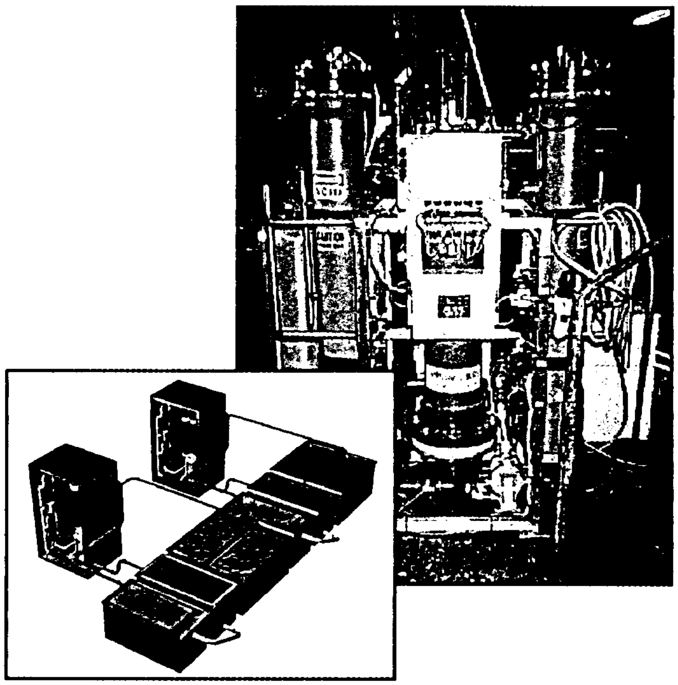
Pollution Prevention Technologies for Metal Finishing Operations

July 22, 1998



Workshop 5

Environmental Training Workshop for Metal Finishers

Sponsored by:

U.S. EPA

Surface Technology Association

Presented by: Tetra Tech EM Inc.

EPA/STA Pollution Prevention Technical Assistance Project

- **Training**
  - Workshop Series (series of 6)
  - Operator Training Series (given multiple times)
- **Mini-Assessments**
  - Working with 6 facilities currently
  - More facilities are being selected (Apply Now!)

Training -- Workshop Series

Workshop Title	Date and Time
Industrial Wastewater Discharge Compliance	✓ February 26
Operator Training	✓ March 12
Hazardous Waste Compliance and P2	✓ March 25
P2 Through Process Control	✓ April 22
Air Emissions Compliance and P2	✓ June 10
Pollution Prevention Technologies	Today
Enviro. Mgmt. System Approaches to P2	August 12, 4-8 pm
Operator Training	August 19, 3 pm

Course Objectives

- Learn what needs to be done before investing in technology
- Understand P2 technologies and their applications
- Review successful case studies
- Identify opportunities for involvement in EPA/STA P2 project activities

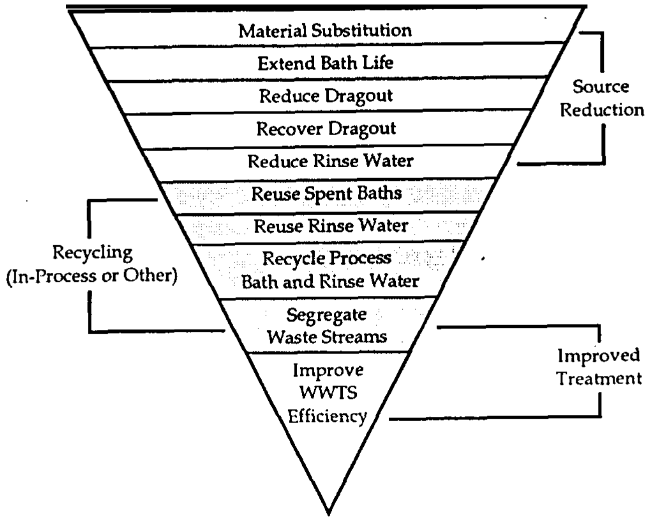
Agenda

- Process Control and P2 Technology Design
- Process Bath Recycling Technologies
  - Electrodialysis
  - Diffusion dialysis
  - Electrowinning
- Rinse Water Recycling
  - Reverse osmosis
  - Ion exchange
- Wrap Up

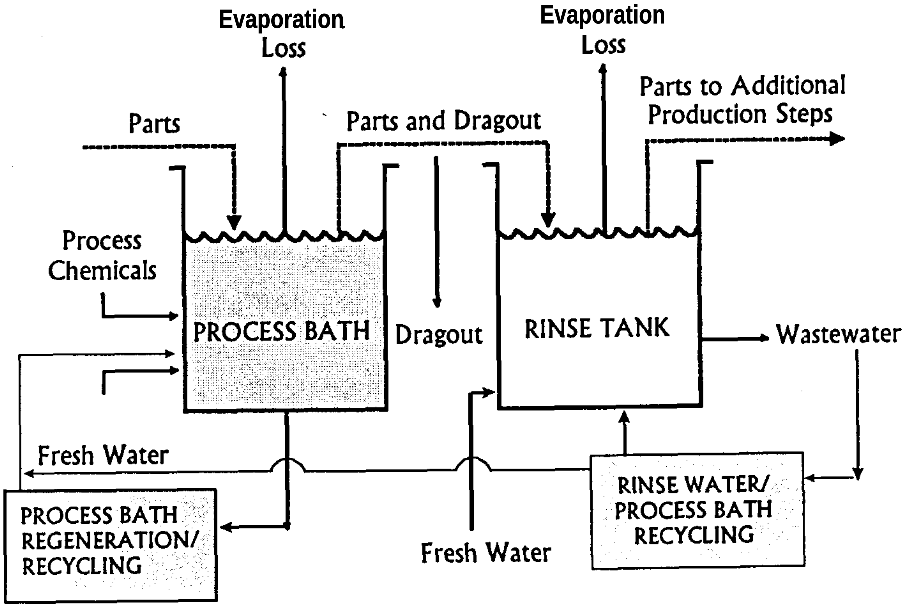
Unit 2
First Things First: Process Control

