Some Successful Applications of Electrodialysis

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Metal recovery from plating solution dragout has become a prime concern for many metal finishers lately. To satisfy the demand for metal recovery, many new recovery systems have been introduced into the market. Electrodialysis (ED) has been one of the more successful systems introduced over the past five years. Some of the most successful applications will be reviewed in this paper.

In order to fully understand the application of electrodialysis, a brief discussion of the theory follows.

Electrodialysis, in the pure sense, is the movement of ions through ion selective membranes, under the influence of an electromotive force (voltage) applied across the membrane area. Ion exchange membranes are the key to this process and exist in two basic distinct forms—cationic and anionic.

Cationic membranes allow only the positively charged ions such as copper, zinc or nickel to pass through them, while conversely, anionic membranes allow only the passage of negatively charged ions such as chloride and sulfate, or cyanide complexes, etc. These membranes are thin sheets of plastic material which have been subsequently impregnated to impart the appropriate ionic characteristic. Membranes then when arranged in parallel cells between two electrodes, positive and negative, along with specifically designed spacers and gaskets to separate the membranes into leak-tight cells, give the basic construction of an electrodialysis stack.

Figure 1 is a schematic operational drawing of such an ED stack. At each end are the electrodes, a cathode of stainless steel and an anode of platinum-clad titanium. Each electrode is in a cell around which flows a compatible salt solution of electrolyte whose purpose is to collect and dispel resultant gases such as hydrogen and oxygen and impart overall electrical conductivity to the stack. Subsequently, there are a number of individual cell compartments of alternating layers of anionic and cationic membranes. The even numbered cells are the paths for the feed solution; the feed solution being the constantly circulated solution from a dragout or reclaim tank. The odd numbered cells are the collecting, or concentrating, cells in which the concentrated plating solution is collected for return to the plating tank. The cations are the metal ions such as nickel, copper, zinc, etc. which are attracted to the left toward the cathode, but can only move into the next adjacent cell where they are prohibited from further migration by an anionic membrane. Likewise, the anions such as the chloride, sulfate, etc. are attracted to the right side, but again are prohibited from further migration by the presence of a cationic membrane. Since the entire system must be electrically neutral, the recovered or concentrated solution is collected in the odd numbered cells while the reclaim rinse solution, that is circulated in the even numbered cells, is constantly being reduced in metal salt concentration.

Figure 2 shows this process in schematic fashion. This ongoing process then is engineered in terms of stack size to remove the same volume of plating solution as is dragged out of the plating tank into the reclaim tank during the normal production operation. The remaining components in an operational electrodialysis unit consist of a rectifier to provide the appropriate potential across the two electrodes, a pump to circulate the electrode rinse, and a pump and filter to circulate the reclaim rinse through the ED stack. This then, along with the appropriate monitoring system and meters, constitutes an operational electrodialysis unit as can be seen in Figure 3.

ED Application in Gold Plating Operations

Circuit-wise

Some of the most successful applications of ED have been on gold plating baths. The high conductivity of typical

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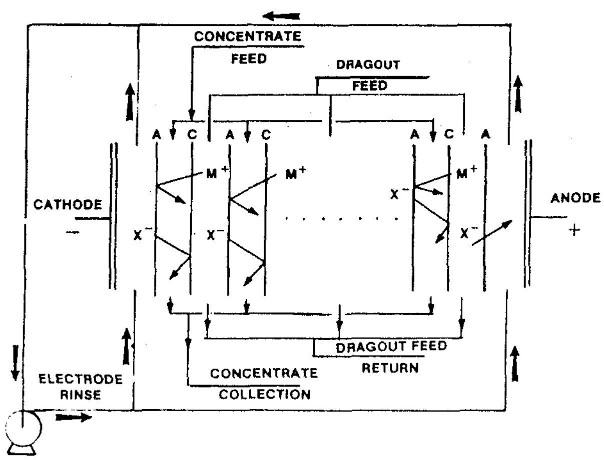


