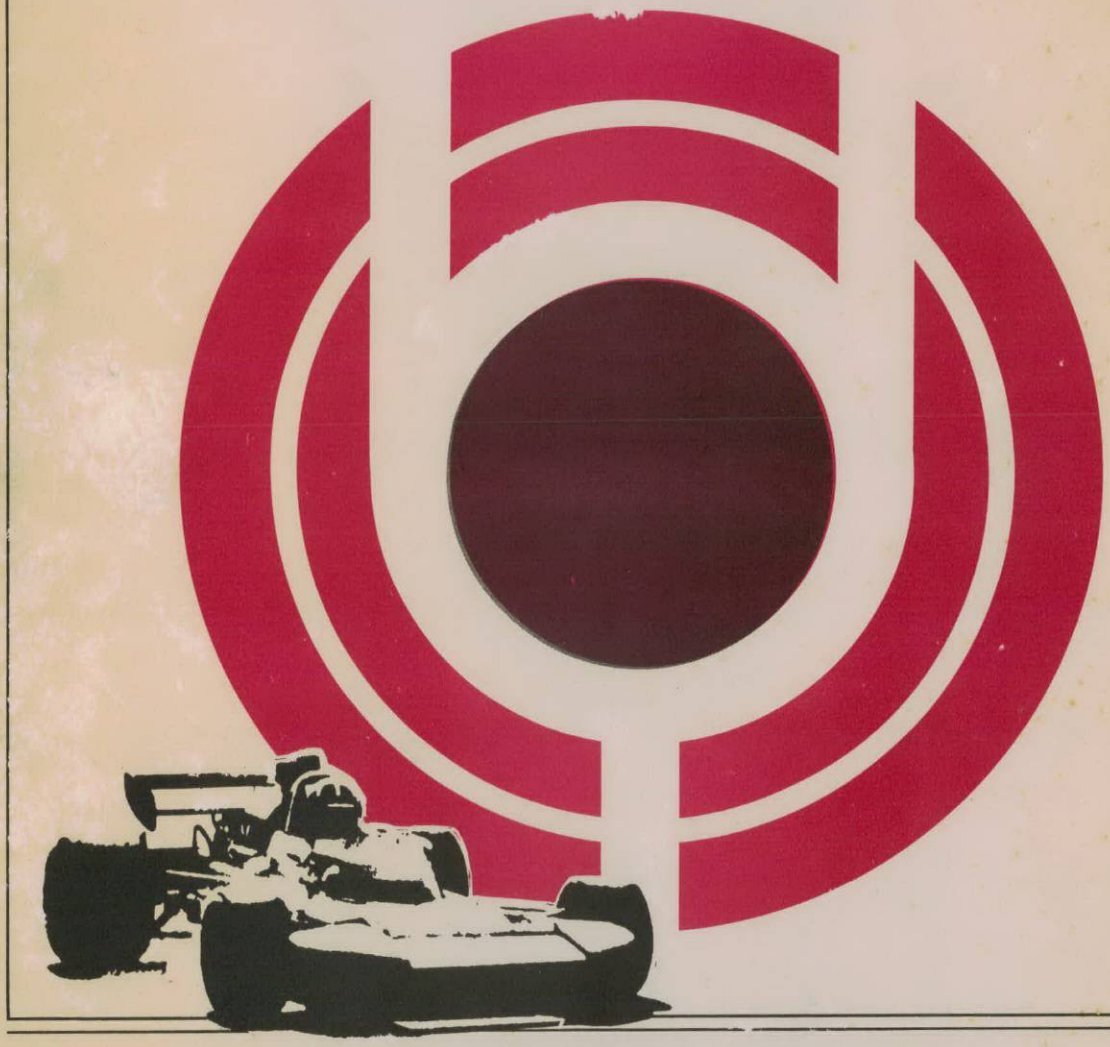
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Session C - Environmental I

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Session C

Process Modifications: The First Step in Wastewater Treatment

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PROCESS MODIFICATIONS: THE FIRST STEP IN WASTEWATER TREATMENT

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General:

The size, scope and complexity of a wastewater treatment system is dictated by both the quantity and quality of the process waste streams, as well as the effluent discharge limitations that a facility is required to meet. Prior to the establishment of wastewater treatment system design criteria, the process operations should be closely studied to determine areas where chemical conservation and rinsewater flow reduction techniques could be implemented. These techniques have a significant impact on reducing the capital and operating costs of a wastewater treament system, and if implemented properly, a negligible effect on product quality.

Chemical Conservation Techniques:

Many articles have been written on various chemical conservation techniques. Some of the more typical techniques that have been applied to electroplating shops are listed in Table 1. Additional information on the minimization of dragout can be found in the references (1, 2).

The reduction of chemical dragout should be the first order of business in implementing a pollution-control program, subsequent to the inventory/data gathering phase. By keeping the chemicals out of the rinse tanks and in the process baths where they belong, a lower water rinse flow becomes acceptable, process chemical purchases are reduced, wastewater treatment facility costs are lowered and treatment sludge generation is reduced.

Rinsewater Conservation Techniques:

Following dragout control, the next step in the pollution-control program should be rinsewater conservation. The quantity of rinsewater utilized in the typical electroplating and printed circuit board manufacturing shop is often excessive and can often be reduced through implementation of more efficient rinsing techniques. Table 2 lists typical rinsewater conservation methods that can have application (references 1, 2).

The familiar rinsing equations, shown in Figure 1 for parallel and series tanks, can be utilized to indicate the benefits from recycling rinsewater. Typically, reductions of between 90 to 95% for a double rinsetank and 95 to 97% for a triple rinsetank can be accomplished, depending on the rinsing ratio of Cp/Cn and rate of dragout (references 3, 4, 5).

Case Studies:

Three case histories will be presented which exemplify the savings in water usage that can be accomplished utilizing accepted rinsewater conservation technology. One company, A, is a printed circuit board manufacturer, while the remaining two, B and C, are electroplating shops.

1. Company A is a New Hampshire-based manufacturer of custom printed circuit boards. The major processes generating wastewater are listed in Table 3. With input on product quality control aspects from the facility chemist, the major thrust was rinsewater flow reduction in the copper/ solder pattern plate line and the solder strip operation with dragout tanks installed in the copper deposition line, copper/ solder pattern plate line, solder strip and hydroetch operation. Table 4 indicates the flow reduction and dragout tank modifications accomplished.

   Overall, a flow reduction of nearly 35% was achieved, with a significant reduction in the treatment system requirements, due to batch treatment possibilities from the implemented dragout tanks. On-going studies will determine the most cost-effective mode of batch treatment/reclaim.

2. Company B is a major electroplating job shop. The process lines are indicated in Table 5. Each line was investigated via dragout studies and laboratory analysis with input on product quality criteria furnished by company personnel (Tables 6 to 12). Total flow reductions are summarized in Table 13. Table 14 indicates the impact on purchase water costs and sewer user charges. The impact on wastewater treatment costs has not been quantifie, but will approach 25-30 percent. Management o f this particular company has implemented all the re- comm endations and is currently acquiring the necessary wastewa ter treatment components from the resale market, further r educing wastewater treatment costs.

3. Company C is a captive electroplating shop. Process rinsewater consumption and subsequent reductions are

summarized in Table 15. These reductions are detailed in Figures 2 and 3. Company personnel are presently implementing the recommendations. Capital cost estimates (equipment and installation) for the industrial wastewater treatment system have been reduced from $343,000. to $162,000., in part by implementing the modifications.

Summary:

The above case histories indicate that by implementing rinsewater/dragout reduction techniques, significant cost-reductions can be accomplished. These methods should be implemented prior to the formulation of design criteria for purchase of a cost-effective wastewater treatment system.

Table 1

Chemical Conservation Techniques

- Mimimize Bath Chemical Concentrations
- Maximize Bath Operating Temperature
- Utilize Wetting Agents
- Efficiently Rack Parts For Best Drainage
- Design Parts To Minimize Dragout
- Withdraw Parts At Slow Rate
- Install Rest Bars Over Process Tanks
- Utilize Drainage Boards
- Utilize Wet Air Knives or Fog Sprays
- Utilize Stagnant (Still) Rinse Tanks

Figure 1

Rinsing Equations

1. $Q = \frac{(Cp\Theta^n)^{1/n}}{Cn}$ PARALLEL TANKS

2. $Q = [(Cp/Cn)^{1/n} + 1/n]\Theta$ SERIES TANKS

where: Q = Rinse flow rate

Cp = Concentration of salts in process bath

Cn = Concentration of salts allowed in final rinse

Θ = Dragout rate

n = Number of rinse baths

Table 2

Rinsewater Conservation Techniques

- Countercurrent Rinsing
- Spray and Fog Rinsing
- Flood Rinsing
- Still Rinsing
- Reuse of Rinsewater
- Rinsewater Agitation
- Conductivity Controlled Rinsing
- Flow Restriction (Regulating) Devices
- Higher Temperature Rinsing

Table 3

Company A
Process Operations

- Electroless Copper Deposition
- Copper/Solder Pattern Plate
- Nickel/Gold Tab Plate
- Immersion Tin
- Hydroetch
- Solder Strip
- Resist Strip
- Developer
- Wave Solder Area
- Screen Wash
- Scrub and Deburr Operations
- Reflow
- Filter Backwash
- Water Treatment Regeneration

Table 4

Company A
Process Flow/Dragout Reductions

1. Copper/Solder Pattern Plate - 24 gpm to 6 gpm

   Instituted double countercurrent rinsing, flow restriction valving and air agitation. Installed dragout rinse following tin lead plating tank.

2. Copper Deposition - No flow reduction

   Installed dragout rinse following microetch and two dragout rinses following electroless copper deposition tank. Batch treat/reclaim as required.

3. Solder Strip - 7.5 gpm to 3.0 gpm

   Installed two dragout rinses followed by a double countercurrent rinse tank.

4. Hydroetch - No flow reduction

   Installed two dragout rinses following immersion etch tank. Batch treat/reclaim as required.

Total Flow Reduction - 71 gpm to 48 gpm
- 33% reduction

Table 5

Company B
Production & Cleaning Lines

LINE	OPERATION	TYPE
1	Zinc Plating	Manual barrel
2	Zinc Plating	Automatic barrel
3	Zinc Plating (Cyanide)	Automatic barrel
4	Nickel Plating	Manual barrel
5	Zinc Plating	Automatic barrel
6	Nickel Plating	Automatic rack
7	Copper Plating (Cyanide) Brass Plating (Cyanide) Tin Plating	Manual barrel
8	Nickel Plating	Manual barrel
Misc.	Alkaline Cleaning	Manual tumblers

Note: Line 6 usage discontinued.

Table 6

Company B
Line 1 Analysis

Tank Identification

1. High Temperature Soap Clean ($150^{o}F$)
2. Rinse
3. H_2SO_4 Clean
4. Rinse
5. Zinc Plating
6. Not used
7. Alkaline Clean
8. Alkaline Clean
9. Alkaline Clean
10. Rinse (Iridite)
11. Rinse-TCC (Iridite)

Wastewater Sources

Tank No.	Present Flow Rate, gpm	Suggested Flow Rate, gpm	Comments
2	3.9	3.0	a - counter-current system at 2.5 gpm
4	5.3	a	
6	0.0	a	
10	3.1	3.1	
11	3.5	2.0	
TOTALS	15.8 gpm	10.6 gpm	

Recommendations

1. Install/calibrate flow restriction valves to tank numbers 2 and 11 as indicated.
2. Fabricate tank numbers 4 and 6 into a double counter-current rinsing system with feedwater flowrate restricted to 2.5 gpm.
3. Supply low level air agitation to rinse tank numbers 2, 4, 6, 11.

Table 7

Company B
Line 2 Analysis

Tank Identification

1. Alkaline Clean
2. Alkaline Clean
3. Rinse
4. HCl Clean
5. Rinse
6. Zinc Plate (80°F)
7. Rinse
8. Rinse
9. Rinse
10. Rinse (Iridite)

Wastewater Sources

Tank No.	Present Flow Rate, gpm	Suggested Flow Rate, gpm	Comments
3	5.9	3.0	a - counter-current system at 3.0 gpm
5	5.3	a	
7	1.2	a	
9	2.4	a	
11	1.0	1.0	
TOTALS	14.4 gpm	8.7 gpm	

Recommendations

1. Install/calibrate flow restriction valve to tank number 5 as indicated.
2. Interconnect tank numbers 7, 8 and 9 to form triple counter-current rinsing system with feedwater flow-rate restricted to 3.0 gpm.
3. Supply low level air agitation to rinse tank numbers 3, 5, 7, 8, 9.

Table 8

Company B
Line 3 Analysis

Tank Identification

1. Alkaline Clean (2-stage)
2. Alkaline Clean (2-stage)
3. Rinse
4. H_2SO_4 Clean
5. H_2SO_4 Clean
6. Rinse
7. Rinse
8. Zinc Plate (Cyanide)
9. Rinse
10. Rinse
11. Rinse
12. Recovery Drip
13. Rinse
14. Recovery Drip
15. Rinse
16. Rinse
17. Rinse (Iridite)

Wastewater Sources

Tank No.	Present Flow Rate, gpm	Suggested Flow Rate, gpm	Comments
3	1.2	1.2	a - assumes 5 gpm
6	5.6	b	total for tank
7	0.0	b	numbers 10, 11,
9	0.0	0.0	15 and 16.
10	a	c	
11	a	c	b - counter-
12	0.0	0.0	current system
13	a	c	at 2.5 gpm.
14	0.0	0.0	
15	a	c	c - counter-
16	a	c	current system
17	3.0	2.0	at 4.0 gpm.
TOTALS	14.8 gpm	9.7 gpm	

Table 8
(Continued)

Recommendations

1. Interconnect tank numbers 6 and 7 to form a double counter-current rinsing system with influent feed rate set at 2.5 gpm.

2. Interconnect tank numbers 10, 11, 13, 15 and 16 to form a five-stage counter-current rinsing system with influent feed rate set at 4.0 gpm.

3. Interconnect tank numbers 9, 12, and 14 to form a dragout recovery system for periodic recycling to zing plating tank.

4. Install/calibrate flow restriction valve to tank number 17 as indicated.

5. Supply low level air agitation to rinse tank numbers 6, 7, 10, 11, 13, 15 and 16.

Table 9

Company B
Line 4 Analysis

Tank Identification

1. Alkaline Clean
2. Alkaline Clean
3. Rinse
4. Not Used
5. H_2SO_4 Clean
6. Nickel Plate
7. Nickel Plate
8. Nickel Plate
9. Nickel Plate
10. Nickel Plate
11. Nickel Plate
12. Nickel Plate
13. Rinse
14. Rinse (heated)
15. Rinse (misc.)

Wastewater Sources

Tank No.	Present Flow Rate, gpm	Suggested Flow Rate, gpm	Comments
3	22.1	a	a - counter-current system at 4.0 gpm.
4	0.0	a	
13	3.5	3.0	
14	0.2	0.2	
15	2.6	2.6	
TOTALS	28.4 gpm	9.8 gpm	

Recommendations

1. Interconnect tank numbers 3 and 4 to form a double counter-current rinsing system with influent feed rate restricted to 4.0 gpm.
2. Install/calibrate flow restriction valve to tank number 13 as indicated.
3. Supply low level air agitation to rinse tank numbers 3, 4 and 13.

Table 10

Company B
Line 5 Analysis

Tank Identification

1. Alkaline Clean (140°F)
2. Alkaline Clean (4-stage)
3. Rinse
4. Risne
5. HCl Clean (3-stage)
6. Rinse (2-stage)
7. Zinc Plate
8. Rinse
9. Rinse (2-stage)
10. Rinse
11. Rinse (3-stage)

Wastewater Sources

Tank No.	Present Flow Rate, gpm	Suggested Flow Rate, gpm	Comments
3	2.0	a	a - counter-
4	0.4	a	current system
6	2.0	2.0	at 1.5 gpm
8	0.0	0.0	
9	0.0	b	b - counter-
10	2.0	b	current system
11	2.0	b	at 1 gpm
TOTALS	6.4 gpm	4.5 gpm	

Recommendations

1. Interconnect tank numbers 3 and 4 to form a double counter-current rinsing system with influent feed rate restricted to 1.5 gpm.

2. Interconnect tank numbers 9, 10 and 11 to form a triple counter-current rinsing system with influent feed rate restricted to 1.0 gpm.

3. Utilize tank number 8 as recovery rinse with recycle to plating tank.

4. Supply low level air agitation to tank numbers 3, 4, 6, 9, 10 and 11.

Table 11

Company B
Line 7 Analysis

Tank Identification

1. Alkaline Clean (150°F)
2. Rinse
3. H_2SO_4 Clean
4. Tin Plate
5. Brass Plate
6. Copper Plate
7. Rinse

Future - Cyanide Rinse

Wastewater Sources

Tank No.	Present Flow Rate, gpm	Suggested Flow Rate, gpm
2	3.9	3.0
7	3.9	3.0
Future	0.0	3.0
TOTALS	7.8 gpm	9.0 gpm

Recommendations

1. Install/calibrate flow restriction valves to tank numbers 2 and 7 as indicated.
2. Install a new tank with influent flow rate set at 3.0 gpm to provide segregation of cyanide bearing wastewaters.
3. Provide low level air agitation to rinse tank numbers 2, 7 and future.

