Copper Research Update

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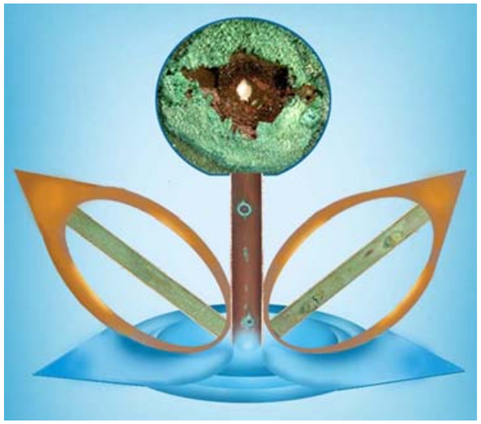
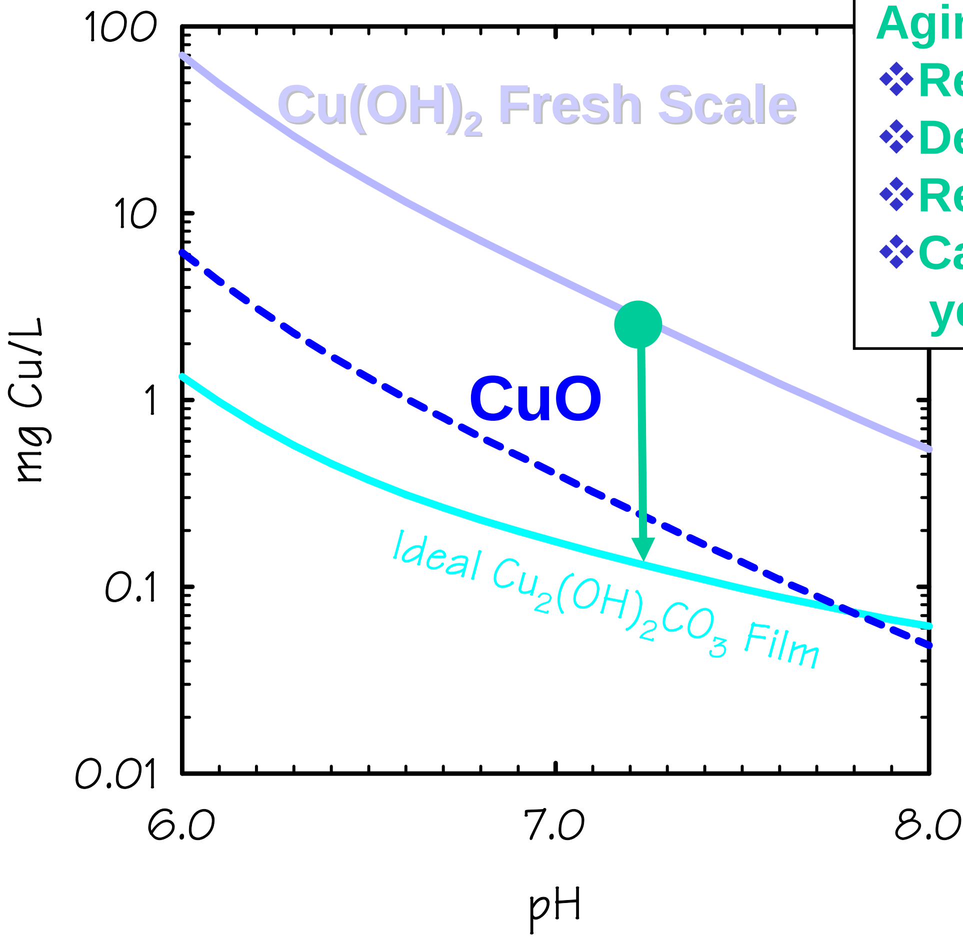
Copper Research Overview

- Role of copper plumbing age on copper release
- Impact of water chemistry on copper solubility
  - *pH*
  - *DIC*
  - *phosphate*
- Copper pitting corrosion and pinhole leaks
- Current research activities



Role of Plumbing Age

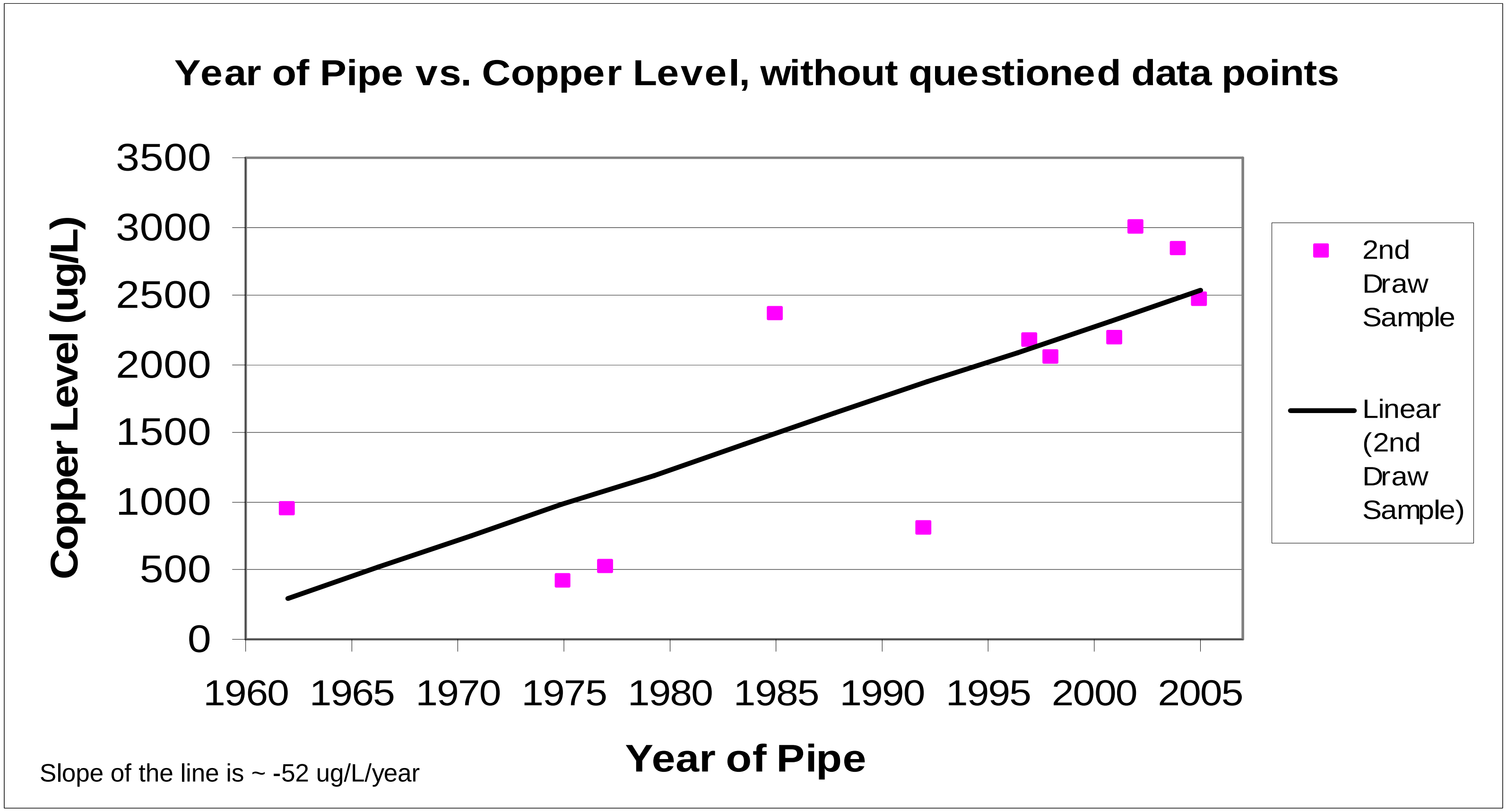
Evolution of Scale Model for High DIC, Low pH Waters