"To Control (and Reduce) Waste, You Must Control the Process"

Hierarchy of P2 and Waste Management Strategies for Metal Finishing



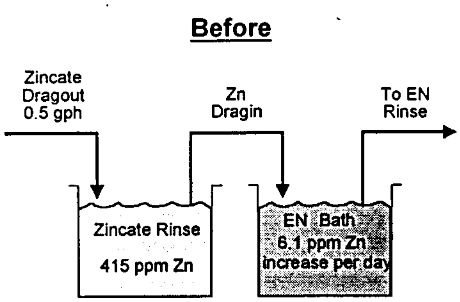
Material Flows for Metal Finishing



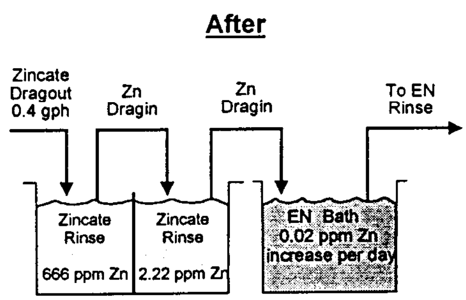
Reducing Contaminant Buildup

- Contaminant buildup reduces process effectiveness and decreases bath life
- Common responses
  - Decant or dummy bath
  - Change bath frequently
- Process control approach
  - Reduce dragin
  - Improve rinse system design and operation

Reducing Contaminant Buildup



- Single-stage zincate rinse
- Rinse water flow rate = 2 gpm
- Dragin rate into bath = 0.5 gph
- Zn buildup in EN bath = 6 ppm/day

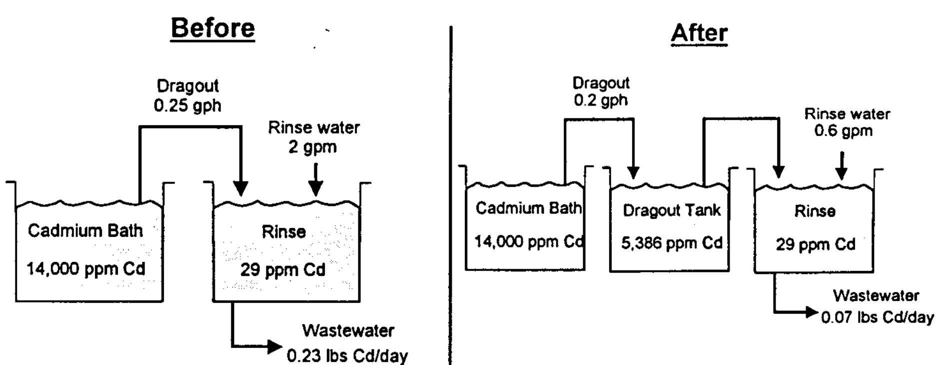


- Two-stage counterflow zincate rinse
- Rinse water flow rate = 1 gpm
- Dragin rate into bath = 0.4 gph
- Zn buildup in EN bath = 0.02 ppm/day

Reducing Rinse Water Flow Rates

- Rinse quality requirements cause high rinse water use
- Common responses
  - Size technology to respond to flow rates
  - Focus on technologies designed for continuous flow
- Process control approach
  - Reduce dragout
  - Improve rinse system design

Reducing Rinse Water Flow Rates



Before

- Single stage rinse
- Rinse water flow rate = 2 gpm
- Dragout rate = 0.25 gph
- Cadmium discharge = 0.23 lb/day

After

- Dragout tank followed by rinse tank
- Rinse water flow rate = 0.6 gpm
- Dragout rate = 0.20 gph
- Cadmium discharge = 0.07 lb/day

Unit 3 - Process Bath and Chemical Recovery

Part 1: Electrodialysis

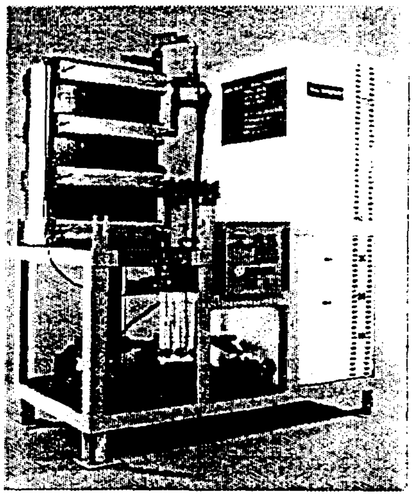
Repurification of Aged Electroless Nickel Baths by Electrodialysis

OMG Fidelity

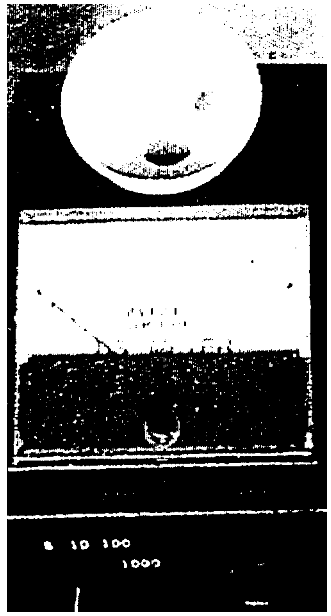
Why Use Electrodialysis ?

