Metal Finishing:
How to Save on Alkaline Cleaners, Acids, and Rinse Water

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Overview

- Typical metal finishing process steps
- Alkaline Cleaners and Acid Etching:
  - use, management, and life extension methods
- Optimizing Rinse Water Use
  - Single tank rinsing vs. double tank rinsing
  - Counterflow rinsing
  - Reactive rinsing

Finishing Methods

- Plating:
  - nickel, zinc, copper, precious metal, etc.
- Conversion coatings:
  - phosphate, iridite, black oxide, anodizing, etc.
- Painting:
  - solvent based, water based, UV curing paints
- Powder coating
- Electrophoretic Coating (E-coat)

Plating or Conversion Coating: Process Steps

Plating or Conversion Coating process flow

Cleaning | Rinsing | Acid Etching | Rinsing | Plating or Conversion Coating | Rinsing | Drying

Anodizing process flow (special variant of conversion coating)

Cleaning | Rinsing | Acid etching | Rinsing | Anodizing | Rinsing | Dyeing | Rinsing | Sealing | Rinsing | Drying

Organic Coating Process Steps

Painting process flow

Cleaning	Rinsing	Phosphating	Drying	Painting	Drying

Powder Coating process flow

Cleaning	Rinsing	Phosphating	Rinsing	Drying	Powder Coating	Curing

E-coating process flow

Cleaning	Rinsing	Acid Etching	Rinsing	E-coating	Rinsing, E-coat recovery	Rinsing	Curing

Rochester Baseline Example

- Water use = 6,310,000 gpy = $32,900/yr. ($5.22/1000 gallons)
- Exhaust blower = 10,000 cfm = $7,899/yr. for 40 hours per week ($.09/kwh)
- Make-up air heating = 431 decatherms natural gas = $2,154 /yr. ($5/decatherm)
- Acid purchases (HCl) = $19,700 ($1.25 /gallon, 15,760 gallons)
- Caustic purchases (NaOH) = $6,400 ($2.10/lb, 3,048 lbs.)
- Sludge disposal = $15,600
- Total cost per year = $66,923/year

Common Cleaning Steps

- First step: Alkaline cleaners
  - Removal of greases, oils, waxes, dirt from the metal parts
  - Typically heated to accelerate the cleaning process
  - May include ultrasonics or agitation to accelerate the cleaning process
- Second step: Acid cleaning/etching
  - Removal of metal oxides (rust, smut, etc.)
  - Makes the metal surface chemically active for the next step (plating, conversion coating, etc.)

Alkaline Cleaner Bath Life

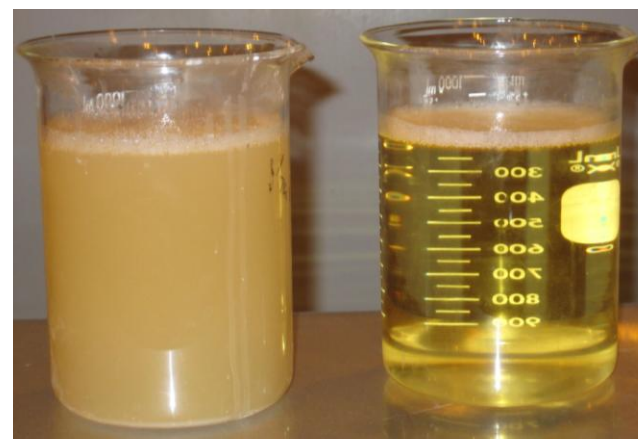
- The cleaner chemical components are lost by:
  - Dragout to the rinse by parts
  - Reaction with the organics (emulsification, chelation, etc.)
- The cleaner effectiveness degrades as the oil and dirt loading goes up with potential redeposition of contaminants

Cleaner Monitoring

- The chemical supplier should be able to provide test kits or test methods to monitor the cleaner chemistry
- Make cleaner chemistry additions based on the test results

Cleaning the Cleaner

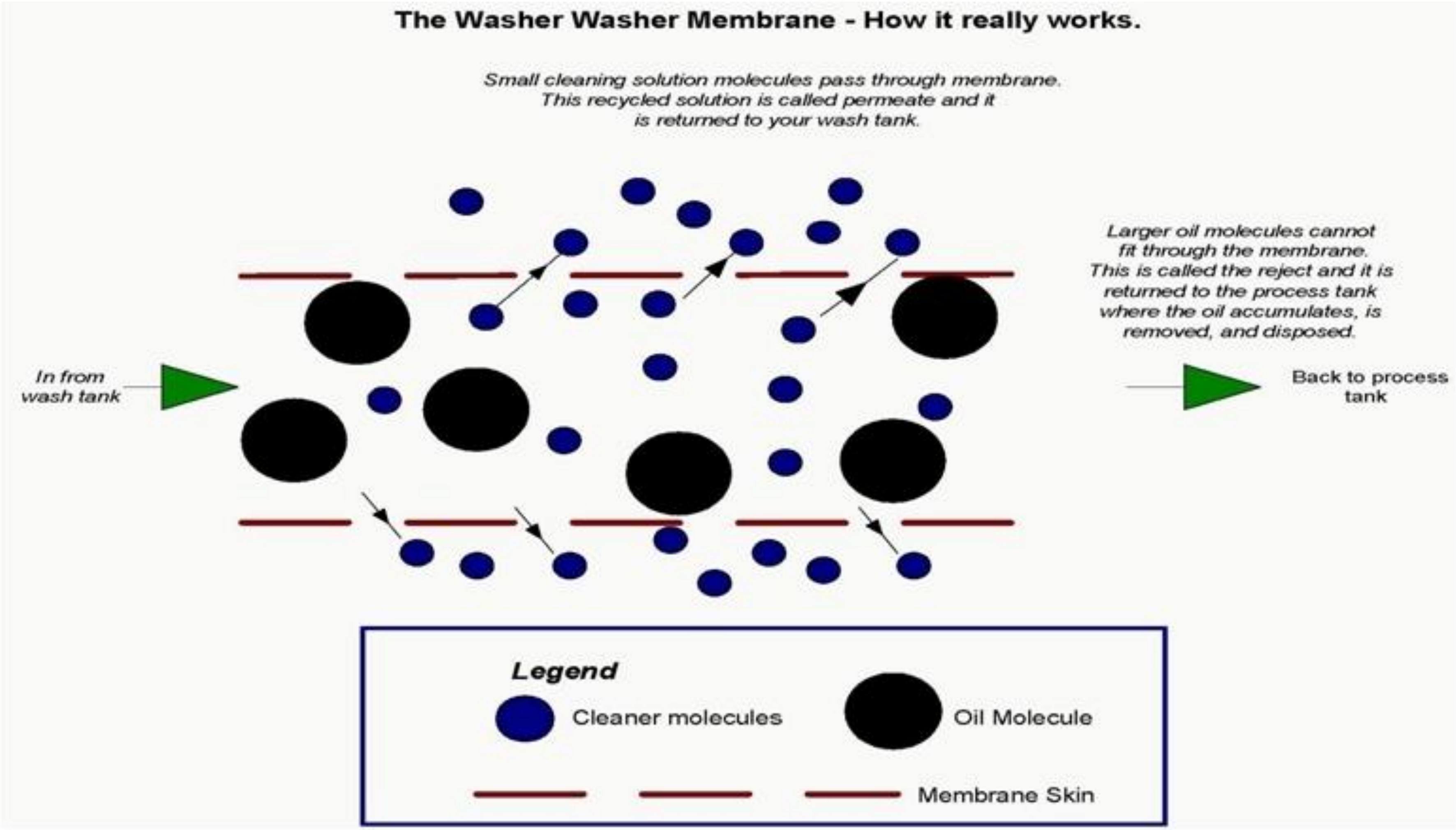
- Cooling a cleaning bath sometimes causes the oils to come out of emulsion and can then be skimmed off (weekend shutdowns)
- Continuous in-tank filtration can usually remove suspended solids (typical polymer filters cannot tolerate solution temperatures >160º F)
- In-tank spargers and weirs can help remove surface oils
- High temperature, high pH tolerant metal or ceramic ultrafiltration can remove colloidal solids and emulsified oils, in most cases without removing any of the cleaning chemistry



