

# A Review of Acid Copper Plating Bath Life Extension & Copper Recovery From Acid Copper Baths

by D. Bless

**Large quantities of hazardous waste, most in aqueous solution or sludges, are being produced at numerous metal plating and processing facilities in the U.S. Regulatory pressures, future liability and limited landfill space have driven the cost of metal waste disposal to levels where it is becoming nonviable. For metal finishing operations to remain competitive and in compliance with environmental requirements, companies must focus their efforts on pollution prevention to reduce waste generation and disposal costs, limit liability and restore maximum profits.**

By applying the pollution prevention concept, metal finishers can reduce the generation of metal bearing wastes at the source.<sup>1</sup> When waste cannot be reduced in the process, the preferred alternative is the recovery/recycling of metals and the maintenance of process solutions used in the metal finishing and primary metals industries. Even though many innovative technologies exist, there is a need to develop and improve sorption-based separation technologies to reduce the discharge of chemicals and minimize the need for wastewater treatment. In 1995, EPA established a Common Sense Initiative (CSI) Subcommittee for the metal finishing industry. The Subcommittee developed a consensus package of cleaner, cheaper and smarter policy actions for the industry as a whole to test innovative ideas and approaches. For this reason, metals recovery/recycle is an important aspect to consider when the risk to human health and ecological consequences are involved. To maximize pollution prevention: (1) water use must be minimized, (2) metals must be source-reduced or recycled "in-process" or (3) recovered contaminants must be removed from the process bath to extend the bath life. This literature search focuses mainly on copper recovery/recycle in acid copper electroplating processes.

## Copper Electroplating Solutions

Copper is one of the most common metals used in the plating industry. The main feature of copper is its high electrical conductivity. Copper is an easy metal to plate from a variety of different bath types. It is also one of the least expensive of the plating metals.

This paper focuses on acid copper baths. Acid copper baths are used throughout the plating industry because of their many advantages over cyanide baths. They cannot be used, however, to directly plate copper onto steel or zinc. If acid copper plating is preferred for these parts, a copper cyanide strike must be applied first.

There are many advantages for using acid copper over cyanide baths. Chemical cost is much lower. The baths are easier to control because their compositions are not as critical as copper cyanide baths, and effluent control is simpler. They have a high conductivity, so bath voltage is low. Anode and cathode polarizations are also low, but their efficiencies are high. Finally their use will reduce cyanide usage, which results in lower treatment and environmental compliance costs.<sup>2</sup>

There are three main types of acid copper baths: the copper sulfate bath, the copper fluoborate bath, and the bright acid copper bath (with organic additives). The typical uses for acid sulfate are: printed wiring boards, undercoat for nickel + chromium plate, printing rolls, electroforming, and plating on plastics.<sup>2</sup>

## Impurities

The copper sulfate electrolyte has good tolerance towards many ionic impurities because of its high acid concentration. For instance, metals such as nickel, cobalt, zinc and iron will tend to build up in solution rather than being plated out with copper. The effects of impurities on the appearance of bright copper deposits are summarized in Table 1.

## Source Reduction

According to the hierarchy of preferred approaches to waste management established by the Pollution Prevention Act of 1990, source reduction options should be investigated first, followed by sound recycling, treatment and disposal. Before turning to methods to recover metals from wastewater, metal finishers should examine processes and operations for opportunities to reduce the generation of waste at the source. Source reduction techniques for metal finishers include:<sup>1</sup>

1. Modifying rack designs to minimize cupping. Fluid will flow together and off the part by the quickest route.
2. Adjusting automatic hoist parameters to include extended drip times. Slow down to allow drain time above tanks to reduce drag-out.
3. Using two-stage and three-stage counterflow rinses.
4. Using stagnant baths for recovery of drag-out from bright nickel baths.
5. Slowing down, reducing the speed of parts removal.
6. Regularly monitoring bath chemistry.
7. Restricting water flow. Simple in-line flow restrictors can limit the water flow rate.