Fig. 1—Schematic Operational Drawing of ED Stack

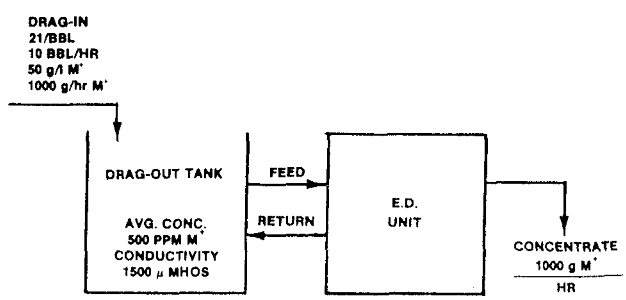


Fig. 2—Schematic of ED Process

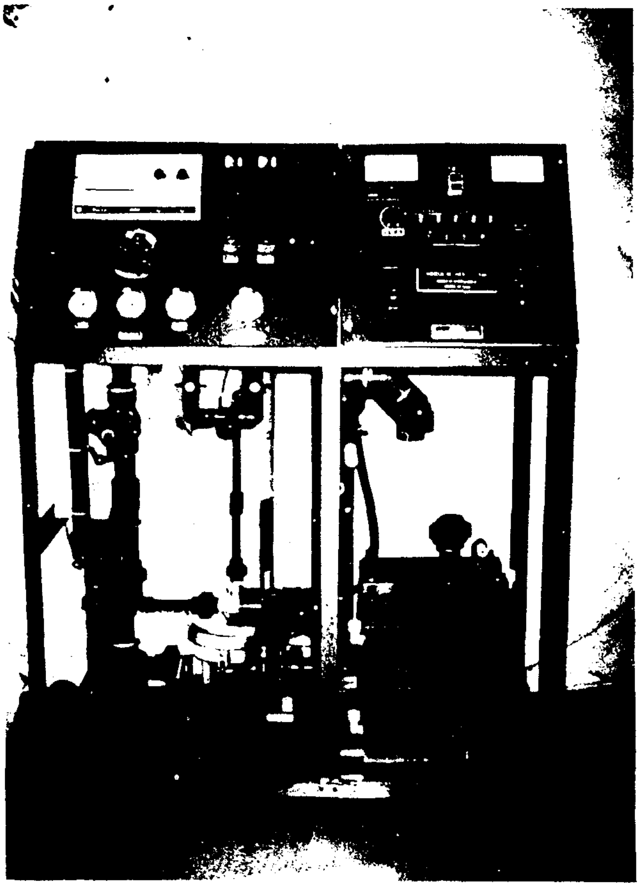


Fig. 3—Operational ED Unit

solutions has produced gold recovery rates over 99%. We have found that gold platers are most resourceful in discovering systems to optimize gold recovery. ED plays a major role in these systems due to low initial cost, low energy consumption, and ability to produce a product suitable for direct recycle to the plating tank.

Circuit-Wise of North Haven, Conn., is one of the larger printed circuit manufacturers in New England. Before they decided on a recovery system for their Mircoplate 7000 Tab Plater, four competing recovery systems were evaluated both by in-plant engineers and by an independent consultant firm. Electrodialysis was chosen as the most applicable process for this installation.

Initially, the ED system was operated on the dragout rinse following the plating station, and a small ion exchange column was installed on the second rinse to recover the last gram of gold. The effectiveness of this system was demonstrated by atomic absorption analysis (AA) on the third rinse which had no detectable gold.

The rinsing in this automatic tab plating machine is very effective and there is very little carryover of contaminants from one process tank to another. Therefore after analysis, the concentrate recovered by ED was returned directly to the plating tank. The system operated in this manner, returning recovered concentrate directly to the plating tank with no buildup of contaminants. Over 35 troy ounces of gold were recovered in the first operation, and with the price of gold at that time, the ED system had paid for itself. Additional savings were building up in the eliminated interest charges which would result from gold in dead inventory on ion exchange resin and at the refiners. Refining charges were also eliminated.

The ED was operated in the constant voltage mode which allows the concentration of the recovered solution to "float", but will recover the maximum amount of gold. Operating in this manner, the concentrate ran from a low of 0.14 troy oz/gal to a high of 5.26 troy oz/gal.

