METAL RECOVERY AND WASTEWATER REDUCTION USING ELECTROWINNING

The Merit Partnership is a joint venture between U.S. Environmental Protection Agency (EPA) Region 9, state and local regulatory agencies, private sector industries, and community representatives. The partnership was created to promote pollution prevention (P2), identify P2 technology needs, and accelerate P2 technology transfer within various industries in southern California. One of these industries is metal finishing, which is represented in the Merit Partnership by the Metal Finishing Association of Southern California (MFASC). Together, MFASC, EPA Region 9, and the California Manufacturing Technology Center (CMTC) established the Merit Partnership P2 Project for Metal Finishers. This project involves implementing P2 techniques and technologies at metal finishing facilities in southern California and documenting and sharing results. Technical support for this project is provided by Tetra Tech EM Inc. (formerly PRC Environmental Management, Inc.). The project is funded by the Environmental Technology Initiative and EPA Region 9 and is implemented, in part, by CMTC through the National Institute of Standards and Technology.

ELECTROWINNING TECHNOLOGY DESCRIPTION

Electrowinning is an electrolytic technology used to recover metals from electroplating rinse waters. Although electrowinning has traditionally been used only for metal recovery, its application in a well designed and controlled rinse system can significantly reduce rinse water use, wastewater generation, and chemical discharge.

Figure 1. Electrowinning Rectifier and Electrolytic Cell

An electrowinning unit has three main components: (1) an electrolytic cell, (2) a rectifier, and (3) a pump. The electrolytic cell and rectifier are shown in Figure 1. An electrolytic cell is a tank in which cathodes and anodes are typically arranged in alternating order (see Figure 2). The cathodes and anodes are attached to their respective bus bars, which supply the electrical potential to the unit. The electrolytic cell may include features to improve rinse water circulation within the cell, such as a flow disperser or air spargers.

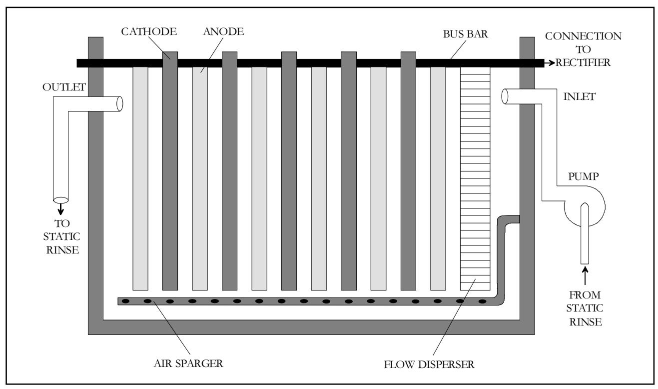

Figure 2. Cross-section of Electrowinning Unit

When an electrowinning unit is in operation, the electrical potential applied to the electrodes causes dissolved metals and other positively charged ions to migrate toward and plate onto the cathodes. As metals deposit on the cathodes, the metal buildup decreases the deposition rate. When the metal deposition rate is no longer sufficient, cathodes are removed from the electrolytic cell for on-site or off-site metal recycling. In some cases, recovered metals are pure enough to be reused in process baths. As metals are chemically reduced at the cathodes, other rinse water components are oxidized at the anodes. If cyanide is present, it is oxidized to cyanate and then to carbon dioxide and nitrogen.

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TECHNOLOGY APPLICATIONS

Electrowinning is most commonly used to recover gold, silver, copper, cadmium, and zinc. Gold and silver are the most successfully recovered metals because of their high electropotential. Chromium is the only metal commonly used in electroplating that is not recoverable by electrowinning. Nickel recovery is possible, but the process is very pH-sensitive as the pH must be maintained within a small range for metal deposition to occur. Some fluoroborate-containing solutions, such as tin and tin-lead solutions, can corrode certain anode materials. Most etchant solutions dissolve metals off the cathodes as quickly as they are deposited.

Most Successful Electrowinning Applications

- Gold
- Silver
- Copper
- Cadmium
- Zinc

DESIGN AND IMPLEMENTATION CONSIDERATIONS

The design and implementation of an electrowinning unit are dependant on the configuration and control of the electroplating and rinse operations for which the unit will be used. Electrowinning can eliminate the need for continuously flowing rinse water in a rinse system if dragout reduction techniques and multiple rinse tanks are used.

