Treatment of Cu-CMP Wastes Using Electrocoagulation

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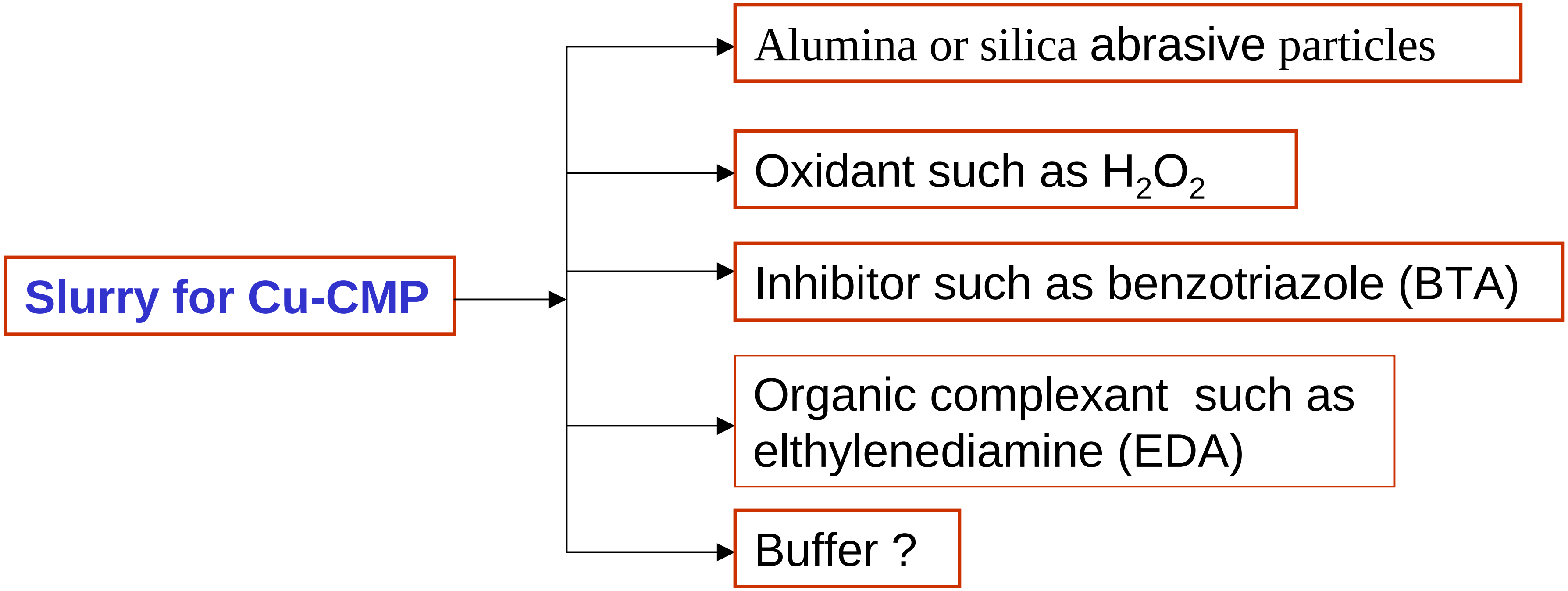
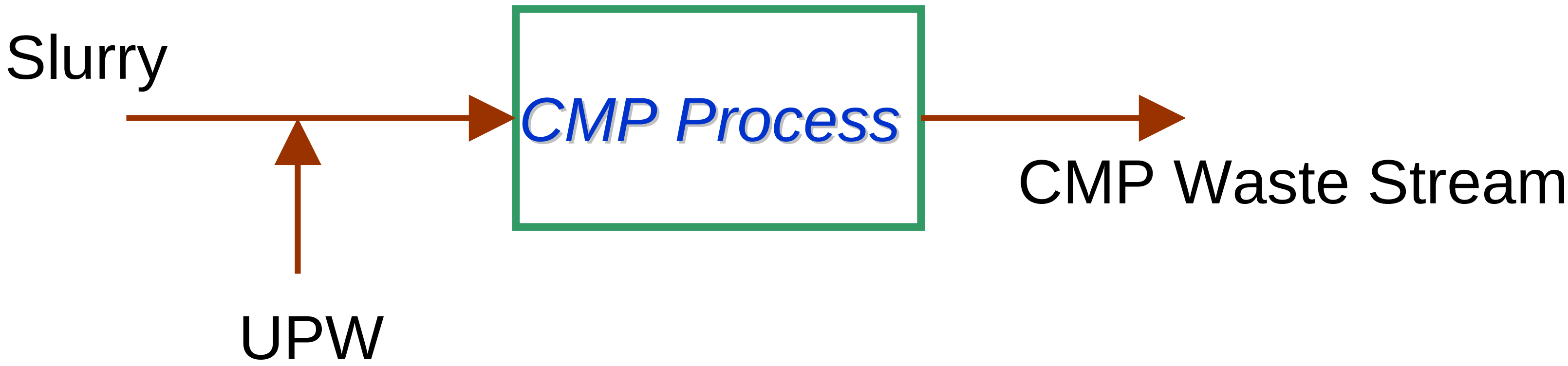
Slurry for Copper CMP



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)

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 $Cu(OH)_2$

Understanding EC/ED

Have worked on two fronts:

1. **Experiments**
2. **Modeling**

Modeling Electrically - Driven Separations

- **Ion and particle conservation**

  convection, diffusion, electromigration

- **Dissociation - association reactions (Equilibrium)**

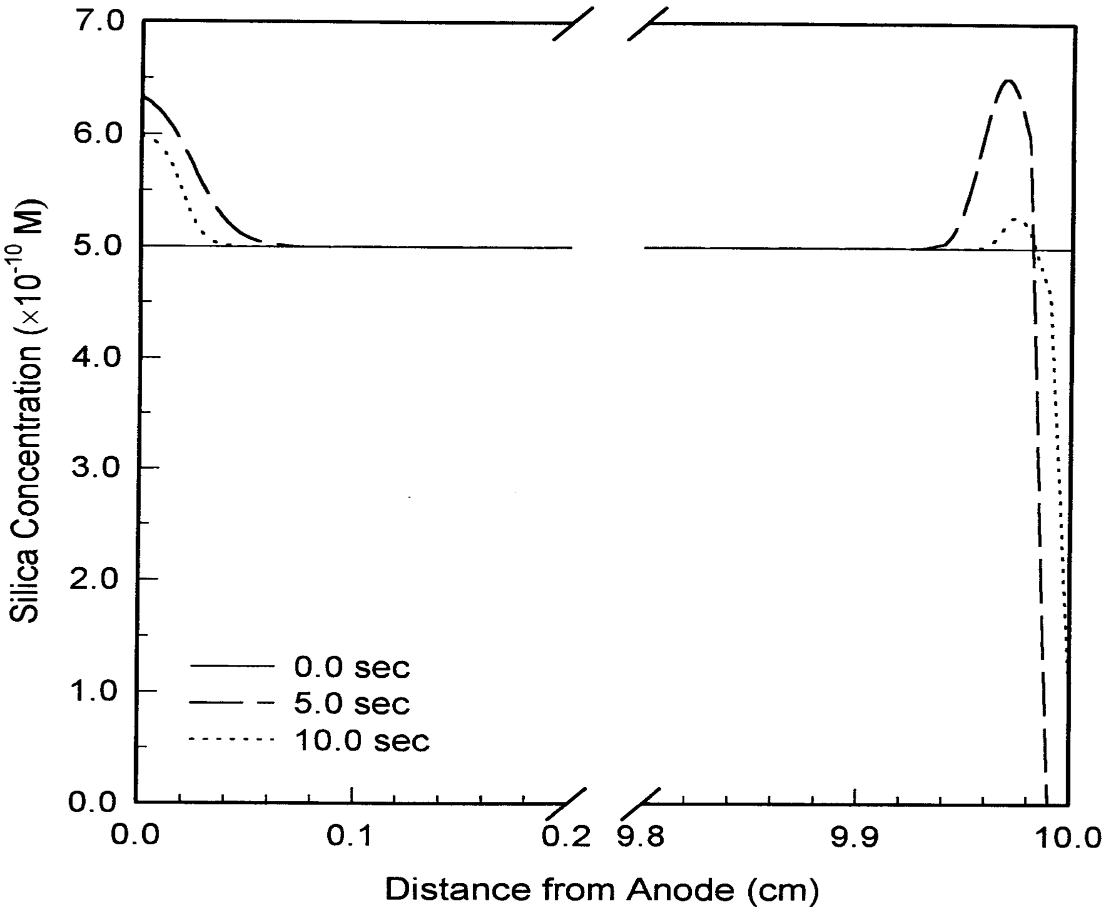
  e.g. $K_w = [H^+][OH^-]$

- **Local electroneutrality + charge balance $\Rightarrow$ local E-field**
- **Momentum balance:**

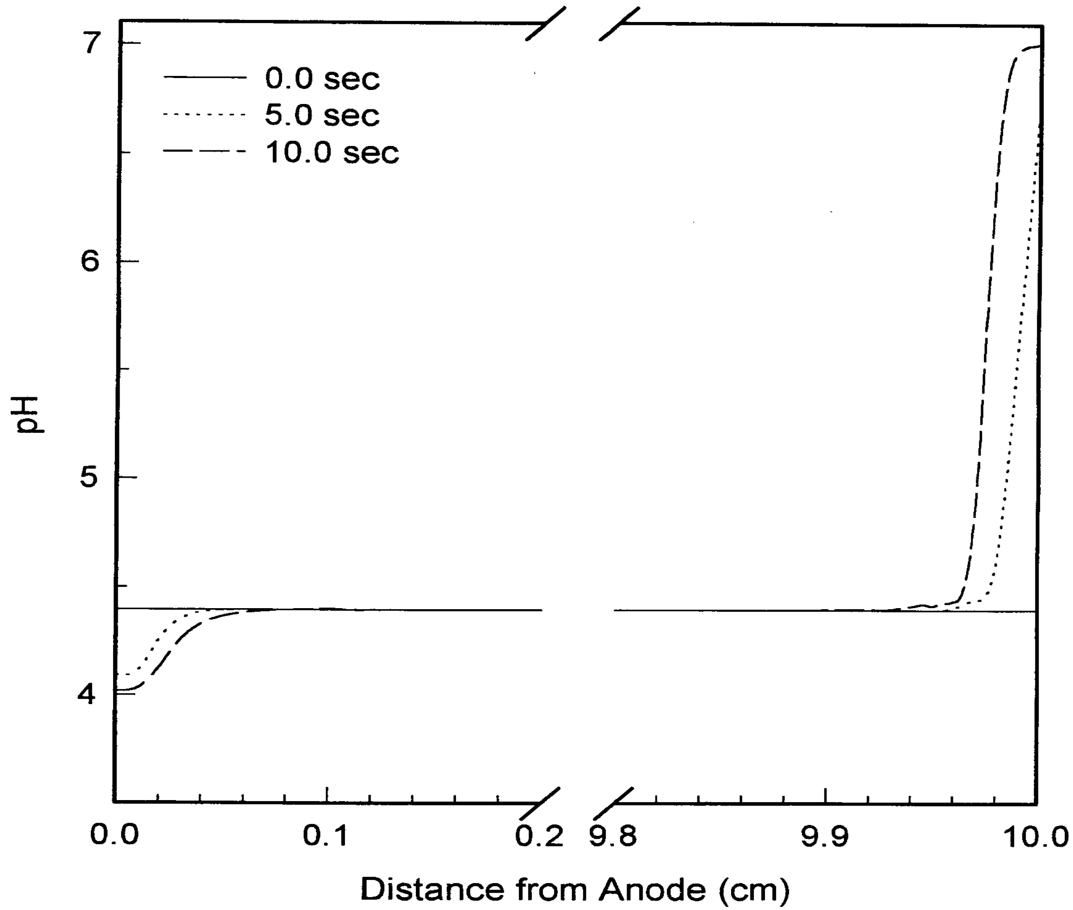
  Navier-Stokes eqns with gravitational body force

