Biological Removal and Recovery of Copper in CMP Effluents

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Research Outline

- Background
- Objectives
- Approach
- Materials and Methods
- Results
- Conclusions

Background

- Cu interconnect technology is rapidly replacing traditional processes.
- Cu-Chemical Mechanical Planarization (CMP) effluents ~ 30-40% water consumed in a fab
- Cu-CMP effluents contain significant quantities of soluble Cu and organic contaminants.
- Environmental biotechnologies offer interesting potentials for metal removal and recovery. Biological treatment could also provide an attractive approach to effectively meet regulatory challenges associated with Cu-CMP.

CMP Wastewater Components

Inorganic

Copper:	Soluble Cu^{+2} (1-50 mg/l)
Inorganic solids:	Abrasives (eg. SiO_2, Al_2O_3)
Oxidizers, strong acids/bases:	H_2O_2, NO_3^-, $KMnO_4$, HF, NH_3, OH^-, etc

Organic

Metal chelators / acids:	Citric acid, oxalic acid, EDTA, peroxy acetic, etc.
Corrosion inhibitors:	Benzotriazoles
Surfactants/dispersants:	PFOS, alkyl sulfates, etc.

Why treat CMP Effluents?

- **To meet environmental standards; eg.**

  BOD: Higher values than permitted often reached

  Cu limit :

  - discharge to wastewater treatment plant: 1- 2 mg Cu/l
  - direct discharge: 5-10 µg Cu/l

- **Enable water reuse**

Treatment of CMP Effluents:

Physico-Chemical Methods

- **Coagulation / flocculation / clarification**
  (Removal of solids, metals, fluoride, soluble silica)

  Requires large tanks, high chemical addition

  Generates (toxic) sludges

  High residual Cu and suspended solids content

- **UF / oxidant removal/ Ion exchange**
  (Removal of solids, oxidants, copper)

  Expensive; No removal of organic fraction

Treatment of CMP Effluents:

Biological Methods

Published work mainly focused on **Biosorption:**

- **Advantages:**
  - Removes copper to ppb levels even when chelators, organics, and particles are present in the waste stream.
  - Further recovery of copper looks feasible.
- **Disadvantages**
  - Breakthrough of columns appears sooner when real CMP wastewater used.
  - No removal of organics or other contaminants has been proved yet.

Source: Stanley & Ogden, (2003) "**Biosorption of copper (II) from chemical metal planarization process**", J. Environ. Management.

Project Objectives

- The goal of this research is to investigate the feasibility of anaerobic treatment for the Removal and Recovery of Copper from CMP Wastewaters.

- Removal of copper will be stimulated by biogenic sulfides produced by sulfate reducing bacteria.

- Copper will be deposited in sand granules inside a crystallization reactor

Microbiological Process

- Process: Use of sulfate as terminal electron acceptor in the oxidation of an organic compound with production of sulfide.
  - **Electron acceptor:** usually an oxidized compound or a compound that can be reduced. It will function as the final receptor of the electron transfer chain. In aerobic reactions is O_2. In anaerobic reactions SO_4^{2-}, NO_3^-, are common terminal e- acceptors.
  - **Electron donor:** compound that gets oxidized. Also known as reductive agent. Often (but not always) in biological reactions an organic compound will play as electron donor.

Our Bioreactor Study

- An anaerobic bioreactor was used to produce sulfide.
- Citric acid was utilized as e-donor (common component of CMP wastewaters) at concentrations of 2000 and 667 mg COD/L.
- Copper (also a common contaminant in CMP) was used in three different periods, at a concentration of 100 mg Cu/L.
- Cu(II) was precipitated and further removed, in a crystallization reactor.

Microbiological Process: Half Reactions

Electron acceptor

$$SO_4^{2-} + 9H^+ + 8e^- \xrightarrow{\text{(Reduction)}} HS^- + 4H_2O$$

Electron donor

$$C_6H_5O_7^{3-} + 5H_2O \xrightarrow{\text{(Oxidation)}} 6CO_2 + 15H^+ + 18e^-$$

(Citrate)

Complete Redox Reaction

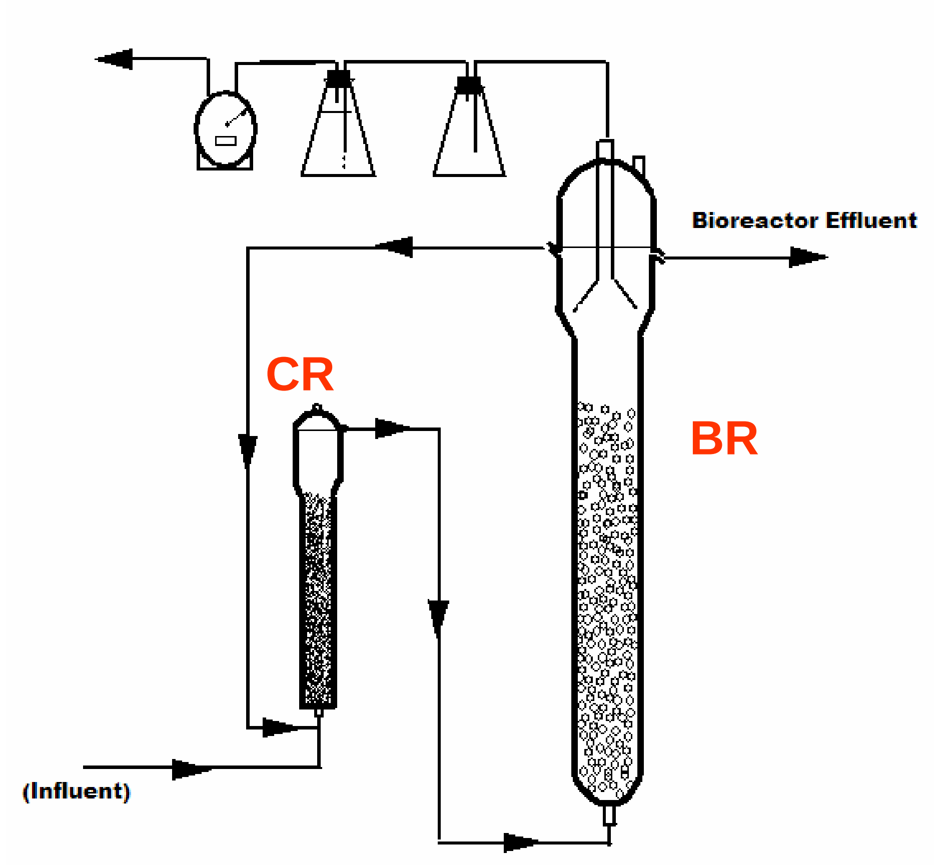
$$9SO_4^{2-} + 4C_6H_5O_7^{3-} + 21H^+ \longrightarrow 9HS^- + 24CO_2 + 16H_2O$$