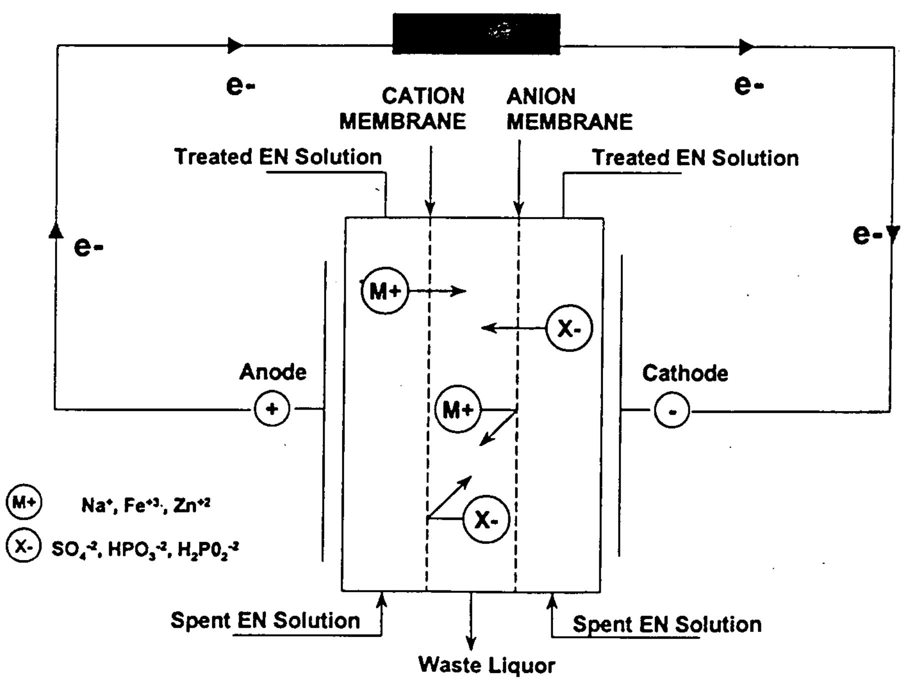
- Maintain consistent deposition rate
- Maintain consistent physical deposit properties
  1) Stress level
  2) Phosphorus content
  3) Deposit structure
  4) Corrosion protection
  5) Magnetic properties
- Lower waste treatment volumes

Electrodialysis Unit



Myron L Meter





Rate of Deposition*

Bath Age	Rate (milc/hr)
0 MT0	0.50
4 MT0	0.28
Dialyzed	0.48

* High Phosphorous EN

Deposit Stress*

Bath Age	Stress (psi)
0 MT0	550
8 MT0	3010
Dialyzed	0

* Bright Medium Phosphorous EN

Cost Assumption

Standard Operation		Dialysis	
25 Makeups	= $13,800.00	1 Makeup =	$551.66
100 MTO's	= $41,000.00	100 MTO's =	$41,000.00
Waste Treat	= $10,000.00	Waste Treat =	$ 1,320.00
(5000 gal @ $2.00/gal)		(2640 gal @ $0.50/gal)	
		Add Backs =	$3,300.00
Total Cost	= $64,800.00	Total Cost =	$46,171.66

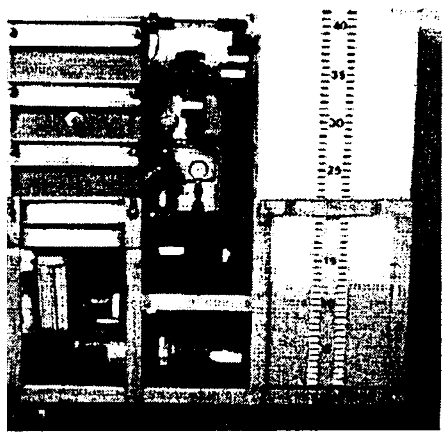
Savings/year = $18,628.34
Payback Period = 10 months

Benefits of Electrodialysis

- Consistent plating bath performance
- Improved deposit consistency
- Reduction in chemical expense
- Reduced waste treatment costs
- Decreased reject rate

Case Study

Full-Scale Electrodialysis Unit



Case Study

Full-Scale Implementation

- 60 hours to reduce 170-gallon bath used for 6 MTOs to 1 MTO equivalent
- 30 diluate and concentrate compartments
- 21 amps of electrical current
- 380 watts per hour of electrical power
- Footprint: 2’ x 4’
- Height: 4.5’
- Capital Cost: $28,000

Case Study

EN Plating Comparison

Parameter	Before Electrodialysis	With Electrodialysis
' EN Baths Per Year	71	3
trodialysis Regenerations Per Year	---	77
l Liquid Waste Solution Per Year	12,070 gallons	6,840 gallons
)s Per Bath	5 to 6	60
ct Rate - Cost	$20,400	$6,280

Case Study

Results

- **Total EN process chemical use decreased by 25%**
- **Total liquid waste generation decreased by 33%**
- **Total liquid waste disposal cost decreased by 77%**
- **Significant decrease in "break-in" time**
- **Reject rates decreased 50%**
- **Total mass of nickel waste decreased by 56%**
- **Normal EN bath additions remained unchanged**

Case Study

Annual Costs

Parameter	Before Electrodialysis	With Electrodialysis
EN Bath Operation		
New Bath Make-Up Chemical Cost	$37,630	$1,590
EN Chemical Additions	$43,380	$43,380
Spent Bath Treatment and Disposal	$31,740	$1,340
Labor for Make-Ups	$1,780	$75
EN Rejects	$20,400	$6,280
Electrodialysis O&M		
Regeneration Additions	—	$15,550
Diluate Disposal	—	$5,930
Labor -Regen. and Membrane Clean	—	$400
Electricity	—	$160
TOTAL	$134,930	$84,340