TiO_2/SS Material Micro-Ultrafiltration

- Filter able to remove solids and oil emulsions from a cleaner at 200º F and pH of 1-14

Image provided by Arbortech



Schematic provided by Arbortech

Case Study

Chromate/E-Coat Paint Line - Midwest Engine Manufacturer

2005 Costs

• Washer Washer	$39,512
• Stands	$2,080
• Miscellaneous (Install Parts & Labor)	$4,000
• Total	$45,592

Client Documented Savings

• Cleaner	$37,901.74
• Waste Treatment	$ 7,108.92
• Total	$45,010.66

R.O.I.

R.O.I. = Costs of Implementation/Benefits
R.O.I. = $45,592/$45,010.66
R.O.I. = 1.01 years

Data provided by Arbortech

Acid Applications

- Acid Pickling
- Stripping baths
- Activation baths
- Deoxidizer Passivation baths
- Anodizing
- Electropolishing
- Etching

Acid Bath Life

- Acid is consumed (expended) as it dissolves metal in the cleaning process
- Acid is consumed by alkali dragged into the bath from previous cleaning tanks
- Therefore, active acid goes down and dissolved metal goes up as the bath is used
- Metal (solid) + Acid (H+, anion -) ⟶ Metal ion (+, dissolved) + nitrate ion or chloride ion or phosphate, etc.(-)
- Acid dragout into acid rinse

Acid Control

- Monitor acid levels, dissolved metal levels
  - Titration
  - Specific gravity
  - Other methods such as spectroscopy, near infrared, viscosity, etc.
  - Automated systems such as the Scanacon Analyzer*
- Make acid additions based on remaining acid in the bath
- Dissolved metal may interfere with the acid reactions (example, sulfuric acid anodizing bath)

*Scanacon.com

Cost of Dumping an Acid Bath

- Cost of neutralizing the remaining acid in the bath
- Cost of replacing all the acid in the new bath
- Cost of rework due to end-of-life poor cleaning of parts
- Cost of metal sludge filtration and disposal in waste treatment
- Labor costs of waste treatment and making up a new bath
- Labor cost of reporting for hazardous material use and disposal

Acid Bath Maintenance

- Maintaining the acid concentration produces more consistent metal etching and cleaning
- Filtration of the solution will remove any suspended solids
- Surface sparging to a weir will remove floating oils and floating dirt

Acid Life Extension

Acid Life Extension involves increasing the usable life of an acid bath while reducing the amount of acid consumed, consequently reducing the number of times the acid bath is dumped and making the process more consistent, over a given time period.

Various Technologies

- Purpose of each technology is to reduce the dissolved metal while recovering the unreacted acid
  - Chemical additives such as PRO-pHx
  - Diffusion Dialysis
  - Acid Sorption (resin column adsorption and flushing of acid)

Acid Life Extension

PRO-pHx:

"PRO-pHx is a catalyzed formulation carried by a proprietary blend of soluble silicates. It effectively immobilizes soluble metals by reacting with them to form insoluble metal silicates.

[It] will also react with volatile and non-volatile organic compounds to produce a non-volatile, non-toxic, non-hazardous waste. The precipitate is then easily filtered."

Information provided by PRO-pHx, Inc.

PRO-pHx Equipment

← In-tank Filtration

Overflow Filtration →

PRO-pHx Study: Coating Technologies, Inc. and Anoplate

- Conducted a 11-month study to assess the performance of PRO-pHx on Muriatic and Nitric acid tanks
- Parameters monitored:
  - Dissolved metals
  - Volume of acid added
  - # of manufacturing defects

Findings

- All baths remained functional through the course of the study
- All baths experienced an increase in life by at least 2x (with some going up to 20x)
- No defects were traceable to poor acid quality
- Current status: Some tanks were run for 3 years without dumping (tanks were dumped for other reasons such as maintenance issues, etc.)

Unexpected outcomes

- Metal concentration in many baths increased beyond typical operating ranges
- No effect on work-piece processing time or cleaning ability (bath activity stayed constant)