$$S^{2-} + Cu^{2+} \longrightarrow CuS \downarrow$$

Metal Sulfide

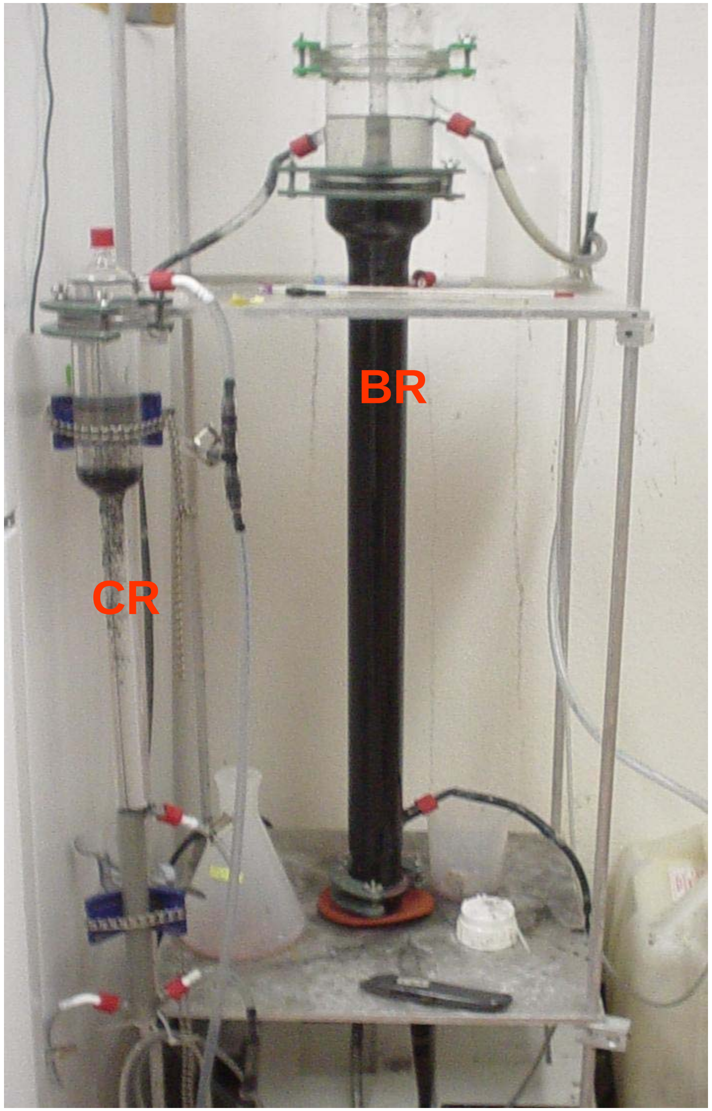
Metal sulfides: very low solubility products, eg. 10^{-36} for CuS

Materials and Methods



Schematic representation of the anaerobic bioreactor (BR)-crystallization reactor (CR) utilized in the treatment of copper

Materials and Methods



Anaerobic bioreactor (BR)-crystallization reactor (CR) utilized in the treatment of the simulated CMP wastewater

Bioreactor Study

Medium Components:

Compound	Concentration (mg/L)
Citrate	2667
Cu^{2+}	100
SO_4^{2-}	3600

↑ PERIOD I and II

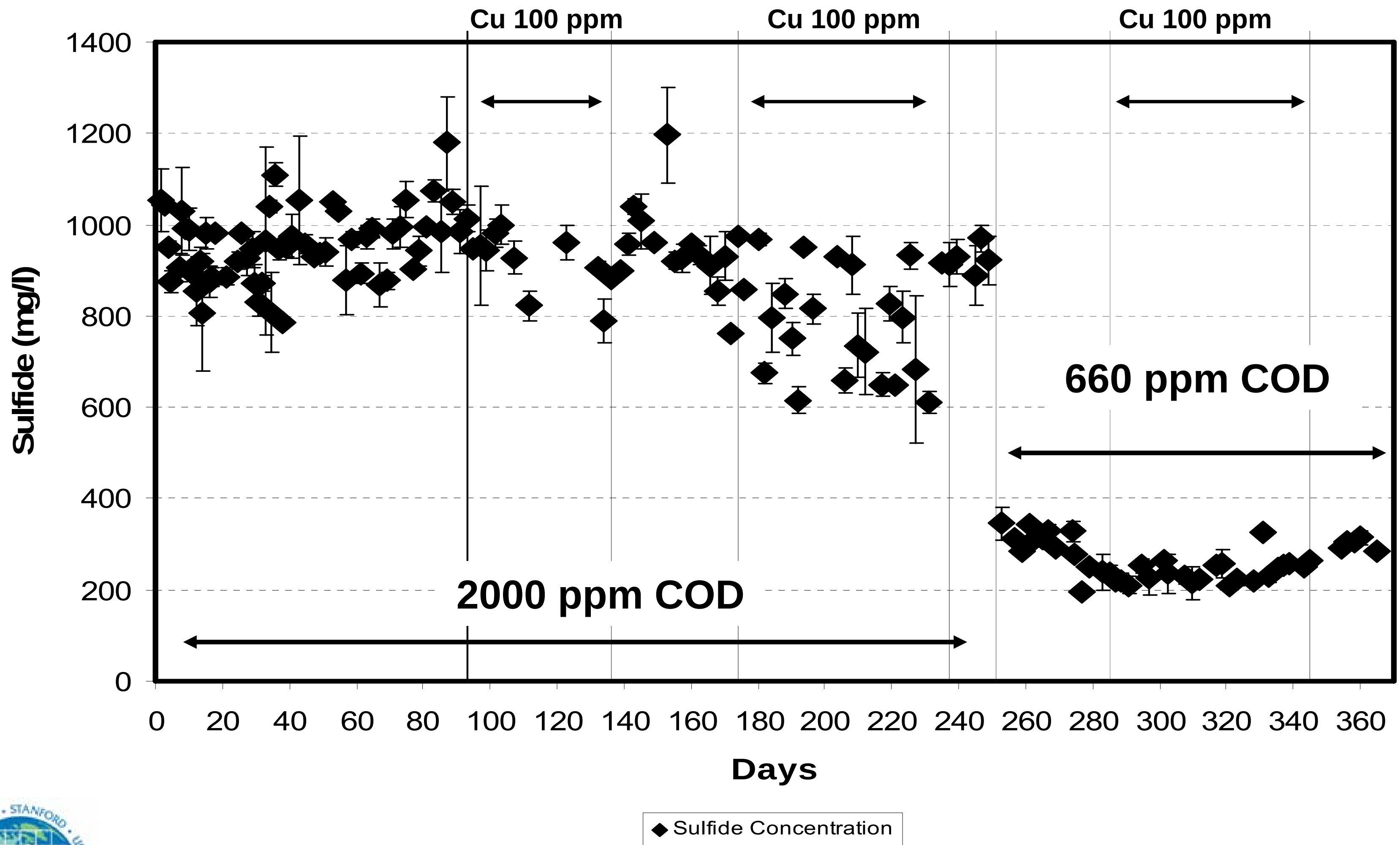
Operating Conditions:

- HRT = 8 hr
- T= 30° C
- Cu^{2+} fed in 3 different periods

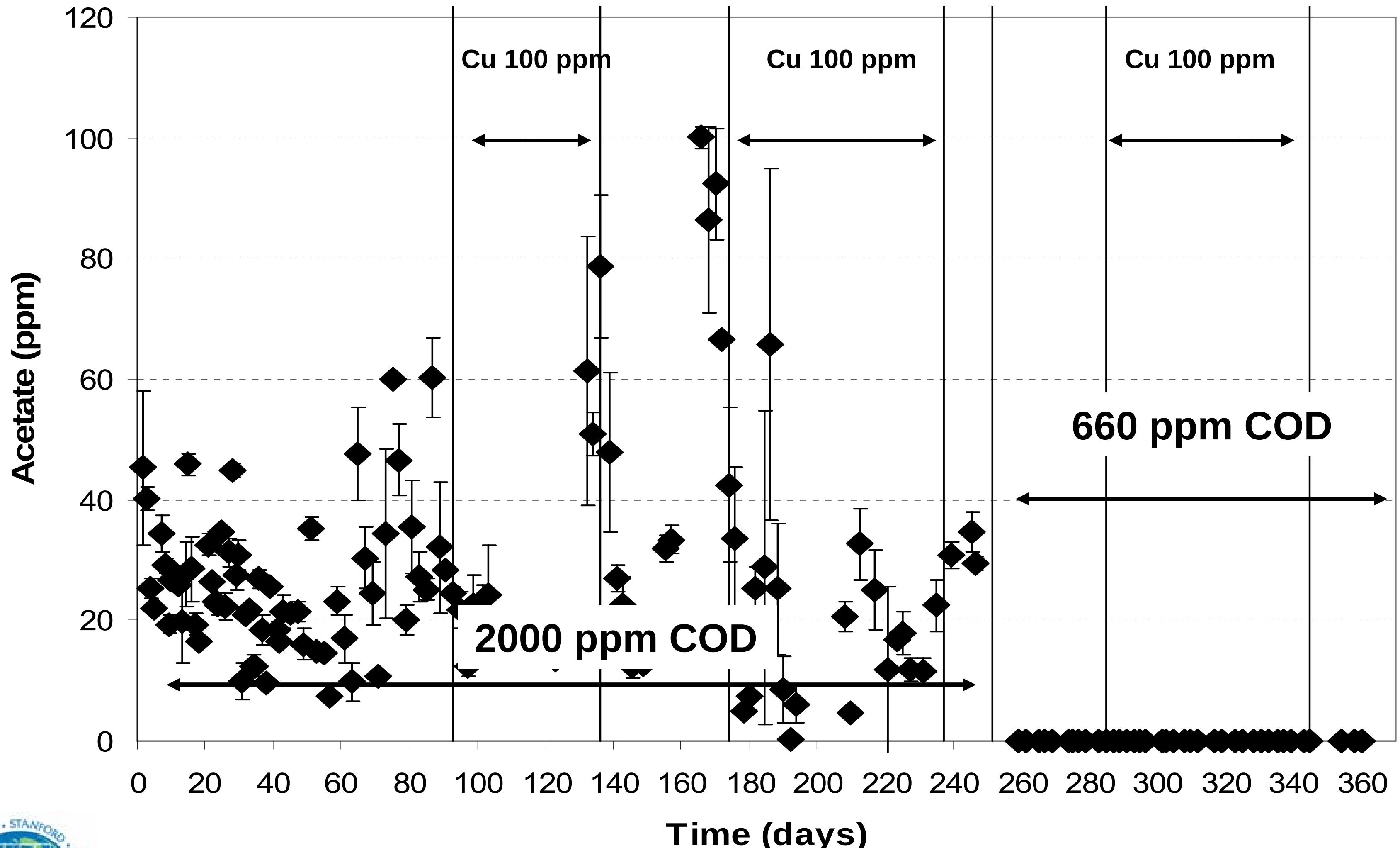
PERIOD III →

Compound	Concentration (mg/L)
Citrate	889
Cu^{2+}	100
SO_4^{2-}	1200

