Cleaning Steps: Control and Chemical Life Extension

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Overview

- Alkaline Cleaners and Acid Etching:
  - use, management, and life extension methods

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

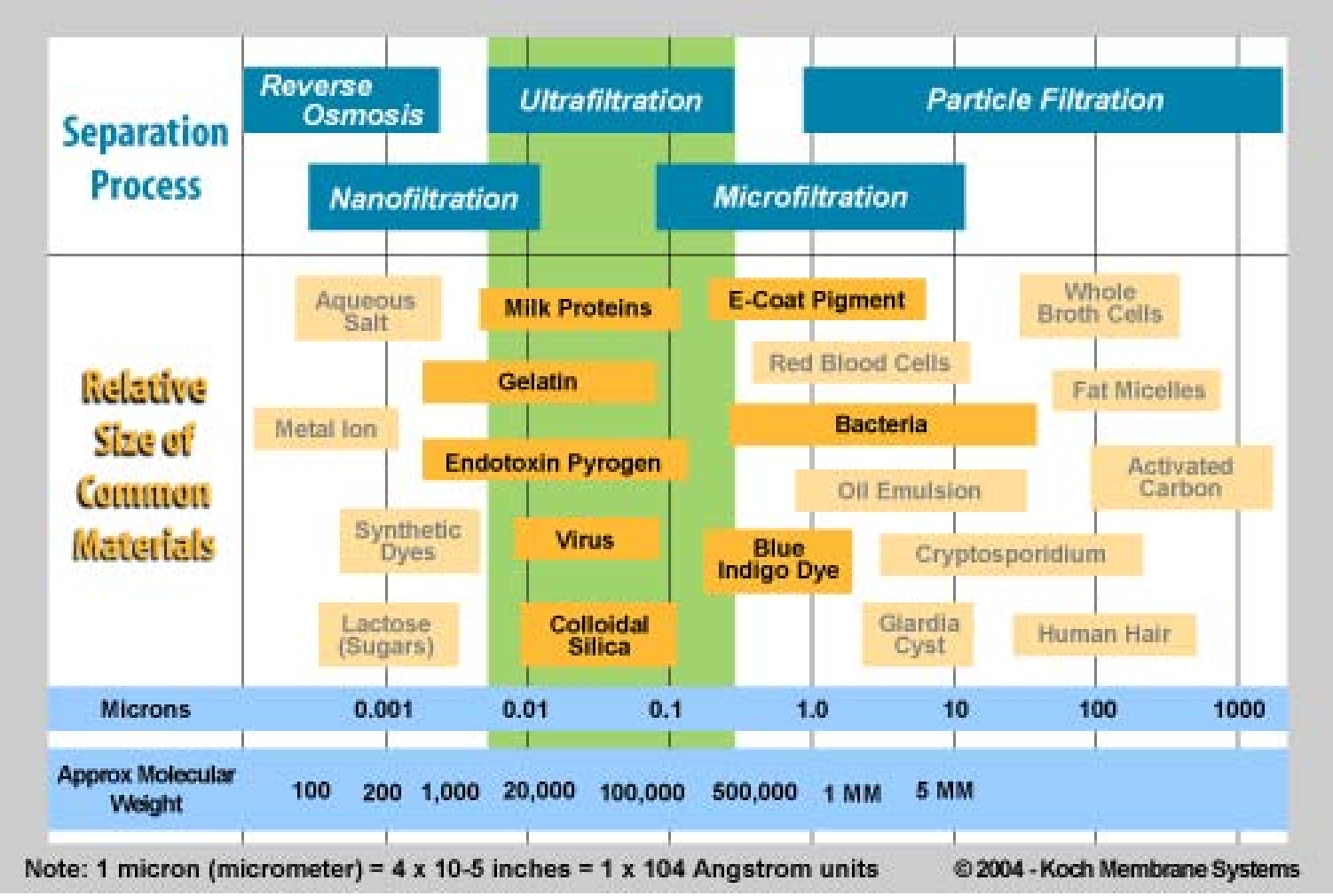
Cleaner Monitoring

- 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

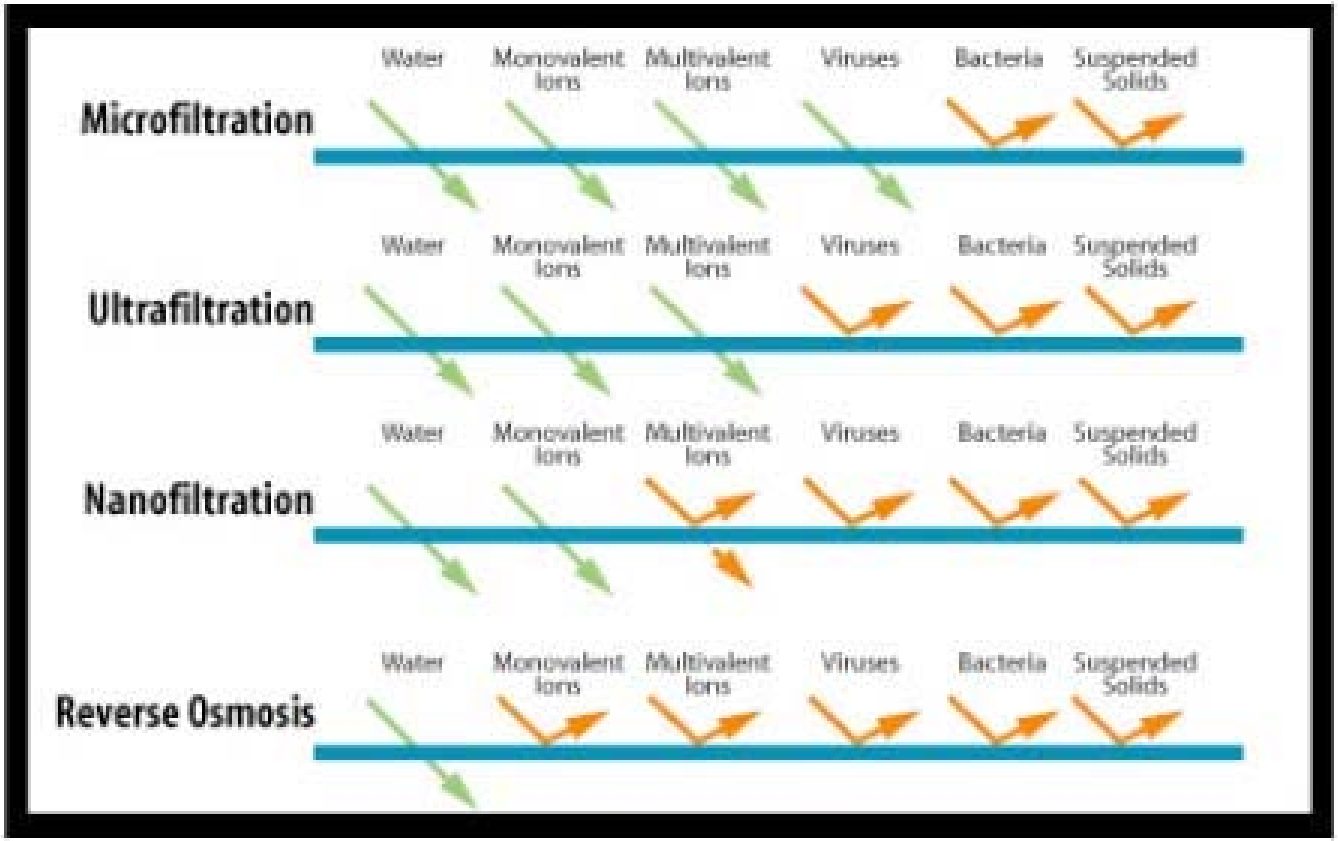
Cleaning the Cleaner

- 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 >120º 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