Table 12

Company B
Line 8 Analysis

Tank Identification

1.	H_2SO_4 Clean	10.	Nickel Plate
2.	Rinse	11.	Nickel Plate
3.	Nickel Plate	12.	Nickel Plate
4.	Nickel Plate	13.	Nickel Plate
5.	Nickel Plate	14.	Nickel Plate
6.	Nickel Plate	15.	Nickel Plate
7.	Nickel Plate	16.	Nickel Plate
8.	Nickel Plate	17.	Rinse
9.	Nickel Plate	18.	Rinse (130°F)

Wastewater Sources

Tank No.	Present Flow Rate, gpm	Suggested Flow Rate, gpm
2	3.2	3.2
17	10.1	5.0
18	0.5	0.5
TOTALS	13.8 gpm	8.7 gpm

Recommendations

1. Install a 5 gpm flow restriction valve on the influent feed line to tank number 17.

2. Supply low level air agitation to rinse tank numbers 2 and 17.

Table 13

Company B
Total Plant Water Consumption Summary

LINE	PRESENT DISCHARGE, gpm	SUGGESTED DISCHARGE, gpm	ESTIMATED REDUCTION, gpm
1	15.8	10.6	5.2
2	14.4	8.7	5.7
3	14.8	9.7	5.1
4	28.4	9.8	18.6
5	6.4	4.5	1.9
6	13.1	0	13.1
7	7.8	9.0	(1.2)
8	13.8	8.7	5.1
Tumblers	22.5	17.5	5.0
TOTALS	137 gpm	78.5 gpm	

Percent reduction in flow = $\frac{137-58.5}{137}$ = 57%

Table 14

Company B
Economic Impact of Water Conservation

OPTION	FLOW RATE gpm	PURCHASE WATER, $/yr[1]	SEWER USER CHARGE, $/yr[2]	TOTAL COST
1. No Change - Present Conditions	137	$37,200	-----	$37,200
2. No Change - Conditions in 1984	137	$37,200	$1,400 to $5,300	$38,600 $42,500
3. Implement Water Conservation Now	79	$24,000	-----	$24,000
4. Implement Water Conservation in 1984	79 79	$24,000	$ 800 to $3,000	$24,800 $27,000

SUMMARY[3]

A. Annual savings available now: $13, 200.

B. Annual savings available in 1984: $13,800 to $15,500.

Notes

1. Present billing structure assumed stable until 1984.

2. Currently under review but expected to be from $0.21 to $0.80 per 1000 cubic feet depending upon type of waste treatment implemented in New Bedford, MA. The higher end of the noted range is expected.

3. Does not include savings from smaller pretreatment system sizing and reduced WWT operation costs.

Table 15

Company C
Rinsewater Consumption Summary

Process[a] Number	Description	Rinsewater Flowrates, gpm Measured Conditions[b]	Following Modifications[b]
1	Cleaning	26.5	5.0
2	Zinc Plating	17.7	5.0
3	Cadmium Plating	11.4	1.5 (5 max.)
4	Silver Plating	(10 max.)	(5 max.)
5	Nickel Plating	5.7	2.0[c] (5 max.)
6	Tin Plating	5.0	2.0[c] (5 max.)
7	Cyanide Dip	6.6	2.0[c] (5 max.)
8	Cadmium Plating	(10 max.)	(2 max.)
9	Copper Plating	(10 max.)	(2 max.)
10	Zinc Plating	(10 max.)	(2 max.)
11	Strip Rinse	2.0	(1 max.)
12	Brite Dip	12.0	2.0
13	Miscellaneous	17.0	4.0 (6 max.)
	TOTALS	103.9	23.5 (50 max.)

PERCENT REDUCTION - 77%

Notes:

a. Numbers coincide with Process Schematics Figures 2 & 3.

b. Intermittent flows shown in parentheses.

c. Estimated average continuous flow due to production.

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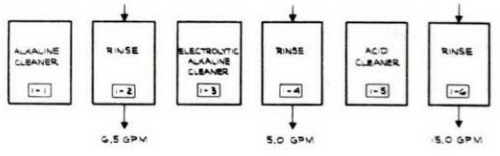
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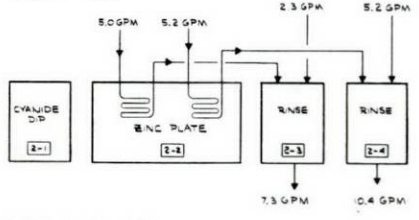
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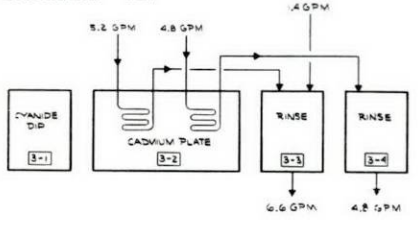
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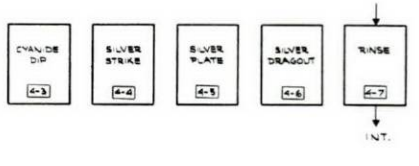
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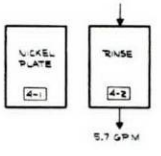


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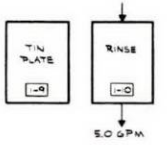


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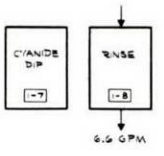
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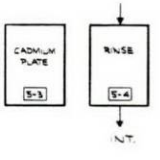
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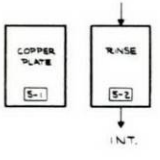
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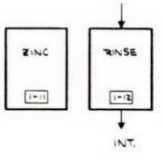
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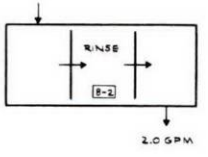
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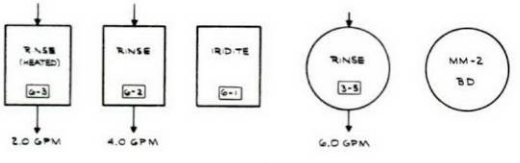
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STRIP RINSE (11)



BRITE DIP (ZN) (12)



MISCELLANEOUS (13)

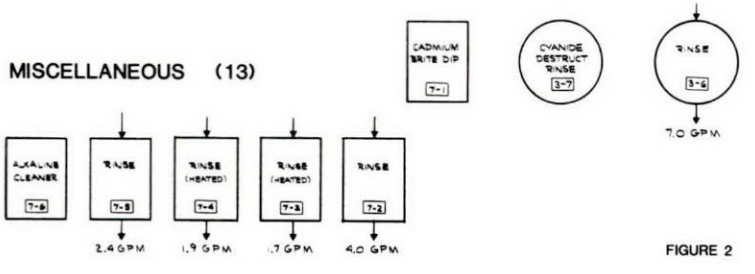
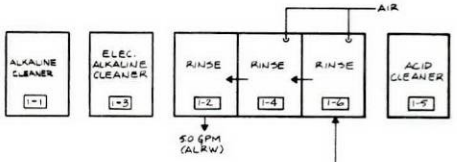
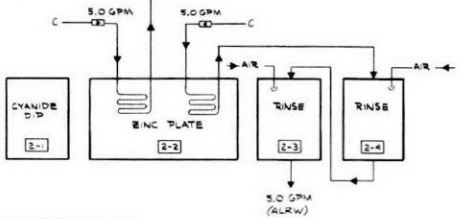


FIGURE 2

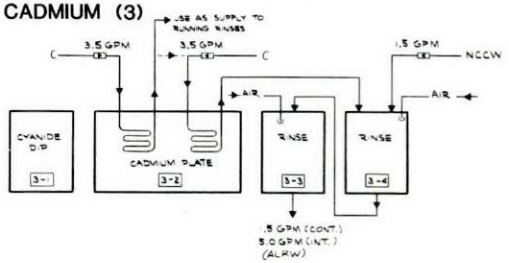
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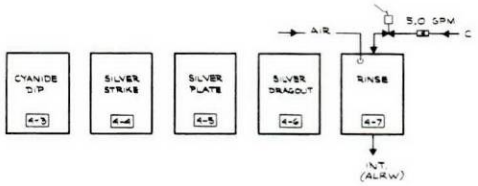
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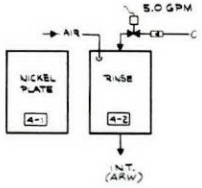
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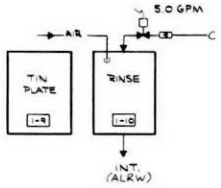
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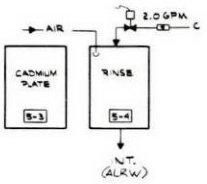
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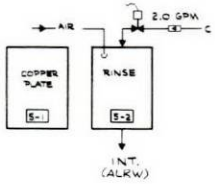
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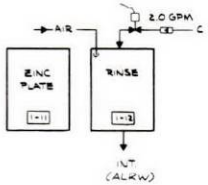
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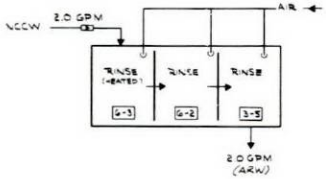
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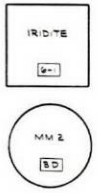


ZINC (10)



BRITE DIP (ZN) (12)





LEGEND

- FLOW RESTRICTION VALVE
- SOLENOID VALVE
- C CITY WATER
- W WELL WATER
- NCCW NON CONTACT COOLING WATER
- INT INTERMITTENT
- ARW ACIDIC RINSEWATER DRAIN
- ALRW ALKALINE RINSEWATER DRAIN

MISCELLANEOUS (13)

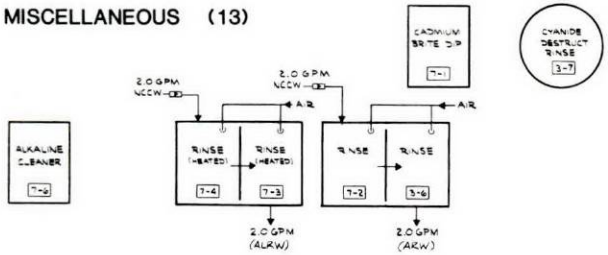


FIGURE 3

C-2

Environmental I
Session C

What's New with Reverse Osmosis in Metal Finishing Waste Treatment

Peter S. Cartwright
C_3 International
Minneapolis, MN

WHAT'S NEW WITH REVERSE OSMOSIS IN METAL FINISHING WASTE TREATMENT

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I. Introduction

The unit operation of reverse osmosis is readily adaptable to the treatment of metal finishing wastes for the following reasons:

- It is a low energy process utilizing pump energy only
- The equipment is simple and easy to maintain
- It is a continuous process as opposed to batch treatment
- It is possible to use this process to continuously return the solute to the plating bath as well as to recover all of the rinse water.

Because reverse osmosis has the ability to separate dissolved solids (both inorganic and organic) from pure water, this process is used to concentrate the dissolved solids portion of the plating rinse stream. In virtually all cases, the pure water can be recycled back to the process, and, depending upon a number of factors, the concentrate stream can be returned to the plating bath, directed to the waste treatment system, or hauled away. Ideally, to achieve "zero discharge:, the concentrate stream should be returned to the plating bath; however, factors such as bath temperature, (which determines the rate of evaporation from the plating bath) degree of contamination of the rinse water, source of rinse water and engineering design considerations of the reverse osmosis system determine its disposition.

The production rate of a particular reverse osmosis membrane is a function of such important variables as:

Feed water temperature

Dissolved solids type and concentration in the feed water

Applied pressure

System Design

Particular membrane polymer characteristics

Obviously, to be effective, the membrane polymer must be resistant to chemical attack by the dissolved solids in the solution in which it is operating. Whereas all of the commercially available polymers exhibit excellent tolerance to certain chemical extremes, none has yet been developed that will satisfactorily function in all extremes, i.e., there is no "optimum" membrane at this time. The chemical factors that present the greatest problems to membrane polymers include pH extremes, strong oxidizing agents and aromatic hydrocarbons. Another polymer characteristic that is important to manufacturers of reverse osmosis membrane is rejection, usually expressed as a percentage. The condition that can most significantly affect membrane performance is "fouling" resulting from suspended or precipitated solids coating the membrane surface. A "fouled" membrane will usually show a reduction in both pure water (permeate) flow and permeate quality. Proper prefiltration is absolutely essential to insure optimum membrane life; however, for baths that are continuously filtered and otherwise properly maintained, the reverse osmosis system usually requires no more than 5 micron prefilter cartridges.

The resistance of a membrane element to fouling is also a function of its configuration. To date, the only practical configurations for most reverse osmosis applications are the hollow fiber permeator (Figure 1) and the spiral wound module (Figure 2). Because of the close packing density and small diameter of the fibers in the permeator, it is much less widely used than the spiral wound configuration.