Circuit-Wise ran for 8 months in this manner, recovering over 150 troy ounces of gold. Typical gold concentrations in the recovered solution and amounts of gold recovered are listed in Table 1. The engineers, encouraged by this performance, looked for ways to recover additional gold from their wide range of processes.

The culmination of this research is now operating at Circuit-Wise. Gold recovery is enclosed in a separate high security area. Within this room, ED is the heart of the recovery system.

On the production floor, each gold plating area is organized with a dragout tank following the plating station. The second rinse tank is also a dead rinse as is the third rinse. The first dragout rinse is withdrawn into drums periodically to maintain the concentraation of gold below 0.1 oz/gal. The second and third rinses are continuously circulated through separate ion exchange cartridges. When the concentration of gold in the third tank exceeds a pre-set level, the resin on the second tank is retired, the ion-exchange on the third tank is moved to the second, and fresh resin is installed on the third tank. This system effectively recovers over 99% of the gold dragout.

Within the recovery area, the drums containing the dragout solution from each plating line are stored and segregated as to type of bath. When a sufficient quantity has been collected, the solution is concentrated through the ED instrument. Analysis of the stripped solution by AA confirms the complete removal of gold before being sent to waste treatment. The concentrate is also analyzed for gold

Table 1
Gold Concentration of Recovered Solutions From Microplate

	Maximum concentrate Troy oz/gal.	*Minimum Concentrate Troy oz/gal.*	*Average Concentrate Troy oz/gal.*	*Troy ounces Recovered*
December 1980	4.48	0.39	1.22	35.5
January 1981	5.26	0.45	2.11	18.3
February 1981	1.97	0.16	0.98	13.0
March 1981	1.86	0.27	0.98	10.1
April 1981	1.26	0.43	0.79	15.8
May 1981	3.04	0.28	1.43	21.4
June 1981	1.87	0.16	1.01	9.5

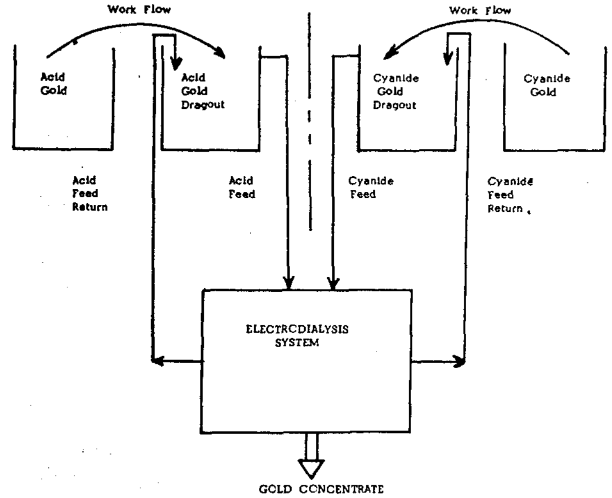


Fig. 4—Recovery system at artistic plating.

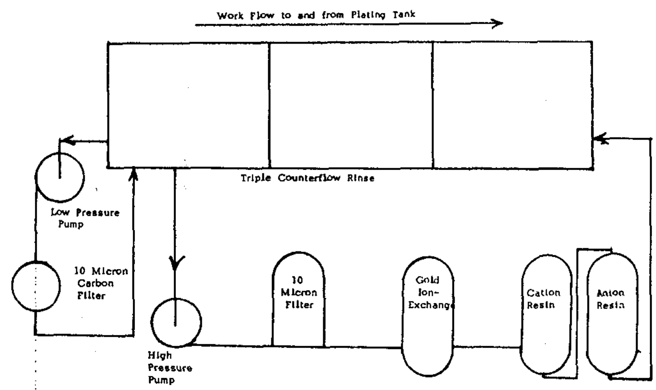


Fig. 5—Rinse purification system at artistic plating.

content and then bottled and placed in stock as replenishment solution for the individual lines. The foreman signs out for the recovered solution just as he does for new products. Very close control is kept over the recovered solutions. In the first ten weeks of operation, over 180 troy ounces of gold were recycled directly into the plating tanks. The analysis of these solutions is tabulated in Table 2.