The most common and cost-effective application of electrowinning involves installing an electrowinning unit on a stagnant rinse tank located after a dragout recovery tank. To maintain a steady-state metal concentration in the stagnant rinse at or below the maximum contaminant concentration, the rate of metal deposition onto the electrowinning cathodes must be greater than or equal to the rate of dragin from the preceding tank. Thus the metal deposition rate is a key design parameter that ultimately affects the capacity, size, and cost of the electrowinning unit.

Helpful Hint

The electrowinning unit should be operated 24 hours per day to maximize metal recovery and to maintain the lowest possible metal and cyanide (if present) concentrations in the stagnant rinse. Operating the unit during nonproduction hours allows it to recover metals and destroy cyanide that accumulate during production.

Because metal and cyanide concentrations in the stagnant rinse are lowered, subsequent rinses will be "cleaner," allowing the rinse water flow rates in these rinses to be reduced or turned off. In many cases, rinse water flow is reduced to a rate equal to the evaporation rate from the stagnant rinse.

MAXIMIZE METAL DEPOSITION RATE

Maximizing and controlling these four factors will improve electrowinning unit performance.

Metal Concentration: To achieve high recovery rates, electrowinning should be applied to concentrated rinse waters. Therefore, electrowinning is most effectively applied to a stagnant rinse.

Current Density: Metal deposition occurs at faster rates with higher current densities. However, if the current density is too high, the solution surrounding the cathodes can become depleted of metals, which limits the metal deposition rate. The "excess" current applied to the electrodes is wasted on converting water into hydrogen and oxygen.

Mixing: Mixing disrupts the metal depletion layer that would form in a stagnant solution, allowing the electrowinning unit to be operated at a higher current density with a corresponding higher deposition rate.

Cathode Surface Area: Metal deposition rate is proportional to cathode surface area. Two main types of cathodes are available: (1) flat plate cathodes and (2) reticulated cathodes. Flat plate cathodes are made of stainless steel, have an effective surface area equal to their apparent area, and are reusable. When deposited metal reaches a thickness of 3/16 to 1/4 inch, flat plate cathodes should be removed and cleaned. The advantage of flat plate cathodes are their reusability and the ability to recover metals on-site. Reticulated cathodes are made of metal-coated carbon fibers and have an effective surface area that is ten times their apparent area. The advantage of using reticulated cathodes is their high deposition rate. Reticulated cathodes are not reusable; fully loaded cathodes are, therefore, sent off site for recycling.

Eventually, dissolved salts that are not removed or oxidized by the electrowinning unit accumulate in the rinse water. If these accumulated salts start negatively impacting rinsing quality, the rinse water tanks should be drained and filled with clean water. Spent rinse water can be evaporated, treated, or disposed of off site.

CASE STUDY: ELECTROWINNING AT ALL METALS

All Metals Processing Company (All Metals) is a small job shop in Burbank, California, that performs cadmium, bronze, and zinc electroplating and black oxide coating for aerospace and other industrial customers. All Metals employs 15 workers, and its facility has about 8,000 square feet of space for plating operations.

In early 1996, All Metals set a goal to reduce water use and eliminate wastewater discharge to the sewer. All Metals was motivated by high city sewer fees and pressure from the mu

Electrowinning Costs

Capital: Electrowinning units typically cost $5,000 to $15,000, depending on the unit's size and design and the type of cathodes used. Reusable, flat plate cathodes cost about $200 each, and "disposable," reticulated cathodes cost about $12 each.

O&M: Labor, electrode replacement, maintenance, and energy costs are low.

nicipal wastewater treatment plant (POTW) to decrease the metal concentrations in treated wastewater. In cooperation with the Merit Partnership, All Metals agreed to pursue its goal in two phases. All Metals and the Merit Partnership decided to focus their efforts on the cadmium electroplating line because it was the most frequently used process line, dragout from this line contributed the largest quantities of metals to the wastewater, and All Metals had exceeded their cadmium wastewater discharge limits on several occasions.

Phase 1 involved evaluating overall process efficiency and control. The purpose of Phase 1 was to reduce dragout and optimize rinse water use to the maximum extent feasible before selecting and purchasing recycling or recovery technologies. Process modifications made during Phase 1 are described in a previous Merit Partnership fact sheet titled "Modifying Tank Layouts to Improve Process Efficiency." Phase 1 modifications resulted in a 50 percent dragout and rinse water reduction, a 60 percent wastewater treatment chemical reduction, improved rinsing quality, and more efficient work flow; the Phase 1 payback period was 1.7 years.

