Reduction of Biochemical Oxygen Demand and Chemical Oxygen Demand of Metalworking Fluid Wastewater by Electrochemical Oxidation

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INTRODUCTION

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- **Many metalworking fluid exhibit high biochemical oxygen demand (BOD_5) and chemical oxygen demand after conventional pre-treatment methods.**
- **Regulators continue to enforce BOD_5 and COD limitations.**
- **Cost effective and user friendly advanced technology solutions are necessary and in demand to resolve BOD_5 and COD issues.**

WHAT ARE CONTAMINANTS IN MWF WASTEWATERS?

Increasing Solubility

- **Hydrocarbon Products (Floatable, Suspended / emulsifiable, and Settleable Organics)**
  - Petroleum Oils, Waxes, Fatty Acid Soaps (Ca, Fe Al), Chlorinated esters and paraffins
- **Floatable, Suspended, and Settleable Solids**
  - Graphite, Vibratory Debur, Floor “dirt”

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- **Non-metals**
  - Arsenic, Selenium

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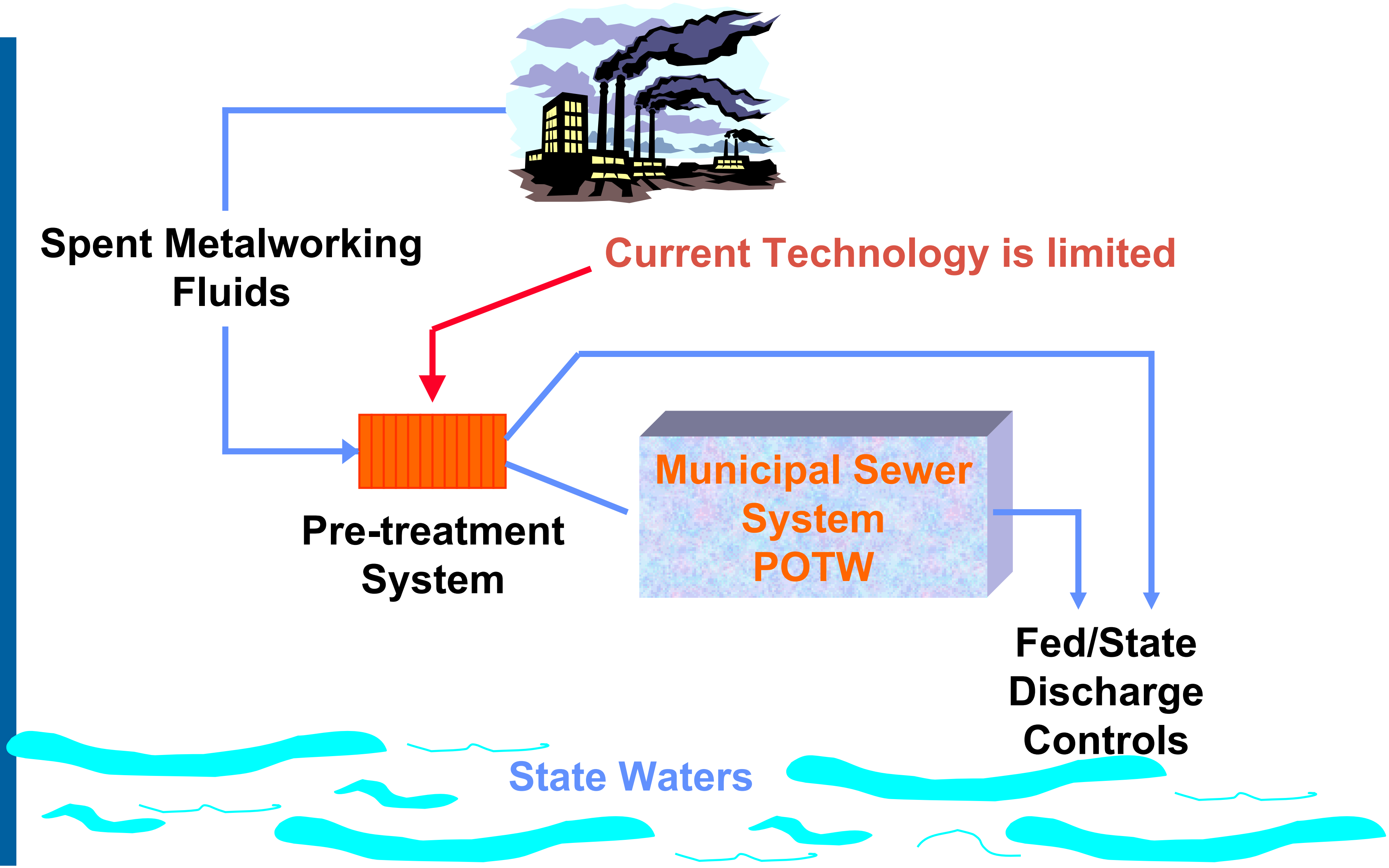
- **Dissolved Solids**
  - Salts (Sodium and Potassium Salts)
- **Dissolved Organics**
  - Amines, Amides, Esters, Glycols, Surfactants, Detergents, Fatty Acids, Fatty Alcohols, biocides, phosphate esters

THE ISSUE



Spent Metalworking Fluids
Current Technology is limited
Pre-treatment System
Municipal Sewer System POTW
Fed/State Discharge Controls
State Waters

Current Established Technology Options

Chemical Treatment
- Salt Splitting
- Polymer Treatment

Membrane Separation
- Ultrafiltration
- Microfiltraion

Evaporation
- Thermal Evaporation
- Mechanical Vapor Recompression

Biological
- Aerobic
- Anaerobic

Adsorption
- Carbon
- Clay

Or Combined technologies from above

Current Options
Combined Technologies

- Chemical / Biological
- Chemical / Carbon or Clay Adsorption

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- Ultrafiltration / Biological / Ultrafiltration (MBR)
- Ultrafilter / Reverse Osmosis (UF /RO)
- Ultrafiltration / Carbon or Clay Adsorption

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Proposed New Option

- Ultrafilter / Electrochemical Oxidative Process

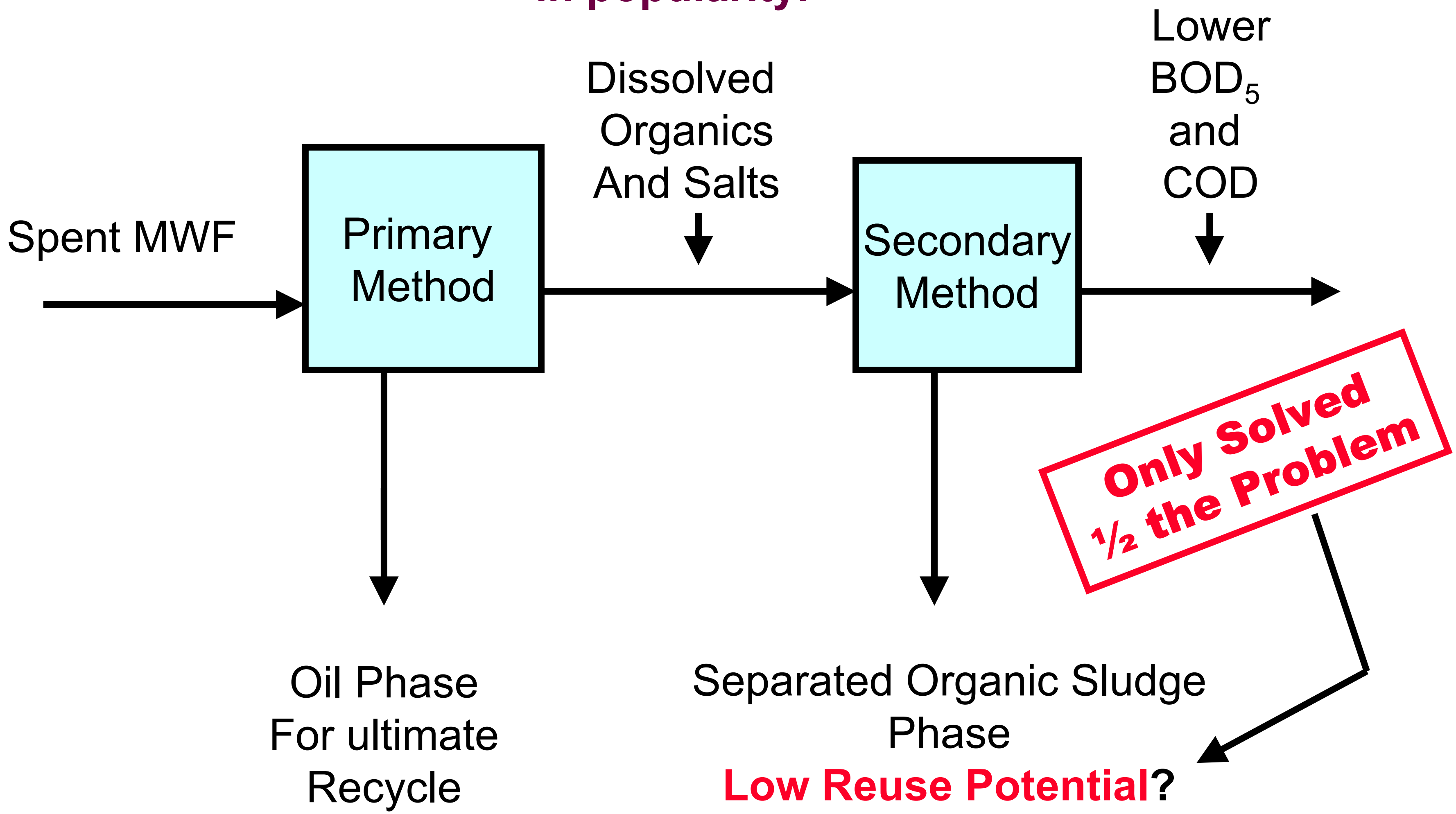
Separation Effectiveness and Costs

Fluid Type @ 5% v/v	Feed BOD5 - mg/L	After Chemical Or Ultrafiltration	Combined Technologies	Combined Technologies Operating Costs USD per Liter
Emulsions	30K –300K	600 – 6,000	20-300	$ 0.25 – 0.45
Semi-Synthetic	4,000 – 25,000	800 – 6,000	30-600	$ 0.25 – 0.45
Synthetic	3,000 – 9,000	500 –5,000	30-600	$ 0.25 – 0.45

