Integrated Electrochemical Treatment of CMP Waste Streams for Water Reclaim and Conservation (Customized Project)

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- Water Resources Research Center

Objectives

- Develop methods for removing Cu^{2+} (electrochemically), H_2O_2 (catalytically), and other contaminants from wastewater generated during CMP.
- Build a prototype reactor and pilot test on real CMP wastewater.
- Estimate total costs of ownership for reclaiming CMP wastewater.

ESH Metrics and Impact

1. *Reduction in emission of ESH-problematic material to the environment*

- Eliminate the disposal problems associated with membrane concentrates.
- Eliminate the disposal of Cu-laden nanoparticles into hazardous waste landfills.

2. Reduction in the use of natural resources (water and energy)

- Reclaim CMP wastewater for reuse.
- CMP wastewater accounts for up to 30% of fab water use.

3. Reduction in the use of chemicals

- Eliminate the need for pH adjusting chemicals and reducing agents that add to TDS load.
- Eliminate the need for activated carbon regeneration.

Opportunity statement

• Natural Resources: Water Conservation

- CMP accounts for ~30% of water use in the fab
- CMP waste water is generated at 25-40m^3/day/tool or 500-750m^3/day for a 20-tool fleet (0.15 to 0.2 MGD)
- CMP waste waters are not broadly reclaimed at present w/in Intel
- Use of reclaimed CMP waste in industrial waters could, for example, easily supply 0.1 MDG for use in cooling towers, or provide feedstock for URW system

• Bulk Chemicals: Reduction of Acid/Base Use

- pH adjustments are done electrochemically and economically ⇨ no need to purchase, ship and store acids and bases to implement the technology

• Equipment and Process: Green Alternative

- electrochemical methods avoid addition of salt (e.g. Cl^- and SO_4^{2-}) and generation of brine streams ⇨ better salinity management in areas such as the Desert SW United States

Current Research and Differentiators

CMP waste characteristics

- 5 - 20 ppm of dissolved copper
- 500 - 1000 ppm of total suspended solids (TSS); 50 to 600nm particles of silica, alumina, ceria and/or polishing pad
- 100 - 400 ppm of total dissolved solids (TDS)
- organic complexants (*e.g.*, citric acid)
- organic corrosion inhibitors (*e.g.*, benzotriazole)
- oxidizing agents (*e.g.*, H_2O_2)

Standard separate treatment steps†

1. oxidizer removal
2. organics removal
3. TSS reduction
4. trace metal removal

†no order implied

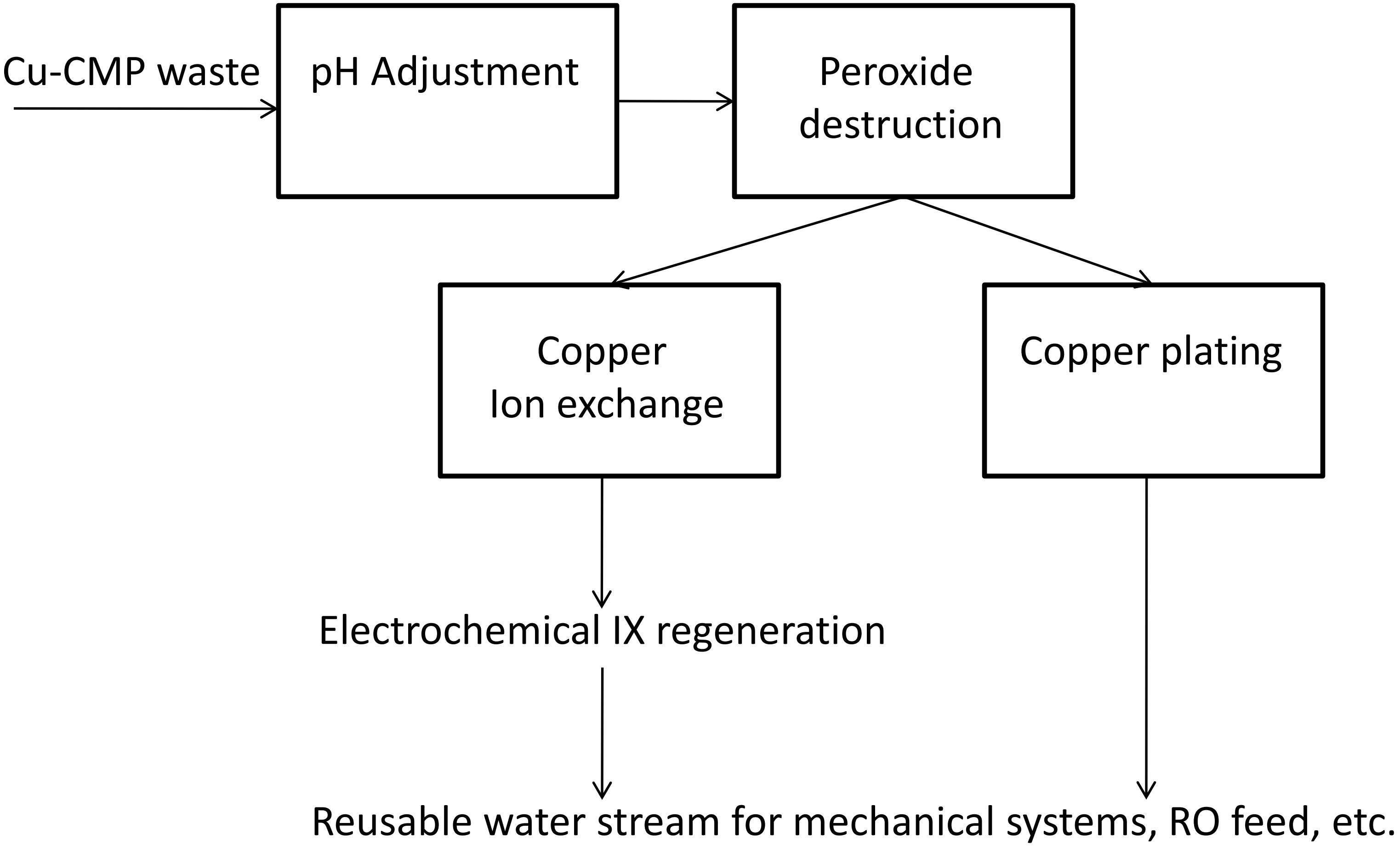
Present treatment methods include:

1. Chemical pH adjustment
2. Addition of reducing agents
3. Solid/liquid separation (MF, UF, RO)
4. Ion exchange

Drawbacks to current methods include:

1. pH adjusting chemicals increase TDS (e.g., Cl^- or Na^+)
2. The need for addition chemical reducing agents to remove H_2O_2 that increase TDS
3. The generation of brine solutions from ion-exchange regeneration
4. The generation of concentrates from solid/liquid separations