Case Study

Payback Period

Total annual savings = $50,600/year

Total capital cost = $28,225

Payback period = 7 months

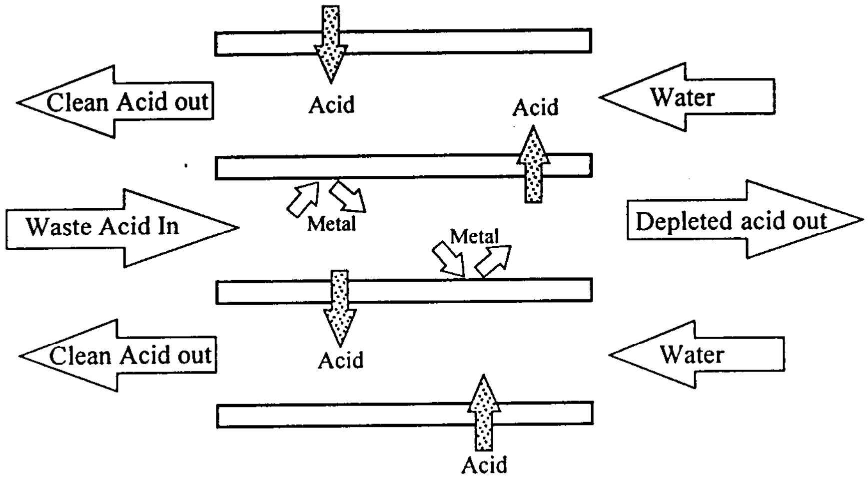
Overview

- Background
- Equipment
- Feed streams
- Results
- Economics
- Conclusions

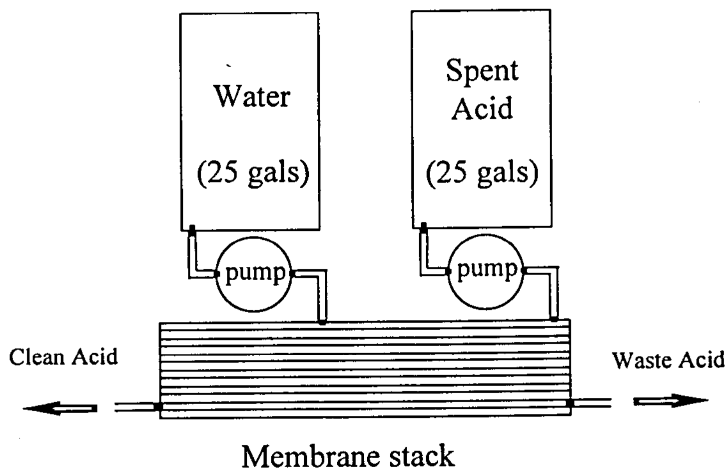
Background

- The human body is the original dialysis system
- Graham in 1861 used parchment paper
- Originally to separate species of different sizes
  - Salts, blood, gelatinous colloids
- Advancements in membrane technology
  - Improved chemical compatibility
  - Increased life expectancy
  - Higher allowable temperatures

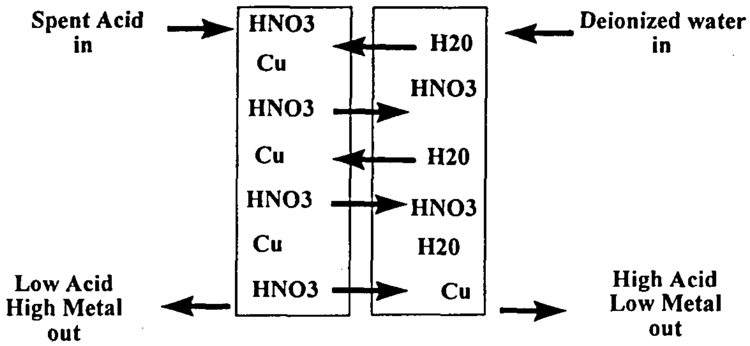
Diffusion Dialysis



Typical Equipment



Waste Acid Recovery (batch)



Acid Feed & Waste Stream Volumes

- 55 gallons waste acid in
- 55 gallons DI water in
- 55 gallons Low Acid High Metal out
- 55 gallons High Acid Low Metal out

Results

Nitric - HF Pickle (9.0 N)

(start)	(finish)
9.0 N Nitric Acid	7.5 N Nitric Acid (83%)
15 gm/l iron	2.5 gm/l iron (-83%)
10 gm/l nickel	1.7 gm/l iron (-83%)

Economics (for 55 gallons)

Nitric Acid ($2.06/lb.)	Dispose	Recycle
–New chemicals	$1300	$260
–Disposal costs	$350	$150

Results

Sulfuric acid activator (5.0N)

(start)	(finish)
4.3 N Sulfuric Acid	3.1 N Sulfuric Acid (72%)
45 gm/l iron	7.9 gm/l iron (-82%)

Economics (for 55 gallons)

Sulfuric Acid ($0.34/lb.)	Dispose	Recycle
New chemicals	$120	$55
Disposal costs	$150	$150

Results

Caustic etch

(start)	(finish)
1.5 N NaOH	1.3 N NaOH (85%)
35 gm/l aluminum	7.1 gm/l aluminum (-79%)

Economics (for 55 gallons)

NaOH ($1.18/lb.)	Dispose	Recycle
New chemicals	$20	$8
Disposal costs	$150	$150

Operation & Maintenance

- Temperature-dependent
  - higher temp = faster processing
- Filtered solutions are a must
  - < 5 micron (< 1 is better)
- Metal / acid ratio must be in range
  - If too low, metal will precipitate and clog
- Both sides of system flushed every 2 weeks
  - Removes metal residue, maintains efficiency
- Should be stored filled with deionized water

Conclusions

- **Acids and bases can be recycled**
  - Waste solutions
  - Tank maintenance
- **Cost-effective depending on volume & controls**
- **Payback times depend on loading and usage**
- **Over 20 vendors offering systems**
- **Over 200 installed systems in U.S.**

Motivation for Pursuing P2

- Process control and efficiency - extending the life of acid bath
- Reduction of reject rate of parts due to rack strip quality
- Reduced operating costs
- Compliance with the Toxic Use Reduction Act (TURA)
- Lower worker exposure to acid
- Concern for the environment

Diffusion Dialysis

- Optimal flow. rate of spent acid stream and recovered acid stream is approximately 15 gallons/day
- Operates directly on-line with continuous process bath flow
- Approximately 10 gallons/week of fresh acid is added to stripping bath

Diffusion Dialysis Results

Savings	
Nitric acid use	$2,761
Hazardous waste disposal	$3,200
TURA fees	$1,100
O & M Costs	
Water, Filter, Electricity	$217
Net Savings	$6,844

