# "Waste & Sludge Minimization from Surface Treatments & Waste Recovery from Industrial Processes"

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This work reviews zinc plating processes, from which alkalines, high-cyanide-content baths are being eliminating. Completed elimination of CN is expected in a three-year time maximum. All white or blues, yellow or dichromate and zinc passivating processes will be substituted with trivalent chrome. The total elimination of hexavalent chrome will be accomplished in 5 years, maximum (2007). Copper and cyanide silver baths will be substituted with non-cyanide baths. Physical-chemical depurator's sludge from surface treatment processes is already used by different industries as by-product or prime material. Anodizing sludge, for example, is used for cement manufacturing. Acid zinc sludge without hexavalent chrome is used to make building material. Almost all other type of depurator's sludge is use by vitrifying plants. Because of this, we will use and study semi-permeable membranes and inverted osmosis units in electrolytic processes.

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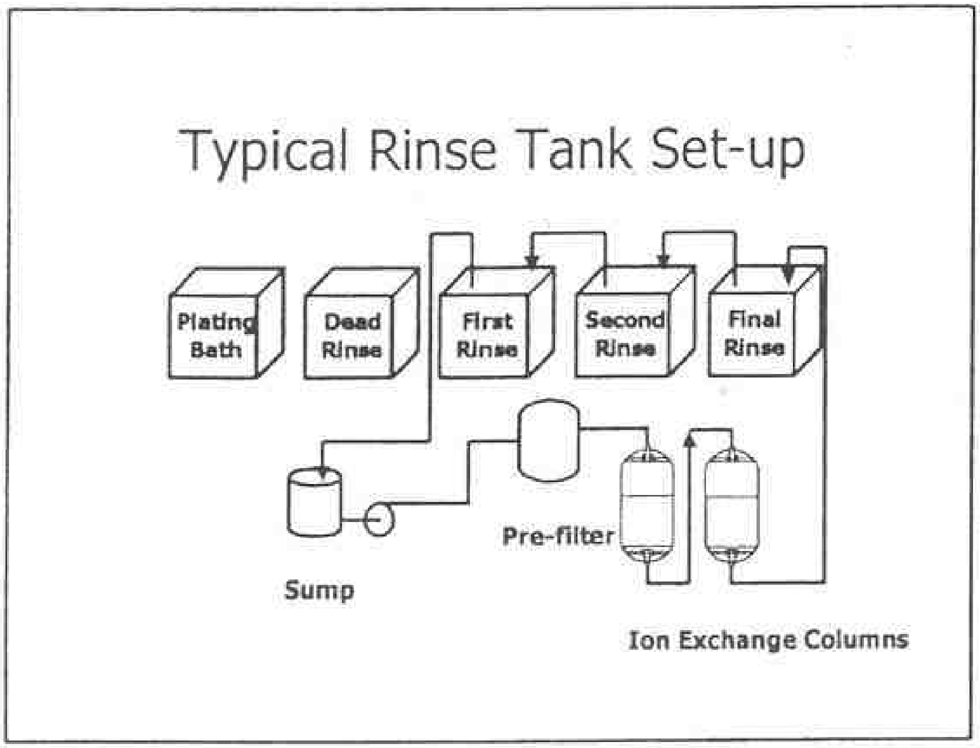
## Introduction

Ion exchange resins are one of the best available and most durable technologies for removing relatively low concentrations of ionised contaminants from water industrial process.

Different metallic contaminants: zinc, nickel , chromium, tin.

Elimination of potential discharge of metals to the environment by elimination.

The need to discharge water waste.