Aging Process (in theory):

- Recrystallizing
- Decreasing surface area
- Reacting with CO_3 or HCO_3^-
- Can take 20, 30 or more years with high DIC

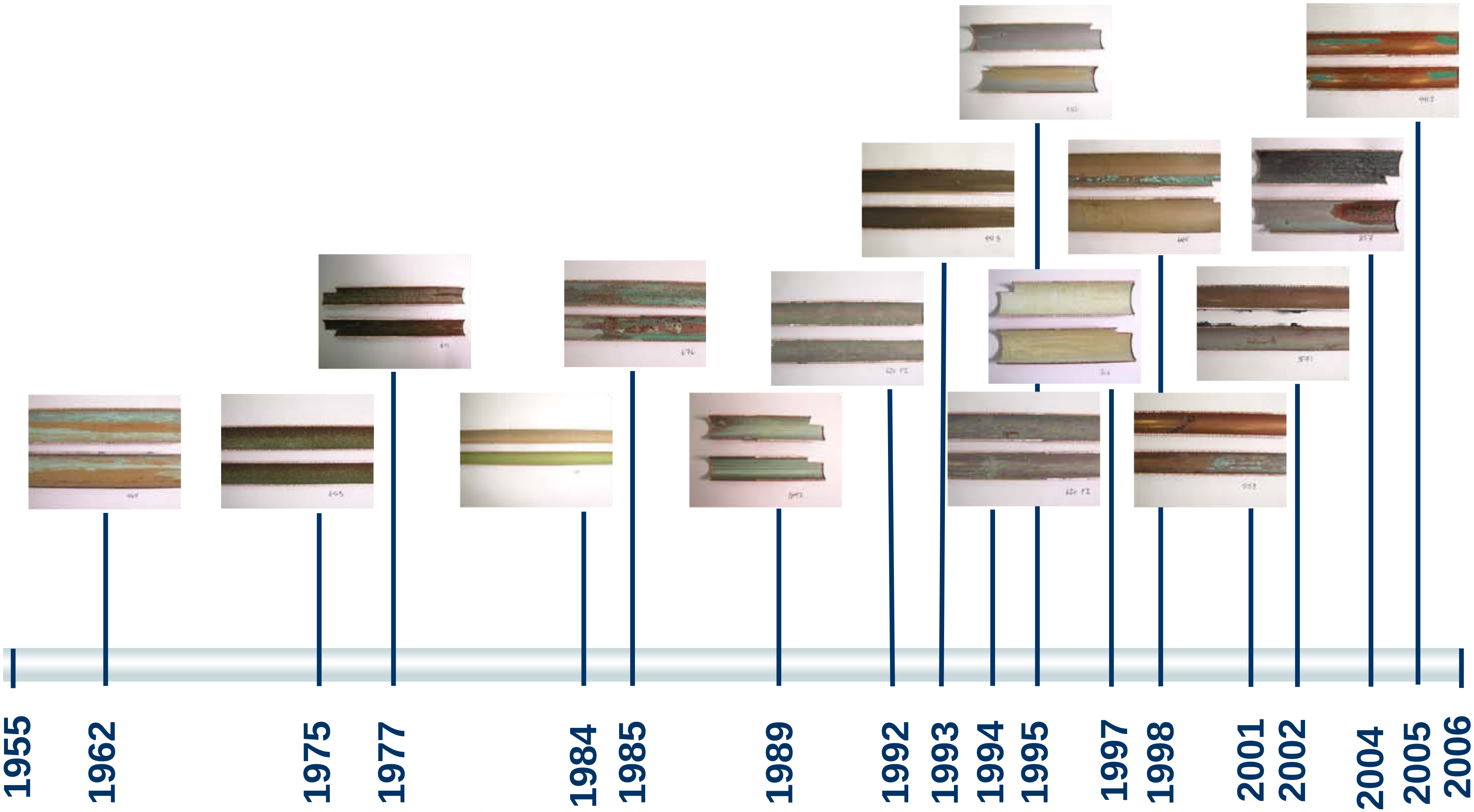
Impact of Plumbing Age on 2nd Draw Copper Concentrations



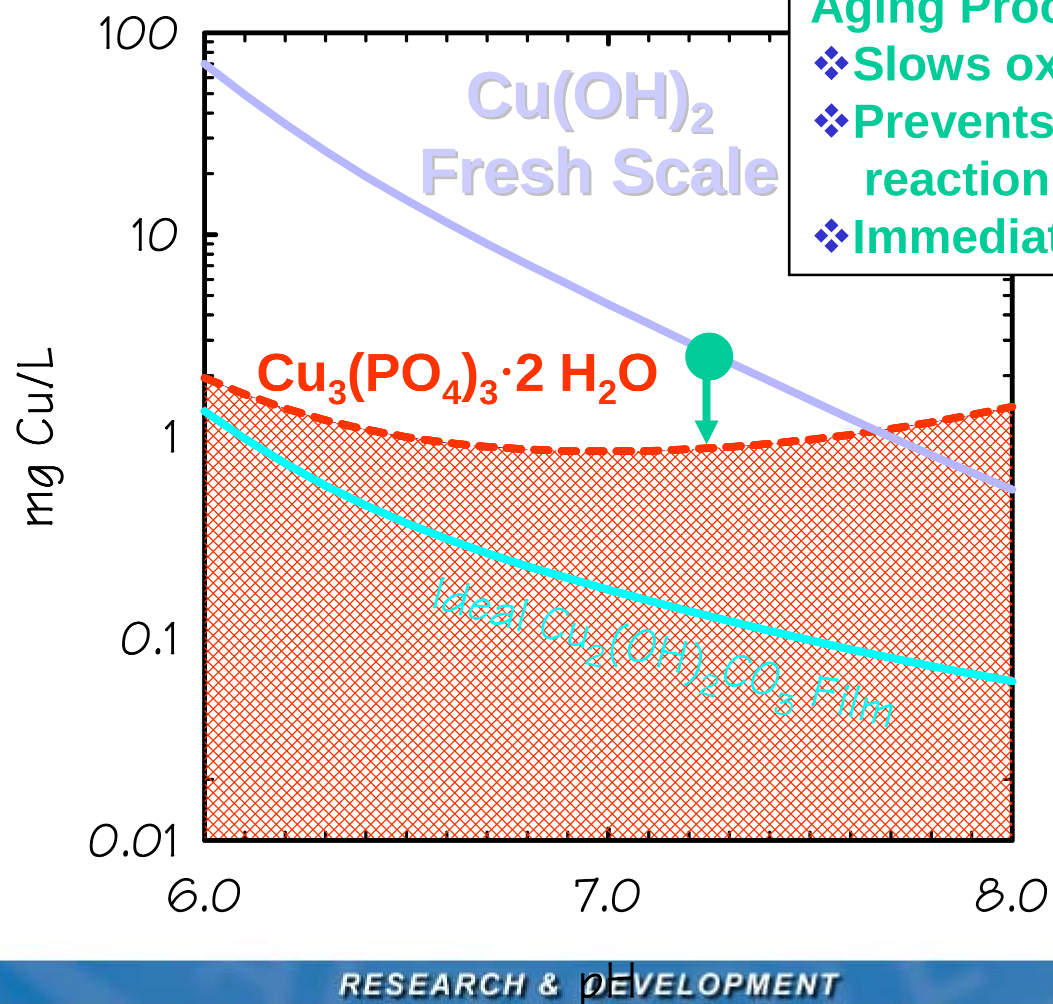
Data from M.S. Thesis of N. Turek, "Investigation of Copper Contamination and Corrosion Scale Mineralogy in Aging Drinking Water Distribution Systems", AFIT, 2006.