Filtration Levels Overview



http://www.kochmembrane.com/sep_uf.html



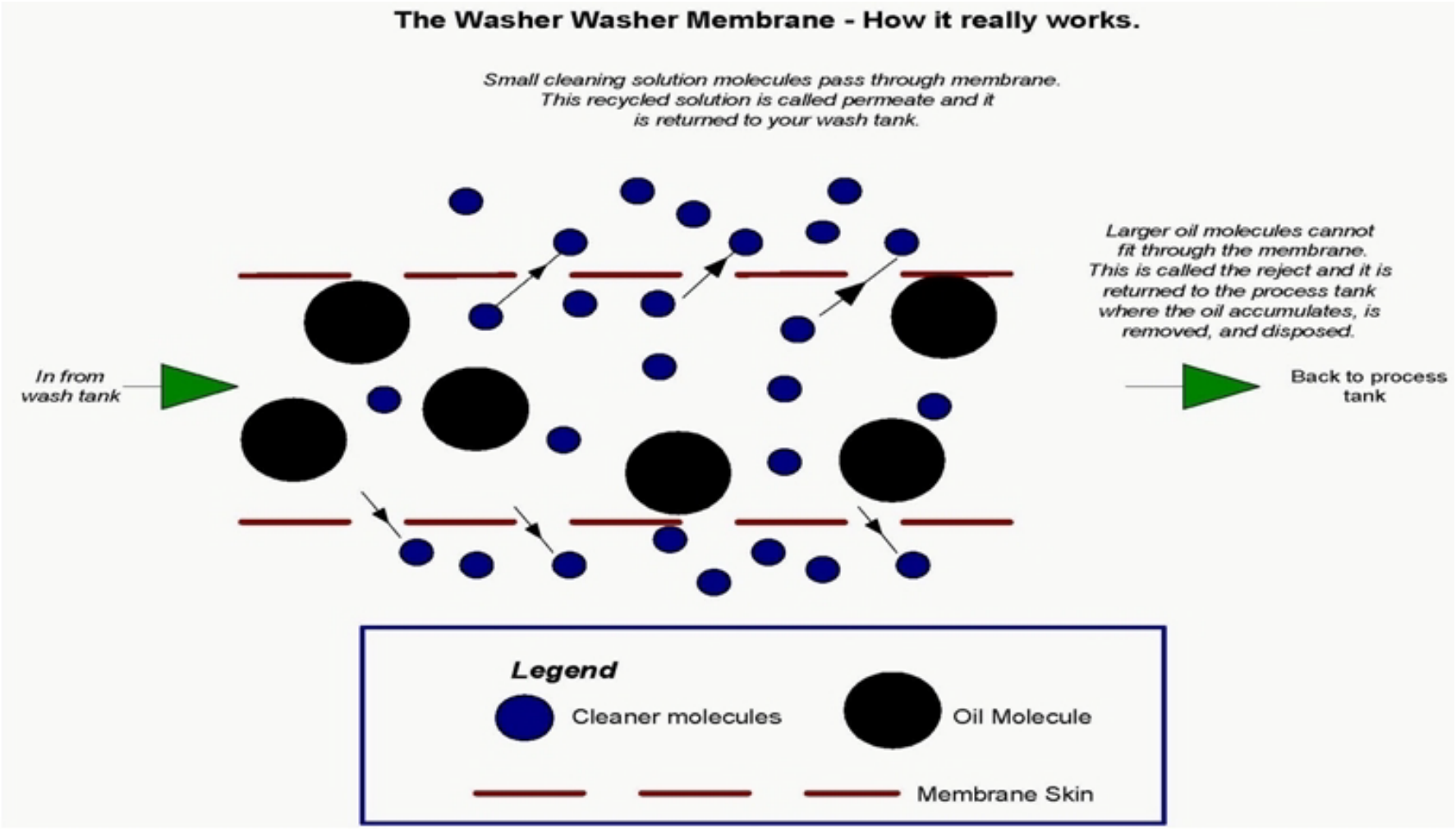
Membrane Process Characteristics

http://www.kochmembrane.com/sep_uf.html

TiO_2/SS Material Micro-Ultrafiltration

- Arbortech equipment (benchtop demonstration)
- 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 -) $\longrightarrow$ 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

