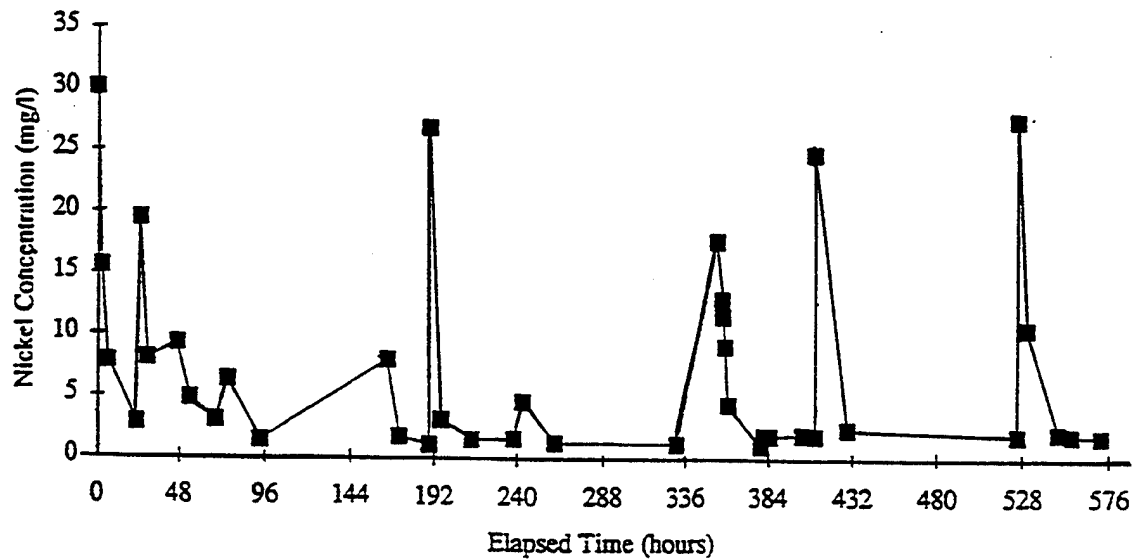


Figure 3-1
Removal of (A) Cu from an acid copper rinse,
and (B) nickel from an electroless nickel rinse.

CHAPTER 4 ELECTROLYTIC RECOVERY UNIT SELECTION

4.1 BASIC ERU DESIGN CRITERIA

Selection of electrolytic recovery units is dependent on the needs of the relatively small job shop plating operations typical of Navy facilities. In addition, ERU selection based on RDT&E modifications for special shop conditions will assure greater recovery rates where low concentrations of drag-out may occur during periods of inactivity. The selection of commercial electrolytic recovery units should include the following minimum design features:

1. A minimum ERU circulation rate of 5 gpm using a sealed magnetic drive pump
2. Corrosion resistant anodes
3. An open electrolytic cell for easy access for removal of individual metal loaded cathodes and for replacement by new cathodes without interrupting the recovery process
4. Materials of ERU construction in contact with the plating solution that are highly corrosive resistant, such as polypropylene, ceramic, and viton
5. A DC power supply (rectifier) that provides for the proper combination of voltage and amperage for the size of the electrolytic cell

The size of the electrolytic recovery unit is site specific and is therefore not included as a basic design criterion for ERU selection. Appendixes C and D discuss sizing requirements for specific sites before procuring an ERU.

4.2 ERU ADVANCED DESIGN FEATURES FOR SPECIFIC SHOP APPLICATIONS

In addition to the minimum design features, the selection of an ERU will depend on site specific requirements such as:

1. Potential contaminants in the rinse stream
2. Known plating bath chemistry
3. Fluctuating or continuous loading of metal/cyanide in the still rinse tank
4. Desired means of recycling/reclaiming of the cathode metal deposit

5. Calibration of ERU meters (amperage and voltage) must coincide with operational usage

For each application certain shop requirements for successful operation of the ERU must be considered aside from technical feasibility as mentioned in Section 2.6.1. For selection of cathodes, anodes and circulation system for optimal performance of the ERU, potential contaminants, plating bath chemistry, and drag-out concentrations must be considered.

4.2.1 Potential Contaminants of Drag-Out in Still Rinse Tank

Potential contaminants in drag-out from plating baths can be obtained to a certain degree by requesting literature from the supplier of the plating bath chemicals, particularly Material Safety Data Sheets (MSDS), a general plating text (Ref 10), or knowledge from shop personnel for make-up of the plating bath. Some known considerations and restrictions for each application discussed in this UDP are given in Table 4-1. Due to the proprietary nature of some commercial plating baths, it is impossible to know all the chemical species (cations, anions, buffering ions, stabilizing species, etc.) that will be contained in the still rinse tank from the plating bath drag-out. However, it is worth the time to obtain as much knowledge as possible of the plating bath chemistry as an aid in ERU selection.

Some minor restrictions for four of the applications were noted during the RDT&E effort. For example, passivation (Ref 8) of the anode occurred if the ERU startup concentration was less than 20 mg/L. However, during continuous operation of the ERU, passivation of the anode did not occur. Table 4-1 details the restrictions of ERU applications to date. If there appears to be a restriction during the ERU operation that is not covered in this UDP, Appendix G gives a listing of NFESC's technical contacts for help in resolving the issue.

4.2.2 Anode Selection Based on Known Plating Bath Chemistry

Table 4-2 gives the choices of material for electrodes. Anodes are chosen based on the plating bath constituents. In most cases, DSA generic anodes (catalytic anodes), as described in Section 2.4.3, are the recommended choice. The exceptions are the following conditions:

1. When complete cyanide oxidation at the anode is desired
2. When anodes, particularly of the halide group, are present

The platinum-clad titanium anodes are more oxidizing for the destruction of cyanide than precious metal oxides.

For extended operation of catalytic anodes, certain ions and organic material in the rinsewater can shorten the life of the anode. Fluoride ions react with the base metal (particularly titanium) and weaken the oxide coating. Thus, it is recommended that fluoride ions must be minimized to less than 2 mg/L. Both manganese and lead can deposit as oxides on the anode surface. The deposition of manganese oxide poisons the anode and lead oxide leads to significant electrical impedance.

For highly oxidizing anodes such as platinum-coated titanium, high halide content, such as chloride, will attack the platinum coating.

Table 4-1
Identification of ERU Application Restrictions

Application	Restrictions/Conditions
Copper cyanide	No restrictions except at very dilute concentrations where passivation of stainless steel flat plates may occur and a copper strike may be needed on the cathode; cyanide destruction occurs at slower rate than copper removal; copper may be recycled as anode in plating bath.
Silver cyanide	No restrictions; silver may be recycled as plating bath anode.
Acid copper	No restrictions on electrowinning, but due to acidic nature of this bath, copper removal may permit algae to grow; recovered copper cannot be recycled back to the plating bath without addition of phosphorous to anode. Anodes must be obtained from a manufacturer.
Tin-lead fluoborate	Selection of anode material restrictive; high halide content will attack anode of the generic DSA type; efficient tin deposition require nonoxidizing anode and addition of an antioxidant; lead removal very efficient.
Electroless nickel	pH adjustment may be required with ammonia to maintain pH above 6.5 with metal concentrations > 500 ppm; bath additives such as reducing agents and stabilizers may cause foaming; nickel cannot be recycled to the plating bath.

4.2.3 Fluctuating Metal Loading in the Still Rinse Tank

If the metal concentration fluctuates greatly, then a large surface area cathode (such as a reticulate cathode) as opposed to a flat plate cathode is recommended in order to maintain low current density for adherent plate. Another consideration at low concentrations is the circulation within the electrolytic cell as discussed in Section 2.4.4.

4.2.4 Cathode Selection Based on a Summary of Recycling or Reclamation

Table 4-3 lists a summary of advantages and disadvantages for using flat plate, wire mesh/expanded metal, and reticulate cathodes. The selection of cathode type may be dependent on the pollution prevention program in the plating shop. ERUs come with a selection of cathode types to accommodate recycling (gold, silver) or reclaim (nickel, acid copper).

Table 4-2
Choices of Materials for Cathodes and Anodes

Application	Cathode Material	Anode Material
Copper cyanide	Copper mesh Reticulated copper Stainless steel flat plate	Platinum clad titanium
Silver cyanide	Stainless steel mesh Stainless steel flat plate	Platinum clad titanium
Acid copper	Reticulated copper	Iridium oxide clad titanium
Tin-lead	Stainless steel flat	Graphite or titania ceramic clad titanium*
Electroless nickel	Reticulated nickel	Iridium oxide clad titanium

*Iridium oxide clad titanium may be used, but the lifetime of the anode is very limited and impacts cost/savings and payback periods for the ERU. Graphite anodes are not favored by platers because of discoloration to the rinse water.

4.2.4.1 Recycle of Recovered Metal to Plating Bath. Flat plate cathodes are ideal for stripping metal to be returned to anode bags in the plating bath.

The wire mesh/expanded metal cathodes may be recycled in the plating bath if there is room in the plating tank such that they do not interfere with the plating process. The material of the wire mesh/expanded metal must be compatible with the plating bath. Note that a titanium cathode cannot be used in a fluoborate bath.

4.2.4.2 Selling Cathodes to Reclaimer. As previously noted, some plating baths such as acid copper, cannot reuse the electrowinned copper due to additives, such as phosphorous in the anode manufacturing process. In other cases, the plating bath may be old and have residual metals such as copper from repeated applied strikes prior to silver cyanide plating, and may not produce a metal cathode deposit of sufficient purity to recycle back to the plating bath.

The option for using reticulate cathodes may be desirable because they have excellent metal recovery in low concentration rinsewaters. However, it can only be sold to a reclaimer for recovery. Higher amperage is required, which will translate into higher energy costs. The purity of the metal is lower due to the carbon fiber content of the cathode and the cathode may also act as a filter for rinsewater particulate matter passing through the electrolytic cell.

Table 4-3
Cathode Selection Summary

Cathode Type	Advantages	Disadvantages
Titanium mesh	<p>Reusable cathode</p> <p>Direct recovery as anode in silver cyanide plating bath</p>	<p>Cannot be used for fluoborate baths</p> <p>Cannot recycle to acid copper plating bath</p>
Copper mesh/ expanded mesh	<p>Copper recovered of high purity and can be used as anode in copper cyanide bath</p> <p>May be sold to reclaimer</p>	<p>Cannot be recycled as anode in acid copper bath</p> <p>Difficult to observe low levels of plating visually by shop personnel</p>
Copper/nickel impregnated reticulate foam	<p>Excellent recovery of copper or nickel at low concentration < 100 mg/L</p> <p>High loading of metal before change cathode, low maintenance</p>	<p>Disposable cathode; cannot be recycled as anode</p> <p>Requires higher amperage than mesh/expanded mesh; results in higher energy costs</p>
Stainless steel flat plate	<p>Metal may be stripped/peeled from cathode</p> <p>Peeled metal can be recycled to anode</p> <p>Excellent visual check of plating rate on cathode by shop personnel</p>	<p>At < 20 mg/L, stainless steel cathode may become passivated and strike may be necessary</p>

4.3 SIZING THE ERU FOR EFFICIENT METAL/CYANIDE MANAGEMENT

In sizing of the ERU, careful consideration must be given to current density requirements, potential drag-out into the still rinse tank, and the rate at which the metal must be recovered to maintain metal/cyanide concentration in the rinsewater at near discharge levels.