Copper Pipe Surface with Age

(from Turek, 2006)



Orthophosphate Effect on Scale Evolution at High DIC

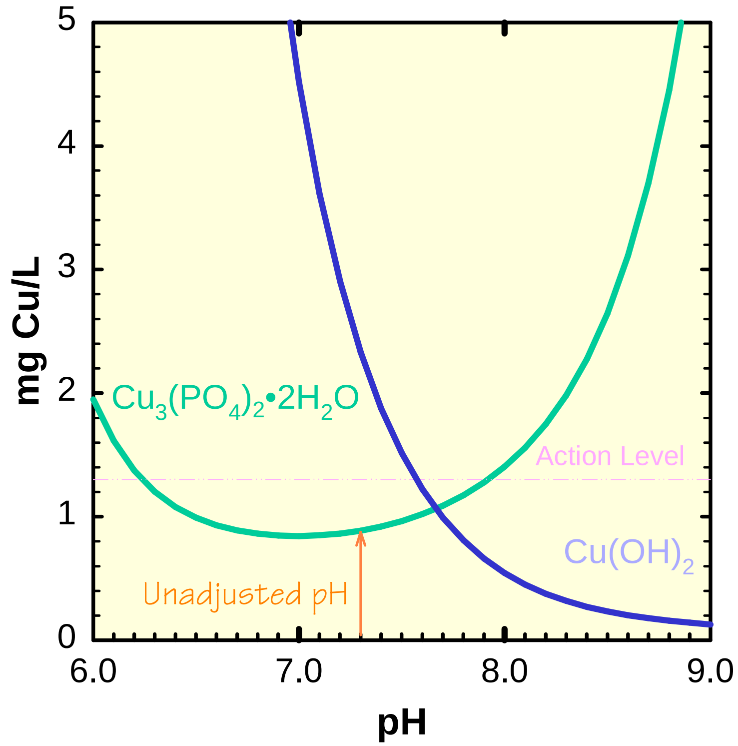


Aging Process is Impeded:

- Slows oxidation
- Prevents or drastically slows reaction with CO_3^{2-} or HCO_3^-
- Immediate benefit

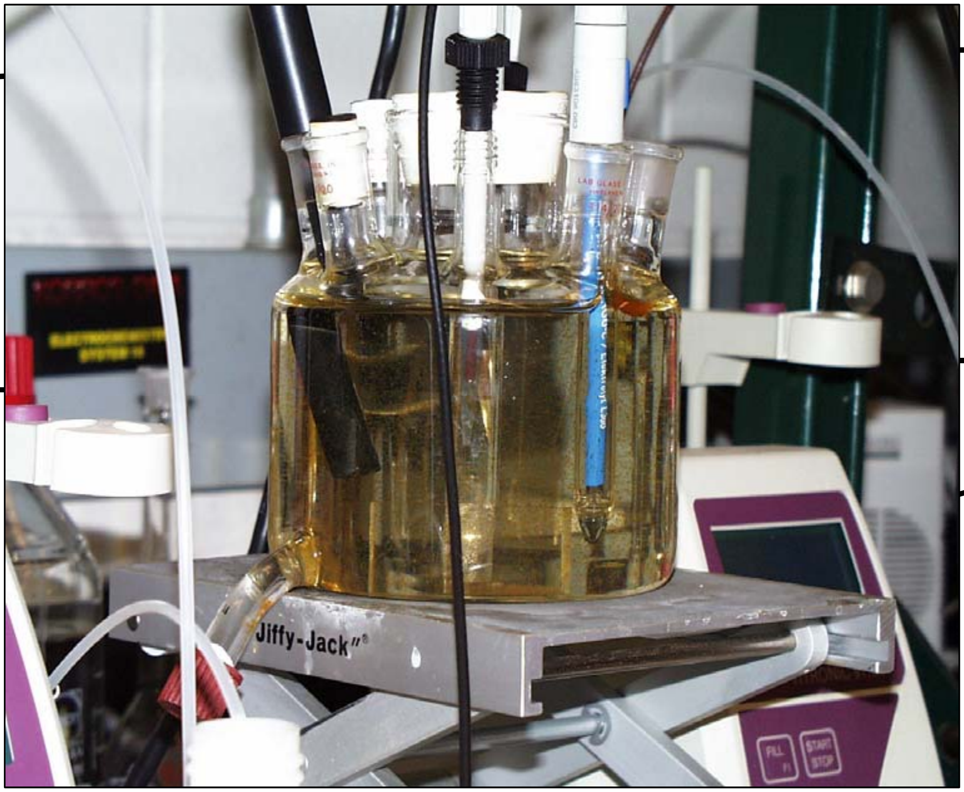
Theoretical Effect of Phosphate on Copper

