Strategies at a Decorative Chromium Electroplating Facility: On-line vs. Off-line Recycling

By James P. Lamancusa, P.E., CEF

The regulatory, as well as moral, obligations to prevent pollution, coupled with the desire to minimize long-term environmental liabilities, present electroplaters with a dichotomy of waste minimization and recycling decisions. Economic and technical restraints, however, usually prohibit recycling all residue materials generated from plating and wastewater treatment processes. Because there will always be a certain quantity of residuals generated in electroplating—hopefully smaller amounts as time goes on—it is more desirable from a long-term environmental standpoint to ship wastewater treatment sludge (EPA waste F006) to off-site recycling facilities, rather than to treatment/disposal (landfill) facilities. To conserve valuable natural resources (chemicals, metals, etc.) it is also important to maximize on-line recycling efforts whenever possible. To avoid creating a wastewater treatment sludge that is not marketable for metal reclamation, a careful balance must be maintained between various on-site and off-site recycling activities. The ratio and concentration of metals and contaminants in the sludge must be of a composition acceptable to the off-site recycler. Ideally, on-line recycling should be implemented so that the maximum volume of sludge is reduced, and any remaining sludge recycled, rather than sent to a landfill.

This article is an edited version of a paper presented at the 16th AESF/EPA Pollution Prevention and Control Conference, February 13–15, 1995, and discusses on-site vs. off-site recycling strategies at a plastic parts chromium electroplating facility.

An electroplater is faced with many process and wastewater treatment decisions. Questions repeatedly facing process and environmental managers regarding changes are:

- How will this change affect the wastewater treatment process?
- Will it adversely affect the recyclability of residues generated either on-line or off-line?
- Will this on-line recycling process result in a buildup of contaminants in the plating tanks, which may adversely affect product quality?
- Will this change increase the potential of long- and short-term environmental liabilities?

In making such decisions, it must be remembered that manufacturing needs to produce high-quality parts at a competitive price. An electroplater, therefore, has a balancing act to perform. For an electroplating facility to survive in the marketplace for the long term, it must efficiently and consistently produce high-quality parts for its customers, while doing a conscientious job of preventing pollution, minimizing waste and reducing environmental liabilities. An overall balance must be maintained between on-line recycling, process contaminant control (*i.e.*, buildup due to recycling), wastewater treatment and off-site recycling of residuals.

An electroplater's ultimate goal is to achieve zero discharge of pollutants to all three environmental media (air, water, and land). In striving to reach this goal, electroplaters must recycle, both on-site and off-site, to the highest degree possible whenever it is technically and economically feasible. Zero discharge is a very admirable goal, but is also somewhat idealistic, and perhaps should be viewed as a general direction or trend, rather than as an achievable goal.

Table 1
Municipal Water & Sewer Costs

	1,000 Gals	Cost/ 1,000 Gal	Annual
Water	50,274	$1.87	$ 94,012
Waste	50,274	$1.23	$ 61,837
Totals	N/A	$3.10	$155,849

If zero discharge is to become a nationwide, enforceable standard, a careful examination should be made of the unique circumstances present at each facility. It should be determined if those at, or near, zero discharge are paying an exorbitant rate for water and sewer service ... or are direct dischargers that must meet stringent standards imposed by an NPDES permit ... or are manufacturing parts where quality and process contaminant control is not that critical.

Plastic Recovery

Lacks Enterprises is a plastic chromium electroplating facility in Grand Rapids, MI, that produces decorative-chromium-plated exterior trim components for the automotive industry. Parts produced must have a high-quality, corrosion-resistant finish meeting very stringent customer specifications. The principal manufacturing materials used in this process include thermoplastics (the substrate), water, acids, alkalis, and metals. Metals consist of copper, nickel, hexavalent chromium, and a tin/palladium complex used as a catalyst.