Diffusion Dialysis Capital Costs

Item	**Cost**
Pure Cycle AJ-20 Acid Recycling System	$15,800
Increased Capacity Tank	$987
Modified Ventilation System	$4,230
Filter Reservoir	$1,473
Flo-King Filter model BX-1200-8	$460
Electrical/Plumbing	$1,000
Barrel Deposits	($4,500)
Total	**$19,450**

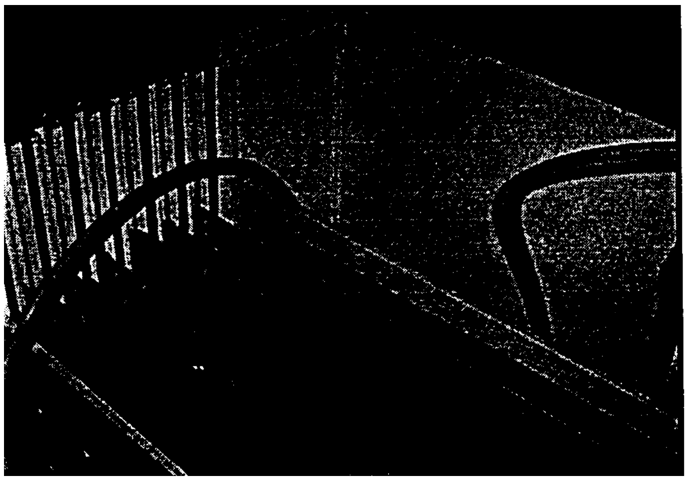
Unit 3 - Process Bath and Chemical Recovery

Part 3: Electrowinning

Electrowinning Use

- Used to recover metals from concentrated solution
- Most commonly installed on dragout rinses
- 19% of shops use electrowinning according to a 1995 NAMF survey

Electrowinning Unit



Common Applications

- Gold
- Silver
- Copper
- Cadmium
- Zinc

Cathodes and Metal Concentration

- **Cathode types**
  - **Flat plate**
  - **Reticulated**
- **Deposition rate is proportional to target metal concentration**

Electrowinning Case Study

Case Study

Phase I: Tank Layout

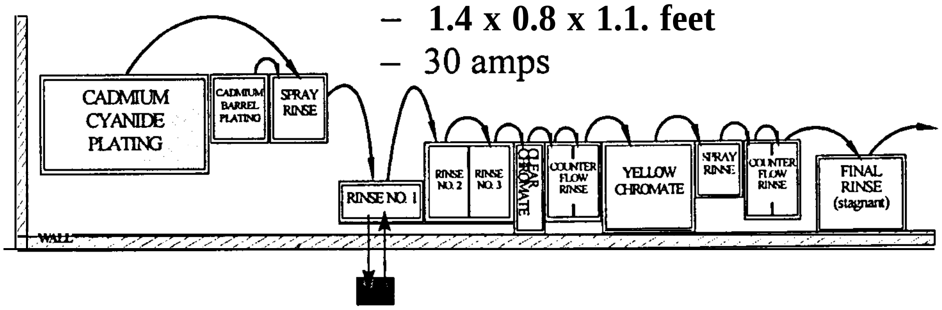
- **Dragout losses reduced 50%**
- **Rinse water flow reduced 50%**
- **Improved rinsing**
- **More efficient work flow**
- **Lower concentration of metals in WWTS discharge**

Case Study

Phase II: Electrowinning

Rented demo unit for 5 weeks ($400)

- **Retec Model 07 by Memtek**
- **1.4 x 0.8 x 1.1. feet**
- 30 amps

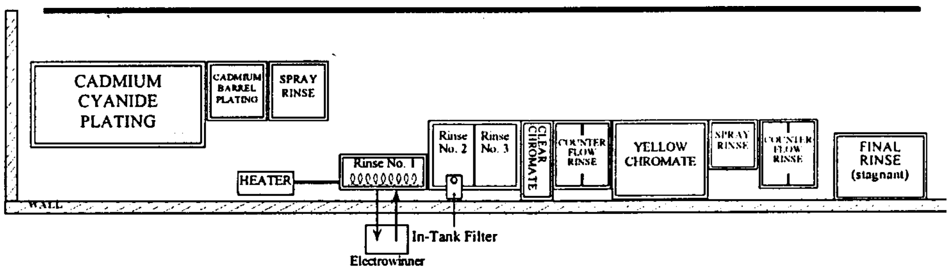


Electrowinner

Electrowinning Trial Conclusions

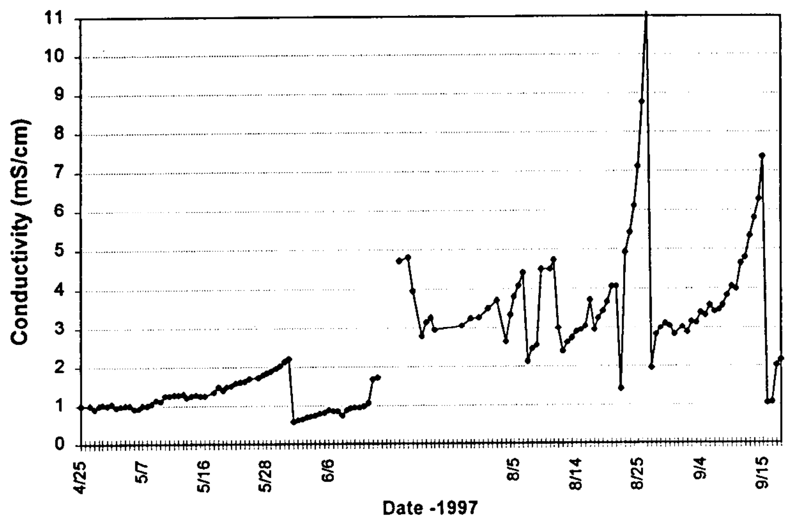
- Rinse water should be moved into Rinse No. 1 at a faster rate
- Rinse No. 1 may need to be periodically poured into plating bath or dumped
- Larger unit may better accommodate production variations
- Water use and wastewater discharge significantly decreased!