3.3 mg PO_4/L at DIC=63 mg C/L

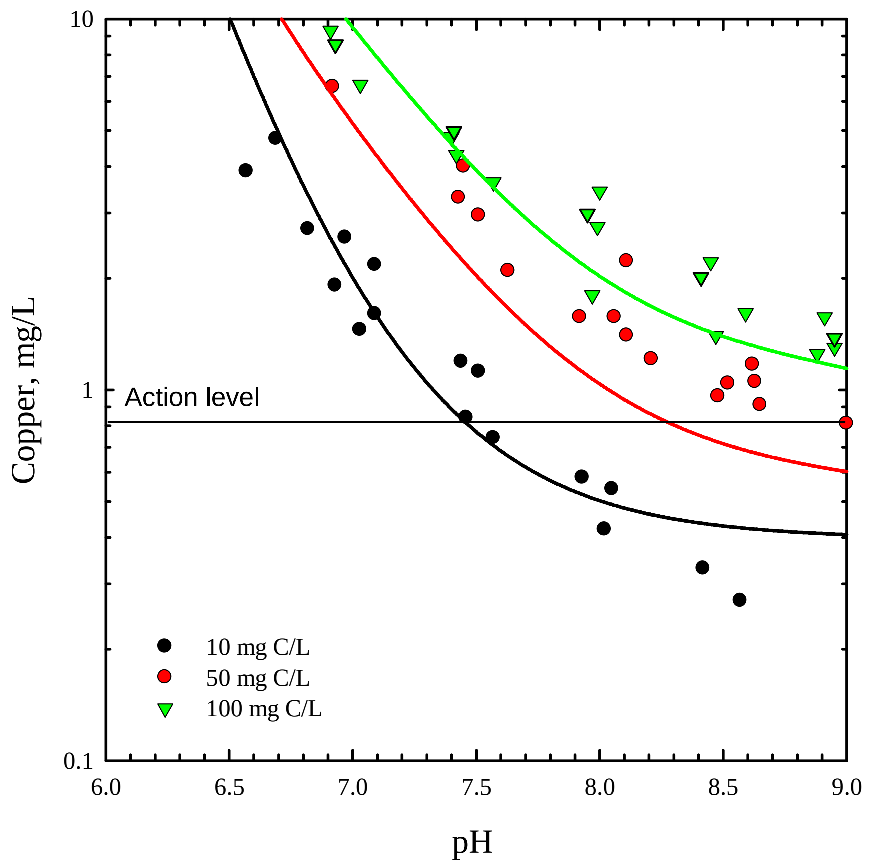


Impact of Water Chemistry on Cu(II) Solubility

Particle Generation Reactor

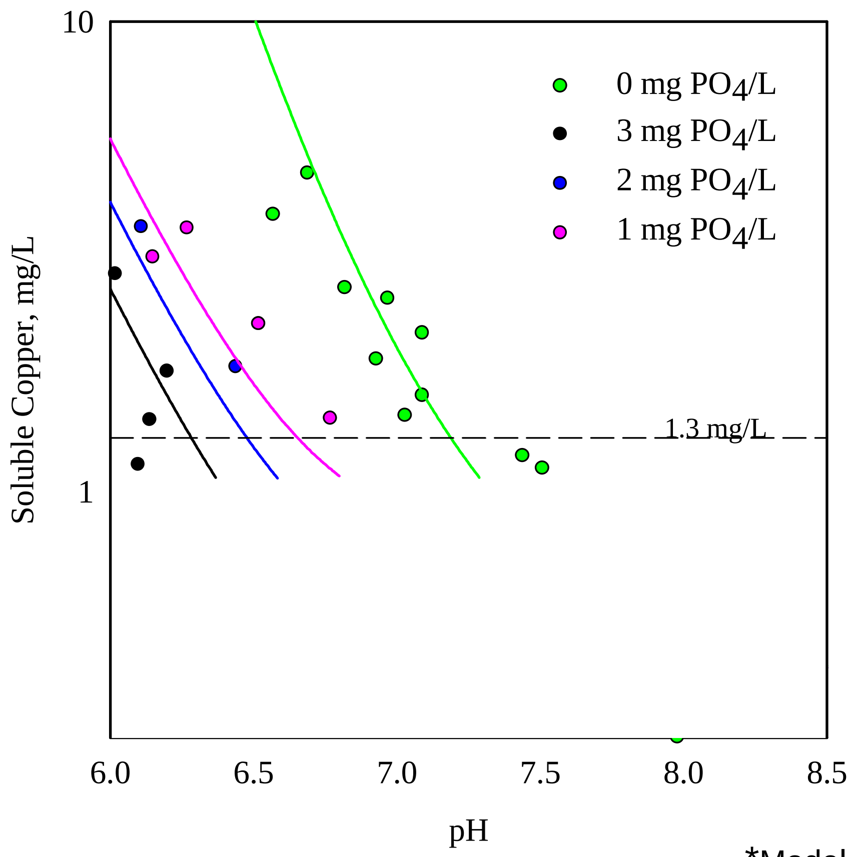


Effect of DIC and pH on Copper Solubility (23ºC)*



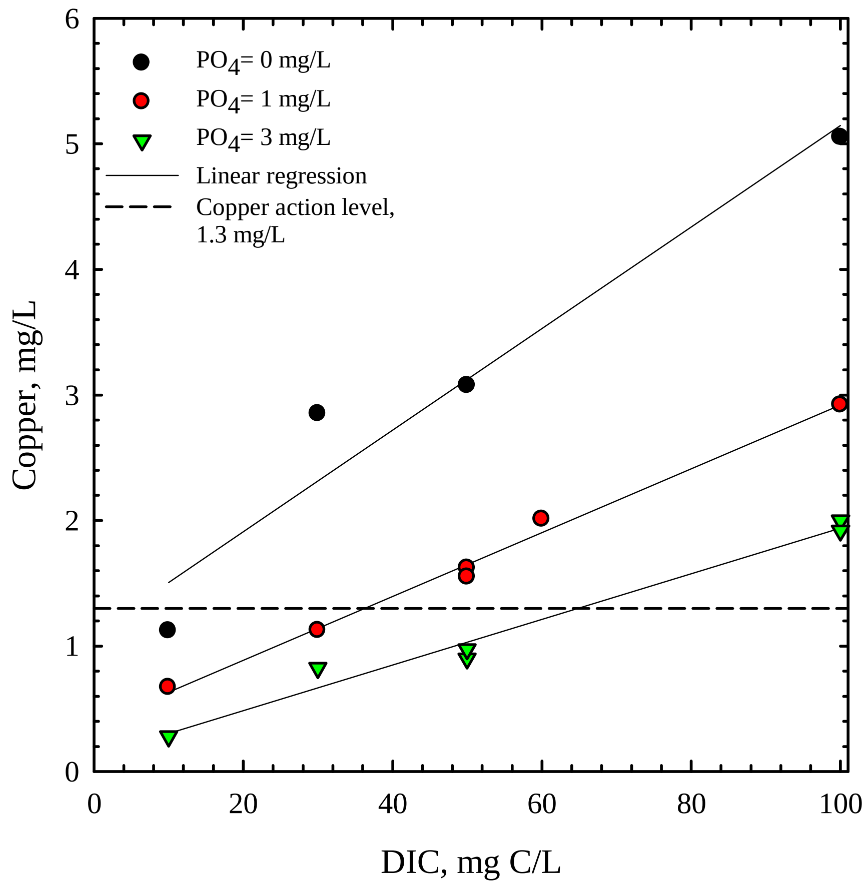
* Model predictions based on $Cu(OH)_2$

Effect of Orthophosphate and pH on Copper Solubility (23°C, 10 mg C/L)