4.3.1 Drag-Out Concentration of Metal/Cyanide in Still Rinse Tank

Drag-out concentration can be estimated by: (1) chemical analysis or (2) conductivity (Refs 14, 15, and 16), as outlined in Appendix D. Once an estimate of drag-out is known for the type of rinse tanks (countercurrent, flowing rinses, etc.) currently installed in the shop, the rate necessary to maintain near-discharge levels of metal removal can then be determined for the ERU.

4.3.2 ERU Rate of Metal Recovery in Dilute Plating Rinsewaters

Under ideal circumstances where there is high concentration in metal in the still rinse tank, the removal rate of metal by the ERU will normally match the expected plate-out rate. That is, the removal rate in g/hr divided by the plating rate in g/amp-hour will match the amperage applied. For example, if 20 g/hr of silver is required to be removed to maintain low levels in the still rinse tank, then 4.96 amps under ideal circumstances would be required as shown in the example below.

$$\frac{20 \text{ g/hr}}{4.03 \text{ g/amp-hr}} = 4.96 \text{ amps*}$$

*Obtained from Table 2-1 in Section 2.5.1 for silver plating rate at 100 percent efficiency (theoretical maximum).

Tests have shown that for dilute solutions, an adjustment must be made in calculating removal rate, as the current efficiency is typically 10 percent. High current levels in electrowinning from dilute solutions leads to poor plate and side reactions. Lower amperage will be required in order to get good adherent plate and, therefore, lower removal rates will occur. Tests showed that amperage settings were one half those suggested by manufacturers once the "maintained concentration" dropped below 50 mg/L, see Appendix A, Table A-3, column 5. One means of increasing the removal rate from dilute solutions, is to increase the surface area of the cathodes. Appendix E illustrates how to calculate the metal recovery rate desired with the number and size of cathodes based on current density requirements in dilute solutions.

In addition, if a high rate of metal recovery is required, then the conductivity may need to be increased by adding non-interfering ions, such as Na⁺.

4.3.3 Estimating ERU Capacity

The ERU capacity specifications are based on the rate of removal desired. Selection of cathodes by type and number can optimize the removal rate in dilute rinsewaters. Cathodes vary on the metal loading capacity, as specified in the manufacturer's manual. For example, the reticulate cathodes need replacement with metal loadings between 3 to 5 pounds. If cathodes are changed every 6 months on a maintenance schedule, then the following example illustrates a case where the ERU capacity is oversized. At a printed circuit board shop, acid copper rinsewaters generated 12.6 pounds of copper per year. For an ERU containing six reticulate cathodes, the system's capacity is:

$$3 \text{ pounds} \times 6 \text{ cathodes} = 18 \text{ pounds of capacity}$$

Therefore, the ERU is probably oversized and a smaller ERU could be procured.

4.3.4 Single Pass Recovery (SPR) Misconceptions

Commercial ERUs can be purchased with as many as 50 cathodes for single pass metal recovery. Manufacturer's SPR results for such systems do not apply for dilute plating rinsewaters (< 1,000 mg/L) and leads to side reactions. If conductivity is not maintained, hydrogen and oxygen evolution may occur at the cathode and anode, respectively. In addition to poor quality plate, the evolution of these gases leads to destruction of the cathodes and anodes well before the calculated payoff period for the ERU. NFESC does not recommend SPR for Navy plating shops, unless special attention can be given to maintain conductivity necessary to prevent side reactions from occurring. A ventilation system should also be considered.

CHAPTER 5 ERU INSTALLATION

5.1 FACILITIES INSTALLATION

Countercurrent rinsing is typically used at Navy facilities to minimize the amount of wastewater generated in the rinsing of plated parts. In order to successfully operate an ERU, the existing system of rinsing must be modified. These modifications will usually be minor, unless remote installation is required of the ERU.

5.1.1 Location of ERU in Plating Process

Figure 5-1 shows a proposed layout for installing the electrolytic recovery unit (ERU). For all configurations, the inlet and outlet piping to the ERU will be connected to the still rinse tank. A single running rinse will follow each still rinse tank to provide a final rinse of plated parts. The ERU, when properly operated, will maintain low concentration levels of metals/cyanides in the succeeding running rinse tank(s) and the concentration may be minimized to the extent that discharge limits may be met.

5.1.2 ERU Installation to Still Rinse Tank

The ERU is typically designed for gravity flow discharge to the still rinse tank. There are usually several choices to maintain gravity feed. The stand of the ERU may need to be modified in height. Figure 5-1 shows the position of check valves, priming tees, and ball valves if the ERU is mounted on the shop floor. Priming tees are not necessary for all ERUs, but some ERUs may have internal check valves which require a priming reservoir. If there is not sufficient space behind the rinsewater tanks for installation, the ERU may be located in an aisle if this placement is not a safety issue.

Installation of the ERU at a remote site or below the shop floor will require that a second pump be installed. This may not be necessary with a remotely sited ERU, if the gravity feed to the still rinse tank proves adequate.

If the ERU is positioned below the shop floor, then a pump will be required on the inlet (as a priming pump) and on the discharge line. The check valve will be installed on the inlet line along with the screen.

5.1.3 Tank and Piping Modifications

The ERUs are PVC piped to each still rinse tank and include ball check valves and unions located to ensure easy access for maintenance. Figure 5-1 shows the incorporation of the ERU into the plating line on the still rinse tank. The ends of both the inlet and the discharge lines should be submerged 8 to 12 inches below the surface of the rinse water to prevent air intake on the inlet side and splashing of the electrowinned rinsewater on the return line.

Figure 5-1 shows the piping configuration for the installation inside the still rinse tank, with screen and ball check valve on the inlet line when gravity feed is possible on the shop floor level. Spring-loaded check valves are not recommended in place of the ball check valves.

5.1.4 Connections to Utilities

As a power supply for the ERU, the rectifier must be chosen to supply sufficient amperage to the electrolytic cell. The rectifier is connected to a standard 115-volt line in the plating shop.

5.1.5 Y-Strainer

The Y-strainer should not be smaller than 1 inch (in Figure 5-1), as its purpose is to filter large solids which would damage the pump, not colloidal material. Colloidal material will build up over time and plug the Y-strainer.

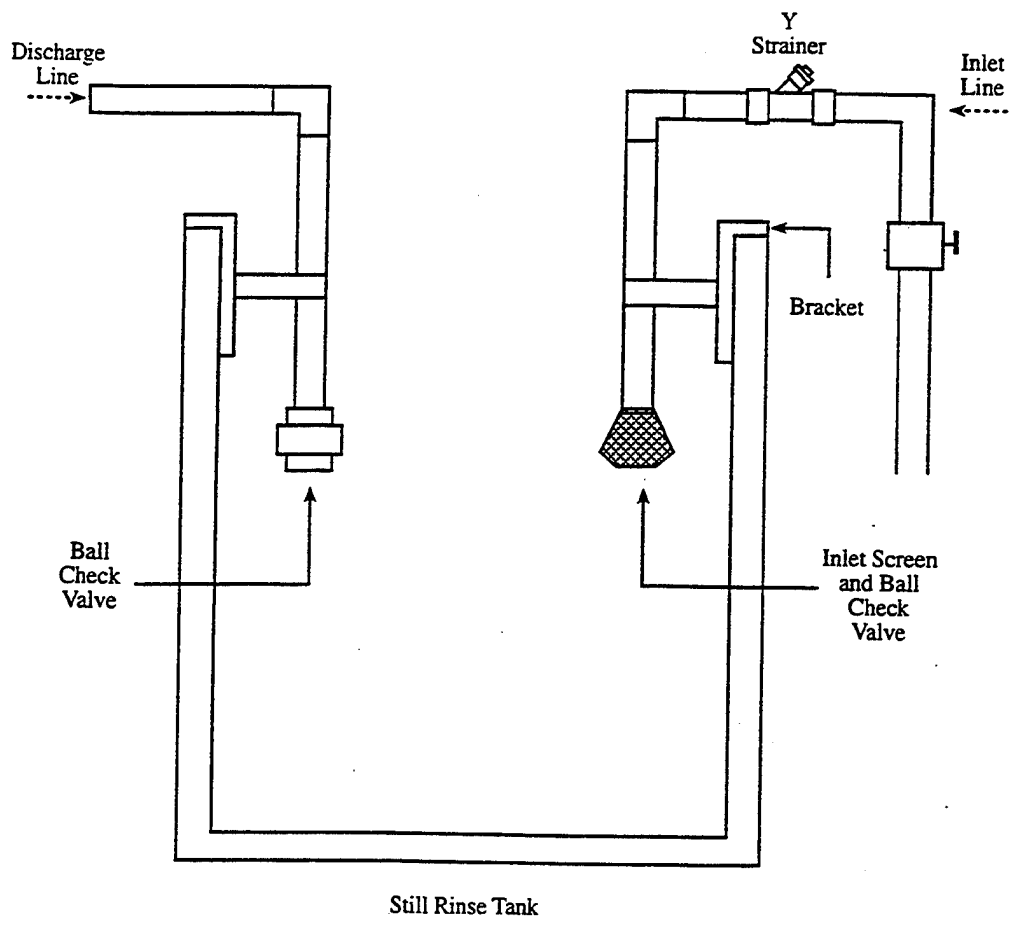
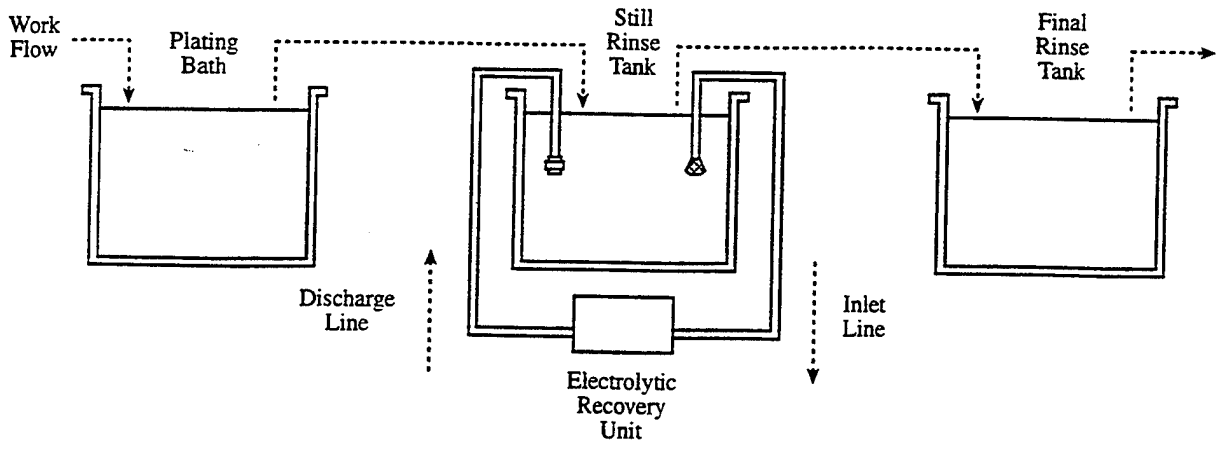


Figure 5-1
 Incorporation of ERU into the plating line with check valves, screens
 on piping leading to still rinse tank, and location of Y-strainers.