Metal Concentrations

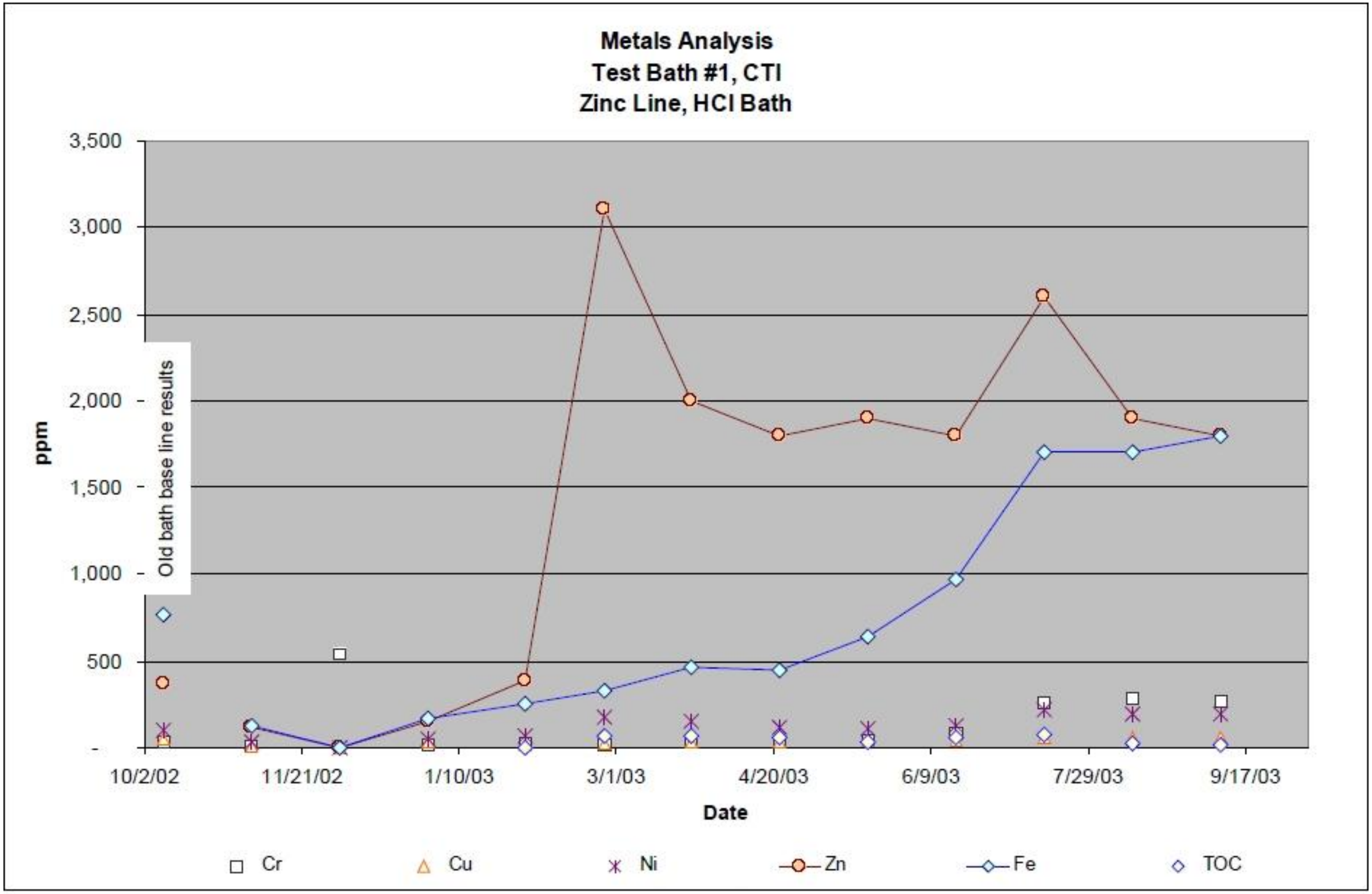


Figure 1

Metal Concentrations

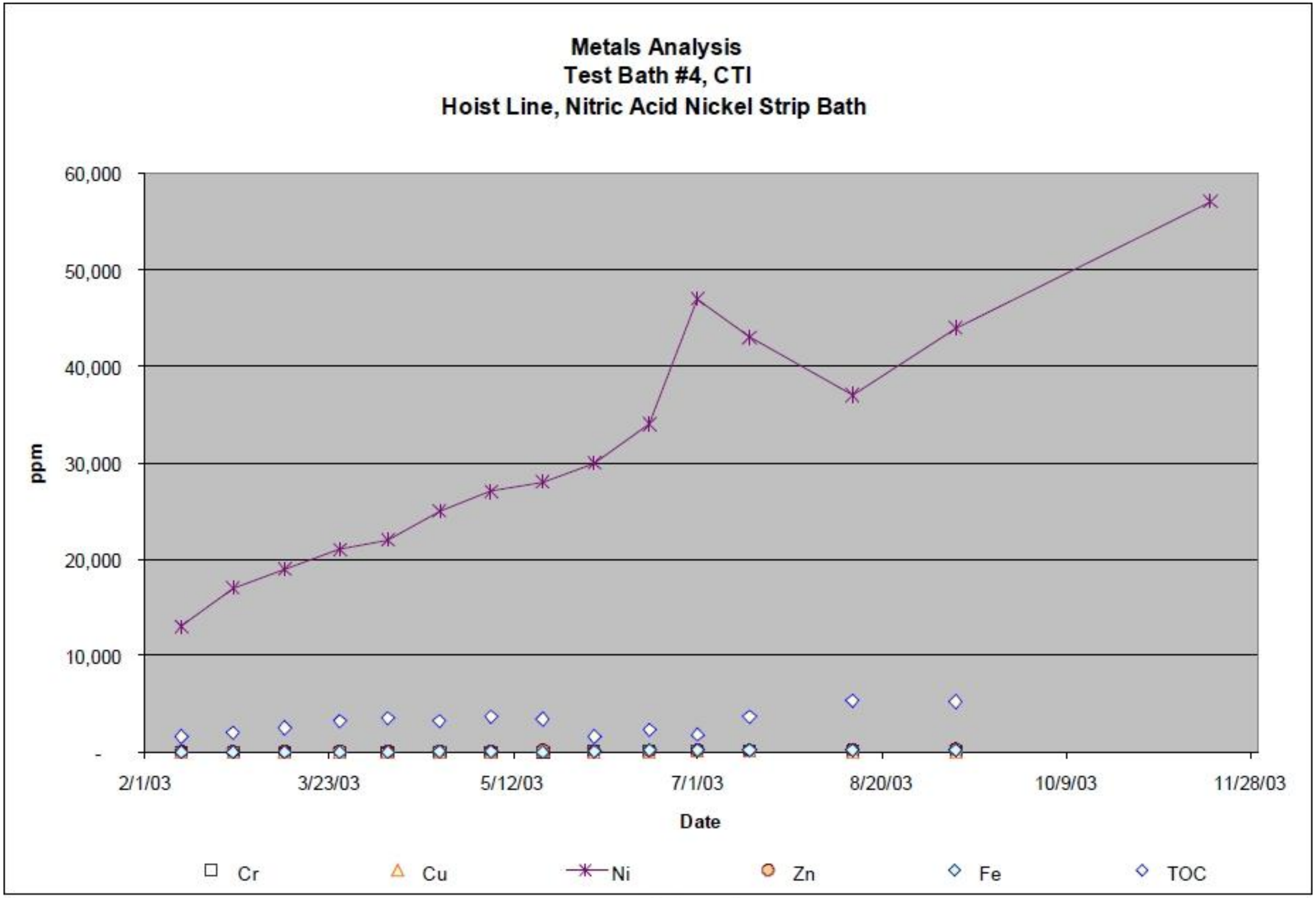


Figure 4

Economic Analysis

For Test Bath1; HCl tank; Dumped every 4 weeks; 250 gallons at 40%

Annualized Data

Before PRO-pHx:

	quantity	$/per	Total
Acid used (gallons)	1430	$ 1.44	$ 2,059.20
Waste treatment ($1.25 for every $1)			$ 2,574.00
Total			$ 4,633.20

With PRO-pHx (first year)

Acid Used (make up)	110	$ 1.44	$ 158.40	
PRO-pHx Used (make up)	2.5	$ 60.00	$ 150.00	
Acid Used (replenishment)	683	$ 1.44	$ 983.52	
PRO-pHx Used (replenishment)	23.89	$ 60.00	$ 1,433.40	
Waste treatment (none required)			$ -	
Filters (2/week @ $2.5 each)	104	$ 2.50	$ 260.00	
Equipment: Filter Pump	1	$ 370.00	$ 370.00	
Total			$ 3,355.32	
First Year Savings			***$ 1,277.88***	28%

Environmental Results

Environmental Summary, CTI

Tank	Acid Gallons			Savings		Percents	
	With out PRO-pHx	With PRO-pHx		With PRO-pHx		With PRO-pHx	
		First Year	Subsequent Years	First Year	Subsequent Years	First Year	Subsequent Years
Test Bath 1	1430	793	683	637	747	44.5%	52.2%
Test Bath 2	1907	506	396	1401	1511	73.5%	79.2%
Test Bath 3	480	166	126	314	354	65.4%	73.8%
Test Bath 4	240	234	194	6	46	2.5%	19.2%
Totals	**4057**	**1699**	**1399**	**2358**	**2658**	**58.1%**	**65.5%**