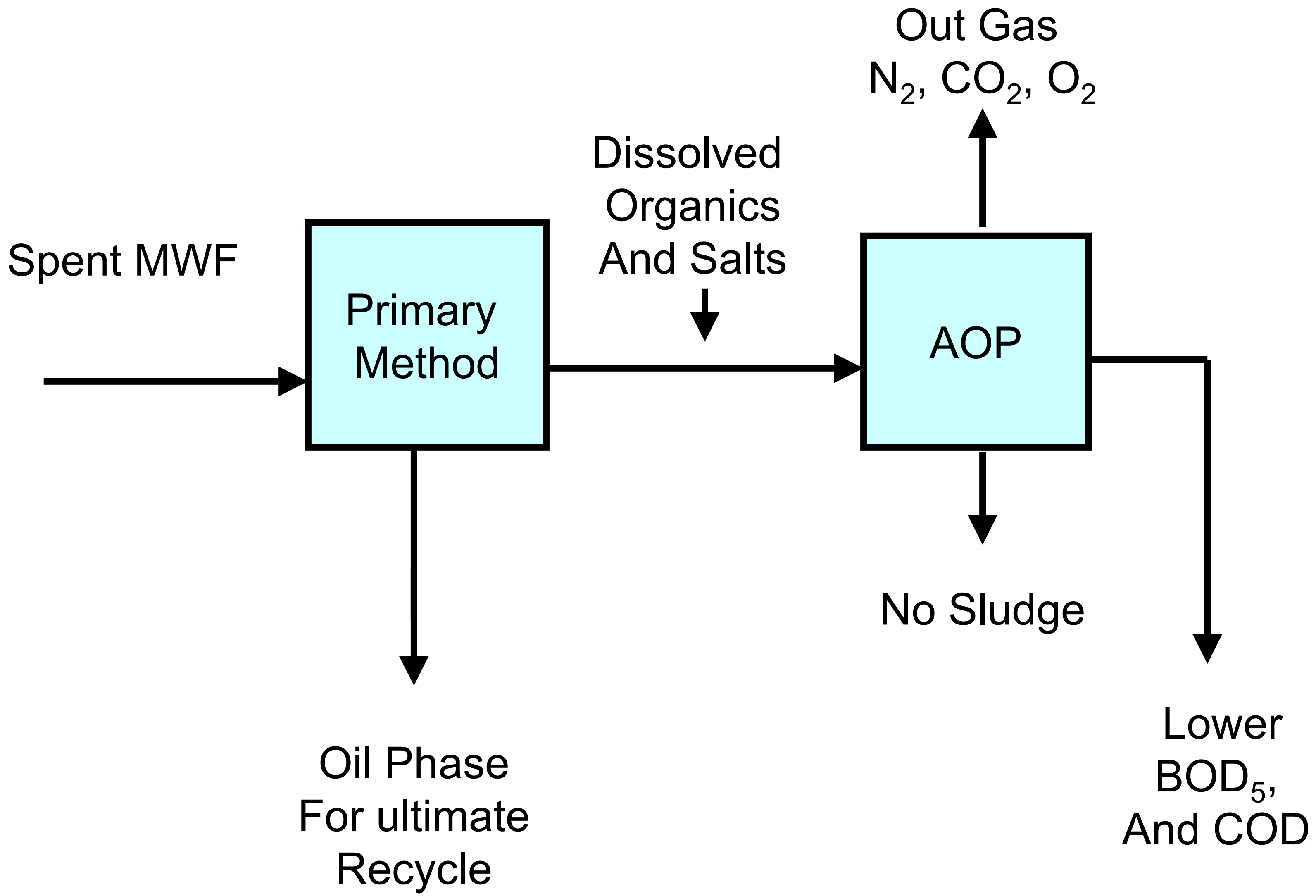
Separation Effectiveness and Costs

Fluid Type @ 5% v/v	Feed COD mg/L	After Chemical Or Ultrafiltration	Combined Technologies	Combined Technologies Operating Costs USD per Liter
Emulsions	500,000 - 1,100,000	2,000 – 9,000	300 – 900	$ 0.25 – 0.45
Semi-Synthetic	20,000 – 55,000	3,000 – 6,000	300 - 1,100	$ 0.25 – 0.55
Synthetic	25,000-35,000	20,000 30,000	250 - 900	$ 0.25 – 0.55

CURRENT TECHNOLOGY IS LIMITED
Combined technologies are gaining in popularity.



Advanced Oxidation Process Technology Option



What are some of the AOP's

- Sodium Periodate
- Sodium Perborate
- Hydroxyl Radical
- Ultraviolet
- Ozone
- Hydrogen Peroxide
- UV / Titanium Dioxide
- Chlorine
- Electrochemical Oxidation

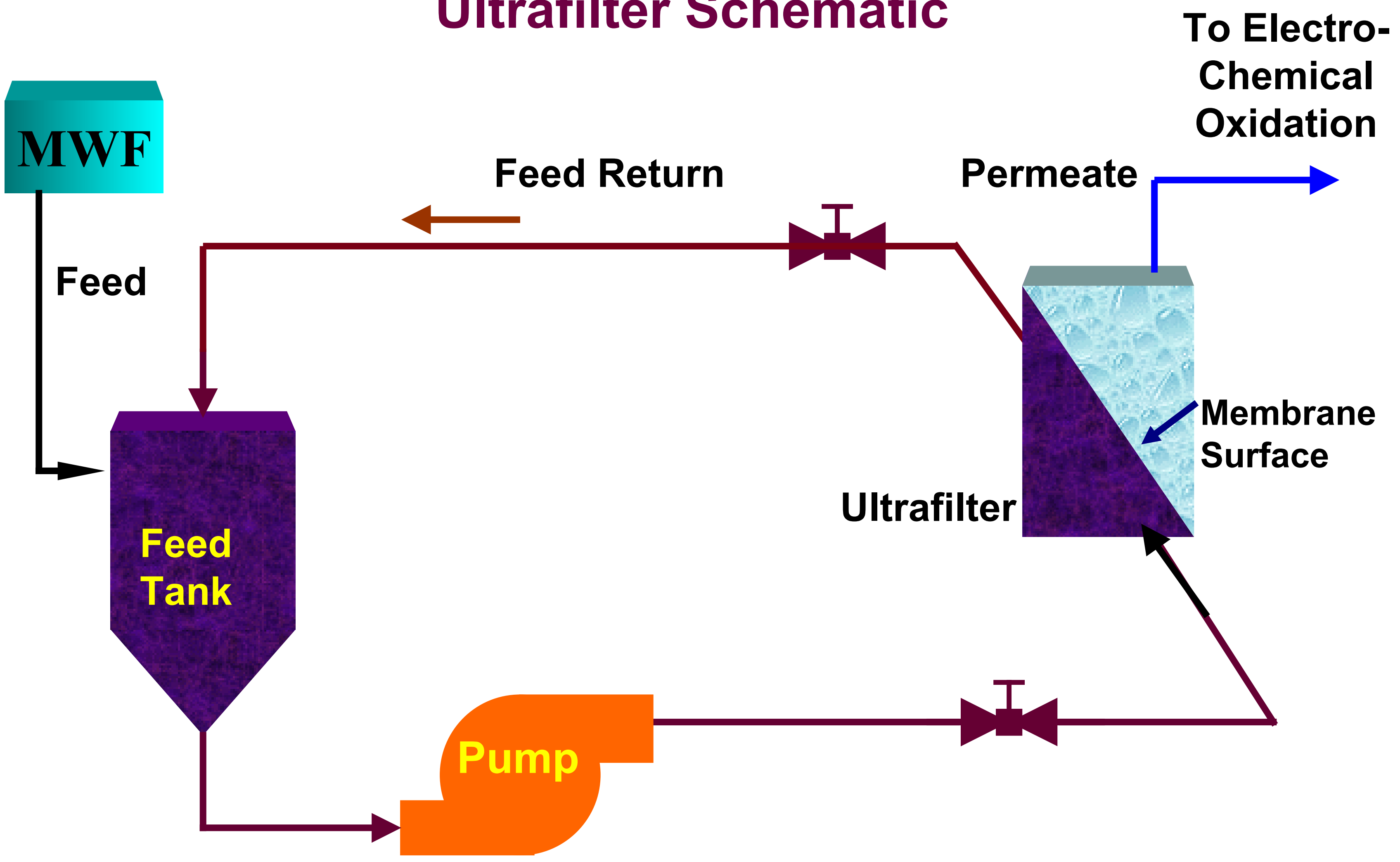
Relative Oxidation Potential of Selected Oxidants

Oxidant	Oxidation Potential, Volts
Fluorine	3.0
Hydroxyl radical	2.8
Ozone	2.1
Hydrogen peroxide	1.8
Potassium permanganate	1.7
Chlorine dioxide	1.5
Chlorine	1.4

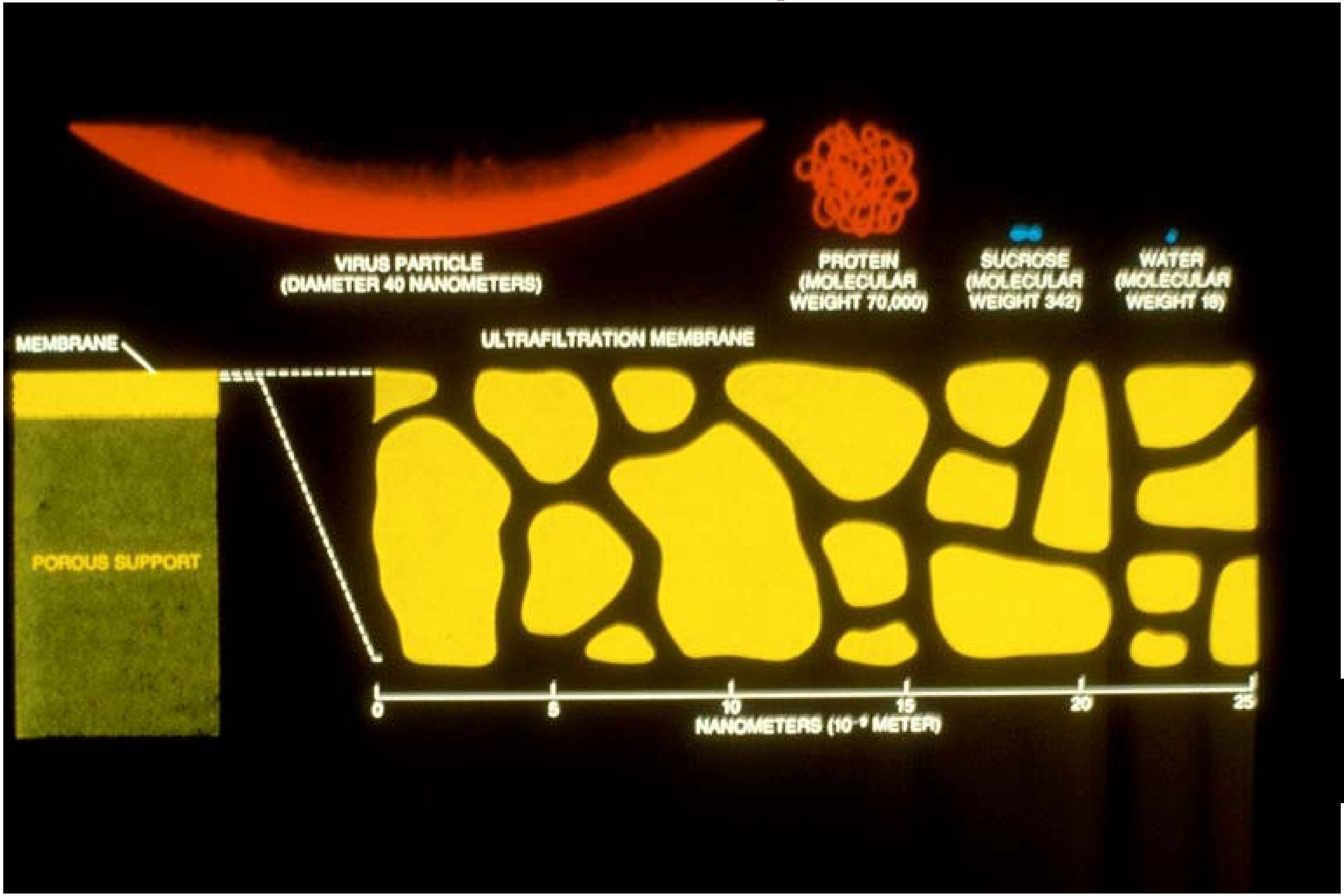
Electrons are Less Expensive

Reagent	Cents/Mole
Electrons @ 6 cents/KWH, 3.5 V	0.6
Hydrogen Peroxide	3.8
Hydrazine	14
Sodium Hydrosulfite	25
Sodium Dichromate	39
Potassium Permanganate	45
Sodium Borohydride	170

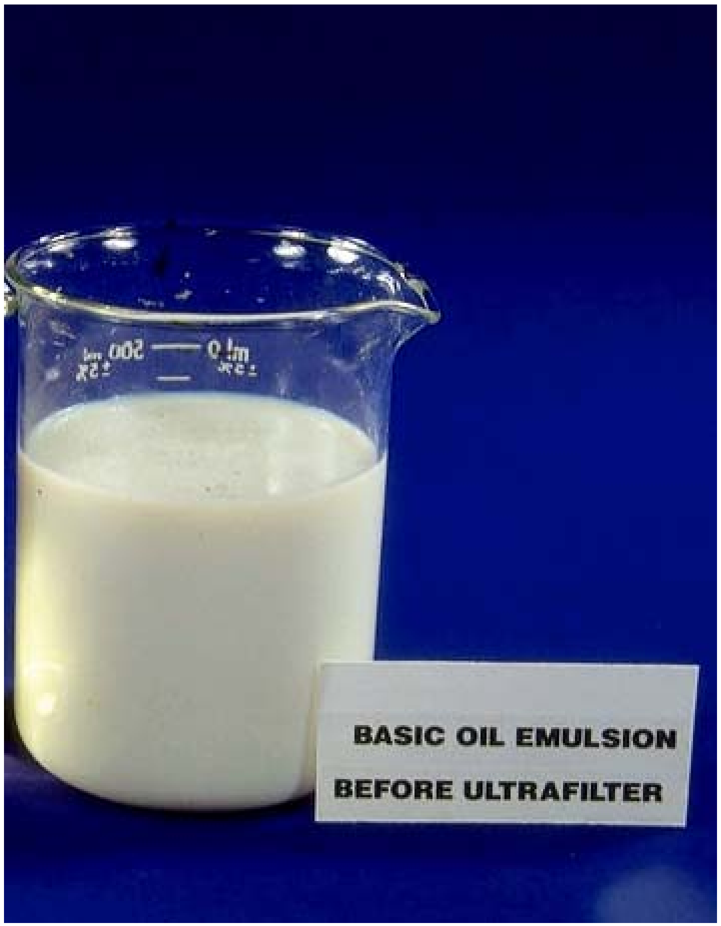
Ultrafilter Schematic



Ultrafiltration – Size Comparison



Ultrafiltration Permeate, Typical



Electrodynamical Oxidation
Multiple Reactions

- Direct Oxidation
  - Reaction occurs directly on the anode surface
- Indirect Oxidation
  - Anode oxidizes a chemical which then oxidizes a substance in solution away from the anode surface