CHAPTER 6 ELECTROLYTIC RECOVERY UNIT OPERATION AND MAINTENANCE

6.1 DETERMINING ERU INITIAL OPERATIONAL PARAMETERS

Initial operational parameters (amperage, voltage, and conductivity) have been recommended by the manufacturer's manual for concentrations that may be unrealistic for Navy plating shops. Because each plating shop may have varying metal concentrations, often less than 500 mg/L, newly installed ERUs need to be adjusted to recover metal at the optimal setting for obtaining adherent plate at low concentrations.

6.1.1 Determining ERU Initial Amperage

Two factors must be considered when estimating the initial amperage: (1) what is the total cathode surface area and (2) what is the metal concentration that is going to be maintained in the rinsewater.

6.1.2 Relationship Between Cathode Surface Area and Amperage

The amperage setting will be dependent of the type and number of cathodes used in the electrolytic cell. The total surface area (type of cathode times the number of cathodes) must be calculated and the amperage adjusted accordingly. As stated in Section 2.4.1, it is the total, or three-dimensional surface area that is to be considered. For a given ERU, greater amperage will be applied as the surface area of the cathode increases. The order of increasing cathode surface area is: (1) stainless steel flat plate, (2) expanded metal/wire mesh, and (3) reticulate. For acid copper rinsewaters, Table 6-1 shows the relationship between cathode type, surface area, amperage applied, and current density for adherent metal plate at the cathode.

Table 6-1
Amperage Setting for Acid Copper

Cathode Type	Surface Area (m ²)	Amperage* Conc > 100 ppm	Amperage Conc < 50 ppm	Current Density Amps/m ² (Conc < 50 ppm)
Expanded titanium mesh	5.20	80 amps	20 amps	15.62 (3.90)
Reticulate	32.00	80 amps	50 amps	2.50 (1.56)

*Amperage recommended by manufacturer for higher concentrations.

As the surface increases from the expanded mesh to reticulate, the current density decreases; at concentrations less than 50 ppm, the current density shows a similar trend. The amperage applied at concentrations less than 50 ppm also drops significantly. To determine initial amperage for a particular application, Table A-3 in Appendix A may be used. The total cathode area and the expected maintained concentration needs to be known. If the initial amperage is too high, bubbles of oxygen will be evolving from the cathode. The amperage should be turned down until these bubbles disappear. While adjusting the initial amperage, the fluidized bed or air spacing system will need to be turned off.

6.1.3 Initial Off-Line Performance Curves With Varying Concentrations

Since many ERUs have a selection of cathodes that may be used by shop personnel, performance curves should be run at the time of installation and the cathodes checked for good plate. When a change of cathode type is made, a new performance curve should be made. A performance curve will track the amount of metal removed from the still rinse tank over time. The performance of the ERU will vary with starting concentration, cathode type, and the amperage applied. Figure 6-1 illustrates the differences in removal rate of metal for three different cathodes tested off-line in acid copper rinsewaters. The slope of the performance curves indicates that the removal rate for copper is significantly higher for the reticulate cathode. The titanium and copper mesh cathode have nearly the same removal rate.

Figure 6-2 shows the configuration for "off-line" testing for initial performance for selected ERU as described in Section 3.0. A range of current density (CD) settings for high and low concentrations are shown in Table 6-2.

Table 6-2
Current Densities for High and Low Metal Concentrations

Cathode Type	Recommended CD > 50 mg/L (Amps/m ²)	NFESC CD at Low Conc (Amps/m ²)
Flat plate	11 - 30	1.54 - 16
Expanded mesh	15 - 37	1.50 - 16
Reticulate	2.5 - 2.8	1.10 - 1.6

Samples should be analyzed hourly for the first four intervals and then every 4 to 8 hours until the concentration is in the low ppm range (<10 mg/L). Visual inspection of the cathode is necessary to determine the quantity and quality of the plate. Correct amperage setting for the ERU has been attained when a good adherent plate without burnish spots is observed. Figure 6-3 illustrates good adherent plate that is easily peeled from the stainless steel flat plate. A written log should be maintained once initial settings for concentration and amperage are determined.

Cathode Type VS Copper Removal From Acid Copper

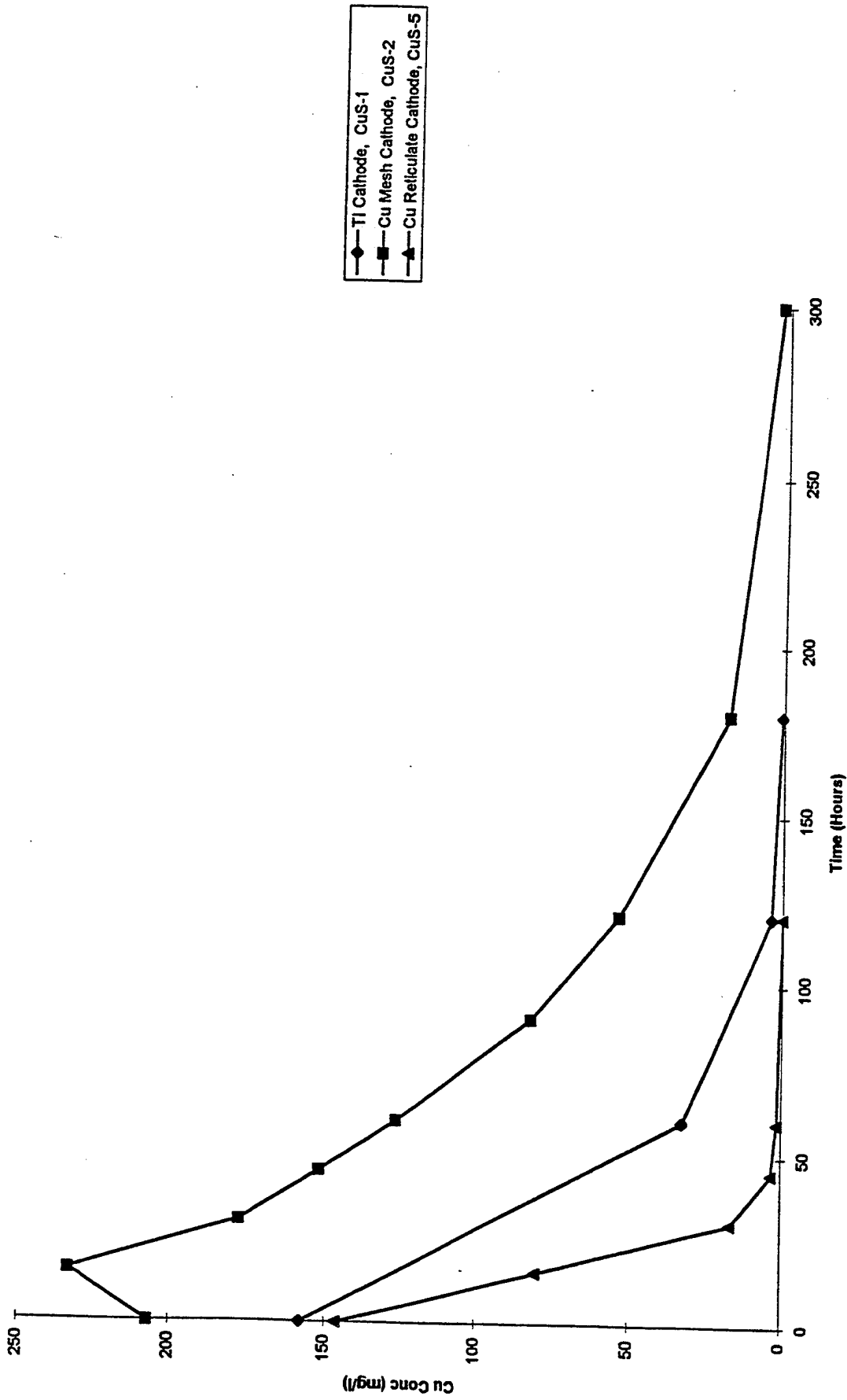
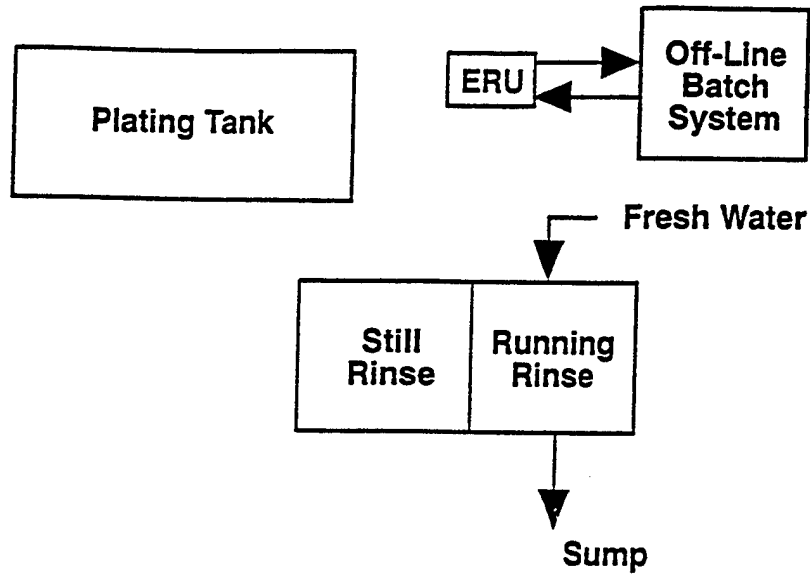
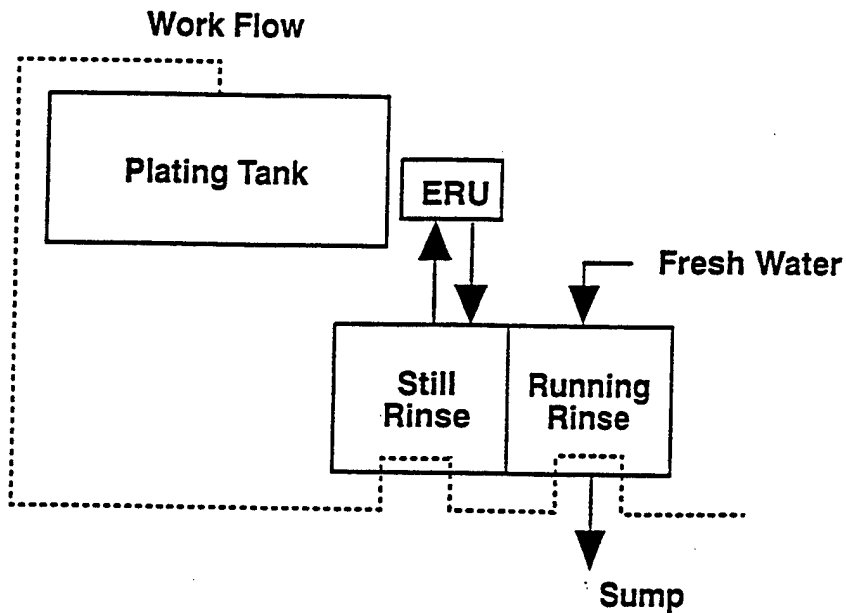


Figure 6-1
Cathode type versus copper recovery from acid copper simulated rinsewaters.