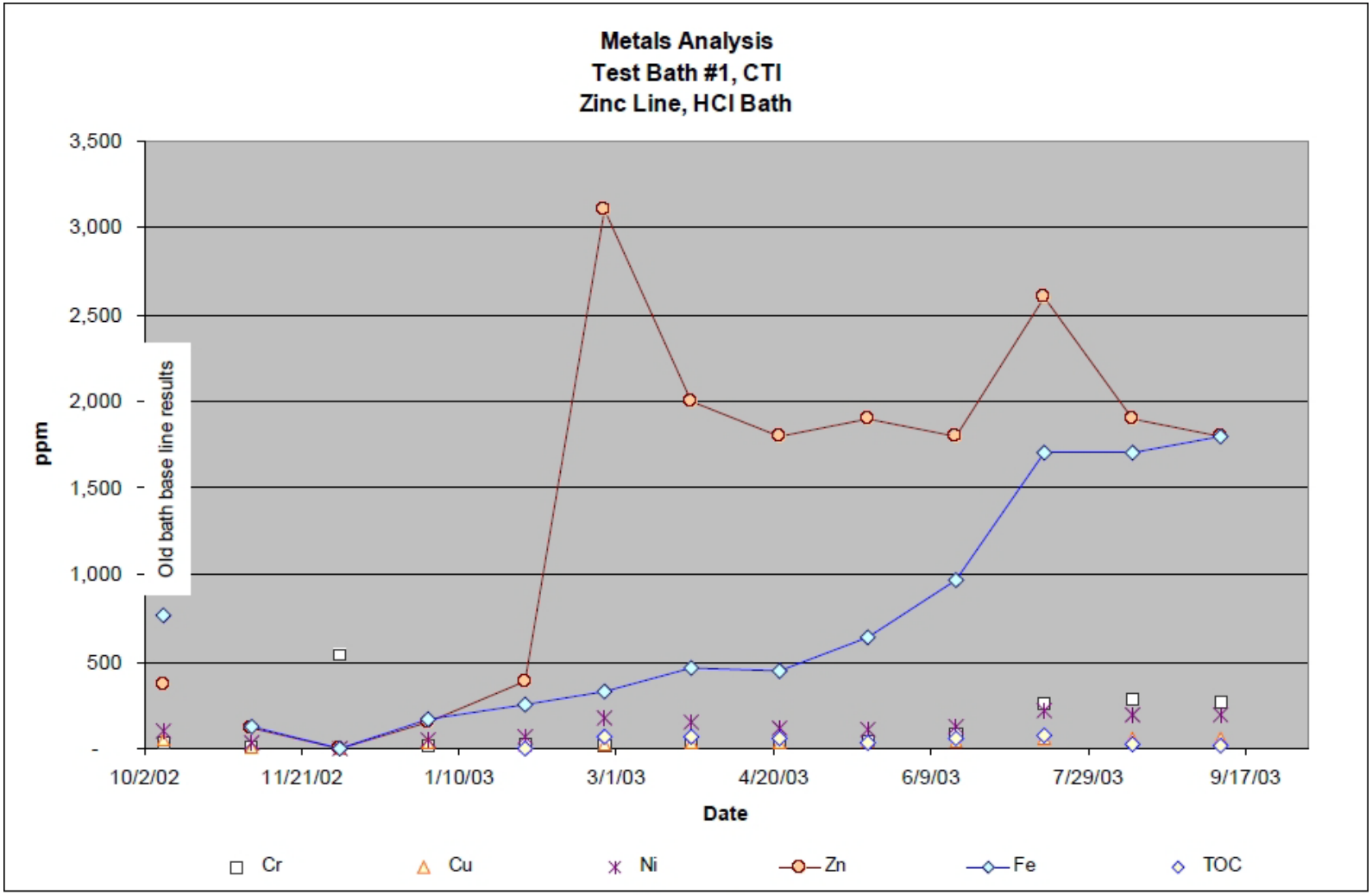


Figure 1

Metal Concentrations

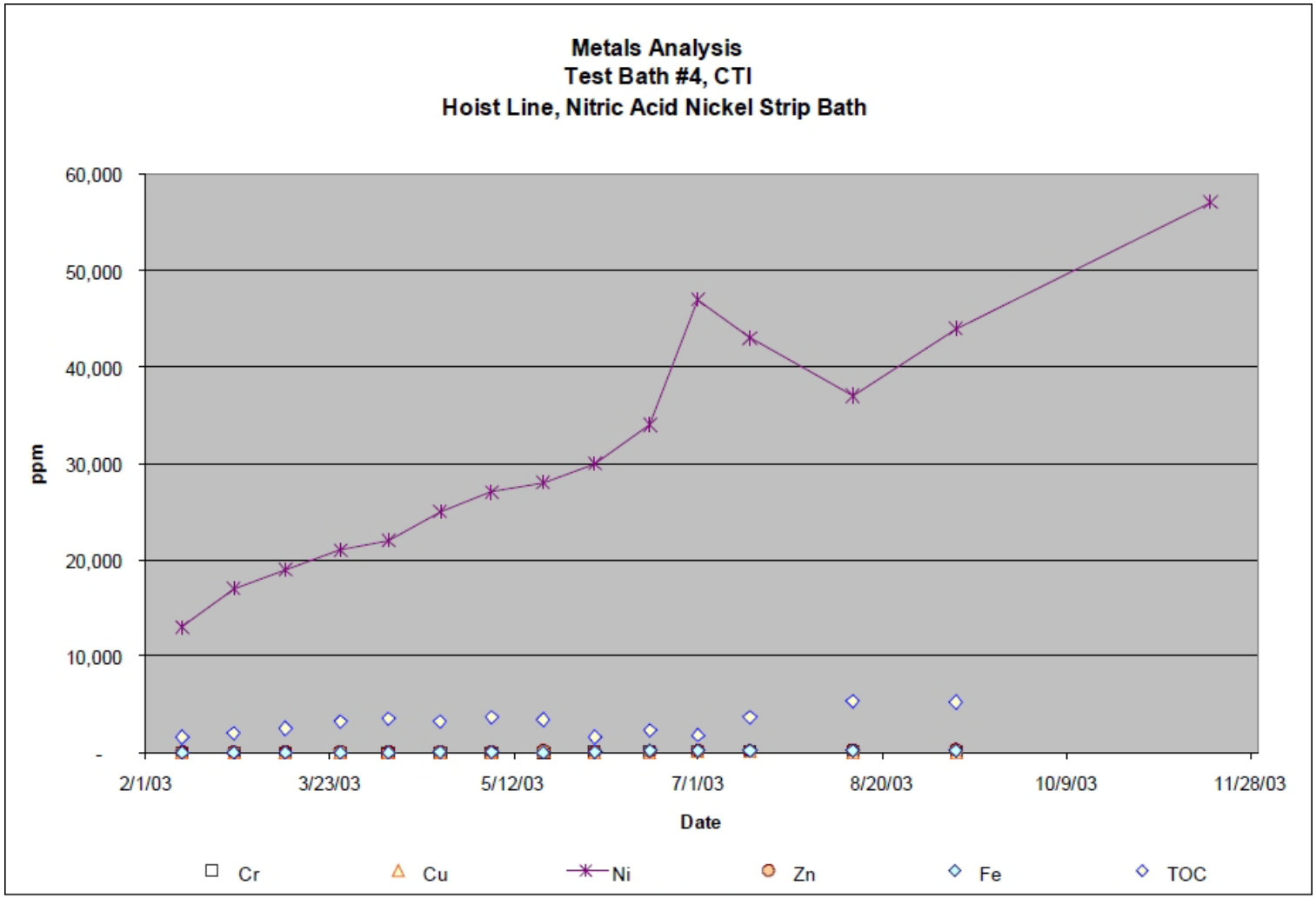


Figure 4

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%**

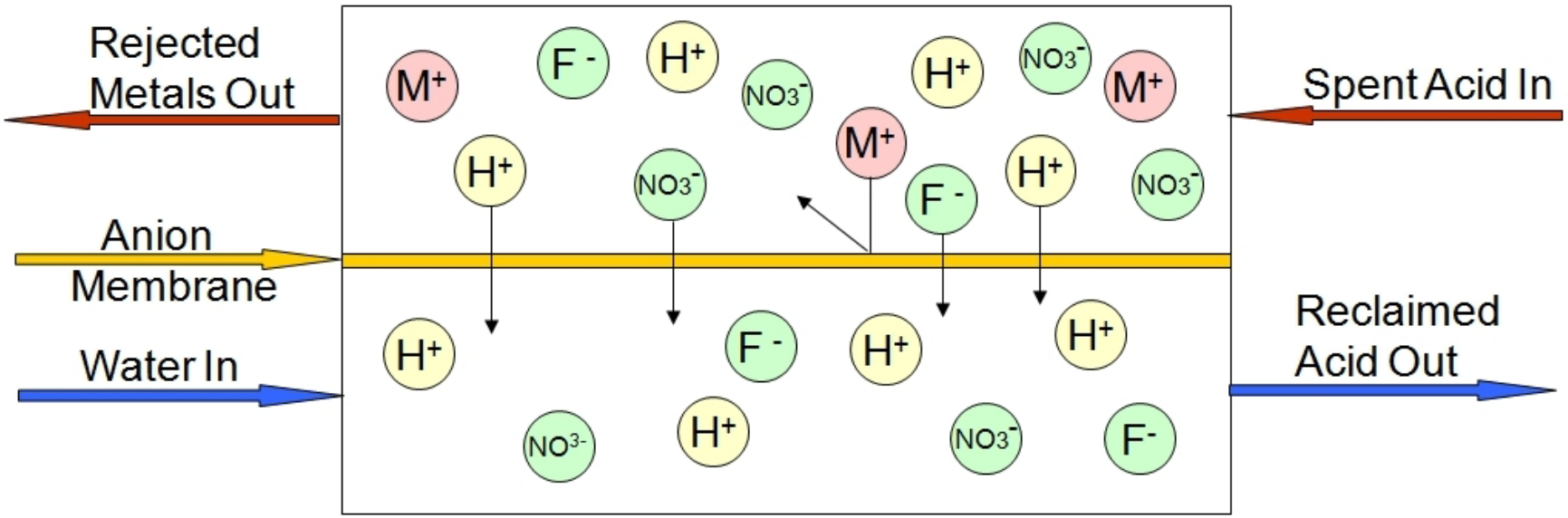
Tank	Caustic Gallons, estimated			Savings		Percents	
	With out PRO-pHx	With PRO-pHx		With PRO-pHx		With PRO-pHx	
		First Year	Subsequent Years	First Year	Subsequent Years	First Year	Subsequent Years
Test Bath 1	2860	1586	1366	1274	1494	44.5%	52.2%
Test Bath 2	3813	1012	792	2801	3021	73.5%	79.2%
Test 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