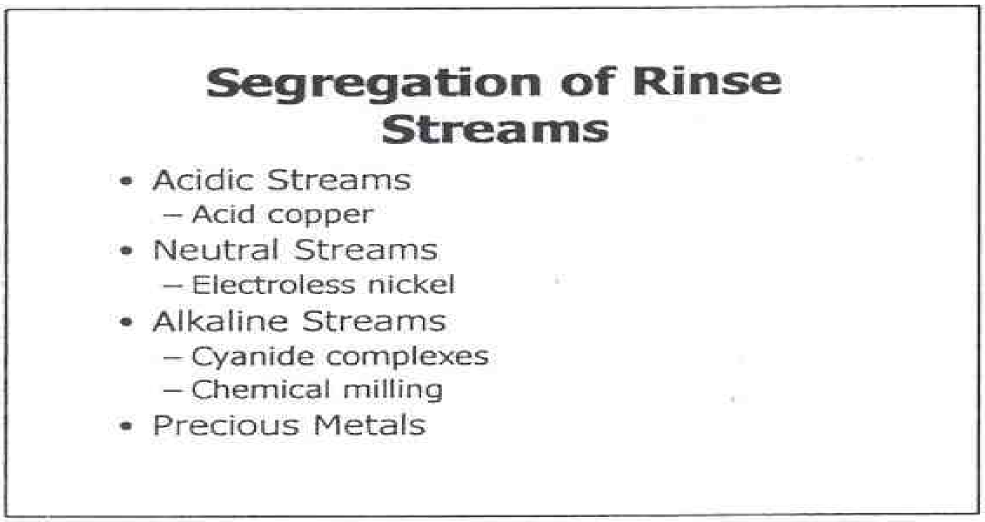

## Recycle Systems

Saving water
Saving contaminants
Saving chemical products
Saving process waste water

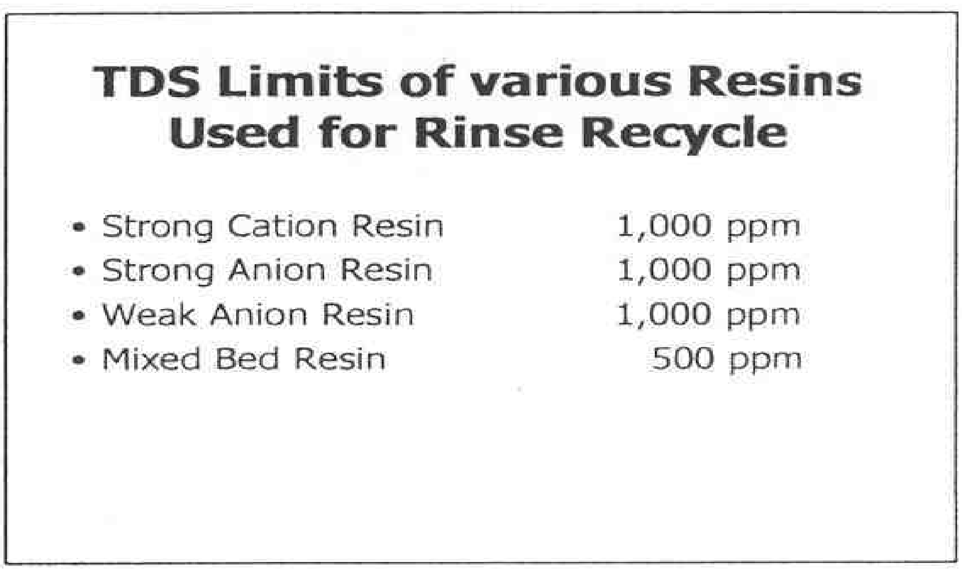
**Segregation of Rinse Water Streams**

For years, most plating shops have combined rinse waters into a common stream for bath treatment.




**Limits Of Ion Exchange**

The ionic concentration of ion exchange resin is in the neighbourhood of 10% (by weight). A rinse water with a concentration of 10% will exhaust a resin in one bed volume, making the process far less than economically viable.




Another limitation of ion exchange systems is that they are relatively intolerant of organic contaminants such as oils and grease.

Ion exchange resins have limited tolerance to ondate chemicals such as bleaches, peroxides, permanganates and other oxidants

## Ion Exchange Resin General Operating Limits

- Sensitivity to inlet contaminants
  - Organic molecules
    - Polar and non-polar solvents are of no consequence. They do not harm ion exchange resins. However, in some cases, solvents can complex with metals and prevent them from being removed by the resin.
    - Polymers and other long chain molecules (particularly if they are only partially water soluble) will coat the resin beads and prevent the exchange of ions.