- **Electrode reactions**

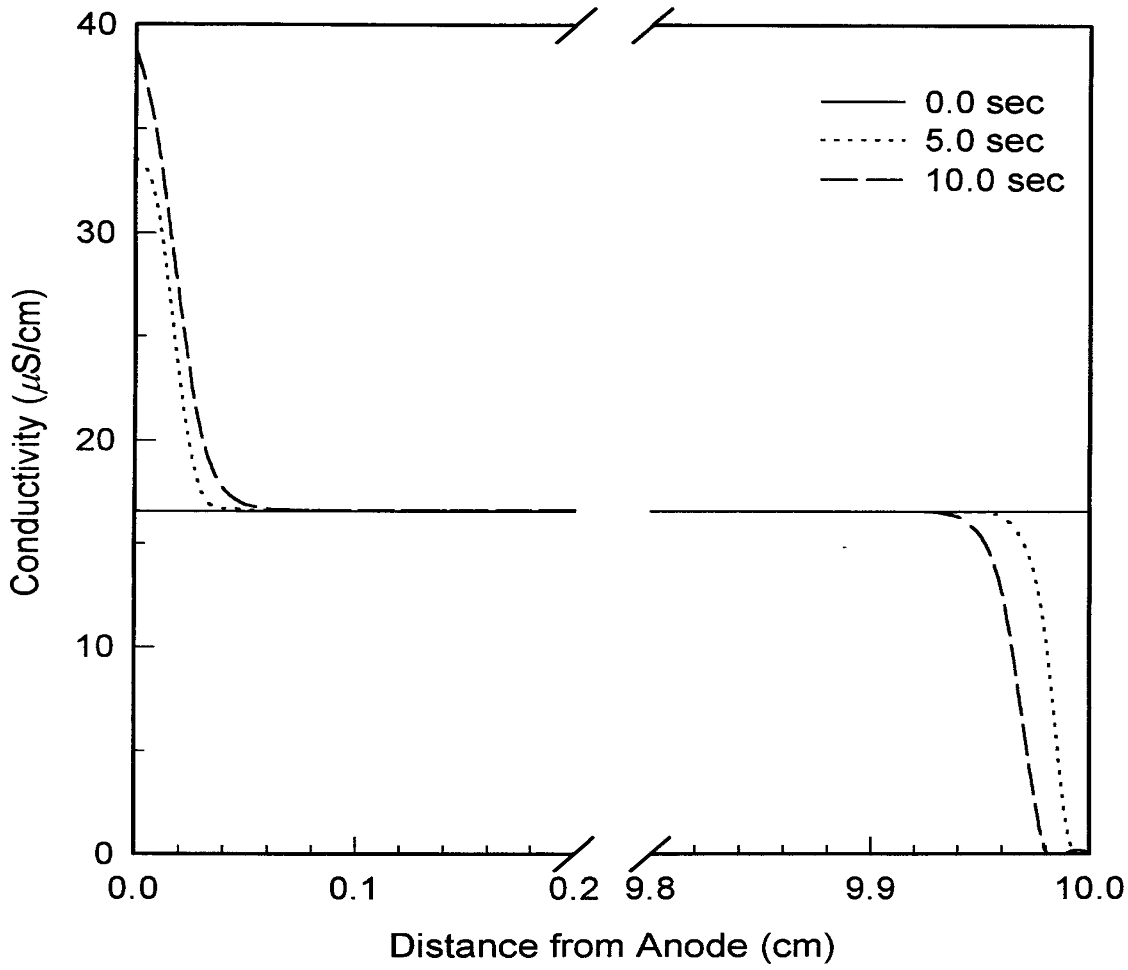
Simulation Result - 1



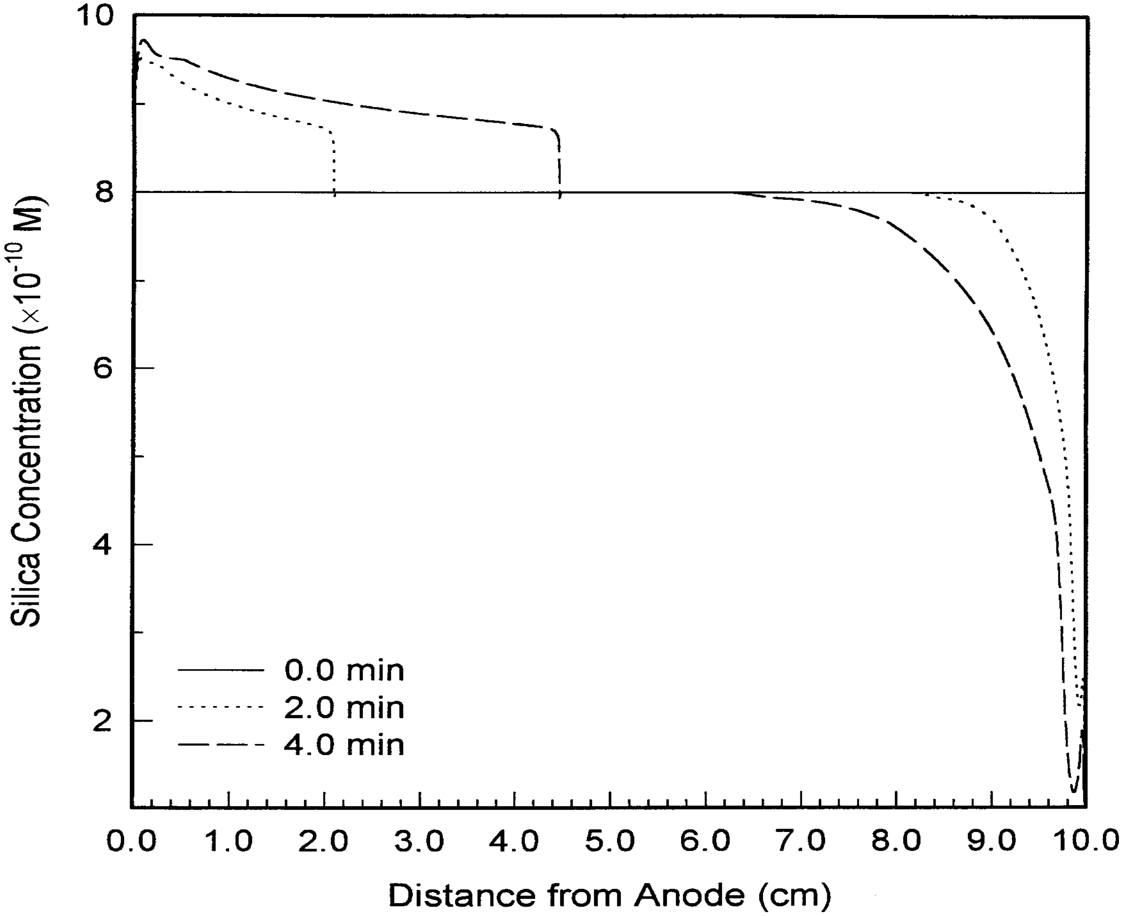
Simulation Result - 2



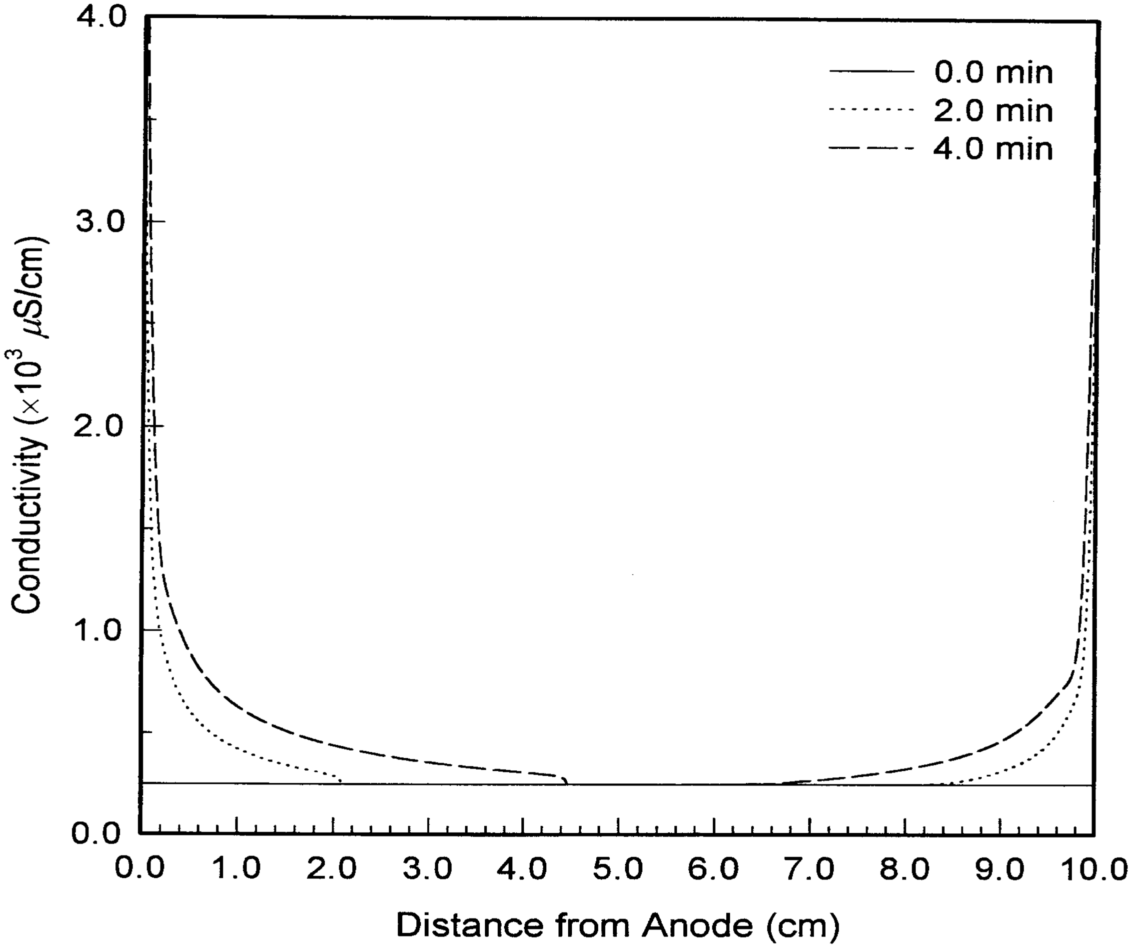
Simulation Result - 3



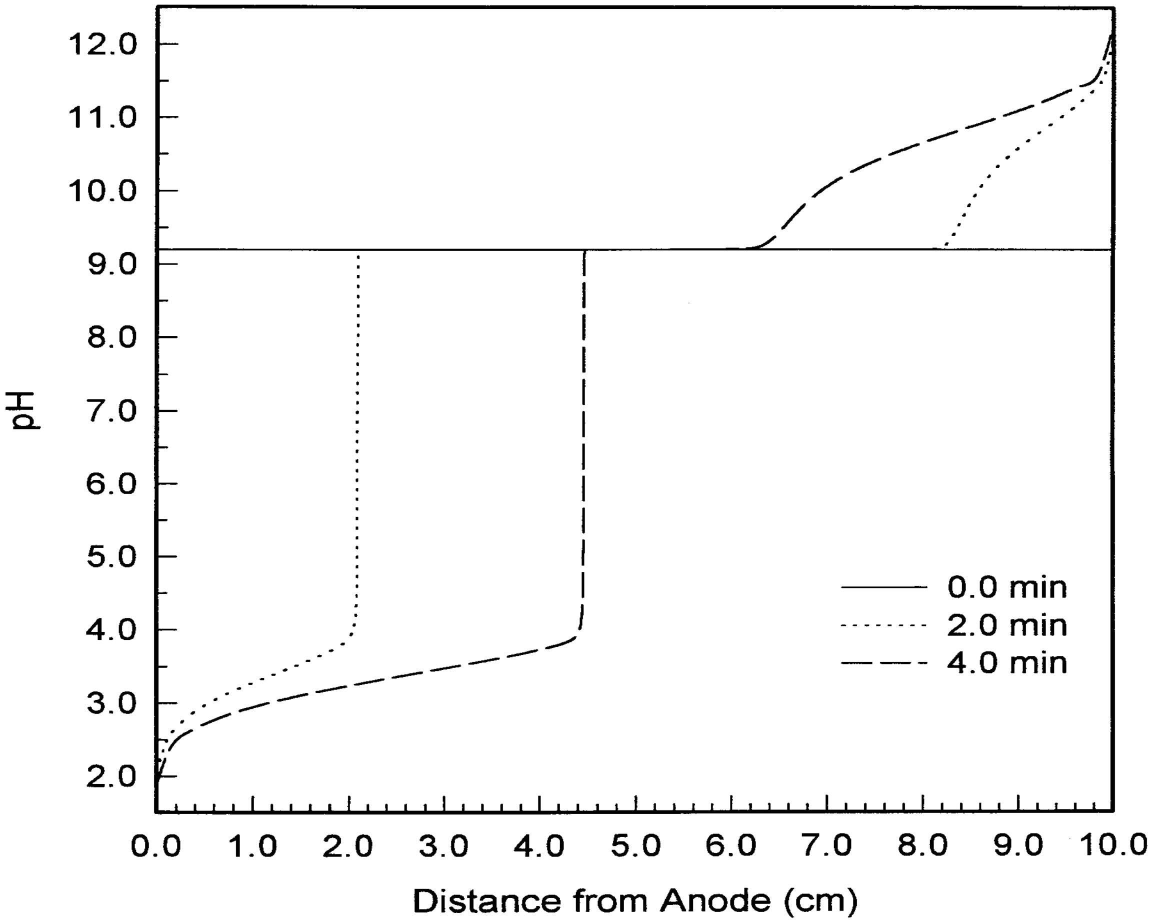
Simulation Result - 4



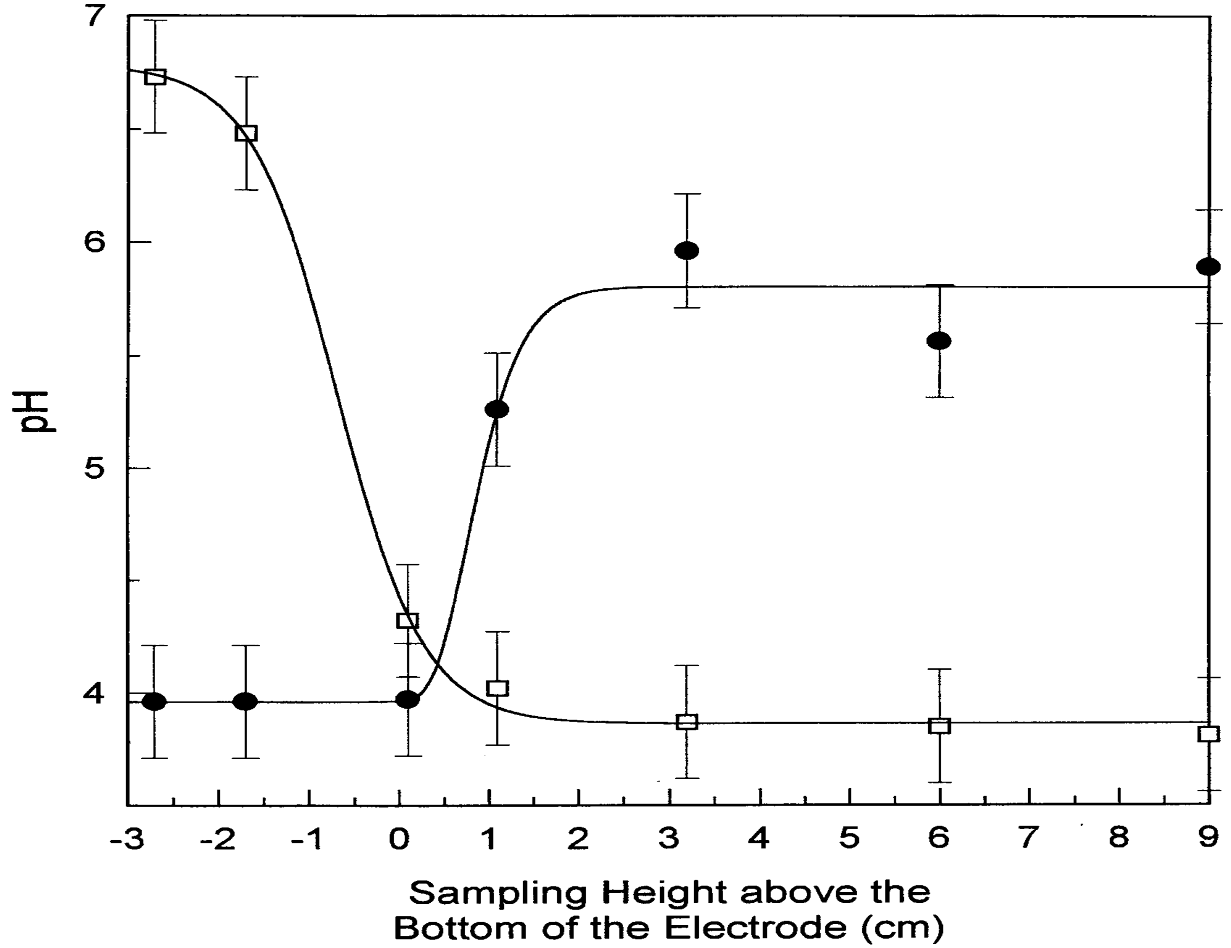
Simulation Result - 5