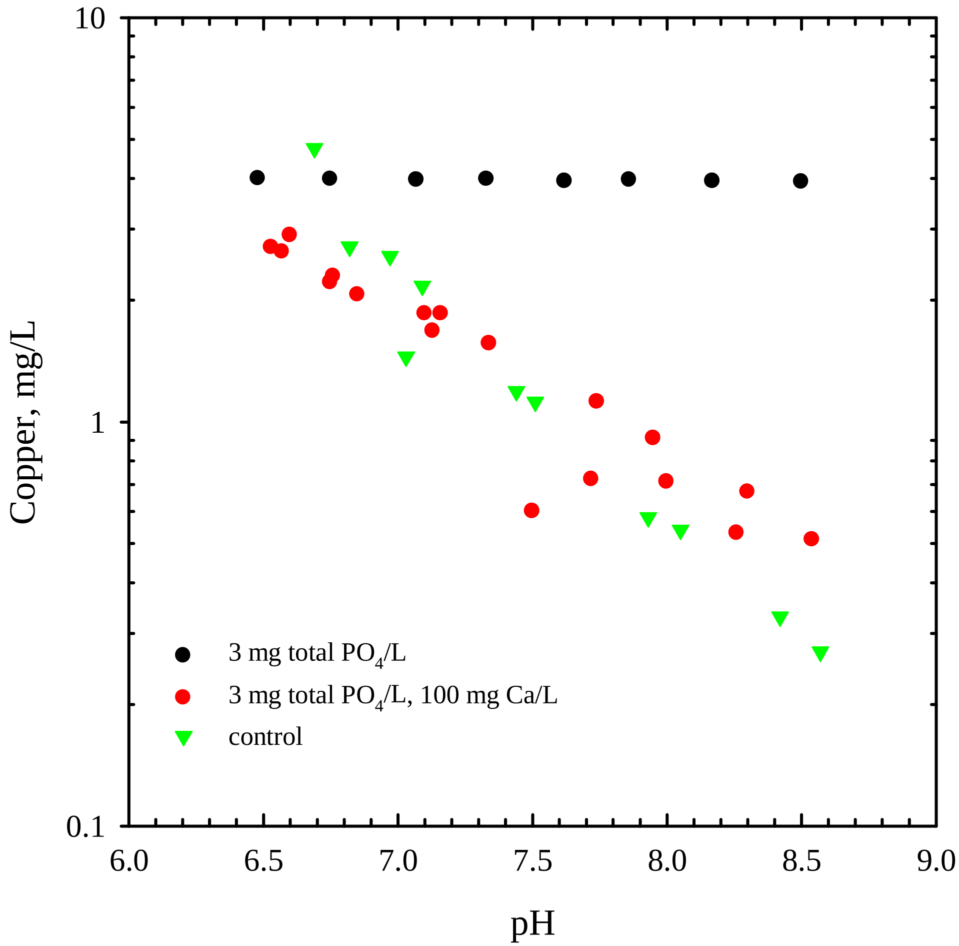
*Model predictions based on $Cu_3(PO_4)_2 \bullet 2H_2O$ and $Cu(OH)_2$

Effect of Orthophosphate and DIC on Copper Solubility (23^{o}C, pH 7.5)*

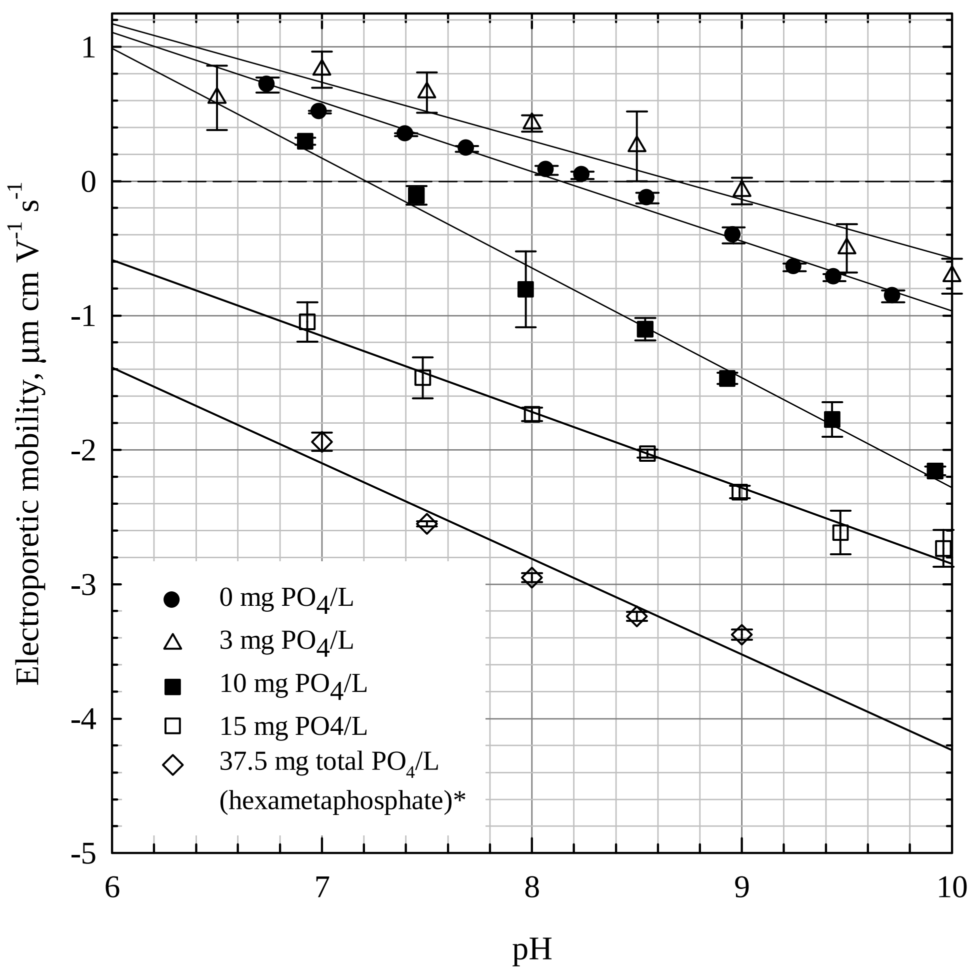


***Based on $Cu(OH)_2$**

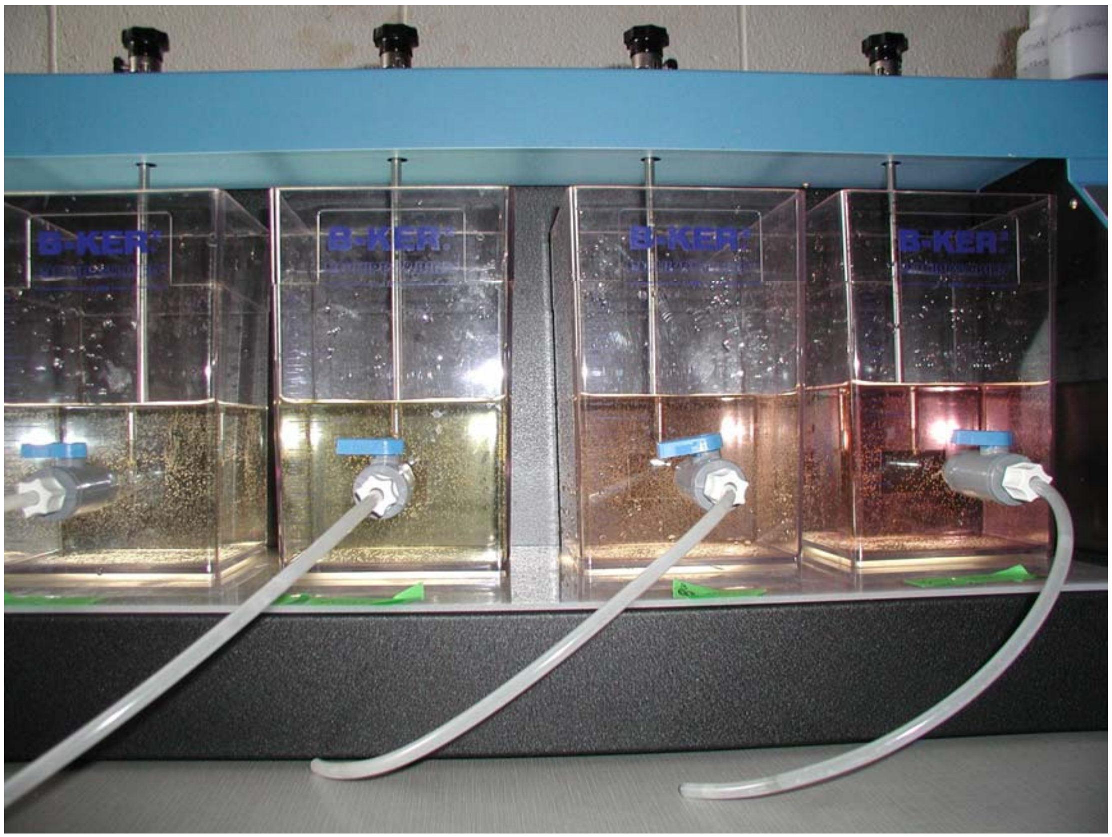
Effect of Polyphosphate and pH on Copper Solubility (23^{o}C, 10 mg C/L)