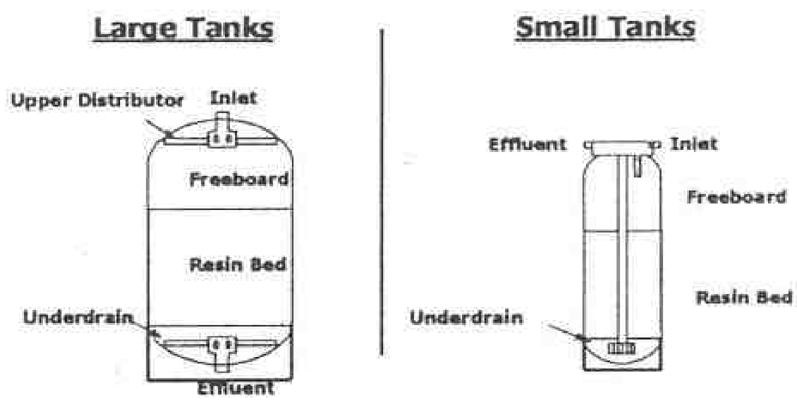
## General Observations about Resin Fouling

- The plastic bag effect
  - Any foulant that coats the resin beads is going to act like a plastic bag and will block the exchange of ions. This will increase leakage and make the resin flow sensitive (OK at low flow, progressively worse as flow increases). It may or may not decrease thru-put.
- The sponge effect
  - Any foulant that collects and surrounds the resin beads is going to act like a sponge and cause long rinses after regeneration. This may or may not cause channeling and high pressure loss. The sponge is a wonderful place for bio-organisms to grow.

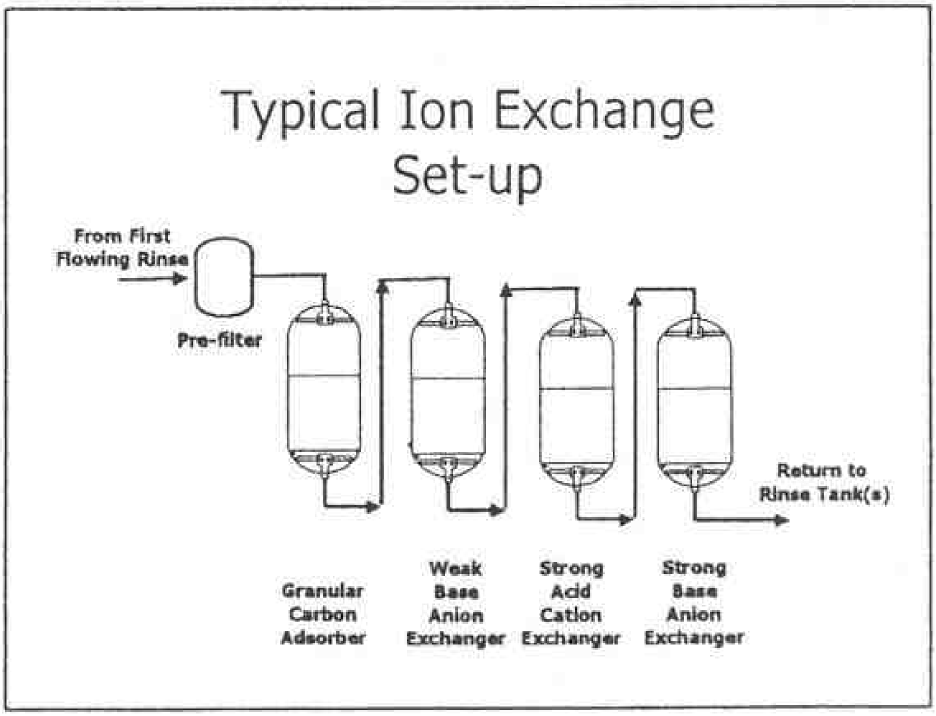
# Ion Exchange Resin General Operating Limits

- pH
  - All ion exchange resins are stable from pH below 0 to above 14. However, their useful operating range is much narrower. This useful range is different for each type of resin. It is usually not advisable to add chemicals to adjust pH ahead of an ion exchange system; far better to use the appropriate resin for the pH expected.
- Temperature
  - Most ion exchange resins are stable to at least 140 °F. In general, capacity increases with increasing temperature.

# Typical Tank Setup






**Acid Baths**

Nickel and copper baths consist of sulphuric acid mixtures with various metal salts. Electroless nickel and other plating baths are slightly acidic and contain additional chelating agents. Anodizing baths contain chromic acid often with dyes and other organic additives.