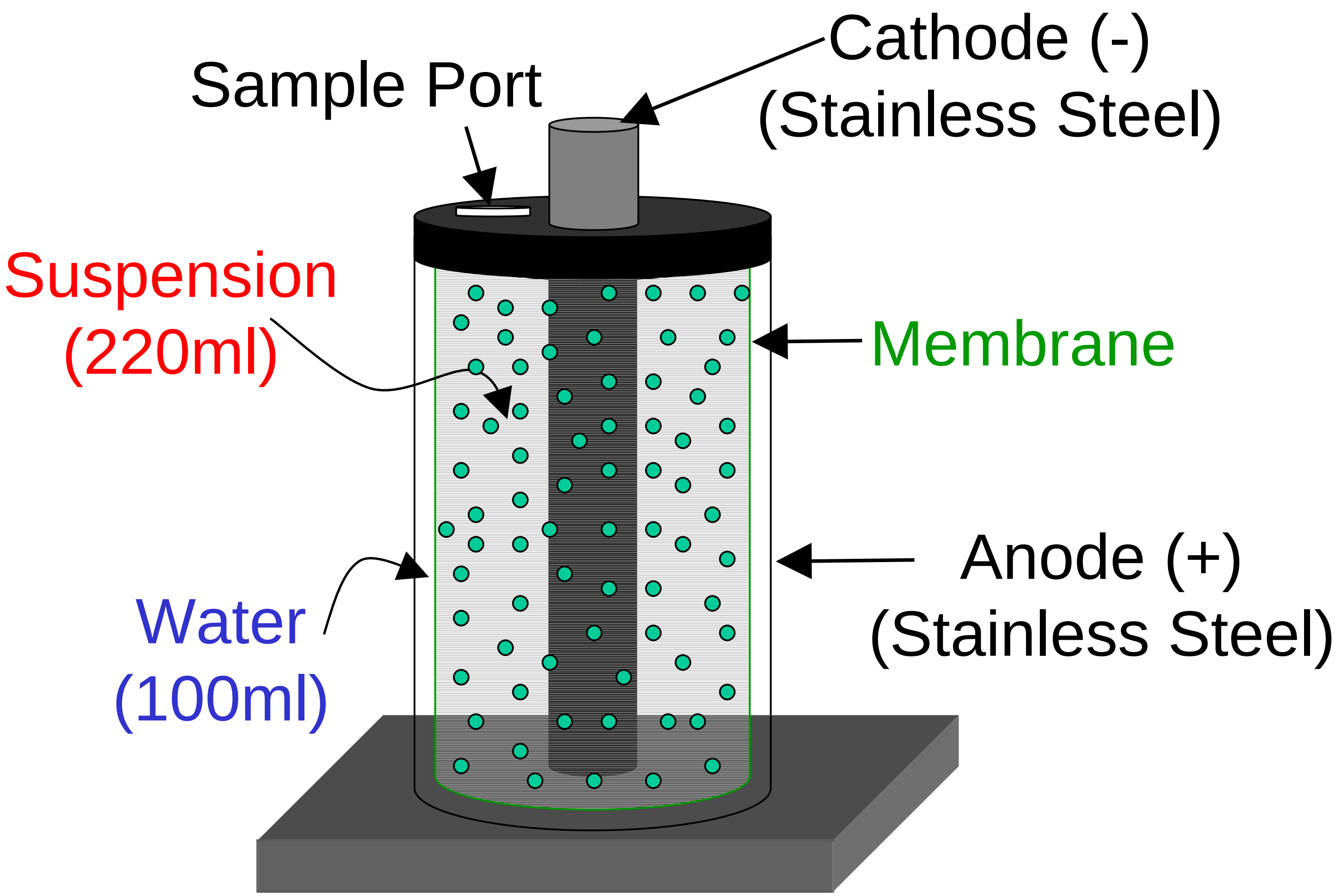
Simulation Result - 6



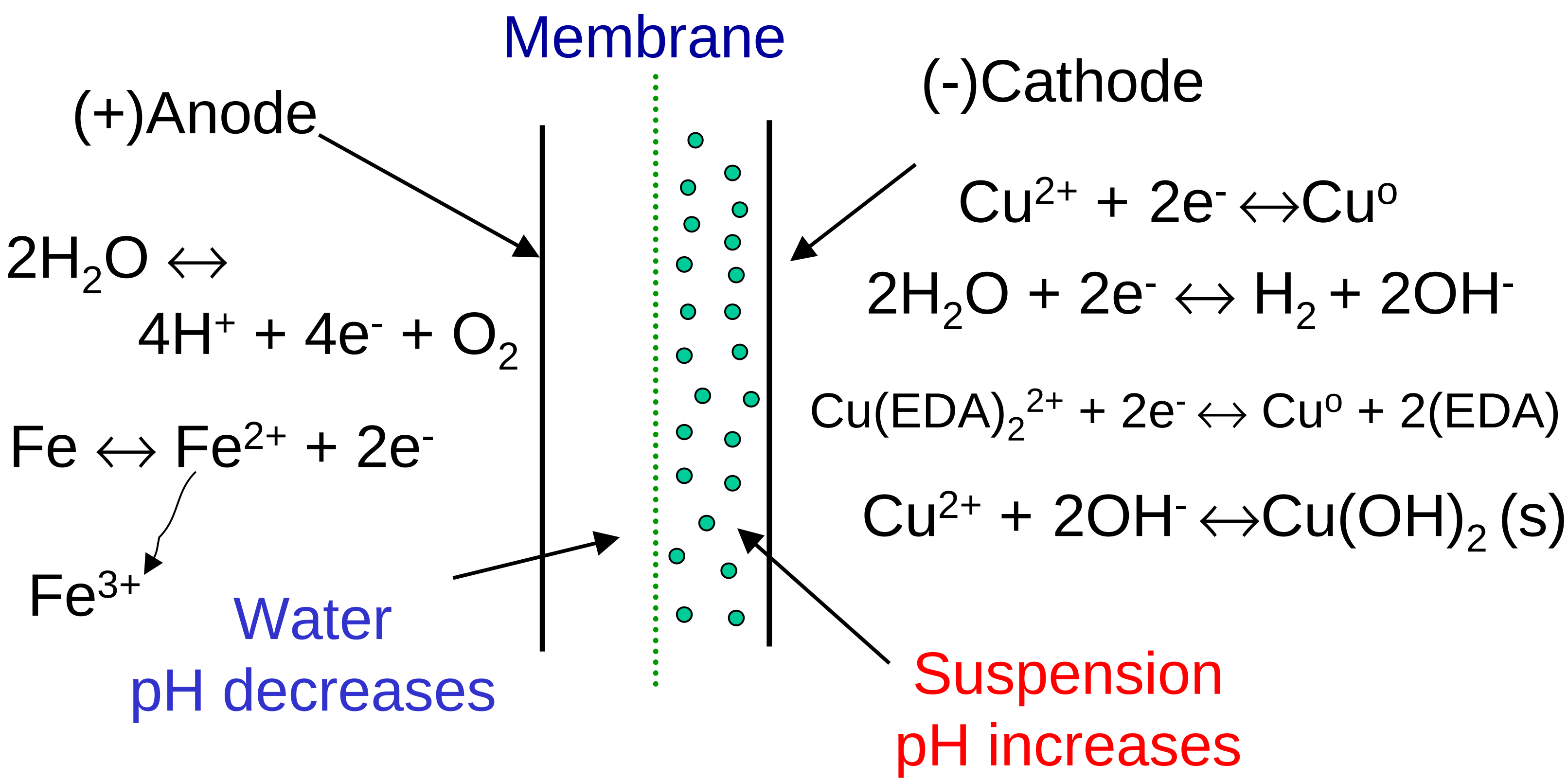
Simulation Result - 7



Experimental Setup



Copper Removal

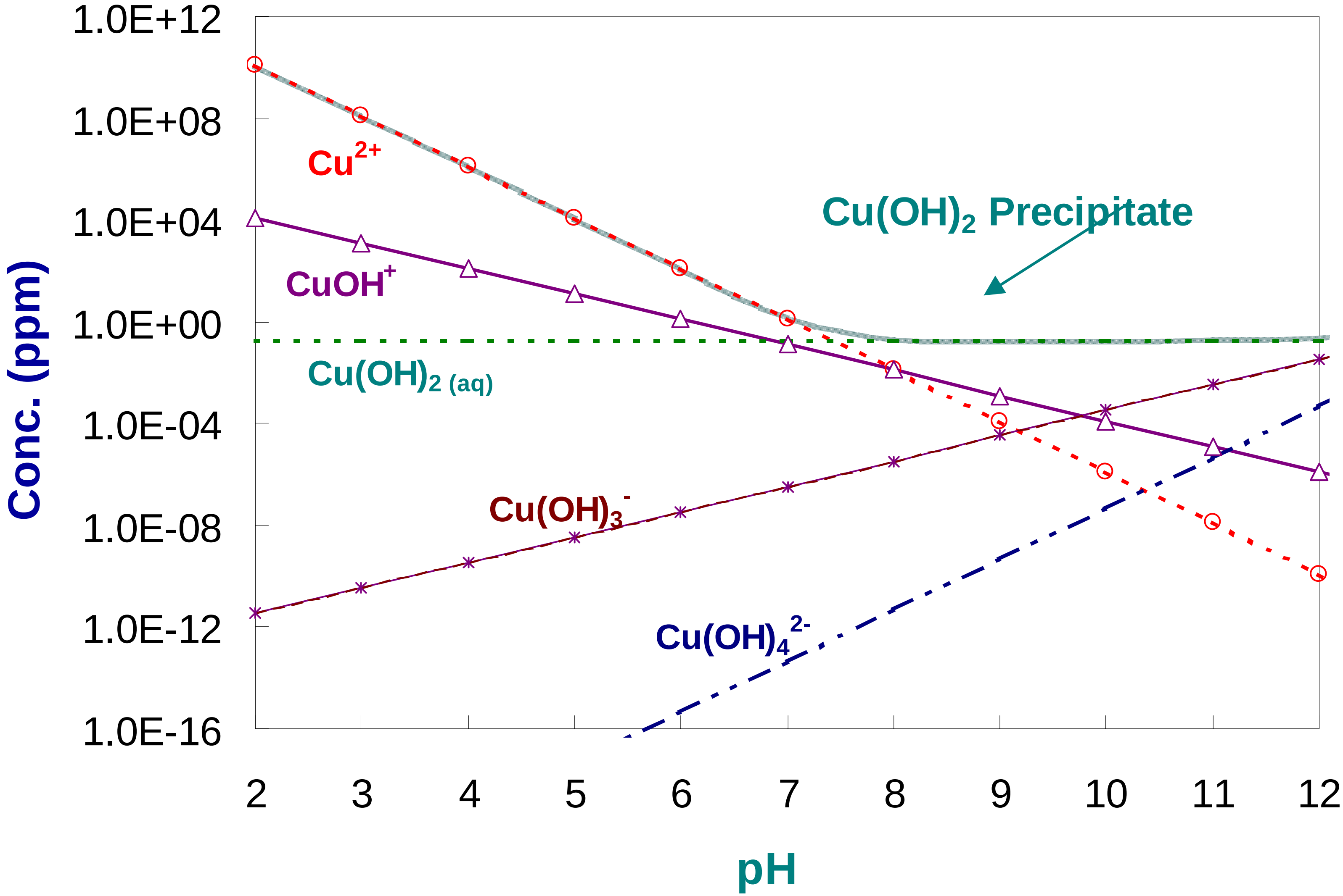


- The membrane partitions the anode and cathode chambers, allowing pH changes to occur in the anode and cathode compartments.