Lacks ships its chromium-plated scrap plastic parts to a local recycler, who in turn grinds the scrap parts prior to shipment to an off-site recycler. The recycled plastic material generated from this process is then used to manufacture products suitable for this lower grade of plastic (*e.g.*, plastic buckets). Sometime in 1995, this same local recycler will begin a trial operation at its facility of equipment designed to separate the plastic and the metal plating. This separation process is expected to produce a purer grade of recycled plastic that will have more uses, and consequently greater value.

Water Recovery & Reuse

Annual water usage and wastewater quantities for the Lacks-Airlane Plant are given in Table 1, along with the associated costs of these services.

Lacks began considering the feasibility of purifying rinsewaters and wastewater effluent to close-loop the system, so that this water could be reused as supply water. The payback for the purification equipment, however, was excessive (simple payback > five yr). At an operation schedule of 250 days/yr, a 200,000 gal/day water purification system would be needed at this facility. Equipment generally includes, among other things, membrane filtration, ion exchange, and reverse osmosis. The capital cost of a such a system would be in excess of one million dollars.

Given the cost of water and sewer service in the Grand Rapids, MI area, it is not cost-effective to purify and reuse all of the water from the plating operation based solely on water and sewer savings. It may, however, make economic sense to do so if an on-line recovery system is recovering plating solutions and valuable metals that can be either reused on-line or shipped off-site to a recycler. An example of this would be an on-line system designed to recover chromic acid etch and/or chromium plating solutions from rinsewaters, using ion exchange and/or electrodialysis.

Other than the closed-looped final de-ionized (DI) rinses following the chromium electroplating process, Lacks does not purify its rinsewater and wastewater for in-process reuse at this time; it does, however, take measures to conserve water, such as:

- Multiple tank counter flow rinsing
- Water rinse sprays (on-demand/ activated for each bar-load)
- Flow restrictors
- Reuse of contaminated rinsewaters, where feasible (scrubber feedwater, intermediate strip tank rinsewater, etc.)
- Use of dry shuttle tanks between pre-plate and electroplating lines.

The plant is in the process of installing water sprays on a majority of the flowing rinse tanks. One tank, using a combination of parts-submergence and water sprays, is equivalent to 1.5–2.0 rinse tanks that use parts-submergence only. This method of rinsing consequently uses less tanks and less water to achieve an equal amount of rinsing.

Recovery & Reuse Of Acids & Alkalis

Unless there is an on-line bath recovery system (*e.g.*, chromium evaporative recovery), most of the acids and alkalis used in electroplating of plastics are lost through drag-out and end up in the wastewater treatment system where it is neutralized. Nitric acid is used to strip copper and nickel from racks at the end of the line. The nitric stripping solution periodically reaches a metal saturation level or becomes diluted with drag-in and must be replenished with fresh acid. Approximately one-third of the nitric strip solution is lost because of bail-out (decant), with the remainder lost through drag-out.

There is no recoverable material (*i.e.*, no bail-out) for the caustic soda chromium stripping solution. Because it is the first step in the rack stripping process, the racks enter this tank dry (no drag-in). Caustic soda and water are added to this tank as needed, to replace solution lost through drag-out. Because of drag-out and the small amount of chromium being stripped, this solution never reaches a point of metal saturation. Decanting the chromium strip tank and replenishing it with fresh caustic, therefore, is not necessary because the strip solution does not become diluted with drag-in, and chromium never reaches a high enough level to significantly reduce the effective stripping capabilities of the bath.

The question then could be asked: Why not recover the nitric acid and the proprietary stripping chemical from the strip bail-out solution by using electrodialysis, electrowinning or some other recovery method? Table 2 shows the annual costs of nitric acid and the proprietary additive associated with replenishing the nitric strip tank because of bail-out losses.