Electrowinning Configuration



- Facility purchased unit in February 1997
  - Retec Model 6
  - $7,500
  - 1.9 x 1.9 x 1.8 feet
  - 100 amps
- Electric heater installed on Rinse No. 1
- Continuous filtration system installed on Rinse No. 2

Conductivity in Stagnant Rinse No. 3



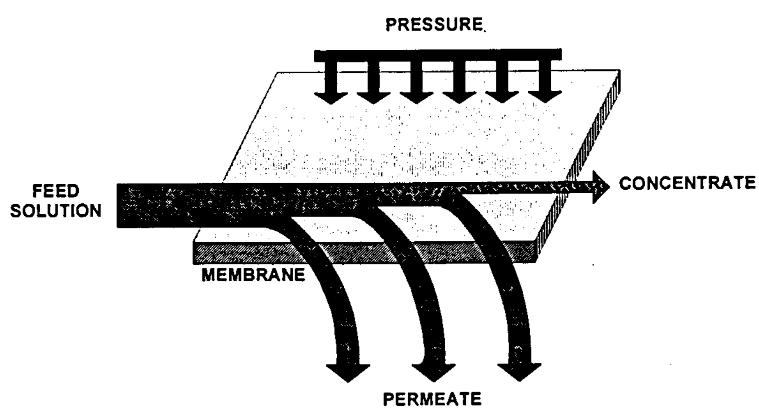
Electrowinning Costs

- Layout Modifications
  - Counterflow and spray rinse = $1,300
  - Installation = $960
- Electrowinning
  - Electrowinner = $7,500
  - Heater = $690
  - Filtration unit = $570
  - Electrical = $250
  - Installation = $400
- O&M
  - Electricity = $20/mo
  - Cathodes = $290/yr

Unit 4 - Rinse Water Recycling

Part 1: Reverse Osmosis

Reverse Osmosis Technology Description

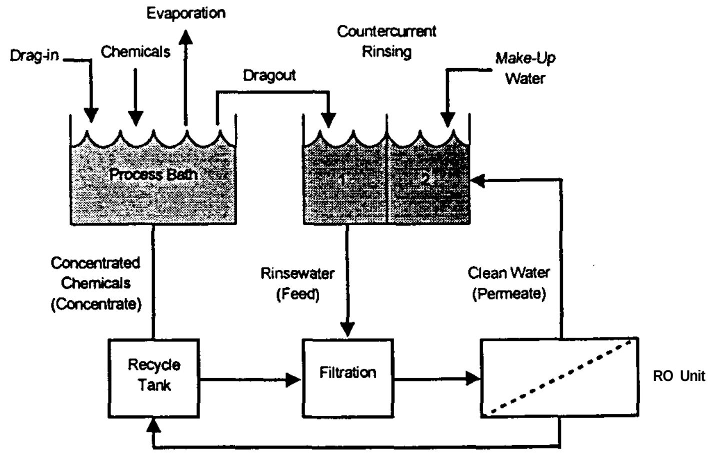


"Crossflow filtration"

Present Uses of RO

- Water purification
- Recycle segregated rinsewaters.
  - Concentrate returned to process bath
  - Permeate reused as rinsewater
  - "Closed-loop" application

Process Flow with RO



RO Membrane Materials

Membrane Material	pH	Maximum Temperature	Other
Cellulose Acetate	2.5 to 7	85 to 122 °F	Biologically Degradable
Aromatic Polyamides	4 to 11	95 to 115 °F	Cannot tolerate chlorine

RO Membrane Designs

Membrane Design	Cost	Membrane Types	Fouling Resistance	Cleanability
Spiral Wound	Low	Many	Fair	Fair
Hollow Fiber	Low	Few	Poor	Poor
Capillary	Moderate	Many	Very good	Very good
Tubular	High	Few	Very good	Very good
Plate and Frame	Moderate	Many	Poor	Fair

RO Cost

- Capital cost: $10,000 to $50,000
- O&M costs (per 1,000 gallons treated)
  - Labor
  - Energy
  - Cleaning chemicals
  - Membrane replacement
  - Total Cost: $2 to $5

RO Advantages

- Concentrate stream can be used to replenish process bath
- Permeate stream can be used as rinse water
- Low energy process
- Low O&M costs
- Easily upgradable
- Low labor required compared to other technologies