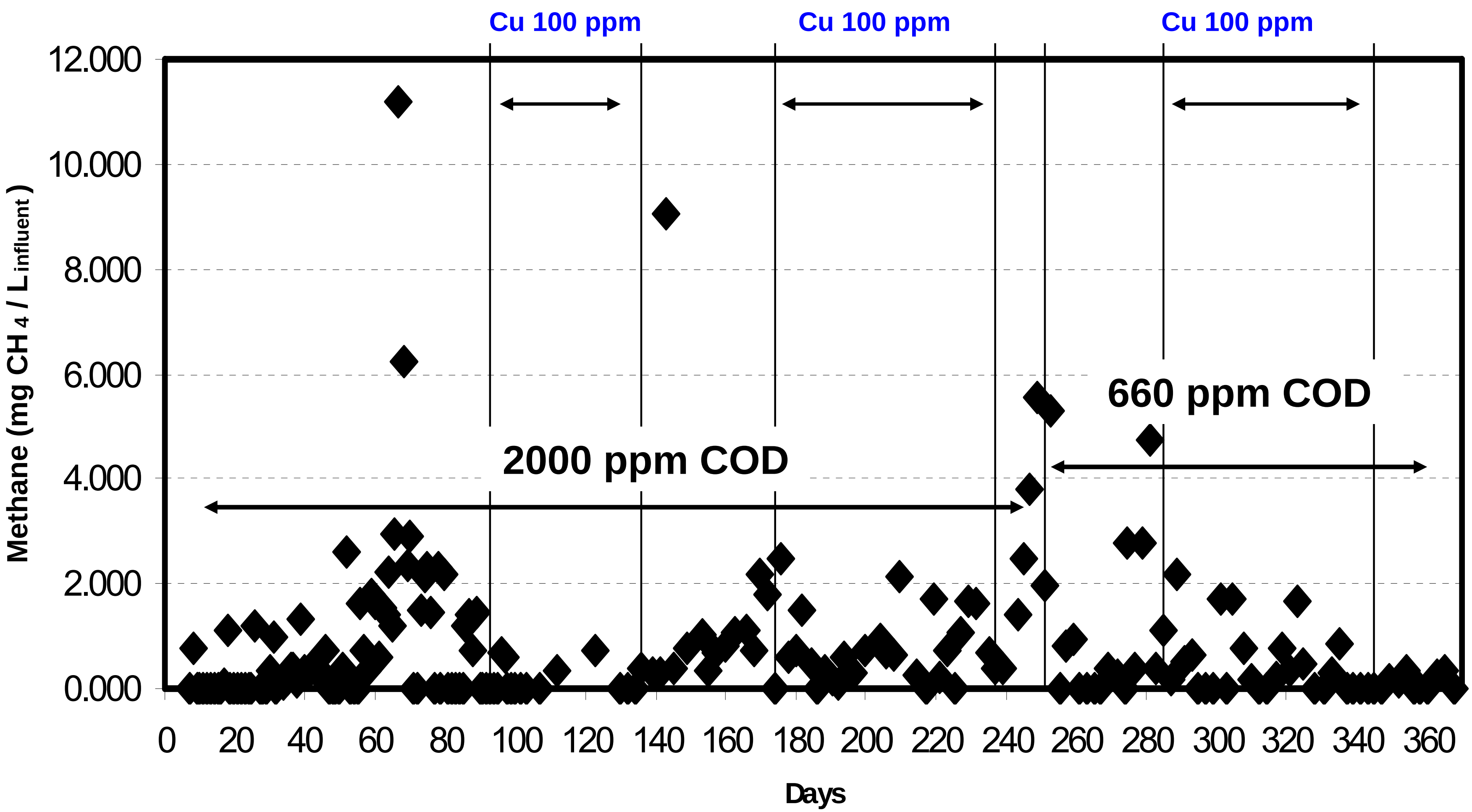
System Performance:
Sulfide Production



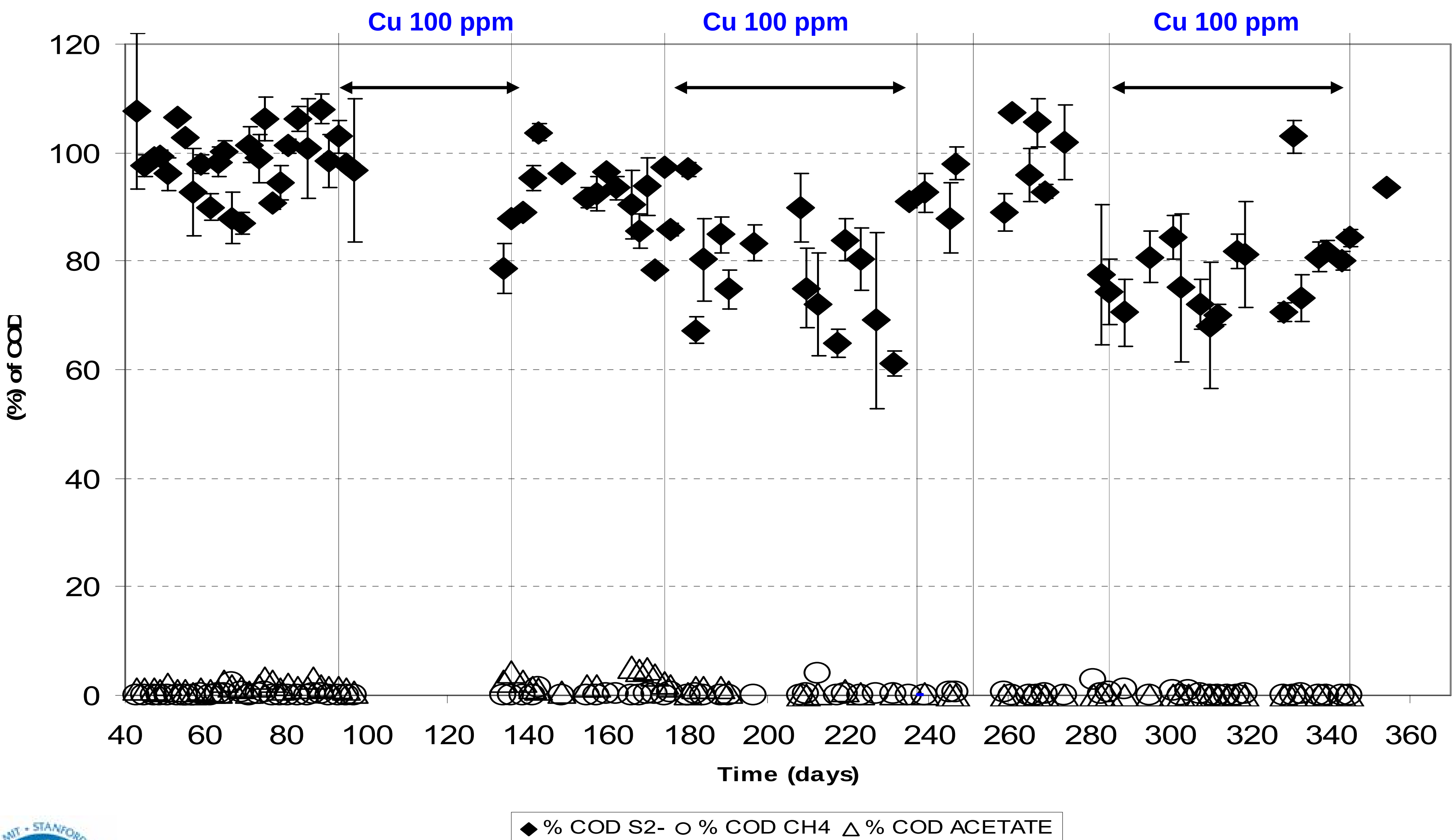
System Performance:
Acetate Residual Concentration