8. Placing a drain board over the lips of two adjacent tanks to catch drag-out.
9. Agitating by manually moving the part, with a mechanical agitator, or with forced air or solution in an immersion tank.
10. Using fogging/spray/air knives. After a part is removed from a bath, these devices can force some of the drag-out off the part and back into the bath.

The point to be stressed here is that drag-out recovery is one of the most important source reduction practices.

### Common Recovery Technologies

The National Center for Manufacturing Sciences (NCMS) sponsored a project in cooperation with the National Association of Metal Finishers (NAMF) to assess pollution prevention and control technology available to the plating industry. The results of the Users Survey show which treatment, recovery and bath maintenance technologies have been most successful for copper plating processes. Various technologies are used by plating shops to separate plating chemicals from rinsewaters and air emissions or to concentrate them, thereby making them available for reuse/recycle.<sup>4</sup>

Table 2 presents a summary of the technologies for copper identified during the Users Survey and the average success rating given by respondents. Technology success was measured by respondents on a scale of 1 to 5, with 1 being the least successful and 5 being the most successful.<sup>4</sup>

### Current & Competing Technologies

The following is a discussion of the technologies identified by the Users Survey which are applicable to bright acid sulfate copper electroplating processes. The applications, restrictions, capital and operating costs will be the main focus of the discussion.

Various technologies are used by copper platers to separate plating chemicals from rinsewaters as well as to concentrate them, thereby making them available for reuse/recycle. The most commonly used recovery and reuse technologies for bright acid sulfate copper plating are electrowinning, atmospheric/vacuum evaporation, and reverse osmosis.<sup>2</sup>

### Electrowinning

Electrowinning is especially efficient in recovering saleable copper scrap from spent solutions and drag-out tanks, as copper is a noble metal that is easily plated from even dilute solutions. Recovery of metals from dilute plating wastewaters by electrowinning is limited by low current efficiency, resulting in high power consumption and unacceptably high effluent concentrate.<sup>2</sup>

The combination of ion exchange and electrowinning potentially has a much higher metal recovery efficiency than just pure electrowinning from a drag-out (still) rinse. The ion exchange unit concentrates the metal into a regenerant stream and the electrowinning unit removes the metal.<sup>4</sup>

Literature indicates that the metals that are most commonly recovered by electrolytic treatment are gold, silver, copper, cadmium and zinc. Metals that have more positive standard electrode potentials plate more easily than the ones with less positive potentials. Although copper has a lower electromotive series than precious metals and it received only moderate levels of satisfaction, this is not to say that this application cannot be successfully performed. Acid copper is included in the group I metals and has a high potential for successful application in electrowinning.

This technology is not labor-intensive nor expensive to run. The capacity requirement for conventional electrowinning depends most heavily on the amount of metal to be recovered and the rate of metal deposition. Factors that affect metal deposition are: electrode type and area, agitation rate (or in general, mass transfer), solution chemistry, electrical variables and temperature. Capital costs can be estimated once capacity requirements are determined. Most vendors refer to capacity in terms of amperage; more precisely, the maximum amperage setting on a unit's rectifier. The rectifier and electrodes comprise the majority of the cost from most units. Other contributing components are the fluid containment tank, pumps, filters and optional metering devices.

Operating costs components are labor, electrode replacement, maintenance and energy, such as in the example shown in Table 3. In the table, data are given for the batch treatment of copper-containing spent process and dragout solution, including acid copper sulfate and potassium persulfate. Labor costs are largely installation- and application-specific. Energy costs will comprise only a small percentage of total operating costs for most applications. For large units, however, energy costs may be more significant in relation to total operating costs. Electrode replacement costs depend on their construction and life expectancy.<sup>4</sup>

**Table 1**  
**Effect of Inorganic Impurities in Acid Copper Plating Baths<sup>3</sup>**

Impurity Element	Effect	Max. Conc., ppm
Al	Dullness	50
Sb	Brittleness	20 - 100
Ca	Roughness	Variable
Fe	Slow plating	22,500
Fe*	Haze	50
Sn*	Rough, dark	60
Zn	Slow plating	22,500
Cr(VI)	Low brightness	100 - 1,000
	Poor adhesion	