(A) Off-Line ERU Testing



(B) On-Line ERU Testing

Figure 6-2
Off-line testing for (A) optimizing initial ERU parameters, and (B) on-line permanent ERU operation.



Figure 6-3
Adherent plate (A) partially peeled on stainless steel
flat plate cathode, and (B) unused mesh cathode.

Once the ERU is running on-line on the still rinse tank, chemical field test kits can be used to track the metal removal to the low ppm range as described in Section 7.0. Laboratory analysis should be done on a schedule that confirms the field test kit results.

6.2 ERU START-UP AND SHUT-DOWN PROCEDURES

These summary instructions are generic with the intent to instruct potential procurer's of this technology of general operational and maintenance procedures. The manufacturer's manual should be consulted prior to installation of the ERU.

6.2.1 Start-Up Procedures

1. Check to make sure the valves are in correct position for start-up. The following valves are to be checked:
 - a. Drain valve in closed position
 - b. Any emergency drain line valves checked for obstructions
2. Check to see that switches for the pump and rectifier are in the off position.
3. If a priming tank is part of the operational set-up, fill the priming tank with rinse water.
4. Turn on the pump. Make sure that rinse water is circulating through the unit and returning to the still rinse.
5. Hang anodes and cathodes onto their respective bus bars. Make certain that good electrical contact is achieved. It is suggested by some manufacturers, particularly those with reticulate cathodes, to turn the rectifier on to standby amperage while installing the cathodes to prevent the possibility of demetalizing the reticulate material.
6. Immediately turn on the rectifier, if not on during installation of cathodes, and adjust to initial amperage.
7. Ensure that cathodes are properly seated in slots and no shorts exist between cathode and anode.
8. Turn on any circulation devices, i.e., open the valve for the air sparging line and adjust to cover the electrode area.
9. Take sample for laboratory analysis or use field test kits for measuring metal/cyanide concentration in the still rinse tank.

6.2.2 ERU Shut-Down Procedures

1. Switch off the rectifier.
2. Close off the inlet ball valve.
3. Remove the electrical leads from the anodes and cathodes and then remove the anodes and cathodes from the ERU.
4. Rinse the anodes and cathodes over the still rinse with fresh water.
5. Inspect the cathode for metal build up. See Section 6.3.3 for cleaning. Inspect the anode for damage, such as burning. Place the anodes and cathodes into storage. Note that cathodes used for cadmium require special procedures.
6. Switch off the pump.
7. If the system requires maintenance, open the drain valves and empty the unit. Open the strainer and permit the suction line to drain on the inlet line.
8. If the system has a priming tank, pump out with a hand pump.
9. Close all valves.

6.2.3 Maintenance, Inspection, and Monitoring

On a daily basis, the plating bath operator should:

1. Check the operation of the pump by observing flow from the discharge line.
2. Check amperage and voltage for unusual changes.
3. General WARNING FOR ALL ERUs:

WARNING

DO NOT LEAVE THE CATHODES IN THE ELECTROLYTIC CELL IN CONTACT WITH THE SOLUTION WITHOUT BEING POLARIZED, I.E., STANDBY AMPERAGE SHOULD BE MAINTAINED.

On a weekly basis:

1. Check amperage and adjust if necessary.
2. Use field test kit to determine concentration of metal/cyanide and record in log book.
3. Adjust pH or conductivity if necessary.

Twice a year, the plating bath operator should:

1. Implement shutdown procedure in Section 6.2.2 and clean system.
2. Scrub the bus bars with Scotchbrite to remove any corrosion.
3. Rinse the tank, bus bars with several gallons of water.
4. Change cathodes if necessary or peel stainless steel flat plate cathodes.
5. Check anodes for corrosion or other damage.
6. Check hoses, fittings, and tank for leaks.

6.2.4 Cathode and Anode Cleaning and/or Replacement

Stainless Steel Cathodes: The stainless steel flat plate cathodes can be used up to several months before the metal plate is removed. The frequency of use of the ERU will depend on the level of production and the amount of drag-out that enters the still rinse. When the metal plate is sufficiently thick that it is separating from the cathode, it is time to remove it. The metal plate will have a thickness of 2 to 5 mils. Peel the metal from both sides of the cathode. Recycle the metal sheet via the recycling program or if compatible with the plating bath, return to an anode sack. A spare standby cathode set may be ordered to insert during this cleaning operation.

Expanded Metal/Wire Cathodes: The copper or titanium expanded metal/wire mesh cathodes can be used for many months until the holes in the mesh have been completely filled in with recovered metal. The cathode facing the front flow distributor will receive the most deposit and will require changing first. During a monthly inspection, personnel may wish to switch the cathodes to maintain even distribution of metal recovery for all the cathodes in the ERU. When loaded with metal, the copper cathodes may be recycled to the plating bath as discussed in Section 2, or disposed of via the activity's recycling program. The titanium cathodes are returned to the plating bath as anodes.

Reticulate Cathodes: Each reticulate cathode can be loaded with 3 to 5 pounds of metal. When fully loaded, the reticulate cathode has lost the major part of its active surface area and may create a barrier to the flow of the effluent. The frequency of replacement varies according to the concentration of the metal ions, flow rate, and the operating conditions. If the cathodes are overloaded, a short may occur between cathodes and shutdown the ERU; a weekly visual inspection of the reticulate cathodes is recommended to mitigate this problem. When the cathodes are fully loaded, they should be removed and sent to the appropriate Navy reclaimer.

Precious Metal or Precious Metal Oxide Anodes: Anodes need to be inspected when the electrolytic cell is cleaned. Special attention should be given to the surface of the anode for damage to the precious metal coating or for organic contaminants. An indication that the anode is no longer functional is the lack of metal plate on the adjacent cathode. Precious metal anodes should not be wire brushed or mechanically cleaned since the precious metal catalytic coating can be lost or damaged.

6.3 MAINTENANCE REQUIREMENTS FOR OPTIMAL PERFORMANCE OF ERUs

6.3.1 Determining Standby Amperage Setting for ERU

Standby amperage is the lowest amperage that must be applied to prevent dissolving of the recovered metal plated on the cathode. Reticulate cathodes are especially sensitive to amperage levels in very dilute rinsewaters. The impregnated metal in the foam cathode will galvanically dissolve and the rinsewater will have the appearance of an increase in metal. To determine standby amperage, if not specified by the manufacturer, turn down the amperage until analytical tests show there is a slight increase in metal concentration in the rinsewater from the plated metal dissolving from the cathode. Turn the amperage up until there is no dissolution of metal from the cathode surface. This amperage is the lowest the ERU should be set during periods of inactivity. The other option is to shut the ERU off and drain the electrolytic cell.

WARNING

Never leave the cathodes/anode in the rinsewater of the electrolytic cell with the current shut off.

6.3.2 Optimal Conductivity for Electrowinning

Conductivity is maintained by drag-out from the plating tank. It is recommended that an initial minimum conductivity of at least 8.5 millimhos. High conductivity allows for higher amperage at lower voltage, which is a far more energy efficient operation. Initial high concentration may require raising the amperage and then lowering the amperage as the concentration stabilizes at < 50 ppm. The user will note a change in voltage as the rinsewater becomes more dilute in metal and cyanide ions, because of the removal of these conducting ions. This change in voltage, if higher than initial starting voltage, is an indication that conductivity of the still tank should be checked and non-interfering ions added in the form of an appropriate acid, base or salt. If such a problem persists, an NFESC point of contact (POC) should be called for consultation.

6.3.3 Maintenance of Cathodes and Anodes for Long Lifetime

Anodes and cathodes may be damaged to varying degrees if left unattended in solution without an applied potential or standby amperage. In an acidic solution there is danger of penetration of the anode precious platinum coating resulting in the platinum layer peeling off. New reticulate cathodes have very little metal impregnated in them and can lose their rigidity and conductivity if left in solution without a standby amperage within a few hours.

NFESC recommends that standby amperage be applied at all times when solution (electrolyte) is present in electrolytic cell.

WARNING

IF A STANDBY AMPERAGE CANNOT BE APPLIED, THE ELECTROLYTIC CELL SHOULD BE TURNED OFF AND DRAINED; THE ELECTRODES THEN CLEANED UP REPLACED IN THE ERU AWAITING START-UP.

6.4 SPECIAL CHEMICAL FACTORS EFFECTING OPTIMAL ELECTROWINNING

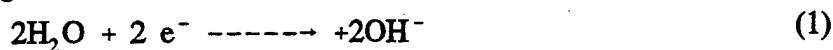
6.4.1 Consequences of Proprietary Plating Bath Chemistry in Dilute Rinsewaters

Plating baths are frequently purchased from suppliers and chemical additives such as wetting agents, conducting salts and buffers, stabilizers, and additions to promote anode corrosion (Ref 8) may react to either enhance or hinder electrowinning of certain applications in dilute concentrations of plating rinsewaters. Many of the additives are proprietary in nature, therefore making it difficult to determine the culprit when the ERU is not operating within performance specifications. In most cases, laboratory analysis can trace the source of the problem. Some examples are cited in the following paragraphs. However, solutions are site-dependent and must take into consideration the quality of plating product before correcting the problem. For example, adding an anti-foaming agent to the rinsewater may leave a film on the plated part. Consult with an NFESC POC if this circumstance arises.

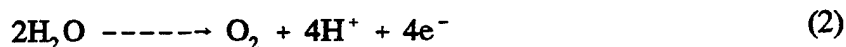
In several reported cases, an odorous smell was generated during periods of heavy metal loading. When electroless nickel baths were electrowinned with heavy loading on the cathode, an oxidized sulfur compound remained after complete nickel recovery. It has also been noted that older tin-lead fluoborate baths contain peptone, which when oxidized at the anode, produces an unpleasant smell.