Proposed Approach



Cu-CMP waste

pH Adjustment

Peroxide destruction

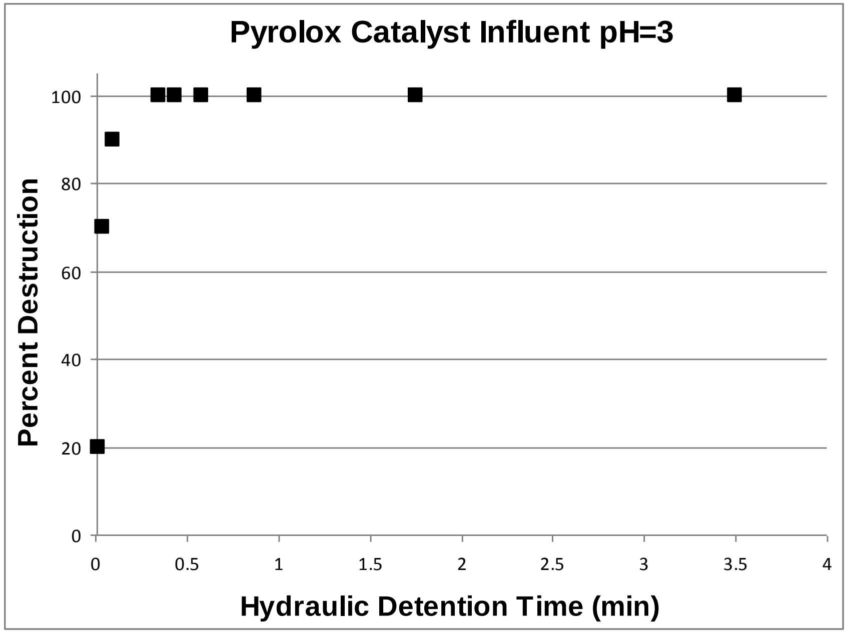
Copper Ion exchange

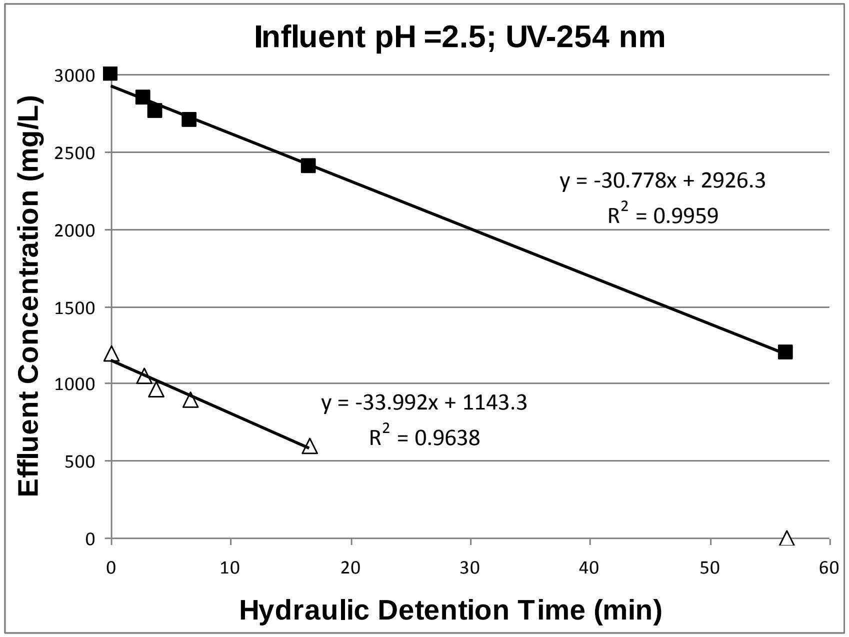
Copper plating

Electrochemical IX regeneration

Reusable water stream for mechanical systems, RO feed, etc.