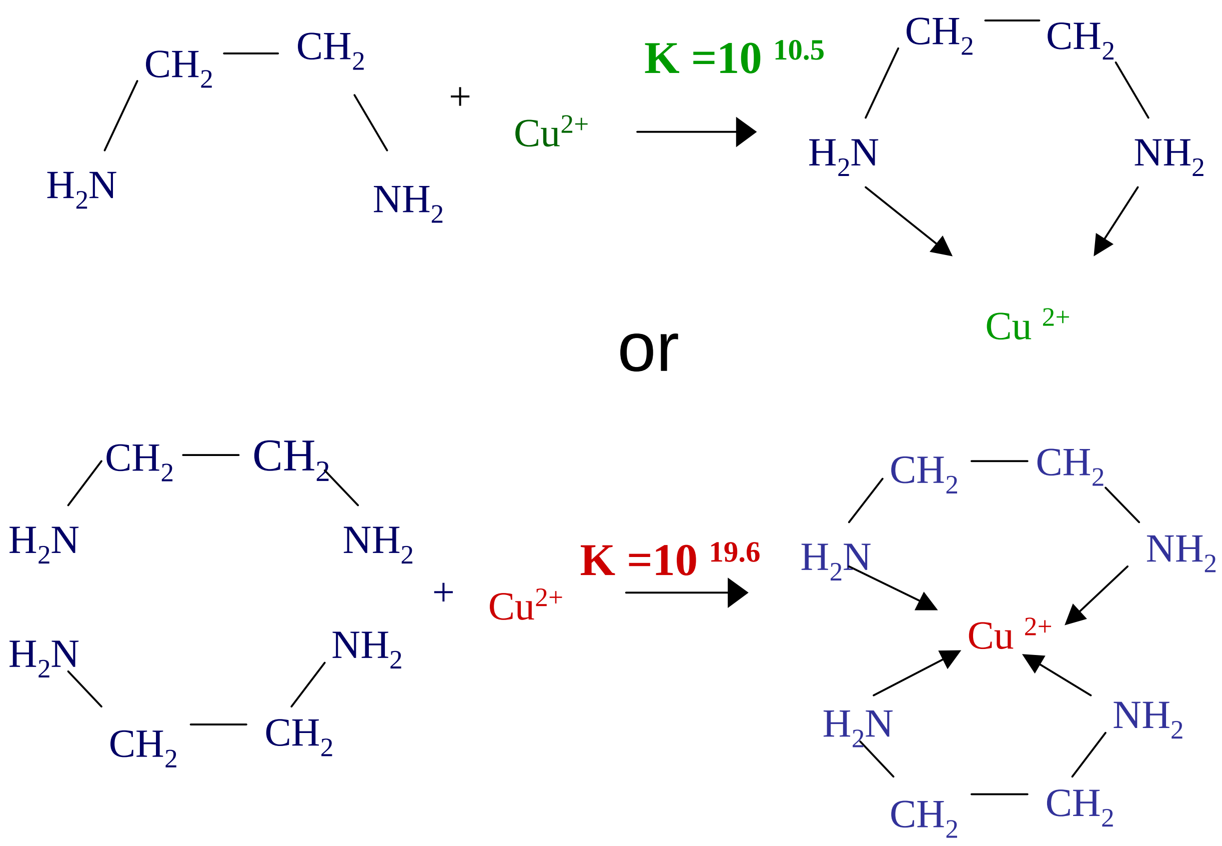
Solids Removal

- Particle-Particle collision rates are enhanced under **E**
- IEP (iso-electric point) mechanism due to pH change
- Coagulation induced by metal ions released from anode
- In-situ chemical precipitation
- Natural convection -- electrodecantation

Speciation Diagram of Cu/H_2O System



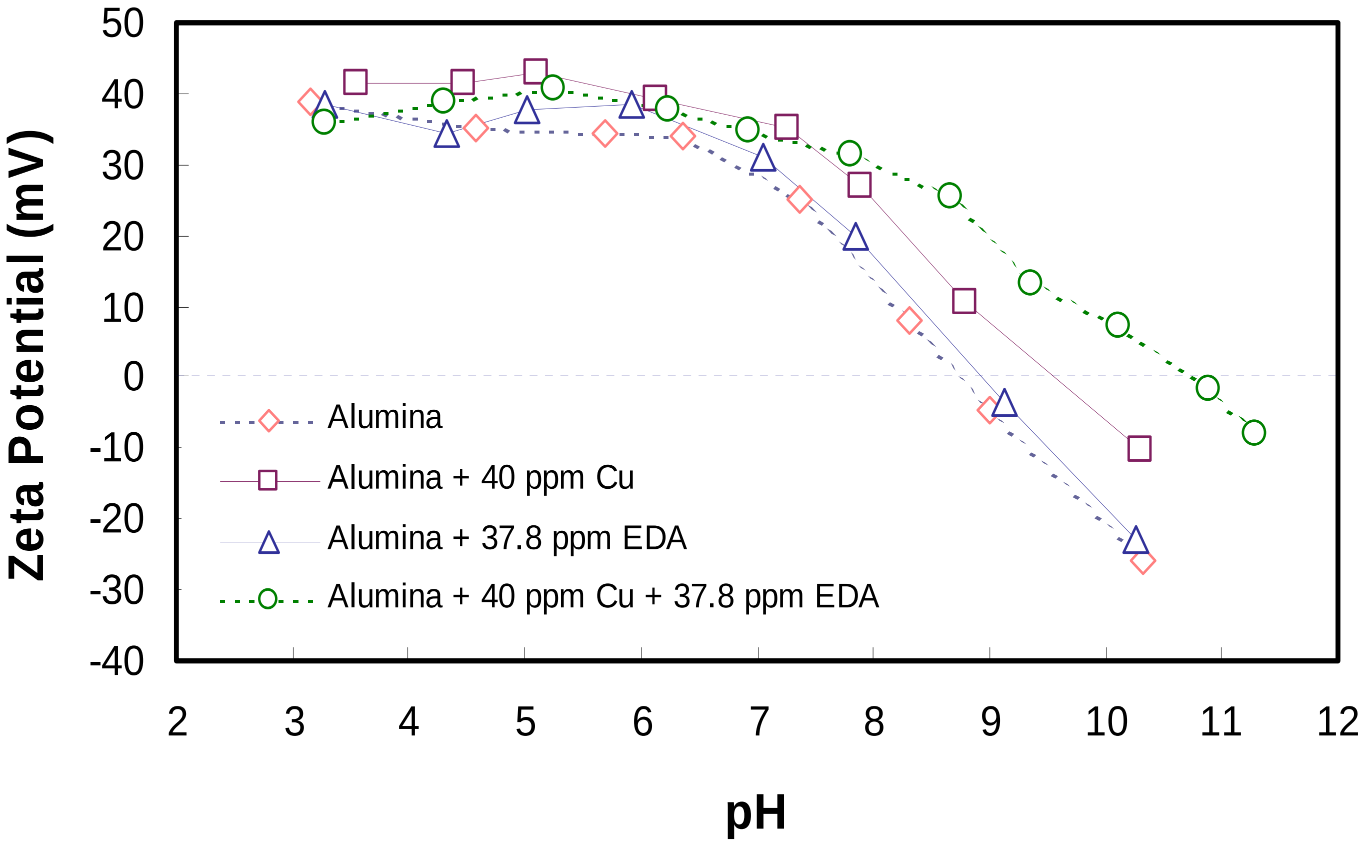
EDA Characteristics



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

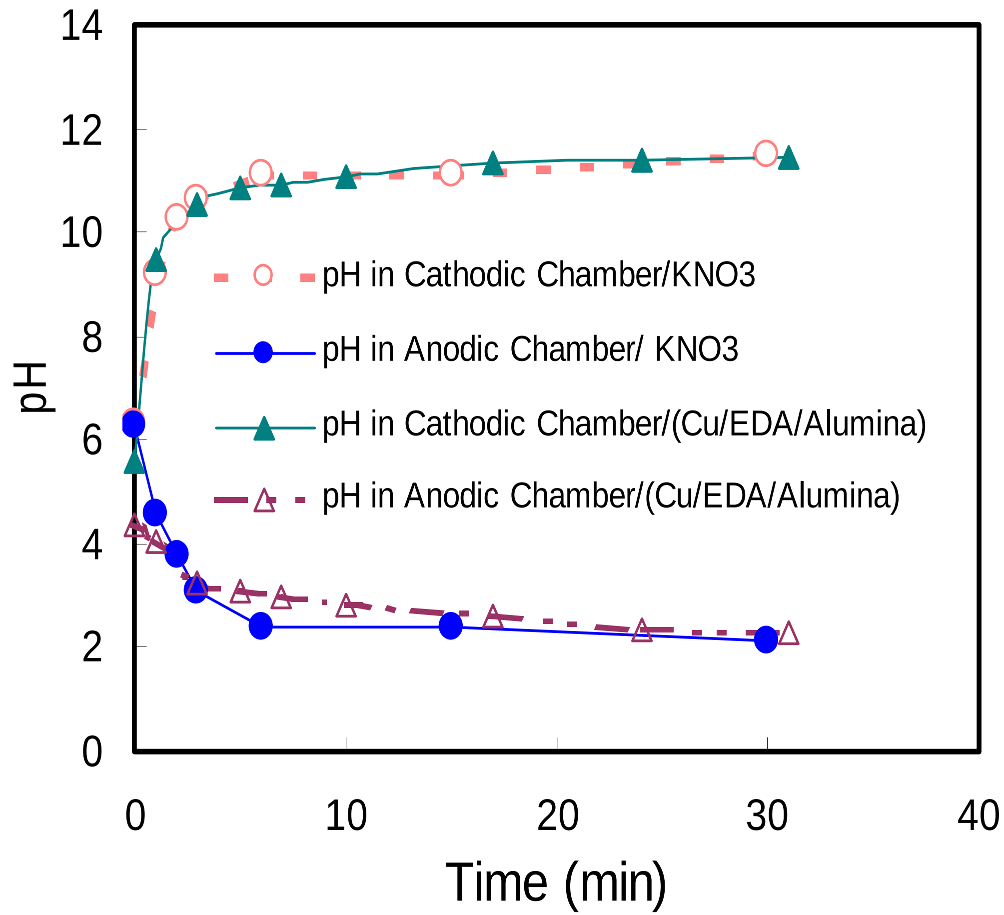
Electrokinetic Behavior of Al_2O_3

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.