Direct Oxidation
Electrode Reactions

- **Desired Anode Reaction**
  - $COOH^- = CO_2 + H^+ + 2\ e^-$
- **Competing Anode Reaction**
  - $H_2O = 2\ H^+ + 1/2\ O_2 + 2\ e^-$
- **Typical Cathode Reactions**
  - $2\ H_2O + 2\ e^- = 2\ OH^- + H_2$ (Base)
  - $2\ H^+ + 2e^- = H_2$ (Acid)
- **May Require Anode with High Oxygen Potential**

More Complex Molecules
More Electrons Required

Methanol

$$CH_3OH + 6\ OH^- = CO_2 + 5\ H_2O + 6\ e^-$$

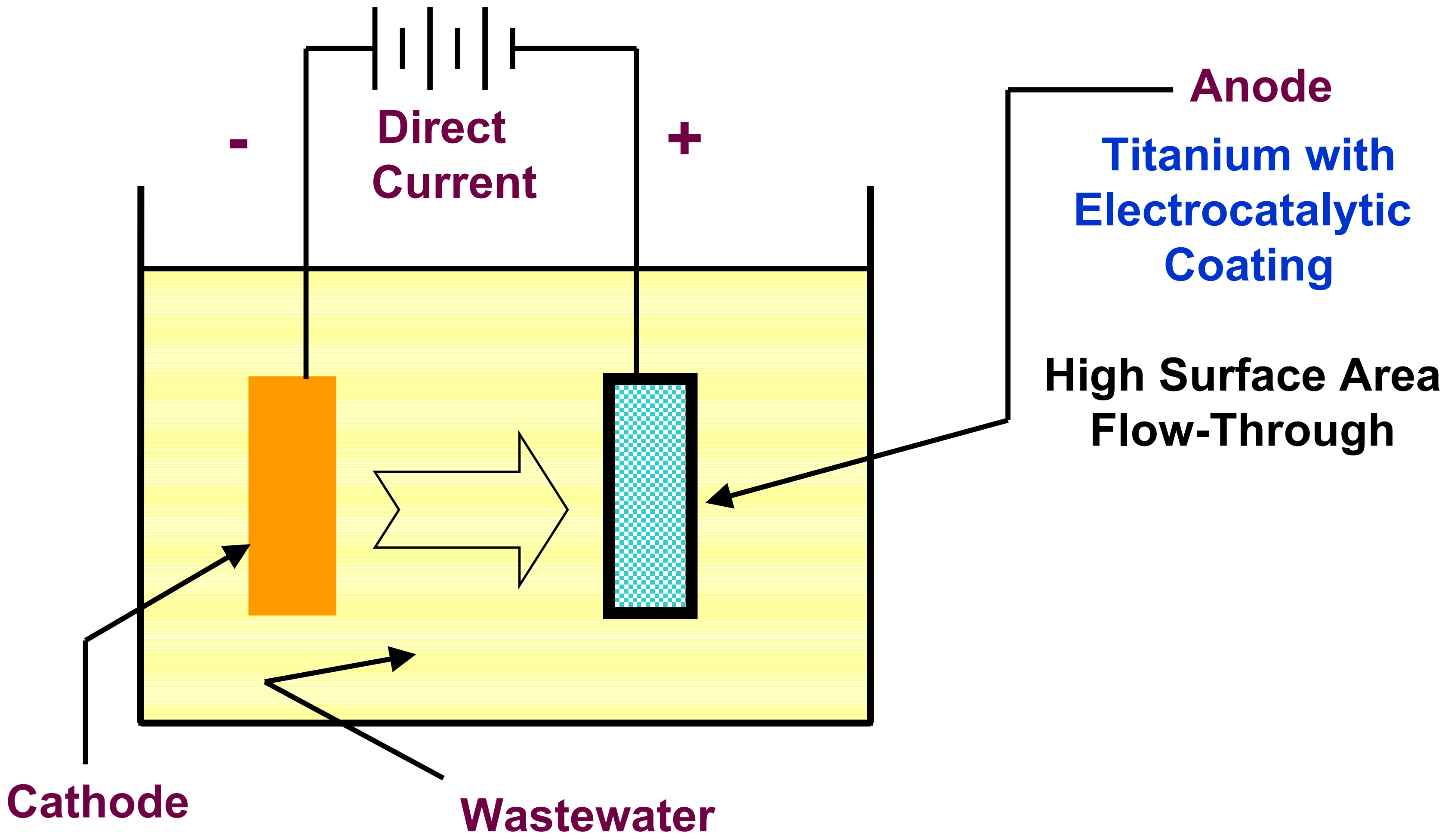
Isopropanol

$$CH_3CH_3CHOH + 12\ OH^- = 3\ CO_2 + 7\ H_2O + 12\ e^-$$

Acetone

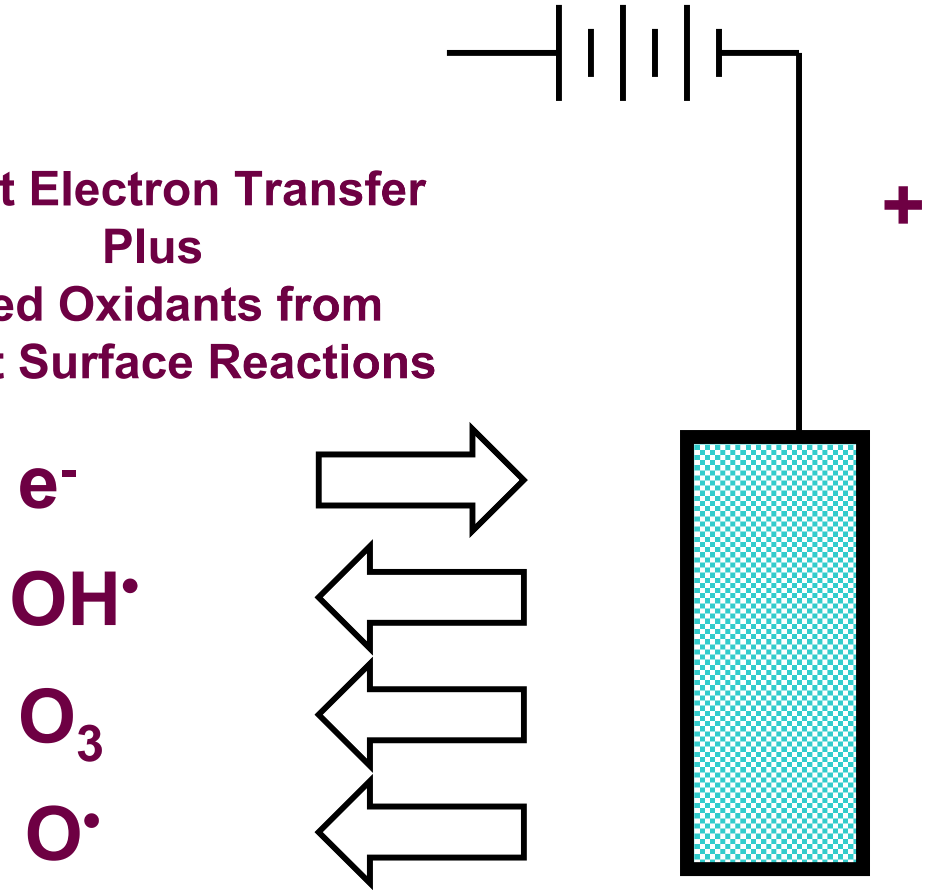
$$CH_3COCH_3 + 16\ OH^- = 3\ CO_2 + 11\ H_2O + 16\ e^-$$