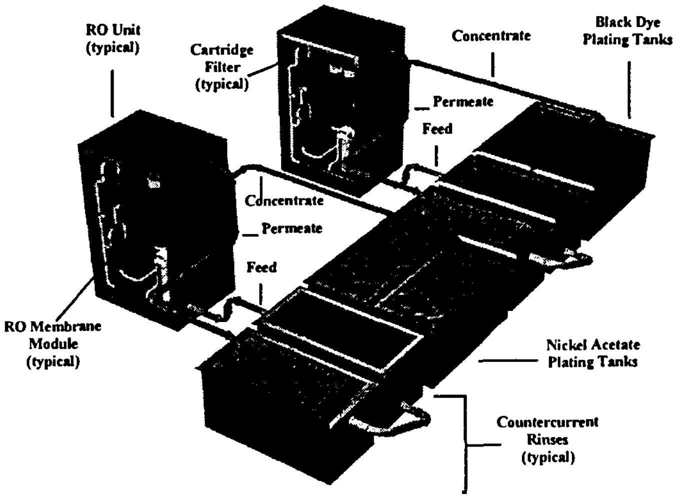
RO Case Study

Case Study

Facility Description

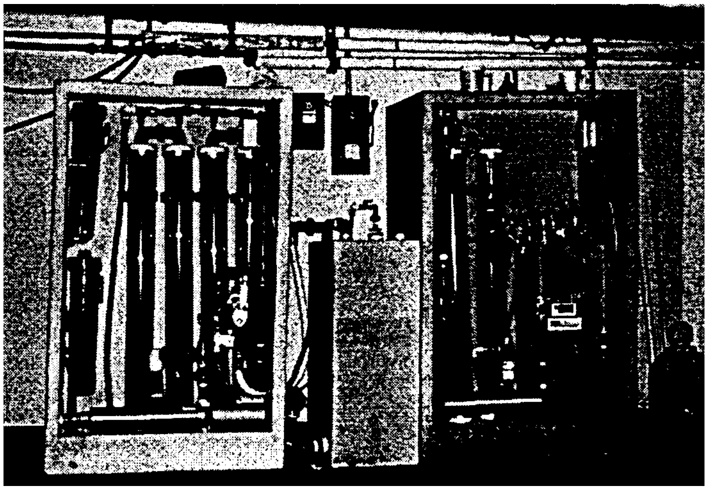
- Specializes in:
  - Standard type 2 and hard type 3 anodizing
  - Chemfilm
  - Stainless steel passivation
  - Dye coloring
- Anodize small- to medium-sized parts
  - Commercial and military parts
  - Flashlight parts
  - Bicycle parts

Case Study: Black Dye and Nickel Acetate Configuration after RO Installation



Case Study

RO Units



Case Study

RO Results for Black Dye Operations

	Before	After	Monthly Savings
City Water	3 gpm	0 gpm	$ 83
POTW Discharge	3 gpm	0 gpm	$133
Black Dye Chemical	21 lbs/mo	9 lbs/mo	$293

Total Savings: $6,100/yr

Total Cost: $10,000

Payback Period: < 2 years

Case Study

Facility Description

- **Wheelchair manufacturer**
  - **Nickel and chrome plating**
  - **Stringent wastewater discharge limitations on total dissolved solids and boron**

Unit 4 - Rinse Water Recycling

Part 2: Closed-Loop Rinsewater Recycling Using an Improved Ion Exchange Process

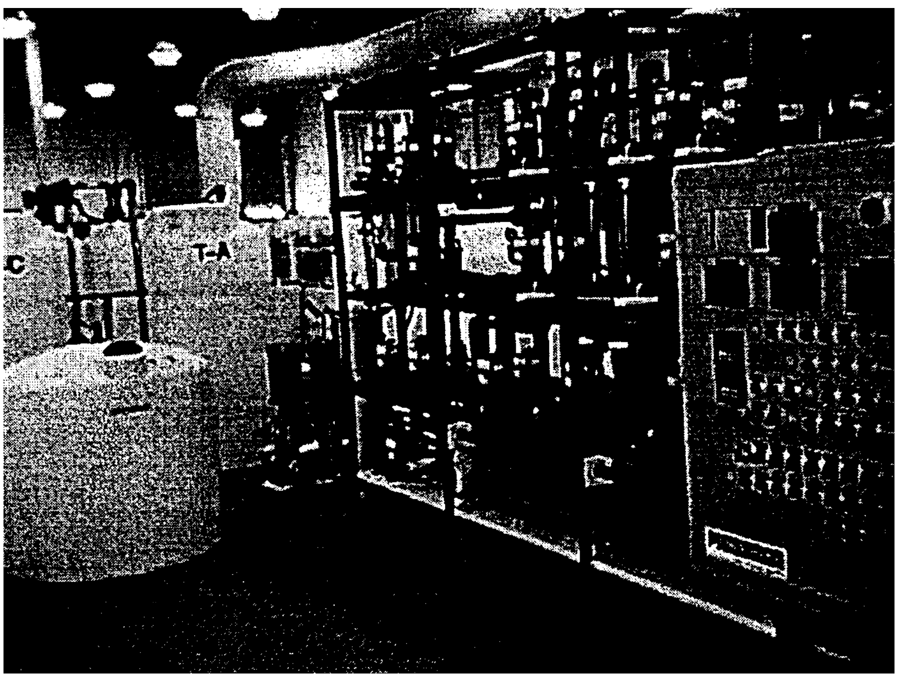
hydromatix

Discussion Topics

- How ion exchange works
- Where ion exchange fits
- Problems with conventional ion exchange systems
- Description of patented 786 Process
- Operating cost comparison
- Gold Seal case study

Metal Selective Ion Exchange

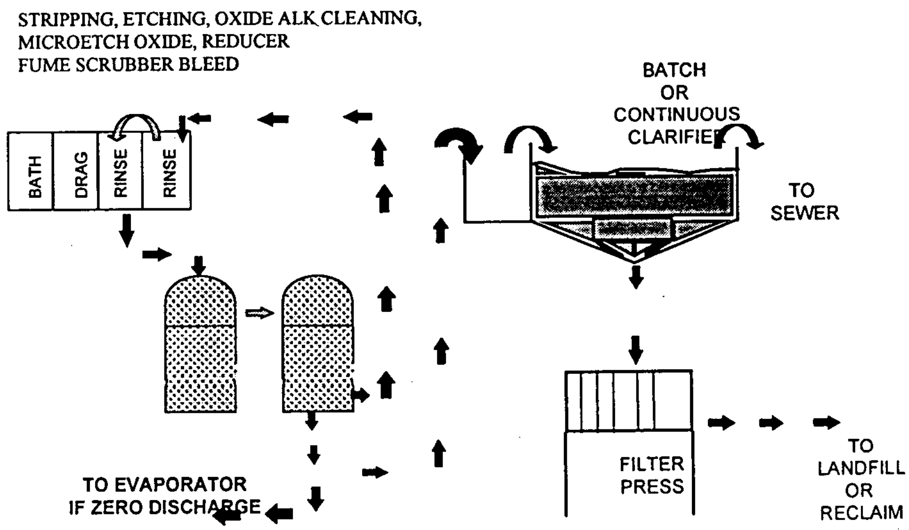
- Used in recovery precious metals
- Found on end-of-pipe systems
- Applications in bath recycling
- Used when electrowinning regenerant
- Not compatible with recycling