The best treatment scheme consist of a three-tanks ion exchange approach. The first tank contains a weekly basic anion exchange resin designed to absorb the excess acidity from the solution. The second tank consist of strong cation exchange resin and the third tank consist of strong anion exchange resin. However, it may be advantageous to separate chrome-containing solutions from other metals from a standpoint of ease of recovery.

**Alkaline Rinses**

Although, the strong cation exchanger does significantly reduce the pH of the rinse water, there is little concern about a gaseous cyanide release, since most of the syanide is chemically bound to the metal and cyanide is very soluble in water.

The anion portion of the exchange removes the cyanide-complexed metal as well as any free cyanide that may be present.

System treating aluminium wastes are also very susceptible to problemas with precipitation and resins fouling since aluminium is soluble at high and low pH but rather insoluble at neutral pH.

| TYPE OF RESIN | TOTAL CAPACITY | OPERATING CAPACITY |
|---|---|---|
| Strong Acid Cation | 2.0 eq/l | 1.0 eq/l |
| Weakly Basic Anion | 1.5 eq/l | 1.0 eq/l |
| Strongly Basic Anion | 1.0 eq/l | 0.6 eq/l |

**Capacity and Doses Rules of Thumb**

| Type of Resin | Typical Operating Capacity | Typical Chemical and Dose |
|---|---|---|
| Strong Acid Cation | 20 kgrns/cuft | 6 lbs/cuft HCl |
| Weak Base Anion | 20 kgrns/cuft | 5 lbs/cuft NaOH |
| Strong Base Anion | 14 kgrns/cuft | 6 lbs/cuft NaOH |

**Regeneration of Spent Resins**

The ion exchange resin have operating lives in the neighbourhood of 100 to 300 cycles unless there is a very strong oxidizing environment, abnormally high temperature or unusually high-flow rate.

## Typical Regeneration Steps

- 1. Backwash
  - Removes physical contaminants and fluffs up the bed so the chemical solution will penetrate the resin evenly
- 2. Chemical injection
  - A dilute chemical solution flows slowly thru the resin, removing accumulated ionic contaminants
- 3. Slow rinse
  - Helps extend contact time
- 4. Fast rinse
  - Purges the last traces of chemicals from the resin, preparing it for the next service cycle

## Backwash

- Relieves compaction of the resin that may have occurred during the service cycle. This allows the chemicals used in the next step(s) to flow smoothly through the resin
- Removes suspended solids that have accumulated in the resin bed
- Air mix may be helpful to remove suspended solids
- 25-50% bed expansion recommended
- Minimum 10 minutes duration (or longer)

## Chemical Injection

- A dilute solution of acid (for cation resin), or base (for anion resin) is passed slowly through the resin.
- The resin gives up the ions collected during the service cycle in exchange for hydrogen (cation) or hydroxide (anion) ions.
- Chemical dose is generally around 4-10 lbs/cuft
- Concentration is generally around 3-6%
- Contact time is generally around 30-40 minutes

## Slow Rinse

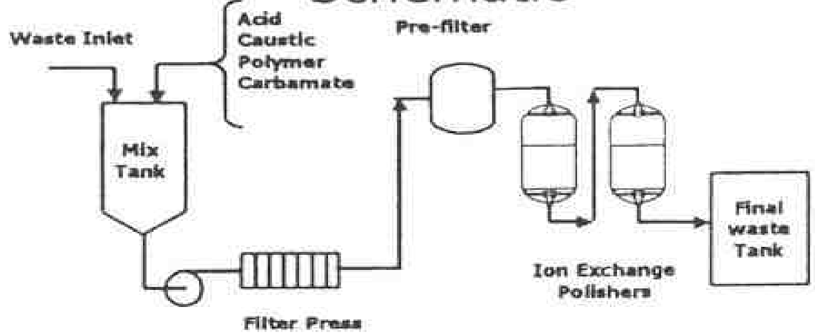
- Pushes the chemical slowly thru the resin, ensuring that the contact time is the same for the resin at the bottom of the bed as at the top
- 1 bed volume (7.5 gal. per cu.ft. of resin) is typical
- Flow rate is the same as the chemical flow rate
- Can be omitted if the chemical contact time is already long enough

