Simultaneous Removal of Alumina Particles and Dissolved Copper from Copper-CMP Waste Streams

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Overview of Copper CMP

- Slurries for copper CMP are either alumina or silica based.
- Hydrogen peroxide is the most commonly used oxidant in the slurries.
- Slurries may contain an organic complexant for copper.
- Benzotriazole(BTA) is added to the slurries to inhibit copper corrosion.
- Copper polishing is typically carried out in the pH range of 6 to 7.
- Barrier layer removal follows copper polishing.
- If the barrier layer used is Ta, polishing at an alkaline pH may be required to remove Ta.
- Some new slurries which can remove Ta at acidic pH values have been developed (EKC).
- An oxide buffing step to remove contaminants may be used.
- In summary, wastes from copper and tantalum removal steps as well as that from oxide buffing fall under the general category of "***Copper CMP WASTES***"

Cu-CMP Waste Characteristics

A typical copper CMP waste contains:

- **0.02 – 0.5 w/v% solids**
- **2 – 40ppm copper ions**
- **An organic complexant? (e.g. EDA, EDTA, CA)**
- **A corrosion inhibitor (e.g. BTA)**

Slurry Waste	Cu level (ppm)	pH	Conductivity (µs/cm)
A	TBD	~6.5	~568
B	TBD	~3.6	~395
C	40	~8.5	~1300

A suspension with the following characteristics was used to simulate copper CMP waste:

- ≈0.4w/v% Al_2O_3 (average particle size ≈200nm)
- ≈40ppm copper ions
- ≈185ppm EDTA (ethylenediamine tetraacetic acid) or 37.8 ppm EDA (ethylenediamine)
- pH ≈ 6.0
- Conductivity ≈ 1300µS/cm

Environmental Regulations

Total Suspended Solids (TSS) level*:

- San Jose Code Limitations: TSS = 0 ppm
- Austin Code Limitations: TSS = 200 ppm
- Puyallup Code Limitation: TSS = 0.015 ppm

Cu Level in Aqueous Phase*:

- San Jose Code Limitations: Cu level = 2.7 ppm
- Austin Code Limitations: Cu level = 1.9 ppm
- Puyallup Code Limitation: Cu level = 0.024 ppm

Cu Level in Solid:

EPA: 40 CFR 503 in RCRA (Resource Conservation Recovery Act):

To qualify for land application, sewage sludge must meet at least the ***Pollutant Ceiling Concentrations*** (PCL):

The land application pollutant limits (PCL) for Copper = 4.3 g/kg

(* Corlett, G.L., Advancing applications in Contamination Control, p.19, Dec. 1998)

Objectives

1. Removal of suspended solids without adding any “additional” chemicals.

2. Simultaneously remove dissolved copper to facilitate water recycle and meet environmental regulations.

Techniques Used

- Electrodecantation/Electrocoagulation

  solid/liquid separation assisted by the application of an electric field.