Basic Concept
Electrolizer

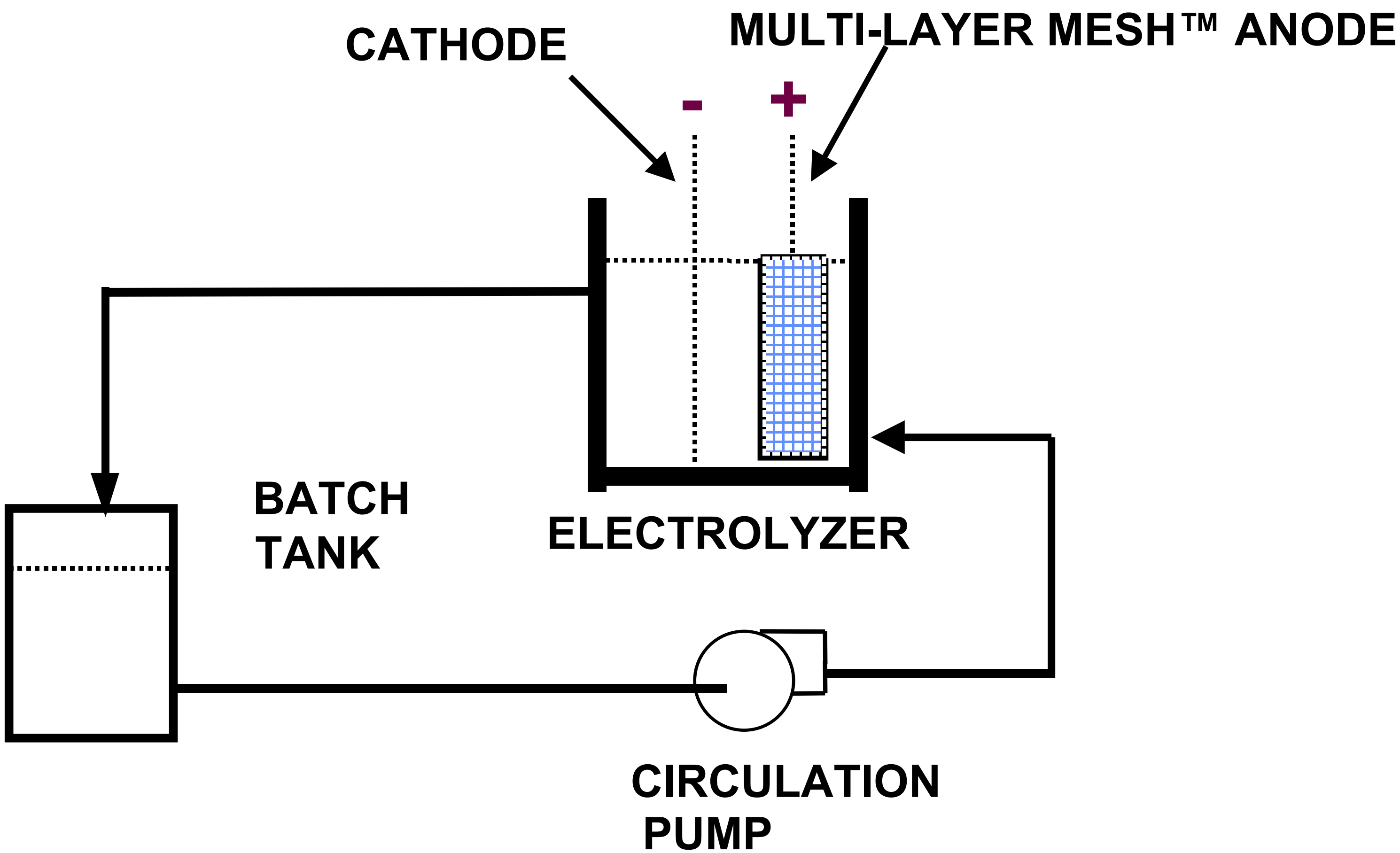


Anode Surface Reactions

Direct Electron Transfer
Plus
Mixed Oxidants from
Direct Surface Reactions

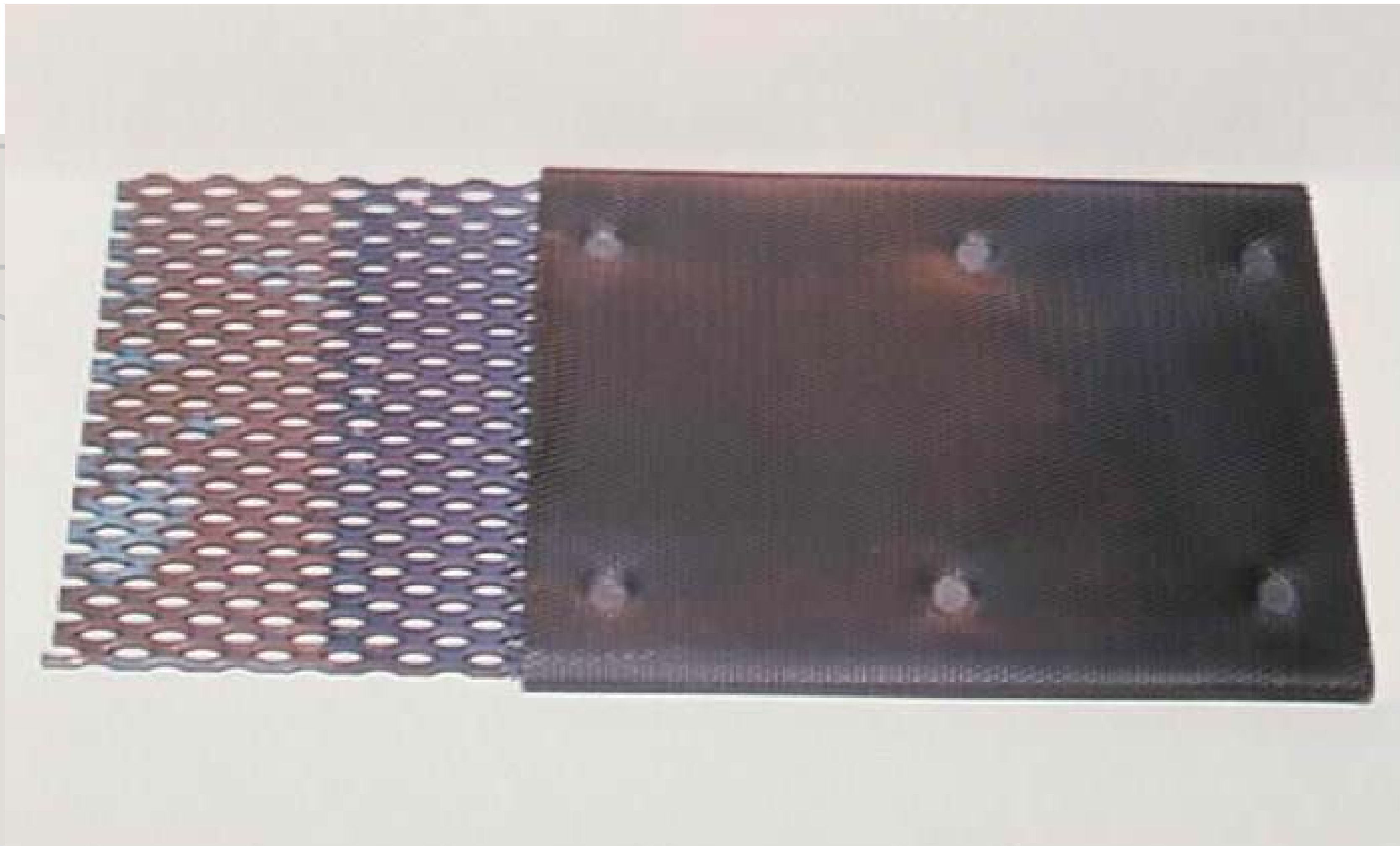


Laboratory Electrochemical Cell



Bench Scale Anode

High Surface Area, Flow Through



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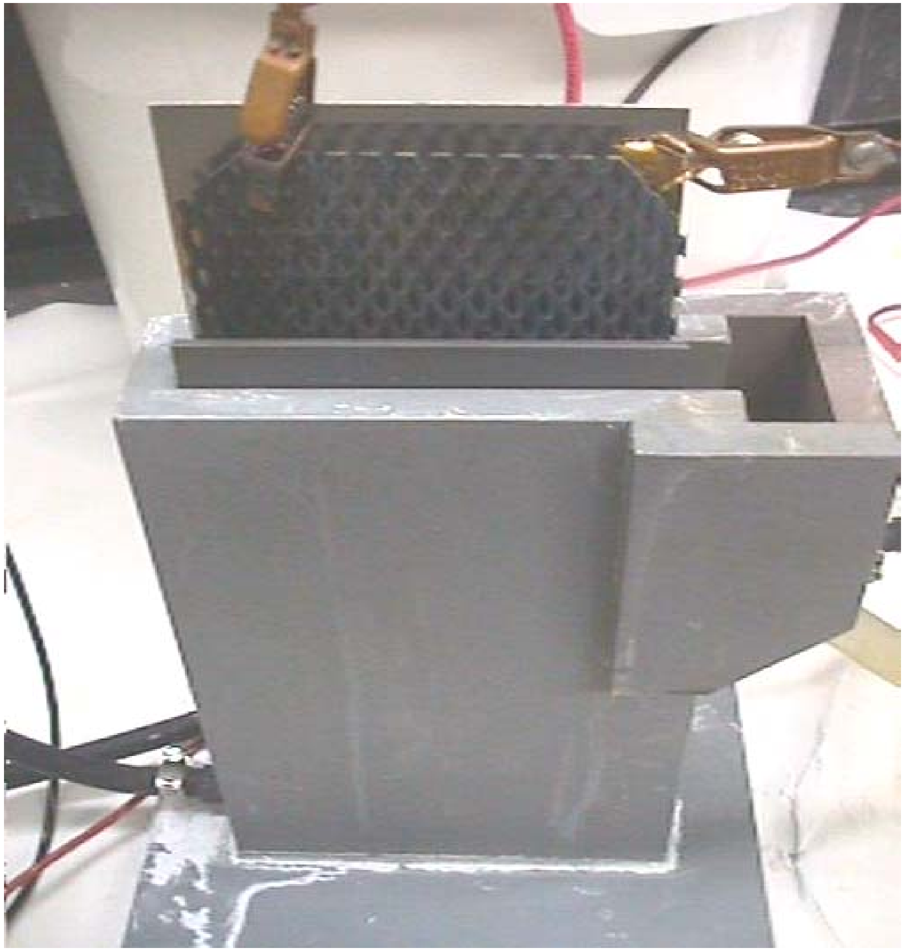
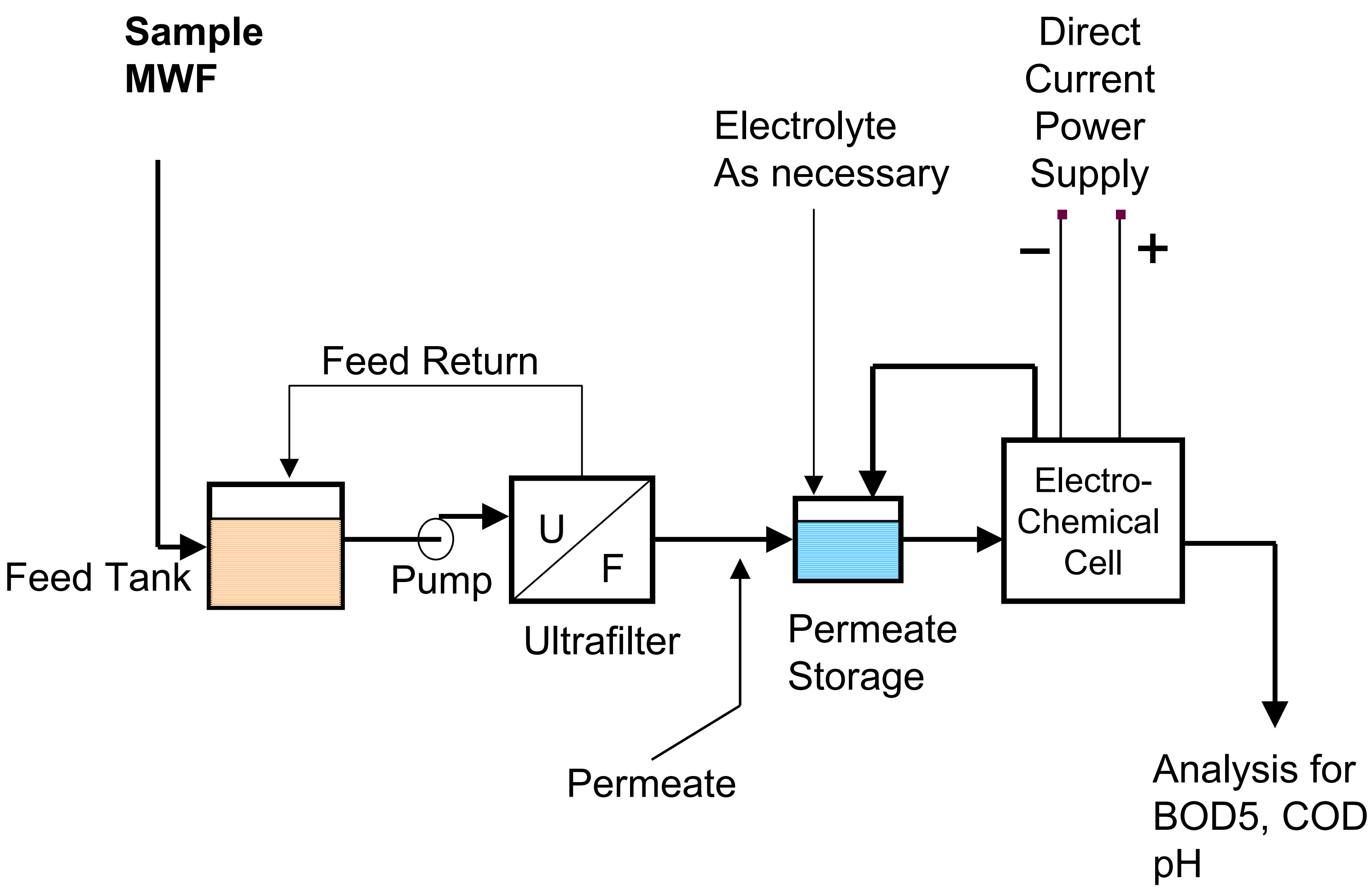
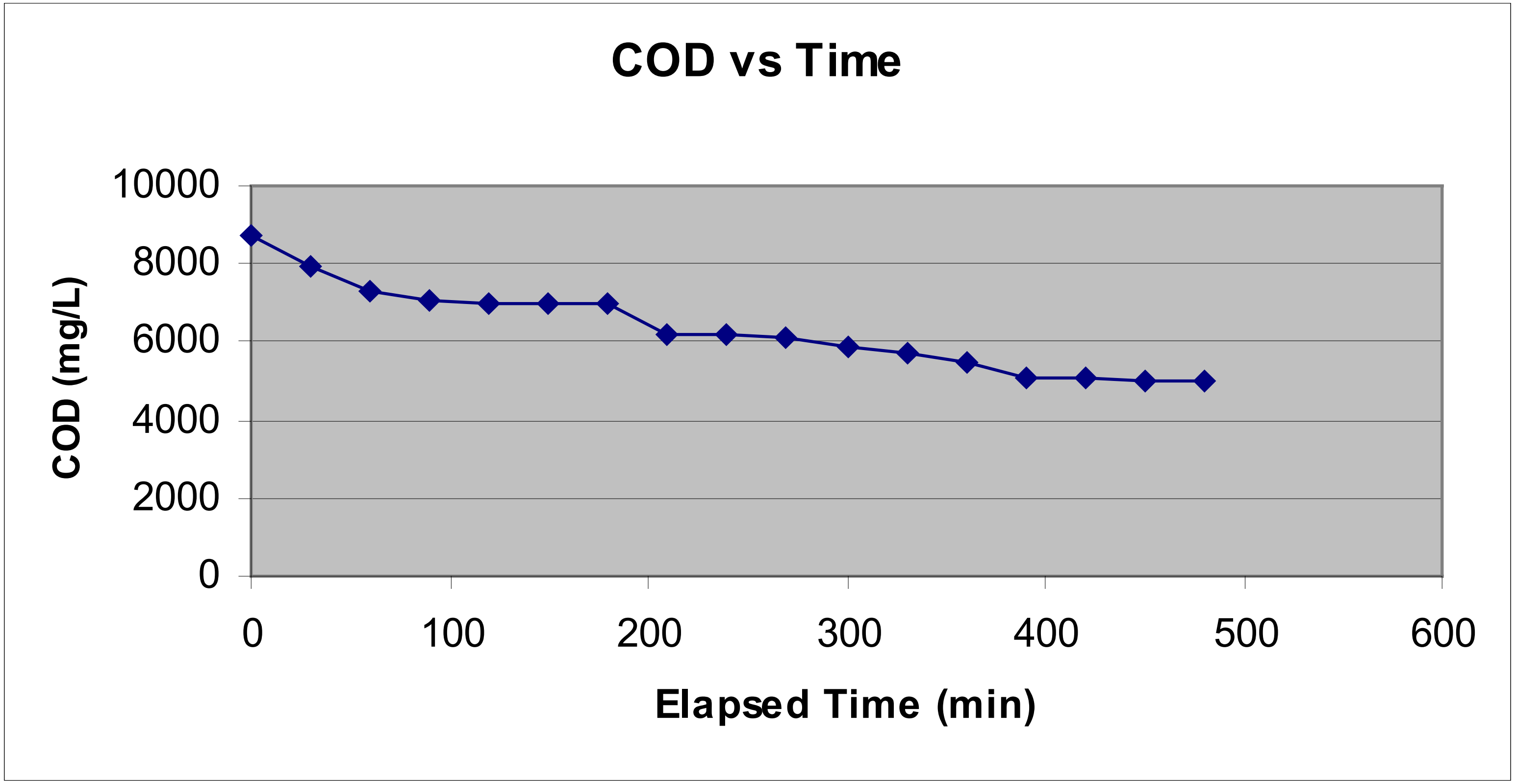
Bench Scale MLM Anode Test Cell