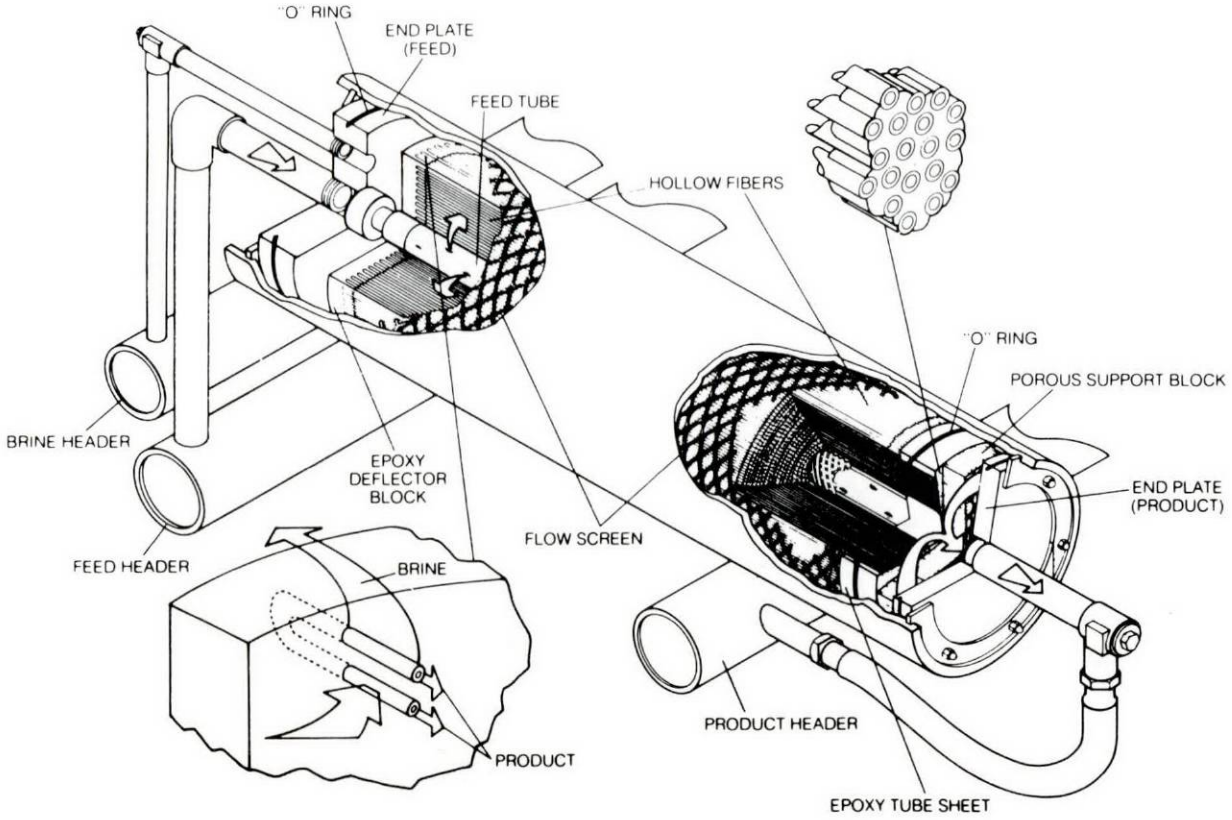


Figure 1. Hollow Fiber Membrane Element

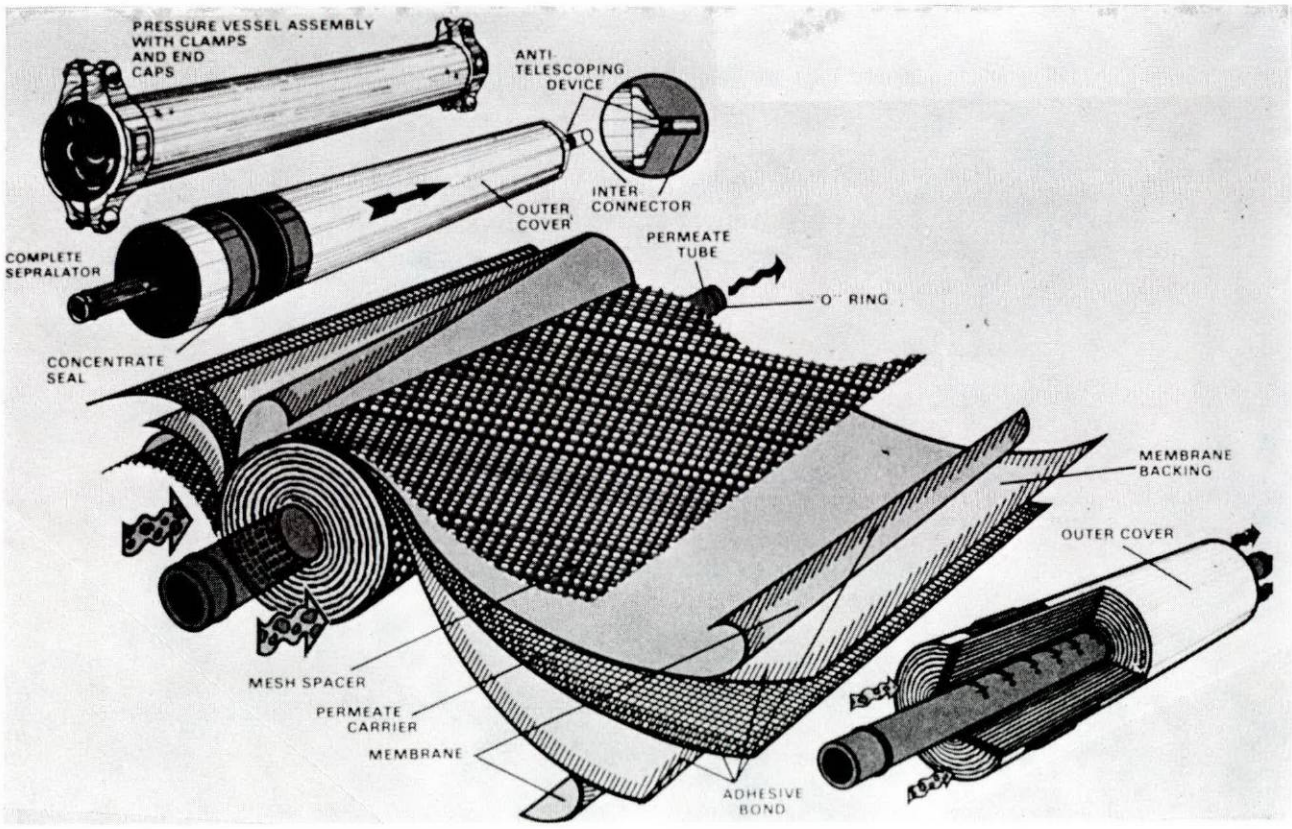


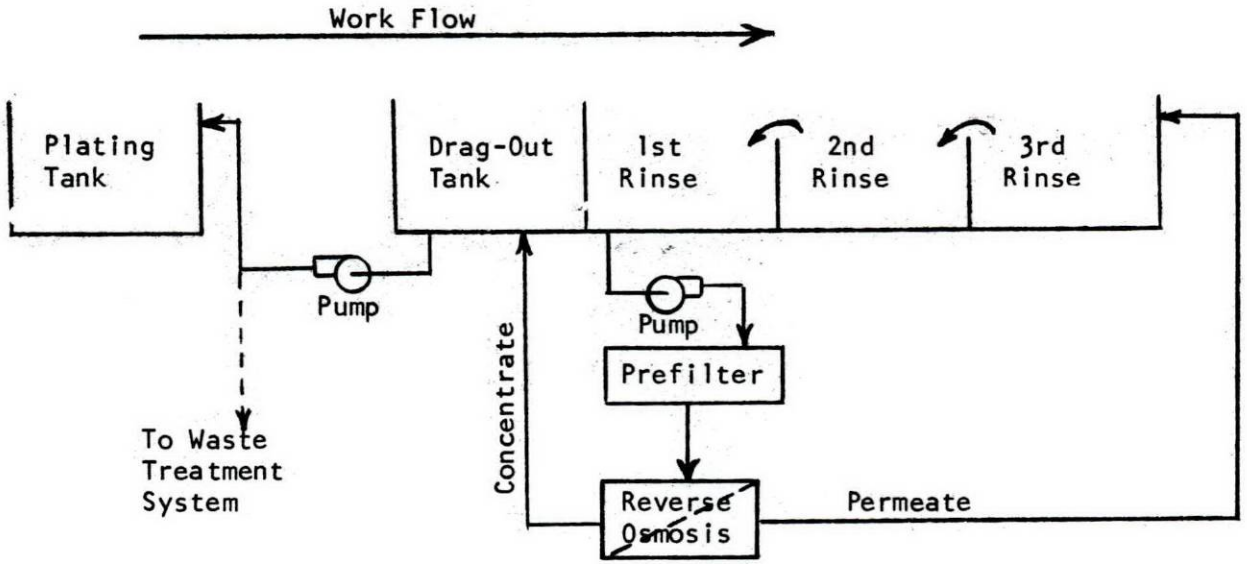
Figure 2. Spiral Wound Membrane Element

Figure 3 represents a typical reverse osmosis system operating on the first rinse and returning the concentrate to the plating tank.

Figure 4 illustrates a reverse osmosis system returning the concentrated bath constituents to a "drag-out" tank for eventual return to the plating tank.

This paper summarizes the existing reverse osmosis installations and addresses the potential applications resulting from the introduction of the new thin film composite membrane polymers.

FIGURE 4 - REVERSE OSMOSIS SYSTEM UTILIZING "DRAG-OUT" RINSE



II. Review of Existing Applications

A. Nickel Installations

There are at least 150 systems operating on various nickel baths, mostly utilizing cellulose acetate membrane elements and with recoveries in the range of 90-97%. The relatively high evaporation rate resulting from the elevated bath temperature generally allows complete recycle of the concentrate stream as well as the permeate stream.

Type of Bath	Membrane Element	Membrane Life	System Payback	Years of System Operation	Items Plated
Watts	Spiral Cellulose Acetate	2 years	12 months	4	Luggage Hardware
Watts	Spiral Cellulose Acetate	1 year	12 months	5	Wire Shelving
Watts	Spiral Cellulose Acetate	1 year	16 months	5	Wire Shelving
Watts	Spiral Cellulose Acetate	1 year	24 months	5	Steel Stamping
Watts	Spiral Cellulose Acetate	1-1/2 years	36 months	7	Job Shop
Watts	Spiral Cellulose Acetate	1-1/2 years	24 months	8	Job Shop
Watts	Spiral Cellulose Acetate	1 year	30 months	5	N/A
Watts	Spiral Cellulose Acetate	2 years	8 months	6	Electrical Devices
Watts	Spiral Cellulose Acetate	4 years	11 months	8	Plumbing Hardware
Watts	Spiral Cellulose Acetate	3 years	8 months	9	Steel Furniture
Watts	Spiral Cellulose Acetate	1-1/2 years	18 months	6	Electrical Devices
Bright Nickel	Spiral Cellulose Acetate	1-1/2 years	14 months	11	Plumbing Hardware

(Continued)

Type of Bath	Membrane Element	Membrane Life	System Payback	Years of System Operation	Items Plated
Bright Nickel	Spiral Cellulose Acetate	2 years	36 months	4	N/A
Bright Nickel	Spiral Cellulose Acetate	1-1/2 years	12 months	5	Automotive Bumpers
Bright Nickel	Spiral Cellulose Acetate	2 years	8 months	9	Hand Tools
Bright Nickel	Spiral Cellulose Acetate	2-1/2 years	20 months	8	Brass Stampings
Sulfamate	Spiral Cellulose Acetate	2 years	13 months	5	Electrical Terminals
Sulfamate	Hollow Fiber Polyamide	2-1/2 to 3 years	N/A	3	P.C. Board Contacts

B. Copper Sulfate Installations

Approximately 12 reverse osmosis systems are operating on rinses from proprietary copper foil manufacturing processes.

Number of Systems	Feed Flow (gpm)	Membrane Element	Concentrate Composition	System Recovery	Membrane Life	Years of System Operation
10	60	Hollow Fiber, Polyamide and Cellulose Triacetate	Waste Treatment	75%	1-3 years	5
2	40	Spiral Wound, Thin Film Composite	Reuse	87.5%	1 year	7

Pretreatment requirements:

Hollow fiber polyamide element - 1 micron filter cartridge

Hollow fiber cellulose triacetate element - 3 micron filter cartridge

Spiral wound thin film composite element - 5 micron filter cartridge

C. Zinc Sulfate Installations

One reverse osmosis system is operating on the zinc sulfate rinse from a proprietary copper foil manufacturing process. The system utilizes spiral wound thin film composite membrane elements with a feed rate of 45 gpm and recovery of 87.5%. Although the system has been in for more than seven years, the thin film composite element has been in for just over a year and is working well.

The concentrate stream is further reduced in volume in an evaporator (operating at 90% recovery) and returned to the bath.

D. Brass Cyanide Installations

Approximately five reverse osmosis systems are operating on the brass cyanide rinses from a proprietary copper foil manufacturing process. Both polyamide and cellulose triacetate hollow fiber membrane elements are utilized. Feed rate is approximately 60 gpm per system at a recovery of 90%. The systems have been operating for five years and the membrane element life is 3-4 years. Pretreatment is one micron filter cartridges for the polyamide elements and 3 micron filter cartridges for the cellulose triacetate elements.

E. Copper Cyanide Installations

1. Printed circuit contact plating application - first flowing rinse fed to a polyamide hollow fiber membrane element at a rate of approximately 210 gph.

   The system is operating at approximately 90% recovery, with a portion of the concentrate recycled to the plating bath and remainder to the waste treatment system. All of the permeate is reused in the rinse stream.

   The system has been operating for more than three years. Pretreatment is one micron filter cartridge followed by activated carbon. Membrane elements have lasted for 2-1/2 to 3 years.

2. Medical device plating application - lead brass substrate, first rinse fed to a polyamide hollow fiber membrane element.

   The system is operating at 93% recovery, with approximately one-half of the concentrate recycled to the plating bath and the rest to the waste treatment system. All of the permeate is reused in the rinse stream.

   The system has been in operation for more than seven years. Pretreatment is by 1.2 micron filter cartridges followed by 0.45 membrane filters, and the membrane life is about 4-1/2 years.

F. Chrome Installations

A copper foil manufacturer has been investigating the use of spiral wound thin film composite membrane elements for use in recovering hexavalent chrome from the rinses in a proprietary manufacturing process. Hollow fiber membrane elements lasted only 1-2 months before irreversibly fouling, while the spiral wound configuration has performed satisfactorily for over 6 months with only 5 micron cartridge filtration as pretreatment.

III. The Promise of New Membranes

The preceding section lists a number of existing applications for zero discharge reverse osmosis systems. It should be noted that with few exceptions, the bulk of the existing installations utilize spiral wound cellulose acetate reverse osmosis membrane elements operating on nickel plating rinses. The viability of reverse osmosis technology in zero discharge applications is a function of the chemical characteristics of the membrane element, and the characteristics of the plating bath.

Until recently, the spiral wound membrane configuration has only been available with cellulose acetate polymer, the chemical characteristics of which have limited its application to low pH baths such as nickel; the temperature of the plating bath determines the evaporation rate of water from the bath, thereby fixing the maximum concentrate rate from the reverse osmosis system.

A new family of polymers known as thin film composites is now available from six or seven membrane manufacturers. These thin film composites exhibit improved application characteristics as indicated on the following chart.

	Spiral Wound Cellulose Acetate	Hollow Fiber Polyamide	Spiral Wound TFC
pH Stability	2-8	4-11	2-12
Fouling Resistance	Good	Poor	Good
Oxidation Resistance	Good	Poor	Fair-Poor
Temperature Stability	95°F.	95°F.	120°F.

An important definition is in order here:

The recovery of a reverse osmosis system is defined as that portion of the feed stream quantity that goes through the membrane and comes out as permeate. Recovery is always expressed as a percentage, so 100 minus recovery is that percentage of the feed stream that becomes the concentrate. Most zero discharge systems operate at recoveries in excess of 95% (the concentrate stream is less than 5% of the feed stream volume). Obviously, for systems

operating on plating baths with lower temperatures, because the evaporation rate is lower, the recovery must be higher in order for all of the concentrate stream to be fed directly to the plating bath. It also stands to reason that as the recovery goes up (the concentrate volume goes down), the concentration of salts in the concentrate stream will increase. This increase can be rather marked; for example, the concentration of salts in a system operating at 98% recovery is 2-1/2 times greater than the concentration in a system operating at 95% recovery.

Thus, the osmotic pressure at these high recoveries becomes the limiting factor in system design.

This means that regardless of the membranes used, lower temperature baths are more difficult to treat with reverse osmosis than those operating above 120°F. In order to overcome this problem, such techniques as air agitation of the plating bath, supplemental evaporation of the concentrate stream, using the concentrate in an air scrubber and bleeding part of the bath into the reverse osmosis unit have all been used with success.

Specific testing of two different thin film composite membranes has been performed on zinc cyanide, copper cyanide and brass cyanide rinses.

Both membranes exhibited excellent rejection of the zinc, copper and cyanide ions; however, the low temperature of these baths require that one or more of the techniques outlined in the preceding paragraph be utilized.

Although some testing remains to be done an all electroplating baths other than nickel, reverse osmosis has proved be be a viable process for "zero discharge" applications, and will continue to become an important waste treatment process in the future.

- END -

C-3

Environmental I
Session C

BPT to BAT

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BPT TO BAT

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Several years ago the General Electric Company decided to upgrade the wastewater treatment system at its manufacturing plant in Florence, South Carolina. The improvements included increasing the hydraulic and chemical treatment capacity, as well as the degree of treatment. Based on discussions with an independent consulting firm, it was decided that a phased program of system improvements should be implemented.

It was also decided that reducing the load being generated, rather than enlarging the existing plant, was the best way to increase the effective hydraulic and chemical treatment capacity. The first phase of the program was a water and waste reduction study of the existing plating facilities. The goal of this study was to reduce water consumption by 30 percent to provide for increased future production, without having to increase the size of the existing treatment plant.

Table 1 lists the various waste producing operations.

Table 1

MANUFACTURING OPERATIONS

1. Printed Circuit Board Fabrication
2. Aluminum and Zinc Die Casting
3. Zinc Plating
4. Chromium (VI) Plating Surface Preparation
5. Copper-Tin Plating
6. Plastic Injection Molding
7. Chemical Polishing and Cleaning
8. Precious Metal Plating

The consultant made a detailed study of each tank in each of the plating lines and proposed a series of general recommendations. Specific recommendations (along with detailed specifications and drawings) were made where major changes were required. The following is a summary of the general recommendations:

a. The water inlet should be changed to add water through a perforated sparger pipe laid along the bottom of the tank, parallel to but on the opposite side from, the overflow weir.

b. Tanks that are used infrequently should have a conductivity controller to actuate a solenoid valve, to start and stop water as required.

c. Tanks that are used on a regular basis should utilize a fixed water flow controller.

d. Rinse tanks should be air agitated with a perforated air sparger pipe laid diagonally across the tank. The sparger pipe should be weighted to keep it in position.

e. Top sprays should be used with a solenoid in the water supply line and actuated by the automatic conveyor, so that water is sprayed only as the rack is lifted up through the zone of influence.

f. Where possible, a master water supply valve should be placed in the water supply to each individual processing line. Thus, whenever a particular line is not in operation, the water supply to that one line can be shut off without disturbing the flow settings.

g. Tank bridges should be provided between tanks so that dragout will drain to the tank of origin.

General Electric implemented the recommendations and realized a reduction of water usage of approximately 40 percent.

Phase II encompassed a detailed study of the existing wastewater treatment system for optimizing its operation and reducing chemical consumption and sludge generation.

The existing system, as shown in Figure 1, consisted of three segregated pretreatment systems followed by combined final treatment. The final stages of treatment consisted of: pH adjustment and precipitation in the final mix tank; addition of lime for coagulation in a secondary final mix tank; addition of polymer; and flocculation followed by settling and sludge dewatering in a solid bowl centrifuge, with centrate return for treatment.

The three pretreatment systems were:

a) Cyanide and copper chelates - Wastewater flowed by gravity to a membrane-lined holding basin and transfer sump. Wastes were then pumped to a two-stage system for alkaline chlorination.

b) Chrome - Wastewater from chrome plating and chromate conversion coating operations flowed to a membrane-lined holding basin and transfer sump. Wastes were then pumped to an acid/sulfonation system for reduction of hexavalent chrome.