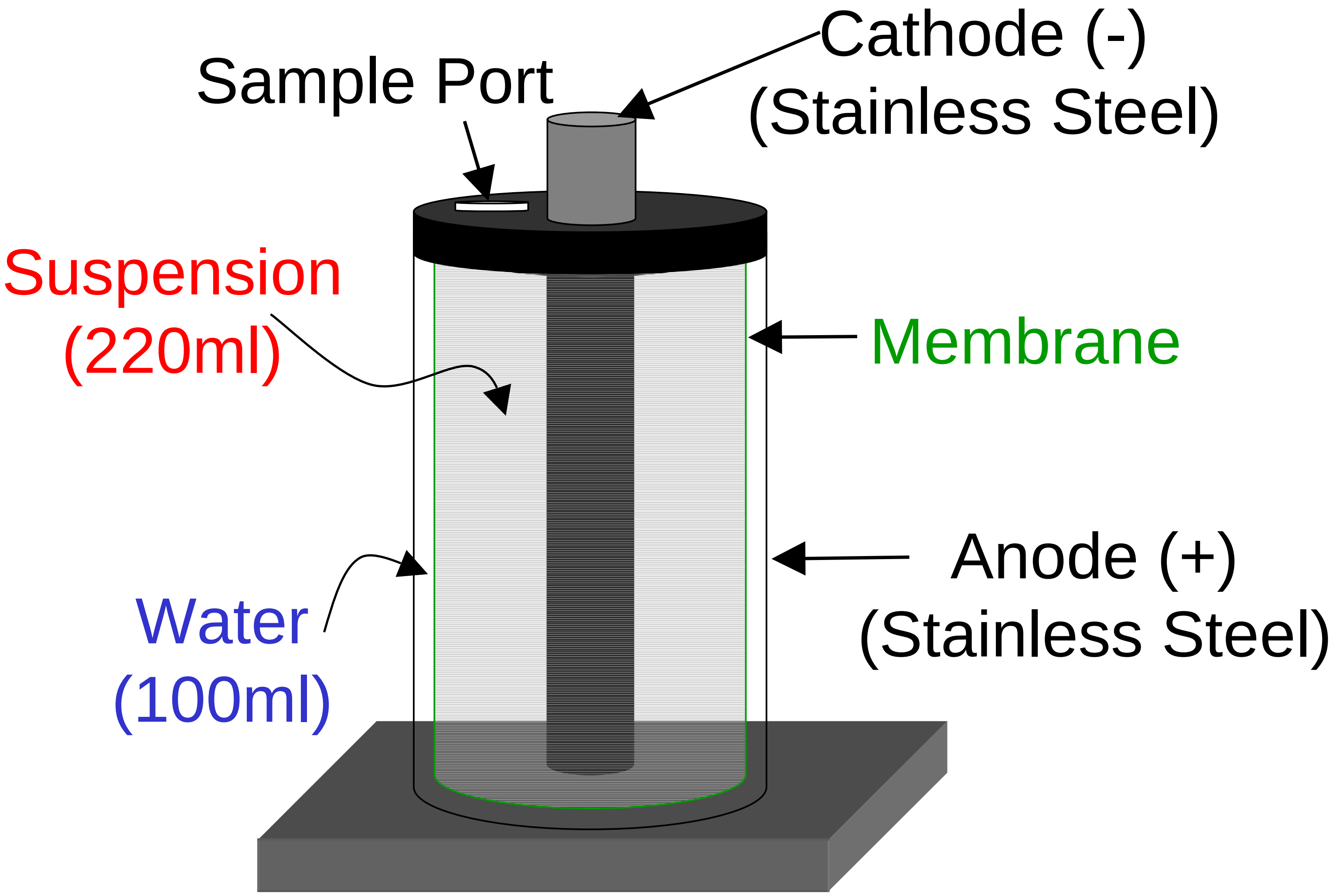
- Electrodeposition

  plate out copper

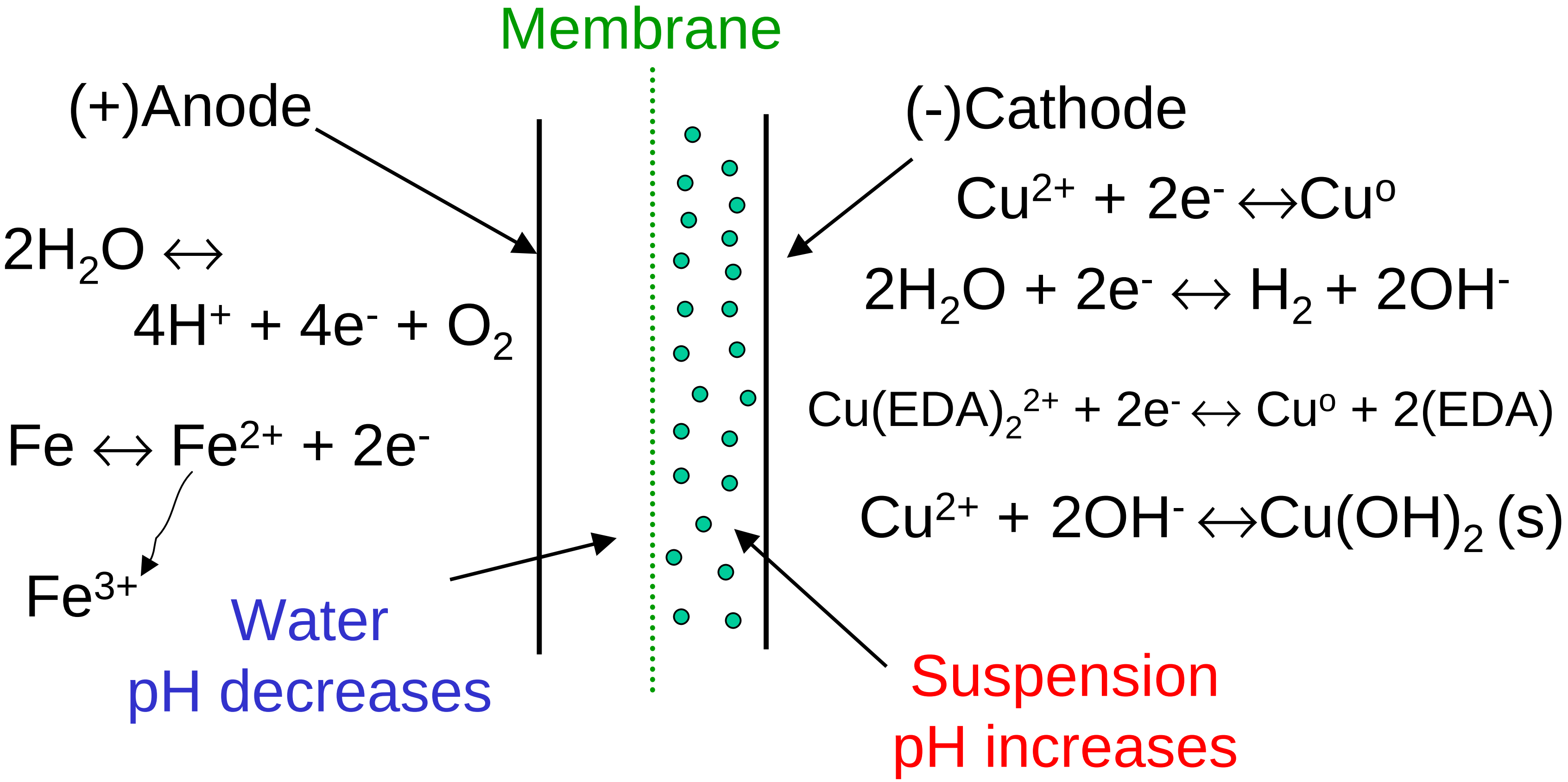
- In-situ chemical precipitation

  remove copper as $Cu(OH)_2$

Experimental Setup



Copper Removal



Membrane

(+)Anode

$2H_2O \leftrightarrow 4H^+ + 4e^- + O_2$

$Fe \leftrightarrow Fe^{2+} + 2e^-$

Fe^{3+}

Water

pH decreases

(-)Cathode

$Cu^{2+} + 2e^- \leftrightarrow Cu^o$

$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^-$

$Cu(EDA)_2^{2+} + 2e^- \leftrightarrow Cu^o + 2(EDA)$

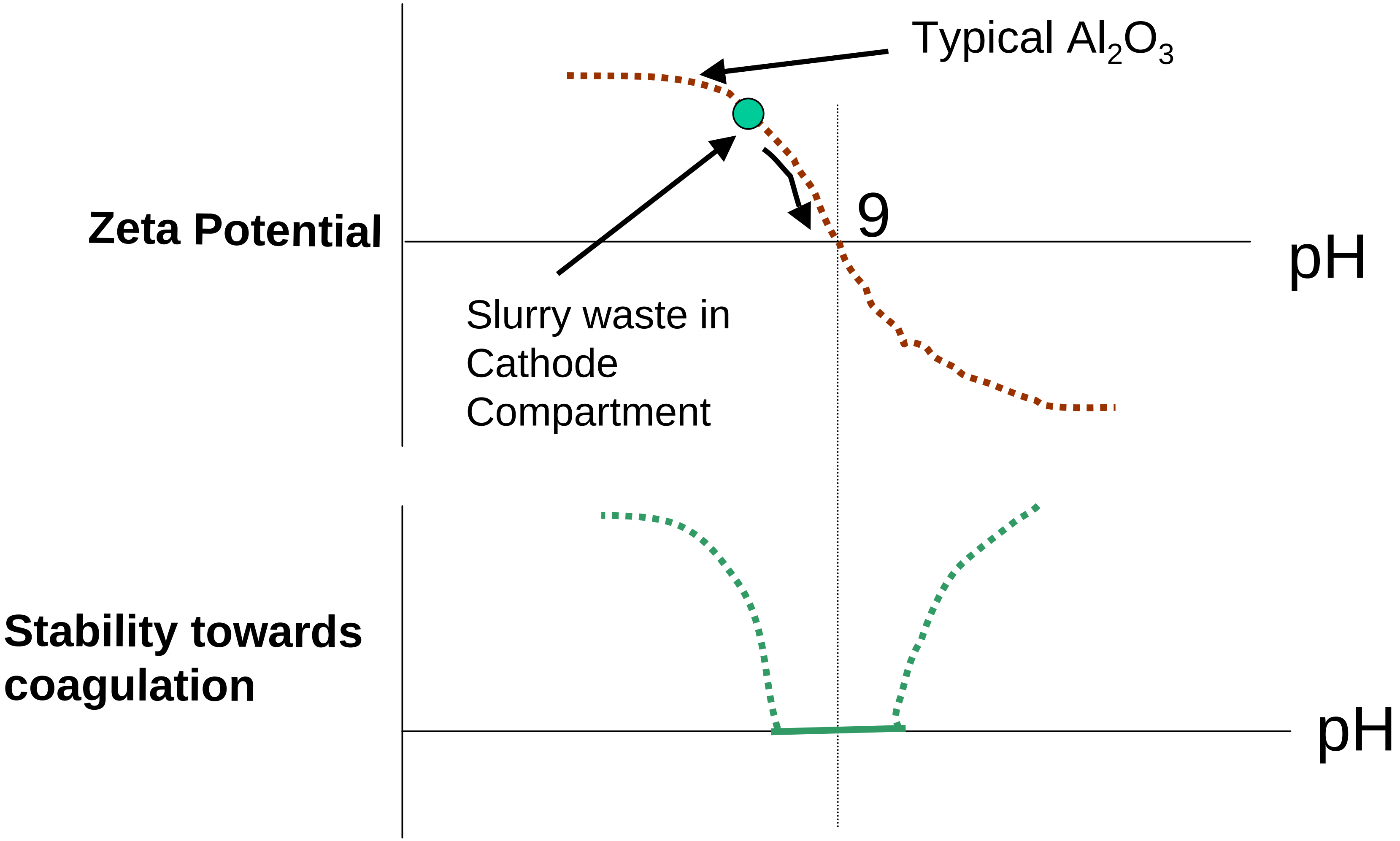
$Cu^{2+} + 2OH^- \leftrightarrow Cu(OH)_2\ (s)$

Suspension

pH increases

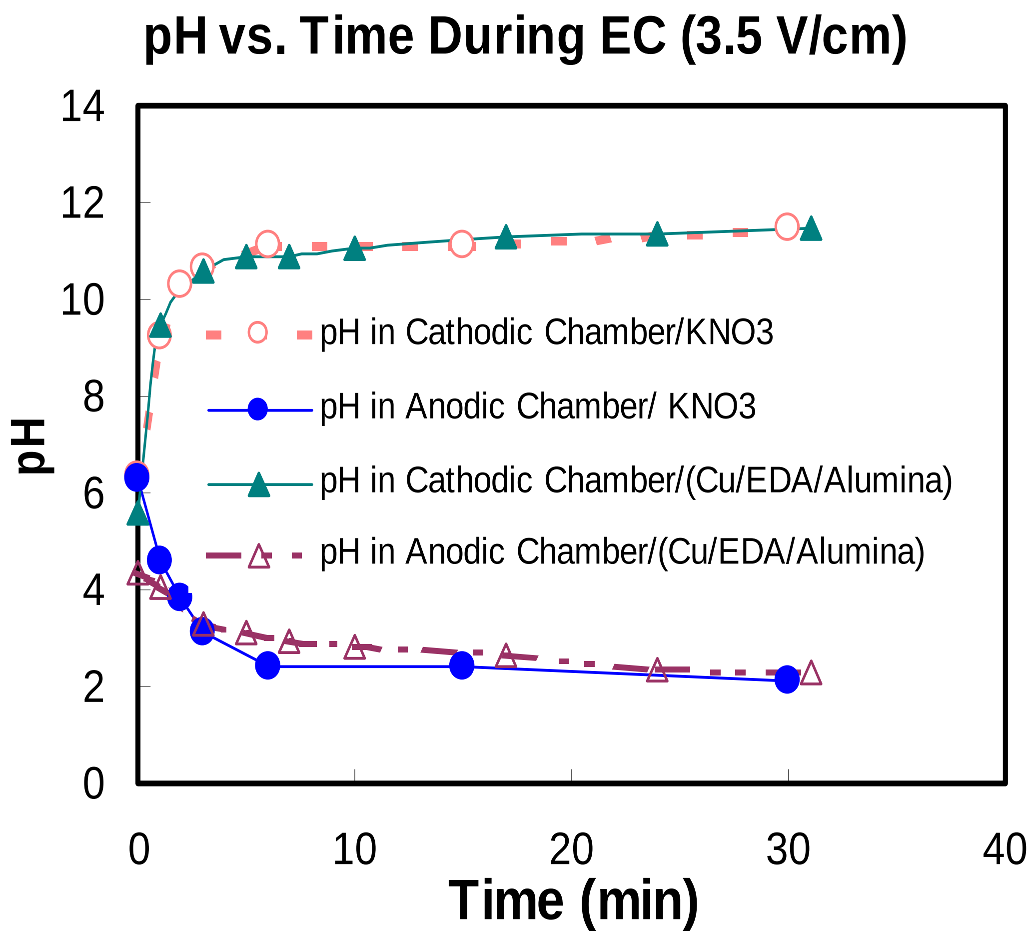
- The membrane partitions the anode and cathode chambers, allowing pH changes to occur in the anode and cathode compartments.