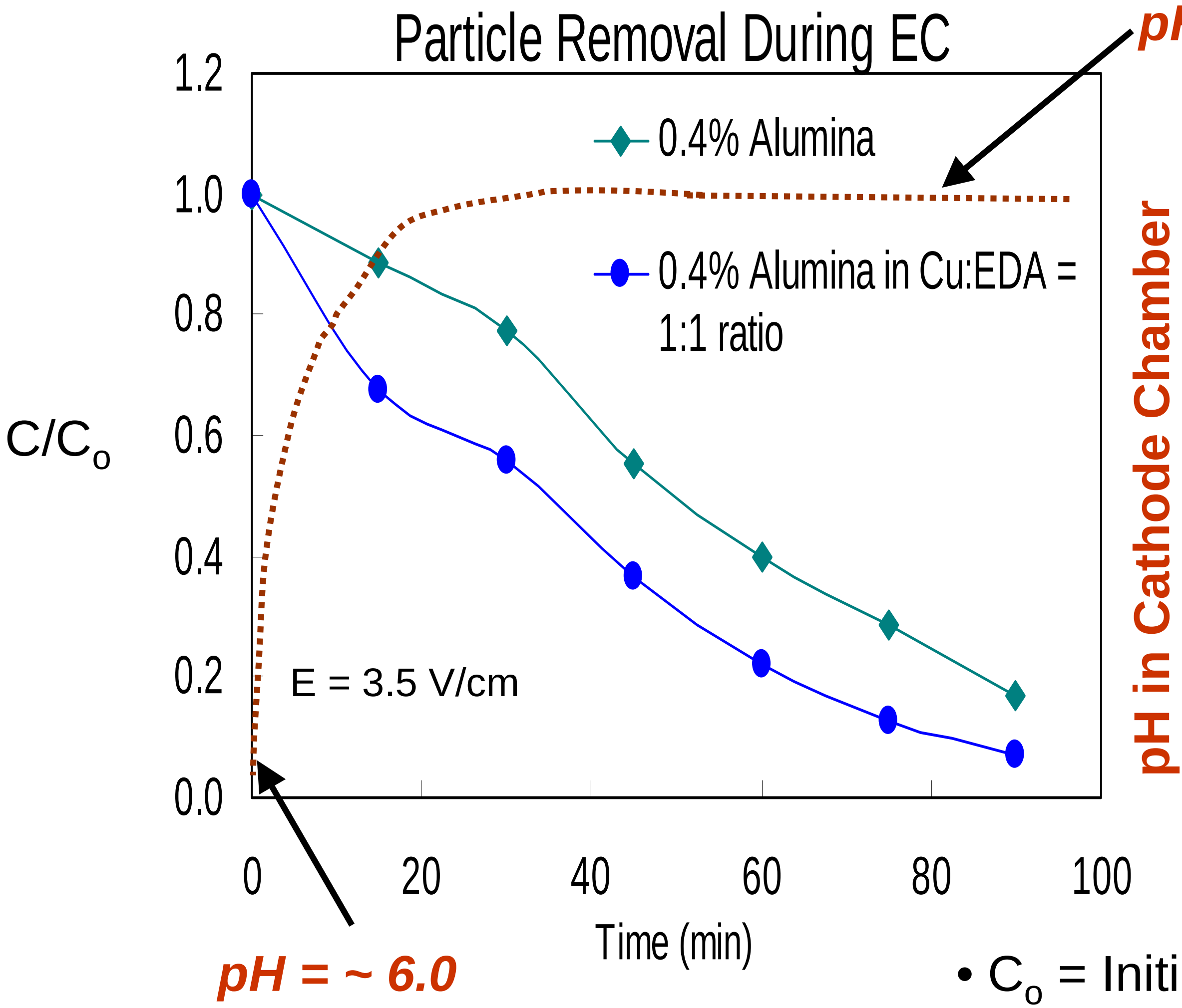
pH Changes during EC

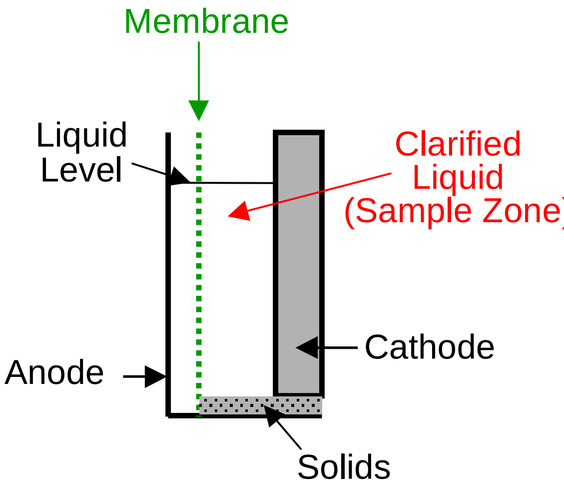


- The suspension pH increases rapidly when an electric field is applied.
- If IEP of particles in the cathode chamber is between *6<pH<10*, coagulation of particles may occur as pH approaches the IEP of particles.

E = 3.5 V/cm

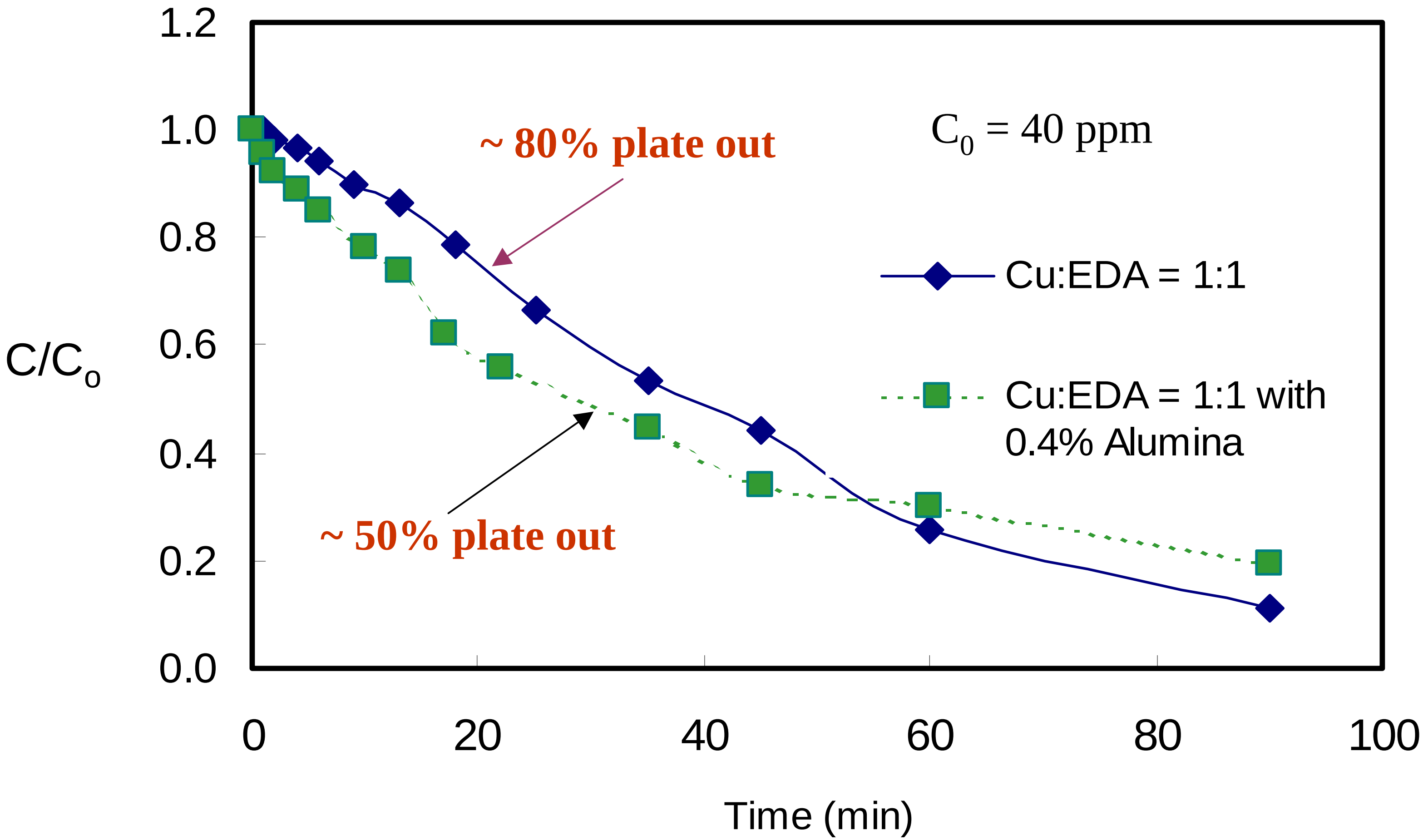
Electrocoagulation of Al_2O_3





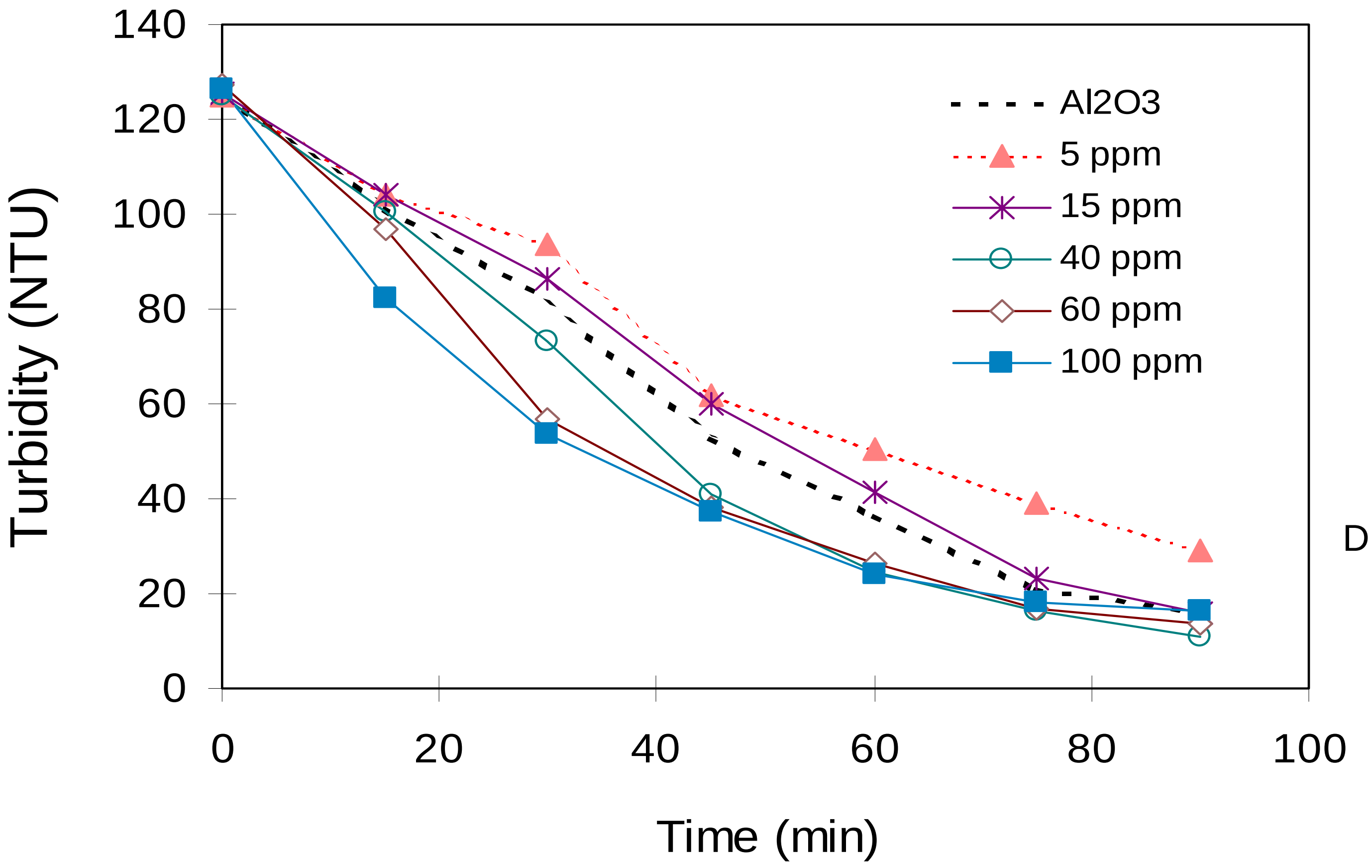
- C_o = Initial Solid Conc. ~ 0.4%
- C = Solid Concentration

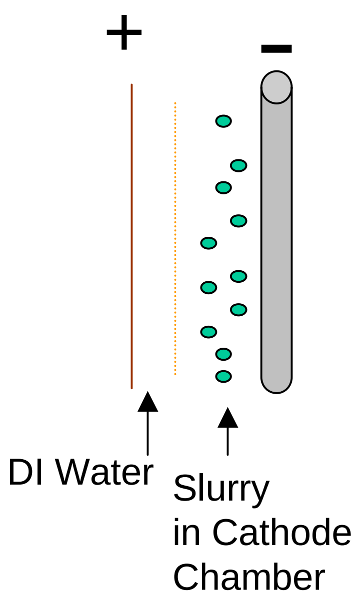
Kinetics of Removal of Dissolved Copper



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

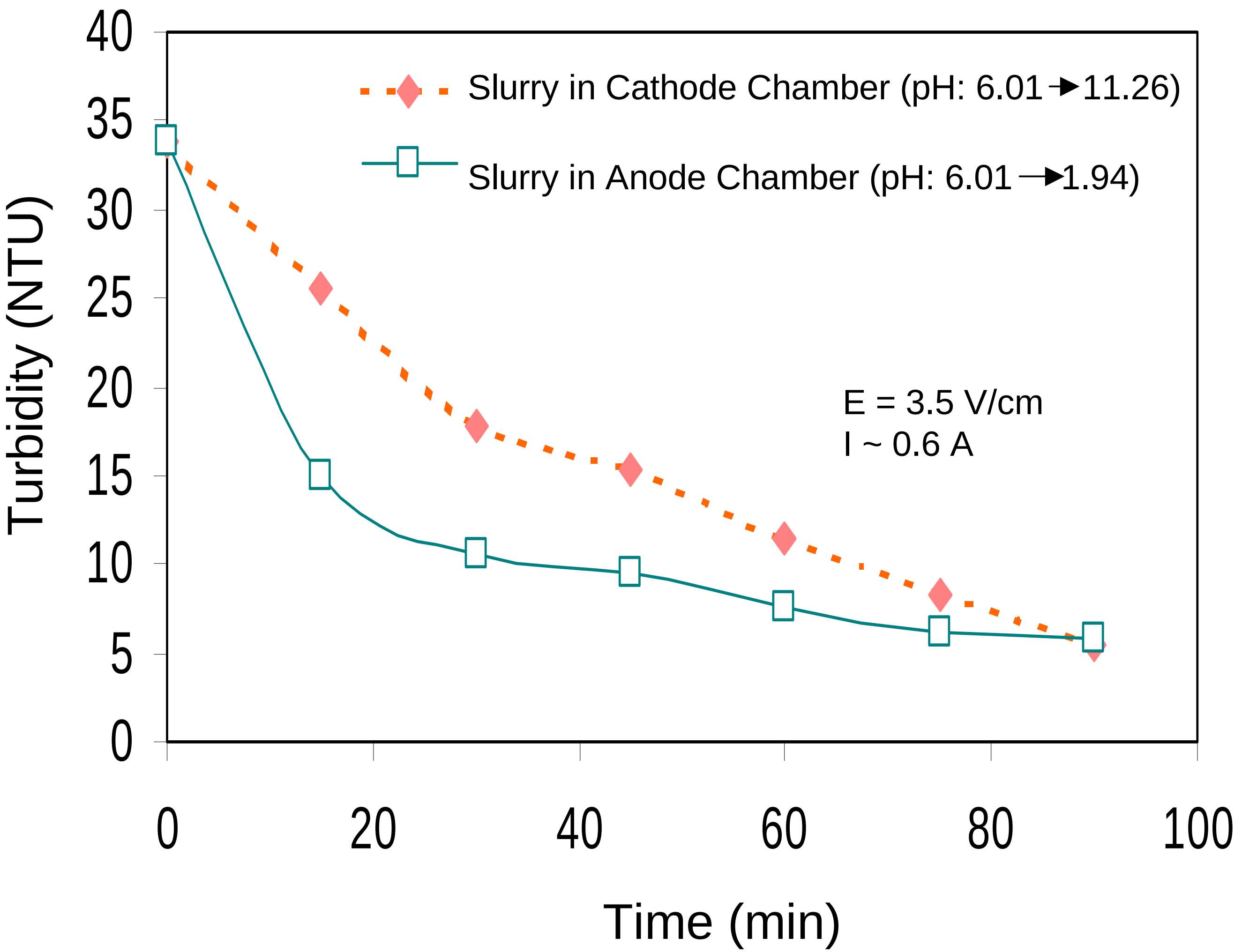
Electrocoagulation Tests on $0.4\%\ Al_2O_3$ (with different Fe^{3+} level)