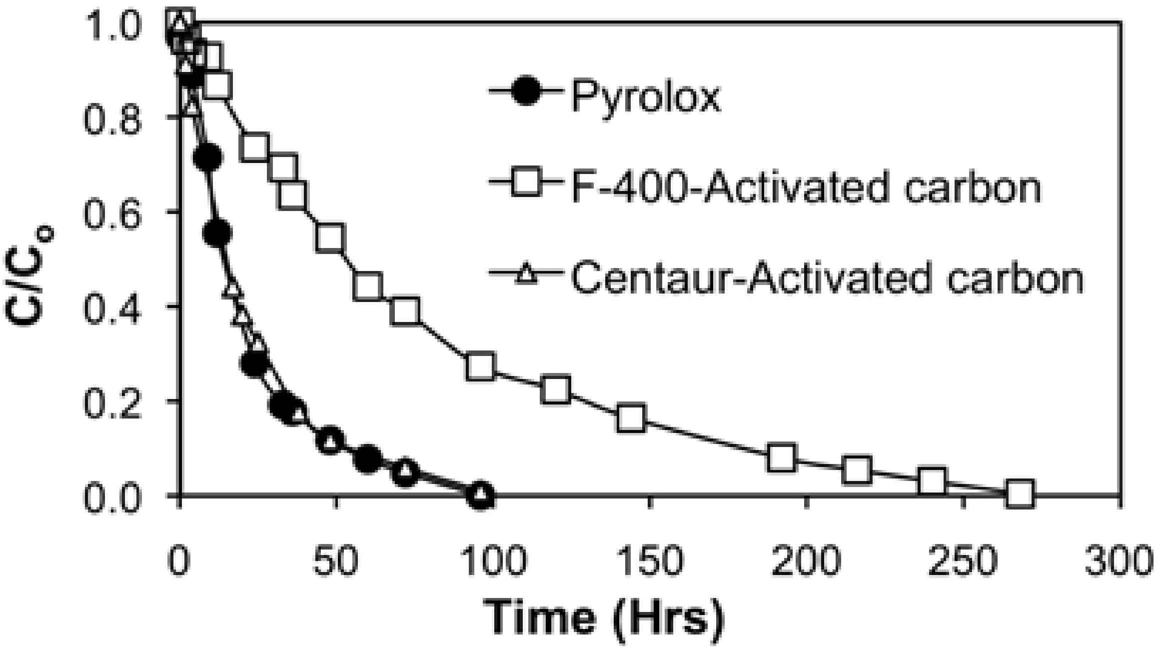
Peroxide Destruction





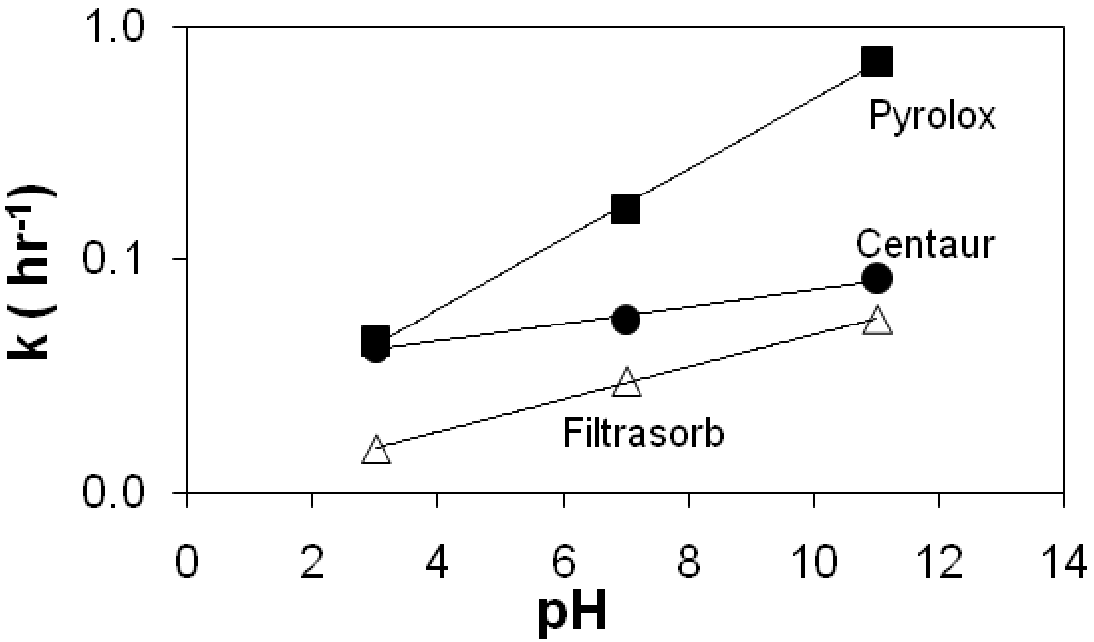
- **Conducted tests on six possible peroxide destruction catalysts.**
- **Conducted tests on ultrasonic and UV-light peroxide destruction.**
- **Pyrolox® (pyrolusite-MnO_2) catalyst determined to be the most effective.**
- **H_2O_2 destruction rates with both 185 and 354 nm UV light were too slow for practical implementations.**

Peroxide Destruction



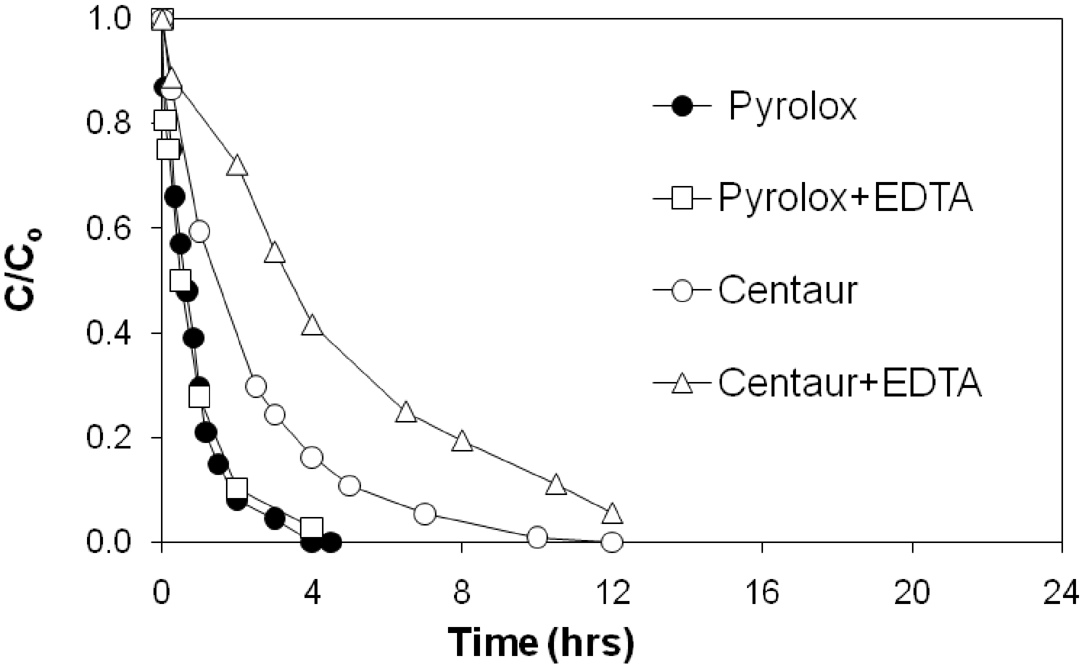
- **Pyrolox catalyst compared to activated carbon catalysts (Filtrasorb® and Centaur®)**
  - **pH 3, in the absence of chelating compounds**
- **Activated carbon and pyrolox can perform identically under these conditions**

Peroxide Destruction



Pyrolox excels as a peroxide destruction catalyst at neutral and high pH values

Peroxide Destruction



Pyrolox maintains its effectiveness in the presence of chelating compounds.

Electrochemistry Background

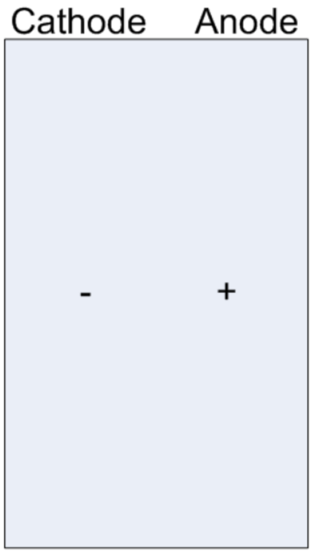
- Why electrochemistry?
  - elimination of chemical additives
  - elimination of secondary waste stream production requiring further treatment or disposal (*e.g.*, ion exchange brines)
  - small footprint, low capital and operating costs

Electrochemistry Background

Copper plating: net result of the process is copper removal from the liquid and a lower pH.