*\*High-throw formulation*

**Table 2**  
**Distribution & Ratings of Chemical Recovery Technologies**

Process name	Recovery Technologies			
	EW	ATM EV	VAC EV	RO
Copper electroplating	3.0 (14)	3.7 (3)	4.0 (1)	2.0 (1)

*Technology Key: ED = electrodialysis, EW = electrowinning, ATM EV = atmospheric evaporation, VAC EV = vacuum evaporation, IX = ion exchange, ME = meshpad mist eliminator, RO = reverse osmosis. Number of applications from the Users Survey is shown in parenthesis. NA = no application. ND = no data.*

## Reverse Osmosis

Reverse osmosis is generally applicable for acidic solutions, but has severe limitations in alkaline solution applications. Reverse osmosis (RO) is a separation process that has been employed in the metal finishing industry to purify raw water (city water) before its use as rinsewater, recover plating chemicals from rinsewater and polish wastewater treatment effluents (usually for reuse as rinsewater).<sup>2</sup>

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

$$\% \text{ Rejection} = \frac{(\text{feed concentration} - \text{permeate concentration})}{\text{feed concentration}} \times 100\%$$

Higher percent rejections will result in better quality (*i.e.*, higher purity) permeate and a higher concentration of the plating chemicals. The permeate is typically reused for rinsing and the concentrated chemicals are typically returned to the bath. There are insufficient data available to account for the various parameters that impact RO system sizing and cost. Therefore, at this time, capital costs are described in terms of feed stream rate.<sup>4</sup>

The most significant operating costs include labor, energy, chemicals (cleaning) and membrane replacement.<sup>4</sup>

## Atmospheric/Vacuum Evaporators

Atmospheric/vacuum evaporation is generally applicable and recovers plating solution, which can be re-used. Vacuum evaporators are currently used less frequently than atmospheric evaporators. This is primarily due to the fact that the average vacuum evaporation unit costs approximately ten times more than the average atmospheric unit. Also, the vacuum units have more sophisticated and expensive operational and maintenance requirements. This is not to mention the key attributes of atmospheric evaporators, which include: (1) low capital cost, (2) simple operation/low maintenance, (3) very high recovery rates (usually 90% to nearly 100%), (4) no additional reagents needed and (5) generation of little or no sludges (when used in recovery application). Atmospheric/vacuum evaporation is not beneficial for acid sulfate plating, as the process builds up in copper content because of higher anode versus cathode current efficiency.<sup>2</sup>

The basic equipment cost for atmospheric evaporators is relatively low. The most common installation cost is for exhausting the air exiting the evaporator. Other installation work includes connecting power and water to the evaporator, rearranging of other equipment or tanks, installation of controls and installation of a transfer tank. Auxiliary equipment may include, for example, a transfer tank, additional recovery rinse tanks, an additional heat exchanger or a deionized (DI) water system.

The major operating costs for atmospheric evaporators include operating and maintenance labor and energy. From the Users Survey, the average operating and maintenance labor is 157 hr/yr. It was assumed that this level of labor is adequate for a unit evaporating 15 gph, 24 hr/day for 260 days/yr. The energy cost accounts for replacement heat in the process tank and for operating a pump.<sup>4</sup>

For vacuum evaporators, equipment costs will vary, depending on the materials of construction. The more popular materials include titanium, tantalum, borosilicate glass,

stainless steel and carbon steel. When selecting a vacuum evaporator, the plater should make every effort to reduce the flow rate of the feed stream by employing pollution prevention measures since the technology is capital intensive.<sup>4</sup>

The primary operating costs for vacuum evaporators are labor, energy and cooling water. Higher operating and maintenance costs can be expected for end-of-pipe applications because the solutions are evaporated to higher solids levels that increase fouling and scaling.<sup>4</sup>