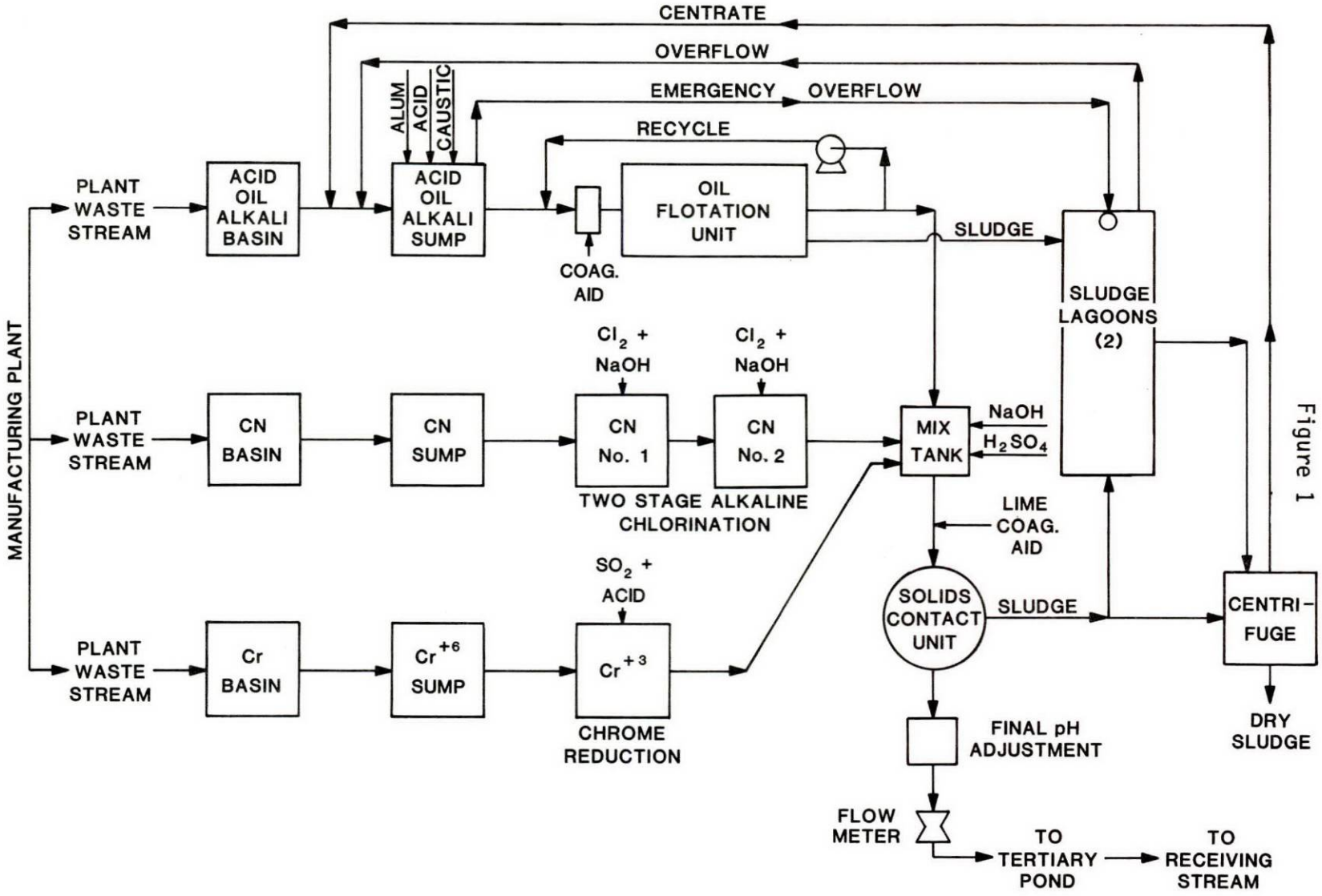

CENTRATE
OVERFLOW
EMERGENCY OVERFLOW
RECYCLE
ALUM
ACID
CAUSTIC
PLANT WASTE STREAM
ACID OIL ALKALI BASIN
ACID OIL ALKALI SUMP
COAG. AID
OIL FLOTATION UNIT
SLUDGE
SLUDGE LAGOONS (2)
MANUFACTURING PLANT
PLANT WASTE STREAM
CN BASIN
CN SUMP
Cl_2 + NaOH
CN No. 1
Cl_2 + NaOH
CN No. 2
TWO STAGE ALKALINE CHLORINATION
MIX TANK
NaOH
H_2SO_4
LIME COAG. AID
PLANT WASTE STREAM
Cr BASIN
Cr^{+6} SUMP
SO_2 + ACID
Cr^{+3}
CHROME REDUCTION
SOLIDS CONTACT UNIT
SLUDGE
CENTRI-FUGE
DRY SLUDGE
FINAL pH ADJUSTMENT
FLOW METER
TO TERTIARY POND
TO RECEIVING STREAM

Figure 1

c) Acid-Alkaline - Oil (A-A-O) - Wastewaters flowed by gravity to a membrane-lined holding basin and treatment/transfer sump where pH was controlled and alum was added as an oil/water emulsion breaker. Wastes were then pumped to a dissolved air flotation (DAF) unit where polymer was added to enhance solids separation.

The following recommendations were made and implemented to optimize treatment and reduce sludge:

a) The holding basins were designed to be operated at one of three levels in the case of cyanide and chrome, and one of two levels in the case of AA-O. All three systems were being operated at the minimum level.

   It was recommended that the cyanide and chrome basins be operated at mid-level and the A-A-O at the upper level, and that air agitation be added to each of the three basins. The goal in each case was concentration equalization, since the plant does not have a separate dump handling system for concentrates.

b) All pretreatment reaction tanks were air agitated, as was the final mix (or neutralization) and precipitation tank. While air agitation in the cyanide and chrome pretreatment tanks increases chemical consumption, it does not affect effluent quality. Air agitation in the final mix tank was affecting effluent quality.

   Enough air was entrained in the flow to produce an excessive amount of floaters in the clarifier. A recommendation was made and implemented by General Electric to replace the air system with a mechanical agitator. This was difficult and expensive, due to tank dimensions and low head room. It was accomplished by using an angle drive and a two-piece shaft. This modification improved the performance of the clarifier but did not eliminate all solids carryover.

c) The 10-year-old existing plant was experiencing difficulties with the pH and ORP electrode assemblies and the reference electrodes, which were of the old remote KCL reservior variety. All pH and ORP electrode assemblies and electrodes were replaced to improve the reliability of these sensors and the control loops they served.

d) Jar tests were conducted on the A-A-O system. Based on these tests, the control pH was lowered and alum dosage reduced. This improved the operation of this subsystem and reduced the quantity of sludge produced.

Phase III consisted of an evaluation of the modified existing system effluent quality. Periodically, the effluent would be out of specification in heavy metals. Studies on filtered and unfiltered wastewater samples indicated that the problem vacillated between metals in solution and metals in fine suspension.

From the above, it was concluded that a polishing filter would resolve the problem of particulate carryover from the clarifier, but that a modification of chemistry would be required to remove the soluble or complexed metal. The resulting recommended system was a combination of insoluble starch xanthate (ISX) and a filter.

Phase IV was a pilot test of this proposed system. Since ISX had become commercially available, a supply was ordered and a refrigerated milk chest was borrowed to prevent deterioration of the ISX.

Parallel tests were run on two different types of filters -- a diatomaceous (D.E.) filter and a moving bed sand filter. In the initial test (see Figure 2), ISX was fed to an agitated reaction vessel, and separate pumps fed the sand filter and a precoated D.E. filter. The D.E. filter produced high clarity water that was low in metals. The filter runs, however, were very short. A body feed system was added that extended the runs somewhat, but significantly added to sludge volume because of the D.E.

The sand filter experienced no pressure drop problems, but did not remove the ISX. Settling tests on an ISX slurry indicated a very fine, almost colloidal, suspension that would not readily settle -- even with polymer addition. Discussions with the manufacturer of the ISX indicated that they were now using a much finer milled starch to make the ISX.

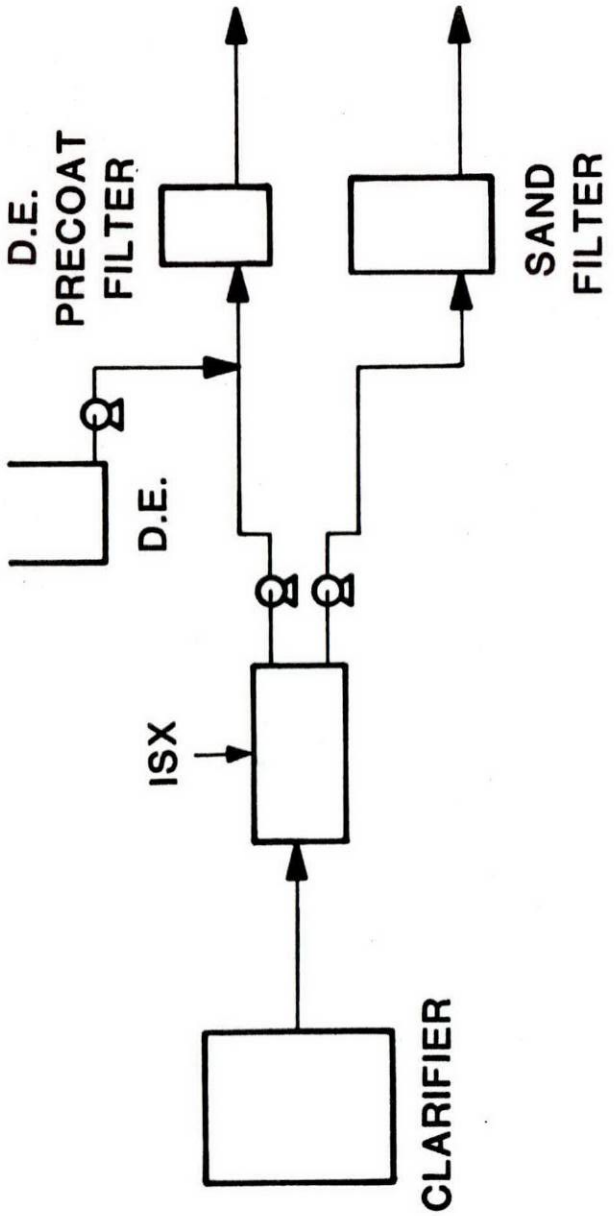
Laboratory jar tests indicated that small additions of alum and polymer after the ISX reactor would produce a separable floc. Despite the fact that our experience with the D.E. filter was not typical of previous experience, we decided to reject it for this particular application because of high consumption of filter aid.

The pilot studies were continued (See Figure 3), with the sand filter preceded by pretreatment with ISX, followed by coagulation with alum, addition of polymer, and flocculation. This treatment train provided repeatable and excellent effluent quality.

Phases V and VI were the detailed design and construction of an add-on polishing waste treatment system (see Figure 4). The new system consists of ISX reaction, alum coagulation, polymer addition, flocculation, and sand filtration. The system has the flexibility to operate in any one of several modes, from the simplest mode of sand filtration for removal of suspended solids, to the full mode for removal of collodial solids and complexed metals.

The final pH adjustment tank was utilized as a wet well for dual transfer pumps. A proportional level control system was utilized to throttle a pneumatically positioned butterfly valve and to provide a proportional modulating control offlow to the polishing system, thus eliminating shock hydraulic loadings. The control signal is also used, with a pneumatic to pulse duration transducer, to provide automatic proportional control of chemical feed metering pumps for ISX, alum, and polymer.

Figure 2



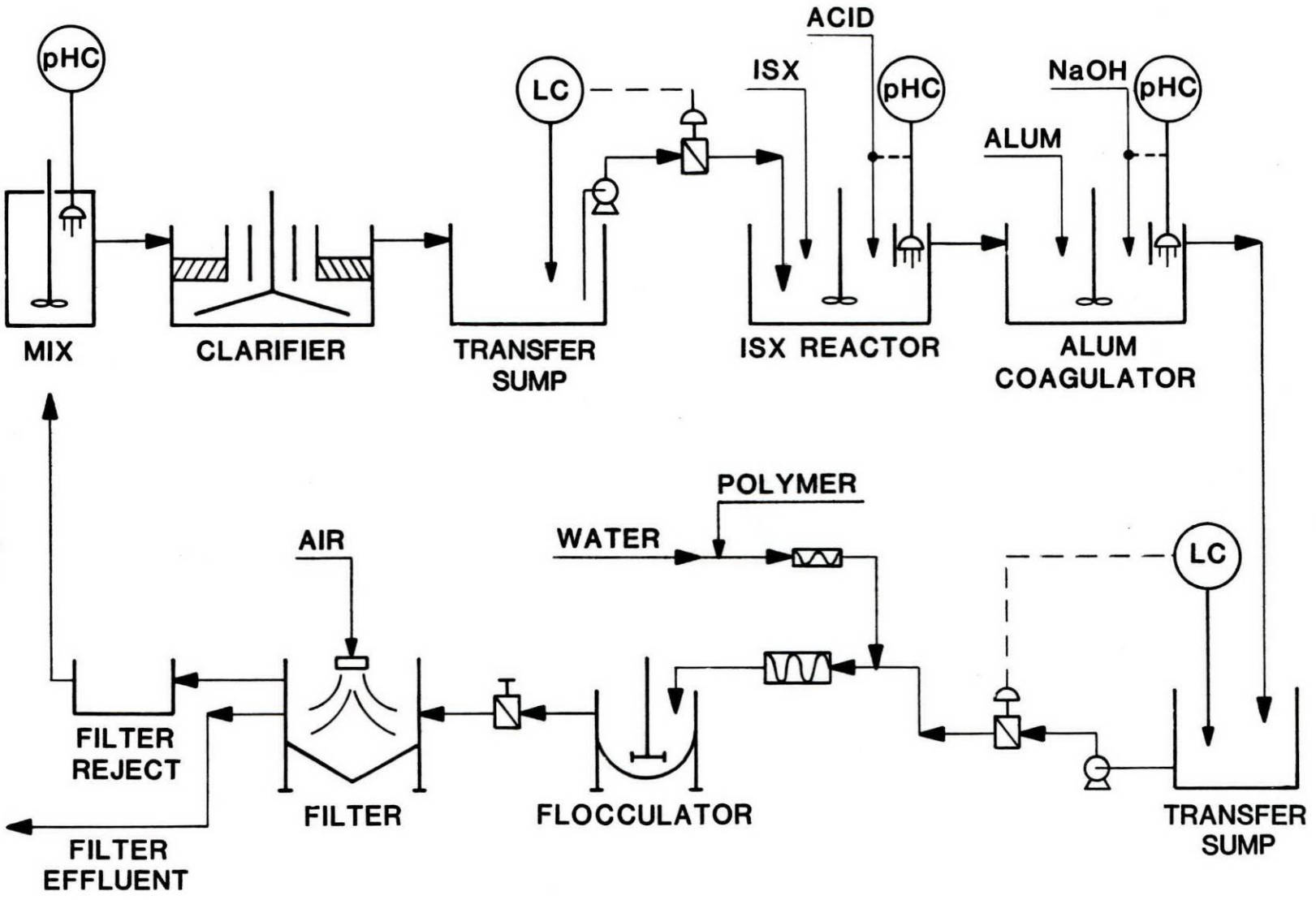

pHC
LC
ISX
ACID
pHC
NaOH
pHC
ALUM
MIX
CLARIFIER
TRANSFER SUMP
ISX REACTOR
ALUM COAGULATOR
POLYMER
AIR
WATER
LC
FILTER REJECT
FILTER
FLOCCULATOR
TRANSFER SUMP
FILTER EFFLUENT

Figure 4

The pumps will transfer the clarifier effluent to the ISX reaction tank. ISX readily reacts with heavy metals by an ionic exchange mechanism to form a very insoluble complex. Its solubility product is considerably less than that of the heavy metal hydroxide; hence, it is better able to precipitate and remove metals in the presence of chelating agents. A metering pump feeds the ISX (see Figure 5) in proportion to flow, and a pH control system is used to automatically and proportionally control the sulfuric acid feed to maintain the desired pH.

The acid feed must maintain the pH in this reactor at approximately 7.0. The acid demand is created by the ISX slurry, which is highly alkaline, plus the fact that the clarifier effluent has a pH of 9.5.

Flow is by gravity from the ISX reaction tank to the alum coagulation tank. To facilitate the removal of collodial suspended solids in the sand filters, alum is added by a metering pump in proportion to flow. A pH control system is used to automatically and proportionally control the feed of caustic soda, thus maintaining the desired pH by overcoming the acidity of the liquid alum.

Following alum coagulation, wastewater flows by gravity to a holding tank where automatically throttled pumps transfer the waste to the flocculation tank. These pumps have the same type of level control system as the clarifier effluent transfer pumps. An in-line static mixer was included in the transfer line, and polymer is fed by a metering pump in proportion to flow just upstream of the static mixer to enhance flocculation. The flocculated waste then flows by gravity to four parallel upflow sand filters that are automatically and continually cleaned. The piping system is designed to provide minimal head loss and to split flow, with only minor adjustment of the filter inlet valves without destroying the floc. Filters were designed at the low end of the design range. Four filters were used, so that with one filter out of service we were still within the upper end of the design range.

Wastewater is introduced into the bottom of the filter, and flows up through the sand bed and over the filtrate weir. An air lift in the filter lifts the dirty sand from the bottom of the filter to a washer, and clean sand is deposited on top of the sand bed. This provides continuous operation without shutdown for backwash. The reject stream containing the solids removed by the sand bed flows by gravity to the reject waste tank, from where it is transferred back to the original system. The reject stream is approximately 10 percent of flow in this particular application. The filtrate flows by gravity and ties back into the original treatment system effluent outfall.

In the original system, lime was added as a coagulant aid. The new system, with its recycle of solids from the sand filter, has enabled General Electric to reduce lime consumption from approximately 400 to 100 pounds per day. This lime reduction reduces chemical consumption and sludge production.