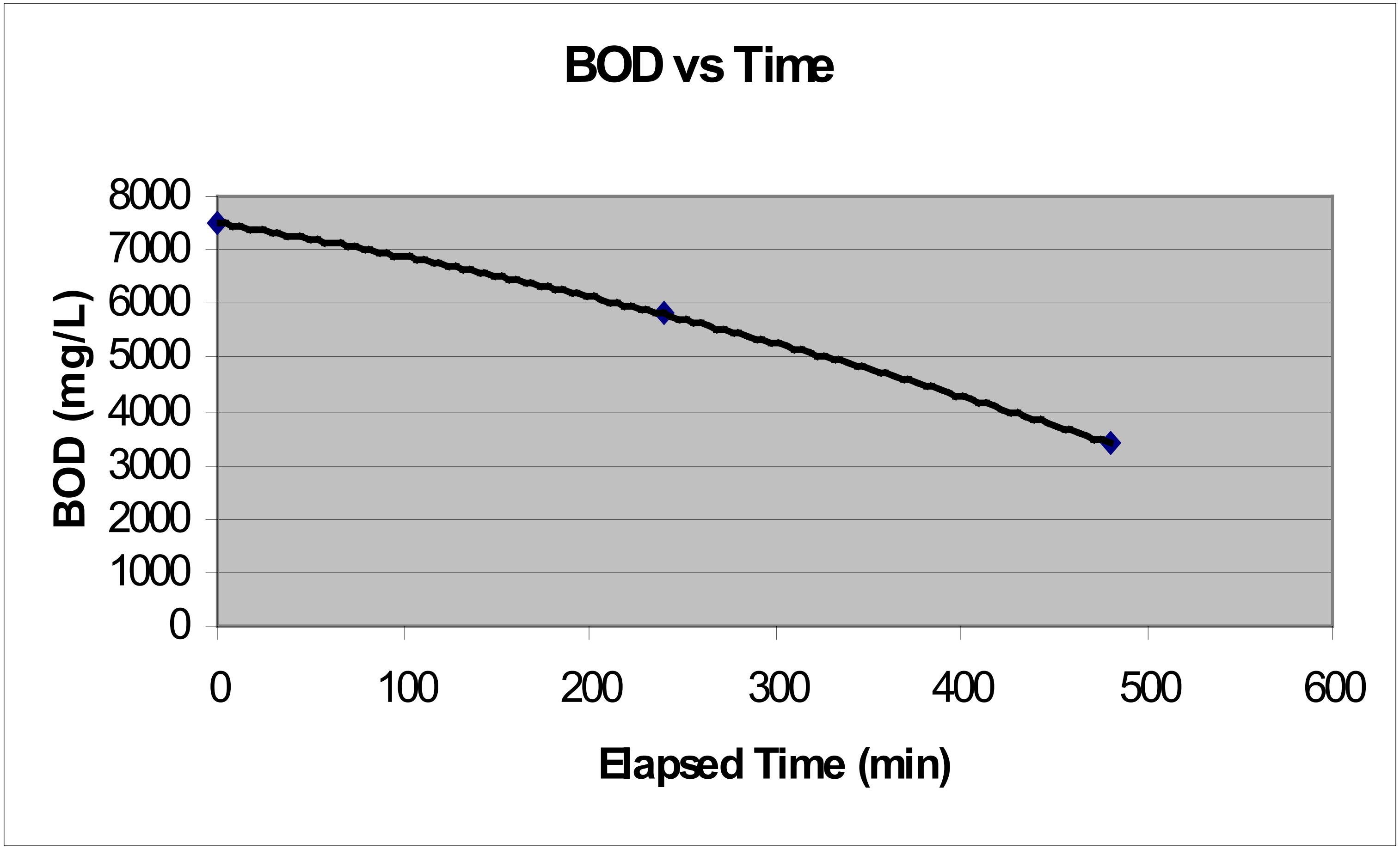
EXPERIMENTAL SET UP



Wastewater After UF
No Added Electrolyte
44% Reduction COD



Wastewater After UF
No Added Electrolyte
53% reduction BOD



INITIAL TESTING SIGNIFICANT VARIATIONS IN WASTEWATER

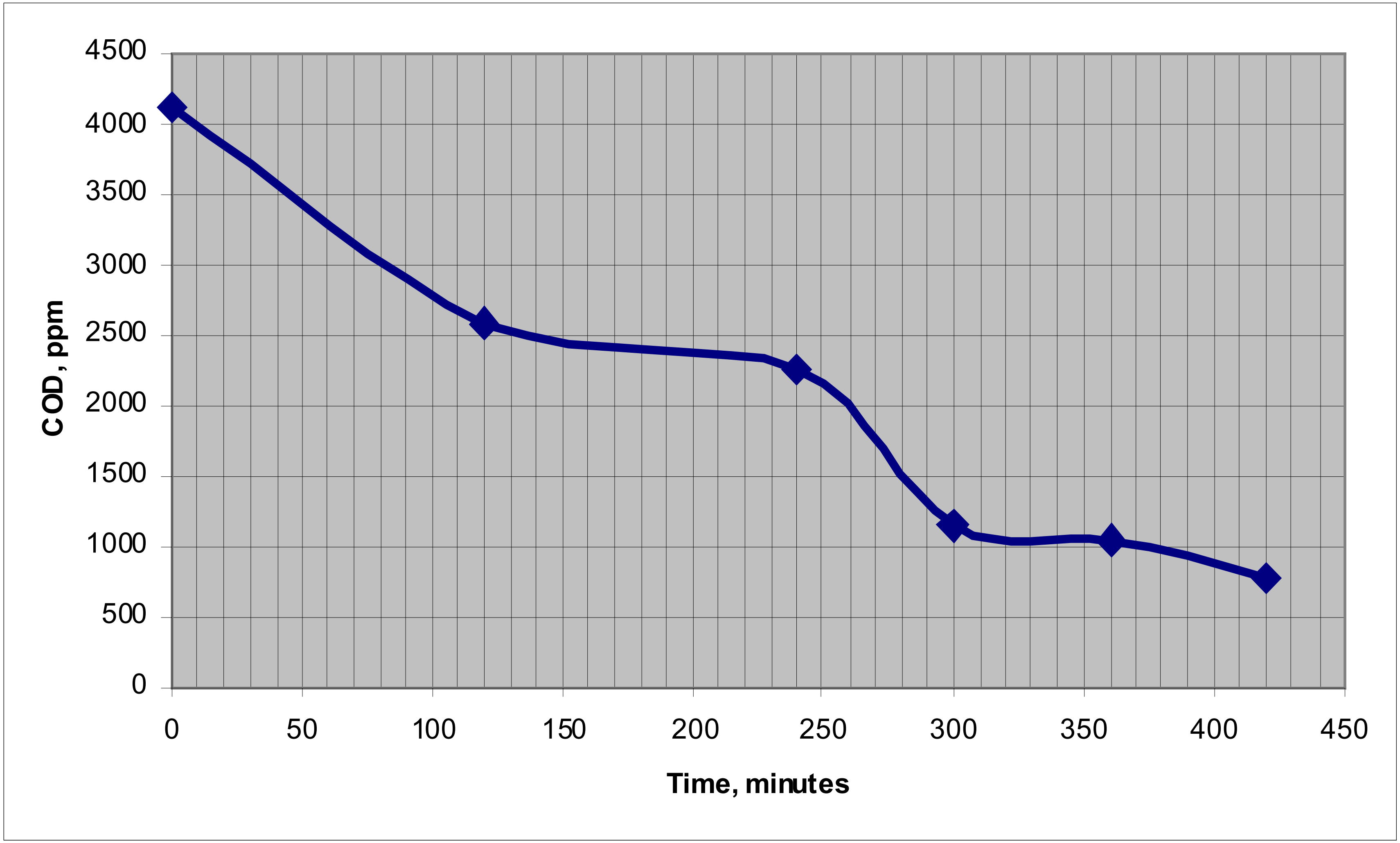
- Very site dependant
- Variations from day to day
- Difficult to “Prove Concept” with excess feed variation
- Need to try a standard
- Three amine blend

Synthetic Feed Mixture and Additive Ratios
The Three Amines

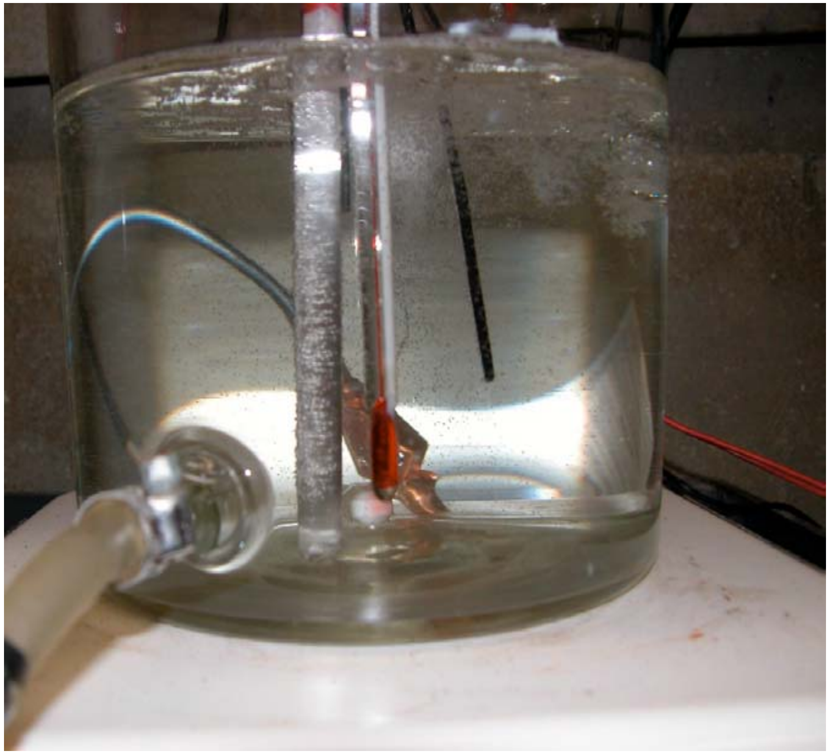
Chemical Mixture	CAS #	% - Volume
Monoethanolamine	141-43-5	30
Triethanolamine	102-71-6	30
Monoisopropanolamine	78-96-6	40