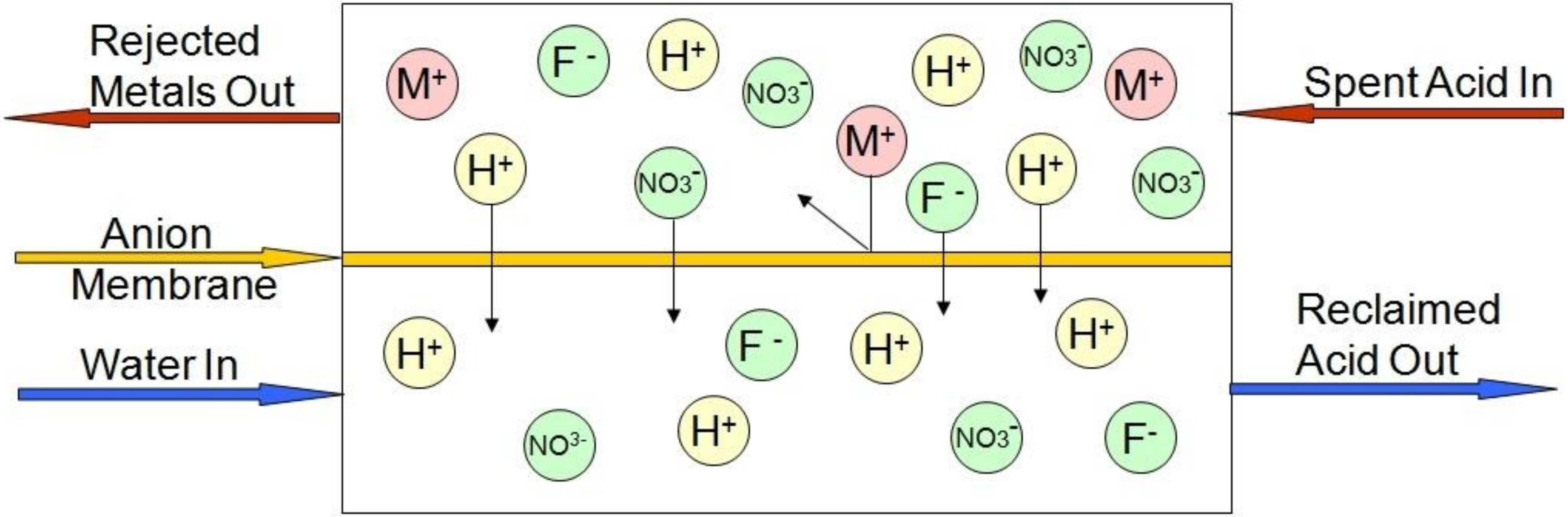
Tank	Caustic Gallons, estimated			Savings		Percents	
	With out PRO-pHx	With PRO-pHx		With PRO-pHx		With PRO-pHx	
		First Year	Subsequent Years	First Year	Subsequent Years	First Year	Subsequent Years
Test Bath 1	2860	1586	1366	1274	1494	44.5%	52.2%
Test Bath 2	3813	1012	792	2801	3021	73.5%	79.2%
Test Bath 3	960	332	252	628	708	65.4%	73.8%
Test Bath 4	480	468	388	12	92	2.5%	19.2%
Totals	8113	3398	2798	4715	5315	**58.1%**	**65.5%**

Diffusion Dialysis

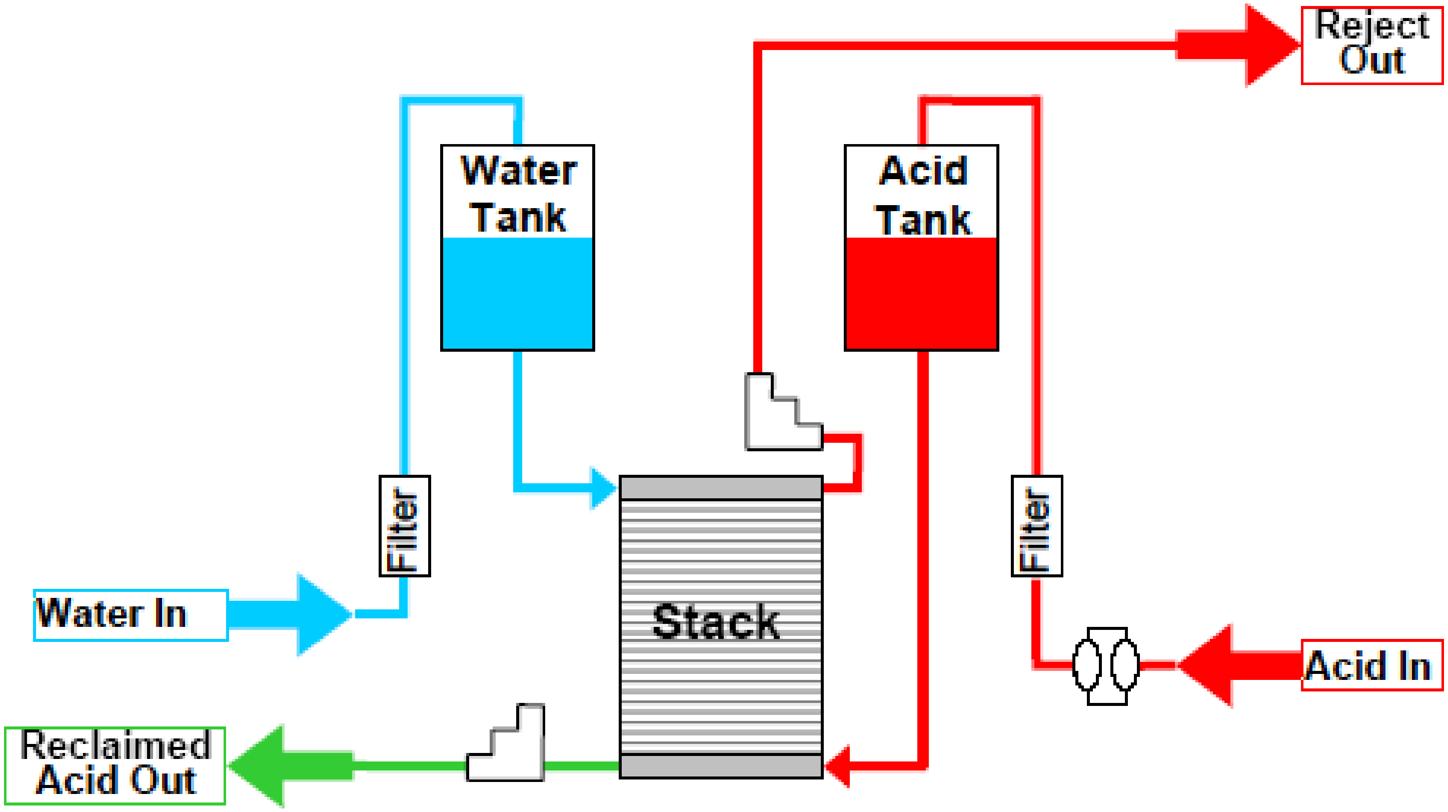
- Diffusion: material movement along a concentration gradient (material moves from high concentration to low concentration)
- Dialysis: Material separation across a membrane based on molecule size and molecule charge. Human kidneys are expert systems at dialysis.