The ISX used in the pilot studies required the use of alum, with a dosage of approximately 50 mg/l as aluminum oxide (AlO_3). A modification in the manu-

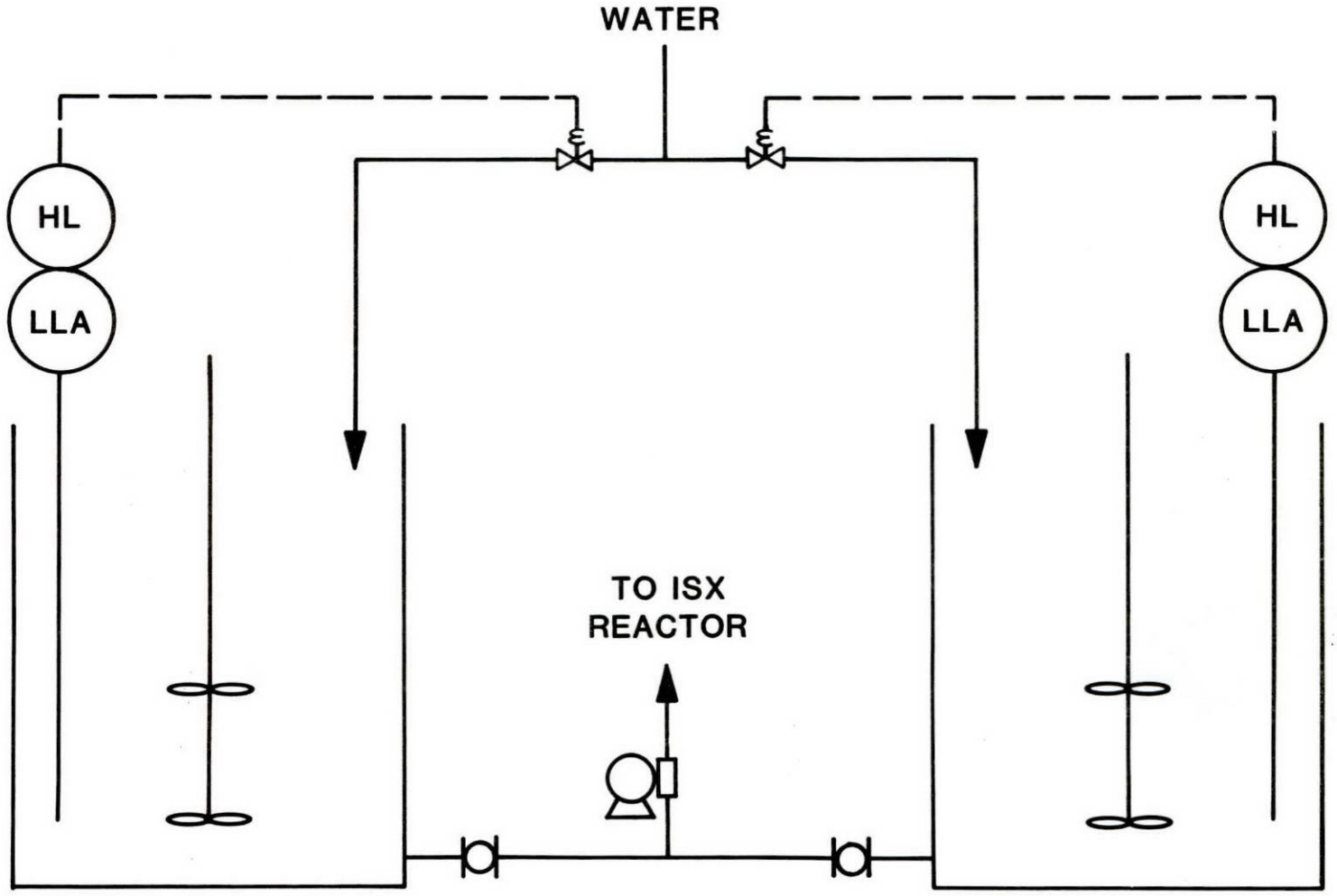


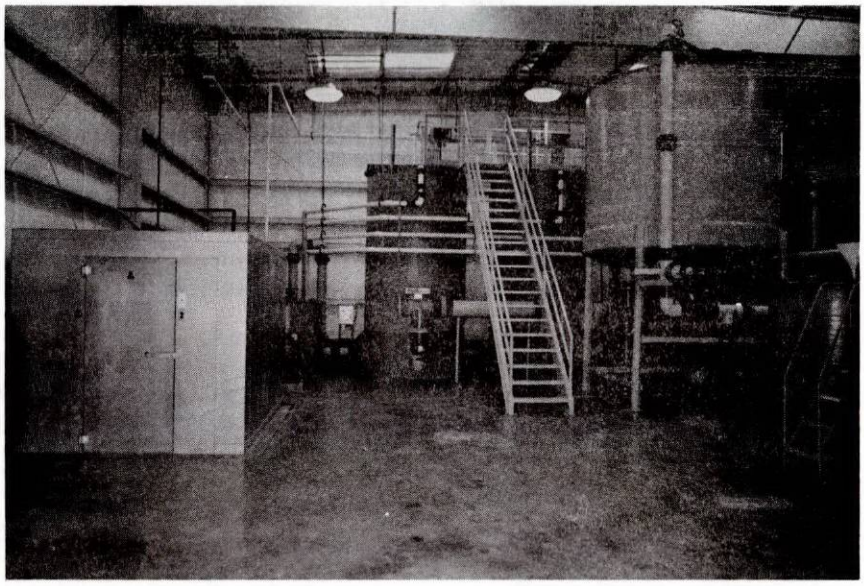
Figure 5

facture of the ISX has eliminated the need for alum. In the full scale system, the use of polymer has been sufficient to produce high clarity effluent in most cases.

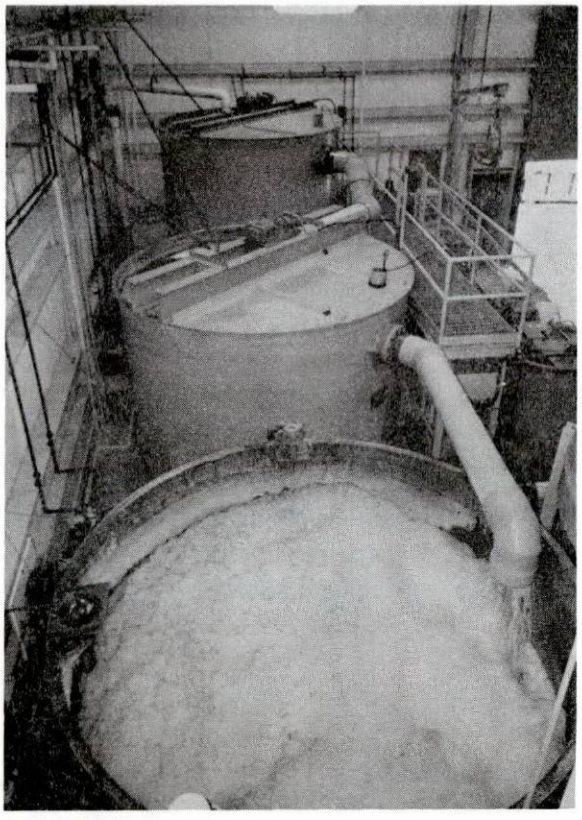
Occasionally, the clarifier effluent will contain fine colloidal-type solids which pass through the filter. When this occurs, the alum feed is reinstated to form the floc necessary for producing the clarity and metal removals required.

The system, then, is highly flexible. If the problem is soluble copper due to increase in the proportion of chelates in the wastewater, ISX feed can be increased to compensate. If, on the other hand, the problem is solids removal in the clarifier, alum feed can be used to solve the problem. Thus, an analysis of clarifier effluent and filter effluent enables the effluent quality to be optimized, and sludge production and operating costs minimized.

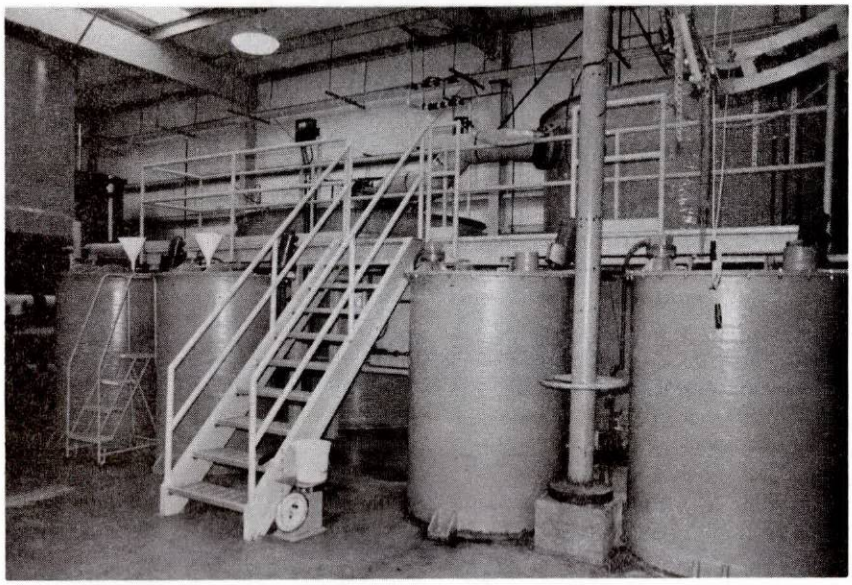
Using a phased approach, General Electric was able to increase the effective capacity of their existing wastewater treatment system. They were also able to add a polishing system capable of meeting variable production needs and environmental standards.



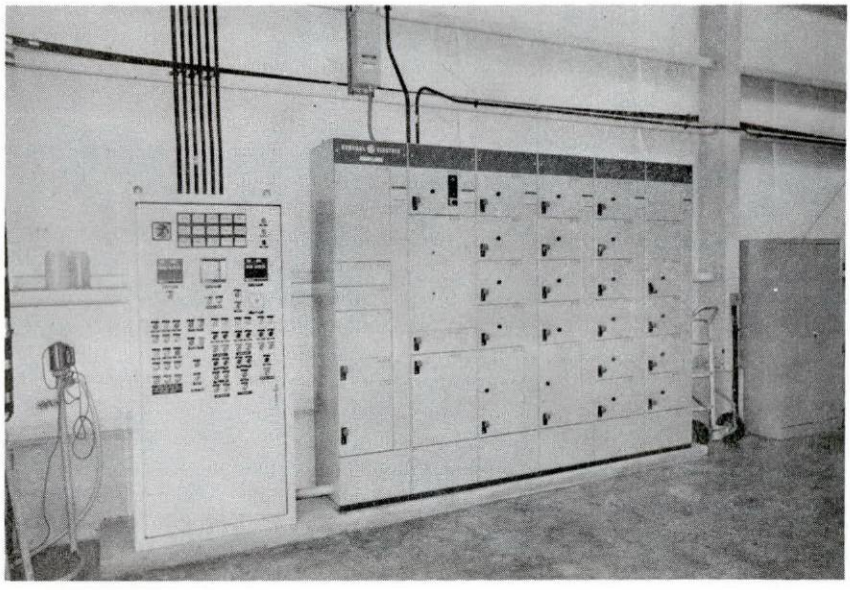
FILTERS



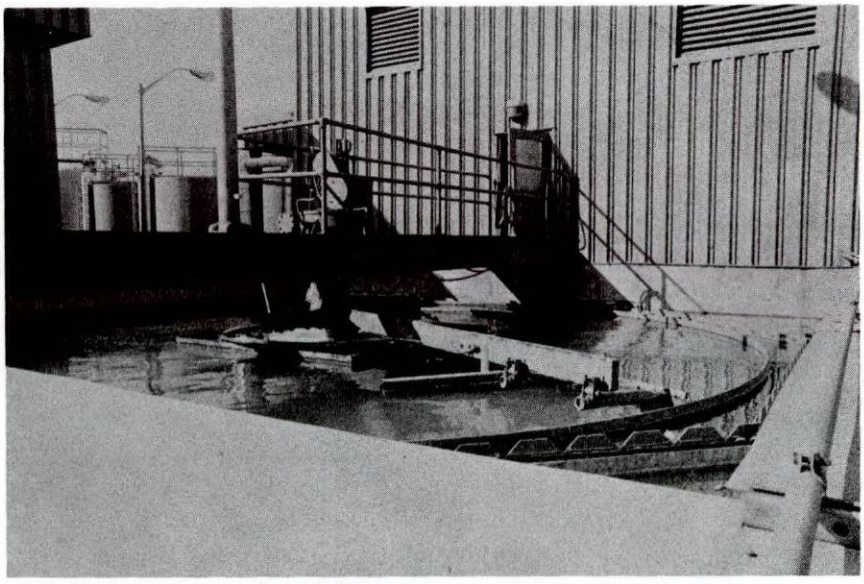
REACTION TANKS



CHEMICAL MAKE-UP TANKS



CONTROL PANELS



CLARIFIER

C-4

Environmental I
Session C

The Recovery and Treatment of Metals from Spent Electroless Processing Solutions

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THE RECOVERY AND TREATMENT OF METALS FROM SPENT ELECTROLESS PROCESSING SOLUTIONS

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Introduction

Electroless plating is a growing segment of metal finishing, finding particular application in the electroplating and electronics industry. The electroless plating process employs a solution in which salts of the metal to be plated are dissolved and held in solution by the use of certain chelating and/or complexing agents. The metal deposition from these baths is an autocatalytic process which proceeds on previously sensitized metal, plastic, or glass surfaces. The rate of metal deposition is controlled by the type and amount of reducing agent present as well as the type of chelating agents used, rather than from an external electric power source. Electroless plating results in a fine-grained metal deposit very similar in appearance and function to that of an electroplated deposit. It is most often used as a starting deposit for subsequent electroplating in the process of plating on plastics, printed circuit boards, electroformed dies, and other metallic objects, with hard-to-reach intricate metal surfaces.

Some electroless plating processes are also known as "immersion plating" systems. These systems are not based on the electron donor being a reducing compound, but depend on an electrochemical exchange reaction. The metal to be deposited is reduced on the surface of the workpiece and a proportional amount of base metal from the workpiece is dissolved. Since the base metal of the object to be plated is replaced by chemical displacement, the electrochemical potential of the metal to be deposited has to be more negative than that of the metal on which the deposit occurs.

The Treatment Problem

As metal is deposited from either electroless or immersion plating solutions, the metal content of the solution is partially depleted. Metal salts and their appropriate chelating agents must then be added to replenish this metal loss. In time, after several chemical replenishment additions, the inorganic salts from the metal additions and the decomposed reducing agents accumulate. This slow accumulation of chemical content of the solution reduces the deposition rate and may affect the crystal structure of the deposit. At this point, a portion must be replaced with fresh solution or all of the electroless plating solution must be discarded.

Discarded plating solutions and waste rinsewaters, because of their metal content, require waste treatment so that the residual metals discharged in the effluent will be at a minimum concentration. Chelated

metal compounds are not responsive to the conventional waste treatment technology of neutralization or high-pH treatment precipitation and settling. For many years now, intensive research on a widespread international scale has been conducted to overcome these difficulties in metal finishing waste treatment. A practical solution should not propose to exchange one problem for another. For example, the treatment of electroless and immersion plating wastes should not generate sufficient quantities of sludge so that this sludge presents its own disposal problem.

Some Typical Solutions

One common method for treating electroless wastes is the addition of reducing agents such as sodium borohydride,[1] sodium hypophosphite or sodium hydrosulfite[2] at elevated temperatures to reduce the soluble metals to their metallic or oxide forms. The sludges produced in these processes contain relatively impure metal powders which are extremely susceptible to air oxidation and require further treatment due to the presence of interstitial waters containing relatively large amounts of free chelating agents. These chelates will over a relatively short period of time cause redissolution of some of the metal oxide in the sludge. This sludge must therefore be considered a hazardous waste and treated accordingly.

The use of conventional ion exchange systems, as well as newly developed resin technology, has been proposed for the treatment of electroless wastes. Conventional cation exchange resins are extremely inefficient due to their affinity for the alkaline earth metals over the heavy metals. Systems involving these resins, therefore, require large columns and frequent regeneration. Most chelating resin systems available today are not effective on all chelate materials. One system, for example, will not remove metals that are complexed with EDTA.[3] In addition, the regenerant from most ion exchange or chelate resin systems will require further treatment in order to reclaim or otherwise remove the metal content.

Electrolytic techniques which utilize high surface area cathodes and/or non-conductive fluidized beds[4, 5] have also been used for the treatment of electroless wastes. These systems fall into the same category as electrodialysis, ultrafiltration, reverse osmosis, or evaporation in that the end result is the generation of a concentrated metal-containing solution. The metallic deposit generated on the high surface area cathodes must be stripped, and the resulting solution treated chemically or by conventional electrolytic means to remove the metal content unless this concentrate can be added back to the processing solution. Each system requires additional equipment before ultimate disposal of the waste can be achieved.

Another Way

A more practical solution to the problem would seem to be the development of a system which minimizes sludge generation by producing directly a usable metallic deposit with minimal operator attention. In order to accomplish this, it would seem reasonable to divide the problem into two areas. First is the concentrated batch dumps of electroless processing solutions which contain relatively high concentrations of metal. The approach here would be to remove the metal electrolytically. The relatively high metal concentration lends itself well to this technique without resorting to high-surface-area-type equipment from which the deposited metal cannot be directly removed. Since the majority of metal waste is produced by these batch dumps, the direct recovery of these metal values seems most reasonable as well as most efficient. The second area involves the treatment of dilute rinsewaters. While electrolytic techniques have been developed for this purpose, the problems encountered that were mentioned earlier often make this approach questionable.

A system has recently been developed which incorporates electrolytic recovery with state-of-the art waste treatment technology for chelated metals. The electrolytic recovery step is performed only on the concentrated batch dumps. Conventional electroplating approaches strip out the metal content of an electroless solution, yielding a coarse, powdery deposit and very low efficiencies, even if the solution has been modified by the addition of various chemicals, pH changes, etc. Recent laboratory investigations, however, revealed that by placing aluminum shapes such as sheet, rods, or wire into spent electroless plating baths, fast recovery and good-quality metal can be deposited. Initially, an electrochemical reaction occurs which deposits a thin metallic layer on the aluminum surface as represented by the following reaction:

$$2\ Al + 3\ NiCl_2 \rightarrow 3\ Ni + 2\ AlCl_3$$

This "strike" layer then provides the base for further metal build-up by the autocatalytic mechanism.

In an attempt to control the dissolution of aluminum, an external cathodic potential was applied to the aluminum sheet. The laboratory cell in this experiment took the form of a conventional electroplating cell in which an aluminum cathode was placed between two steel anodes. This modification proved to be highly successful. The electrodeposition was very rapid. The cathode plate was fine-grained and was built to a sufficient thickness so that the deposit could be periodically removed and reused. The dissolution of the aluminum was also significantly inhibited by the cathodic potential. The process can be illustrated by the following examples.