6.4.2 pH Control to Prevent Hydroxide Ion Formation

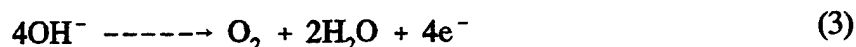
Low current efficiency can affect the pH of a dilute plating rinse solution by the electrolysis of water. At the cathode, hydrogen evolution is accompanied by the production of hydroxide ions in the following reaction:



If the anodes are insoluble and, as the rinsewater becomes depleted in metal ions near the anode, the following reaction occurs in acidic solution:



or in alkaline solution:



Increasing pH of a solution during electrowinning means that the cathode efficiency is lower than anode efficiency (Equations 2 and 3). Decreasing pH means that anode efficiency is lower than cathode efficiency (Equation 3). Substantial pH changes during electrowinning may cause the formation of metal hydroxides as noted from Equation 1. The hydroxide ion, present from the electrolysis of water, may precipitate metal cations instead of electrowinning them at the cathode. Sludge below the cathodes will indicate that hydroxide ion is present and forming a metal hydroxide precipitant.

6.4.3 Micro-Organisms Growth Preventative Steps

Plating shop atmospheres are often humid and, thus, an ideal location for algae and other micro-organisms to flourish. Micro-organisms occur because many metals, particularly copper, are antifungicides. Once the copper ion has been electrolytically removed, micro-organism growth may set in and result in a warm acidic environment. At a printed circuit board shop where acid copper rinsewaters are electrowinned, addition of sodium chloride to the rinsewater and subsequent formation of hypochlorous acid by oxidation at the anode, cured the problem. Other remedies will be site-dependent, but good housekeeping practices are a must. When the ERU is not in operation, the unit should be drained and cleaned. A filter to the plating rinsewater adds additional maintenance time, so it is recommended as a last resort to solving the problem.

CHAPTER 7 ANALYTICAL LABORATORY SUPPORT

In order to test the performance of the ERU after installation, rinsewater samples must be taken from the still rinse baths at intervals to determine the concentration of metals. For cyanide processing baths, analytical tests for free cyanide, total cyanide and cyanate need to be measured to develop initial ERU performance curves. Once the performance of the ERU is satisfactory in both metal recovery and cyanide destruction, only sampling of free cyanide may be necessary. Field kits may be used for cyanide determinations on analytical laboratory samples taken during routine plating bath operations.

7.1 ANALYSIS OF METALS

Analysis of metals is typically performed by inductively coupled plasma (ICP) or atomic adsorption (AA) is shown by the methods listed in Table 7-1. In order for the analytical laboratory to set up their instruments for quick turn around time, it is suggested that the expected metal concentration range be given the laboratory so they can prepare appropriate standards for the analytical instruments.

7.2 ANALYSIS OF CYANIDE CONCENTRATION IN STILL RINSE TANK

The tests for cyanide and cyanate are suggested as given in Table 7-2.

Cyanide analysis will vary according to the test used. For cyanide plating rinsewaters, the total cyanide test should be performed initially. For example, copper is highly complexed with cyanide and has several forms in the rinsewater, i.e., $[\text{Cu}(\text{CN})_2]$ and $[\text{Cu}(\text{CN})_3]^{2-}$, and possibly the tetracyano complex $[\text{Cu}(\text{CN})_4]^{3-}$ as well. Therefore, if a test for free cyanide is analyzed at the start of electrowinning and then at a later time interval, the cyanide level may appear to be increasing as the copper is plated on the cathode and releasing cyanide from the copper complex. However, once very low concentrations of metal are reached, it is assumed that most of the cyanide bonded with the metal is broken as the metal is reduced at the cathode with the release of free cyanide. It is appropriate to measure free cyanide under these latter conditions.

The method for the total cyanide analysis takes longer due to the additional distillation step and is usually more costly at commercial laboratories.

Table 7-1
Methods for Laboratory Analysis of Metals By ICP or AA

Analysis	Method	Concentration Range (ppm)
Nickel	ICP or AA EPA (6101/7870)	1 - 500
Silver	ICP or AA EPA (6101/7210)	1 - 500
Zinc	ICP or AA EPA (6101/7420)	1 - 500
Tin	ICP or AA EPA (6101/7870)	1 - 1000
Copper	ICP or AA EPA (6101/7210)	1 - 500
Lead	ICP or AA EPA (6101/7420)	1 - 500

The laboratory should provide sample bottles with the appropriate label and add preservatives for metals if needed.

7.3 METAL ASSAYS FOR RECYCLING METALS TO PLATING BATH

Each plating shop will evaluate the purity of the recovered metal to determine if the metal is acceptable to be returned to the plating bath in anode bags.

7.4 FIELD TEST KITS FOR METALS AND FREE CYANIDE

Several field test kits are now on the market to determine the levels of metal and cyanide in the plating rinsewaters. The field strip tests for copper, nickel, zinc, iron, and tin have concentration ranges from 10 to 1,000 ppm, as shown in Table 7-3. The silver test (as of this writing) is not appropriate for use with plating rinsewaters. Other types of field test strips may be desired depending on the plating application for detection of fluoride or chloride ions.

The field test is designed for detection of free cyanide or complexes that can be decomposed by chlorine. This test of cyanides is questionable since "total cyanide" may need to be measured. For example, this test cannot tell you how much nickel may be complexed with cyanide. As noted in Section 7.2, once very low levels of metal concentration are reached, then the free cyanide analysis (instead of the total cyanide analysis) is appropriate and the test strips may be used to determine within the error specified by the kit, the concentration of cyanide remaining.

Table 7-2
Methods for Laboratory Analysis of Cyanide and Cyanate

Analysis	Method	Concentration Range (ppm)
Total cyanide	Distillation/Titration (412 B, C)*	300 - 3,000
Free cyanide	Titration (412 C)*	200 - 2,000
Free cyanide	Ion Selective Electrode (413 E)*	
Cyanate	Wet Chemical (412 K)*	0 - 200
Preservation of cyanides	413 A*	Cyanide must be treated with pH change (> 12) if not analyzed immediately

*Methods from "Standard Methods for the Examination of Water and Wastewater," 16th edition (Ref 17).

Table 7-3
Analysis by Field Test Kits Metal and Free Cyanide

Analysis	PPM Range of Metal*
Zn ²⁺	0, 10, 40, 100, 250
Free cyanide	1, 3, 10, 30
Fe ²⁺ /F ³⁺	2, 5, 10, 25, 50, 100
Cu ²⁺	10, 25, 100, 250, 500, 1,000
Ni ²⁺	10, 25, 50, 100, 250, 500, 1,000
Sn ²⁺	10 to 500

*See Vendor List in Appendix F for ordering field test kits.

CHAPTER 8

TRAINING FOR OPERATION AND MAINTENANCE

The training for operation and maintenance for ERUs should include plating operators, engineers, supervisors, chemical laboratory personnel and maintenance personnel. Part of the training should include an explanation of the ERU accomplishments as discussed in Section 3.1.1.1 in relation to the Navy's Pollution Prevention Program. The training instructor may be personnel from NFESC or activity personnel familiar with electrowinning technology.

8.1 TWO-HOUR ERU TRAINING

During a 2-hour training period the following subjects are recommended to be demonstrated in detail with the ERU: peeling recovered metal and cleaning electrodes; daily check procedures; safety clothing; preventive maintenance procedures; discussion of MSDS listed hazards and hazard mitigations; and discussion of pump, electrical, and leak repairs. Procedures for start-up and shut down of the ERU should include the specific recommendations by the manufacturer as well as those found in this UDP. Particular attention should be given to standby amperage for the ERU during periods of inactivity in Chapter 6.

8.2 ERU INSTRUCTION MANUALS

A copy of the ERU UDP should supplement areas covering topics where the manufacturer's manual is non-specific. A manufacturer's manual should be provided for all personnel being trained in addition to the manual being accessible in the plating shop area with POCs for consulting when problems arise.

CHAPTER 9 SAFETY

9.1 SAFETY CONSIDERATIONS

The hazard associated with the electrolytic recovery unit primarily involve the treatment and handling of hazardous material wastes. ERUs operate where heavy metal liquid wastes containing silver, copper, lead, nickel, and other toxic chemicals may be present. However, these systems will not add any new chemical hazards to the plating shop that are not already present.

9.2 PRE-EXISTING HAZARDS

The installation and operation of the electrolytic recovery unit will be conducted in the electroplating shop. This shop environment includes chemical hazards associated with each process bath, electrical hazards associated with the rectifiers and electrical equipment located in the shop, and mechanical/physical hazards associated with equipment that may be used in the plating shop.

9.3 POSSIBLE NEW HAZARDS

Electrolytic recovery is a process very similar to electroplating. In electroplating, metals are plated onto a part during immersion in concentrated electrolyte solutions. In electrowinning, metals are being plated from dilute wastewaters onto a cathode for future recovery. In very dilute rinsewaters with low conductivity, generation of hydrogen and oxygen is possible at the cathode and anode respectively. By using the correct operational parameters in this UDP recommended by NFESC in Section 6, generation of these gases should not occur. If the ERU is located in a well ventilated Navy shop, the potential hazard from these gases should be mitigated. ERUs can be designed with specialized hood systems that can be easily connected into the plating shop ventilation system. Caution should be exercised when scrapping the recovered metal from the cathode as with any other operation involving parts in the shop. Normally, the shop parts preparation area is also used for scrapping the metal from the cathodes. General shop air usually serves the prep area and it acts to dilute low level contaminants. If the recommendations for producing adherent plate are followed by operating the ERU at correct amperage, the metal on the cathode will be a solid metal plate and will peel as illustrated in Figure 6-3. However, if other conditions exist where personnel may be exposed to heavy metals during this scrapping operation, an industrial hygienist should monitor the personnel for short-term exposure limits (STEL). Consult NFESC Code 425 for engineering controls when the local industrial hygiene office identifies exposures above the action level.

9.4 MATERIAL SAFETY DATA SHEETS

Applicable MSDS should be read for each plating process where an electrolytic recovery unit is being installed and operated. Such MSDS are located on the tank in the plating facility. If the MSDS lists any potential hazards, prepare mitigation measures as required for the application where the ERU is located.

9.5 APPROPRIATE PERSONNEL PROTECTIVE EQUIPMENT (PPE)

Appropriate personnel protective equipment (PPE), including safety glasses with side shields and neoprene gloves, should be worn during the handling and sample collection of metal/cyanide rinsewaters. In addition, safety shoes should be worn in the plating shop area as required by the activity.