## Ion Exchange

The Users Survey data indicate that there are no ion exchange applications for acid copper plating. On the other hand, the Vendors Survey data include six responses to using ion exchange for acid copper plating. Therefore, the Users Survey is not inclusive of all the available alternatives.<sup>4</sup>

Copper plating from copper sulfate solutions is a primary and integral process in the manufacture of printed circuit media. These copper electroplating operations involve the generation of copper contaminated rinsewaters that usually cannot be discharged without undergoing some form of treatment. The preponderance of copper as the contaminating metal allows shops to take advantage of the powerful ion exchange/electrowinning combination. Together, these two technologies combine to separate, concentrate and recover copper from rinse streams. Ion exchange offers shops the ability to close-loop some rinses and reduce the need for downstream treatment.<sup>5</sup> Carboxylic acid resins show highest capacities for copper removal.

Generally, ion exchange is limited to dilute rinsewater streams, although scavenging resins can be used to treat more concentrated wastes under certain circumstances. As concentrations increase, ion exchange becomes impractical due to the increasing frequency of regenerations and the declining difference between the concentration of the regenerant which is a constant (typically 5-10 g/L) and the concentration of the stream being treated.<sup>5</sup>

When the sole objective of using ion exchange is to remove metal from a waste stream, a metal scavenging resin is used. This system uses only one type of ion exchange resin, either selective anion or cation, depending on the charge of metal or metal complex being targeted for removal (*e.g.*, a cation-type resin is used for most copper removal applications). Because this system does not have both cation and anion resins, the rinsewater will not be fully "deionized" and cannot be reused as rinsewater for common rinsing purposes.<sup>5</sup>

Deionization is used when the objective is to recover metal and recycle rinsewater (*i.e.*, closed-loop). The configuration uses a combination of cation and anion exchange columns in series to remove all ions from the rinsewater. A good candidate for deionization is the electroplating copper rinse system. With this application, rinsewater containing copper is sent to the cation and anion exchange columns and deionized water is returned as fresh rinsewater to the rinse system. The anion regenerant, usually NaOH, can usually be pH-treated and discharged. The cation regenerant stream is interesting because of its similarity to the plating bath make-up: sulfuric acid and copper sulfate. While it is possible to return the regenerant to the plating bath, thereby closing the loop for most of the process, this is generally not done for two important reasons: (1) the performance of the printed wiring board (PWB) through-hole plating in various stress tests is quite sensitive to small variations in bath chemistry making additions of regenerant inadvisable and (2) the copper sulfate plating bath is operated at too low a temperature to create

sufficient evaporative headroom for the regenerant additions. The regenerant is an ideal electrowinning candidate and this is the most common treatment option.<sup>5</sup>

Drag-out recovery tanks are used in conjunction with ion exchange systems whenever feasible to reduce the load on the ion exchange system. In operation, the drag-out tanks return the bulk of the plating chemicals directly to the plating bath and an ion exchange unit connected to a subsequent flowing rinse captures only the residual chemicals. The needed size of the ion exchange unit and its regeneration frequency are therefore reduced.<sup>5</sup>

Table 4 provides some general guidelines on the type and capacity of resin used for acid copper electroplating, the chemicals used for regeneration and the method of recovery.<sup>4</sup>

The installed costs are estimated based on the projected costs for electrical and piping, including two components of electrical costs (service module and regeneration station) and three components of the piping costs (service module, regeneration module and service/regeneration module interface). For small, manual applications, capacity is usually expressed in terms of resin volume, to which capital costs are directly related. Larger system capacities are more often expressed in terms of flow rate, but direct vendor-to-vendor pricing comparisons based only on capacity units such as gallons-per-minute can be quite misleading. The Users Survey did not account for several cost factors including the amount of customization, the precise level of automation, the type and quality of metering and monitoring instrumentation and the general design strategies and criteria pursued by the manufacturer. Manual systems are often sized to provide an acceptable service period. Larger columns offer the benefit of fewer regenerations or replacements, less downtime and less labor expense. Automatic systems, on the other hand, are sized to handle the expected flow rate. Water recycling systems are, in general, more expensive than metal-scavenging units. Installation expenses are site-specific but can be significantly typically 5 to 40 percent or more of basic equipment costs.<sup>4</sup>