Diffusion Dialysis Process

- Want to separate the dissolved metal from the acid
- Want to have a relatively high acid concentration at least close to that of the original acid, i.e. don't want a dilute acid stream



System Schematic



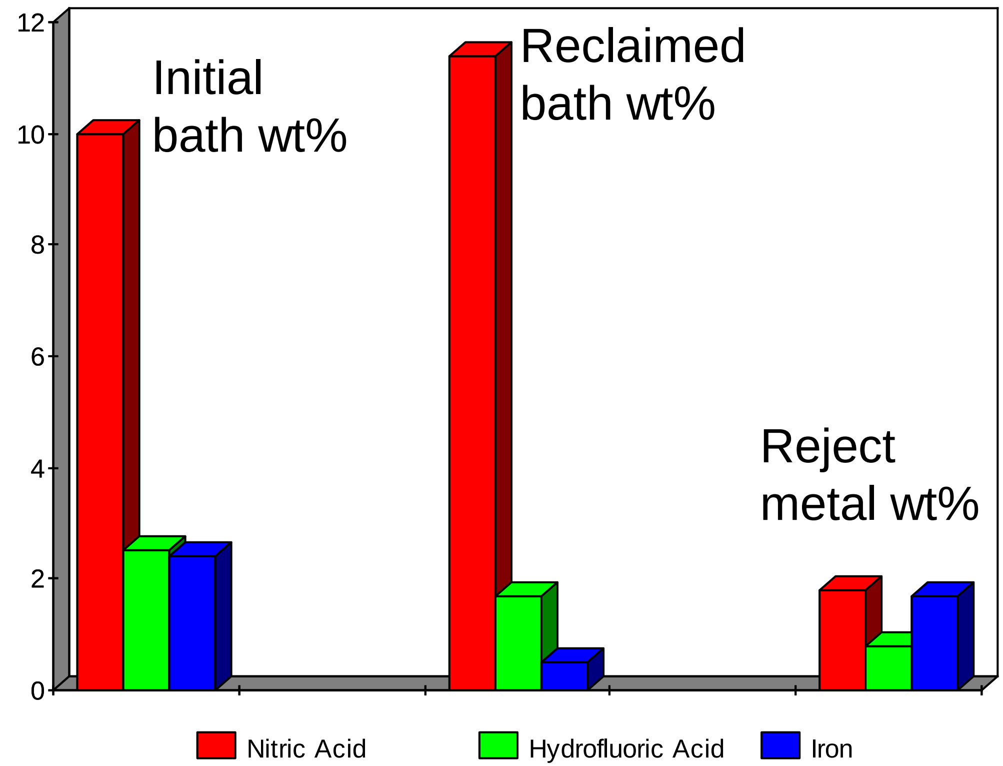
Schematic provided by Mech-Chem Associates, Inc.

Case Study: Nitric-Hydrofluoric Acid, A Common Stainless Steel Pickling Solution:

Expected System Performance:

- 80 – 90% Nitric Acid Recovery,
- 65 – 75% Hydrofluoric Acid Recovery,
- 70 – 90% Metals Removal.