Then dilute above mixture 99:1 with H_20
To create COD ≈ 4,000

SYNTHETIC FEED / With Electrolyte #1
83% reduction COD

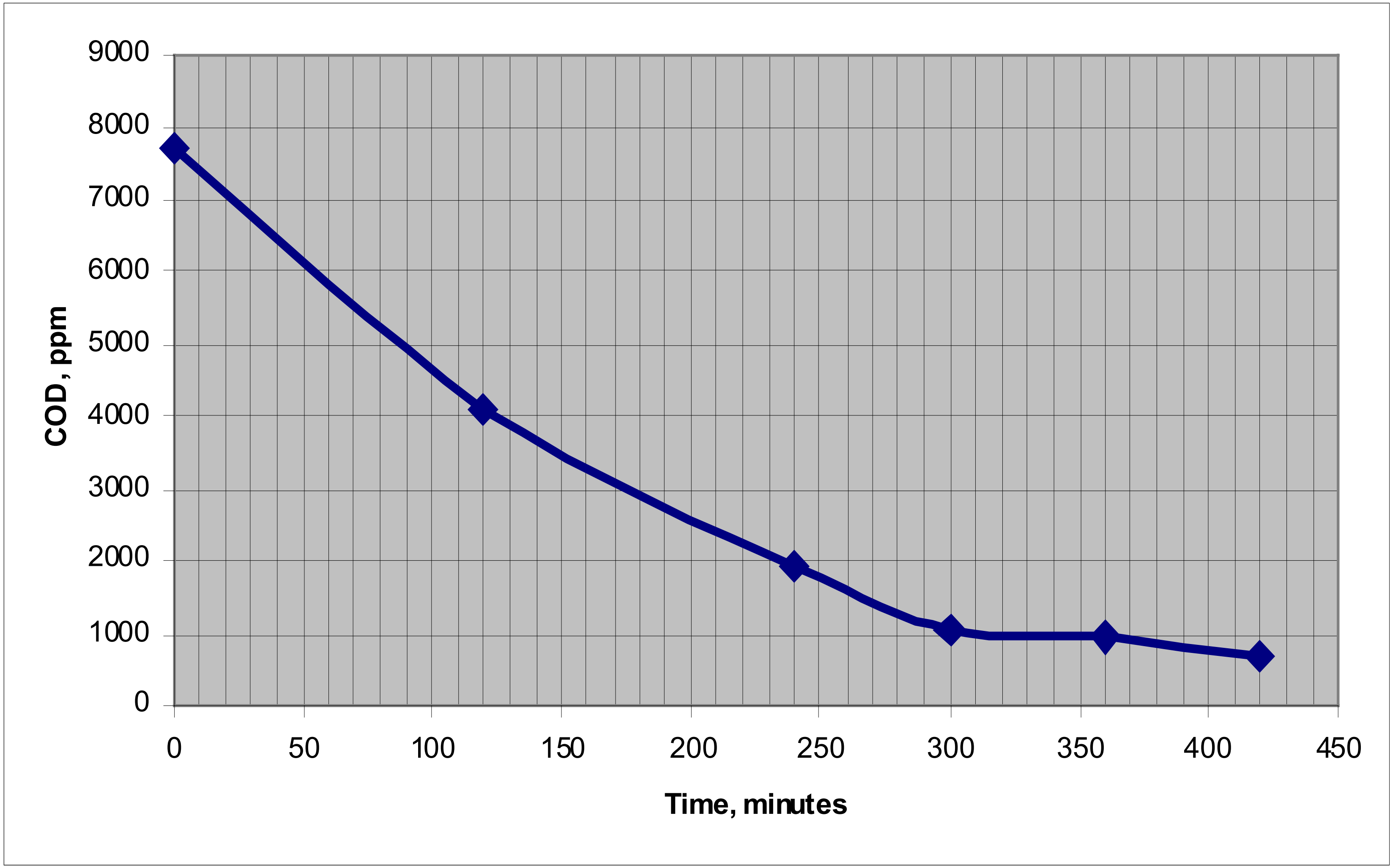


SYNTHETIC FEED / With Electrolyte #1

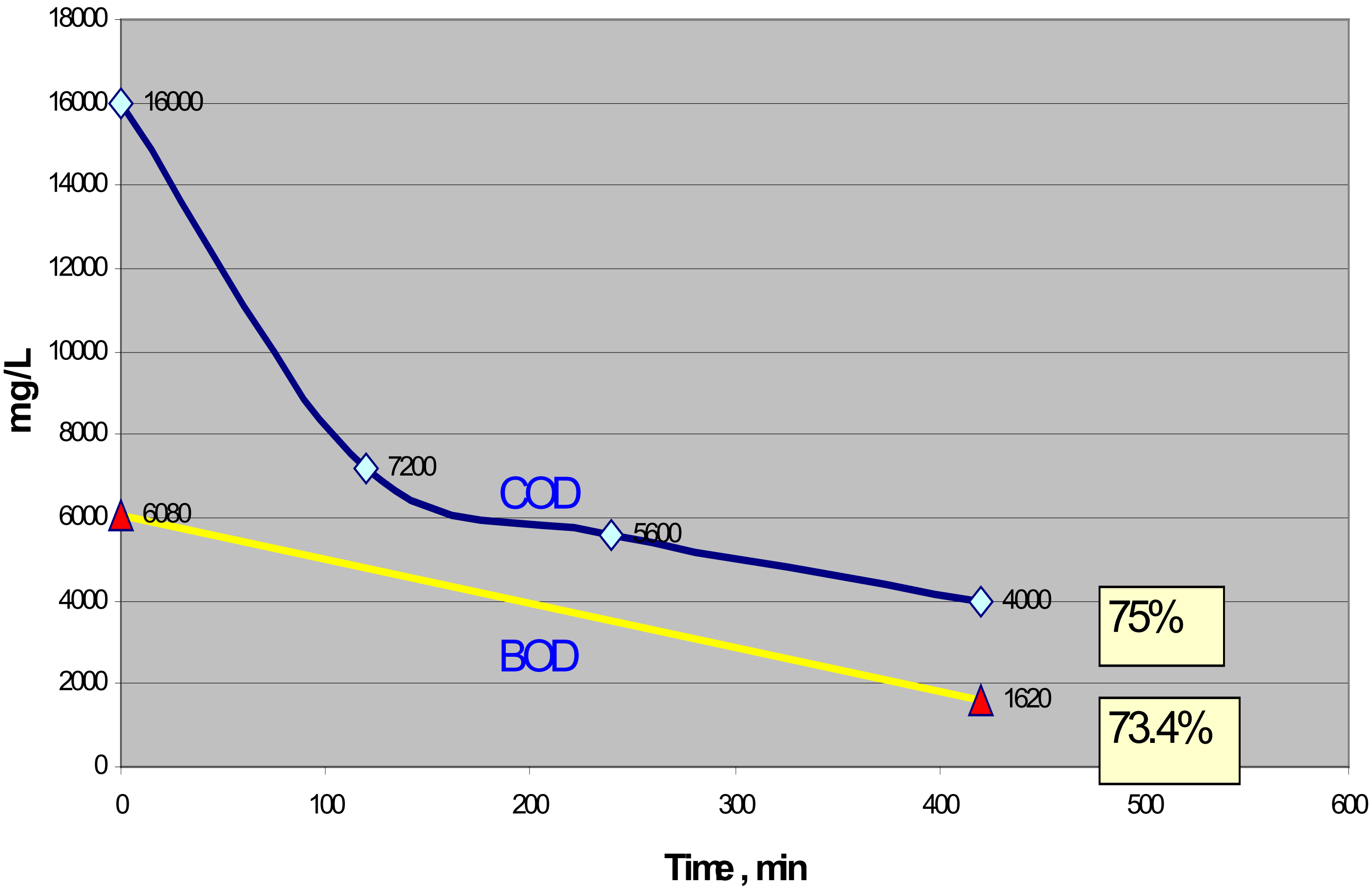


60 Minutes **460 Minutes**

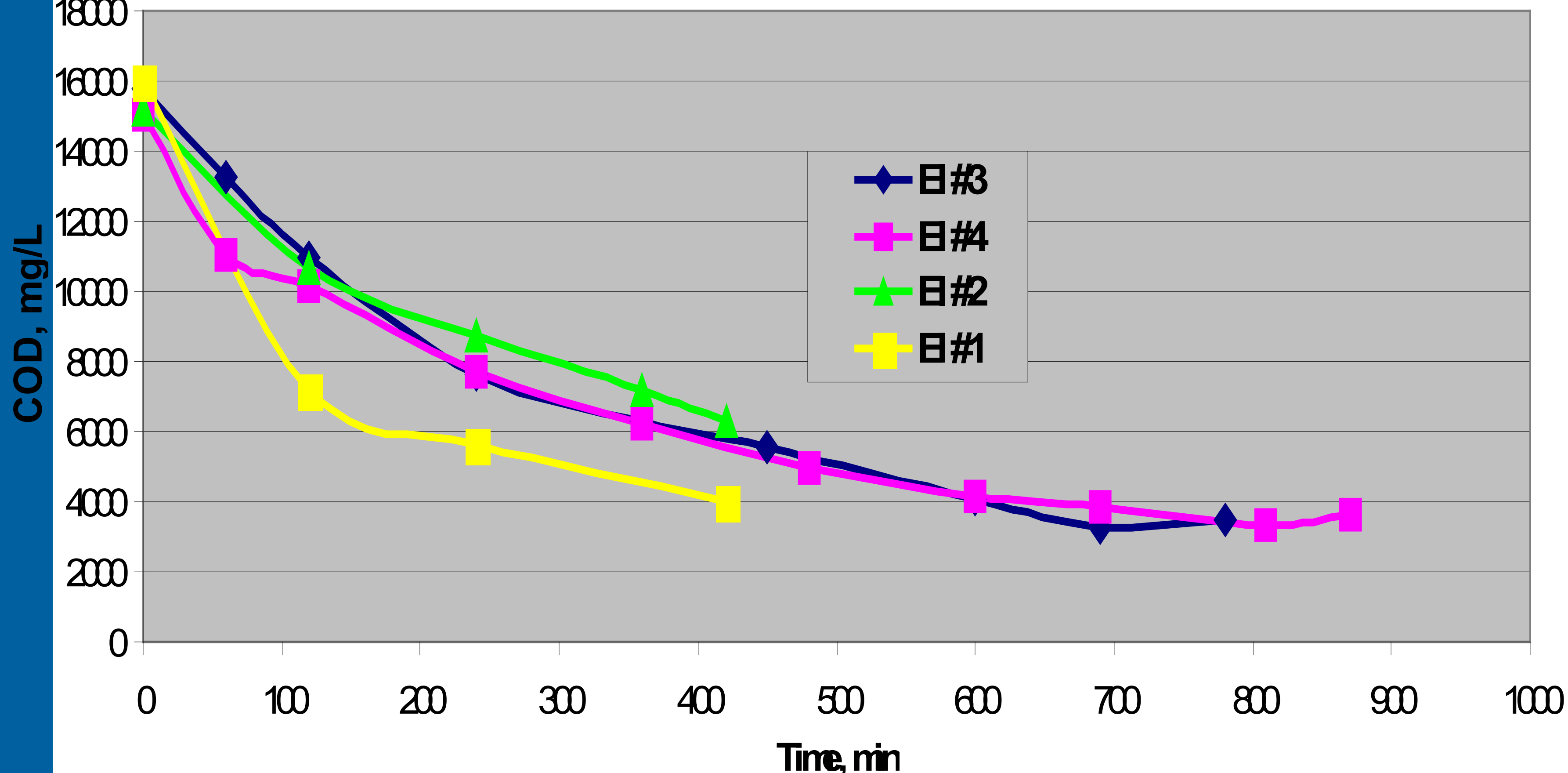
UF Permeate
Premium New MWF at 2% with Electrolyte #1
91.0% COD reduction