CHAPTER 10 REFERENCES

1. Naval Facilities Engineering Service Center. Technical Report, Operational Test Report for Testing and Evaluation of Electrolytic Recovery Units at Naval Aviation Depot Cherry Point, Naval Air Warfare Center Indianapolis, and Norfolk Naval Shipyard, by Katherine Ford and Jennie Koff, Port Hueneme, CA, in publication.
2. _____. Technical Memorandum TM-2118-ENV (CR): Testing and Evaluation of Electrolytic Metal Recovery Units at Naval Air Depot Cherry Point, CAI Engineering, Oakton, VA, Mar 1994.
3. _____. Technical Memorandum TM-2119-ENV (CR): Testing and Evaluation of Electrolytic Metal Recovery Units at Naval Air Warfare Center Indianapolis, CAI Engineering, Oakton, VA, December 1993.
4. _____. Technical Memorandum TM-2120-ENV (CR): Testing and Evaluation of Electrolytic Metal Recovery Units at the Norfolk Naval Shipyard, CAI Engineering, Oakton, VA, Nov 1993.
5. Naval Civil Engineering Laboratory. Technical Note N-1787: Hazardous Waste Minimization Initiation Decision Report, by R.M. Roberts, J.L. Koff, and L.A. Karr. Port Hueneme, CA, Jun 1988.
6. J. Koff. "Minimization of Cadmium Cyanide Wastes Using Electrolytic Treatment," *Military Engineer*, Aug 1989, vol 81, no. 530.
7. Naval Civil Engineering Laboratory. Technical Memorandum M-74-88-04: Phase 2 Developmental Test Report (DTRII) on Electrolytic Treatment of Navy Cyanide Wastewaters, by J.L. Koff and T. Torres, Feb 1988. Program No. Y0817-004-01-4172, Port Hueneme, CA 93043.
8. Naval Facilities Engineering Service Center. Technical Memorandum TM-2134-ENV (CR): Technology Assessment for Electrowinning Applications, Applied Engineering Management Corporation, Camarillo, CA, 1991.
9. J.P. Wiaux, "The Recovery and Recycling of Metal Utilizing Electrolytic Techniques," *Titalyse*, S.A., 8 Rue Bergere, CH-1217 Meyrin/Geneva, Switzerland.
10. F.A. Lowenheim. "Modern Electroplating," 3rd ed., John Wiley and Son Inc., NY, 1974.
11. K.L. Hardee, L.K. Mitchell, and E.J. Rudd, "Catalytic Anodes for High-speed Electroplating and Electro galvanizing," *Plating and Surface Finishing*, Apr 1989.

12. R.M. Skomoroski, R. Baboan, R.G. Zobbl, and E.K. Camp, "Performance of Platinum-clad Tantalum Anodes in Electroplating," *Plating*, Nov 1973.
13. G.C. Cushnie. *Pollution Prevention and Control Technology for Plating Operations*, National Center for Manufacturing Sciences, 3025 Boardwalk Drive, Ann Arbor, MI, 1994.
14. J.B. Mohler. "Survey Your Rinse Tanks," *Metal Finishing*, Jul 1977.
15. _____. "Dual Purpose Rinsing," *Plating and Surface Finishing*, Sep 1979.
16. G.A. Ryder. "Rinse Management Techniques," *Metal Finishing*, Nov, 1986.
17. "Standard Methods for the Examination of Water and Wastewater," 1985, 16th ed., American Public Health Association, Washington, DC.
18. J.B. Mohler. "Art and Science of Rinsing," Electroplater's Society, Inc. Orlando, FL, copyright 1985.

Appendix A

TABLES

The degree which a metal can be recovered by electrowinning is in part reflected by its position on the electromotive series (Ref 10). The more positive the metal the more likely it can be electrowinned, as shown in Table A-1, where recovery is highest for gold and lowest for aluminum:

Table A-1
Electrochemical Potential Series

Metal	Potential
Gold	+1.69
Silver	+0.80
Copper (+) ^a	+0.52
Copper (++) ^b	+0.34
Lead	-0.13
Tin	-0.14
Nickel	-0.25
Cadmium	-0.40
Zinc	-0.76
Aluminum	-1.66

^aCu (+) as found in copper cyanide.

^bCu (++) as found in acid copper.

The electrochemical potential series closely resembles Table A-1 for potential applications for electrowinning of plating rinsewaters. Metals with cyanide anions are in Group 1 such as zinc cyanide. Other metals without the cyanide anions may fall in either Group 2 or 3. See Reference 10 for further explanation of cyanide as an anion in electroplating.

Table A-2
Current Efficiency/Power Consumption for Copper and Silver Cyanide

Test	Metal (Concentration)	Average Current Density	Current Efficiency		Power Consumption
			(%)	(gr/amp-hr)	
1	Cu (2680)	1.391	37	0.9	6
2	Cu (1280)	0.686	13	0.3	15
3	Cu (421)	0.774	8	0.2	40
4	Cu (21)	0.573	2	0.05	200
1	Ag (856)	1.281	4	0.17	15
2	Ag (405)	2.315	2	0.10	40
3	Ag (99)	0.950	7	0.30	134

Table A-3
**ERU Cathode Surface Area and Related Current Density
and Amperage Settings at High and Low Concentrations***

Cathode Type	Cathode Total Area (m ²)	Application	Manufacturer's Suggested Amperage (amp) (Maintained Concentration > 50 mg/L)	NFESC's Suggested Amperage (amp) (Maintained Concentration < 50 mg/L)	Current Density (amp/m ²) (< 50 mg/L)
SS flat plate	0.10	Silver cyanide	3 (50-100 ppm)	1.0-1.5 (< 50 ppm)	30 (12.5)
SS flat plate	2.27	Copper cyanide	25 max (500 ppm)	3-4 (< 50 ppm)	11.0 (1.54)
SS flat plate	0.10	Tin-lead fluoborate	3 (100 ppm)	1.5-1.75 (< 50 ppm)	30 (16.3)
Titanium mesh	0.08	Silver cyanide	3 (50-100 ppm)	0.75-1 (< 50 ppm)	37.5 (10.93)
Copper mesh	1.82	Copper cyanide	25 max (500 ppm)	2.5-3.0 (< 50 ppm)	13.75 (1.51)
Expanded titanium mesh	5.20	Acid copper	80 (100 ppm)	20 (< 50 ppm)	15.62 (3.90)
Reticulate	32.00	Acid copper	80 (100 ppm)	50 (< 50 ppm)	2.50 (1.56)
Reticulate	32.00	Electroless nickel	90 (5,000 ppm)	35 (< 50 ppm)	2.81 (1.09)

*Data from References 2, 3, and 4.

Appendix B

ECONOMIC BENEFITS/ACQUISITION COSTS

Capital investment for electrolytic recovery systems include the initial cost of the ERU, labor, and materials required for installation. NFESC's RDT&E effort required that the ERU cost less than \$15,000, the average cost being \$11,000. Cost variations from this analysis may be due to site specific differences such as: (1) metal to be electrowinned (gold, silver, copper, lead), (2) type of rinsing system, and (3) current water treatment costs. The assumptions for this cost/benefit analysis were obtained from NADEP Norfolk in an earlier ERU study. Activities will need to consult personnel at their IWTP for complete site specific cost information.

ASSUMPTIONS FOR COST/BENEFIT ANALYSIS:

Work year	=	260 day/year
Labor	=	\$40 per hour
Electricity Cost	=	\$ 0.07 per kW
Cost of Water	=	\$ 1.65/1000 gal
IWTP Treatment Cost	=	\$53.53/1000 gal

Number of gallons rinsewater from a counterflow rinsing system:

Counterflow rinse	=	2 gal/min x 60 min/hour x 24 hr/day x 260 days/yr
Gallons to IWTP	=	748,000 gal/yr

CAPITAL INVESTMENT

1. Cost of Electrolytic Recovery Unit, Associated Equipment, and Installation

ERU	=	\$15,000 maximum cost
Installation (labor)	=	3,500
Materials	=	400

Total Capital Investment \$19,046

ANNUAL MAINTENANCE COSTS

2. Estimated Annual Maintenance Costs

a. Annual Cleaning of the ERU

Annual draining and cleaning of the ERU. Required time for this task is 2 hours per year.

$$\text{Annual cleaning of ERU: } 2 \text{ hrs} * \$40/\text{hr} = \$80$$

b. Cleaning Cathode

Stripping and cleaning of the electrodes is performed eight times annually and requires 1 hour of labor each time the electrodes are stripped and cleaned. Alternatively, if disposable cathodes are used, then ordering and selling to reclaimer costs are estimated to be approximately the same.

$$8 \text{ cleanings/yr} * \$40/\text{hr} = \$320/\text{yr}$$

$$\text{Total Costs: } \underline{\quad\quad\quad} \$400.00$$

ESTIMATED ANNUAL OPERATIONAL COST

3. Estimated Annual Operational Costs

a. Daily Spot Checks

One spot check is required every other day when the ERU is continuously running. Each check required 10 minutes.

Annual Spot Check Cost:

$$0.5 \text{ checks/day} * 5 \text{ day/week} * 52 \text{ weeks/yr} = 130 \text{ checks/yr}$$

$$130 \text{ checks/yr} * 10 \text{ min/check} * 1 \text{ hr}/60 \text{ min} = 22 \text{ hrs/yr}$$

$$22 \text{ hr/yr} * \$40/\text{hr} = \$880$$

b. Energy Usage

The energy usage is dependent on the type of cathode used. For stainless steel flat plate, the average energy usage was:

$$2 \text{ volts} * 2 \text{ amps} = 4 \text{ watts}$$

4. Estimated Annual Savings for Installed ERU

a. Annual Savings on Water Consumption

Utilization of the ERU limits yearly water consumption at an estimated 75 percent, but can be higher in plating shops where there is an evaporative makeup bath or a three bay rinse-system. For a countercurrent rinse tank, an estimated 2 gal/min or 748,000 gals/yr (based on 260 work days/yr).

Savings on Water Consumption

$$\text{Without ERU: } 748,000 \times \$1.65/1000 \text{ gal} = \$1,234$$

$$75 \text{ percent reduction with installed ERU: } 187,000 \times \$1.65/1000 \text{ gal} = \$113.33$$

Annual Water Savings

$$\$1,234 - 113.00 = \$1,121$$

b. Annual Savings on Wastewater Treatment

Due to the reduced water consumption resulting from the utilization of the ERU, the amount of wastewater that requires treatment decreased. An estimated cost of \$53.53/1000 gal for treatment of plating rinsewaters includes chemical, labor, and energy costs.

Savings on Treatment Costs

$$\text{Wastewater treatment cost (w/o ERU): } 748,000 \times 53.53/1000 \text{ gal} = \$40,040$$

$$75\% \text{ reduction with installed ERU: } 187,000 \times 53.53/1000 \text{ gal} = \$10,010$$

Annual Wastewater Treatment Costs

$$\$40,040 - 10,010 = \$30,030$$

$$\underline{\text{Total Annual Savings}} = \underline{\underline{\$31,151}}$$

5. Payback Period

The initial investment, using the estimated savings total, will be recovered in approximately 6.1 months. This figure does not include recycling the recovered metal into the plating bath.

ERU-Investment and Associated Equipment: \$18,900
Annual Maintenance and Operation Costs: 3,546/yr
Annual Savings: \$31,151 - 3,546 = \$27,605/yr
Payback Period: \$18,900/\$27,605 * 12 months = 8.2 months

6. Savings Investment Ratio (SIR)

Over an economic life cycle of 10 years, using the estimated savings total, each dollar of the ERU investment will generate approximately 12.0 dollars in savings. The actual SIR may be significantly higher if lower amperage were used and the cost of the metal recovered were part of the calculation.