By improving overall process efficiency first, All Metals was able to more cost-effectively apply a metal recovery technology and move toward eliminating cadmium wastewater discharges to the POTW. For Phase 2, electrowinning was determined to be the most feasible technology for All Metals to reduce or eliminate wastewater discharges from the cadmium electroplating operation.

ELECTROWINNING UNIT INSTALLATION AND OPERATION

All Metals purchased a Retec Model 6 electrowinning unit from U.S. Filter/Memtek, of Billerica, Massachusetts. The Model 6 holds six cathodes and has a 100-ampere capacity. The electrolytic cell and rectifier were mounted on a shelf above a stagnant rinse tank (Rinse 1) that follows a spray dragout recovery tank (see Figure 3). Reticulated cathodes were used in the electrowinning unit. Anticipating that the electrowinning unit would reduce cadmium and cyanide concentrations in Rinse 1, All Metals turned off the rinse water flow in the subsequent counterflow rinse and converted it into a two-stage stagnant rinse (Rinses 2 and 3). Rinse water was manually transferred from Rinse 2 to Rinse 1 in order to make up for evaporative losses; rinse water in Rinse 3 flows through a weir into Rinse 2 when clean water is added to Rinse 3.

Helpful Hint

Ideally, a heater should be installed on the rinse tank connected to the electrowinning unit. This design feature concentrates the influent to the electrowinning unit, which increases the metal deposition rate. It also increases the countercurrent flow of rinse water from subsequent rinses.

In addition, All Metals installed an electric heater on Rinse 2 to increase evaporation, thereby increasing the countercurrent flow of clean water from Rinse 3. A heater could not be installed on Rinse 1 because it is a plastic tank that could not tolerate higher temperatures. All Metals also installed an in-tank filtration system on Rinse 2 to remove suspended solids from the rinse water.

RESULTS

The electrowinning unit is operated at the All Metals facility 24 hours a day, 7 days a week. The cathodes are replaced every 3 months on average. Based on the start and finish weights of the cathodes, about 2 kilograms (4.4 pounds) of cadmium was recovered on the six cathodes after 2 months of operation. Spent cathodes are picked up by a scrap metal dealer for recycling.

Before the electrowinning unit was installed, rinse water flowed through the counterflow rinse tank at a rate of 0.5 gallon per minute. Since the electrowinning unit was installed,

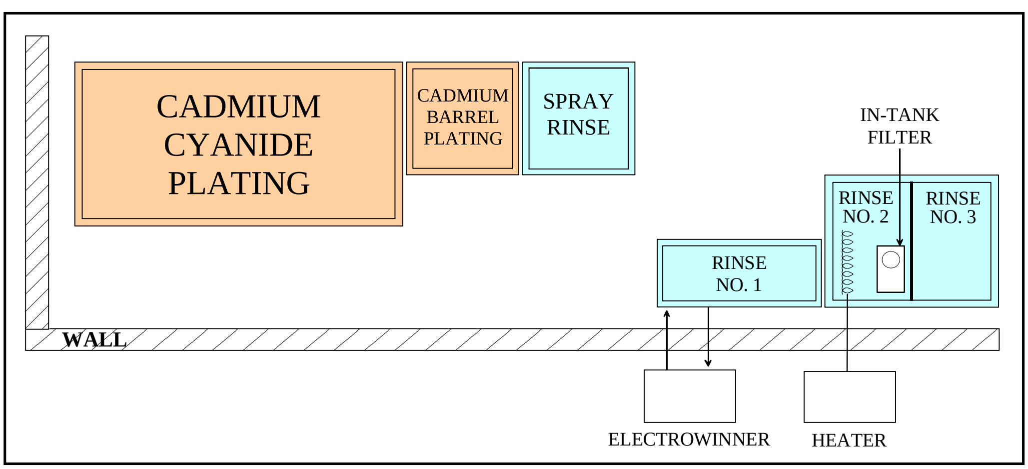

Figure 3. All Metals' Cadmium Electroplating Line

Benefits of Electrowinning on All Metals' Cadmium Line

- 94% water use reduction
- Elimination of cadmium-bearing wastewater
- No cadmium discharge limit violations
- Simplified wastewater discharge permit
- Decreased WWTS O&M and filter cake generation

all the rinse tanks have been operated in a stagnant mode, and the temperature of the rinse water in Rinse 2 has been maintained at about 115 °F, resulting in the evaporation of about 15 gallons of rinse water per day. Consequently, 15 gallons of clean water per day is added to Rinse 3 in order to compensate for the water transferred into Rinse 2 to make up for evaporative losses. Based on comparison of water use on the cadmium electroplating line before and after installation of the electrowinning unit, rinse water use has been reduced by 94 percent and wastewater is no longer generated from the rinses.