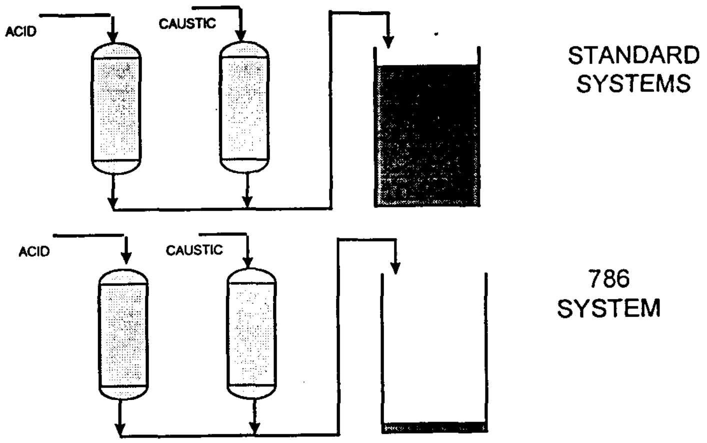
Recycling Incentives

- Achieve zero sewer discharge
- Achieve batch treat mode to assure compliance
- Have high flow rates through rinse tanks for better quality
- Lower operating costs

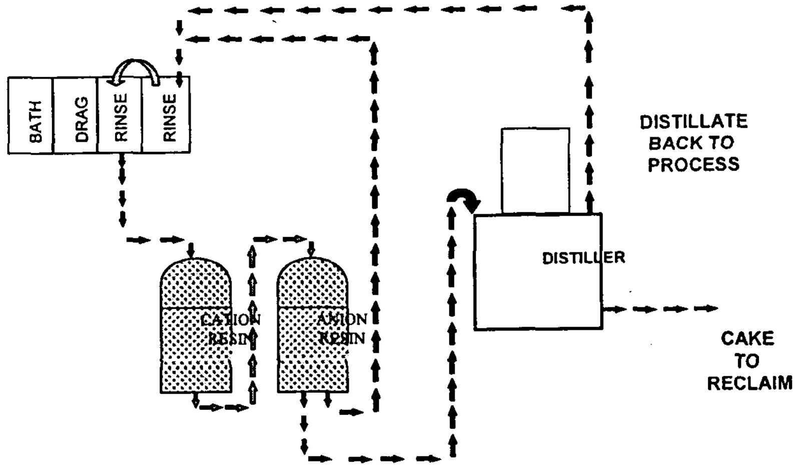
Where Ion Exchange Fits (Inorganic Rinses)



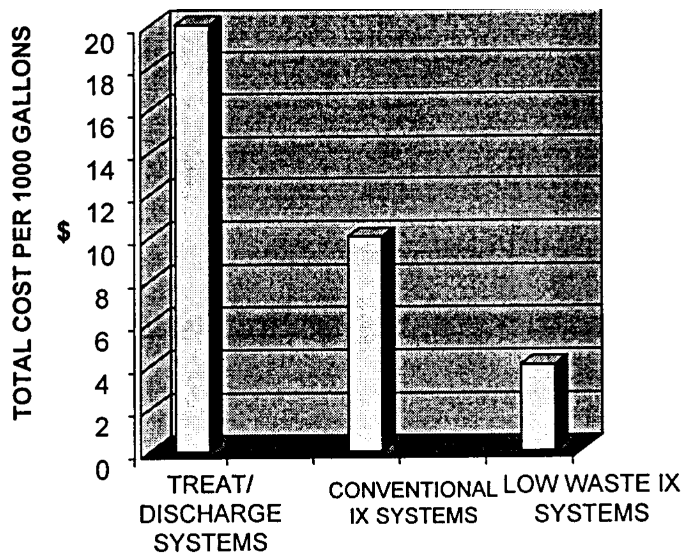
Regenerant Comparison



Zero Sewer Discharge



Operating Cost Comparison



Case Study

Gold Seal Background

- **Initiated by Cal EPA - Department of Toxic Substances Control (DTSC)**
- **Motive to highlight technology with significant environmental impact**
- **Completed in December 1996**
- **Received CWEA Industrial & Hazardous Facility of the Year Award - 1996**

Case Study

California EPA - Gold Seal Plating

W/O Recovery System (6 gpm)	Annual Amount	Unit Cost	Annual Cost
Incoming City Water (Rinse)	2,170,000 gal	$0.0045/gal	$9,800
Wastewater Treatment	2,170,000 gal	$0.007/gal	$15,500
Sludge Recycling	73,150 lbs	$0.33/lb	$24,100
Permit	---	---	$11,400
Outside Lab Testing	---	---	$2,200
TOTAL			$63,000

Case Study

Recycling Plus Zero Discharge to Sewer

With Recovery (12-15 gpm)	Annual Amount	Unit Cost	Annual Cost
Incoming City Water (Make up)	260,000 gal	$0.0045/gal	$1,200
Chemicals (Regenerant)	11,400 gal	$1.42/gal	$16,200
Energy (Evaporators)	70,200 gal	$0.034/lb	$2,400
Sludge Recycling	36,000 lbs	$0.36/lb	$13,000
Permit	---	---	$0
Outside Lab Testing	---	---	$0
TOTAL			$32,800

Company Background

- Established in 1989
- Ion Exchange based on specialty separations
- 786 technology was introduced in 1995
- Worldwide patents applied for - 2 U.S. patents approved

Partial Users List

- Gold Seal Plating - Oakland
- QLP Laminated Division - Santa Ana
- Allied Signal - Irvine
- MEKTEC - Milpitas
- Hughes Research Labs - Malibu
- Aero Electric Connectors - Torrance
- Electrochem - Hayward (In construction)
- Packard Hughes - Irvine (In construction)

Unit 5
Wrap Up

Pollution Prevention Technologies

- "First things first"
- Process bath regeneration/recycling
  - electrodialysis
  - diffusion dialysis
  - electrowinning
- Rinsewater recycling
  - reverse osmosis
  - ion exchange

Mini-Assessments

FREE technical assistance to motivated facilities to help them select and implement <u>cost-effective</u> Pollution Prevention "fixes"

6 facilities already selected
More will be selected (Apply Now!)