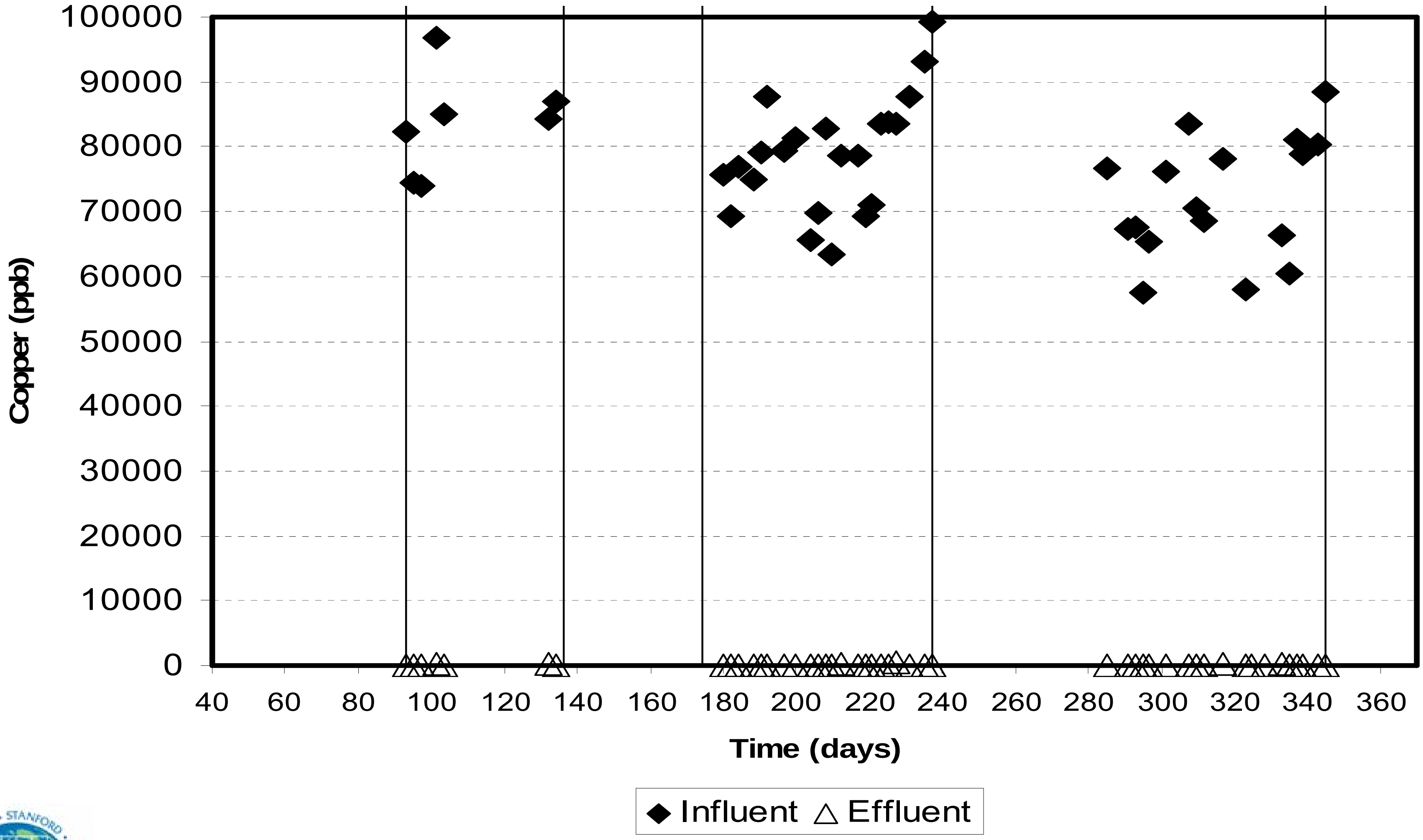
System Performance:
Methane Production



System Performance:
ThOD Removal Percentage

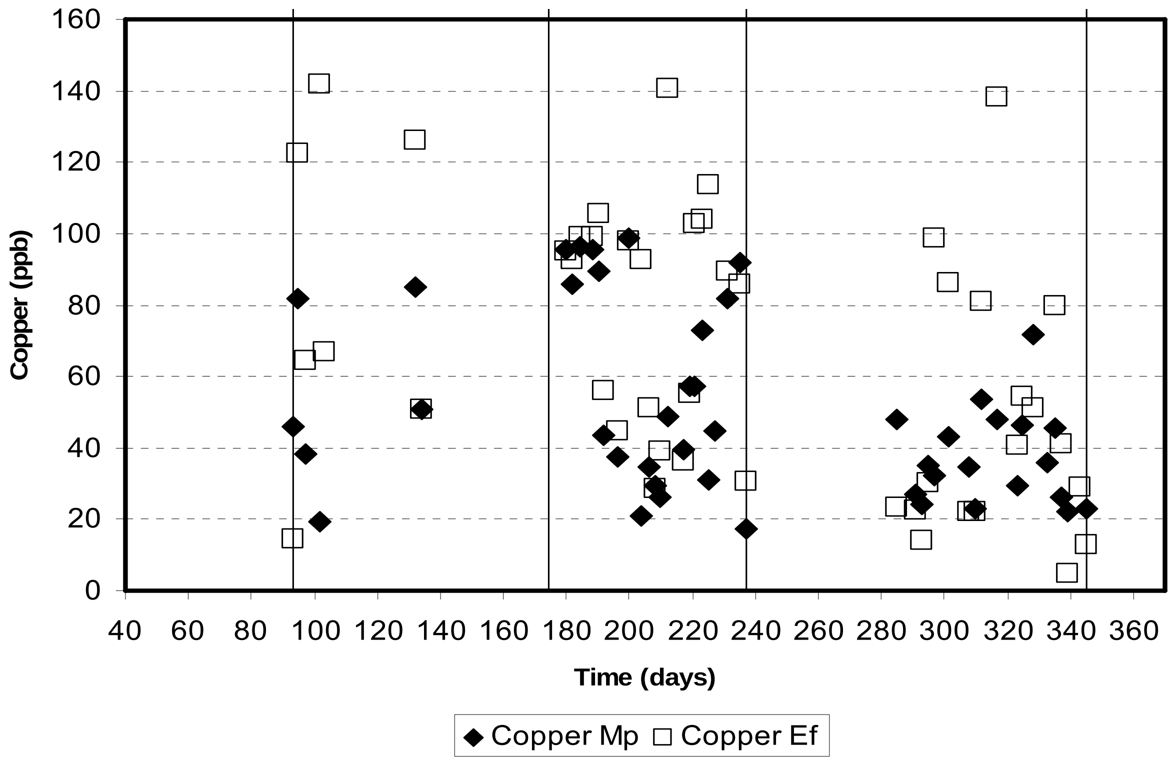


System Performance:
Removal of Copper

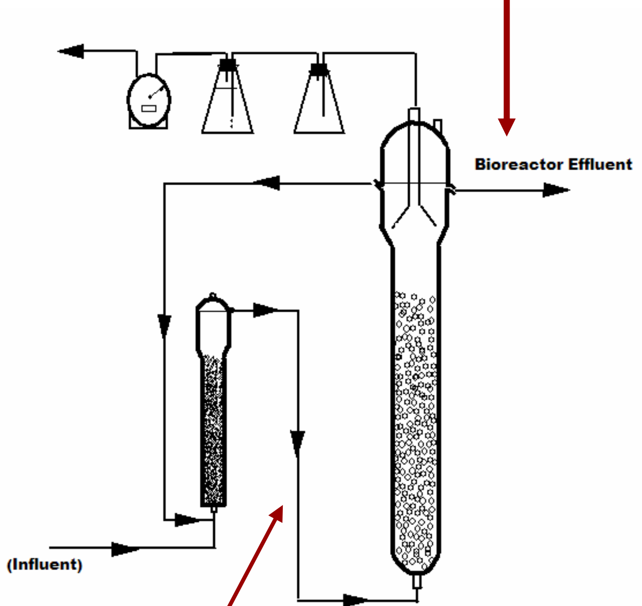


System Performance:

Soluble of Copper



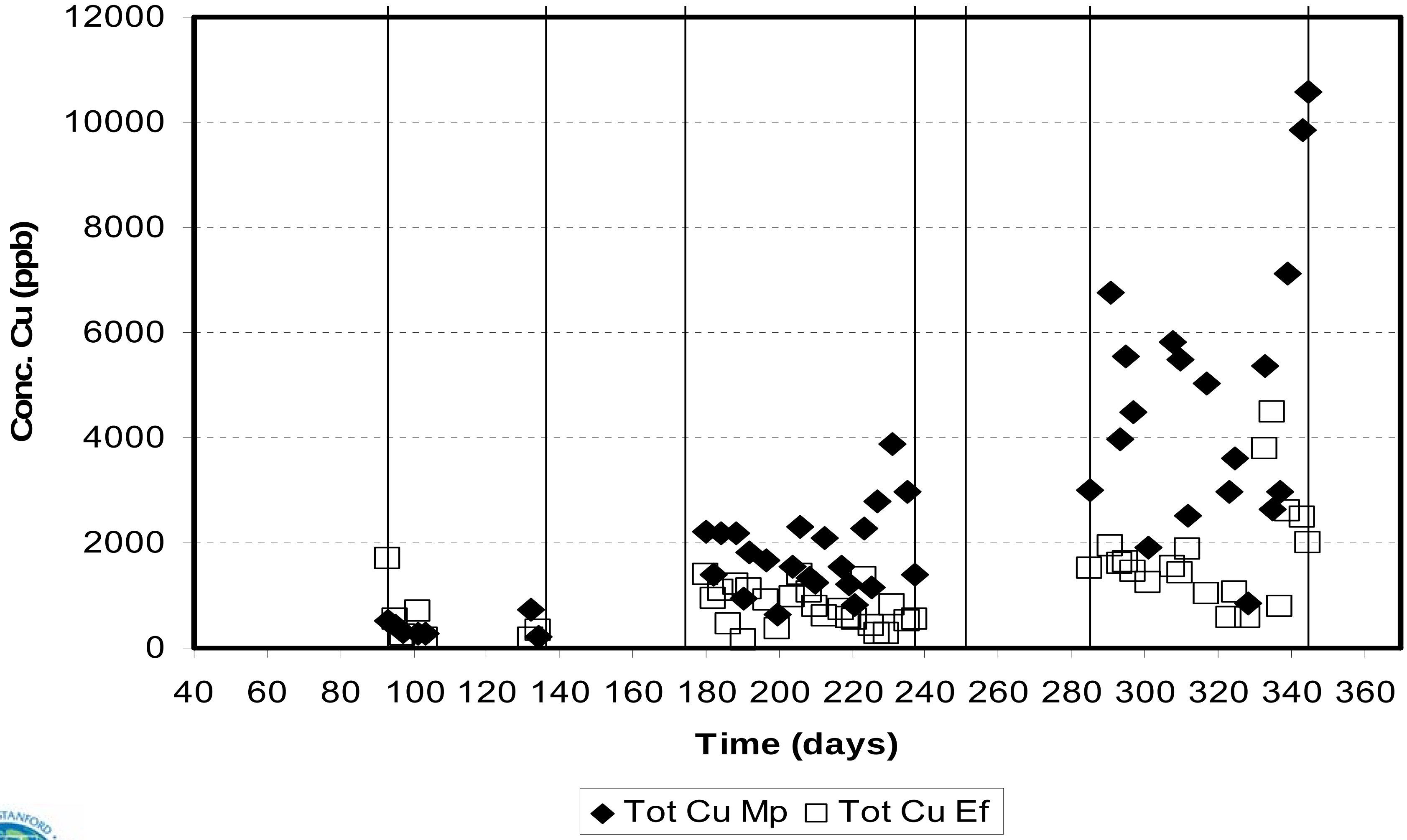
Ef= Effluent



MP= Middle Point

System Performance:

Total Copper

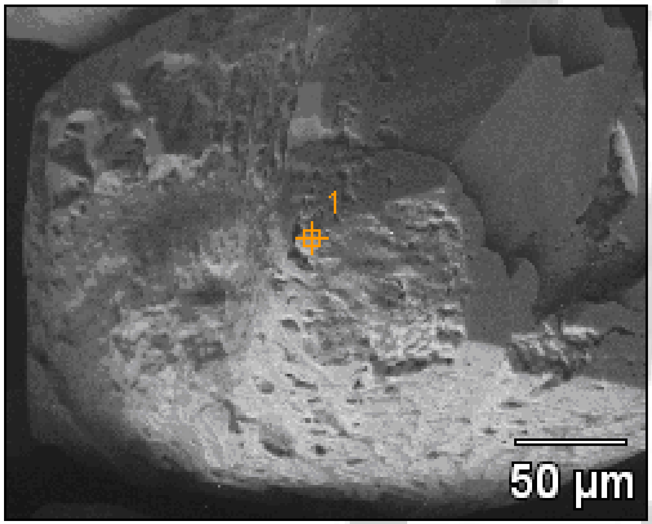


System Performance:

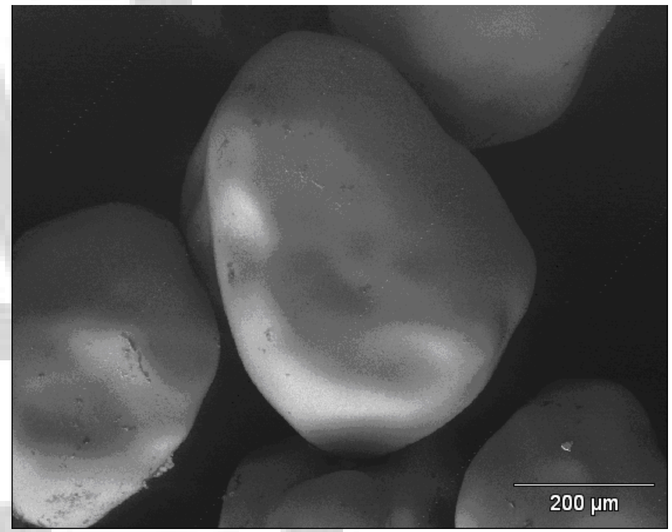
Removal of Copper

	Period I		Period II		Period III	
Cu^{2+}	Soluble	Total	Soluble	Total	Soluble	Total
Removal Efficiency CR	100.0 ± 1.6%	102.0 ± 9.5%	101.0 ± 1.4%	80.7% ± 12.0%	100.2 ± 1.3%	34.3 ± 50.3%
Removal Efficiency BR	-0.1 ± 1.7%	-2.9 ± 10.1%	-0.7 ± 1.5%	19.6% ± 13.3%	-0.3 ± 1.4%	63.2 ± 50.7%
Total Removal	100.0 ± 0.1%	99.3 ± 0.7%	99.9 ± 0.1%	99.0% ± 0.5%	99.9 ± 0.1%	97.5% ± 1.7%

Is Copper being recovered on Sand?