Copper removal:
$Cu^{2+} + 2e^- \rightarrow Cu^0$

Competing reaction:
$2H^+ + 2e^- \rightarrow H_2$

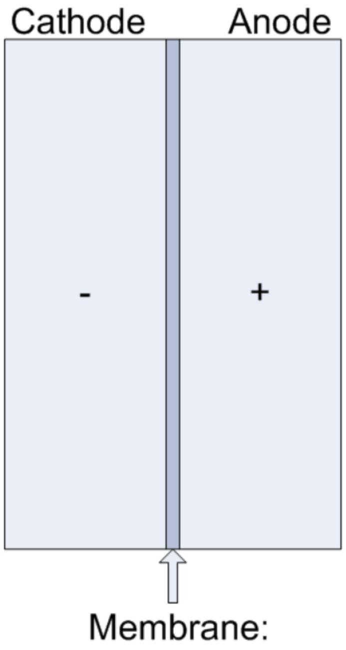


Counter-reaction:
$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$

Electrochemistry Background

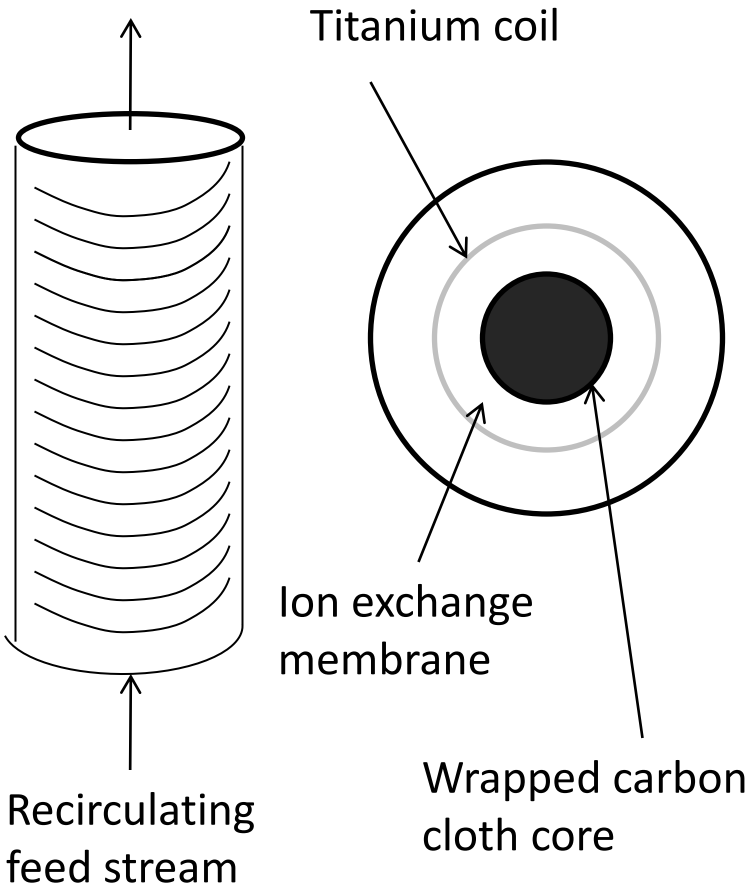
Electrochemical pH adjustment: pH is increased on one side of the membrane and lowered on the other side

Acid consumption (base production):
$2H^+ + 2e^- \rightarrow H_2$



Acid production:
$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$

Electrodeposition of Cu^{2+} in Flow-through Reactor

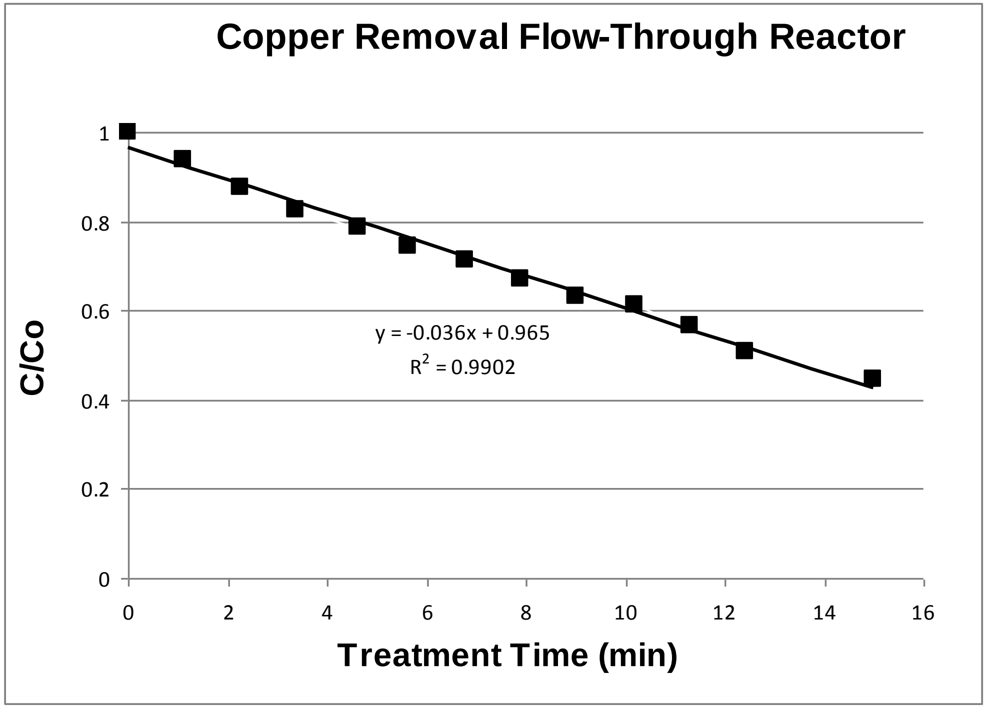


Titanium coil

Ion exchange membrane

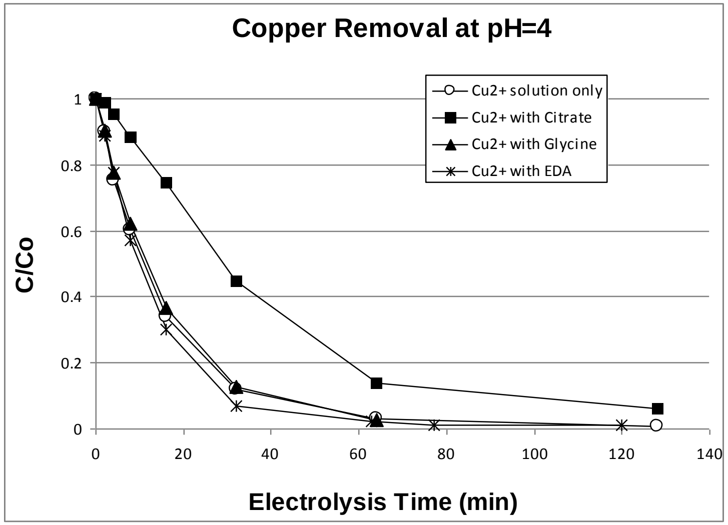
Wrapped carbon cloth core

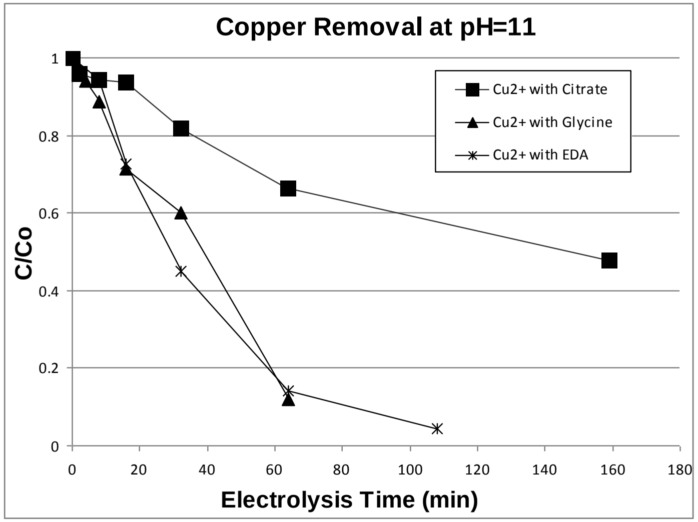
Recirculating feed stream



Cu deposition occurs rapidly in flow-through reactor. (Initial concentration of 40 mg/L.)