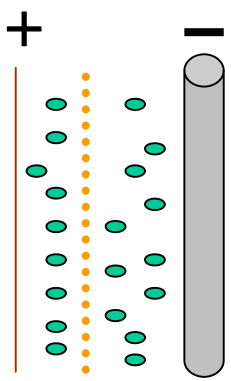




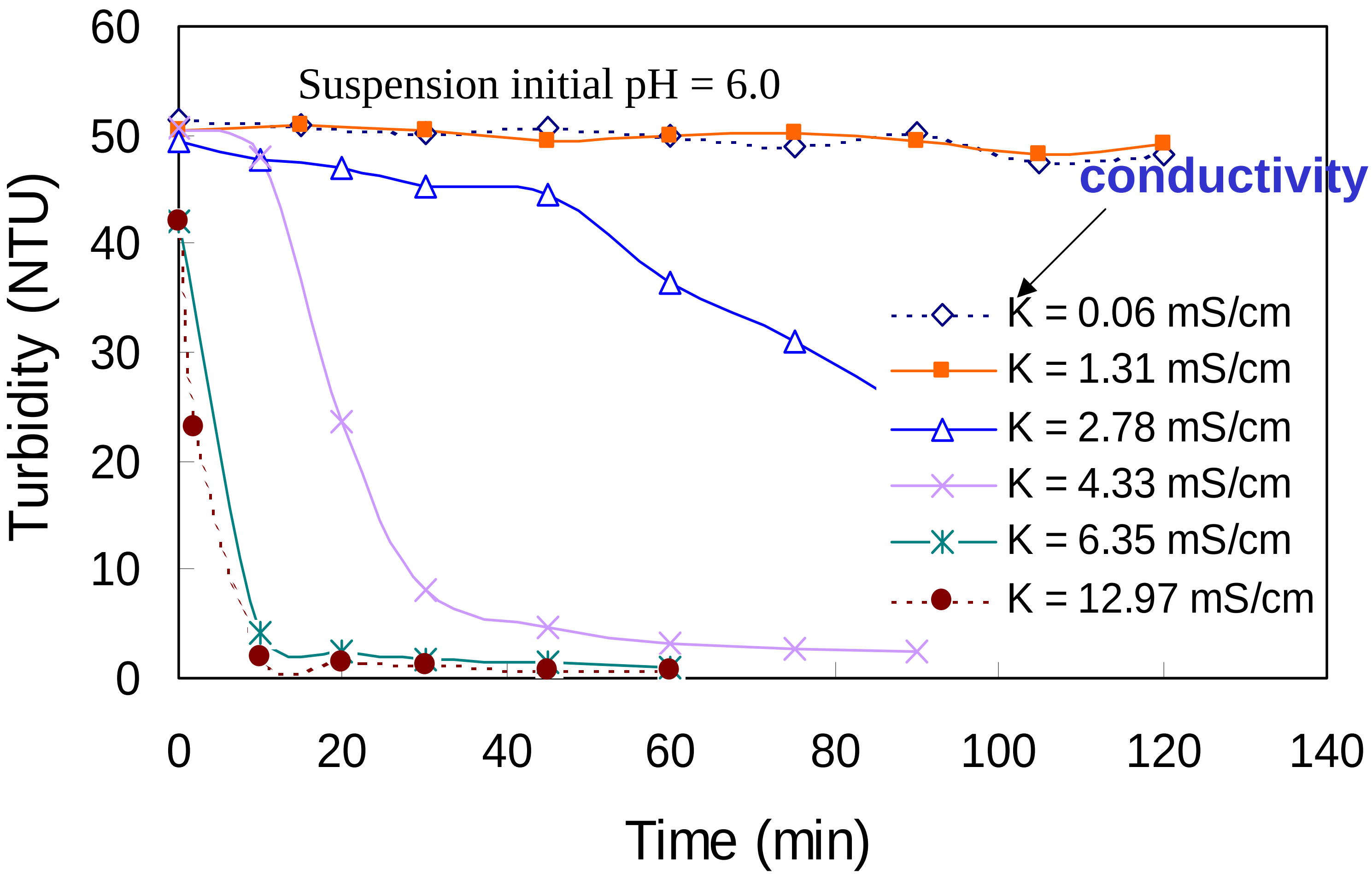
The presence of Fe^{3+} in slurry slightly increases the rate of Al_2O_3 coagulation

Electrocoagulation Tests on 0.1% Al_2O_3 (in both chambers)



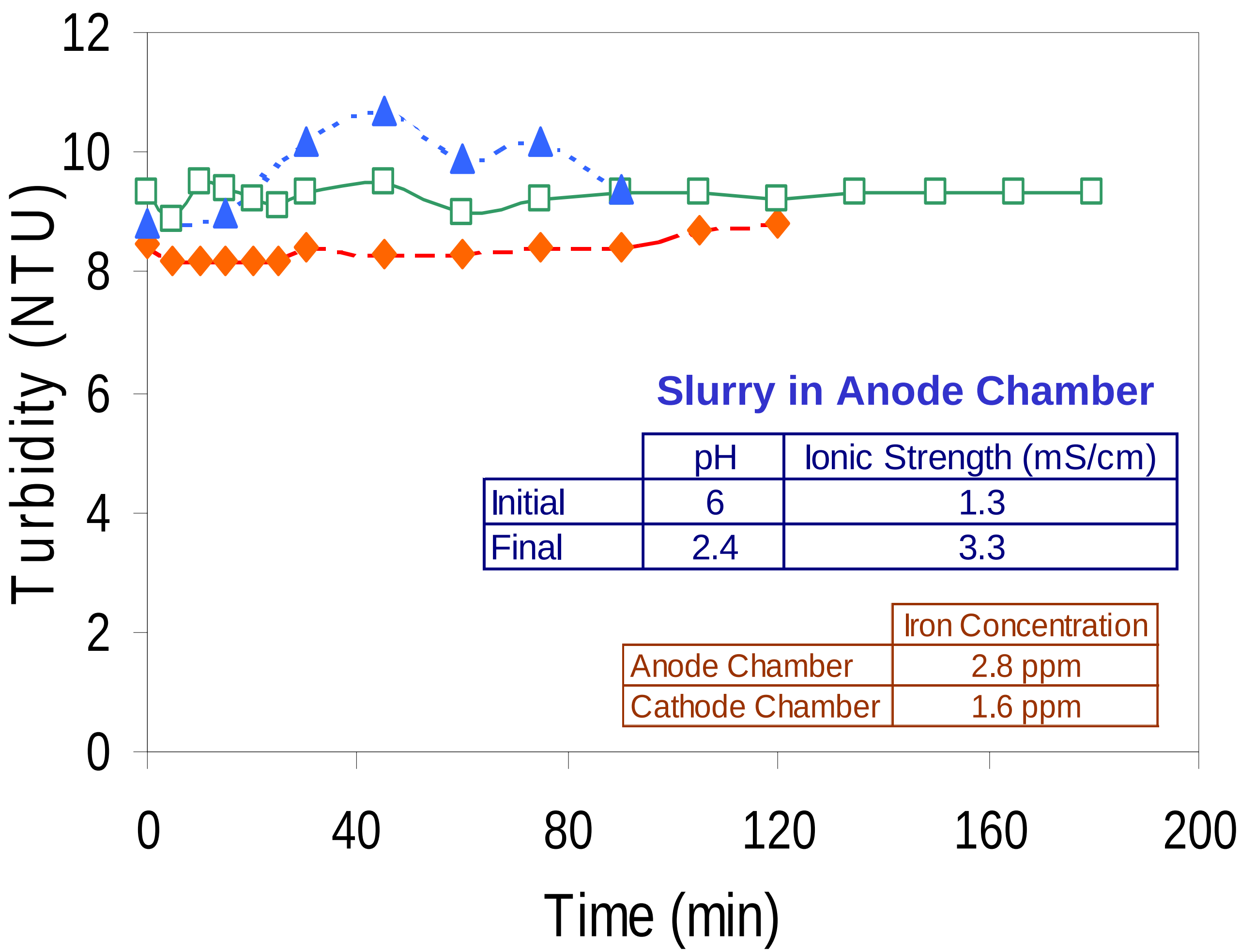


Stability of 0.2% Al_2O_3 (no applied field)



- When K ≥ 2.78 mS/cm, Destabilization starts to occur.

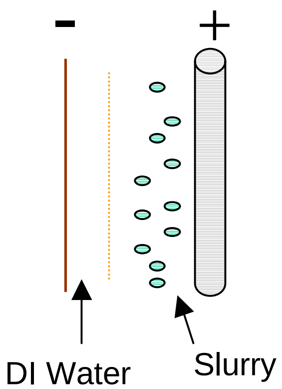
Electrocoagulation Tests on 0.1% Klebosol SiO_2 Slurries



Slurry in Anode Chamber

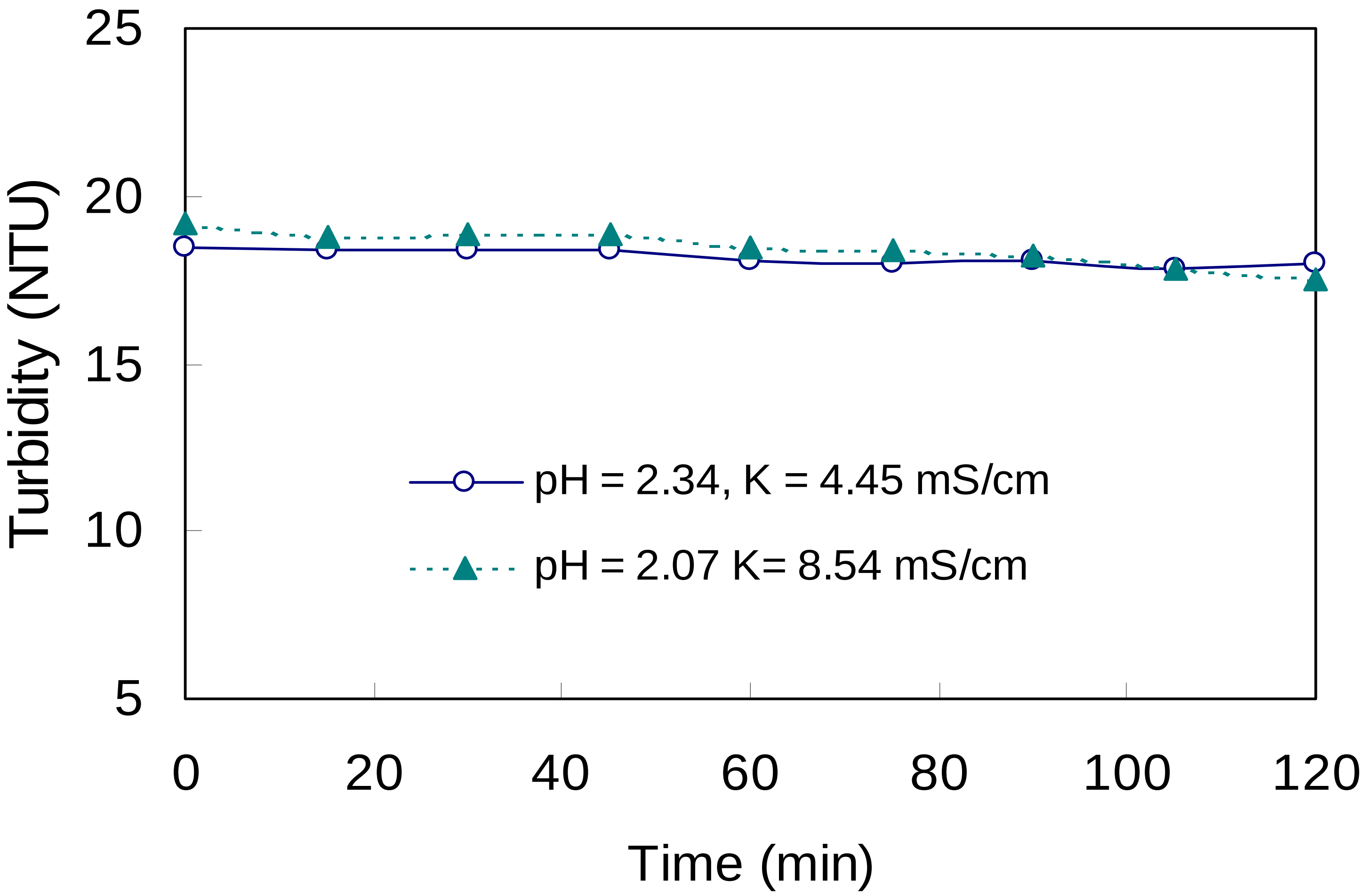
	pH	Ionic Strength (mS/cm)
Initial	6	1.3
Final	2.4	3.3