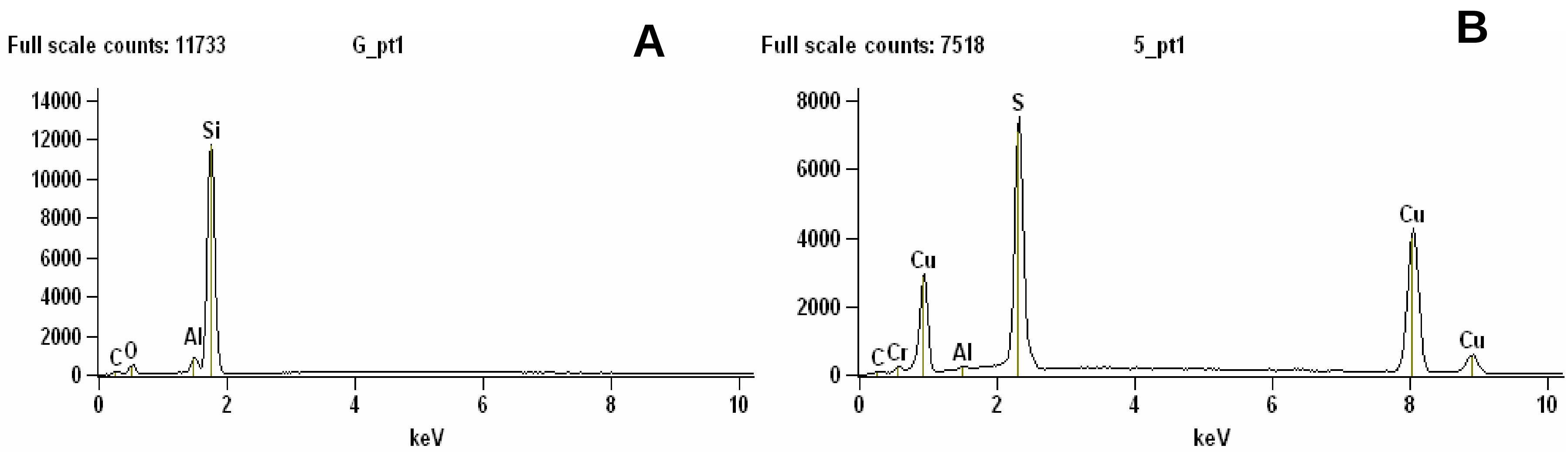
(a)



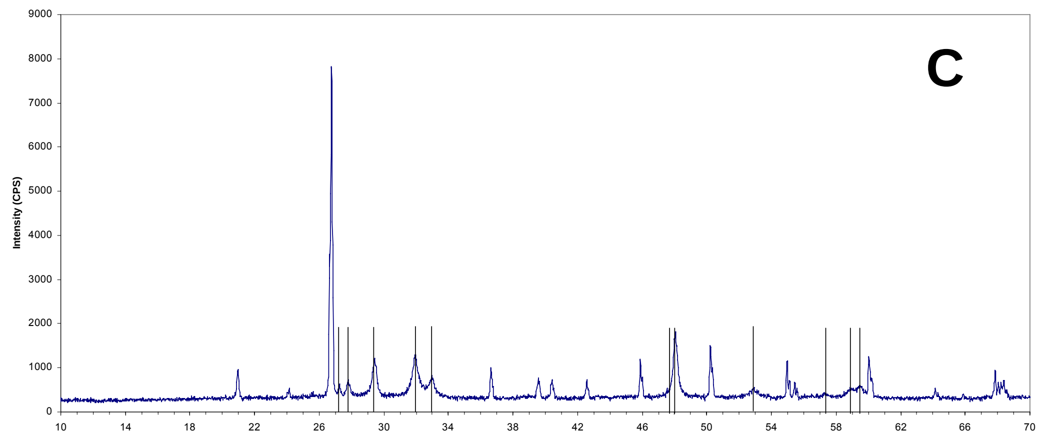
(b)

SEM images from sand. (A) Sand granule before treatment (B) Sand Granule evenly coated after treatment (influent = 100 mg Cu/l)

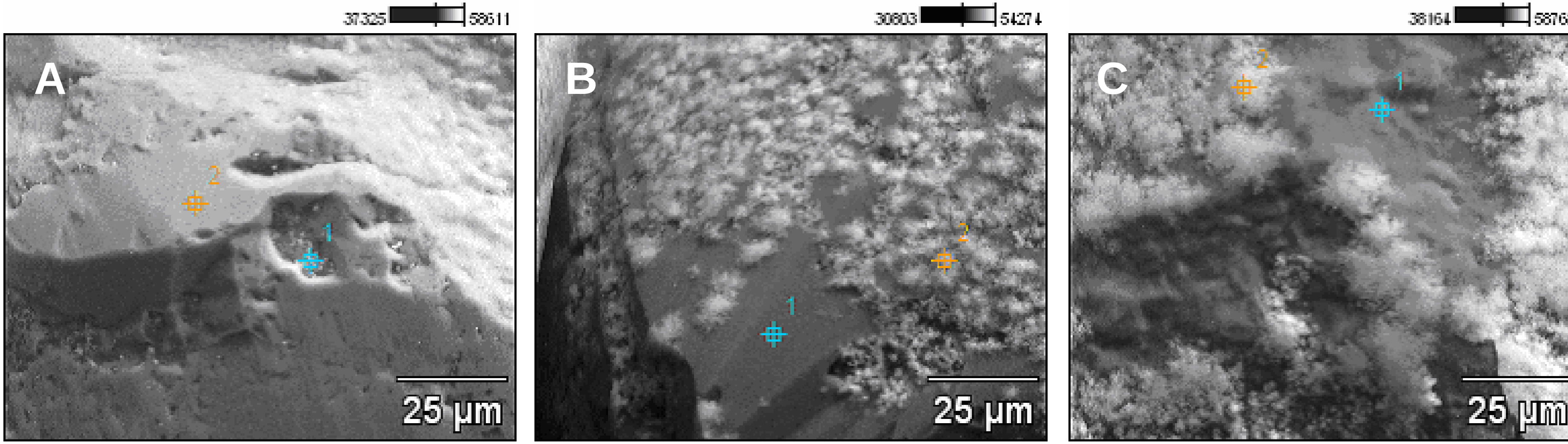
How is copper being recovered?