The savings in interest charges due to immediate recycle are significant. Even with an 8-week return of gold recovered by ion-exchange or plating out, there would still be about 150 troy ounces of gold held as unusuable inventory in various stages of recovery. At today's high interest rates, the savings over one year would be over $13,000.

Circuit-Wise also recovers gold from their rejects. After stripping the gold, ED is used to concentrate the gold in the solution to 8 oz/gal for ease of handling and control of gold content. Gold present in ion exchange resin is recovered as a solid after burning off the resin.

Artistic Plating Co.

Artistic Plating Co. Inc. is an upper midwestern job shop specializing in precious metal plating. Of particular interest

Table 2
Analysis of Recovered Solutions—July-Sept. 1981

Lot #	*Volume*	*Concentration*	*Troy ounces*
1	63 l	1.44	24.0
1A	38 l	0.556	5.6
2	68 l	1.39	25.0
2A	54 l	0.28	4.0
3	69 l	0.92	16.8
4	31 l	1.74	14.3
4A	32 l	0.31	2.6
5	36 l	2.23	21.2
5A	36 l	0.37	3.5
6	30 l	3.12	24.8
6A	36 l	0.55	5.2
7	61 l	1.25	20.2
7A	54 l	0.12	1.7
8	43 l	0.98	11.2
			180.1

Table 3
Installation Cost

Components	*Cost*
E D System	$16,000
Pumps	700
Piping	1,000
Controls	1,200
Resins/Filters	650
Installation Labor	1,500
Total	$21,050

Table 4
Annual Operating Cost

Components	*Cost*
Electrical Power	$300
Chemicals	175
Filter Cartridges	150
Replacement Membranes	750
Labor	1,000
Resin (Gold Selective)	70
Resin (H-OH)	900
Total	$3,345

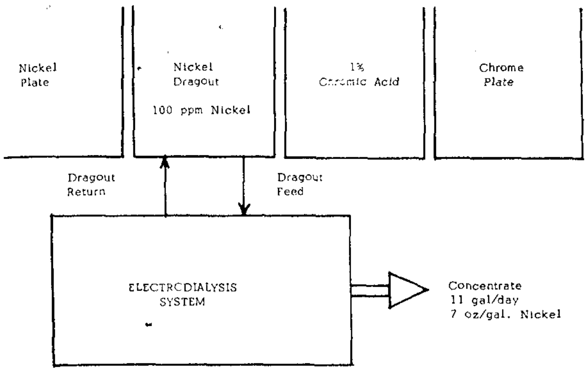
Table 5
Silver Recovery Justification Oneida Ltd.

Operating conditions Before E.D.

Operating Hours	8 hrs./day
Dragout	20,000 Troy oz/yr.
Recovery Method	Precipitation as Silver Chloride

Savings With E.D. Recovery

Cyanide Treatment @ 2.60/#	$ 5,200/yr.
Refining Charges @ $.56/Troy oz.	$11,200/yr.
Interest Charges for Silver at Refiners - 4 months @ 12% Annual Interest	12,800/yr.
Refining Loss 5% Difference between Oneida's Assay and Refiners Return	$16,000/yr.
Total Savings with E.D.	$45,200/yr.
Installed Cost of E.D.	$30,450/yr.



. 6—Recovery system at Stratford Metal Finishing.

the large volume of plumbing hardware which is gold ated. Seventy percent of their gold consumption is used ı a large assortment of plumbing accessories ranging from ·ass and zinc castings to stainless steel stampings to six ıot brass extrusions. Due to the varying nature of the raw aterials received for processing, impurity build-up in ›stly gold baths has been a problem of continuing concern. ı the past several years, fluctuations in the cost of raw ıaterials have been no where more dramatic than in the recious metal market where changes of up to 100% have een seen in a matter of months. To combat these problems, rtistic Plating has designed a system which effectively iminates the buildup of bath impurities and maintains in-ouse control of all gold recovered.

The closed loop system is designed to recover gold from a rag-out tank, continuously removing impurities and llowing reintroduction of gold concentrate into various aths. It additionally purifies and reuses its rinse water by ıeans of several techniques common in the metal finishing ıdustry. The system is unique in that it uses a closed-loop pproach to a plating system generally not thought to be daptable to that mode of operation.