Electrodeposition of Cu on Carbon Cloth Cathode

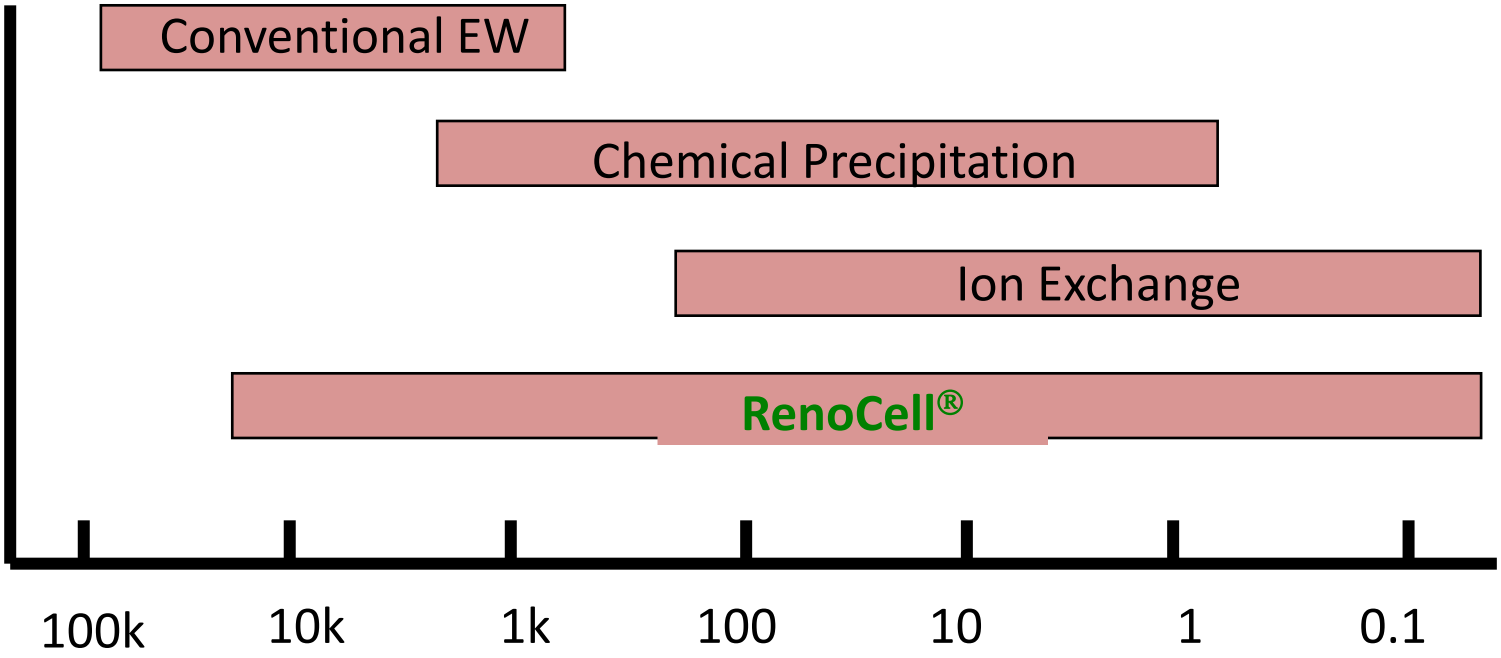




- **Investigated the effect of chelating agents on electrodeposition of Cu in batch reactors in solutions with low and high pH values.**
- **Ethylenediamine (EDA) and glycine do not affect Cu deposition rates.**
- **Cu deposition occurs at both low and high solution pH values.**

Commercial Scale Reactors

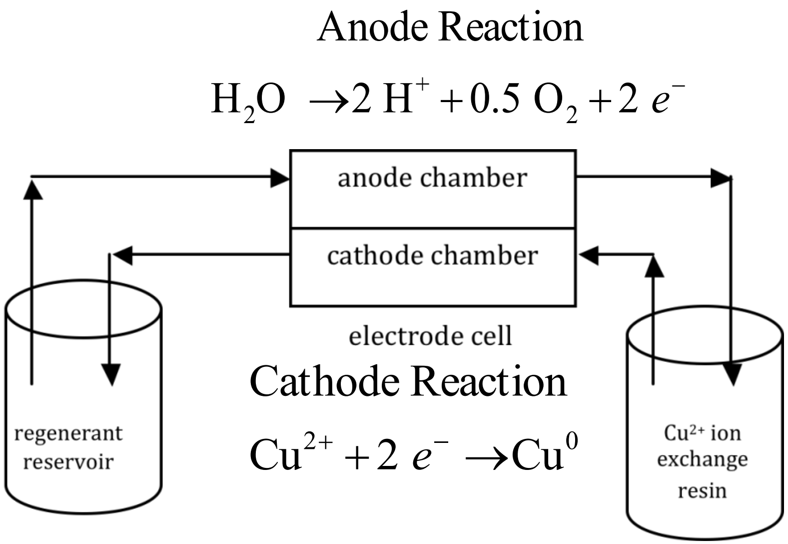
Effective Operating Ranges for Metal Removal Technologies



Copper Remaining (mg/l)

Experimental System

- Copper plating system:
  - Renovare M100 RenoCell (bench scale test system)
- S-930 Purolite cation exchange resin
  - Chelating, iminodiacetic functional groups