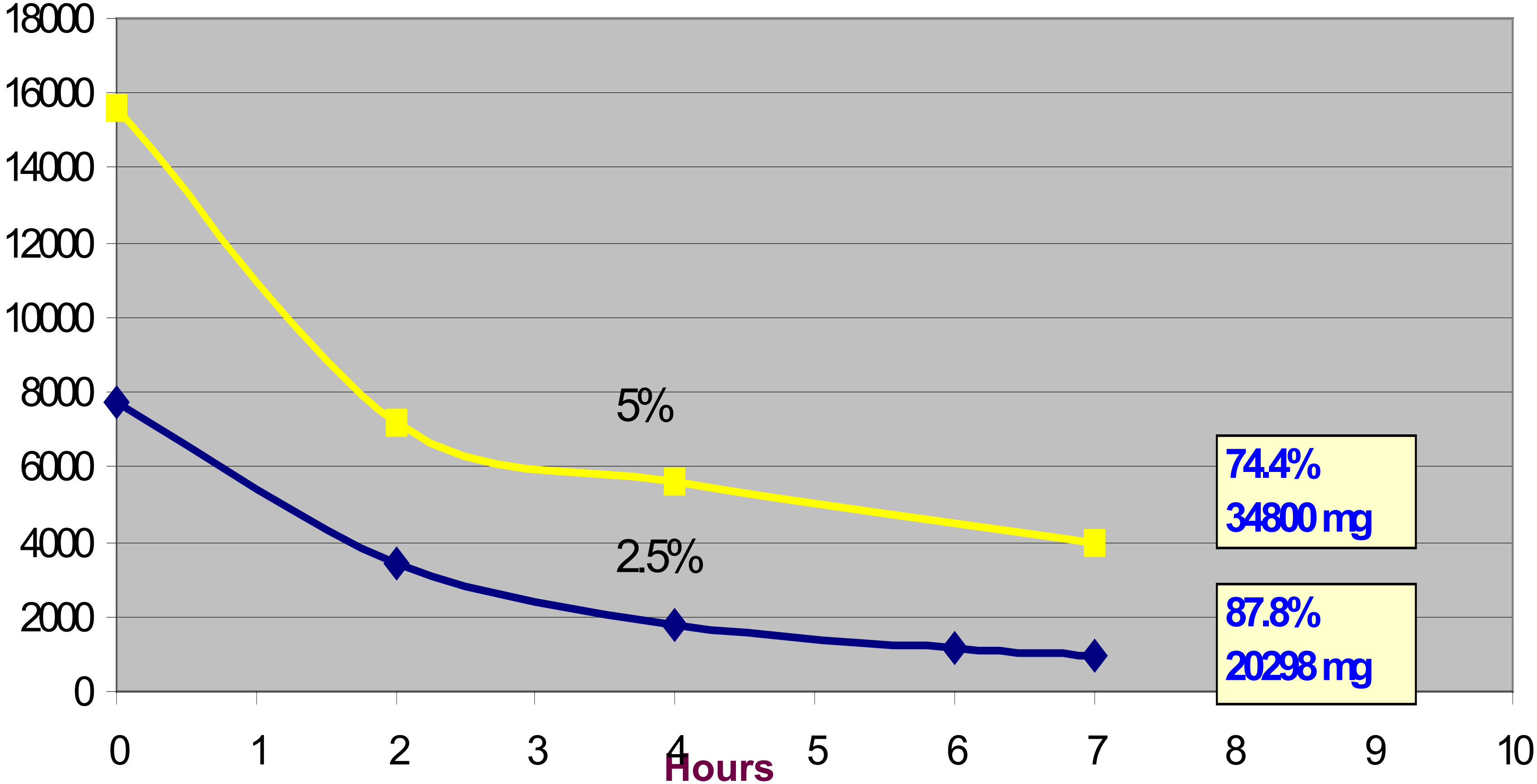
UF Permeate
COD and BOD5 Reduction versus Time.
Virgin MWF,5%; Electrolyte #1



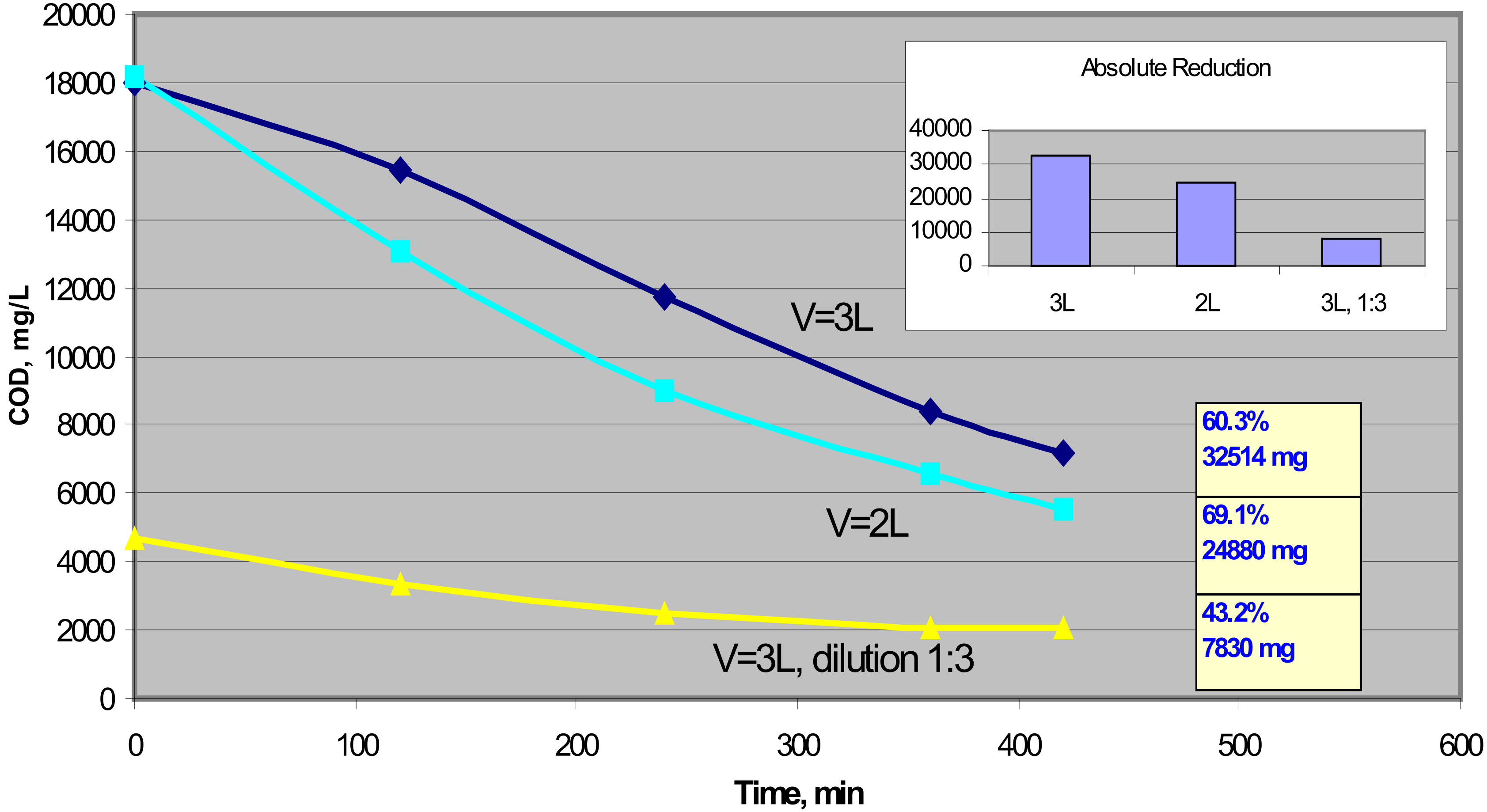
UF Permeate
COD Reduction Versus Time
Effect of Electrolytes
Virgin MWF, 5%



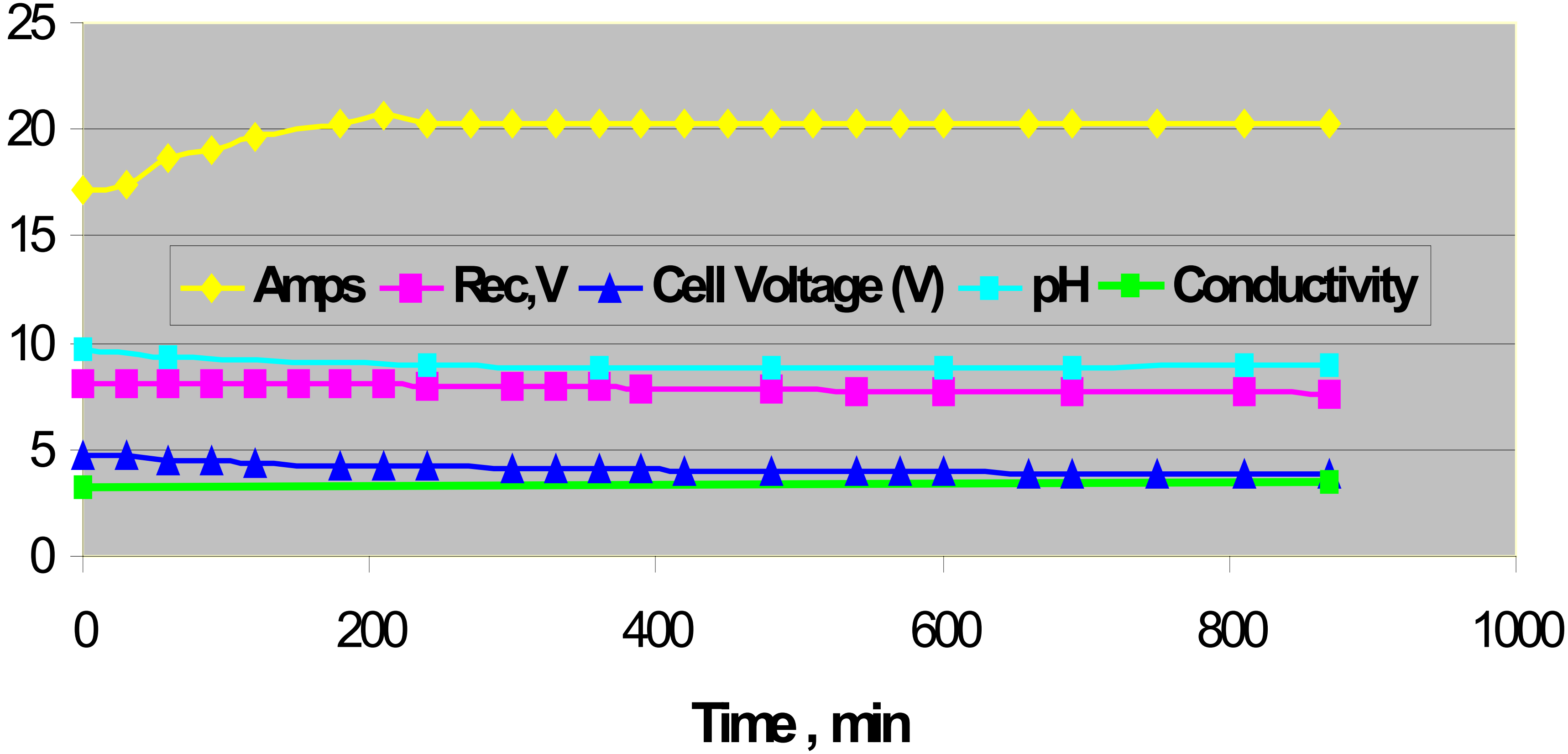
UF Permeate
Relative and Absolute Reduction of COD
Concentration Effect.
Virgin MWF, 7 hours, Electrolyte #1