Effect of Phosphate and pH on the EPM of Fresh Copper Solids (23^{o}C, 10 mg C/L)

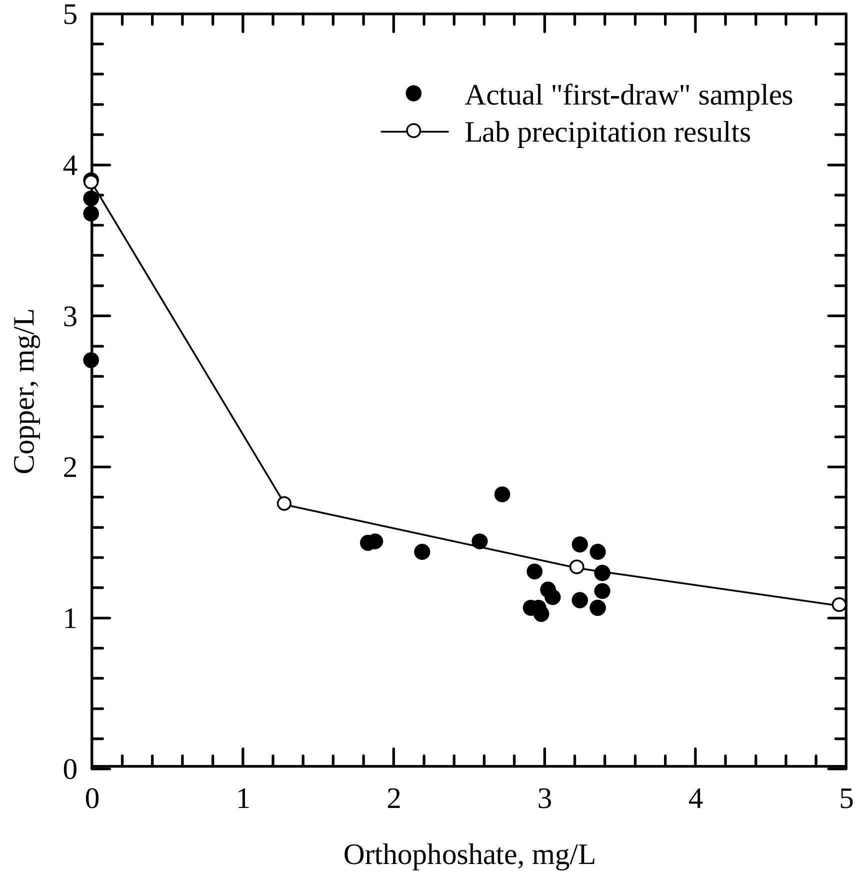


Value of Jar Tests in Predicting Copper Solubility in the Field



Value of Jar Testing to Predicting Copper Solubility in the Field

Case Study (pH= 7.4, 73 mg C/L DIC)



Copper Pitting and Pinhole Leaks

Copper Pitting

The consequences…

- *Costly repairs*
- *Undetected leaks in walls and/or basements*
- *Pinhole leaks*
    - Mold and mildew
    - Liability issues

- ***Note:*** *Copper pitting does* not *cause high copper levels at the tap.*

Pinhole Leaks

Result of copper pitting

Copper Pitting Corrosion
Reasons

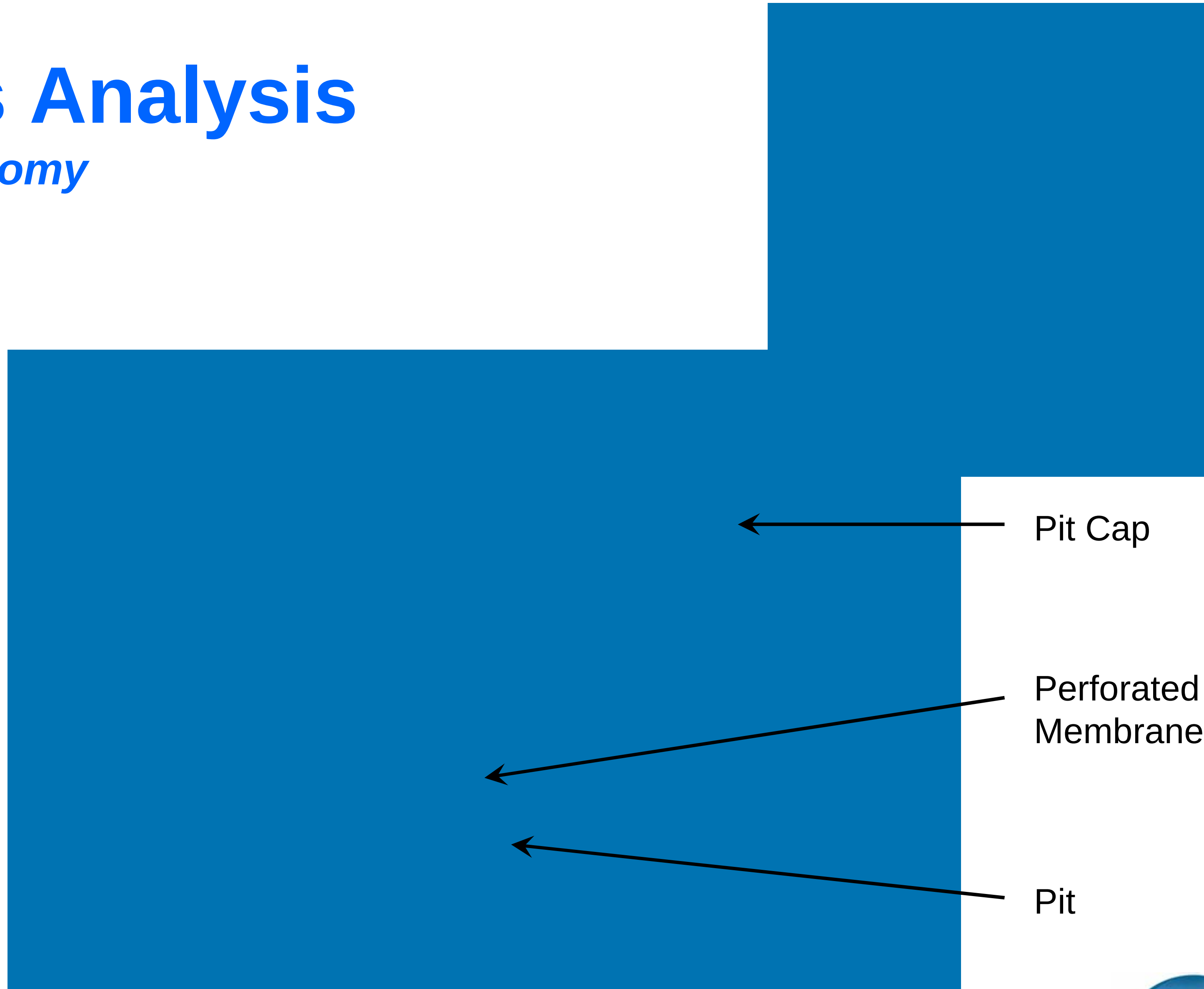
- Defects in material
- Organics left from pipe manufacturing
- Plumbing practice
- Particles
- Microorganisms
- Electrical Grounding
- Water flow
- Water quality (DIC, pH, sulfate, chloride, others)
- Others