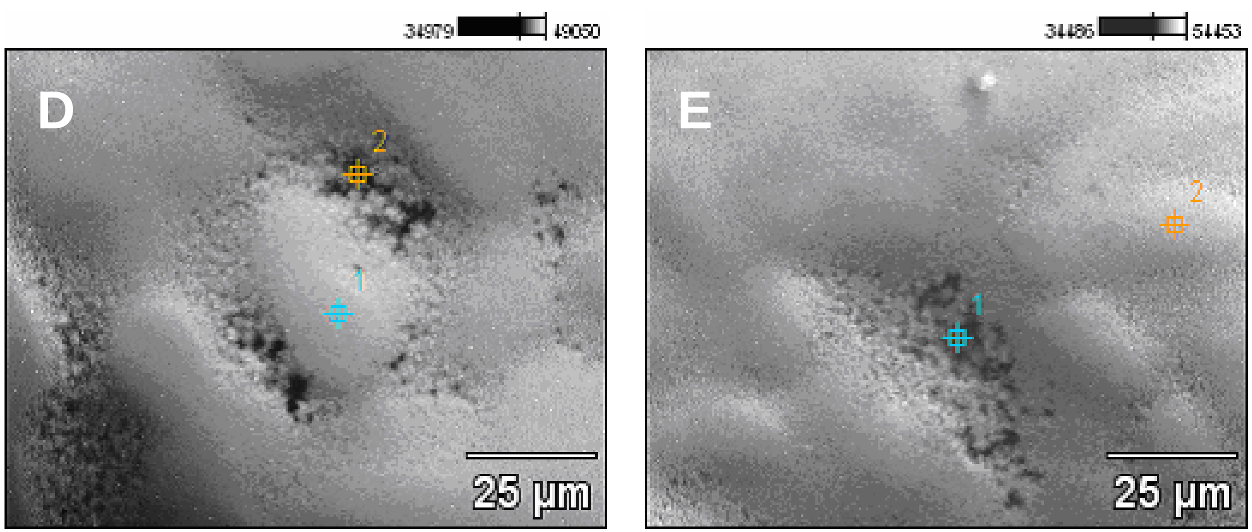
EDS from sand. (A) Sand granule before treatment (B) Sand granule evenly coated after treatment (influent = 100 mg Cu/l) (C) XRD image from sand, the peaks show the presence of ***covellite*** *(CuS)*



Crystal Growth in Sand

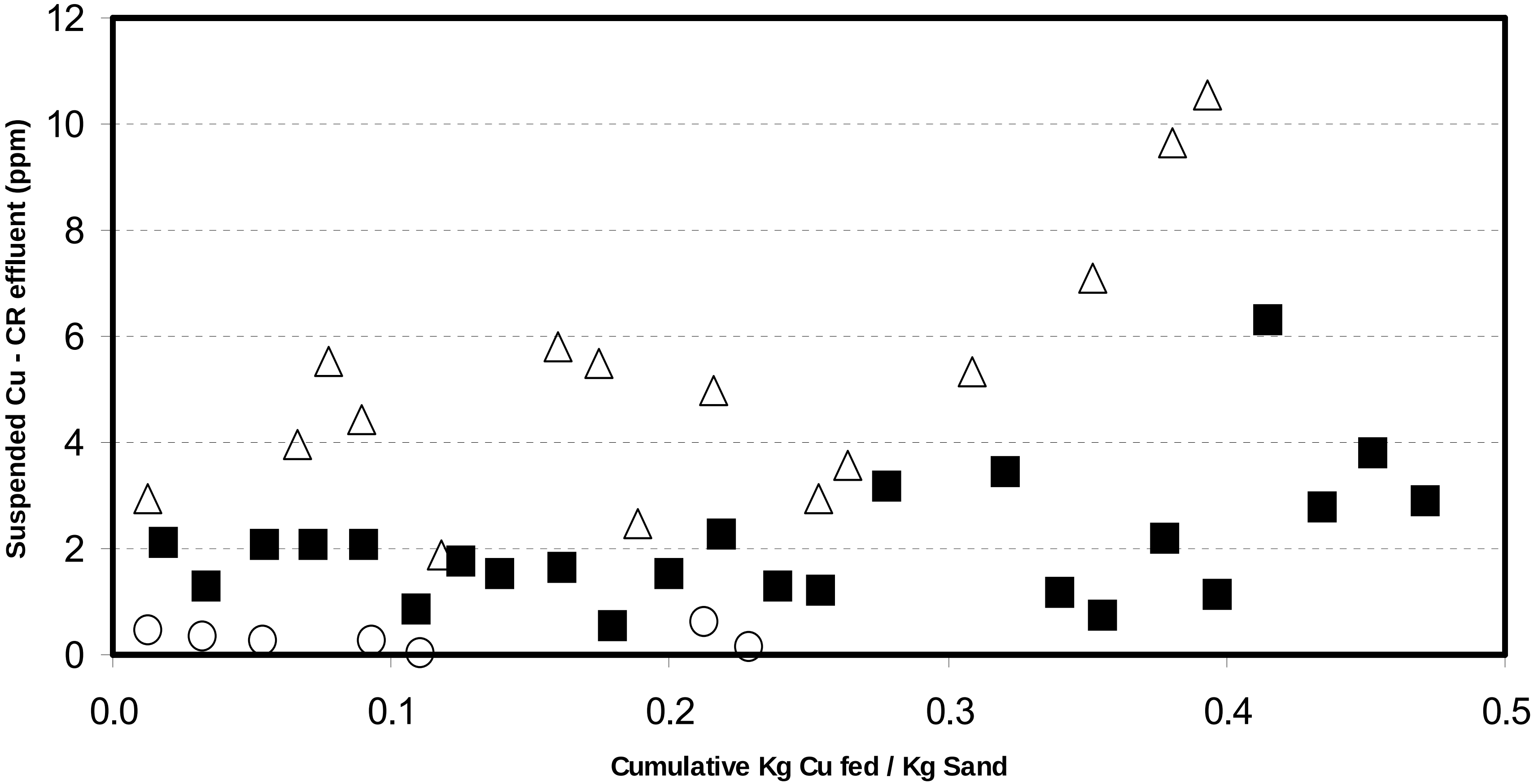


*EDS from sand. (**A**) Sand granule before treatment (**B**) Sand Granule after 24 h (**C**) Sand granule after 51 h (**D**) Sand granule after 1 week (E) Sand granule after 2 weeks. (100 mg Cu/L)*



System Performance:

Sand Retention Capacity



System Performance:
Copper Recovery on Sand

Mass Balance for Period II

Copper in Sand			Copper Fed		
Final Sand Mass	126.3	g	**Volume Treated**	499.96	L
Initial Sand Mass	75	g	**Average Cu Conc.**	0.79	g/L
Difference (CuS)	51.23	g	**Removal Efficiency**	80.7%	
Cu^{2+} recovered	34.07	g	**Cu^{2+} Fed**	31.8	g

Percentage Recovered in Sand 107%

Conclusions (I)

- Treatment of wastewaters containing citrate and Cu is feasible in a crystallization reactor – sulfate-reducing bioreactor system.

- Organic removal efficiencies above 90% can be achieved by the system even at influent Cu concentration > 75 mg/L.

- No significant copper inhibition was observed in the bioreactor. Soluble Cu(II) was successfully removed by the crystallization reactor, avoiding toxicity and process failure in the bioreactor.

- Total removal efficiencies in the system, for soluble and total copper had average values of 99.9% and 98.0%, respectively

Conclusions (II)

- Total Cu removal efficiencies of 100% for period I, 80% for period II, and 34% for period III were measured for the crystallization reactor.
- Sand granules served as nucleation points for copper sulfide.
- Covellite (CuS) was the main form of copper sulfide found on the sand surface.

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