Because not all dissolved solids are removed by the electrowinning unit, conductivity is monitored in Rinses 1 and 3 (see Figure 4). Rinse 3 is drained to dispose of the dissolved solids buildup and replenished with clean rinse water every 6 weeks on average. The drained rinse water is evaporated onsite by All Metals. In addition, cyanide concentrations are periodically measured in Rinse 1; these concentrations have been significantly reduced by the electrowinning unit.

All Metals purchased the Retec Model 6 electrowinning unit for $7,500; the electric tank heater for $690; and the in-tank filtration system for $570. All Metals spent an additional $250 on electrical hardware such as wiring and a fuse box and a total of 20 labor hours for unit installation and startup. Operation and maintenance (O&M) expenses include about $20 per month for electricity and $290 per year for reticulated cathode purchase.

Lessons Learned

Cathode installation and maintenance is critical to the electrowinning units performance. All Metals experienced two incidents in which the cathodes dissolved into the circulating rinse water when the electrical connection between the bus bar and cathodes was disrupted. The first incident occurred when three cathodes were improperly placed in the electrowinning unit. The second incident was caused by reuse of cathode connectors. As the connectors gradually became corroded, the electrical connection between the cathodes and bus bar was lost. **All Metals now replaces the cathode connectors every time that the cathodes are replaced and periodically checks the cathodes to assure their proper connection to the bus bar.**

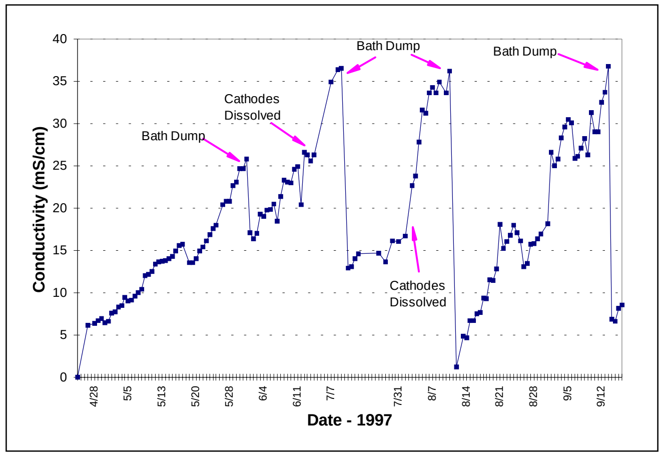

Figure 4. Conductivity Measurements in Rinse 1

After installation of the electrowinning unit, no increase in the number of reject parts occurred, and no adverse impacts on production were observed. Motivated by the success of the electrowinning unit for the cadmium operation, All Metals has installed another electrowinning unit in a copper electroplating stagnant rinse.

Cost Savings

	Before	After	Savings
Water Use - Cd	240 gal/day	15 gal/day	$110/yr
Sewer Discharge - Cd	240 gal/day	0 gal/day	$480/yr
WWTS O&M	$11,080/yr	$10,220/yr	$860/yr
Filter Cake Disposal	760 lb/mo	700 lb/mo	$114/yr

Annual Savings = $1,564/yr*

Total Costs = $9,010

O&M Costs = $530/yr

Payback Period = 8.7 yrs

***Annual savings does not include potential reclaim value for recovered metals**

The estimated 8.7-year payback period is relatively high because it considers only direct costs and savings. **Other beneficial outcomes may lower the payback period.** For example, the electrowinning unit takes All Metals one-step closer to its goal of zero discharge to the sewer, which will eliminate the $2,860 annual wastewater discharge fee. Also, All Metals is no longer susceptible to cadmium discharge violations, which can result in $1,000 fines.

For more information on this case study or the Merit Partnership, contact the following individuals:

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