Solids Removal (underlying concept)



- pH in the Cathode compartment increases due to the generation of OH^-

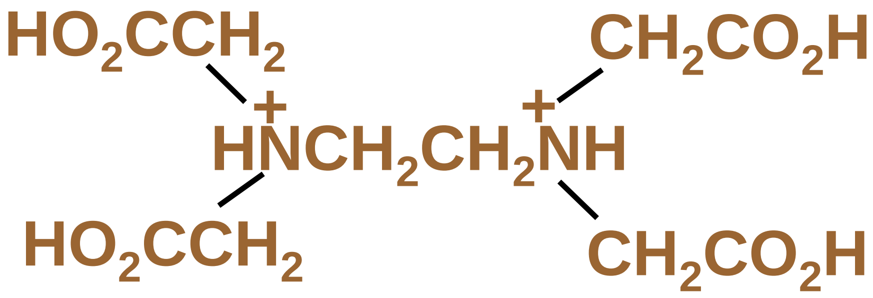
pH Changes during Electrocoagulation



- **The suspension pH increases rapidly when an electric field is applied.**

- If IEP of Al_2O_3 particles in the cathode chamber is between ***4<pH<10***, coagulation of particles may occur as pH approaches the IEP of particles.

EDTA Characteristics



$$\begin{matrix} HO_2CCH_2 & & CH_2CO_2H \\ & H\overset{+}{N}CH_2CH_2\overset{+}{N}H & \\ HO_2CCH_2 & & CH_2CO_2H \end{matrix}$$

p$K_1 = 0.0$

p$K_2 = 1.5$

p$K_3 = 2.0$

p$K_4 = 2.7$

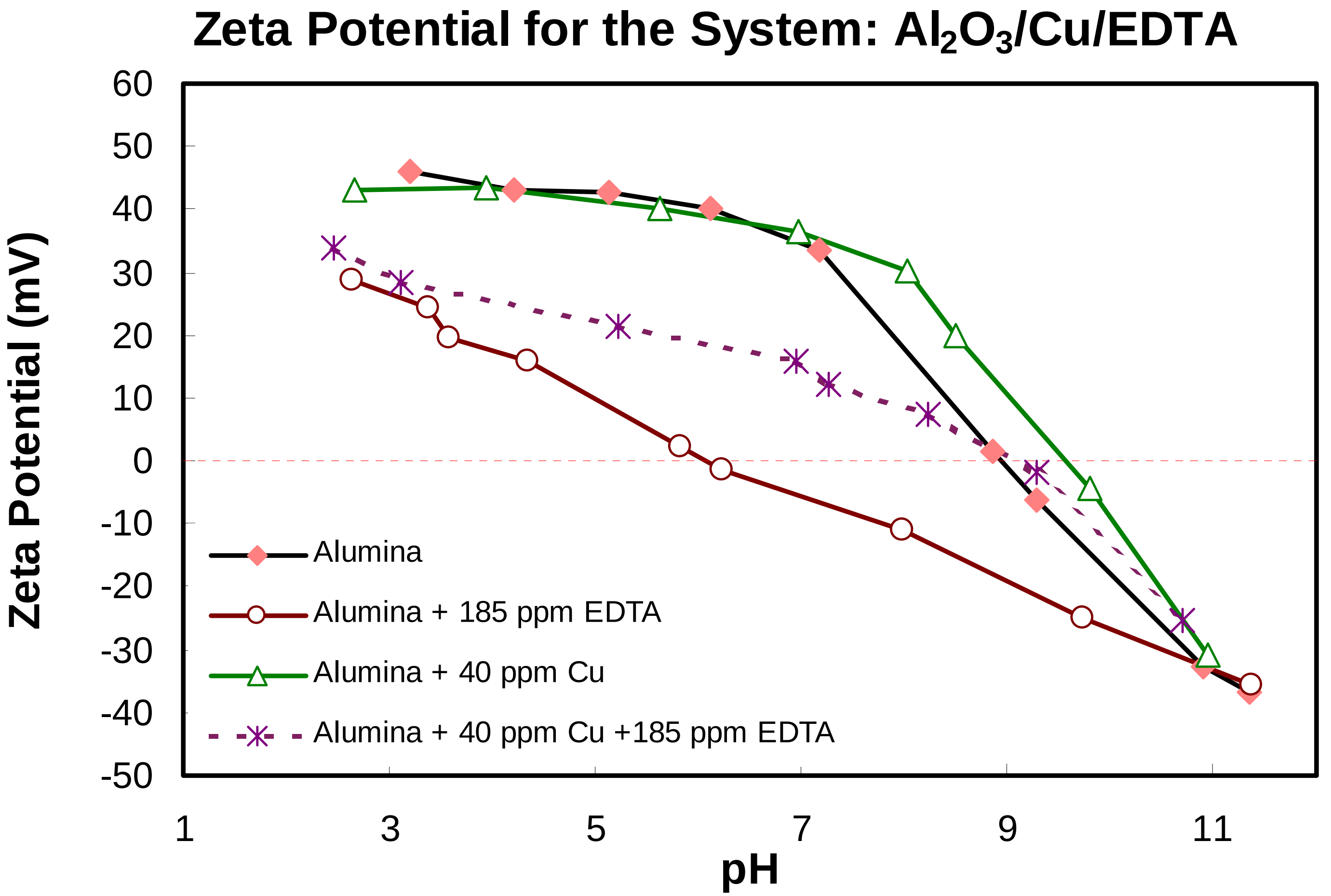
p$K_5 = 6.2$

p$K_6 = 10.2$

pH	Charge of Cu(EDTA) complex
1.0	+3
1.7	+2
2.5	+1
5.0	0
8.0	-1
11.0	-2

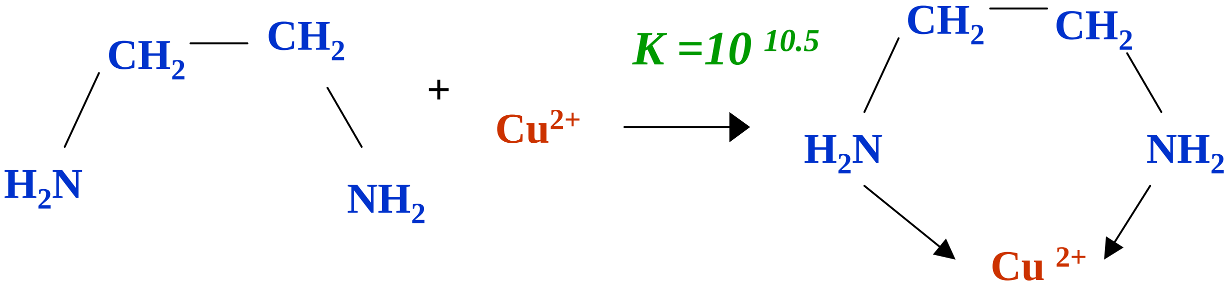
- EDTA forms a 1:1 complex with Cu
- The charge of the Cu(EDTA) complex depends on the suspension pH