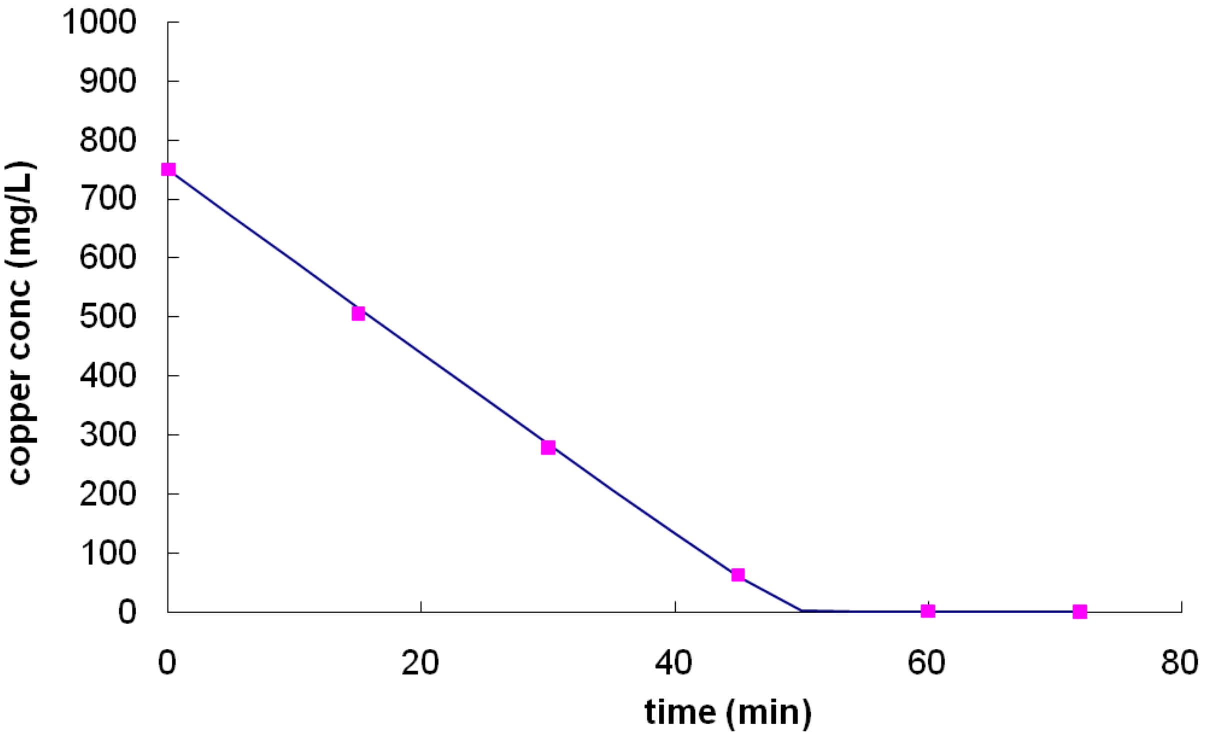
Anode Reaction

$H_2O \rightarrow 2\,H^+ + 0.5\,O_2 + 2\,e^-$

Cathode Reaction

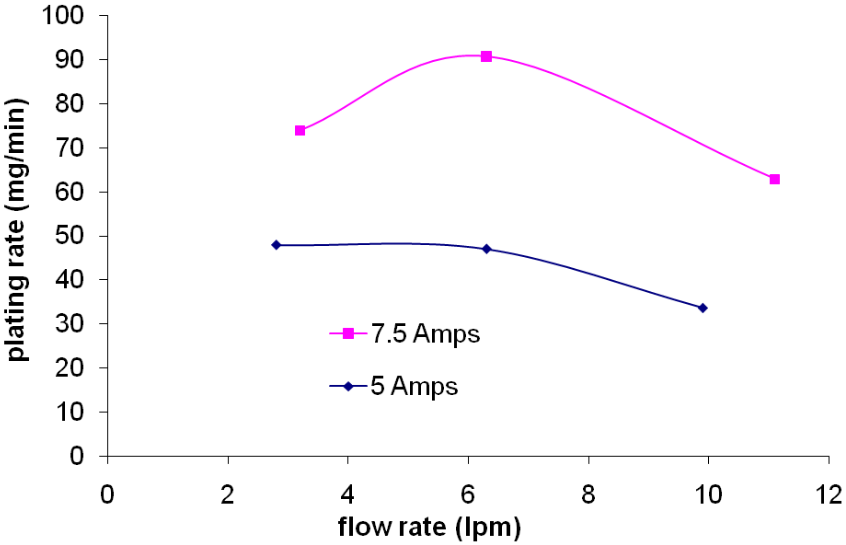
$Cu^{2+} + 2\,e^- \rightarrow Cu^0$

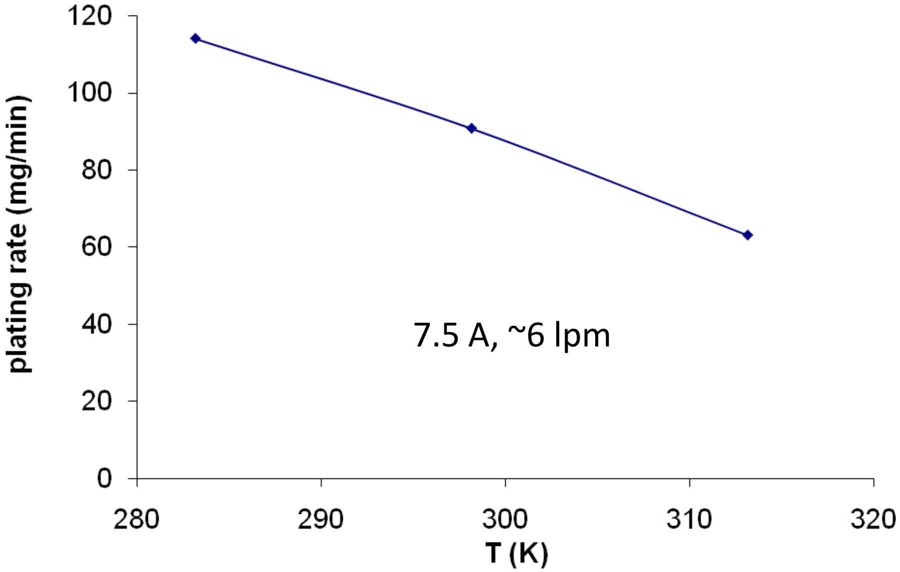
Copper Plating Only



Copper plates at a constant rate at high concentrations, and follows a first-order rate law at low concentrations.