Example 1

A spent electroless nickel plating solution was placed in a laboratory plating cell consisting of an aluminum cathode centered between two mild steel anodes. The solution pH was adjusted to 8.0-8.5. This pH was maintained by periodic additions of sodium hydroxide during the electrolysis. The solution volume electrolyzed was 2.5 liters, and the temperature maintained at 140° F. The cathode current density used was 4 Amperes/sq. ft. The results of this test are contained in Table I below.

Table I

Time hour	Soluble Ni (g/l)	Cathode Efficiency	Cumulative Cathode Efficiency
0	5.23	--	--
1	4.11	1534%	1534%
2	2.85	1726%	1630%
3	2.25	812%	1358%
4	1.29	1324%	1349%
6	0.70	399%	1033%
7	0.40	416%	944%
8	0.35	73%	836%
9	0.29		

After nine hours of electrolysis, the cathode deposit was inspected and found to be adherent, bright, and metallic. Analysis of the resulting solution showed 27.4 ppm aluminum and 14.0 ppm iron.

Example II

In a second example, a 500 ml sample of spent electroless copper plating solution was treated. During electrolysis, the pH is maintained at 11.0-11.5. The plating cell was the same as that used in the previous example with a current density of .2 to .4 Amps/sq. ft. on the cathode being maintained. The results of this test are contained in Table II below.

Table II

Time hour	Soluble Ni (g/l)	Cathode Efficiency	Cumulative Cathode Efficiency
0	2.99		
1	1.63	819%	819%
2	1.21	252%	536%
5	0.175	208%	339%
6	0.064	67%	294%
7	0.0059	35%	256%

The deposit obtained on the cathode was bright and metallic, with good adhesion. The aluminum content of the solution after 7 hours of electrolysis was 1,800 ppm, during which time 2.9 g/l of copper were removed.

As can be seen from the extremely high current efficiencies in these two examples, the aluminum cathode was protected from excess dissolution, while the bulk of the metal deposition was due to the electrolytic and autocatalytic processes. The result is a practical electrolytic recovery technique for metal values contained in spent electrolysis processing solution.

Since the quantity of electroless processing solutions being used is relatively small, the metal value recovered from these spent baths in itself cannot easily amortize the cost of the equipment at a fast rate. It must be remembered that if we do not make a good-quality metal deposit from the spent electroless processing solution, that metal content must be turned into sludge. There is, of course, disposal cost associated with the generation of this sludge. This cost must also be considered in our evaluation of the economics of the electrolytic recovery equipment.

The second stage of this new system approach deals with the treatment of the rinsewaters following the electroless process solutions. The technique used combines the advantages of sulfide precipitation with adsorption and filtration. The rinsewaters are diverted to a reaction tank in which sodium sulfide is added. The additions of sodium sulfide are closely controlled and monitored by a newly developed sulfide control instrument. From here the rinsewaters are passed through a specially designed filter onto which an adsorbing media has been coated. As the solution passes through the media, metal sulfides are filtered out and any residual soluble metals are adsorbed. The spent batch dumps following electrolytic recovery are also diverted through this system where residual metals, including any dissolved aluminum, are removed. Approximately 4 lbs. of media is used for each pound of metal removed. The effluent discharge from this system is able to meet total metal and free sulfide concentrations of less than 1 ppm. The following table shows the approximate capital and operating costs for this recover/treatment system. The complete package occupies a total floor space of approximately 50 sq. ft.

Table III

Typical Operating Costs

	EL/EMR/Sorption Filter system	Sorption Filter Unit Only	No Treatment
Equipment Costs	$ 65,600	$ 61,200	--
Operating Costs (media usage, energy, chemicals, labor)	7,000/yr.	16,400/yr.	--
Hauling Costs	38/yr.	150/yr.	37,500/yr.
Total	$ 72,638	$ 77,750	$ 37,500

The optimum approach for the recovery and treatment of electroless processing wastes is when the first rinse following the electroless processing step is considered as a dragout solution which is allowed to increase in metal content and made up with fresh water each time the electroless solution is dumped. In this manner of processing, the metal would be recovered electrolytically by adding the dragout rinse to the dumped process solution and electrolyzing the whole, somewhat diluted solution mix. The advantage is a more complete metal recovery with very minimal additional equipment or operating cost and at the same time a significantly reduced volume of filter sludge generation.

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Environmental I
Session C

Electrochemical Removal of Heavy Metals from Wastewater

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ELECTROCHEMICAL REMOVAL OF HEAVY METALS FROM WASTEWATER

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and
Joseph G. Duffey, P.E.
Andco Environmental Processes, Inc., Buffalo, New York

Environmental regulations are quite specific in limiting the amount of dissolved heavy metals in electroplating and printed circuit board wastewater discharged to municipal sewers or streams. Generally, two or more heavy metals are present, and since each metal hydroxide has its own pH point for minimum solubility, it is quite difficult to meet the EPA regulations consistently with traditional chemical precipitation methods. Chelating agents further complicate the problem.

About ten years ago, the electrochemical process for removing heavy metals was developed and today nearly 100 plants are in operation with flow rates from 5 to 1400 gallons per minute. This technology overcomes the basic theoretical problems of multiple metal chemical precipitation and results in a more cost-effective wastewater treatment system.

A number of articles on the process have been presented (1,2,3,4,5) and three U.S. patents (6) describe the technology.

Electrochemical Heavy Metal Removal Process

The process may be thought of as being the reverse of electroplating. In the case of electroplating, a plate is lowered into a tank and attracts the chrome solution, thus attaching or coating the plate and simultaneously weakening the remaining tank solution.

In wastewater treatment, the tank solution is the waste chrome, and the iron plate is once again lowered into the solution. However, this time the iron migrates from the plate to the solution, and after the attachment takes place, the properties of the chrome change, making it denser, and subsequently settles to the bottom of the tank and simultaneously weakens or uses up the plate.

In the electrochemical process, a direct current is conducted through a cell containing carbon steel electrodes. This generates the ferrous ion, which in the case of hexavalent chrome, reduces it to trivalent chrome. The overall reaction is as follows:

$$Na_2Cr_2O_7 + 6Fe(OH)_2 + 7H_2O \longrightarrow$$

$$2Cr(OH)_3 + 6Fe(OH)_3 + 2NaOH \qquad (1)$$

While this reaction indicates the chemical reduction taking place if hexavalent chrome is present, it is not at all necessary that chrome be present for the removal of all other heavy metals. It will be noted that no sulfates are formed as in chemical precipitation thereby making the treated water suitable for recycling to the plating operation.

Other heavy metals such as copper, nickel, zinc, lead, tin, vanadium, etc. are coprecipitated with the ferric hydroxide, resulting in a mixture of insoluble metal hydroxides. The reaction proceeds quite favorably in the pH range of 6 to 9, which is the pH level prescribed by the EPA for wastewater discharge. Since some excess hydroxyl ion is present, the pH will increase 0.5 to 1.0 units in passing through the cell. No other chemicals are added. Table 1 shows typical plant operating data.

Figure 1 illustrates the configuration of an electrochemical cell. A bipolar arrangement is used wherein one side of each electrode is the anode and the other side is the cathode. The ferrous ion produced at the anode and the hydroxide ion produced at the cathode diffuse into solution and react forming ferrous hydroxide. A small amount of hydrogen gas formed is vented from the cell. In the process of the reaction, the carbon steel electrodes are consumed and theoretically 3.22 pounds of iron would be required to react one pound of hexavalent chrome to the trivalent state. Actual sludge analysis shows about 3.5 pounds of iron per pound of chrome, and generally, the electrodes are changed after about 75 percent of the metal has been consumed, which is around once a month. To assure even wearing on the plates, the polarity is reversed once a day, converting the anode to the cathode, and visa versa. Since metals other than chrome do not require reduction and are simply coprecipitated with the iron, lesser amounts of electrode are needed, usually in the order of 1 to 2 pounds of iron per pound of heavy metal.

Sludge generated by the electrochemical process is slightly greater, on a stoichiometric or theoretical basis, than the chemical process. However, in actual operation, the chemical precipitation method uses substantially greater than theoretical chemicals, whereas the electrochemical process is very nearly theoretical in electrode usage. Therefore, the electrochemical process generally produces less sludge than the chemical method.

Only a small amount of electric current is needed, as very high Faraday efficiencies are achieved. Only about five kilo-

watts are required per pound of heavy metal removed. The amperage can be calculated from Faraday's Law and a typical cell would operate at about 25 amps DC. The voltage on the cell is a function of the electrical conductivity of the wastewater and can vary from 50 to 400 volts DC. The plants are supplied with 220 or 440 volt AC power and rectification equipment within the unit makes available the necessary direct current.

The amperage required is a function of the flow of wastewater and the heavy metal concentration. As the flows or concentrations change, the amperage is modified so that the effluent heavy metal concentration is within specification.

Normal operation on a once-through basis requires that the wastewater be delivered to the cells at about 25 psig, and after setting the proper amperage on the cells, no further attention is needed by the operator. In order to keep the electrodes clean and operating at proper efficiency, the flow to a given cell is turned off once a day for a period of about twenty minutes so that the cell can go through an acid wash procedure. Wastewater is drained from the cell and then a dilute sulfuric acid or hydrochloric acid solution is recycled from the acid tank through the cell and back into the acid tank for about five minutes. This cleans any residual material off of the electrodes. The acid solution is then drained into the acid tank and the cell is put back on the line. About once a month, the dilute acid solution is changed.

Chelating agents represent a serious problem for traditional chemical precipitation methods of heavy metal removal since the metals are kept in solution by the chelating compound. It is well-known that iron breaks chelates, and in the electrochemical process this takes place in the cell, making removal of chelated metals quite simple.

Methods of Operation

The Electrochemical Heavy Metal Removal Process can be operated in two distinct modes, depending upon the wastewater treatment requirements. Figure 2 illustrates the process flow diagram.

1. Continuous Once-Through Mode

Many electroplaters have rinsewater streams containing a fairly constant heavy metal concentration in the range of about 10 to 50 mg/l. Under these conditions the wastewater in a pH range of 6 to 9 is pumped through the electrochemical cell with the proper amps being applied. Residence time in the cell is only about 10 seconds. Treated water leaving the cell contains the metal hydroxides as suspended

solids which were formed in the reaction.

These suspended solids must be removed in a clarifier. Prior to entering the clarifier, about one mg/l of anionic polyelectrolyte is added as a flocculant which aids in the separation of solids in the clarifier. Lamella-type clarifiers are frequently used since they require less floor space than the traditional circular clarifiers. The effluent from the clarifier will have less than 20 mg/l suspended solids, and of course, the effluent water will meet EPA discharge requirements.

Underflow from the clarifier will be about one percent solids and will contain the heavy metals as metal hydroxides. Most plants run the clarifier underflow through a sludge pump into a filter press where it is dewatered to about thirty percent solids. The filtrate is recycled back to the clarifier and the filter cake is dumped, usually once per shift.

2. Batch Recirculation Mode

When platers have heavy metal concentrations above 50 mg/l, it is frequently more cost-effective to operate the electrochemical process on a batch recirculation basis. Wastewater is collected in a holding tank or sump, and at convenient intervals a predetermined quantity is transferred to a treatment tank. As usual, the water to be treated is brought up to a pH of 6 to 9 to satisfy EPA discharge requirements and is pumped through the electrochemical cell and clarifier. Since all of the heavy metals will not have been removed in one pass due to the high initial concentration, the water from the clarifier is recycled back to the treatment tank for additional recirculation through the system. The recirculation continues until the material in the treatment tank meets specifications for discharge or recycling back to the plating line.

It was mentioned earlier that the electrochemical process generates excess hydroxyl ions thereby increasing the pH slightly as the water passes through the cell. When operating in the recirculation mode, some acid must be added through a pH controller to keep the pH in the optimum 6 to 9 range. This acid can be raw, untreated wastewater from the holding tank, assuming it is low pH.

Non-Hazardous Sludge

The Environmental Protection Agency has established criteria whereby sludges are determined to be toxic or non-toxic (7). A sample of the sludge is tested using the Extraction Procedure

Toxicity Test for leachability. The sludge sample is acidified to a pH of 5 with acetic acid and allowed to stir for 24 hours, and then the resulting liquid is analyzed for heavy metal content. In the case of chrome, the test permits 5.0 mg/l in the leachate and the electrochemical process regularly shows a chrome content in the order of 0.02 to 0.05 mg/l, which means it is safe by a factor of 100. Other heavy metals produce similar results.

If a sludge meets the Extraction Procedure Toxicity Test, an application is made to the Environmental Protection Agency for delisting of the sludge from the hazardous to the non-hazardous status. Sludge from the electrochemical process easily meets the Extraction Procedure Toxicity Test and has been formally delisted in the Federal Register (8) so that the sludge is considered non-toxic and non-hazardous by the EPA. This facilitates easy and economical disposal of the sludge even though chrome as chromic hydroxide is present. Any non-hazardous landfill can be used as far as the Federal EPA is concerned, but some localities may impose additional testing requirements prior to granting a disposal permit.

Operating Costs

Table 2 shows the operating cost for the electrochemical process. This is based on a plant removing several heavy metals simultaneously with an average electrode consumption of three pounds per pound of heavy metal as the elements, i.e. Cu, Ni, Cr, Zn, Pb, etc., not as the hydroxides. The cost will increase or decrease slightly as the chrome concentration varies since chrome is the only metal undergoing chemical reduction and this element consumes iron electrodes as shown in equation (1).

Capital Cost

The capital cost of an electrochemical heavy metal removal plant is completely dependent on the quantity of wastewater to be treated and the concentration of heavy metals present. An analysis of capital cost of electrochemical versus traditional chemical precipitation plants designed with equivalent equipment standards and similar degrees of automation indicate the following:

1. Basic equipment cost of the electrochemical process is competitive with, or slightly higher than, chemical precipitation.

2. Since the electrochemical process is a compact "packaged" plant, the building space requirements are significantly less than chemical precipitation. Batch

or continuous mixing tanks and dry, curbed areas for raw chemical storage for sodium metabisulfite, lime, sulfur dioxide, etc. makes floor space with chemical precipitation much greater.

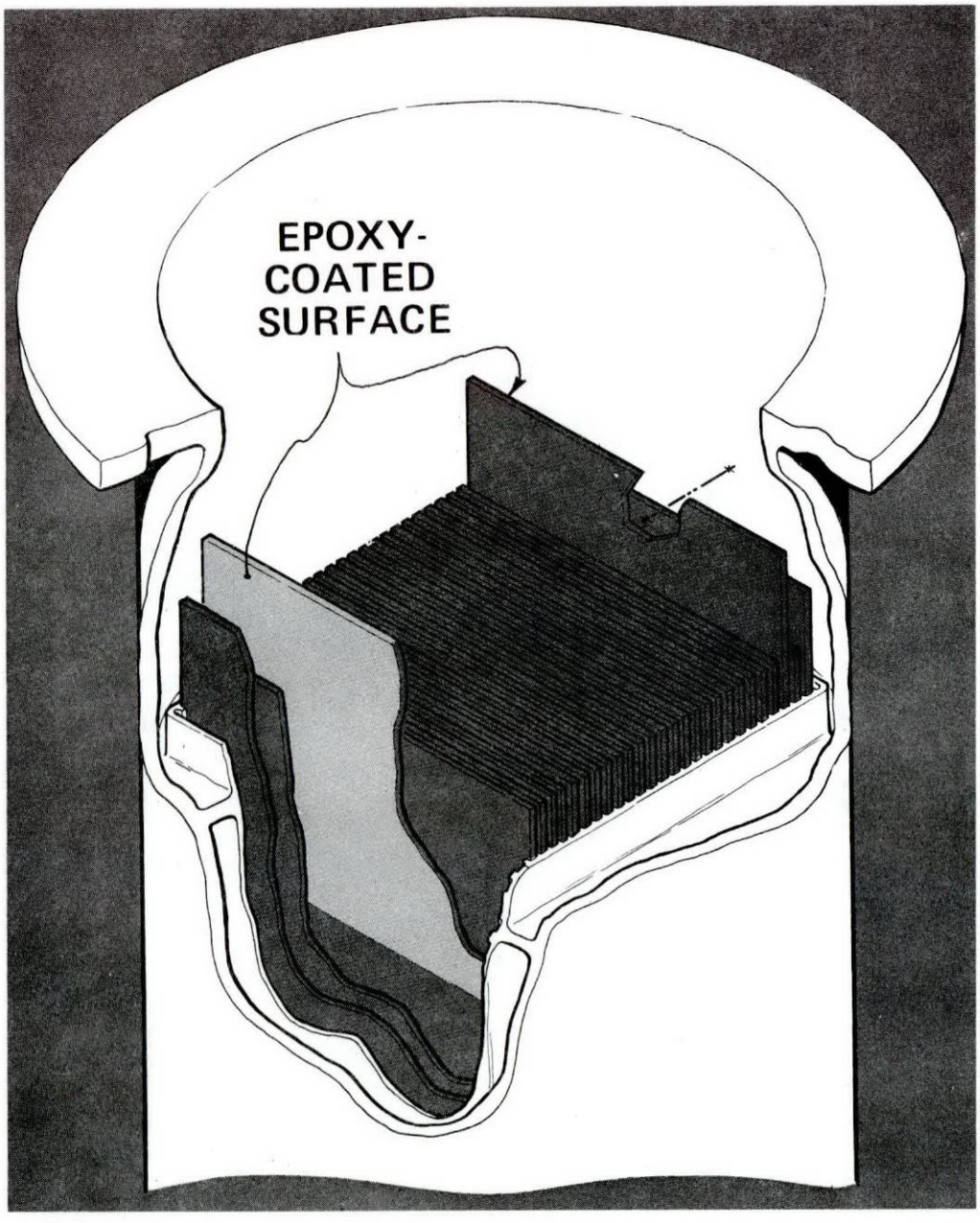
3. In the chemical precipitation process, raw chemical unloading, storage, make-up, and testing for proper dosage are labor intensive. Unplugging chemical lines, cleaning valves, pumps, and mixer blades involves man-hours above and beyond what most plants are willing, or even prepared, to accept. Maintenance costs of plants handling dry chemicals with mechanical devices are invariably high. Suitable ventilation must be provided for chemical storage and make-up areas, particularly with powder-type chemicals. Operation and maintenance costs for the electrochemical process are about one-half that for chemical precipitation.