The heart of the recovery system is the electrodialysis ecovery system operated on the dragout rinses. The ED ystem is piped directly into both the acid gold dragout and yanide gold dragout. Only one dragout is concentrated at a ime. The system is equipped to rapidly flush from itself any esidual acid or cyanide remaining before alternating ›etween dragout tanks. The concentrate is collected and ıvailable for direct recycle into the plating tanks. This may ›e seen schematically in Figure 4.

Work being processed in gold plate is rinsed prior to and ıfter plating in the same closed loop counterflow rinse station. This rinse station is continually purified by two separate systems. Organic impurities are removed by continuous filtration through activated carbon. The second system provides a high flow to rapidly circulate purified water for rinsing.

This system is also equipped with a gold selective ion exchange resin to collect any gold which escapes ED recovery.

Removal of solids is accomplished by use of a 10 micron filter. Residual ionic species are removed with an anion-cation H-OH resin. This procedure is demonstrated in Figure 5.

The ED unit is operated as required by monitoring percent conductivity settings on the dragout rinse. The concentrate from this contains over 95% of all recovered gold. This concentrate is analyzed and added as required to gold strike tanks in non-critical, decorative applications, where the main criteria is the appearance of the plate.

The installed cost of the ED rinse system was $21,050. The annual operating cost is $3,345. The initial payback occurred after 9 months of operation. The average gold recovery rate is 3.9 troy oz/month. Although Artistic Plating recognizes the cash flow advantages of direct recycle, they did not directly use this in the payback justification. The complete figures are tabulated in Tables 3 and 4.

ED Application in Nickel Plating

Stratford Metal Finishing of Winston-Salem, North Carolina had a serious problem. Their shop is situated over a stream, and the discharge limits were below 1 mg/l for all metals. The shop has been in existence for many years and the space available for effluent treatment was minimal. In fact, the available space was so small that they did not have room to segregate the nickel rinses from the cyanide-bearing rinses.

This resulted in nickel complexing with the cyanide giving excessive treatment times, chemical usage, and nickel in the discharge.

The solution devised by Stratford Metal Finishing was the treatment of plating rinses to allow recycle of the treated water for use in rinsing. Although Stratford terms their water use "closed loop", there is the inevitable discharge of water to reduce the build-up of dissolved solids. Occasionally certain solutions such as spent strippers and floor spills are barrelled and shipped to a licensed hauler.

Electrodialysis plays an important role in the total effluent treatment package. The only way Stratford could have made this system functional was to eliminate nickel mixing with the cyanide in the treatment tanks. They were not as concerned with the recovery value of the nickel solution, as in eliminating nickel from their rinses so their recycle system would work.

The ED was oversized for the amount of nickel dragout expected. This would allow Stratford to operate the ED in the constant voltage mode to effect the greatest extraction of nickel ions from the dragout while allowing the concentration of nickel in the recovered solution to float. The concentration of the recovered solution was unimportant as there was considerable evaporation from the plating tanks, therefore sufficient room for recycle.

ED Application in Chrome Plating

The chrome plating solutions are also operated in a "closed loop". A proprietary membrane separation process is used for the concentration and recovery of chrome plating solutions. The recovered concentrate is used to replenish the plating tanks.

Rinses from the cyanide plating tanks are handled by conventional chemical treatment to oxidize the cyanide and precipitate the metals. Rinses from the cleaning and pickling operations are neutratlized by conventional means also. The entire effluent flow is then passed through a large filter press to remove solids. The clear effluent is then partially deionized through the use of an H-OH ion exchange unit before reuse.

This system does not save any money compared to a conventional system; in fact it costs more to operate. But the peace of mind obtainable by being able to cement over all the drains in the building has been more than worth the expense to the owners.

Table 6
Silver Recovery at Oneida Ltd.