Saving-Investment-Ratio:

$$\frac{(\$31,151 - \$3,546) (8.216)}{\$18,900} = 12.0$$

$$\text{Saving-Investment-Ratio} = 12.0$$

AMORTIZATION COST

7. Amortization Cost

The Future Value (FV) is equal to P (value today) in return for $P(1 + i)^n$ dollars (n) years from today. An accumulation schedule on the following Accumulation Schedule Table is based on a lifetime of 10 years for the ERU and interest rate of 6.0 percent. The FV of the ERU is 10 years at \$26,862.

Calculations from NAVFAC P-442 Economic Analysis Handbook

$$\text{Future Value} = \$26,862 \text{ in 10 years}$$

SUMMARY

● ERU Capital Investment	\$18,900
● Annual Operation	1,068
● Annual Maintenance	400
● Materials Analytical Laboratory	2,080
● Annual Savings	32,271
● Payback Period	8.2 months
● Saving-Investment-Ratio	12.0
● Amortization Cost	\$26,862

Appendix C

ERU SELECTION WORKSHEET

This ERU Selection Worksheet is designed to ask the questions that need to be addressed by plating shop personnel before making a final decision for using electrolytic recovery technology. For assistance with this worksheet, call a POC at NFESC listed in Appendix G.

DATE: _____

ACTIVITY: _____

ADDRESS: _____

SHIPPING ADDRESS: _____

POC: _____ POSITION: _____

TELEPHONE NUMBER: _____

FEASIBILITY OF ELECTROWINNING

- a) What potential plating bath rinsewaters are to be electrowinned:

Acid Copper ____
Copper Cyanide ____
Electroless Nickel ____
Silver Cyanide ____
Tin-Lead Fluoborate ____
Cadmium Cyanide ____

Other ____

- b) If "Other" is given as an answer, is the plating bath rinsewater feasible for electrowinning? ____
UDP Section 1.7.1
- c) Is cyanide destruction a major reason for installing the electrowinning recovery unit? ____

PLATING SHOP PROCESS FLOW

- a) Is there a still rinse tank on the lines designated for electrowinning?
- b) Are the rinse tanks: Countercurrent ____
Spray ____
- c) If countercurrent, are they double ____ triple ____
- d) If still rinse tanks are not on the lines, can they be installed ____
- e) Can the countercurrent rinse tank be sectioned off so as to provide a still rinse tank ____
- f) What is the total amount of rinse water used per 8 hour shift ____ per day ____ for each application
- g) Are there any evaporative make-up still rinse tanks ____
- h) Other types of recovery, if any, in-line or off-line such as:

Ion Exchange ____
Reverse Osmosis ____
- i) Are the rinse lines, Manual ____, Automatic ____
- j) Are there conductivity meters in the rinse bath ____

POTENTIAL CONCENTRATION LOADING OF METAL/CYANIDE IN STILL RINSE TANK (See Appendix D)

- a) Calculate the concentration of each application per day:

Application _____ Tank # _____ Conc _____ ppm

Application _____ Tank # _____ Conc _____ ppm

Application _____ Tank # _____ Conc _____ ppm

- b) Classify Concentration as LIGHT, MODERATE, HEAVY usage by the following scale:

VERY LIGHT: less than 50 ppm per day
LIGHT: greater than 50 ppm but less than 250 ppm
MODERATE: greater than 250 ppm but less than 500 ppm
HEAVY: greater than 500 ppm
VERY HEAVY: greater than 1000 ppm

EQUIPMENT SELECTION

CATHODES

- a) Are the cathodes to be sold to reclaimer ___ or recycled in plating bath ___

- b) If recycled, see section 3.2.5.1 UDP for options:

Stainless Steel Flat Plate Cathodes ___
Metal stripped and returned to plating tank in anode bag
Recommended for Moderate to Very Heavy Metal Concentrations

Expanded metal/wire mesh cathodes ___
Mesh cathode hung in plating tank
Recommended for very light to moderate concentrations

- c) If sold to reclaimer, see section 3.2.5.2 UDP for options:

Reticulate Impregnated Metal Cathodes ___
Cathode dried and sold to reclaimer
Recommended for very Light to Heavy Concentrations

Expanded Metal/wire mesh Cathodes ___
Cathode may be sold to reclaimer where high purity may be required
Recommended for Light to Moderate Concentrations

- d) Is there persulfate in the rinsewater ___ If so, metal will be removed from the cathode.

ANODES

- a) Types of Anodes available and Materials, see UDP Section 3.2.2.

<u>Anode Type</u>	<u>Example</u>
Catalytic Anodes:	Titanium Iridium Oxide
Highly Oxidizing Anodes:	Platinized Titanium
Neutral Anodes:	Graphite, Antimony-Lead

Do rinsewaters contain any of the following halide ions or strong oxidizing agents which may cause damage to anodes:

Chloride ion	___	(halide ion)
Fluoride ion	___	(halide ion)
Fluoborate ion	___	(break down products form halide ion)
Manganese	___	(passivates anode)
Hydrogen Peroxide	___	(strong oxidizing agent)
Sodium Persulfate	___	(strong oxidizing agent)

- b) If chlorine ion is present, use catalytic anodes.
- c) If fluoride or fluoborate ion is present, catalytic anodes may be used, but their life is limited. Otherwise graphite anodes are recommended. Graphite anodes are known to gradually exfoliate carbon particles into the rinse water. The discoloration may be objectionable.
- d) If strong oxidizing agents are present, a reducing agent must be added before electrowinning.

CIRCULATION SYSTEM

- a) Does the ERU come with a pump that will circulate the still rinse tank at 5 gallons per minute ___
- b) Inlet dispersion or air sparged is recommended for most applications except for those incidents listed below for the fluidized glass bead bed.
- c) Fluidized glass bead bed circulation is recommended if:
1. Plating a precious metal (gold or silver)
 2. Concentration of metal is light
 3. Height purity of recovery of metal is required
 4. Shop personnel have technical background in plating

INSTALLATION

- a) Does the plating shop have adequate space so that the ERU may be located such that the rinsewater leaving the ERU may gravity feed back to the still rinse tank ____
- b) Will the ERU be installed below the plating shop floor?
- c) If gravity feed is not possible, then a second pump will have to be installed. If yes to b) a second pump is absolutely required.
- d) Is there sufficient ventilation around the ERU ____
- e) Is the electrical supply in the plating shop adequate to supply the rectifier of choice for the ERU ____

REGULATORY REQUIREMENTS

- a) What are the discharge concentrations the shop is required to meet for each metal:

Appendix D

CONCENTRATION IN RINSING TANKS FROM DRAG-OUT

In order to select a ERU with the required capacity, an estimate is needed of the drag-out from the plating tank into the rinse tanks is required. The method for determining metal/cyanide drag-out concentration is dependent on the plating shop's facilities; either chemical analysis or the conductivity method (Refs 13 through 16) may be used to determine metal ion concentration. In some cases, if the nominal composition of the plating bath is known, an estimate of the drag-out and the rinsewater concentration may be sufficiently accurate under non-equilibrium conditions to determine ERU capacity. Appendix D explains how to determine the cathodes surface area (number of cathodes * area/cathode) needed for a selected ERU.

1. Countercurrent Rinse Tanks Under Equilibrium Conditions

The basic rinsing equation (Ref 18) is used with metal concentration being determined by chemical analysis or using a conductivity meter. The basic rinsing equation at **equilibrium** is:

$$D \times C_r = F \times C_R$$

C_r = Concentration in the previous tank and solution dragged in

D = Volume of dragout

C_R = Concentration in the rinse

F = Flow of water to the rinse tank

For example calculate drag-out for 10 parts/hour leaving the process plating tank:

Drag-out = 0.004 L/rack

Conc of metal in plating bath = 40 g/L

Flow Rate = 20 L/hour

Plated part Process Rate = 10 parts/hr

Flow rate per part = 2 L/part

Conc of rinse water = 0.08 g/L

Flow rate per part = 20 L/hr/10 parts/hr = 2 L/part

The drag-in (D) times the concentration in the preceding process tank (C_R) equals the flow (F) times the concentration in the following rinse tank (C_r). For one rack:

$$\begin{aligned}
 0.004 \text{ L/rack} * 40 \text{ g/L} &= 2 \text{ L/rack} * 0.08 \text{ g/L} \\
 0.160 \text{ g} &= 0.160 \text{ g}
 \end{aligned}$$

Therefore, an equilibrium is established so that the rinse tank always contains 0.160 grams of metal. However, a flow rate of 20 liters/hour (5.9 gallons) of water must be used in order to maintain this equilibrium.

2. Still Rinse Tank at Non-equilibrium Conditions

For a still rinse tank at non-equilibrium condition, a good estimate of the rinse bath concentration that will build up over time is:

$$\frac{0.004 \text{ L/rack} * 40 \text{ g/L} * \# \text{ of racks} * 8 \text{ hrs/day}}{\text{Vol } C_r} = C_r$$

Therefore, if 50 racks are plated per hour in an 8 hour day, then the concentration in a still rinse tank of 1000 liters is:

$$\frac{0.004 \text{ L/rack} * 40 \text{ g/L} * 50 \text{ racks} * 8 \text{ hrs/day}}{1000 \text{ liters}} = C_r$$

$$C_r = 51.2 \text{ ppm/day}$$

Can an ERU remove 51.2 ppm/day of metal overnight to maintain the still rinse below discharge levels. See Appendix E to determine the cathode surface area necessary to answer this question.

Appendix E

CALCULATIONS TO MAINTAIN DESIRED METAL RECOVERY RATE

Appendix E is designed to determine if the size of the ERU is consistent with the desired rate of metal recovery to maintain low metal concentration in the still rinse tank. Add the number of cathodes necessary to maintain a balance between total active cathode surface area and amperage. If a higher amperage is required to maintain a desired rate of metal recovery from the still rinse tank, then the surface area of the cathode must increase.

NOTE: DATA USED IN THIS EXAMPLE ARE FOUND IN TABLE 3, APPENDIX A.

Silver Cyanide Rinsewater

Cathode	Cathode Total Area (m ²)	Manufacturer's Amperage (>50 mg/L)	NFESC Amperage (<50 mg/L)	Current Density (<50 mg/L) Amps/m ²
Stainless steel plate	0.10	3 amps	1.0 - 1.5 amps	30 amp/m ² (12.5 amp/m ²)

- 1) Determine the concentration in (mg/L) in the still rinse tank. Use the conductivity method (Ref 2 and 16) or analytical tests as described in Section 7.0.

Calculate the number of grams of metal present in the rinsewater (volume of 1000 liters) due to dragout from Appendix C:

$\text{Vol} \times \text{mg/L} = \text{grams of metal (Vol=vol still rinse tank)}$

$1000 \text{ liters} \times 0.0512 \text{ g/L} = 51.2 \text{ grams of silver}$

- 2) Estimate the number of grams per hour that is required to be plated out on the cathode to maintain low concentration.