4. At chemical precipitation plants, laboratory equipment is necessary to monitor raw chemical dosages. Where constant monitoring is not performed, there is a tendency to overdose to assure completion of the chemical reaction. This results in higher costs of raw chemicals and additional sludge generation. Surges from the plating plant will occur and chemical dosages must vary to reflect these changes, buffered somewhat by holding tanks.

5. The overall annualized cost of the electrochemical process is approximately half of the chemical precipitation cost.

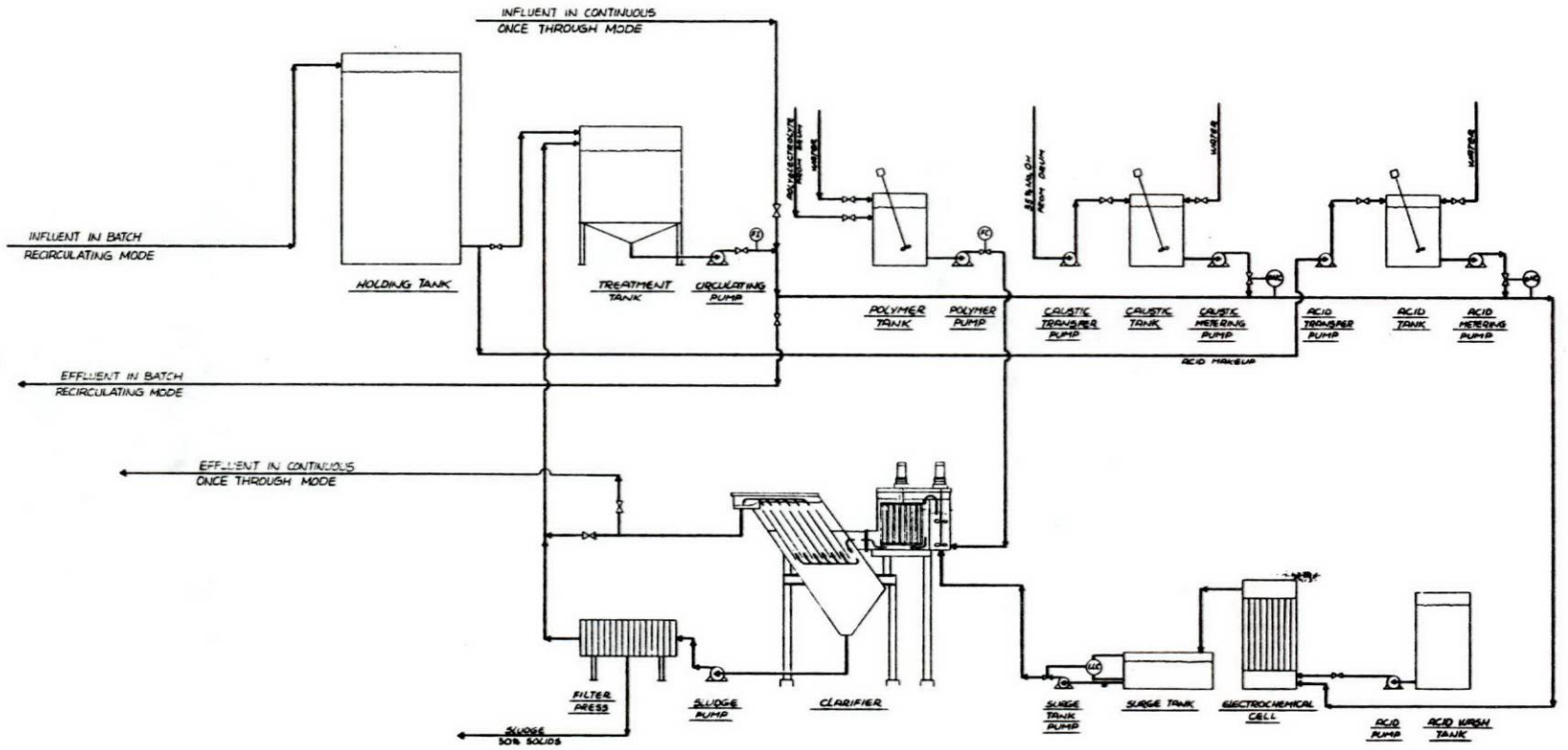
Summary

Field operating experience over many years with a large number of electrochemical heavy metal removal units has proven the cost-effectiveness of the technology. In addition, the sludge resulting from the process has been found to be non-toxic and non-hazardous by Environmental Protection Agency criteria. Treated water using this process can be recycled back to the electroplating plant for water conservation.



ELECTRODE
ARRANGEMENT

Figure 1



PROCESS FLOW DIAGRAM
ELECTROCHEMICAL HEAVY METAL REMOVAL PROCESS
FIGURE 2

Table 1

TYPICAL PLANT DATA

Plant	Influent/Effluent, mg/l				
	Hex Chrome	Zinc	Copper	Nickel	Lead
A	9/0.04	2.3/0.1	--	--	--
B	--	--	11/0.7	--	--
C	178/0.01	--	--	189/0.8	--
D	6.7/0.05	10.4/0.23	0.2/0.05	9.4/0.4	1.51/0.01

Table 2

OPERATING COST

Basis: Multiple heavy metal removal with average electrode consumption of 3 lbs/lb heavy metal.

	Quantity/lb Heavy Metal	Cost/Unit	Cost/lb Heavy Metal
Electrodes	3 lbs.	$0.30/lb	$0.90
Power	5 kwh	$0.04/kwh	$0.20
			$1.10

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Environmental I
Session C

Copper Removal from Metal Finishing Waste Solutions

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COPPER REMOVAL FROM METAL FINISHING WASTE SOLUTIONS

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The presence of complexing agents in waste solutions increases the difficulty of removing heavy metals, such as copper. This fact is of vital importance to the metal finishing industry because of the growth in the use of printed circuit boards for consumer products and telecommunications equipment, and to the growing utilization of plated plastics for shielding electronic enclosures such as office equipment and personal computers. These growth markets require electroless copper which means that the waste solutions will contain significant levels of an organic chelator such as EDTA or Quadrol. One consequence of these developments is that it is becoming increasingly difficult for many manufacturers to meet existing and proposed requirements for the amount of copper discharged to publicly owned treatment works (POTW) or to receiving surface waters.

The EPA regulations for the Metal Finishing Industry which were proposed August 31, 1982, set the copper pretreatment standards for new and existing metal finishing sources at a maximum for any one day of less than 3.72 milligrams per liter (mg/l) copper and an average of daily values for 30 days, which shall not exceed 1.09 mg/l copper.

For existing job shop electroplaters and printed circuit job shops, the pretreatment standard is 4.5 mg/l maximum for any one day and 2.7 mg/l for the average of 4 consecutive monitoring days. However, many POTW's and receiving streams have required limits for copper much more stringent than EPA Guidelines, and values of <0.1 mg/l copper occasionally must be met.

Treatment methods for electroless copper rinse waters depend greatly on the particular chelate/copper complex used in the electroless copper process. Treatment methods to be discussed include (a) recovery of the chelate/copper complex and recycle to the plating bath, (b) destruction of the chelator and removal of copper by conventional techniques, and (c) removal of copper by proprietary techniques.

BACKGROUND

The advantages of using electroplated plastics over their metal counterparts include more freedom in part design, reduced weight, lower raw material costs and the elimination of costly surface preparation operations such as polishing and buffing.

Although many plastics can be plated, adhesion varies widely. Only those which provide the best adhesion are used for electroplating applications. The basic electroplating cycle for plastics is divided into two stages. The first stage is called the preplate cycle. The purpose of this cycle is to provide an adherent, conductive metallic film on the surface of the plastic part so that the second stage, electroplating the decorative or functional finish, can be added by conventional electroplating technology.

The last step of the preplate cycle is to cover the surface with a thin layer of nickel or copper. This layer is deposited autocatalytically from an electroless solution, which contains the nickel or copper salt, a reducing agent, a complexing agent, a stabilizer and a pH buffering system. The chemistry of this electroless solution is such that the copper or nickel is reduced spontaneously as the catalyzed plastic surface contacts the solution, and a very thin uniform metallic coating is then formed. In many applications, a copper deposit is preferred to a nickel deposit due to its superior adhesion, ductility, corrosion performance under both wet and dry conditions, and its electrical properties.

The nature of the electroless copper plating solution is such that the copper ion is held in solution by the complexing agent until a catalyst initiates the action of the reducing agent. Hence, any solution going to waste treatment that is pulled out of the bath through surface tension, or lost due to spills or bath dumps, will contain the metal ion tightly held in solution by the complexing agent. The complexing agent is used in molar excess to ensure that the metal ion is not reduced, and thus precipitate out of solution under normal operating parameters.

The two principal complexing agents predominantly used in electroless copper solutions are EDTA (ethylenediaminetetraacetic acid) or Quadrol (N,N,N',N'-tetrakis (2-hydroxypropyl)-ethylenediamine) as shown in FIGURES 1 and 2.

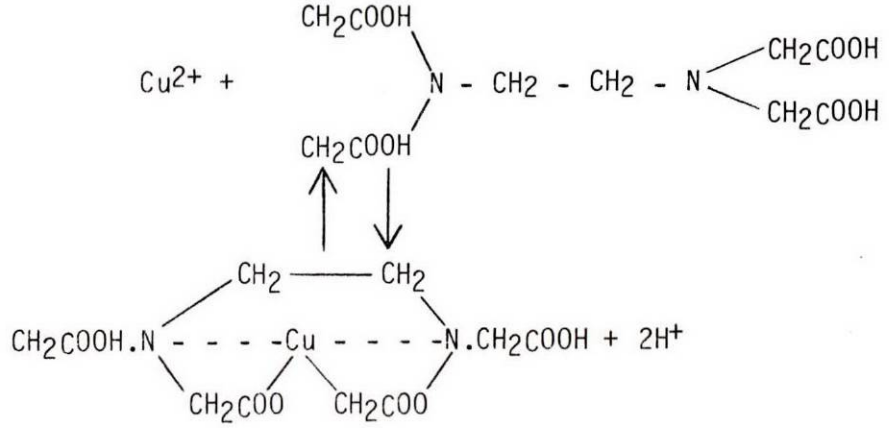


FIGURE 1. EDTA-CU Chelated Complex Mechanism

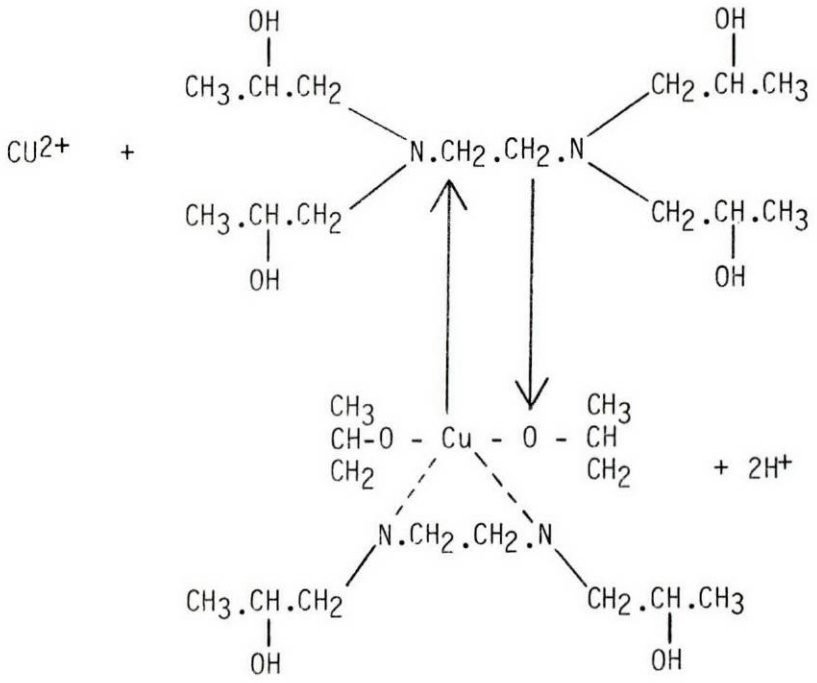


FIGURE 2. Quadrol-Cu Chelated Complex Mechanism

The complexing agent, because of its nature, will complex with cations in other effluent streams. Thus it is obligatory that the electroless copper effluent stream be segregated from other plant wastes and treated separately to remove the copper. The concentration of the copper in the stream is usually too high to be suitable for direct discharge. Restrictions usually do not apply regarding the discharge of organic chelators, since these organic compounds are biodegradable in the presence of light.

TREATMENT USING CONVENTIONAL TECHNOLOGY

Electroless copper treatment methods, used traditionally in industry to remove the copper, generate voluminous amounts of sludge, require costly capital expenditure and are labor-intensive. The treatment of electroless copper-containing rinse wastes of either EDTA or Quadrol have been thoroughly discussed by Wing[1]. Wing and his co-workers found that these complexes can be treated with calcium hydroxide, calcium oxide, calcium chloride or calcium sulfate at a pH of 11.6 to 12.5. In work done at our facility, we found that to effectively reduce copper to a concentration of less than 1 mg/l from an original concentration of 50 mg/l, a large excess of calcium is required (up to 15X stoichiometric excess). This is because the equilibrium constant, k, for the equation:

$$Ca^{2+} + Cu\ EDTA \underset{}{\overset{k}{\rightleftharpoons}} Ca\ EDTA + Cu^{2+}$$

Excess Ca →

FIGURE 3. Equilibrium Equation for EDTA-Cu-Ca

was found to lie between 5.6 and 14.0 (with a mean of 10), thus providing a rough measure of the amount of calcium required for adequate copper displacement.

This calcium treatment is not effective for Quadrol-copper complexes. The copper displaced from the complex precipitates from the solution as copper hydroxide.

Another effective method of displacing the copper from the EDTA or Quadrol complex is to lower the pH to between 2.7 and 5.0 and add ferrous sulfate or ferric chloride. The reduction in pH weakens the copper complex bond and facilitates the substitution of the copper for iron. Approximately one gram of ferrous sulfate or ferric chloride was added per 50 mg. of copper present, indicating a 7X stoichiometric excess of iron is necessary to displace the copper. The pH was then raised to 9.0, using lime or caustic, and the precipitated copper hydroxide filtered from the solution.

$$Fe^{2+} + Cu\text{-}Complex \rightleftharpoons Fe\text{-}Complex + Cu^{2+}$$

Excess Fe →

OH^- ↓

$Cu(OH)_2$ ↓

FIGURE 4. Equilibrium Equation for Copper Removal Using Iron

The high pH, calcium substitution treatment procedure and the iron substitution procedure reduce the copper concentration to an acceptable level for discharge. However, large amounts of sludge which require disposal are generated.

The copper has also been removed from the complex by using strong reducing agents such as sodium hydrosulfite, Kamperman[2], or sodium borohydride, Jula[3]. Sulfide precipitation of the copper is also discussed by Scott[4] and Anderson and Weiss[5]. Starch-based products, such as Insoluble Starch Xanthate, have been developed by Wing[1] and are presently commercially available. All these processes, however, generate a sludge that has to be disposed of in an environmentally acceptable manner.

Tests carried out in our facility (shown in Table I) indicate that these methods produced only partially acceptable results for copper removal from solutions containing initially 50 mg/l of copper.

TABLE I. Copper Removal from EDTA or Quadrol Complex Using Sodium Hydrosulfite, Sodium Borohydride and Insoluble Starch Xanthate

TECHNOLOGY	EDTA* mg/l	QUADROL* mg/l
SODIUM HYDROSULFITE	7.2	0.46
SODIUM BOROHYDRIDE	14.0	2.4
INSOLUBLE STARCH XANTHATE	.7	.31

*Initial copper concentration 50 mg/l.

TREATMENT USING ADVANCED TECHNOLOGY

As a result of more stringent government regulations regarding disposal of hazardous materials, and the increased emphasis on zero discharge, several new approaches to the treatment of electroless copper-containing rinse waters have evolved. It is convenient to classify these approaches as follows to facilitate discussion of the technology issues involved:

1. Recycling of the copper-complex back to the bath.
2. Destruction of the complexor so that the copper can be removed by conventional techniques.
3. Removal of the copper by proprietary techniques.

RECYCLING TECHNIQUES

Conventional recycling techniques such as evaporation, reverse osmosis or electrodialysis, cannot be used to concentrate the dilute electroless copper effluent stream to give a concentrate which can be returned to the electroless copper bath. This is because changes in bath chemistry can be anticipated on reconcentration, which could initiate copper deposition, thus rendering the recovery equipment inoperative. Also, the electroless copper bath is extremely sensitive to contaminant build-up. The return of recovered concentrate back into the bath will be accompanied by the return of recovered contaminants, and operation of the bath will become increasingly difficult.