	Silver (Tr. oz/gal.)		*Potassium Cyanide (oz/gal.)*		*Potassium Carbonate (oz/gal.)*	
	Dragout	*Concentrate*	*Dragout*	*Concentrate*	*Dragout*	*Concentrate*
11/11	0.56	4.19	1.9	6.7	1.0	0.47
11/19	0.50	8.0	1.3	4.5	0.45	<.10
11/24	.35	6.4	1.1	6.1	0.55	<.10
11/30	.58	8.2	1.8	6.6	0.60	<.10
12/4	.44	7.0	1.7	7.4	0.40	<.10
12/10	.52	8.3	1.9	6.6	0.45	<.10
12/71	.34	5.7	1.3	8.5		

The description of operation is sure to raise a few eyebrows among the readers of this paper. This method of recycle is not being recommended as general practice. Stratford Metal Finishing was faced with the option of reducing the metal content in the effluent to virtually unattainable levels or closing down. They chose a third option; elimination of all discharge and sealing all the drains in the building. Hard work, constant attention to details, and an owner determined to make the system work have contributed to its success. This example is presented not as an operating recommendation, but only to demonstrate how electrodialysis is contributing to successful recovery and recycle.

In operation, the system consists of a single dragout rinse following nickel plate continuously purified by ED, followed by a 1% chromic acid solution as an activator before chrome plate. Sulfuric acid is added to the dragout tank to maintain conductivity and allow the greatest recovery of nickel. The operation is shown in Figure 6. The 1% chromic acid solution is sent to a licensed hauler about once a month.

This system has been in operation for 6 months. During this period the average concentration of nickel in the dragout rinse has been below 100 mg/l. On the average a nickel solution at 75% of bath strength is recovered at 11 gallons per 16 hour day. There has been no significant drag-in of nickel or chloride into the chrome plating tank. And there has been no nickel detected in the effluent treatment system.

ED Application in Silver Plating

Oneida Ltd. located in Sherrill, New York is a major manufacturer of silver plated tableware and holloware. As their production increased due to both increased sales and acquisition of new product lines, economical recovery of dragged out silver became a top priority.

The approach taken by the engineers at Oneida Ltd. was very conservative. After evaluating many systems, the most promising were installed for on-site evaluation. As a result of these tests, the equipment justification figures were revised and electrodialysis was chosen as the most promising method. The justification breakdown is given in Table 5.

Once the electrodialysis recovery system was installed, periodic analyses were made to determine if the system was living up to expectations. The results of these were tabulated in Table 6. The most interesting item revealed from analyzing this table is the apparent order of recovery of the ionic species.

The major components of a silver bath are silver cyanide, potassium cyanide and potassium carbonate (from the breakdown of potassium cyanide). When the dragout containing these chemicals was passed through the electrodialysis unit, the silver cyanide passed through the membrane in a greater proportion to the potassium cyanide than present in the dragout. The potassium carbonate, which is weakly ionized compared to the cyanides, was recovered in only very small amounts.

The major conclusions that can be drawn from these results are (1) the silver may be recovered at concentrations over 2 times bath strength; (2) carbonates do not tend to be concentrated by electrodialysis; and that (3) the recovered concentrate may be added directly to the plating bath for reuse. Since the dragout is high when plating holloware, the concentration of the highly conductive cyanide ions is sufficient to block the transfer of the carbonate which has been a problem with other direct recycle recovery methods. Thus the concentrated dragout may be directly recycled without fear of accelerated build-up of carbonates.

Electrodialysis systems are also operating on palladium chloride, acid tin (sulfate) and cyanide cadmium. In total, there are more than fifty operating electrodialysis systems in the field, and this total is expected to more than double in 1982. Systems designed for the recovery of fluoborate solutions and chrome plating solutions are expected to be released from development into full production during 1982. The wide range of applications and economical cost have established electrodialysis as the preferred method of recovery for many solutions. The many successful applications in the field will insure its continued growth.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

EPA-600/9-82-022
December 1982

Fourth Conference On Advanced Pollution Control For the Metal Finishing Industry

PRESENTED AT:
Dutch Inn, Lake Buena Vista, FL
January 18-20, 1982

Co-sponsored by:
- The American Electroplaters' Society
- The United States Environmental Protection Agency

Industrial Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268