From Table 2-1, approximately 4 grams per hour can be removed at 100% current efficiency.

Determine the amperage at the theoretical maximum (100% current efficiency)

$$\frac{\text{gr/hr}}{\text{gr/amp.hr}} = \text{Amps}$$

Example for silver cyanide plating out on flat plate cathode at 10 grams/hr, the amperage required is:

$$\frac{10\text{gr/hr}}{4.025 \text{ gr/amp.hr}} = 2.48\text{Amps}$$

- 3) Using current density of 30 A/m² meter (Table A-1, Appendix A) at concentration >50 mg/L:

$$\frac{2.48 \text{ Amps}}{30 \text{ Amps/m}^2} = 0.085 \text{ m}^2 \text{ for cathode area}$$

- 4) However, at low concentrations, <50 mg/L, current efficiency is about 10% and the amperage required will be twice as much to maintain a rate of 10 g/hour.

$$2.48 \times 2 = 4.96 \text{ Amps}$$

- 5) To maintain a higher rate of plating at a lower concentration (<50 mg/L) the cathode area must increase correspondingly to maintain good adherent plate:

$$\frac{4.96 \text{ Amps}}{30 \text{ Amps/m}^2} = 0.16 \text{ m}^2 \text{ of cathode area}$$

- 6) For concentrations less than 50 g/L, the current may be turned to half with the current density lowered to approximately 12.5.

$$\frac{\text{Amps}}{0.16 \text{ m}^2} = 12.5 \text{ Amps/m}^2 = 2$$

Therefore, the plating rate will be: 2 Amps x 4.025 g/amp.hr or approximately 8 grams/hr.

Note: The actual surface area of the flat plate cathode was 0.1 m². Therefore the rate of recovery may be slightly slower than 10 grams/hr desired.

Summary

First, add the number of cathodes necessary to maintain a balance between total **active** cathode surface area and amperage for the ERU. See Table 6-2 for recommended current density (CD) ranges. If a higher amperage is required to maintain a desired rate of metal recovery from the still rinse tank, then the cathode surface must increase in order to stay within recommended current density (CD). If amperage is raised while not increasing the surface area of the cathodes, then poor plate on the cathode may be the result.

Appendix F

LIST OF VENDORS¹

The following three electrolytic recovery units were tested and evaluated at NADEP Cherry Point, Naval Air Warfare Center Indianapolis, and Norfolk Naval Shipyard. Detailed information regarding these ERUs can be obtained from the Technical Report "Operational Test Report for Testing and Evaluation of the Electrolytic Recovery Units at Norfolk Naval Shipyard, Naval Air Warfare Center, and NADEP Cherry Point" (Ref 1).

PMR-25 CHEMELEC VENDORS (Company Name BEWT)

Ralph Coxon (Technical East Coast USA)
BEWT
Phone (410) 357-5327
FAX (410) 357-5328

Philippa H. Lock (Technical)
BEWT Recovery Technologies
Phone 01144 (789) 763-669
FAX 01144 (789) 400-274

BEWT Water Engineers Limited (Technical)
Attention: Dr. R.R. Kellner
Arden Forest Industrial Estate
Alcester
Warwickshire, B49, 6ES, England

¹This report has been reviewed by NFESC and approved for publication. The mention of trade names or commercial products does not constitute endorsement or recommendation for use.

RETEC VENDORS

Dan Heggan
Hegyan Corporation
P.O. Box 7000-187
Palos Verdes Peninsula, CA 90274
Phone (310) 373-6755
FAX (310) 375-2793

(Eltech representative)

James J. Stewart
Eltech International
625 East Street
Fairport Harbor, OH 44077
Phone (216) 357-4037
FAX (216) 257-4077

(Technical)

ACCA VENDOR

Ron Chappel
ACCA Technologies
P.O. Box 1266
Atteboro Falls, MA 02763
Phone (508) 699-4655
FAX (508) 699-2717

FIELD TEST KITS & TEST STRIPS

Gallard-Schlesinger Industries, Inc.
Research Department
Attention: Henry Medollo
584 Mineola Avenue
Carle Place, NY 11514
Phone (576) 333-5600
FAX (516) 333-5624

Appendix G

NFESC POINTS OF CONTACT

The Naval Facilities Engineering Service Center (NFESC) is located in Port Hueneme, CA. The Pollution Prevention Division (Code 42) provides responsive engineering and informational management support for the reduction of any hazardous substance, pollutant, or contaminant entering a wastestream. The Pollution Prevention (P2) Technology Development Branch (Code 421) identifies Navy P2 needs and is tasked with RDT&E efforts to meet those needs. The Information/Technology Transfer Branch (Code 423) implements P2 technologies Navy-wide.

ELECTROLYTIC RECOVERY TECHNOLOGY POINTS OF CONTACT

Technology Implementation/Transfer POC: Mr. Michael Viggiano, NFESC (Code 423), DSN 551-4895, Commercial: (805) 982-4895/4897.

Mailing Address:

Naval Facilities Engineering Service Center
Information/Technology Transfer Branch, Code 423
560 Center Drive
Port Hueneme, CA 93043-4328

Technical POC: Dr. Katherine Ford, NFESC (Code 421), DSN 551-1470, Commercial: (805) 982-1470/1685.

Mailing Address:

Naval Facilities Engineering Service Center
Pollution Prevention Technology Development Branch, Code 421
560 Center Drive
Port Hueneme, CA 93043-4328

Safety POC: David Chavez, NFESC (Code 425), DSN 551-5314, Commercial: (805) 982-5314.

Mailing Address:

Naval Facilities Engineering Service Center
Pollution Prevention Technology Development Branch, Code 421
560 Center Drive
Port Hueneme, CA 93043-4328

DISTRIBUTION LIST

AF / AFMC/ENX, BLACK, WRIGHT PATTERSON AFB, OH; AFMC/ENX, HERRING, WRIGHT PATTERSON AFB, OH; AFMC/LGPW, WRIGHT PATTERSON AFB, OH; AGMC/EM, NEWARK AFB, OH AMARC/LABC, DAVIS MONTHAN AFB, AZ; HSC-YAQ, SAN ANTONIO, TX; MAXWELL, BROOKS AFB, TX; OC-ALC/EMV, TINKER AFB, OK; SA-ALC/EMP, KELLY AFB, TX; SM-ALC/EMPM, MCCLELLAN AFB, CA; WR-ALC/TIEAC, ROBINS AFB, GA

ARMY / SFIM-AEC-ETD, ABERDEEN PROVING GROUND, MD

ARMY CRREL / ISKANDAR, HANOVER, NH

ARMY DEPOT / DEREAL, SACRAMENTO, CA; LETTERKENNY, AMSDS-IN-E (REED), CHAMBERSBURG, PA; LETTERKENNY, SDSLE-EN (SMITH), CHAMBERSBURG, PA; SDSAN-DEL-EMD, ANNISTON, AL; SDSRR-WE, TEXARKANA, TX; SDSTE-IRE, TOOELE, UT; SDSTO-EM-H, TOBYHANNA, PA; SDSTO-ME, TOBYHANNA, PA

ARMY ENGRG DIV / ED-SY (LOYD), HUNTSVILLE, AL

BUREAU OF RECLAMATION / D-1512 (GS DEPUY), DENVER, CO

CNO / CODE N45, ARLINGTON, VA; CODE N451H, ARLINGTON, VA

COMSUBPAC / CODE 44A1, PEARL HARBOR, HI

DEFENSE DEPOT / FACILITY ENGINEER, OGDEN, UT

DLA / BEDDOES, ALEXANDRIA, VA; COFFIE, ALEXANDRIA, VA

JOINT DEPOT / SMITH, DAYTON, OH

MCAS / ENVIRONMENTAL AFFAIRS, CHERRY POINT, NC

MCLB / CODE 88-4, ALBANY, GA; CODE 883, RIVERS, ALBANY, GA; CODE 883, WOODWARD, ALBANY, GA

NAD / CODE 0015, JACKSONVILLE, FL; CODE 340, JACKSONVILLE, FL

NAD / CODE 342, NAS JACKSONVILLE, FL

NAD / CODE 343, JACKSONVILLE, FL

NAD / CODE 640, CHERRY POINT, NC

NAD / CODE 647, CHERRY POINT, NC

NAD / ROBERTS, CHERRY POINT, NC

NAD NI / CODE 670, SAN DIEGO, CA

NAVAIRSYSCOM / AIR-530TE, ARLINGTON, VA

NAVAIRSYSCOM / AIR-09Y, ARLINGTON, VA

NAVIRWARCENACDIVWAR / CODE 832, WARMINSTER, PA

NAVIRWARCENACDIVWAR / SPADAFORA, WARMINSTER, PA

NAVFACENGCOM / CODE 40D, ALEXANDRIA, VA

NAVMAG / CODE 09, LUALUALEI, HI

NAVSEA / SEA-071&E, ARLINGTON, VA

NAVSHIPYD / CODE 106, PEARL HARBOR, HI; MILTON, PHILADELPHIA, PA; STRICKLAND, PORTSMOUTH, VA; TAYLOR, PORTSMOUTH, VA; VOZZELLA, PORTSMOUTH, NH

NAVWPNCEN / CODE C833, CHINA LAKE, CA

NAVWPNSUPPCEN / CRANE, IN; CODE 095, CRANE, IN; CODE 7067, CRANE, IN; CODE SF, CRANE, IN

NAWC / CODE 507, INDIANAPOLIS, IN; CODE OIH, INDIANAPOLIS, IN

NOARL / CODE 440, NSTL, MS

NORDA / CODE 1121SP, NSTL, MS

NRL / CODE 2530.1, WASHINGTON, DC

NSWC / CODE 6301, ANNAPOLIS, MD; CODE OE, INDIAN HEAD, MD

NSWC-1HD / CODE 095, INDIAN HEAD, MD

NUWC / CODE 041, KEYPORT, WA; CODE 043, KEYPORT, WA; CODE EDX4, KEYPORT, WA

NWS / CODE 09203, CONCORD, CA; CODE 0923, SEAL BEACH, CA; CODE 096, COLTS NECK, NJ;
CODE H1, YORKTOWN, VA

PUGET SOUND NAVSHPYD / BREMERTON, WA

PUGET SOUND NAVSHPYD / CODE 106.33, BREMERTON, WA; CODE 134.6, BREMERTON, WA;

CODE 245, BREMERTON, WA; CODE 248.313, BREMERTON, WA

PWC/ CODE 400, WASHINGTON, DC

US GEOLOGICAL SURVEY / J BALES, RALEIGH, NC

USAMC / AMCLG-MJ (BARTON), ALEXANDRIA, VA; AMCLG-MJ (DELL-OMO), ALEXANDRIA, VA

USCG / WASHINGTON, DC; G-EAE-391, BELTSVILLE, MD; G-ECV-4B, WASHINGTON, DC