	Iron Concentration
Anode Chamber	2.8 ppm
Cathode Chamber	1.6 ppm



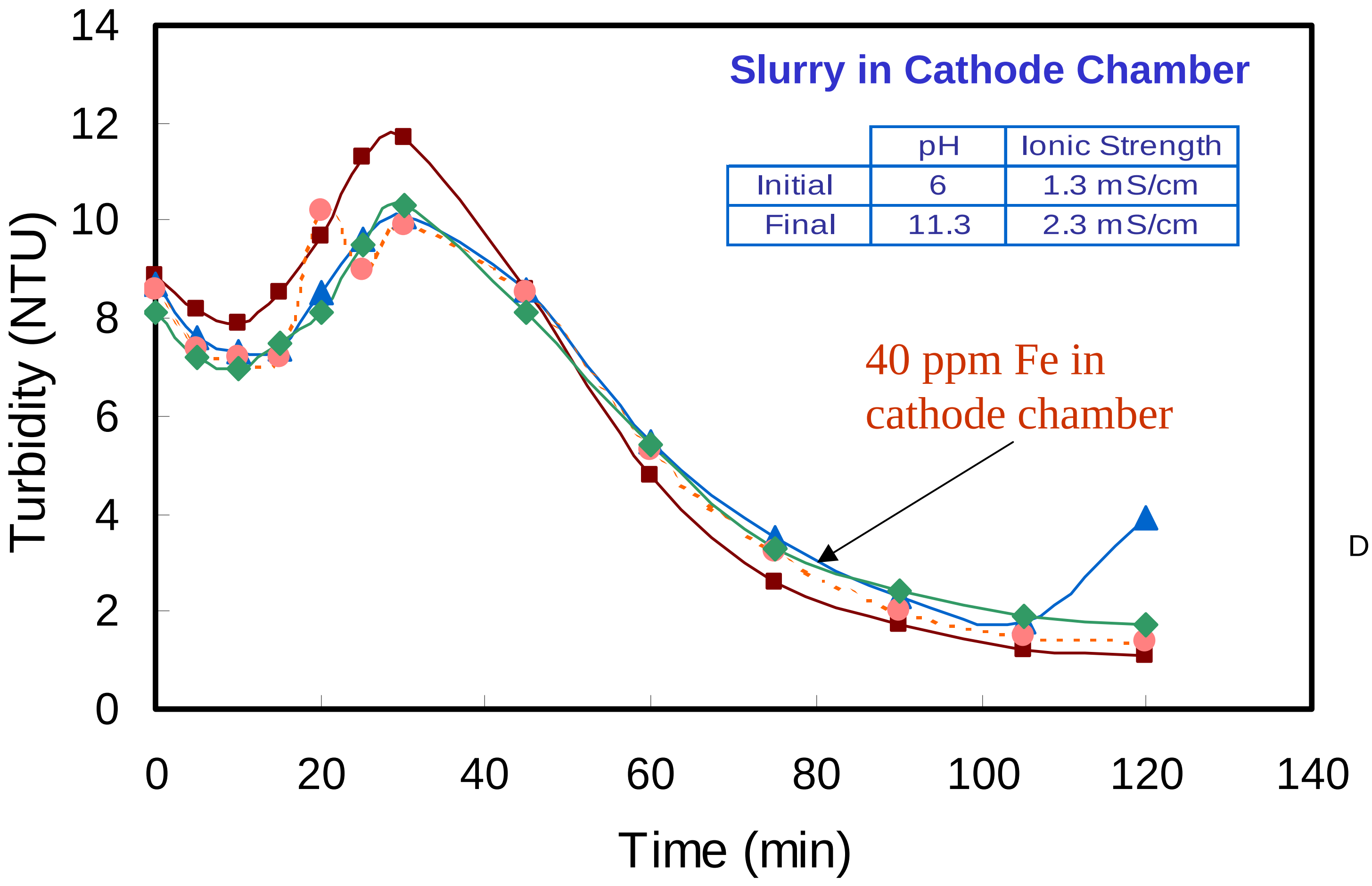
Note: EC treated slurries remained stable when stored for 48 hours.

Stability of 0.2% SiO_2 (no applied field)

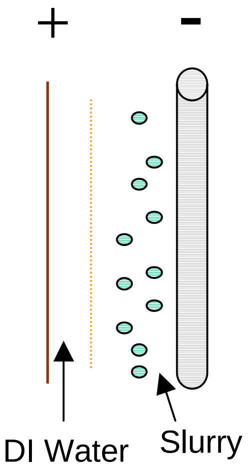


- Suspension of Klebosol SiO_2 is very stable.

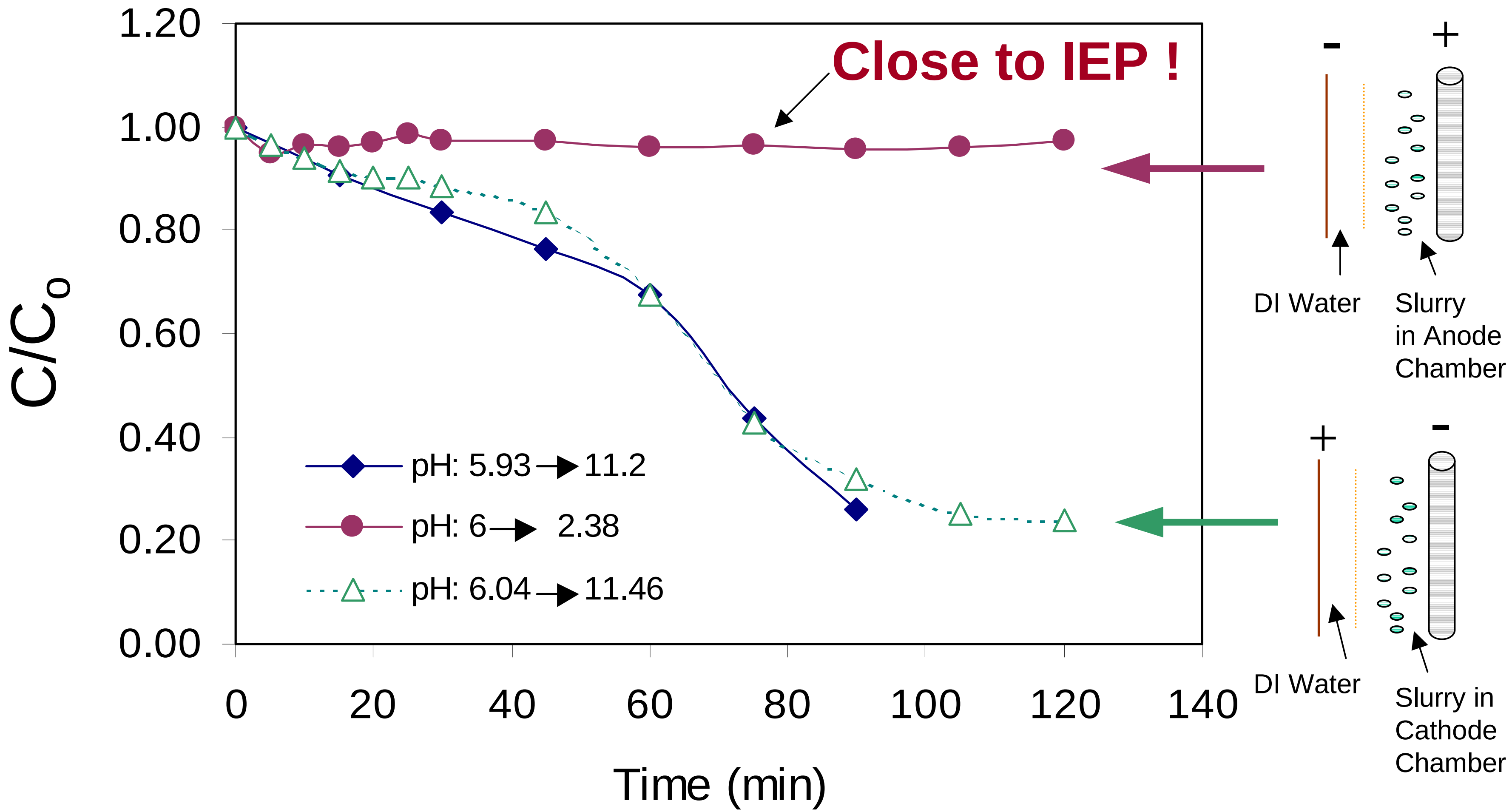
Electrocoagulation Tests on 0.1% Klebosol SiO_2 Slurries



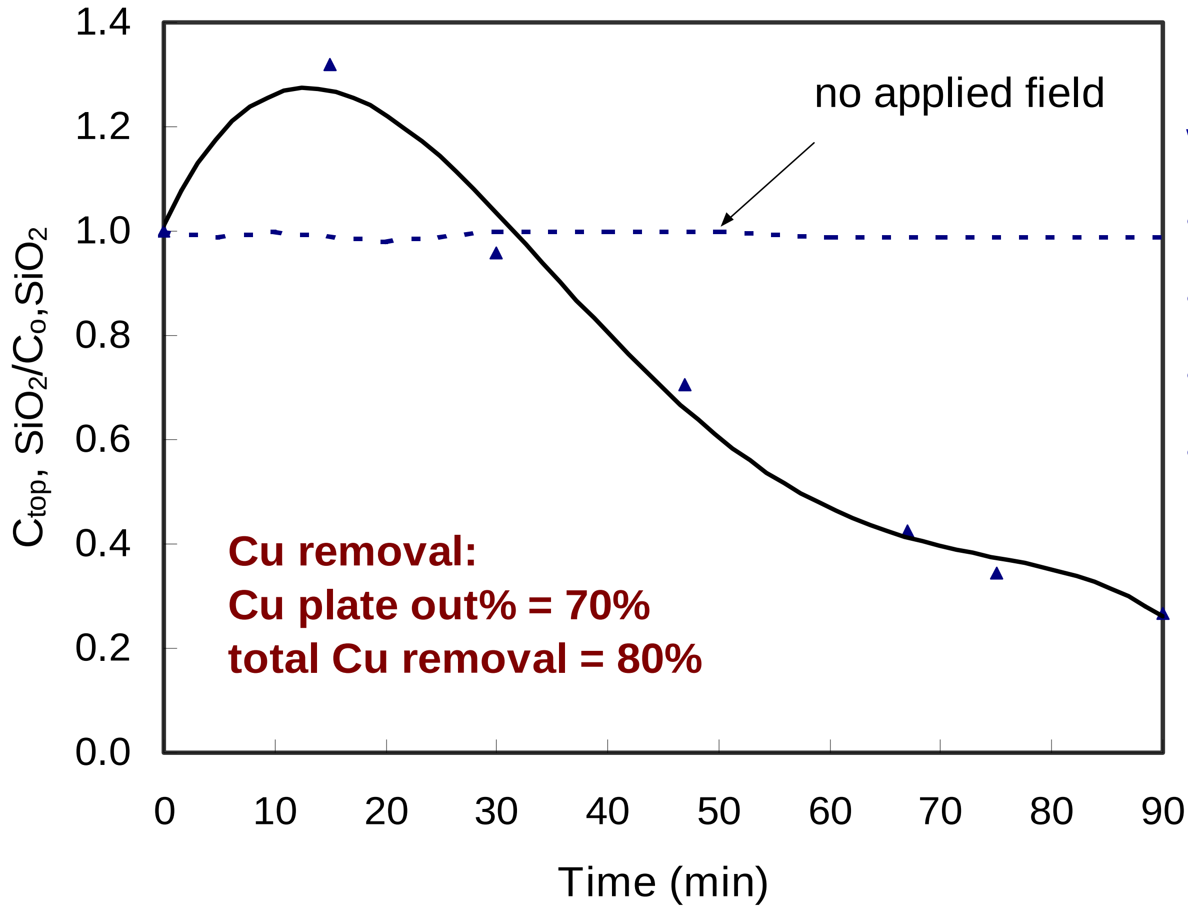
	pH	Ionic Strength
Initial	6	1.3 mS/cm
Final	11.3	2.3 mS/cm