Electrokinetic Behavior of Al_2O_3 (1)

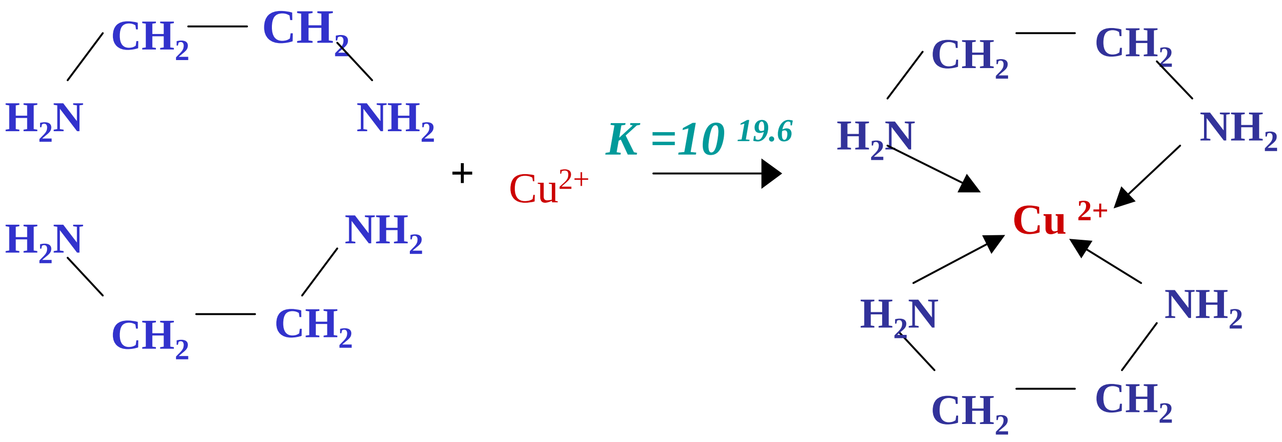


- EDTA shifts the isoelectric point of Al_2O_3 to lower pH values.
- Cu(EDTA) complex has no significant effect on the IEP of Al_2O_3

EDA Characteristics



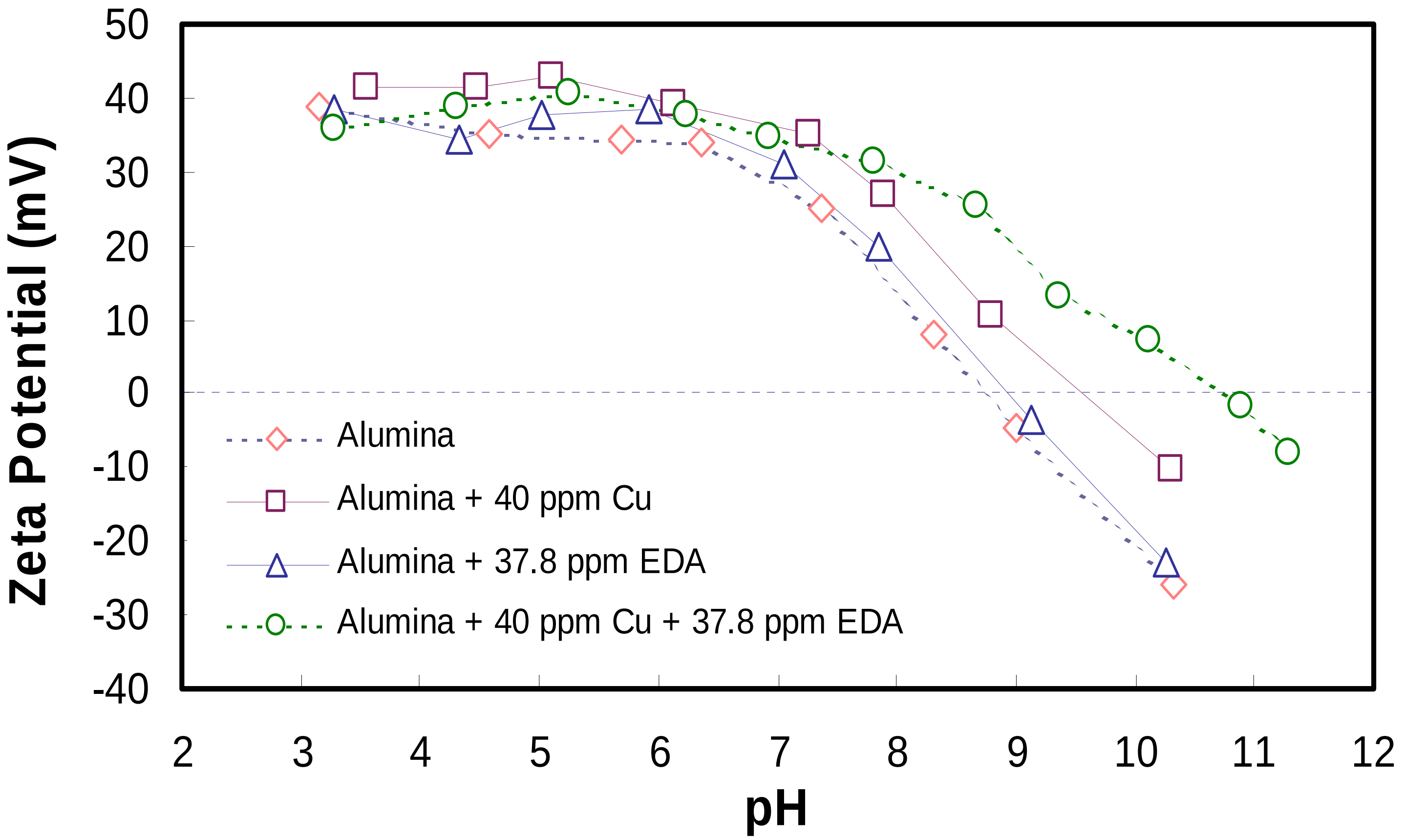
or



- EDA forms a 1:1 or 2:1 complex with Cu
- The charge of the Cu(EDA) or Cu(EDA)$_2$ complex is positive.

Electrokinetic Behavior of Al_2O_3 (2)

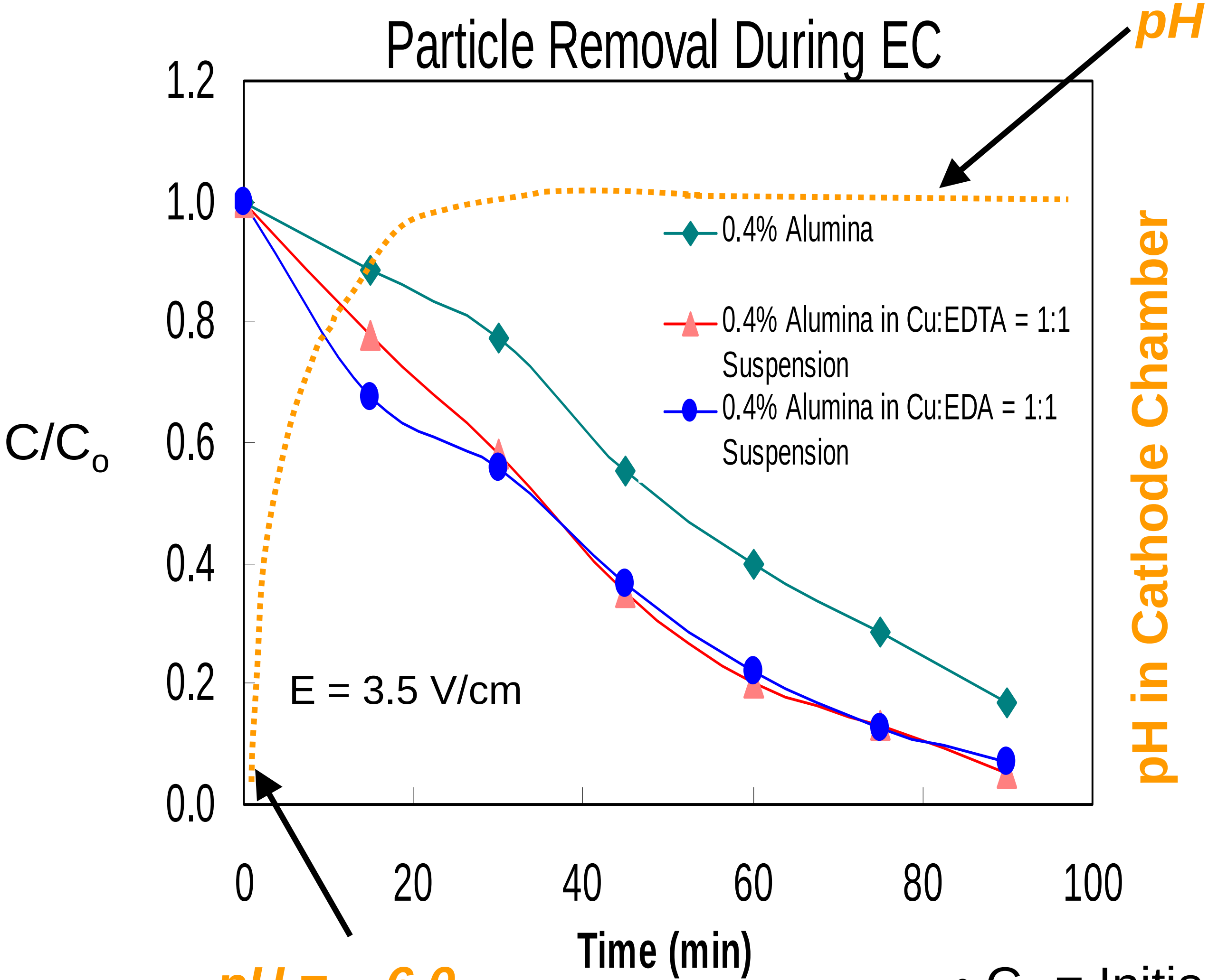
Zeta Potential for the System: Al_2O_3/Cu/EDA