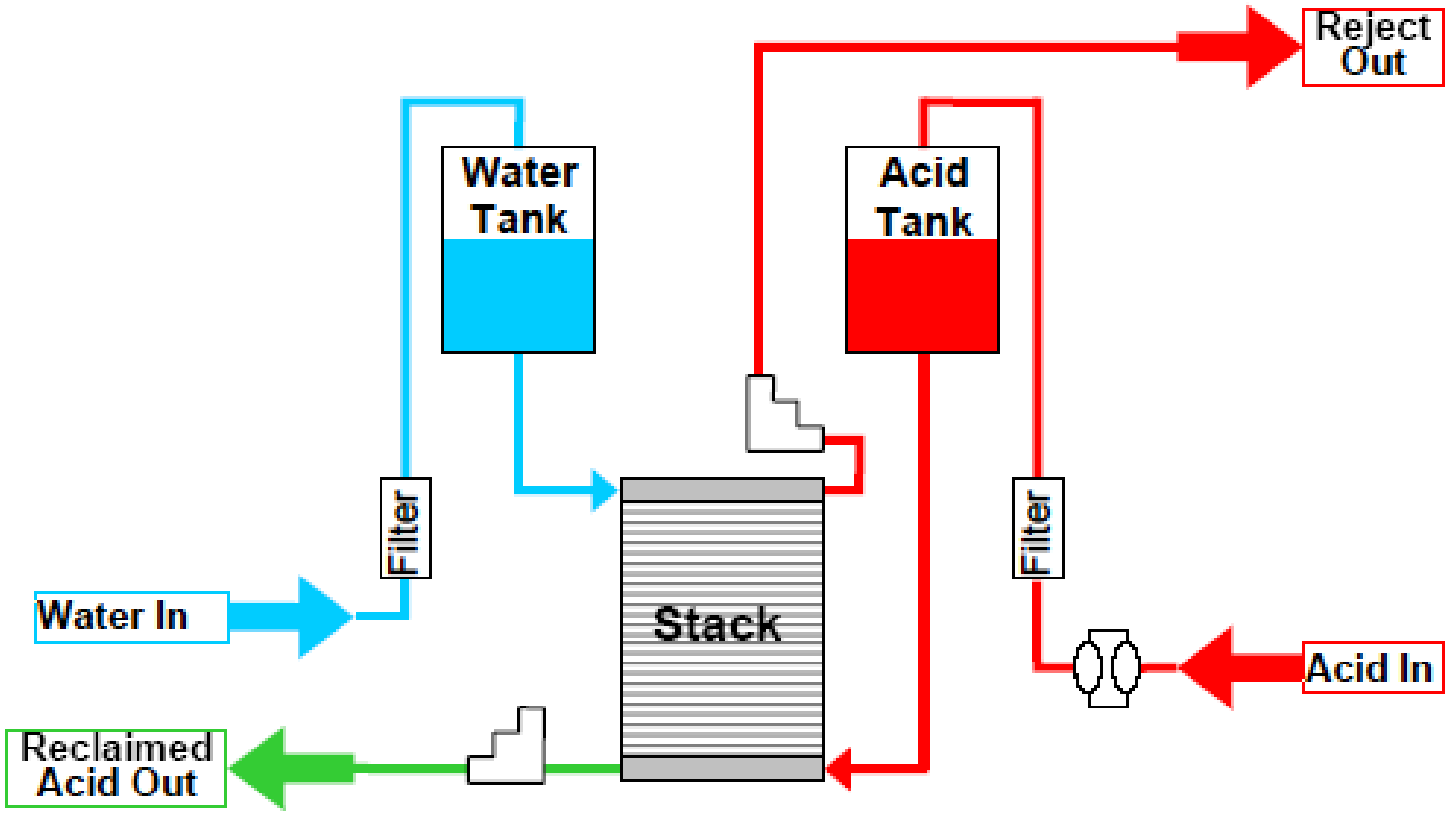
- Diffusion: material movement along a concentration gradient (material moves from high concentration to low concentration)
- Dialysis: Material separation across a membrane based on molecule size and molecule charge. Human kidneys are expert systems at dialysis.