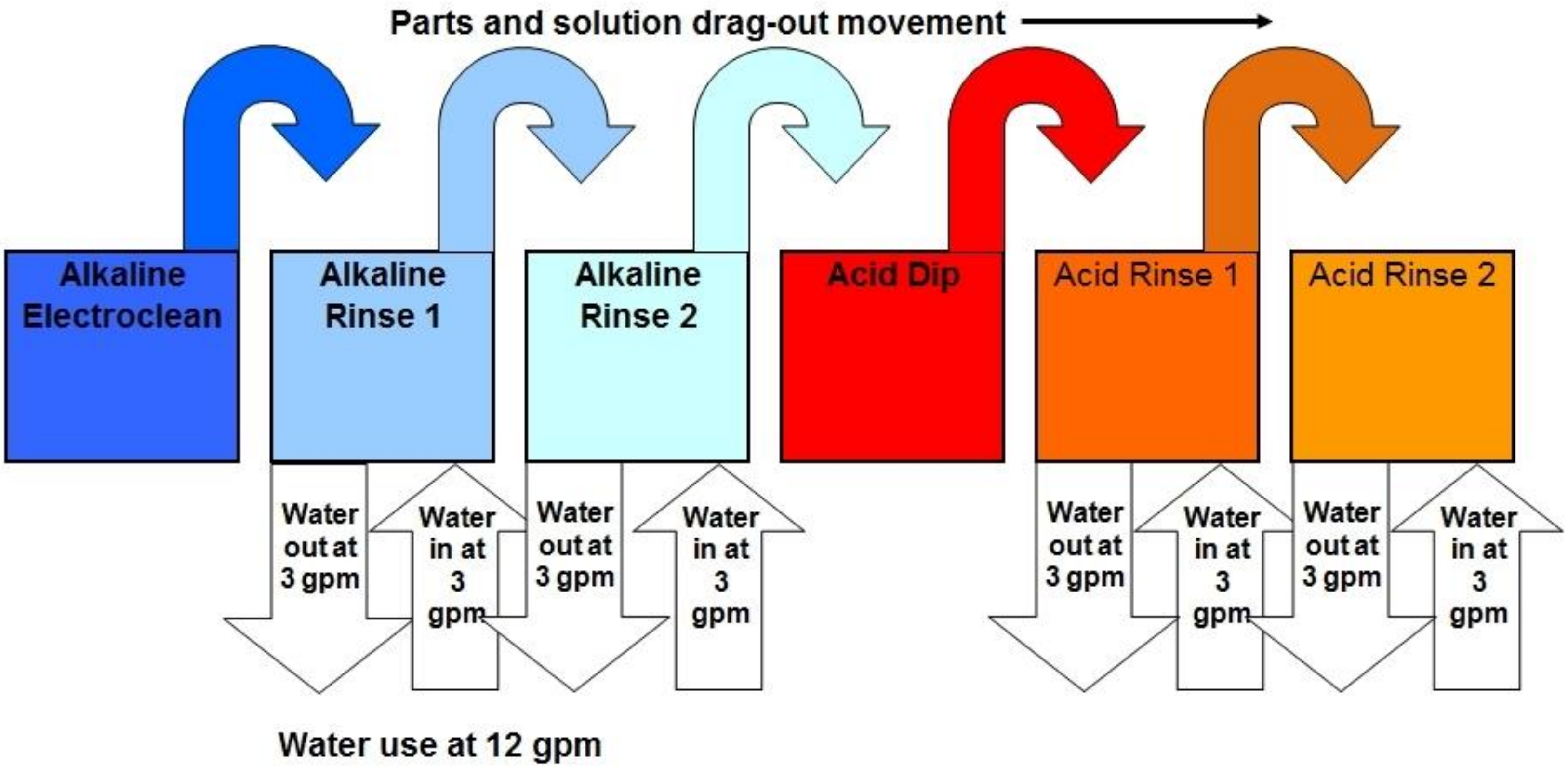
Actual System Performance



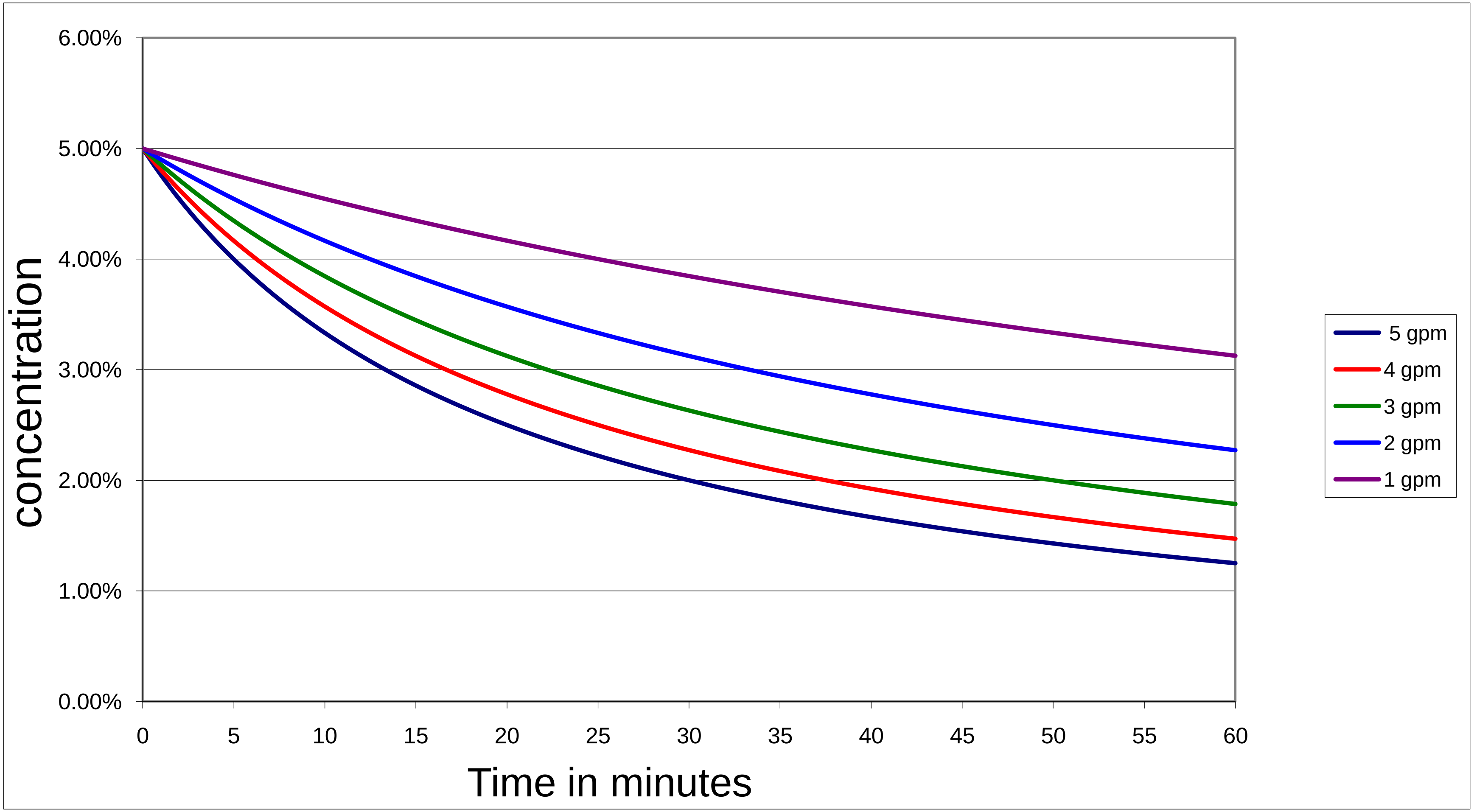
Typical Cleaning Steps

1. Alkaline cleaner, could include ultrasonics, agitation, or electrocleaning to assist the cleaning chemistry in contaminant removal. Contaminants are typically oil, dirt, buffing compound, fingerprints, etc.
2. Rinses (parts drag alkali into rinse water)
3. Acid etch, to remove light rust or oxides
4. Rinses (parts drag acid into rinse water)
5. Sometimes a repeat of the alkaline and acid steps including rinses