Currently, only one technology exists which can successfully recycle the copper-complex to the bath. This process is detailed by Zeblisky[6] and is only applicable for alkanolamine and copper-alkanolamine type complexes such as (ethylenedinitrilo)-tetra-2-propanol, triethanolamine, ethylenedinitrilotetraethanol, nitrilotri-2-propanol, etc. which can protonate and therefore have a net positive charge. At high pH values, these complexes will deprotonate and become species with no electrical charge, as shown in Figure 5.

$$\text{Cu-Complex}^{+2} \rightarrow \text{Cu (Complex-H}^{+})^{+1} \rightarrow \text{Cu (Complex-2H}^{+})^{0}$$

pH<7.3 pH 7.7-10 pH>10

FIGURE 5. Effect of pH on Copper Complex Charge

The free ligand also reacts in a similar way. Therefore, the complexed copper and ligand in an alkanolamine type electroless copper bath such as (ethylenedinitro)-tetra-2-propanol can be removed and recovered from waste electroless copper solutions using a cationic exchange system. The pH of the waste electroless copper bath is lowered to form the cationic copper-complexor species. The copper-complexor is retained on a cationic exchange resin and then reclaimed from the resin, either by using standard resin regenerating techniques or by raising the pH of the resin bed with hydroxide. Raising the pH of the resin bed reclaims the copper complex by converting the complex to a zero charged species and releasing it from the ion exchange resin in a form suitable for additions to an electroless copper bath. This process is shown schematically in FIGURE 6.

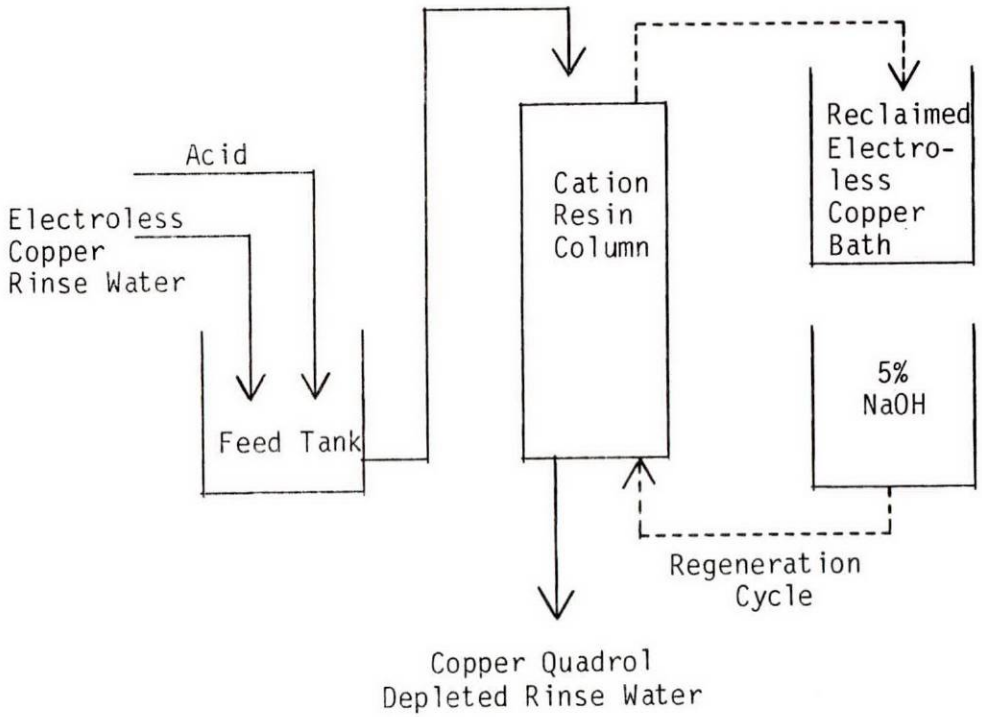


FIGURE 6. Schematic for Copper-Quadrol Recovery[6]

An alternative method of regenerating the Cu-Quadrol complex is to pass sulfuric acid over the loaded resin, and then wash the copper complex from the resin, using water. The process is used mainly to reclaim Cu-Quadrol from concentrated solutions and not from rinse water. The Cu-EDTA-type complex does not protonate on pH change; thus, this process is not applicable. If the pH of an EDTA-Cu bath is lowered to a pH of 2.5, the EDTA-Cu complex dissociates and the EDTA separates to form a lower layer. The EDTA can be thus recovered and reused to replenish the bath EDTA concentration. The resulting supernate is an acidic solution containing large amounts of copper and small amounts of EDTA. Depending upon the degree of copper removal required, the solution should be segregated from other plant effluents so that it can be treated, using techniques discussed previously.

TECHNIQUES INVOLVING DESTRUCTION OF THE COMPLEXING AGENT

If the organic complex is destroyed by oxidation techniques, the copper-containing stream may then be mixed with other plant effluent streams for conventional treatment. Cullivan[7] has investigated the economics of using either chlorine or ozone to oxidize large quantities of organic containing effluents. However, this survey was for large quantities of organic containing wastes. For electroless copper containing wastes it would prove uneconomic. Work carried out in our laboratory, using sodium hypochlorite to oxidize the

EDTA or Quadrol, prior to copper precipitation using lime, yielded less than 60% removal of the copper from an initial concentration of 50 mg/l copper to 22.4 mg/l for the EDTA and 16.7 mg/l for the Quadrol based solutions, respectively.

The addition of UV activation to the ozone oxidation process has been investigated by Prengle and Mauk[8], who found that promising oxidation of the organics occurred. Macur et al[9], further discussed the ozone/UV destruction of EDTA. This method is currently in commercial use. However, it is important, during the ozone/UV process, to remove the copper as it is released from the complex. If this is not done, the released copper will selectively initiate the ozone degradation and thus no oxidation of the EDTA will occur. In general, oxidation of the organic complex is not a practical method of treating an electroless copper waste stream.

PROPRIETARY COPPER RECYCLE AND REMOVAL TECHNIQUES

Ion exchange can be used as a method to remove copper from a complexed solution, thus rendering the solution depleted in copper and able to be discharged directly. Development of suitable ion exchange techniques has been delayed because the specialty resins required to remove the copper have only recently been available for industrial use.

The resin used to remove the copper has to be a powerful chelator which will selectively remove copper from the copper-chelate complex in the electroless copper effluent. A process has been recently developed by Courduvelis et al[10], and Whalen[11], using a resin with an iminodiacetic acid functional group.

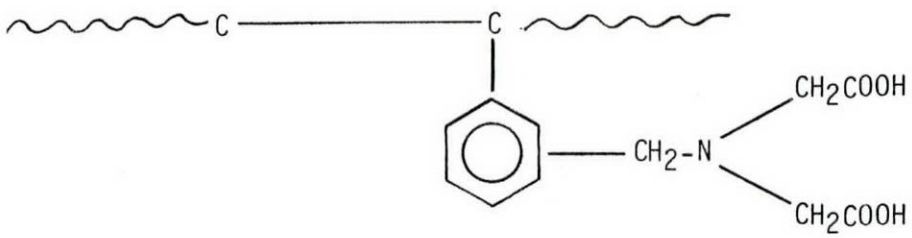


FIGURE 7. Polystyrene Bearing Iminodiacetic Acid Functional Groups[11]

This resin has been found to remove copper from a variety of chelators such as carboxylic acid and alkanolamine type chelators.

However, no separation of copper takes place in the presence of ethylenediaminetetracetic acid (EDTA), and other amino acid type chelators.

This result appears to agree with the expectation based on the respective chelating constants[11], shown in Table II.

TABLE II. Relative Strength of Chelating Constants for Copper with Chelating Compounds[11]

CHELATING COMPOUND	CHELATING CONSTANT k
EDTA	$10^{18.8}$
Iminodiaceticacid	$10^{10.55}$
Tartaric Acid	$10^{9.9}$

The efficiency for copper separation from Quadrol is greater in an acidic solution, pH=2.7-7.0, than it is in an alkaline solution. When the resin is exhausted, it is regenerated with dilute sulfuric acid, which redissolves the copper retained on the resin. Thus copper bearing acid solution can then be treated by conventional hydroxide precipitation, or the copper can be plated out and the acid recycled to be used in the next regeneration sequence. As with most ion exchange procedures, copper removal is extremely sensitive to process variables such as pH, flow rate, copper loading and temperature.

An alternative method of removing copper from the copper complex is by plating out the copper. A variety of processes have been developed to plate out the copper either as a copper sheet, Stewart et al[12], or as a non-complexed copper containing solution, DasGupta et al[13]. However, the effluent as a result of these processes normally has a copper concentration of between 10-50 mg/l. We have developed a method by which the copper is selectively removed from a solution containing copper in a complexed form, Arcilesi et al[14]. The mechanism of the removal is shown below.

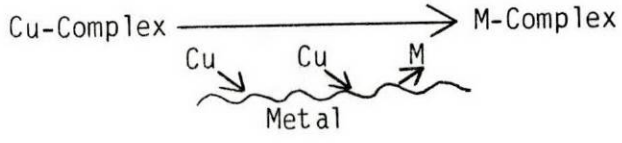


FIGURE 8. Selective Electrochemical Displacement Mechanism

The process is shown schematically in Figure 9.

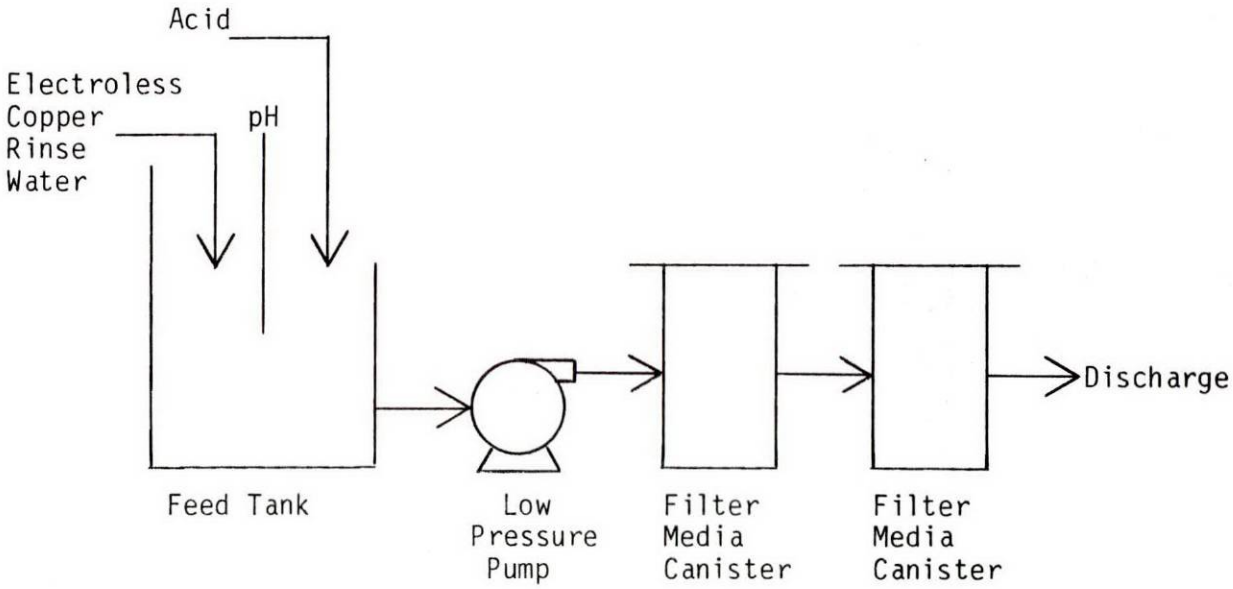


FIGURE 9. Schematic of Copper Removal Process

The electroless copper containing rinse water flows into a feed tank in which the pH is adjusted by the addition of acid to the optimal level for selective electrochemical displacement. The residence time allowed in the feed tank permits adequate blending. The pH adjusted rinse water is then pumped through a pair of filter media containing canisters in which the copper is selectively removed from the solution and replaced by a metal complex. The use of the canisters in series is alternated to optimize the removal media use. The majority of the copper is removed in the first canister and the stream is polished in the second canister. Removal rates of greater than 90% are achieved in each canister.

Field results to date indicate that copper is removed to a level of less than 1 mg/l from an initial level of 100 mg/l from solutions such as, EDTA copper, Quadrol copper, Tartrate copper, pyrophosphate copper, ammonium persulfate etch, and peroxide sulfuric copper etch.

The results are summarized in Table III.

TABLE III. Summary of Field Results.

Time In Service	8 Hours	40 Hours
Canister #1	0.5 mg/l	1.5 mg/l
Canister #2	0.05 mg/l	0.05 mg/l

The results were achieved on a solution of electroless copper rinse water* with an initial copper concentration of 58 mg/l at a flow rate of 5 GPM, at a pH of 4, and an ambient temperature. Six pounds of copper was removed in the forty-hour period.

When the copper concentration exiting the lead canister exceeds 4 mg/l; its media is replaced and the flow through the canisters is alternated to make this the second canister in the series.

The copper plated base metal is classified as non-hazardous and the media can be either sold or disposed of as scrap metal.

The effluent from this process still contains complexor and must be segregated from other plant waste streams until they have been treated prior to discharge.

The equipment** for this process is shown in Figure 10. The unit is skid mounted, prepiped and prewired for easy installation. The only hook-ups that have to be made are electroless copper waste waters, city water for intermittent flushing of the canisters and a line to take away the effluent from the equipment; also required is an electrical hook-up to the panel of 440 volt, 3 phase power.

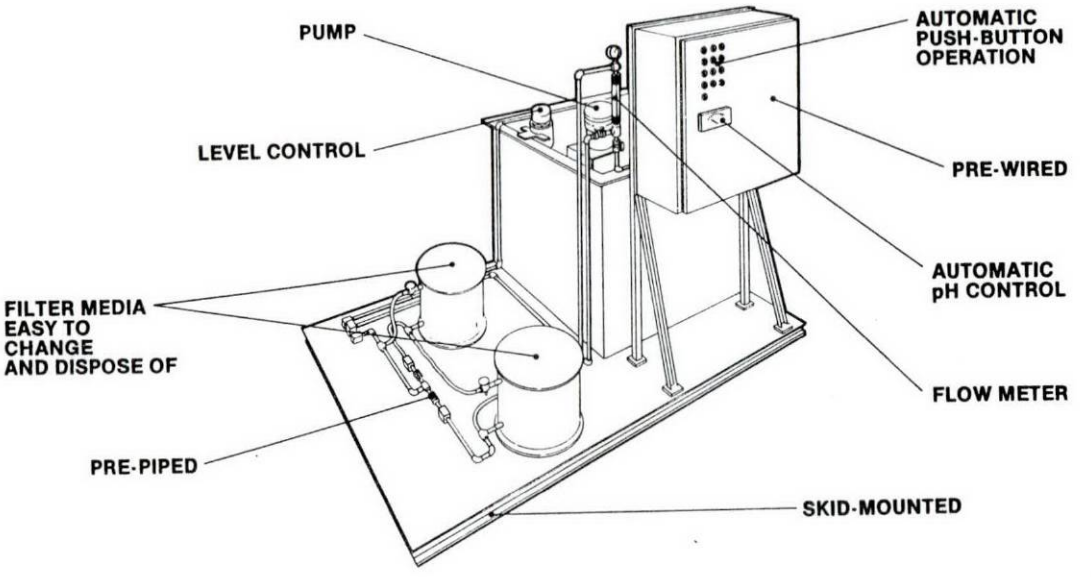


FIGURE 10. Apparatus to Remove Copper from Copper Containing Complexed Solutions[14]

*UDIQUE® 820
**CUPRATROLLER™

DISCUSSION

The main disadvantages of current waste treatment methods for copper removal are the following:

- Calcium or iron displacement produces large amounts of hazardous sludge which should be disposed of in classified landfills. The costs for hazardous landfill are increasing daily, and even though the calcium or iron displacement methods are very effective on treating certain electroless coper waste streams, it can be seen that in the future processes which produce large amounts of sludge will actually become a liability to the companies using them.

- Sodium borohydride and sodium hydrosulfite when used to effect copper removal, both prove to be costly from the chemical and process viewpoint, as well as producing a sludge which has to be disposed of in an environmentally acceptable manner.

- ISX is an effective copper removal method but only becomes cost effective as compared to other known methods for final polish water containing less than 10 mg/l of copper.

- The recycle of the copper complex using ion exchange is presently only applicable to copper Quadrol solutions; it is not effective on dilute streams, and has an extremely high operating cost due to the complexity of the process and the equipment that has been developed.

- Destruction of the complexing agent is not economical for small quantities of rinse, and it is not effective on all copper complexes.

- Removal of the copper by ion exchange is not an effective method on all electroless copper streams and the regenerant still requires further processing to remove the copper.

- Removal of the copper by electrowinning requires equipment that has a high capital cost. Also, the efficiency of the electrowinning process is very low at very low concentrations of copper.

The advantages of copper removal using selective electrochemical displacement are:

- Selective electrochemical displacement is effective on any copper containing stream.

- It is a simple direct copper removal method.

- The copper plated onto the base metal can be classified as non-hazardous for disposal purposes and may be sold or reclaimed.

- Equipment has been developed that offers low maintenance, and low capital and operating costs.

SUMMARY

Conventional methods of removing the copper from metal finishing waste streams prior to discharge, generate large quantities of hazardous sludge with associated disposal problems. Newer technologies recently introduced provide economical recovery of the copper which may be used for other purposes, but not for reuse in the bath. The resulting copper-depleted rinse solutions can then be discharged with other treated metal finishing wastes to POTW or receiving waters as required. Of these newer technologies, selective electrochemical displacement appears to be the best approach in terms of operational efficiency and cost.

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