Electrocoagulation Tests on 0.4 % Klebosol SiO_2 Slurries



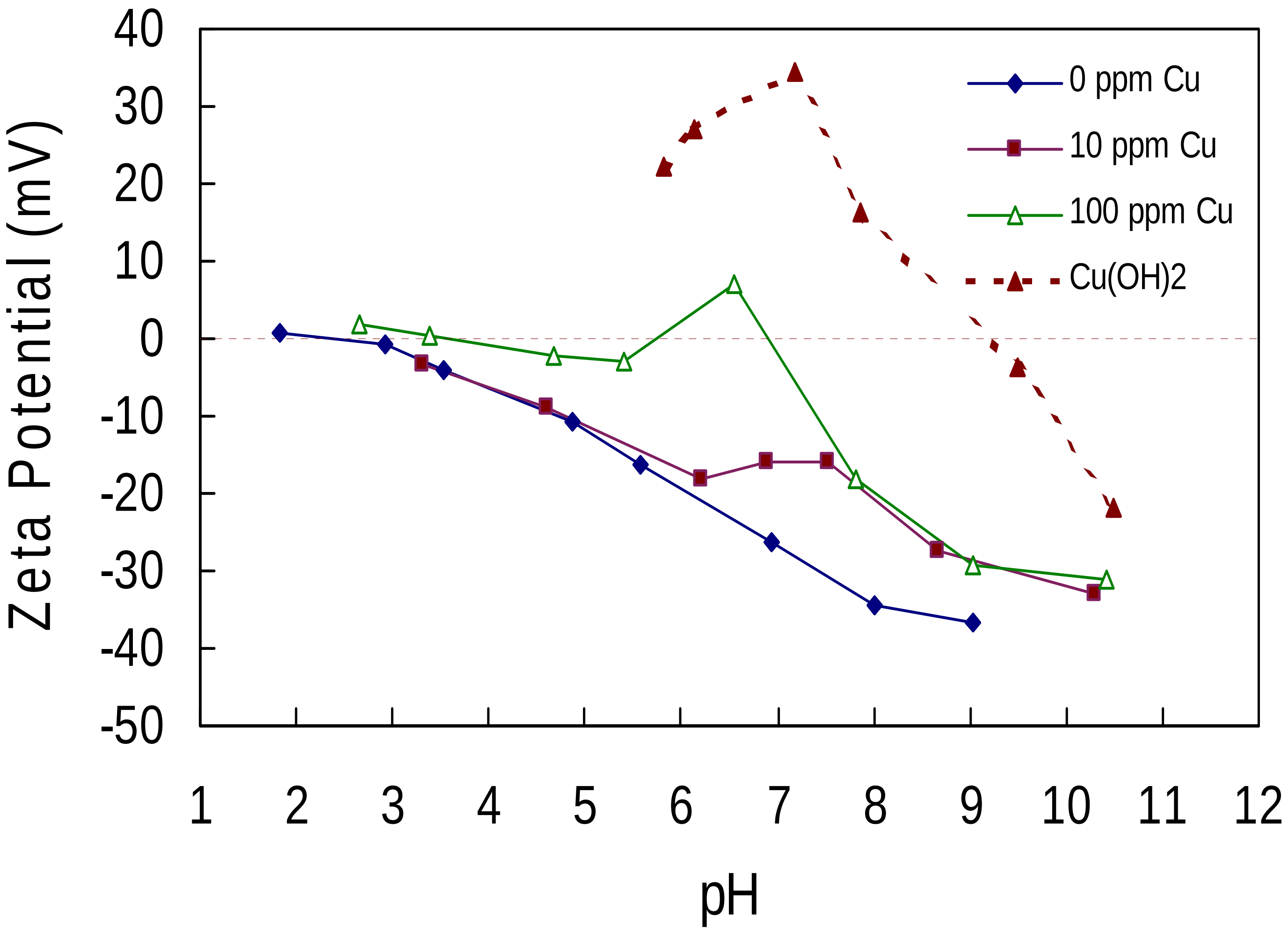
Electrocoagulation Tests on Klebosol SiO_2 Slurries



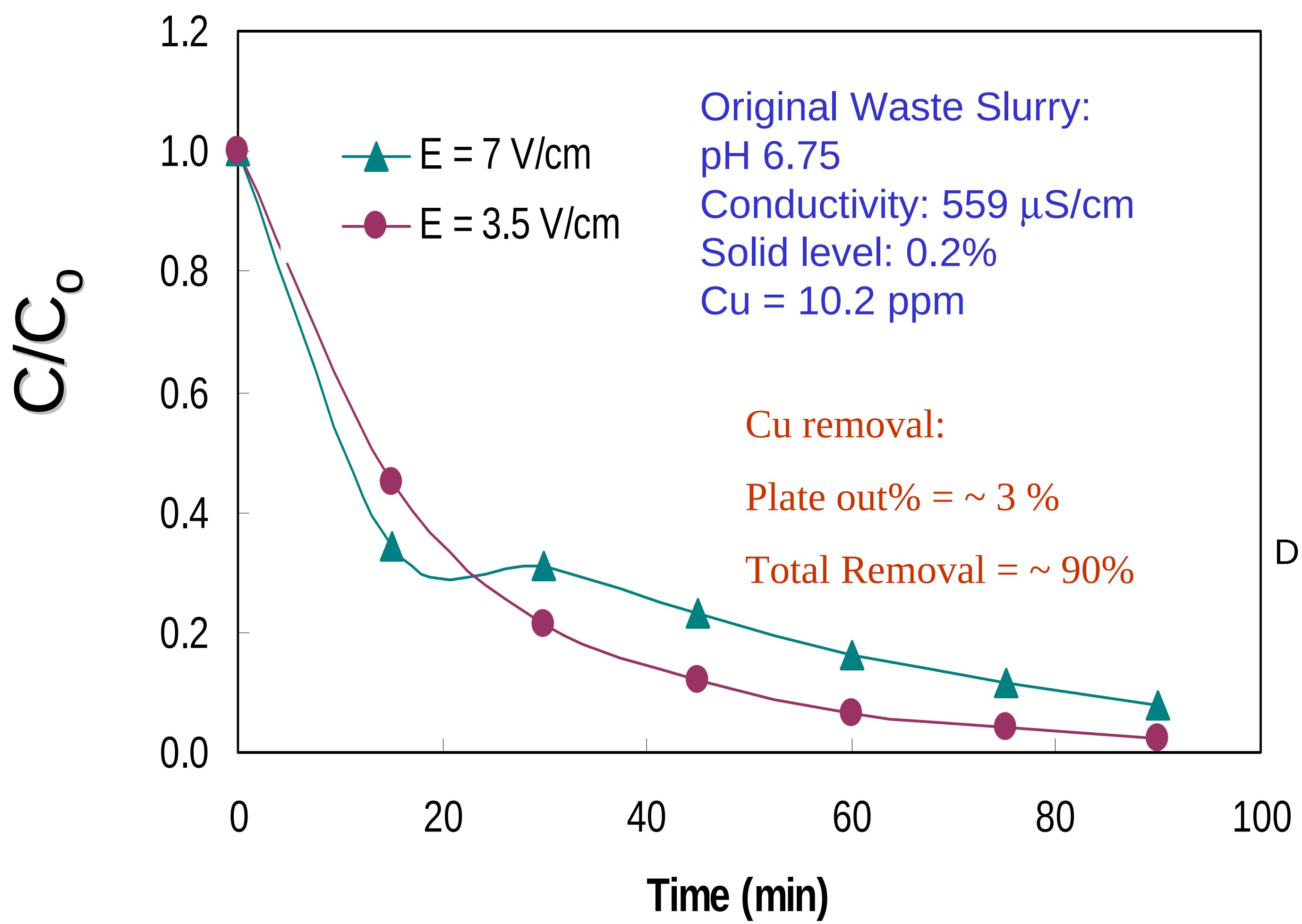
Waste Characteristics:

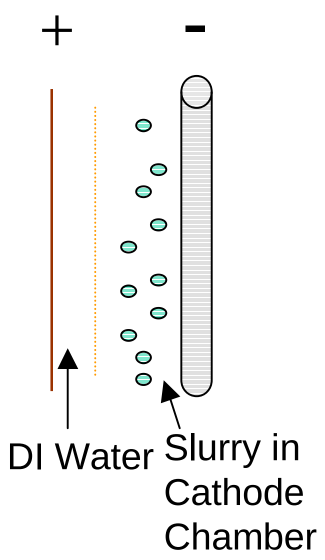
- 0.1w/v% SiO_2
- 20 ppm dissolved Cu
- 19 ppm EDA
- Initial suspension pH = 6.0

Electrokinetics Behavior of SiO_2

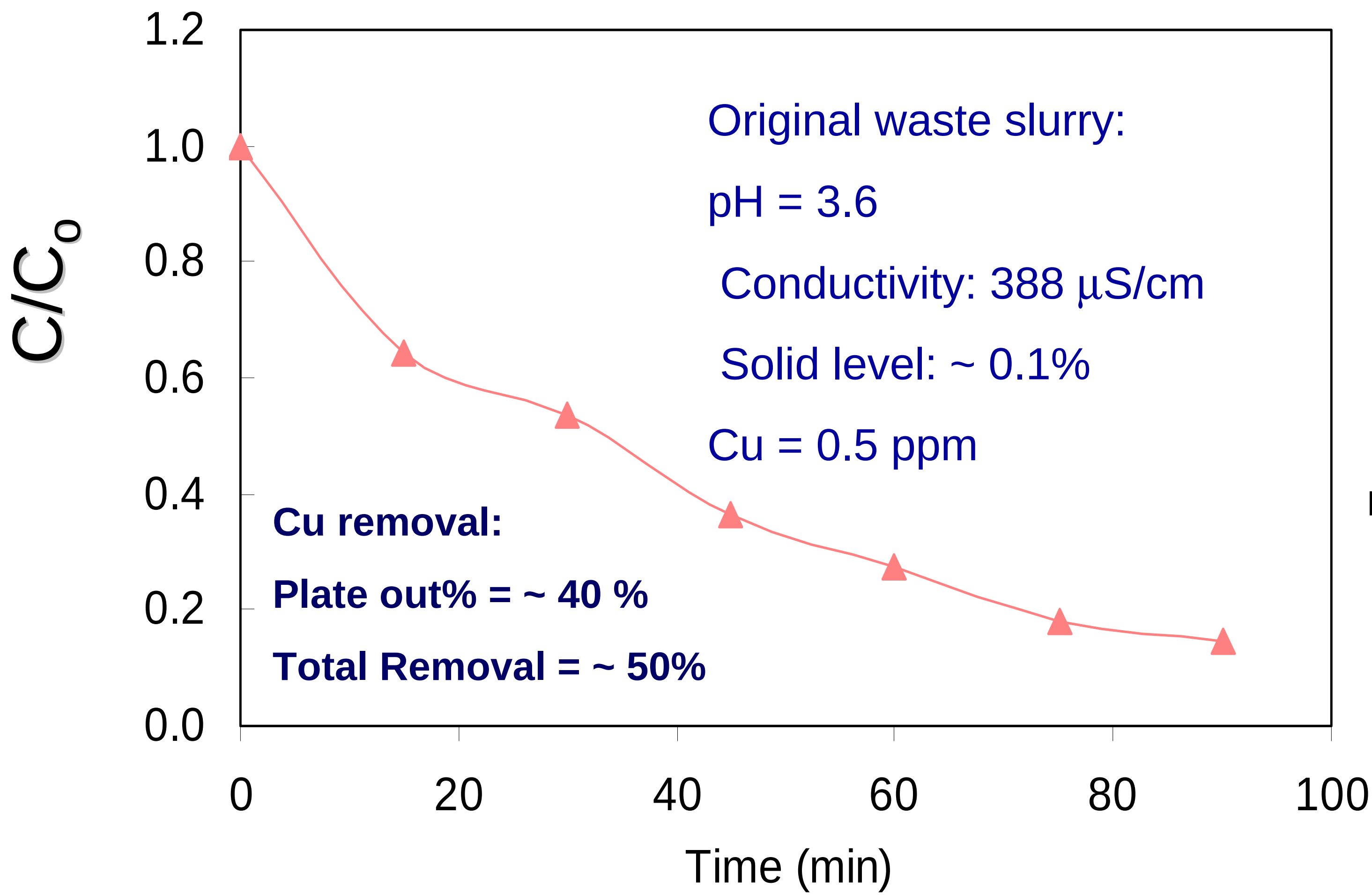


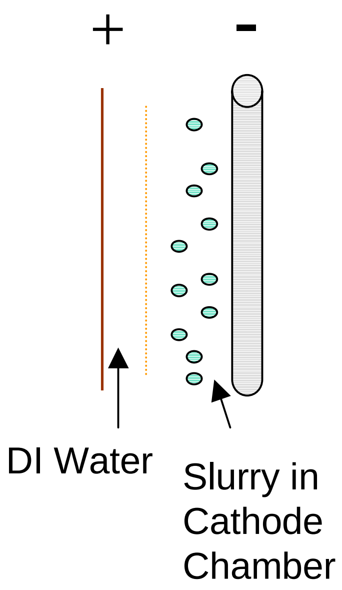
Electrocoagulation (EC) Tests on Actual CMP Waste Slurry -1





Electrocoagulation (EC) Tests on Actual CMP Waste Slurry-2





Summary

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

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

3. When Al_2O_3 slurry is put into cathode chamber, the Al_2O_3 particles coagulate via “IEP” mechanism. When it is put into anode chamber, coagulation may be caused by “Ionic Strength Increase” or locally high particle concentration.

4. The presence of Fe^{3+} (up to 100ppm) may not dramatically enhance the Al_2O_3 coagulation.

Summary

5. Klebosol SiO_2 in cathode chamber appears to coagulate by the presence of ferric iron that migrate from the anode chamber.

6. When either 0.4% or 0.1% SiO_2 is contained in the anode chamber, no coagulation is observed, this indicates that "IEP" mechanism can not be used to explain SiO_2 coagulation, a new explanation needs to be found.

Acknowledgements

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