Typical Cleaning and Rinsing Layout

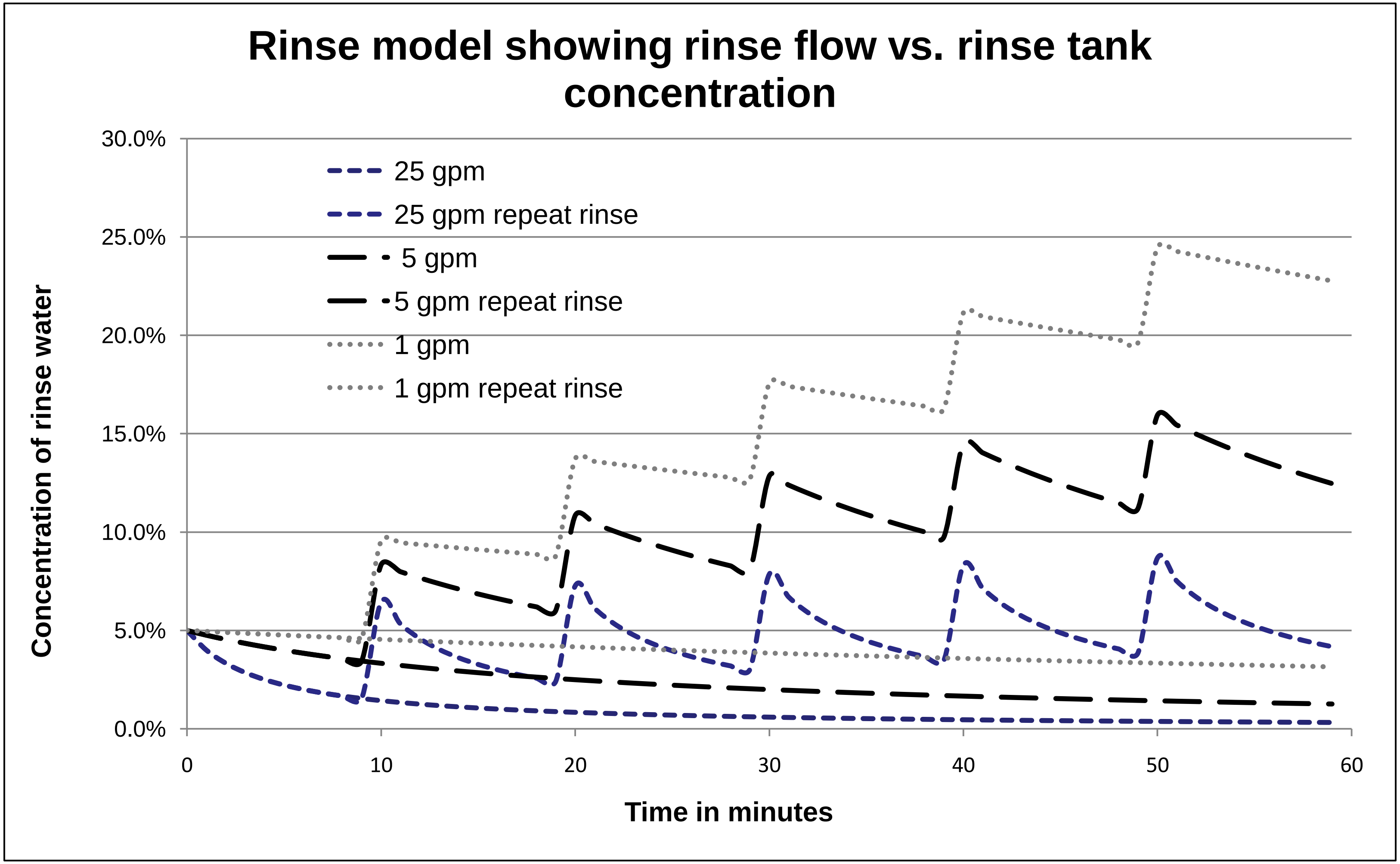


Single Rinse Dilution Model



100 gallon tank, .05 gal. dragout, 100 gm/gallon in dragout

Single Rinse Dilution Model



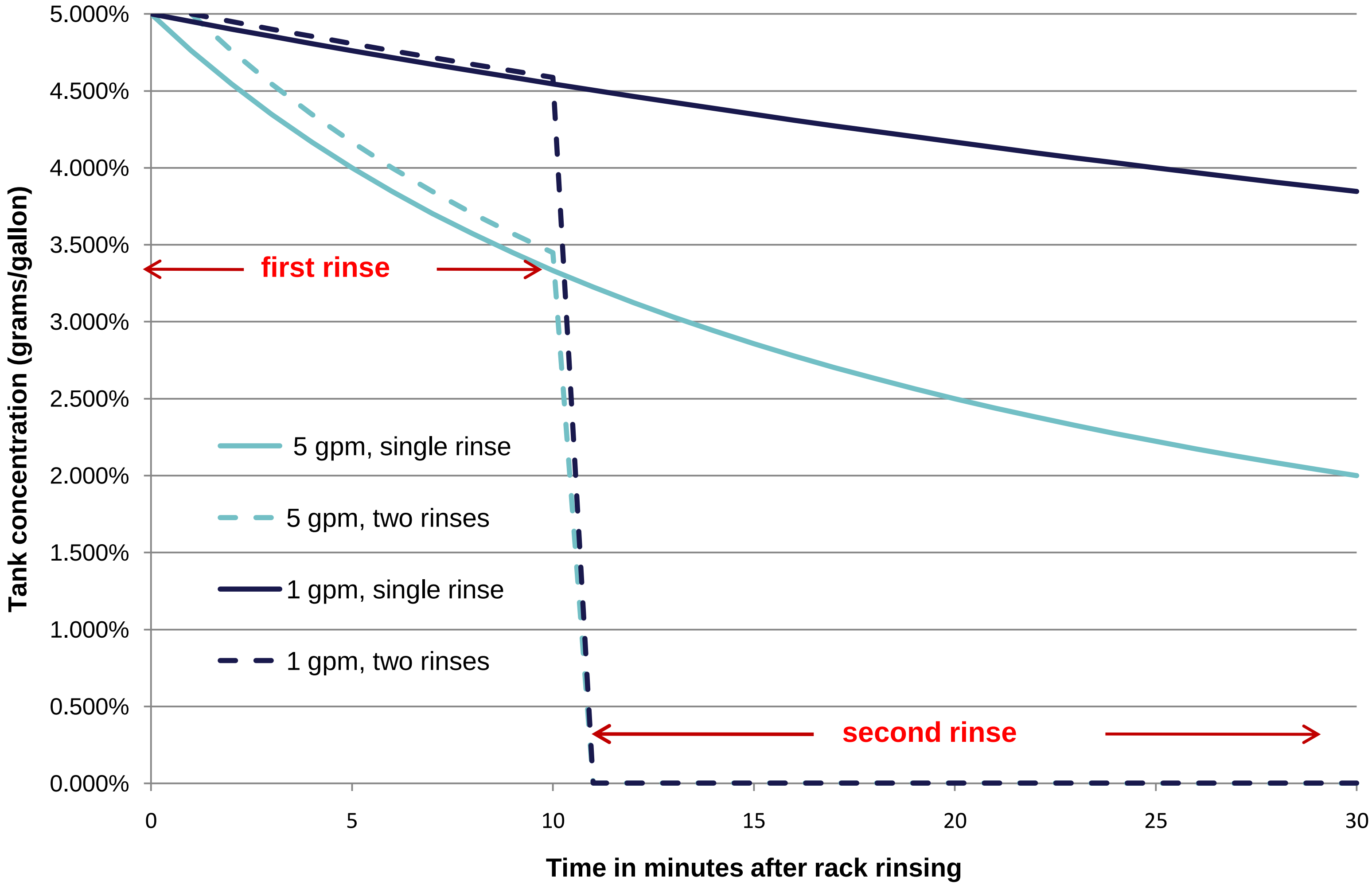
Single Rinse

- Conclusion: Based on the rate of dilution in even a small tank (100 gallons), it is very difficult to obtain good rinsing with a single rinse tank. Even relatively high flow rates of 5 gpm cannot keep up with the contamination loading from parts dragout.
- Therefore, there really needs to be a second rinse tank for critical rinsing.
- And……it becomes very important to determine your real rinse tank dynamics by measuring flow and conductivity/TDS

Double Tank Rinsing

- First rinse tank
  - remove most of the previous tank's chemicals from the part
  - Stop the chemical reaction from the previous tank
- Second rinse tank
  - Final rinse to remove additional chemicals and maximize part cleanliness
  - Minimize contamination of next chemical tank