Labor, regeneration chemistry, resin replacement and energy are the major operating cost categories. Labor costs are significantly affected by the automation level of the system and automation capital costs are often quickly returned. Undersized or misapplied equipment can greatly impact

**Table 3**  
**An Example of Calculating Operating Costs**  
**For an Electrowinning Application**

<b>Capital Costs</b>	
Cost of Unit	\$22,000.00
<u>Installation</u>	<u>\$5,100.00</u>
<b>Total</b>	<b>\$27,100.00</b>
<b>Operating Costs/Year</b>	
Energy	\$450.00
Labor	\$3,900.00
Cathodes	\$895.00
Anodes	\$1,650.00
Parts	\$300.00
Chemistry	\$750.00
<u>Scrap metal value</u>	<u>(\$643.00)</u>
<b>Total</b>	<b>\$7,302.00</b>
<b>Savings/Year</b>	
Waste treatment savings	\$2,700.00
Metal recovered	1,702 lb.

labor and costs. Resin life is usually measured in years, but can be shortened by misuse and improper application. Resin fouling, mentioned by several respondents, is usually a result of marginal application, misuse or insufficient upstream filtration or pretreatment.<sup>4</sup>

The operating costs estimates are based on the following assumptions:<sup>4</sup>

**Feed Characteristics (rinsewater)/Resin Capacity**

- Copper sulfate plating process generating rinsewater containing 50 mg/L Cu<sup>++</sup>.
- Resin capacity of 38 equivalents of Cu<sup>++</sup>/ft<sup>3</sup> (12,900 gal between generations for a 2 ft<sup>3</sup> column).
- Assume two anion regenerations for each cation regeneration (1.79 days between regenerations for 2 ft<sup>3</sup> column).

**Energy**

- 1 hp-hr/300 gal
- \$10/kW-hr (\$0.25/1,000 gal)

**Table 4**  
**Resin Guidelines for Acid Copper Plating**

Plating Solution	Resin Type	Capacity, lb. metal/ft <sup>3</sup>	Regenerant	Typical Recovery Method(s)
Acid copper	Strong acid cation	2.0	H <sub>2</sub> SO <sub>4</sub> or HCl	Electrowinning

**Table 5**  
**Users Survey Data Addressing Common Solution Maintenance Techniques<sup>4</sup>**

Process Name	Total Number of Processes	Batch Carbon Treatment	Cont. Carbon Treatment	Dummy Plating	Carbonate Freeze	In-Tank Filtration	External Filtration	High pH	Precipitation
Copper Fluoborate	3	0	1	1	0	1	0	0	0
Copper Sulfate	61	16	10	10	0	27	17	0	0

### Regeneration Chemicals

- Assume four-bed volumes for concurrent (Vendor 1—Modular) and two-bed volumes for counterflow (all others).
- H<sub>2</sub>SO<sub>4</sub> (Modular 1): 12 gal (conc.) @ \$2/gal per 12,900 gal flow (\$1.9/1,000 gal)
- NaOH (Modular 1): 24 gal (conc.) @ \$2/gal per 12,900 gal flow (\$3.8/1,000 gal)

### Resin Replacement

- Assume five-year life with 3% mechanical loss per year.
- Cation: \$200/ft<sup>3</sup> (\$0.03/1,000 gal)
- Anion: \$400/ft<sup>3</sup> (\$0.06/1,000 gal)

### Labor

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

The total costs, in \$/lb. Cu, are: \$20.96 for Modular 1, \$13.00 for Modular 2, \$20.96 for semi-automatic labor and \$17.73 for automatic labor. The total cost includes the assumption of feed characteristics given above along with the energy costs, regeneration chemicals costs, resin replacement costs and labor costs.