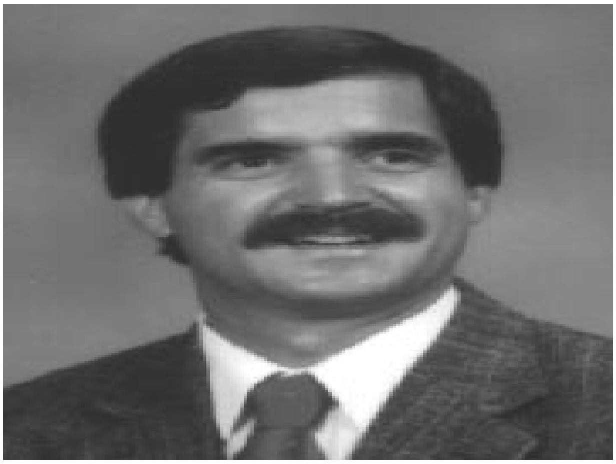
Processes being considered at Lacks for acid recovery include membrane electrodialysis and diffusion dialysis. The capital cost of electrodialysis for this application is estimated at $100,000 or more. Because of the low costs of the stripping chemicals, installing and operating electrodialysis recovery equipment for these materials cannot be economically justified. Diffusion dialysis, on the other hand, is a simpler, less costly process, and may be cost-effective, depending on the acid recovery rates.

The capital cost of a diffusion dialysis unit for this application is $35–40,000, with an estimated simple payback calculated at 1.5–2.0 years. Capital, operation and maintenance costs of a recovery unit such as this are offset not only by savings in nitric acid purchases, but also by savings in sodium hydroxide usage (used in wastewater treatment for neutralizing spent acid). The next step at Lacks will be to lease a pilot diffusion dialysis unit to evaluate nitric acid recovery rates, and also to determine if there will be incidental recovery of the proprietary stripping chemical.

Table 2
Cost of Cu/Ni Stripping Chemicals

Description	Cost for bail-out replenishment
Nitric acid (42 Be, 67.2%)	$ 8,000
Proprietary additive	$ 4,000
Total	$12,000

1994 Water & Wastewater Rate Survey*
(By Ernst & Young LLP)



*Rates given in $1,000 for 11.22 MG & 8-in. meter.

Table 3
Marketability of Sludge Materials

Good	Limited
• Nickel/Copper, w/Chromium < 2.0% • Chromium/Nickel, w/Copper < 2.0% • Copper only • Nickel only	• Chromium only • Nickel/copper, w/chromium > 5.0% • Nickel/chromium, w/copper > 5.0%

Table 4
Market Value of Dried F006 Sludge At Lacks-Airlane Plant

	Price (11/10/94)	Dry Basis Composition, %
Nickel	\$3.35/lb	12–20
Copper	\$1.20/lb	10–15
Chromium	minimal value	10–15
Palladium	\$156/troy oz	0.01–0.025
Water	N/A	10–20 (@ 105 °C)

Other measures being taken at the facility to reduce plating solution usage and losses, which in turn conserve on acids, alkalis and metals, include:

- Pre-dip tanks
- Efficient parts racking to minimize drag-out
- Design part drain holes/slots to minimize drag-out
- Wetting agents to minimize drag-out
- Using less concentrated plating baths where feasible (*e.g.*, nickel)
- Drip-off tanks
- Splash guards and drip trays
- Hoist delays

Recovery of Metals

Off-site Recyclers

On-line methods to recover metals/plating solutions at Lacks include evaporative recovery of chromic acid etch and chromium plating solutions. Since the late 1980s, the company has thermally dried the metal hydroxide sludge generated in the wastewater treatment process (EPA waste F006) and has shipped this granular material to off-site recycling facilities. The off-site facilities used were interested in this material primarily because of its nickel content (the principal product produced by the metal recyclers is nickel anodes—99.99 percent pure). One of the off-site facilities gives metal credits not only for nickel, but also for the copper and palladium.

Another off-site recycling facility gives credit for nickel and copper only. Most facilities of this type charge secondary material suppliers a process or treatment fee, as well as various surcharges for excess water content and impurities in excess of a specified concentration (see Tables 3–5).