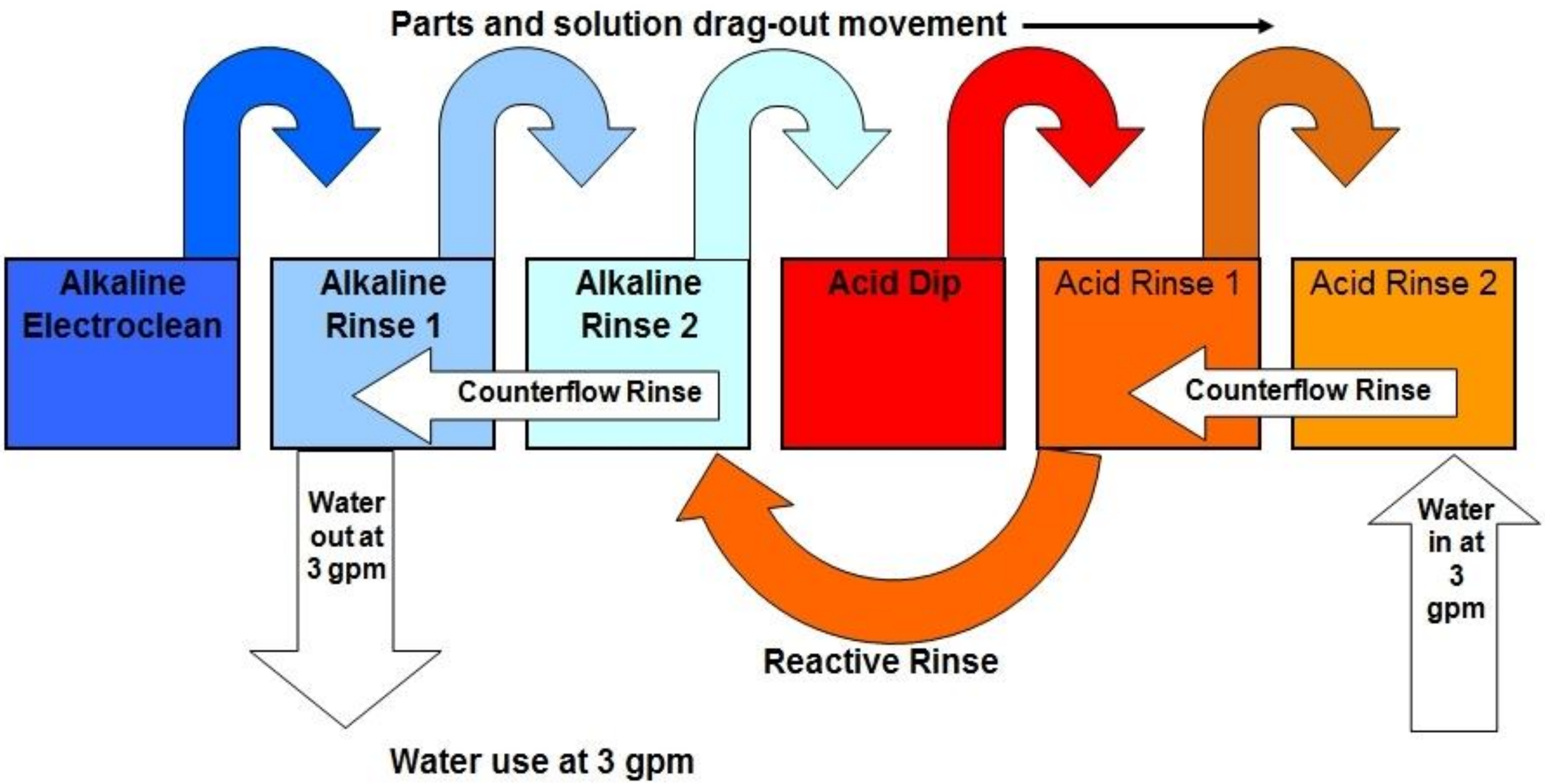
Double Tank Rinsing



Reactive Rinsing

- Divert rinse around a process tank into a previous rinse tank
- Called reactive rinsing because typically there is a chemical reaction between the chemicals, typically an acid-base reaction
- Allows some chemical recovery by re-introducing a chemical back into a process tank

Optimized Cleaning and Rinsing



Flow Controls in Immersion Rinsing

- In-line flow restrictors: the hand operated valve has an aperture to restrict the flow to some maximum value at maximum valve opening.
- Conductivity controls: rinse valve opens and closes based on TDS value of rinse tank

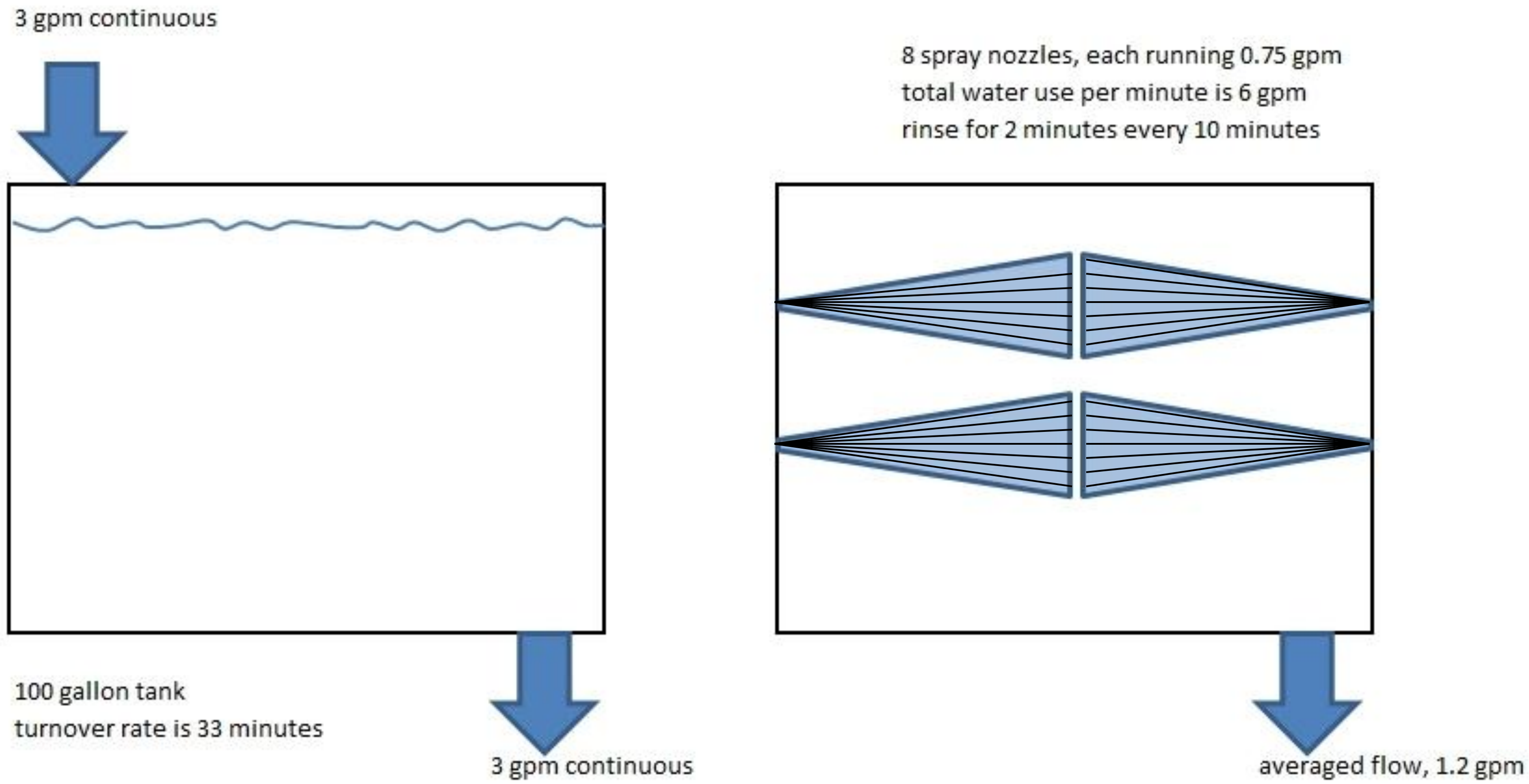
From:
www.freshwatersystems.com

From: Myron L Company, Controlstik Systems

Conductivity/TDS Controls

- Finding the best TDS set points (valve opens when water reaches maximum TDS set point, valve closes when water reaches minimum TDS set point)
- Measure the TDS with a meter in the critical rinse tanks. Knowing the existing flow rate also helps.

Immersion vs. Spray Rinsing



Sources

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   www.pro-phx.com

2. Research, Development & Demonstration Project Report:
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