### Bath Life Extension

Chemical solution maintenance includes a range of pollution prevention practices and technologies that preserve or restore the operating integrity of metal finishing process solutions, thereby extending their useful lives. Because of rising costs for chemicals, energy and treatment/disposal and increasingly more stringent environmental requirements, solution maintenance has become a greater priority to plating shops. In addition to extending bath lives, solution maintenance often improves the average operating efficiency and effectiveness of a process solution and therefore has a positive impact on production rates and finish quality.<sup>4</sup>

Table 5 shows results from the Users Survey addressing commonly used solution maintenance methods. Some common preventative and corrective measures include but are not limited to:

- Promptly removing all dropped parts.
- Taking special care to prevent introducing contaminants from cleaners or from poorly maintained racks.
- Where metallic contamination is a chronic problem, such as with small zinc castings, using a continuous electrolytic purification, or “dummying,” cell.

### U.S. EPA Effluent Limitations Guidelines, Pretreatment Standards, & New Source Performance Standards: Metal Products & Machinery

The latest Code of Federal Regulations are Part 433, 413 and they are from the early 1980s. The new Guidelines were to be out for review in the year 2000 and finally out in the year 2003. The guidelines are based on chemical precipitation and in some in-process practices such as counter-current rinses. According to a representative from the U.S. EPA, ion exchange is being used more for recovering precious metals such as gold and silver, although some semi-conductor industries are using ion exchange for high quality copper.

Also, electrolysis is being used more often than ion exchange for metals (non-precious). The standards for copper are 1.3 mg/L/day total and a monthly average of 0.60.

### Concluding Remarks

Overall, the most efficient pollution prevention measures for electroplating copper rinsewater are accomplished through a recycling system which employs a combination of previously implemented source reduction practices (i.e., dragout recovery, two- or three-stage counterflow rinses) along with a configuration of two or more bath treatment technologies. The figure shows a plating tank followed by three counterflow rinse tanks for drag-out recovery. A filter follows the third rinse tank where the solution is fed to an ion exchange unit. There are two treatment units in the square indicating the option of using either one. Electrowinning recovers the metal from the regenerant and sends it to a recycling plant. The other option uses an atmospheric evaporator to concentrate the dilute solution which is fed back to the plating bath.

### References

1. G.C. Cushnie Jr., *Source Reduction and Metal Recovery Techniques for Metal Finishers*, State of Ohio Environmental Protection Agency, 1994.
2. A. Yazdani & F. Altmayer, *AESF/EPA Pollution Prevention for Copper Plating Processes: P2 Concepts & Practices for Metal Plating & Finishing*, AESF, Orlando, FL, 1997.
3. AESF Educational Course, *Training Course: Electroplating and Surface Finishing*, Volume I, AESF, Orlando, FL, 2000.
4. G.C. Cushnie Jr., *Pollution Prevention and Control Technology for Plating Operations*, National Center for Manufacturing Sciences, 1994.
5. EPA Handbook, *Guides to Pollution Prevention The Metal Finishing Industry*, EPA/625/R-92/011, October 1992.
6. S. Geil, U.S. EPA, personal communication