Credits for metals present in this sludge are then deducted from the process/treatment charges, resulting in either a net charge or a net credit to the material supplier. One of the recyclers previously used had been imposing strict limits for chromium and tin. The tin was eliminated from the sludge by simply diverting the catalyst rinsewater (tin/palladium complex) around the wastewater treatment plant, and discharging it directly to the final effluent tank. The final pH was then adjusted prior to discharge to the Grand Rapids municipal sewer system. The tin and palladium contained in the catalyst are not regulated by the city of Grand Rapids or by the EPA, and neither metal poses a problem to the treatment process at the publicly owned treatment works (POTW). The downside of this is that palladium, a precious metal with a market price of \$100+/troy oz, was being washed down the sewer, and consequently no palladium credits were given.

This was very unfortunate, because the concentration of palladium in the catalyst rinsewater is only 1.0 to 1.5 ppm, which at such a low level is not practical to recover using on-line recovery equipment. If it were technically and economically feasible to recover the palladium on-line, there are off-site domestic and foreign precious metal refineries that are more than willing to accept this material based on a “process charge/metal credit” formula.

The nickel recycler imposing the stringent tin and chromium limits has since relaxed these requirements, making it possible once again to discharge the catalyst rinsewater to the wastewater treatment system, and receive credits for the palladium content of the sludge.

With the exception of stainless steel manufacturers, most off-site recyclers are not interested in receiving scrap trivalent chromium metal; therefore, credits for the chromium present in the sludge are generally not given. In addition, some off-site recycling facilities will not accept secondary materials if the chromium is greater than 5.0 percent, and others restrict chromium to a maximum of 1.0–2.0 percent. Facilities that will accept dried sludge containing chromium and nickel usually do not want copper present, or otherwise restrict it to a maximum allowable concentration of 1.0–2.0 percent. Most off-site recyclers that will accept dried F006 sludge generated at Lacks are only interested if the nickel content is greater than 10 percent.

On-Line Recycling Options

Because selling the dried metal hydroxide sludge had been so successful, and because long-term environmental liabilities made landfilling this waste unacceptable, it was decided that additional on-line recycling equipment would not be installed unless it would improve—and not compromise—the company’s current situation. It was therefore necessary that the on-line recovery methods adopted achieve the following objectives:

- Reduce the overall quantity of F006 sludge generated
- Make the composition of the F006 sludge more suitable to potential buyers, and therefore more valuable/marketable
- Recover pure metal or process solutions on-line to allow reuse of these materials in-process where feasible, or to allow selling these purer-grade materials to off-site recyclers.

With these objectives in mind, the company decided to investigate methods to recover copper from the acid copper rinsewaters, as well as secondary methods of recovering chromic acid from the etch and chromium plating rinsewaters.

Lacks currently has on-line recycling equipment to recover etch and chromium plating solutions. This equipment, which could be catego-

Table 5
Typical Recycler Requirements for Metal Hydroxide Sludge

Domestic

Recycler A	**Recycler B**	**Recycler C** ***(accepted as Ni/Cr Sludge)***
Moisture < 5.0% Nickel > 12% Copper > 12% Volatile Organic Carbon < 1,000 mg/l Mercury, arsenic, thallium, titanium, and/or bariu: all < 10 mg/l each	Silica: Surcharge above 10% Copper: Surcharge above 5% Phosphorous: 0.15% max.; Surcharge above 0.05%	Nickel > 10% Copper < 0.6% Cobalt < 0.6% Phosphorous < 0.03% Chromium < 15% Silica < 5% Water < 35% Tin < 0.02% Sulfur < 5% Lead < 1% Arsenic, bismuth, antimony, selenium: all < 0.% each