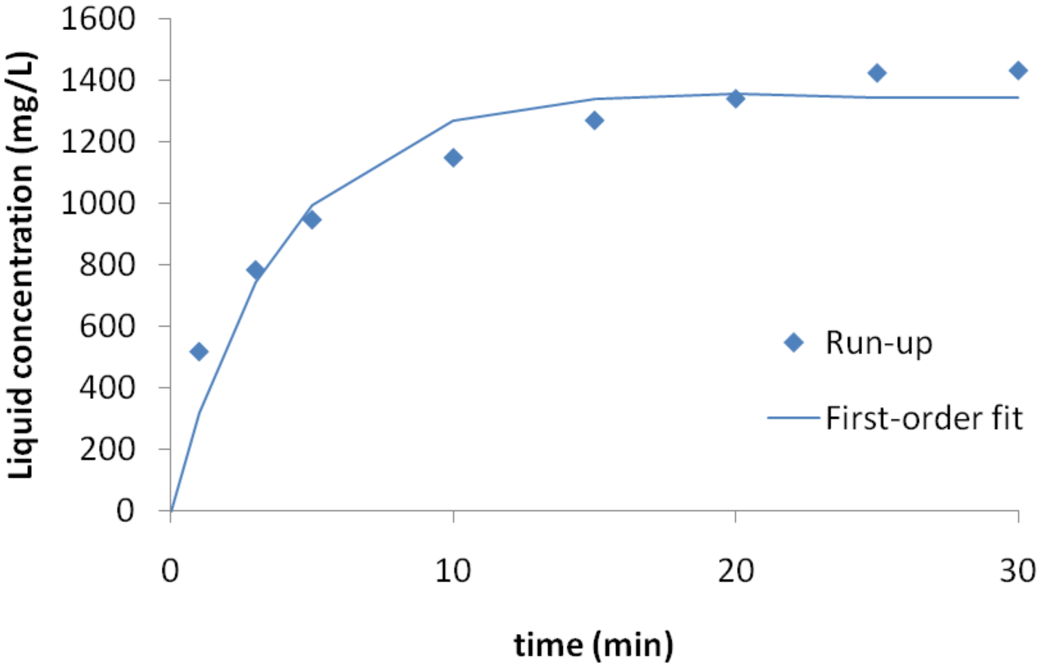
Copper Plating Only





Copper plating rate depends on temperature, flow rate, current

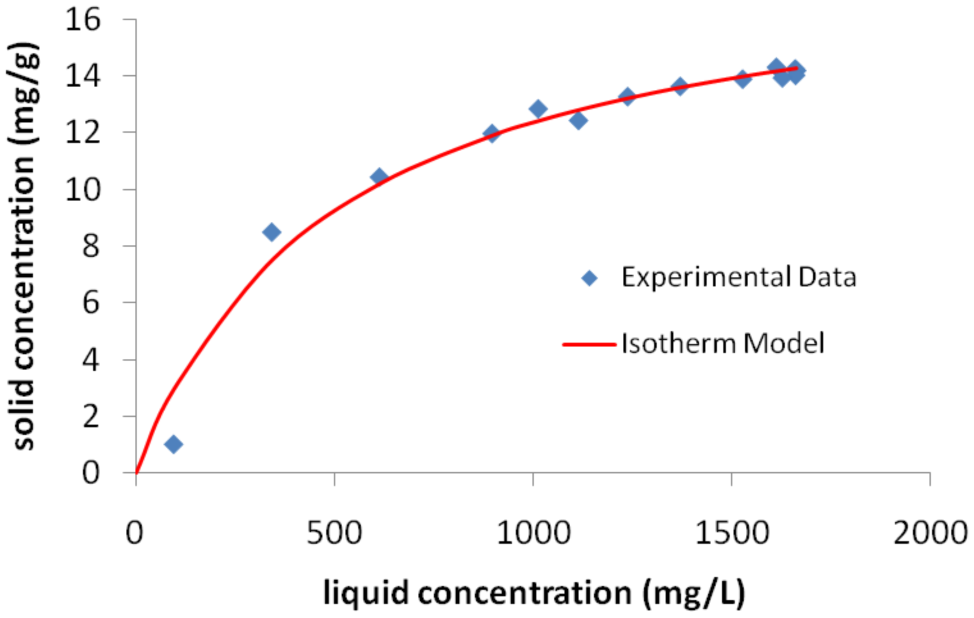
Ion Exchange Resin Regeneration Only



Copper removal from the ion exchange resin can be approximated using first-order models, although knowledge of the isotherm can improve the description of the process.

Finding the Isotherm

Copper removal from the resin happens quickly compared to copper plating → the liquid concentration stays close to equilibrium with the resin



Combined Resin Regeneration Process

Process model:

Liquid mass balance:

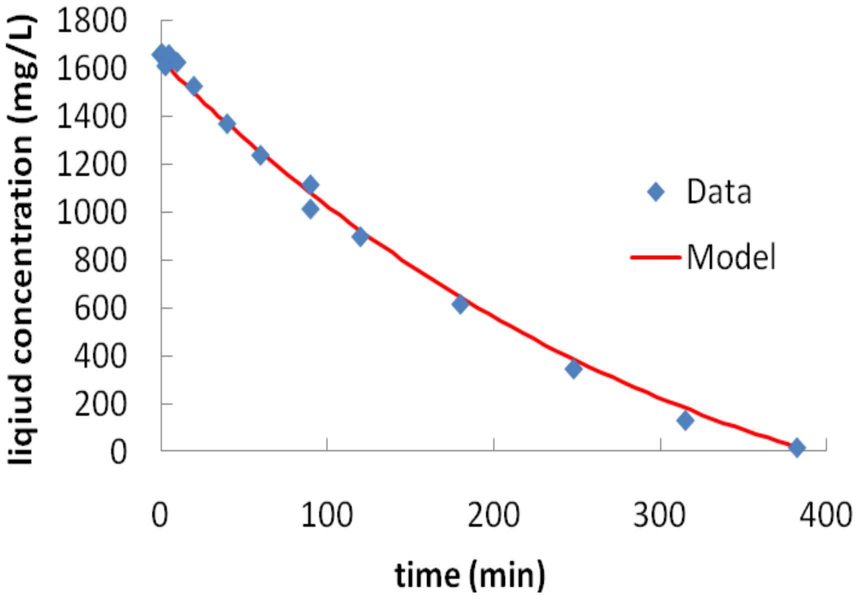
$$\underbrace{\left(V_{MIX}+V_P+\varepsilon V_{RR}\right)\frac{dc}{dt}}_{\text{change in copper in the phase}}=-\underbrace{\frac{k_0 c}{k_0/k_1+c}}_{\text{amount of copper plated}}A+\underbrace{V_{RR}K_m\left[c_{eq}^{l}(c_s)-c\right]}_{\text{copper pulled off resin}}$$

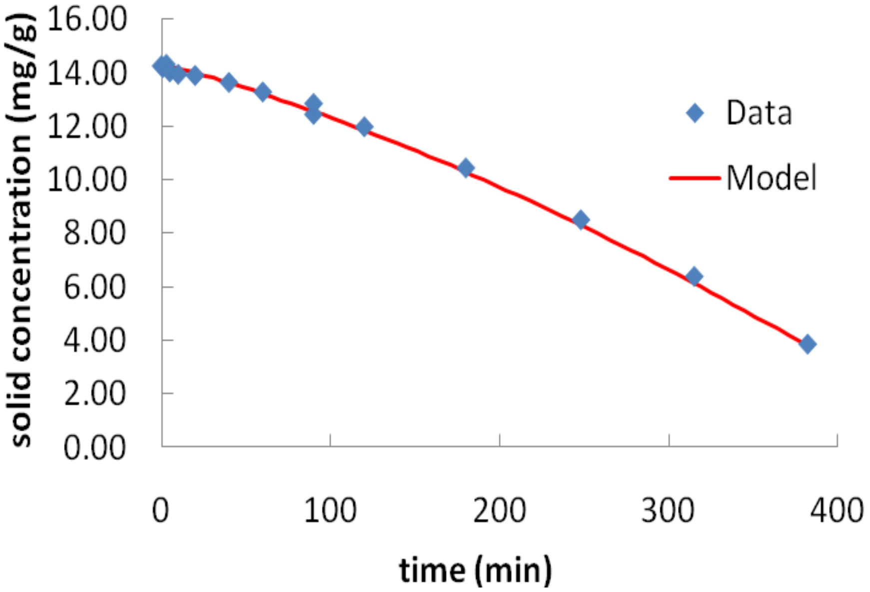
Solid mass balance:

$$\underline{V_{RR}\frac{dc_s}{dt}}=\underline{-V_{RR}K_m\left[c_{eq}^{l}(c_s)-c\right]}$$