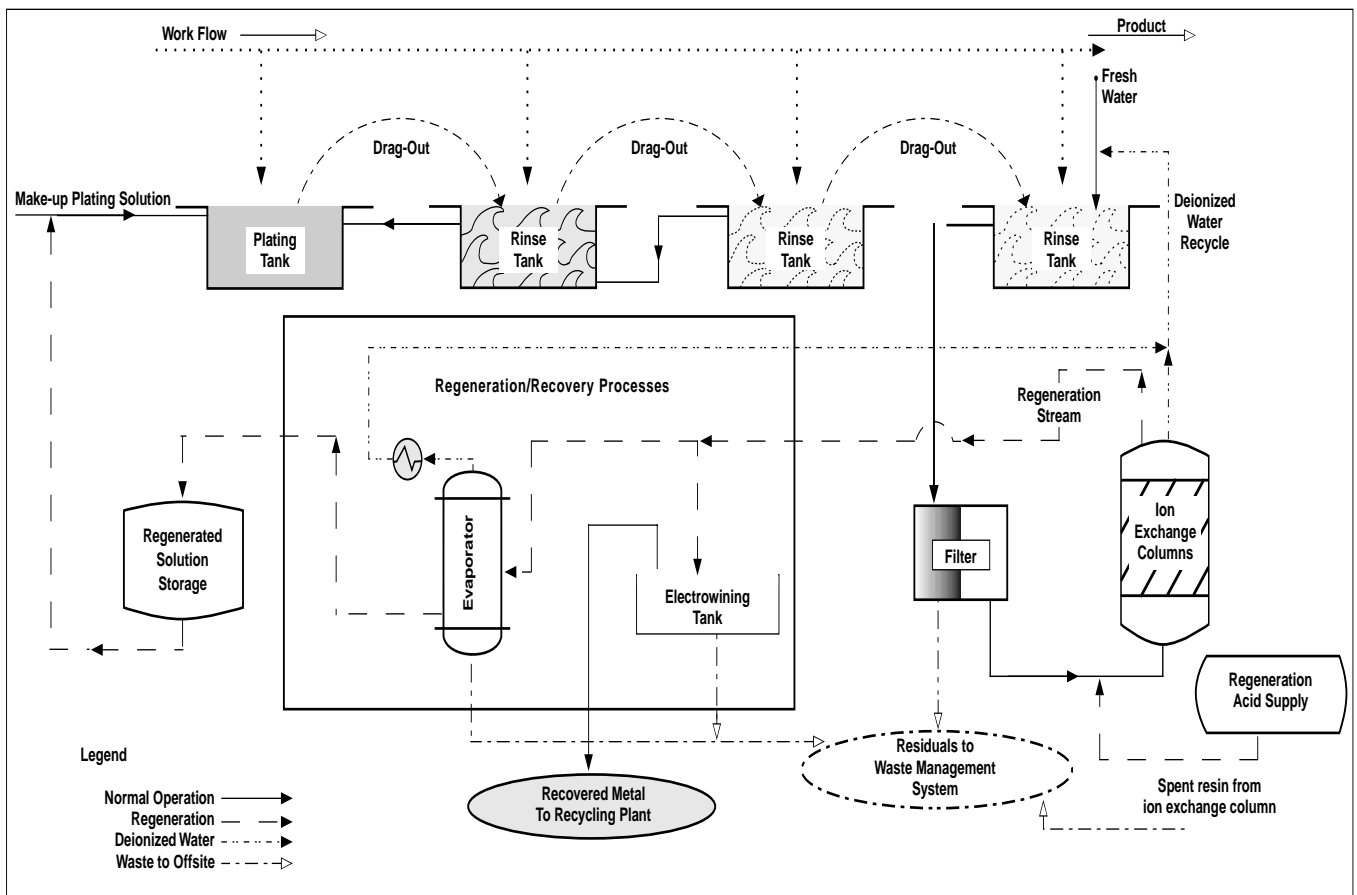
### Bibliography

- F.A. Steward & C.G. Ritzert, *Waste Minimization and Recovery Technologies*.  
EPA, *Effluent Limitations, Guidelines, Pretreatment Standards, and New Source Performance Standards: Metal Products and Machinery*, 1998.  
A.E. Olsen, *Bright Acid Sulfate Copper Plating*, AESF, Orlando, FL, 1986.  
Printed Wire Board Resource Center, *Ion Exchange*, <http://207.207.205.214/bmr/ix.htm> (April 13, 1998).

### About the Author

Diana Bless is a staff member of the National Risk Management Research Laboratory, 26 W. Martin Luther King Dr., Cincinnati, OH 45268. She has conducted research for the prevention and clean-up of toxic/hazardous waste. Her research interests focus on low-cost technologies for metals recovery/recycling in metal finishing, biological removal of metals in mine drainage and the ecological/health impacts of mercury and arsenic contamination in abandoned mines. She holds a BS in chemical engineering with a minor in biochemical engineering from New Mexico State University.





Schematic diagram of a regeneration/recovery system implementing source reduction practices.