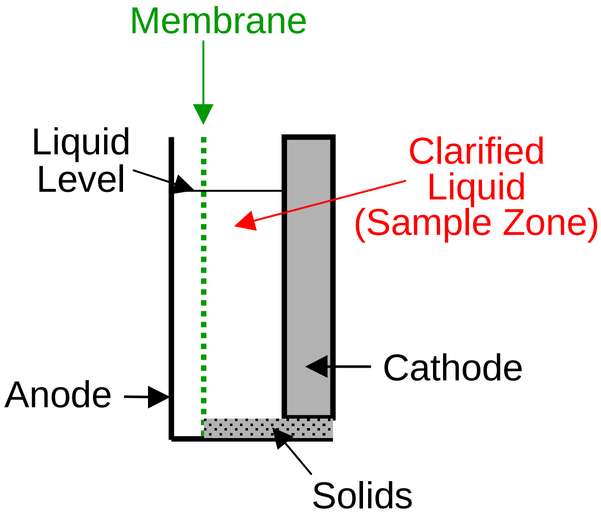
- EDA does not effect the isoelectric point of Al_2O_3.
- Cu(EDA) complex shifts the IEP of Al_2O_3 to higher pH values.

Electrocoagulation of Al_2O_3

pH = ~11.60

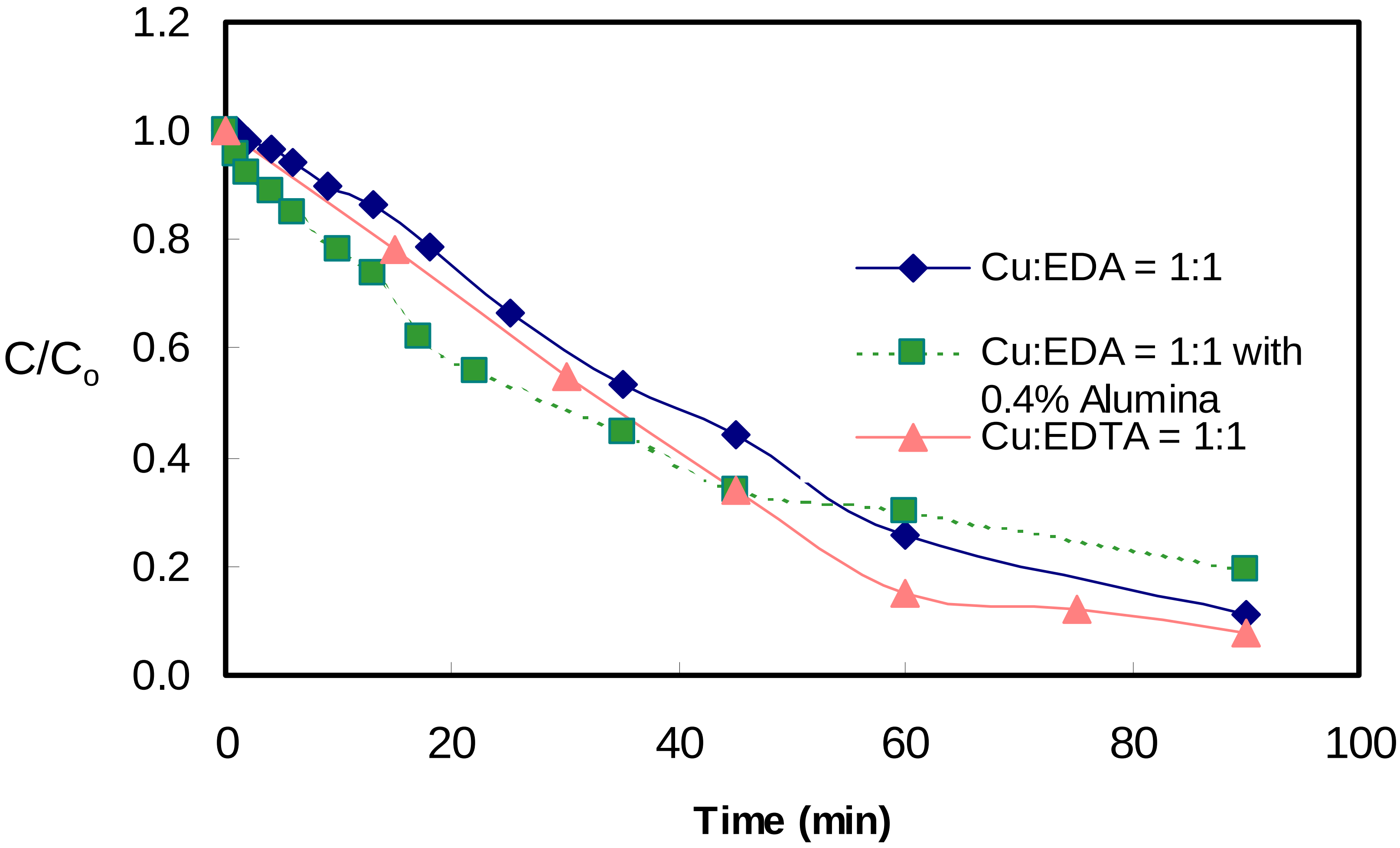


pH = ~ 6.0



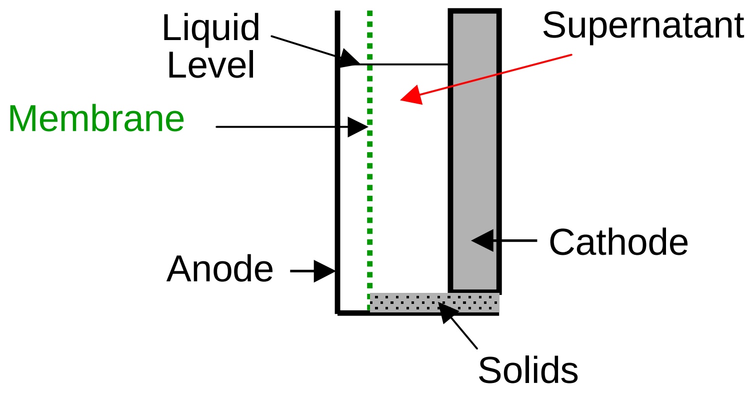
- C_o = Initial Solid Conc. ~ 0.4%
- C = Solid Concentration