## Fast Rinse

- Flow rate as it suits (often the same as for service)
- 5-10 bed volumes (40-80 gal per cuft) when rinsing to quality before return to service
- Time is as required to achieve necessary volume at the flow rate selected

## Bulk Waste Treatment Schematic





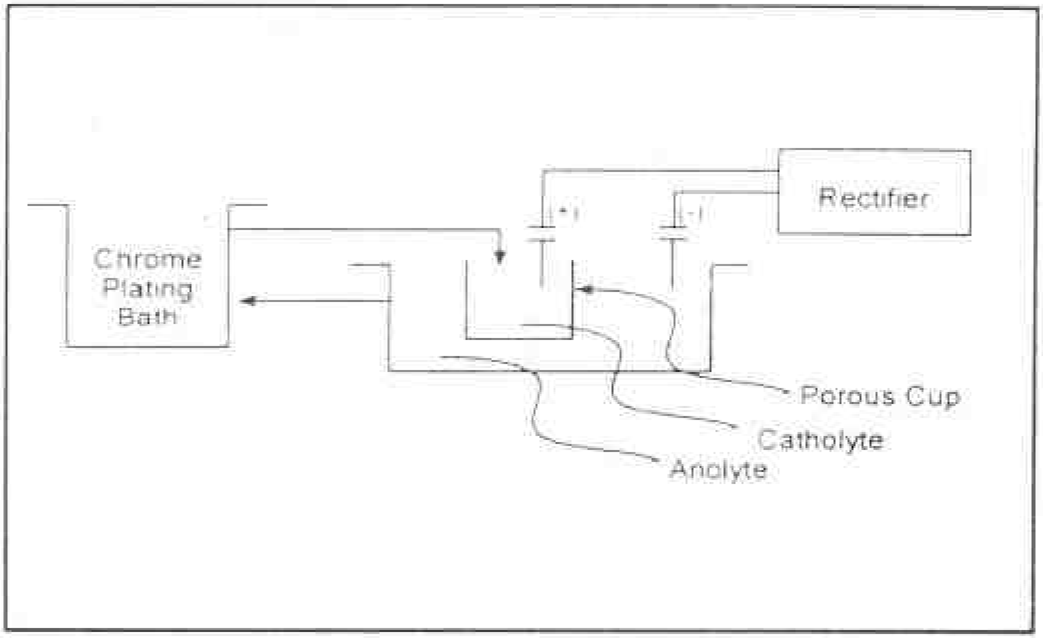



Figure 1- Porous Pot Purification

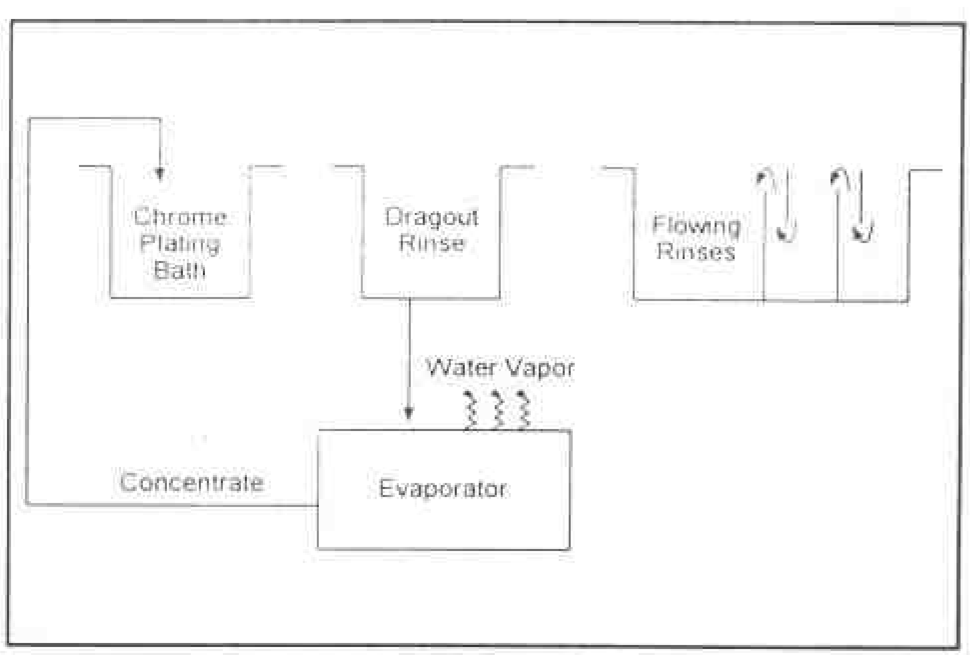



Figure 2 – Evaporation Recovery

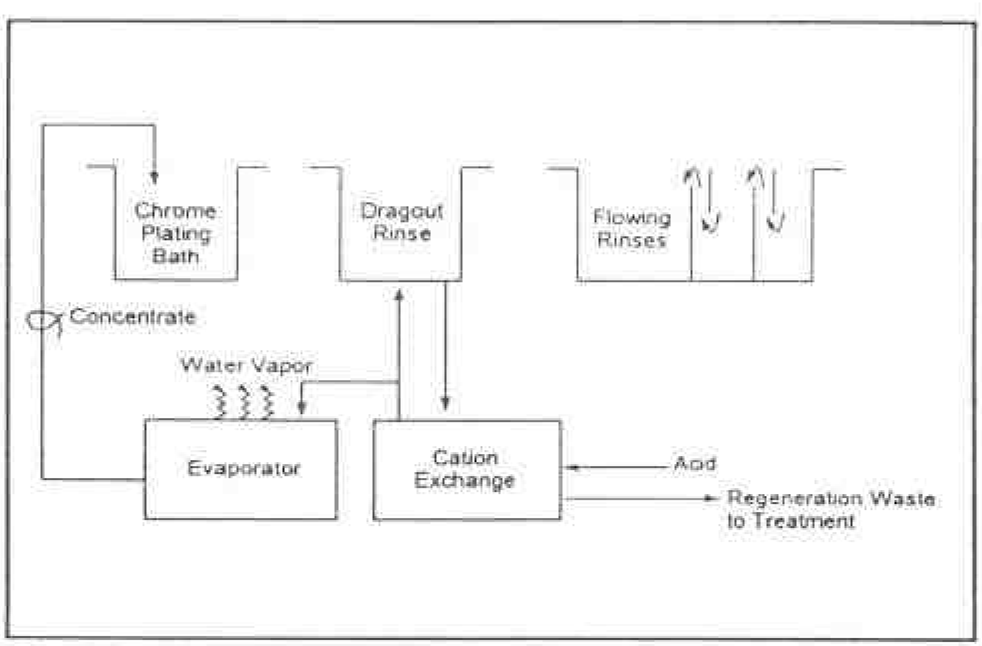



Figure 3 – Evaporation Recovery and Ion Exchange Removal of Contaminants

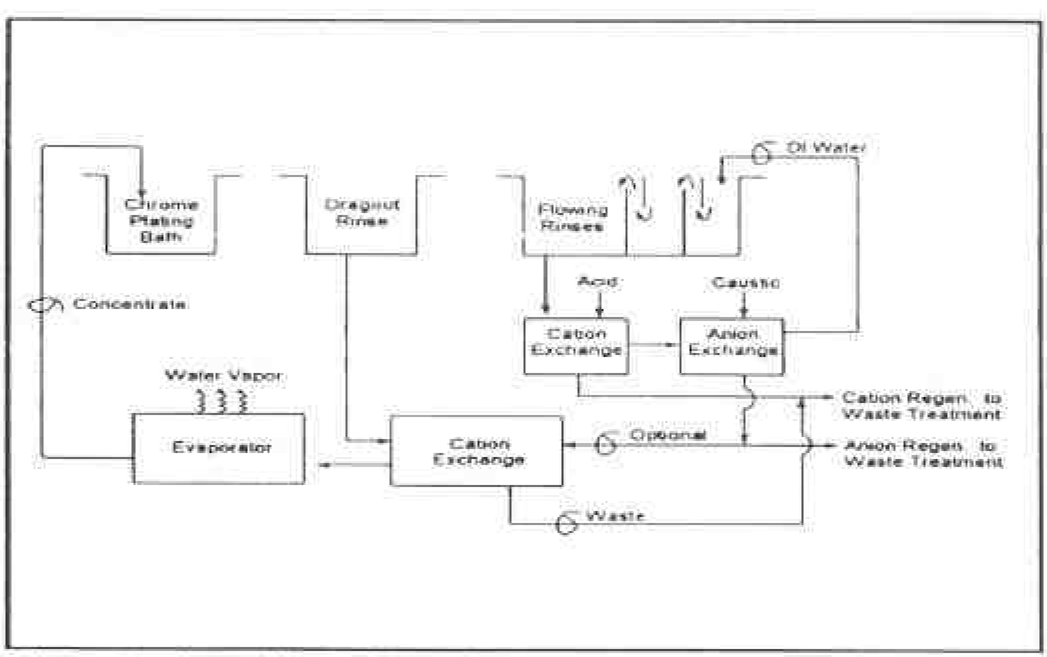



Figure 4 – Rinse Water Recycling

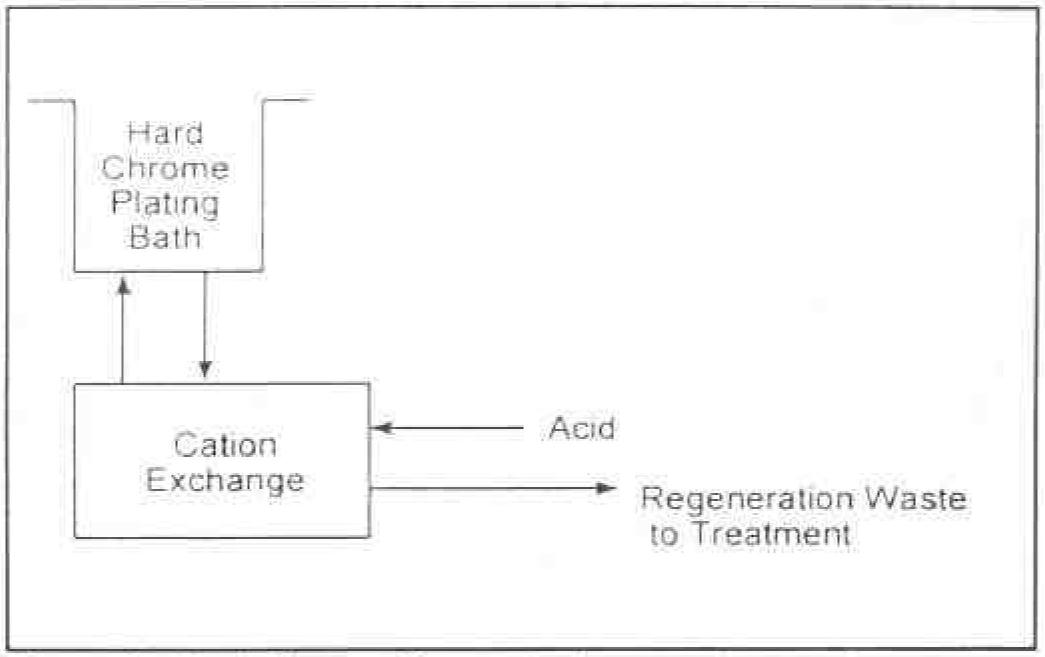


Figure 5 – Hard Chrome Plating Application

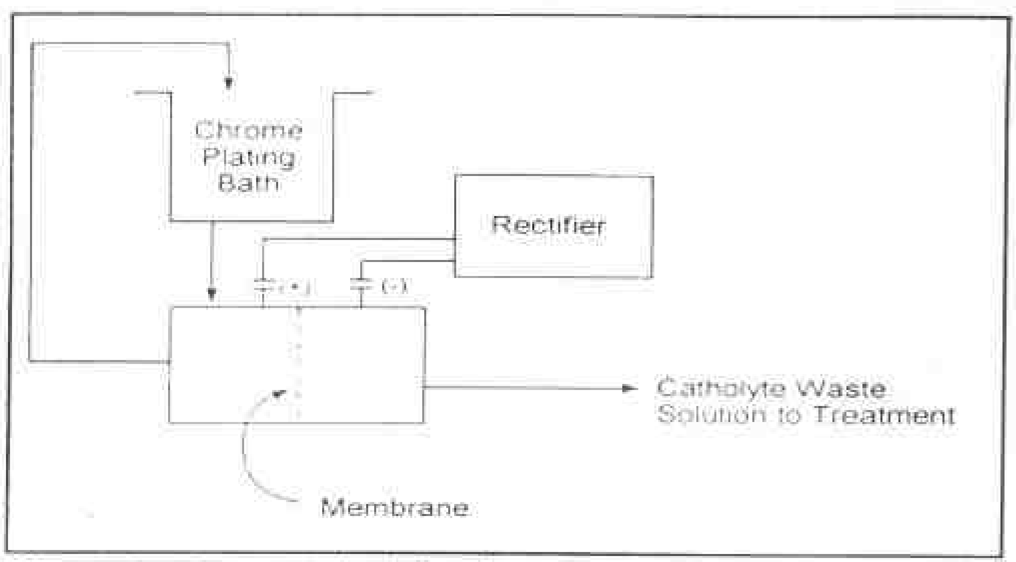


Figure 6 – Alternative Bath Purification Method