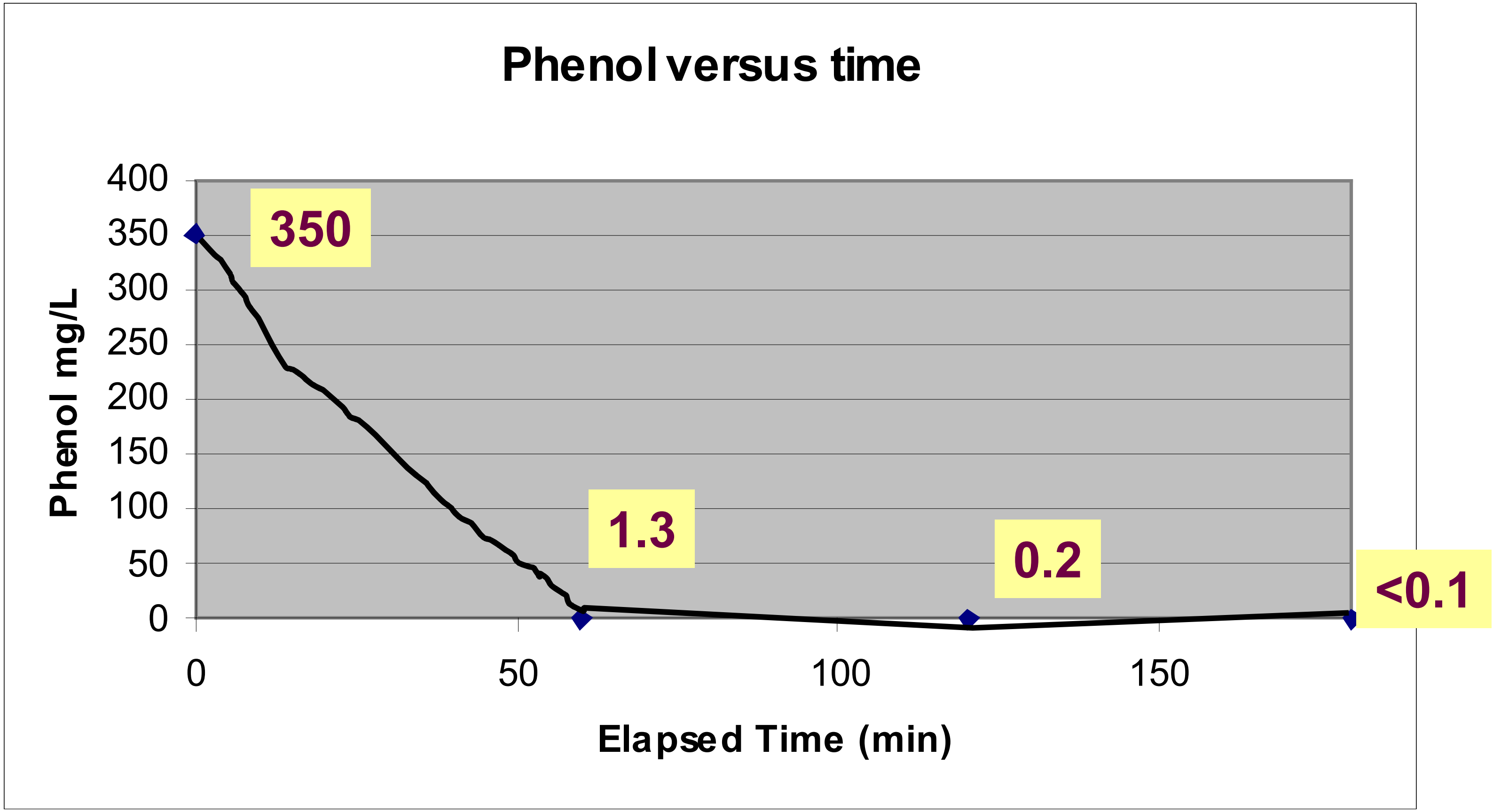
Relative and Absolute Reduction of COD Concentration and Treated Volume Effect Used MWF, 7 hours, Electrolyte #3



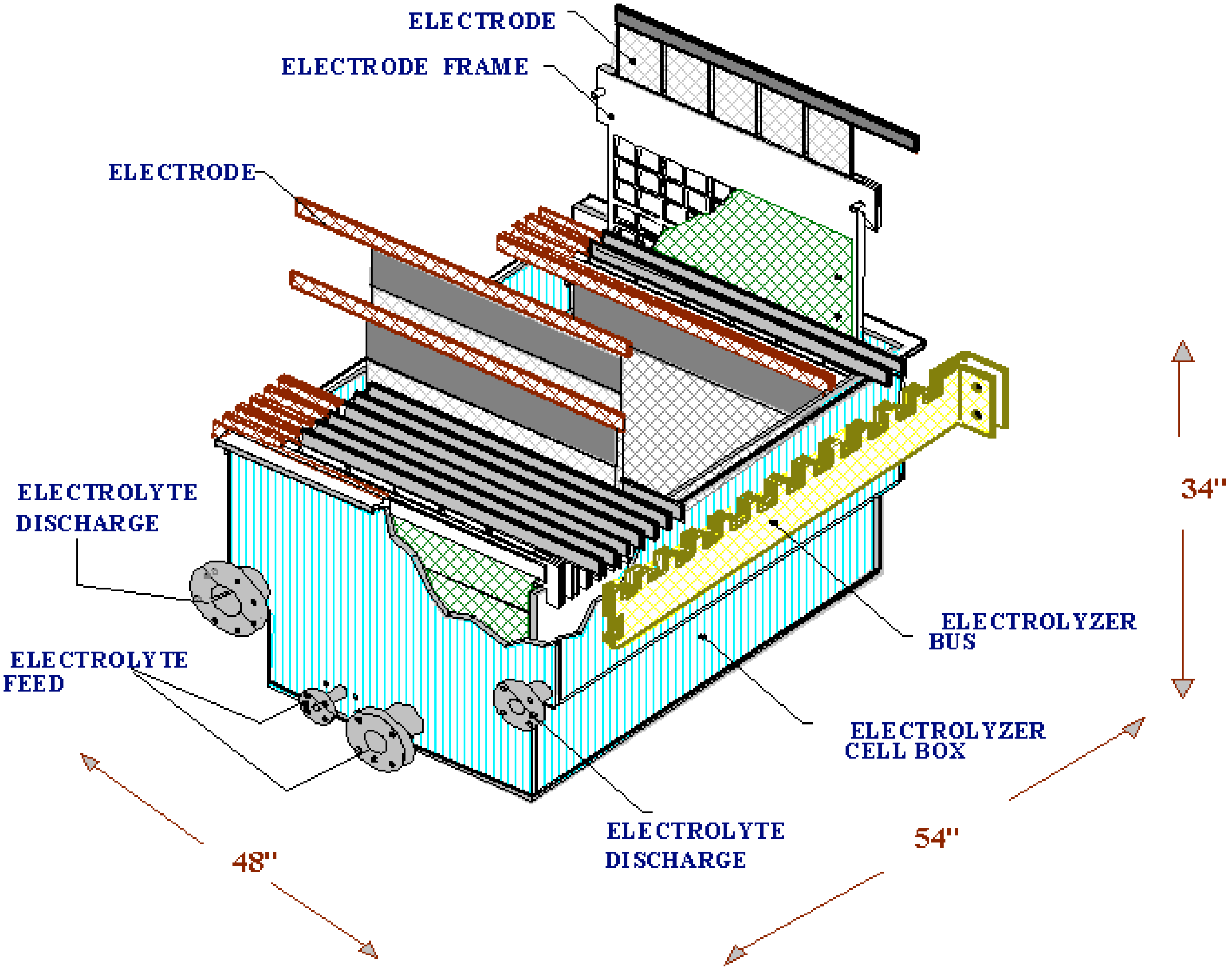
Process Control Data
Electrolyte #3



Premium MWF #3 @ 5% 100 ppm hard water, UF Permeate, Electrolyte #3 99.9% Reduction of Phenol (4AAP)

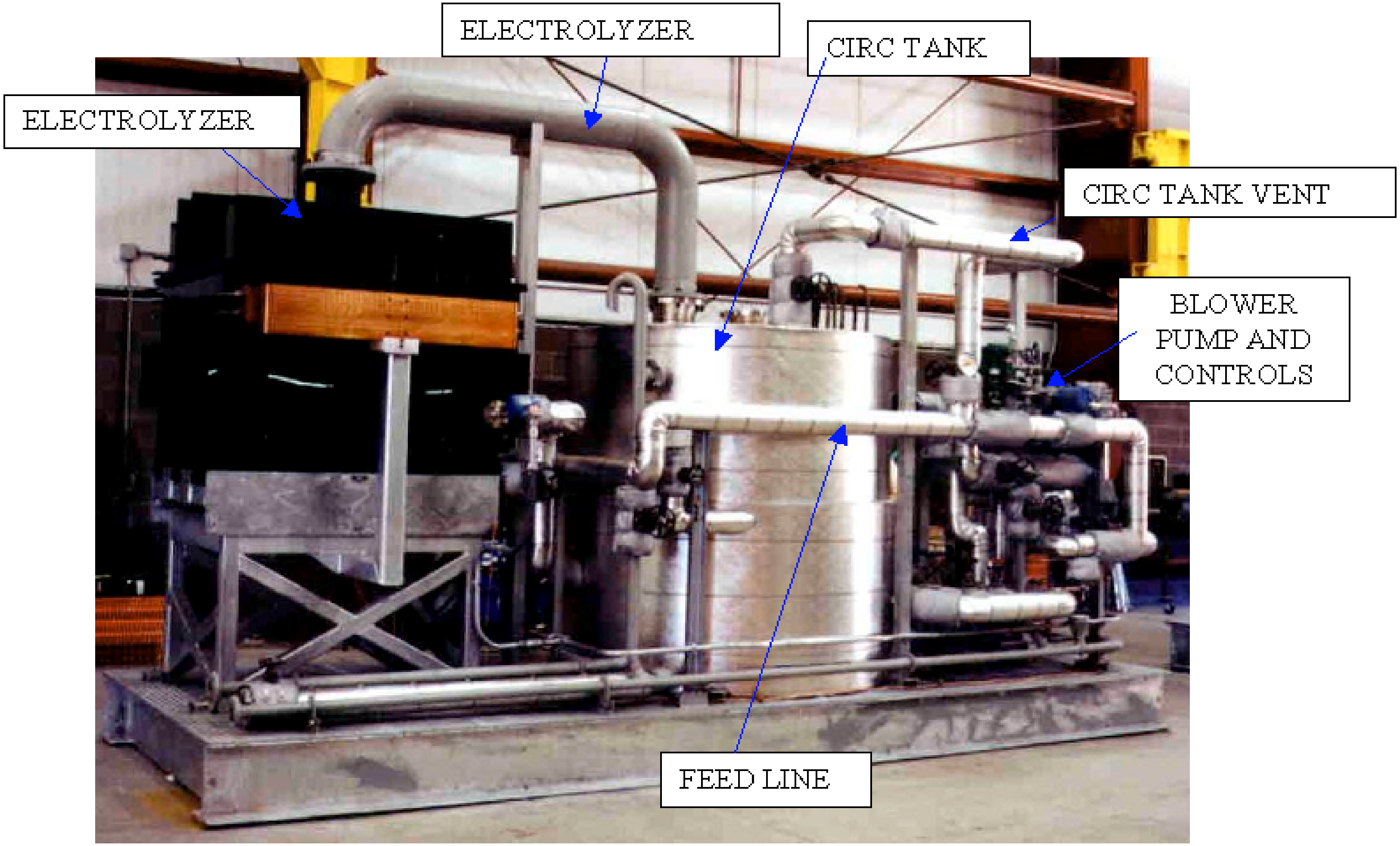


Electrolyzer



Full Scale Electrolyzer

Skid Mounted System



Some Engineering System Considerations

- Chemical resistance to oxidation
- Current density
- Anode / cathode lifetime
- Current efficiency – electrolyte addition
- Solution concentration
- Mass transfer
  - Fluid velocity
  - Concentration
  - Volume
- Footprint of physical equipment
- Oxidation reduction by-products to air
- Available operating area
- Fits with partner processes and industry comfort factor
  - UF / Chem treat vs. biological
- Ease of operation and maintenance
- Capital and operating cost

Summary

- Additional experimental work still in progress.
- Electrolyte addition increases the efficiency of the overall process - electrolyte cost is insignificant.
- BOD_5 and COD reductions in the range of 60% to 80% in 7- 8 hours are achievable.
- Operating cost (energy and anode life) to drive electrolytic cell estimated to be $ 0.012- $0.017 per liter at rate of $ 0.06 / KWH, per 8 hours of run time.
- Compact design.
- No sludge to dispose of.
- Can selectively oxidize certain organic compounds (phenol) in the presence of more difficult to oxidize organic compounds .
- Ultrafiltration with Electrochemical Oxidation is a promising method.