Kinetics of Removal of Dissolved Copper



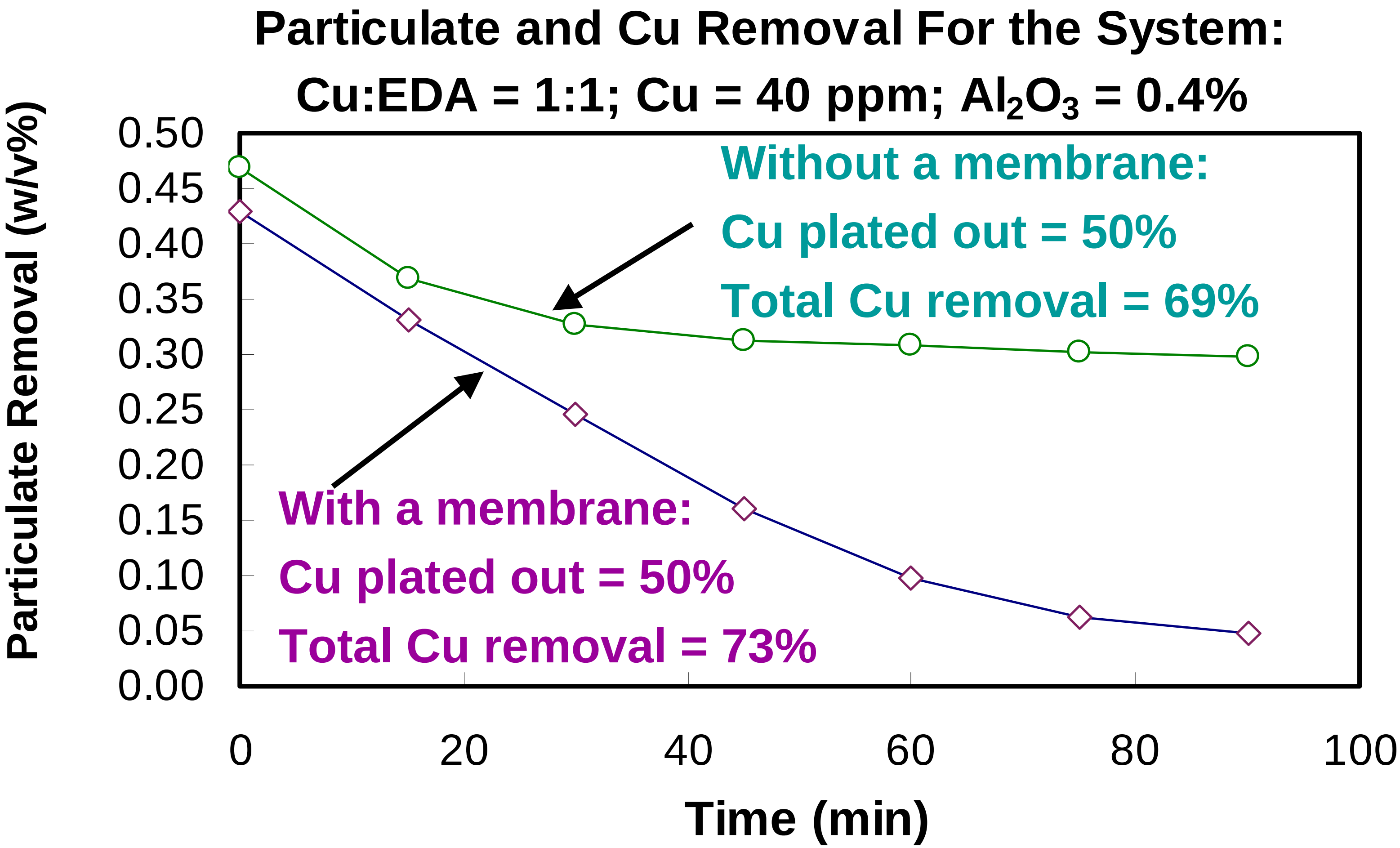
- **Copper is removed by plating and/or by copper hydroxide formation in the bulk.**

Effect of EDTA & EDA on Cu Distribution



EDTA (Cu:EDTA = 1:1; Cu_{oCu} = 40 ppm)		EDA (Cu:EDA = 1:1; Cu_{oCu} = 40 ppm)	
Forms negatively charged Cu-EDTA complexes.		Forms postively charged Cu-EDA complexes.	
Electric potential restrains Cu-EDTA complexes from approaching cathode		Electric potential attracts Cu-EDA complexes to cathode	
$Cu(EDTA)^{2-}$; log K = 20.5	E = -0.27 V	$Cu(EDA)^{-}$; log K = 10.5	E = 0.03 V
% Cu plated out	16.3%	% Cu plated out	50.2%
% Cu Collected with solid	39.4%	% Cu Collected with solid	25.3%
% Cu in anode chamber/supernatant	20.5/9.7 %	% Cu in anode chamber/supernatant	0.0/15.3%

Effect of Membrane on Particulate and Cu Removal



Particulate and Cu Removal For the System:

Cu:EDA = 1:1; Cu = 40 ppm; Al_2O_3 = 0.4%

Without a membrane:

Cu plated out = 50%

Total Cu removal = 69%

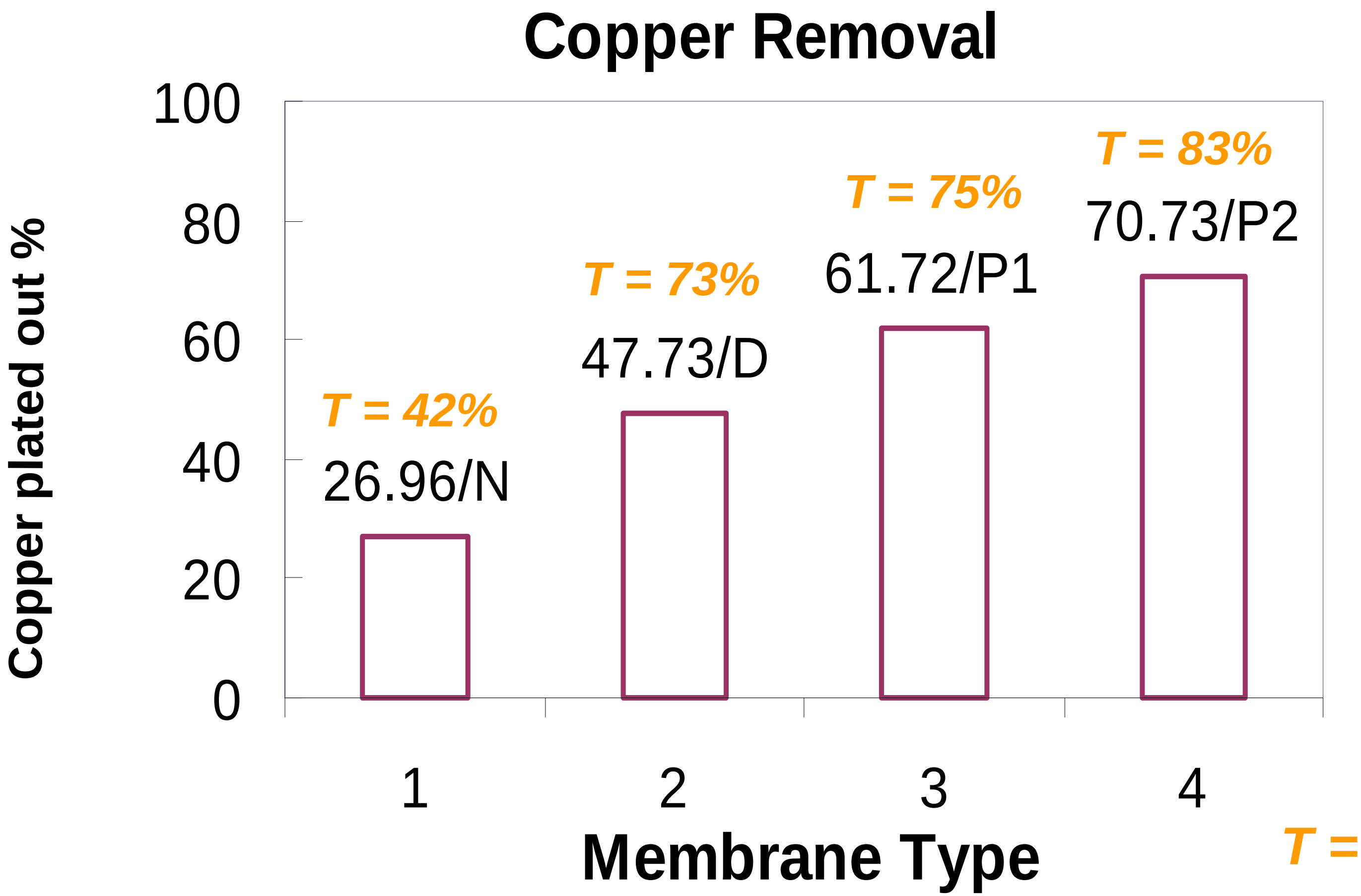
With a membrane:

Cu plated out = 50%

Total Cu removal = 73%

- **The presence of a membrane enhanced the removal of particulate.**

Effect of Membrane Type on Particulate and Cu Removal

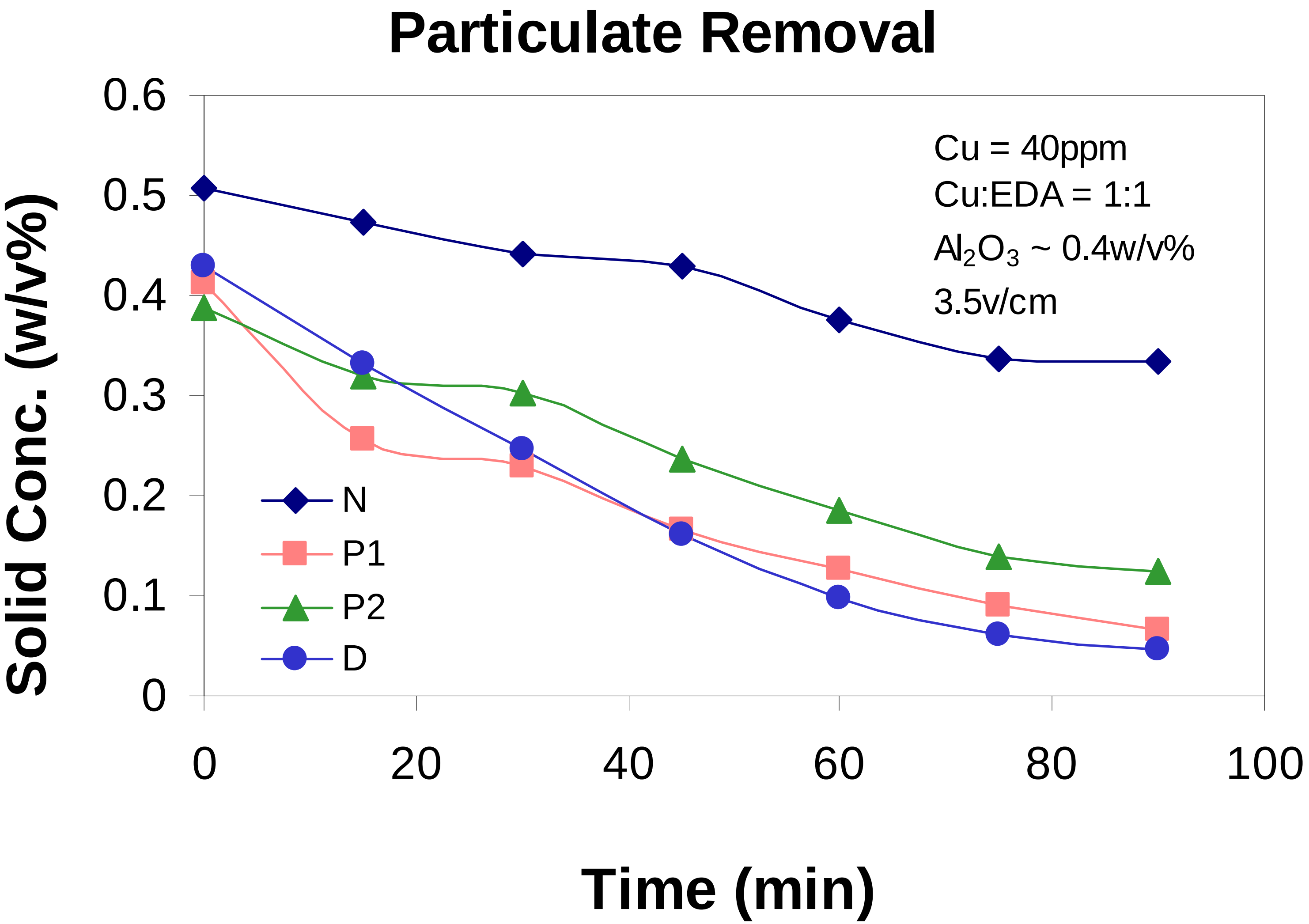


- Type of membrane affects Cu removal

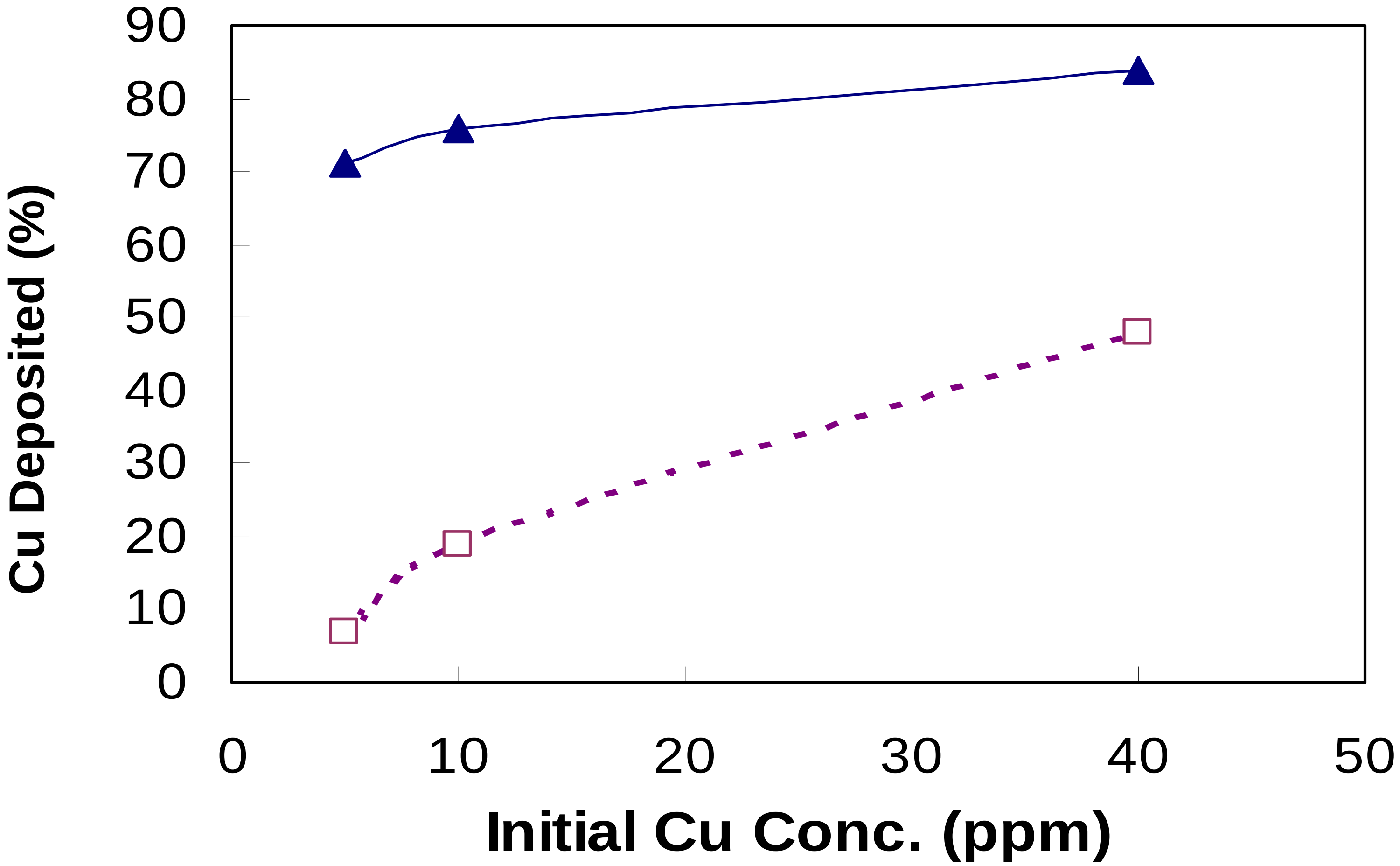
T = Total removal

N -- negatively charged membrane; D -- dialysis membrane
P1-- positively charged membrane; P2 -- positively charged membrane

Effect of Membrane Type on Particulate & Cu Removal -- (2)