**Table 1 - Chrome Plating Solution Recovery – Relative Cost Comparison**

| Recovey Technic | Capitol Equipment | Labor | Recovery Efficiency | Utilities | Chemicals | Miscellaneous |
|---|---|---|---|---|---|---|
| Porous Cup | Low | Low | Low | Low | Low | Bath Purification Recovery |
| Evaporation | Low | Low | Moderate | High | N A | Bath Recovery |
| I X Evaporation | Moderate | Moderate | High | High | Low | Bath Purification Recovery |
| IX Evaporation With Rinse Water Recycled | High | Moderate | High | High | Moderate | Bath Purification Recovery & Rinse Water Recovery |
| Electrodialysis | Moderate | Moderate High | Moderate | Moderate | Low | Bath Purification Recovery |
| Conventional Treatment | Moderate | High | N/A | Low | High | No Recovery & High Disposal Cost |

**Table 2 - Economic Comparison**

| Item | Conventional Treatment | Off-Site Treatment | Evaporation | IX/ Evaporation | Rinse Water Recycle |
|---|---|---|---|---|---|
| Sulfuric Acid ($0.05 lb) | $83.00 | N / A | N / A | $62.00 | $26.00/day |
| Sodium Hdroxide ($0.15 lb) | $119.00 | N / A | N / A | $50.00 | $18.00/day |
| | $1,838.00 | N / A | N / A | N / A | $10.00/day |
| Electricity ($0.05 / K WH) -see note 1- | NIL | N / A | $4,380.00/ yr (evaporate -10 gph) | $4,389.00/ yr (Evaporate - 10 gph) | $5.00/day |
| Water Sewer Disposal ($5. / 1,00 gal) | $4.00 | N / A | Nil | $37.00 | $7.00/day |
| Solid waste Disposal ($300.00 /ton) -see note 2- | $1,625.00 | N / A | N / A | $150.00 | $3.00/day |
| Liquid Waste Disposal | N / a | $5.00/ gallon -see note 1- | N / A | N / A | N / A |
| Resin Replacement | $120.00 | N / A | N / A | | Nil |
| Labor $15.00/Hr | $3.500.00 | $60.00 | $ 780.00/ yr (-1 hr/wk) | $780.00/ yr (- 1 hr/ wrk) | $15.00 (1 hr/day) |
| Bath Replacement @$3.50/gal) | $3.500.00 | $3,500.00 | N / A | N / A | N / A |
| TOTAL COST | $7,589.00 | $8,560.00/ yr (1) | $5,160.00/ yr | $5,459.00/ye | -$84.00/day |

BASIS:
Assume 1,000 gallons (3,785 liters) of chromium plating solution at 250 g/ $C_RO_3$+ and 15 g/l total cation contamination
Bath dump schedule IX / year
Total metal contamination at dump – 15 g/l
NOTES:
(1) Assume - $0.06/gallon of water evaporated
(2) Does not include transportation.

## Conclusions

When properly designed and operated, rinse recycle systems provide two major benefits. They eliminate the need to discharge waste water than might contain hazardous contaminants and they generally provide a better quality rinse environment and a mores stable condition.

In the ever-tightening world of environmental regulation, liquid-waste discharge can be a huge headache that never needs to happen.

**References**

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