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

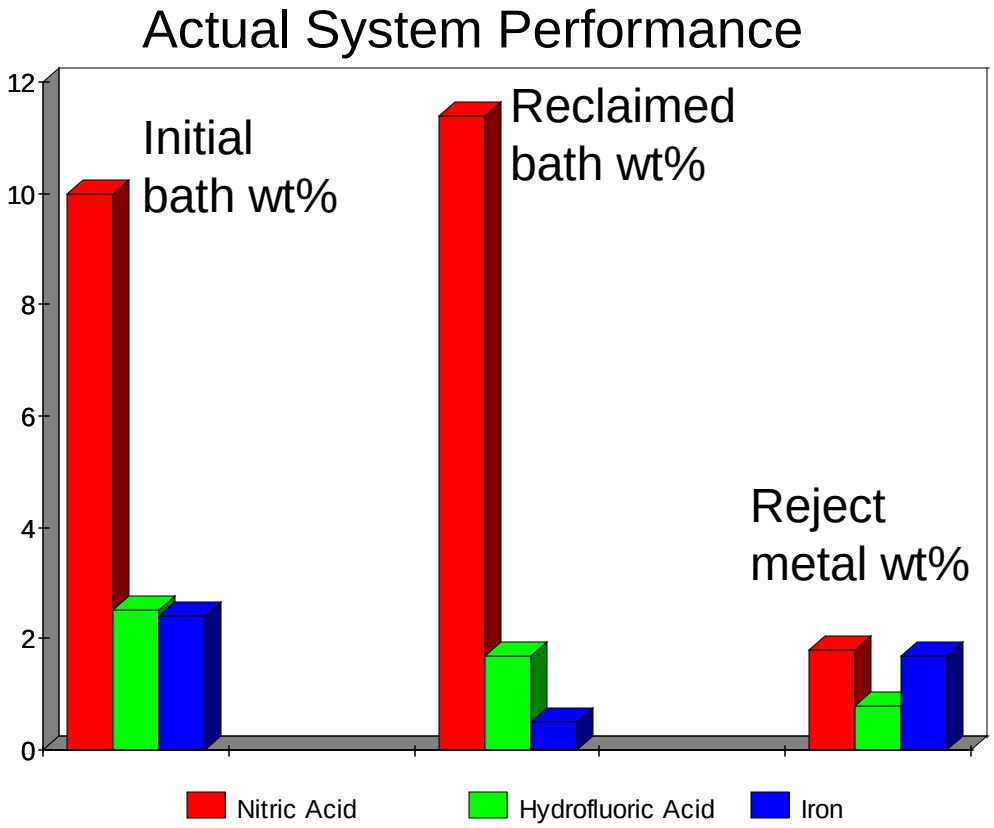


Schematic provided by Mech-Chem Associates, Inc.

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.



Sources

1. PRO-pHx Acid Life Extender: Zero Acid Disposal
Providing Environmentally Sustainable Technology
Eliminating Acid Disposal (Presentation)
www.pro-phx.com

2. Research, Development & Demonstration Project Report:
Acid Life Extender Test Application At Coating Technology & Anoplate
(Final Report)

3. Presentation for NYSP2I
Arbortech Corporation
www.arbortech.com

4. Steel Acid Presentation
Mech-Chem Associates, Inc.
www.mech-chem.com

Questions?