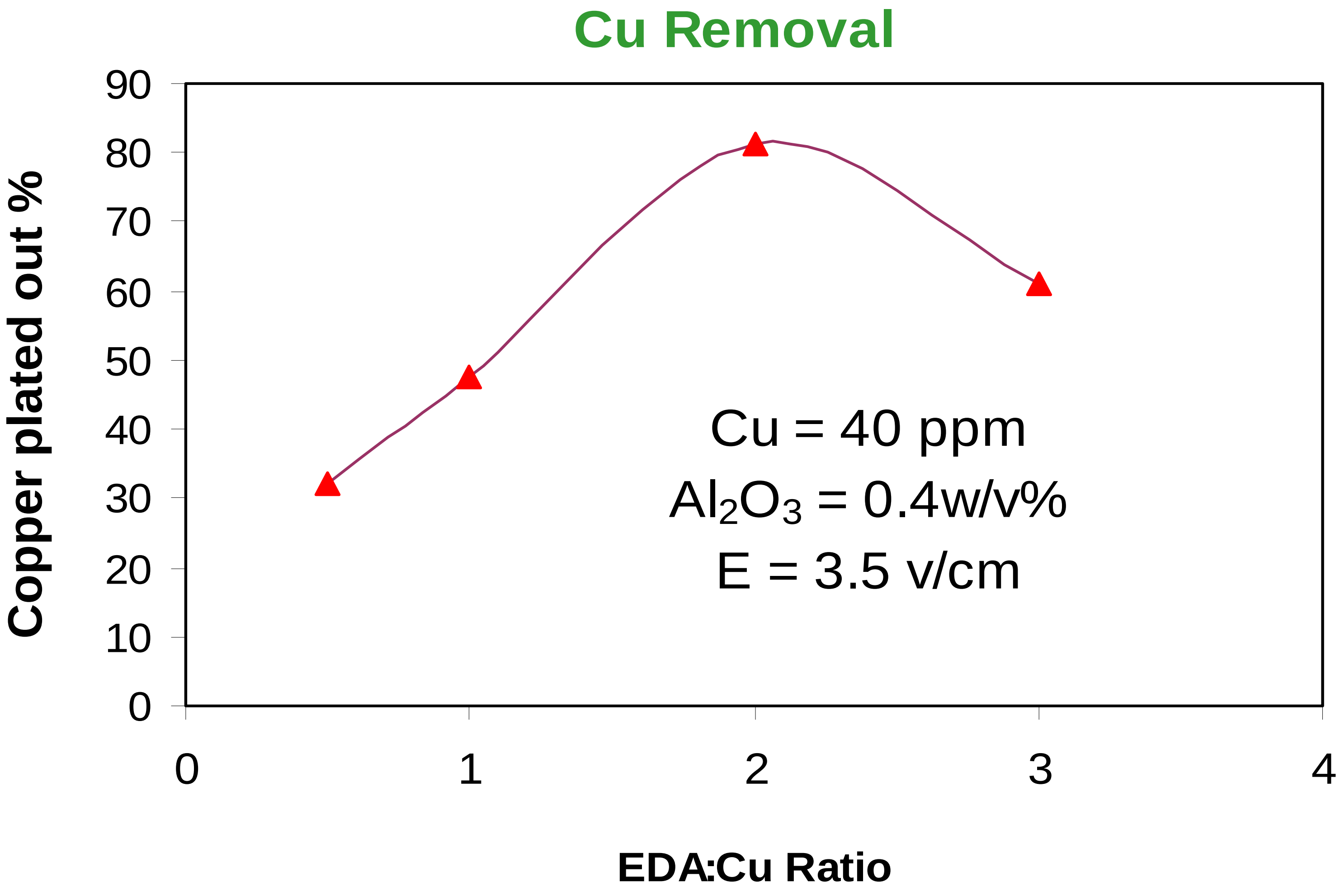


Effect of Copper Level on Cu Removal by Deposition



- Extent of Cu removal by deposition is adversely affected by the presence of particles.

Effect of EDA:Cu Ratio on Particulate & Cu Removal -- (1)



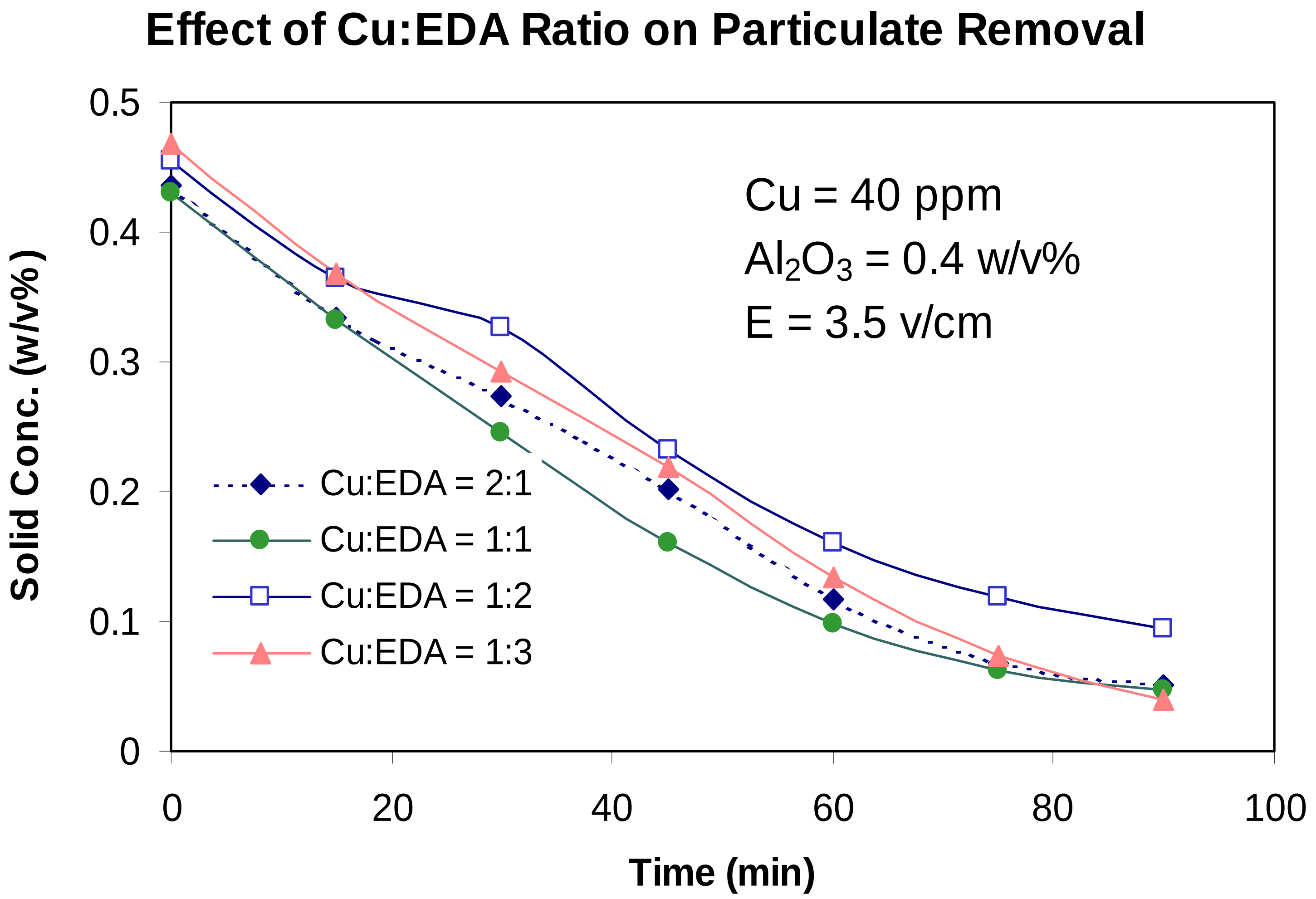
Cu = 40 ppm

Al_2O_3 = 0.4w/v%

E = 3.5 v/cm

- The EDA:Cu Ratio appears to influence the extent of copper removal by plating

Effect of EDA:Cu Ratio on Particulate & Cu Removal -- (2)



- The EDA:Cu Ratio does not appear to influence particulate removal

Summary

- Aqueous Alumina suspensions can be destabilized by the application of an electric filed.

- The pH changes created and maintained by the use of membranes is critical to the success of the electrocoagulation process.

- Copper can be removed simultaneously with the solids, either by in situ precipitation or by plating out onto the cathode.

- The extent of copper removal by plating is affected by the type of the organic complexant that may be present in the CMP slurry as well as the charge on the membrane used.