Foreign

Recycler I	**Recycler II**	**Recycler III**	**Recycler IV**	**Recycler V** ***(rec'd as copper sludge)***
Nickel > 10% Copper: no req. Chromium < 1.4% Zinc, Lead, Arsenic: all < 1.0% ea. Cadmium: nondetectable	Ni > 10% Copper: Ni/Cu Ratio > 15/1 Chromium < 5.0% Zinc, Lead, Arsenic: all < 1.0% Cadmium: nondetectable	Iron 5.0% max; surcharge above nondetectable Chromium: 20% max; charge above 14% Tin: 1.0% max; surcharge above 0.50% Moisture: 65% max; surcharge above 35% Manganese: 0.20% max; surcharge above nondetec. Lead: 0.20% max.; surcharge above nondet. Arsenic: 0.10 % max.; surcharge above nondet. Zinc: 1.0 % max.; surcharge above nondetectable Copper: credit given Palladium: credit given	Surcharge assessed for less than full load;< 20 short tons (40,000 lbs) Nickel: 10% min; Surcharge below 11% LOI: 30% max. (loss on ignition @1000 °F) Chlorine: 0.6% max. Fluorine: 0.20% max. Chromium: no req. Copper: credit given	Water < 35% Heavy Metals < 0.05% ea. Zinc < 0.5% Chromium < 0.5% Nickel < 1% Mercury < 20 ppm Fluorine < 100 ppm Toxic Organics < 400 ppm Heating Value < 5000 Btu/lb

rized as primary chromium recovery equipment, is a vacuum-type evaporative recovery system. Vacuum and atmospheric evaporative recovery technology applied for the recovery of chromium solutions has been used by many hard and decorative chromium electroplaters throughout the U.S. for many years. If applied properly, evaporative equipment is capable of recovering 90+ percent of the chromium present in the chromic acid etch and chromium plating rinsewaters. These evaporators are sometimes preferred over atmospheric evaporators, because they take up less space and are more adaptable to automation.

The secondary chromium recovery system is one that should increase chromium recovery efficiency from the current level of approximately 90 percent to more than 99 percent. The two pilot systems tested during the past year have shown promising results, and it appears that one of these systems, or a combination of the two, will be technically feasible. The next question is whether the secondary chromium recovery system will be cost-effective. An ion exchange resin-bed system and a membrane electrodialysis system are being investigated.

Lacks is now field-testing an acid copper recovery (electrowinning) system, which is an electrolytic process, to determine the recovery efficiency and the expected costs of a full-scale unit. Copper recovered at the cathode of this unit will be sold to a copper scrap dealer. The company currently treats electroless copper through immersion deposition on an iron fabric material. The copper displaces the iron metal, and the iron goes into solution. Untreated iron may be discharged directly to the sewer because it is not detrimental to operation of the POTW. Neither the EPA nor the city of Grand Rapids has an effluent standard for iron. The use of this same immersion deposition process for treatment and recovery of copper from the acid copper process is also being evaluated. Segregation of the acid copper waste stream, followed by conventional chemical precipitation/sedimentation, is another method being investigated to facilitate offsite reclamation of the copper contained in the acid copper rinsewater.

Plans are to combine the copper scrap material from these two processes (*i.e.*, acid copper and electroless copper) and sell it to an off-site recycler. Shipping scrap copper residue generated from the electroless copper treatment system alone has been difficult in the past, because of the relatively small amount (less than truckload quantities) generated during the EPA-mandated 90-day accumulation period. Combining the two scrap materials—if the electrowinning process is determined to be economical and goes on-line—will make it more practical to ship copper scrap materials to an off-site recycler.

Once the concentration of chromium and/or copper is reduced in the wastewater treatment sludge, it will then be possible to examine on-line recovery methods for nickel drag-out. Just as evaporative recovery is adaptable for recovery of heated chromium plating and etch reclaim solutions, it may also be suitable for the recovery of heated nickel reclaim solutions. One problem with a nickel recovery system such as this, is the difficulty associated with the build-up of organic contaminants. This occurs because organic brightening compounds tend to break down into different organic chemicals as they are used and reused. This breakdown is caused by energy-intensive cathodic reactions and by the elevated process temperatures.