isotherm

Combined Resin Regeneration Process



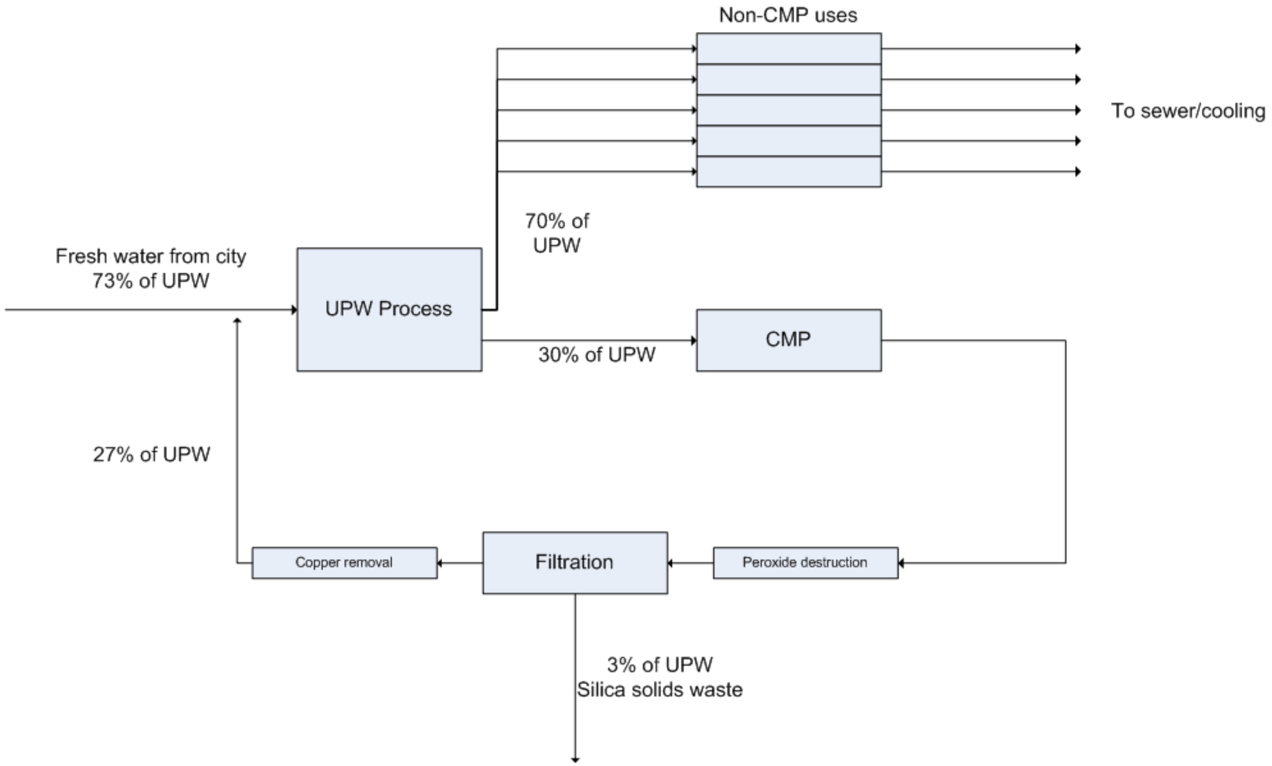


- Modeling can predict both liquid and solid phase Cu^{2+} concentrations
- Modeling will be used to scale-up from prototype to full scale system

Parameters: V_{MIX} = 6.0 L; V_{RR} = 3.4 L; V_P = 3.0 L; ε = 0.3; K_m = 0.162 min^{-1}

Isotherm: $c_{liq} = (1/(1.97 \times 10^{-3})) \times (c_{sol}/(18.6 - c_{sol}))$, c_{liq} in mg/L, c_{sol} in mg/g

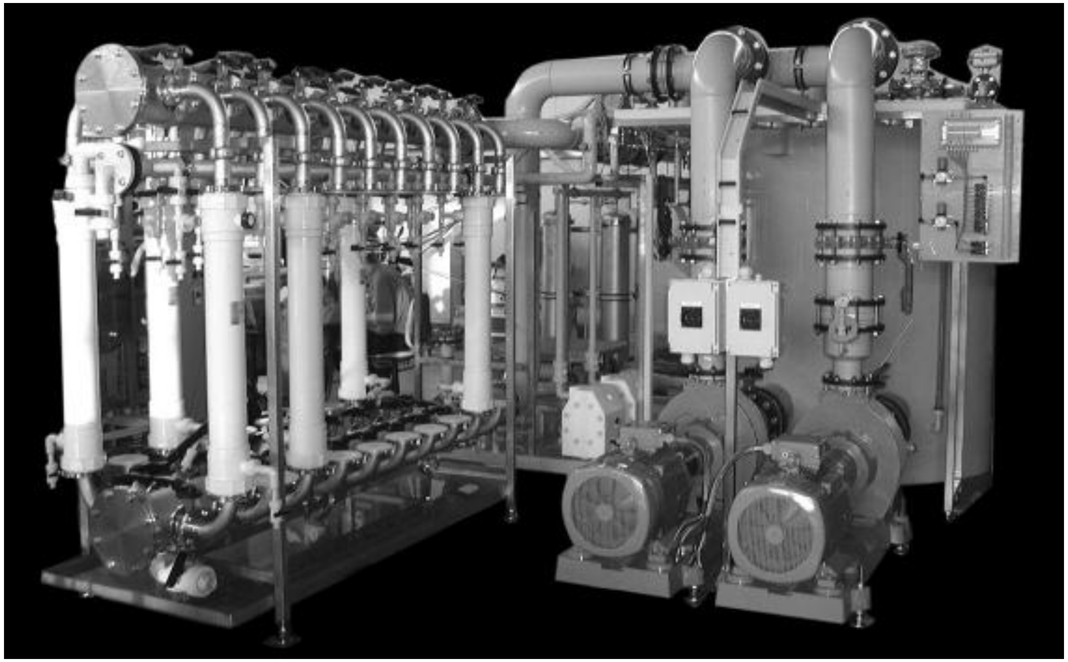
Proposed Treatment System (e.g.)



1. *Peroxide is oxidized using Pyrolox catalyst*
2. *Copper is removed via ion exchange, the resin for which can be regenerated*
3. *Result is a clean water stream and concentrated solid slurry*

Proposed Treatment System

- Biggest economic concern is the filtration
  - Pall Corp. filters - \$1.80-\$3.20/1000 gallons



- Other costs:
  - Electricity for plating
  - Initial investments for pyrolox and ion exchange media

Proposed Treatment System

- Economic benefits:
  - Recovery of copper

Power cost = \$8.40/m^3-resin
Cu value = \$240/m^3-resin

  - Recovery of water stream – avoids costs for municipal sewer and fresh water
    - e.g. Rio Rancho, NM, sewer costs are \$6.30/1000 gal and water costs are \$3.24/1000 gal
    - After filtration, at least \$6.34/1000 gal for other treatment
    - At 300,000 gallons/day, this is about \$700,000/year for recovery of capital costs or as savings
- Environmental benefits:
  - Reduced water "footprint"
  - Potential contaminants are kept out of sewer system

Conclusions

- Hydrogen peroxide and copper can be effectively removed from CMP wastes using catalytic and electrochemical methods.
- Regeneration of ion exchange resins can be effectively modeled to predict system performance.
- Water reuse can be accomplished in economically feasible systems, with costs comparable to municipal treatment fees.

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