Another potential problem with recovering nickel, regardless of the recovery method used, is that more nickel may be recovered than can be utilized in the process (because of anode/cathode imbalance). It may be possible to correct this imbalance by installing insoluble anodes in place of some of the nickel anodes. (This expense would have to be added to the cost of the recovery equipment.)

Other methods of recovering nickel include reverse osmosis and ion exchange. Similar to the secondary chromium recovery system, an ion exchange system could serve as a secondary system for nickel bath recovery. Lacks plans to take a closer look at all of these options once full-scale copper electrowinning and/or secondary chromium recovery systems are installed and operating.

Summary & Conclusions

A priority system should be developed to determine which on-line recovery systems to investigate. Priorities should be based, in part, on controlling the composition of the sludge generated in the wastewater treatment process to ensure that the sludge is marketable (*i.e.*, able to be shipped to an off-site recycler). If the sludge has no value, it may have to be sent to an off-site treatment/land disposal facility, which is an unacceptable alternative because of the associated long-term environmental liabilities.

Recovery systems should be able to recover materials that can be reused in the process, or are suitable for acceptance by an off-site recycler. For the Lacks-Airlane facility, the metal hydroxide sludge was considered valuable primarily because of its nickel content. Based on concentration and market value, palladium was the second-most-valuable metal present in the sludge, followed by copper, and then chromium, which has little or no value.

Because of the low concentration of palladium present in the catalyst rinsewater, on-line recovery of palladium was not considered economically feasible. (Some off-site recyclers will give credit for the palladium content of the sludge, if the concentration is significant.)

Priorities for investigating and installing economically feasible on-line recovery equipment at the Lacks-Airlane plant include:

- Secondary recovery of chromium solutions from etch and chromium plating rinsewaters.
- Electrowinning, immersion deposition, or segregation/ chemical precipitation of copper from acid-copper rinsewaters.
- Recovery of nitric acid from stripping solutions using diffusion dialysis.
- Primary (possibly secondary) recovery of nickel plating solutions from nickel rinsewaters, depending on implementation and success of chromium and copper recovery systems proposed.

New Plant Considerations: Recommendations were made regarding the layout of a new plant, including suggestions on whether it would be advantageous to segregate any of the waste streams. Considering the market value of different forms of electroplating sludge, for example, individual piping and wastewater treatment systems could be constructed to separate different metal streams, thereby facilitating the generation of single- or dual-metal sludge materials.

Based on proposals received from a number of off-site recyclers, however, it does not appear advantageous to segregate the nickel and chromium waste streams (*i.e.*, after chromium reduction). On-line chromium recovery methods should be used to reduce the chromium content in the wastewater treatment sludge to < 5.0 percent, making the sludge more marketable. Even if the chromium content in the sludge is > 5.0 percent, it would be preferable to combine the chromium with the nickel so an off-site recycler would be more willing to accept chromium-bearing materials.

Copper has a relatively low market value compared to nickel, so there is no advantage to combining it with the nickel waste stream. In fact, for some off-site recyclers, copper is considered undesirable and troublesome to the metal reclamation process. There are good markets for copper-only waste streams, so it would be advantageous to keep those streams separate. Full truckload quantities of copper-bearing materials could then be created, including copper cathode material from electrowinning, copper residue material from treating electroless copper, and copper sludge from the separate treatment of copper wastewater (using conventional treatment methods, such as chemical precipitation/sedimentation). ❏

***Editor's Note:** The full text of this paper is available in the* Proceedings *of the 16th AESF/EPA Pollution Prevention and Control Conference. Price, excluding shipping, to AESF members is $50; $70 to non-members. Call AESF Publications Sales (1-800/334-2052) to order by credit card.*

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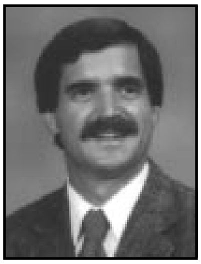

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