Solids Analysis

Pipe cross-section

Solids Analysis

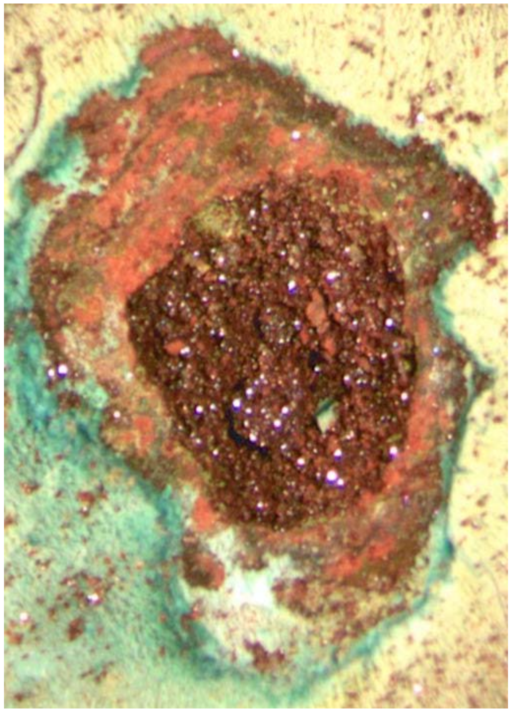
Cu pit anatomy

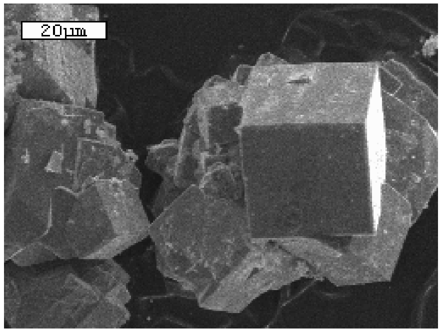


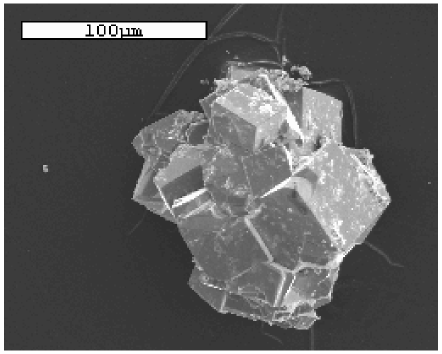
Solids Analysis

Pit- cuprite crystals

Pits are loosely packed with cuprite crystals beneath the permeable membrane



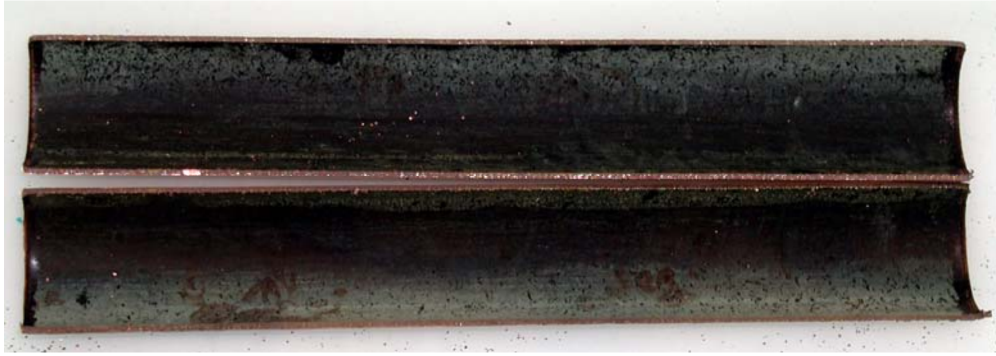




Solids Analysis

"Non-problem" sites: Hot vs. Cold Water Plumbing

Hot Water Plumbing



Cold Water Plumbing

Pilot Scale Research

Copper Recirculation ("Recirc") Study

- Early 1990's, EPA research was conducted to study copper release (uniform corrosion)
- Foundation for current thinking on copper levels at the consumer's tap
- Unintentionally, some experimental conditions produced localized corrosion which was attributed to water chemistry
- Synthetic waters used in most experiments- water quality closely controlled

Pilot Study- Copper Recirc Study

Experimental system

Pilot Study- Copper Recirc Study

Water chemistry from lab experiments

pH	SO_4 (mg/L)	pH	Temp	Ca	Cl	Cl_2	SO_4	TIC
7	0	7.02	22.6	4.7	61	0.63	3.9	10.4
	5	7.00	22.8	4.3	66	0.65	6.8	9.9
	50	6.99	22.9	4.4	63	0.63	49.2	10.2
	150	7.00	22.8	4.4	66	0.59	150.2	9.8
8	0	7.98	23.0	3.8	56	0.56	0.2	10.5
	5	7.99	23.2	5.0	60	0.59	3.8	10.4
	50	7.99	23.1	4.9	53	0.62	50.2	10.1
	150	7.98	23.0	4.9	53	0.72	148.2	10.4
9	0	8.98	22.9	5.3	28	0.65	0.1	10.8
	5	8.97	23.1	4.9	28	0.66	4.7	10.5
	50	8.98	23.0	4.9	26	0.78	47.7	10.3
	150	8.98	22.8	5.0	23	0.81	143.5	10.3

Pitting

* All units are in mg/L, TIC is in mg C/L units

Problem real waters:

Florida water: pH= 8.5 to 8.9 , SO_4= 121 mg/L, Cl=47 mg/L, TIC= 9.8 mg C/L

Ohio water: pH= 8.9, SO_4= 120 mg/L, Cl=64 mg/L, TIC= 9.8 mg C/L

Pilot Study- Copper Recirc Study

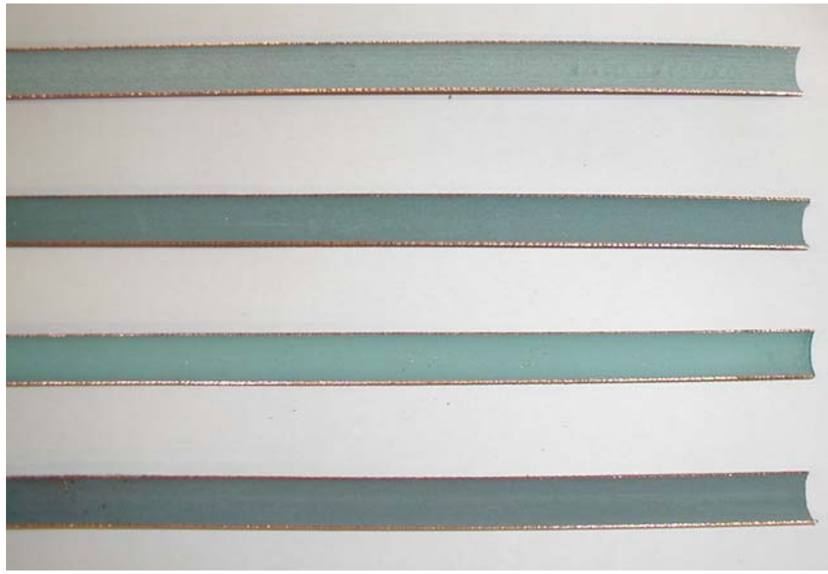
Pipe cross-section at pH 7

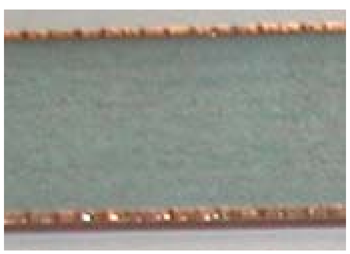
0 mg $[SO_4]$/L

5 mg $[SO_4]$/L

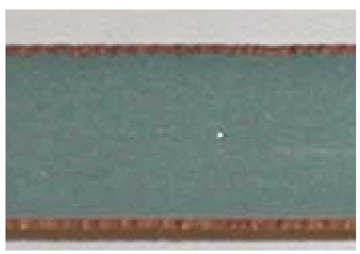
50 mg $[SO_4]$/L

150 mg $[SO_4]$/L



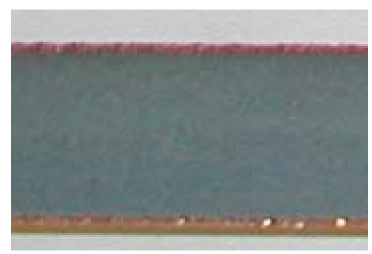


0 mg [SO4]/L



5 mg [SO4]/L

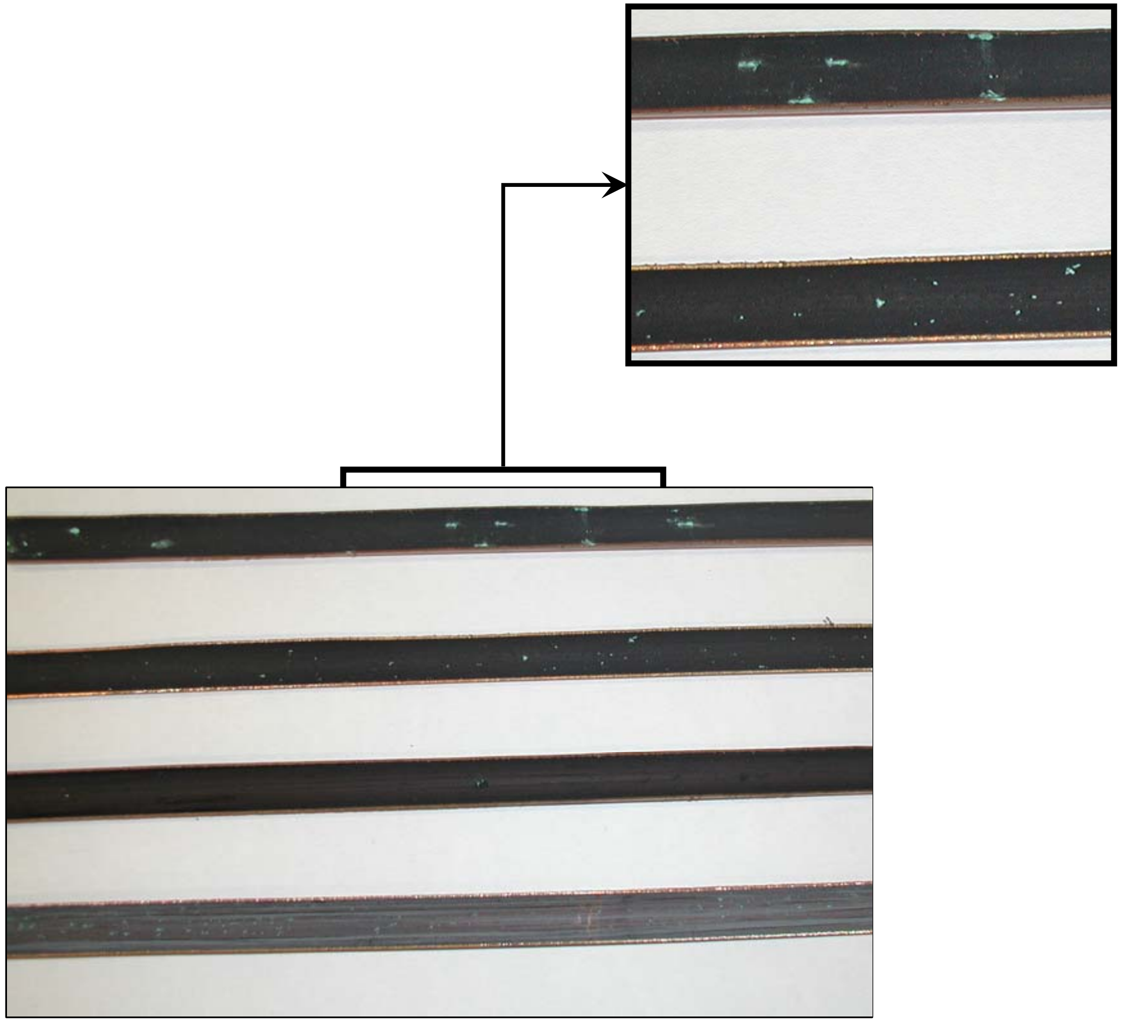
50 mg [SO4]/L



150 mg [SO4]/L

Pilot Study- Copper Recirc Study

Pipe cross-section at pH 9



0 mg $[SO_4]$/L

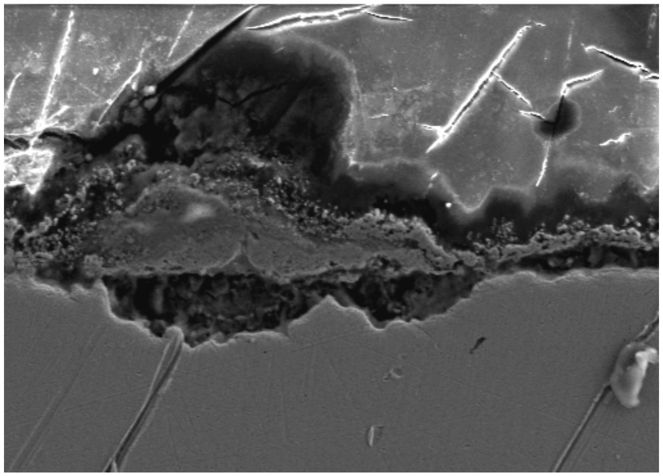
5 mg $[SO_4]$/L

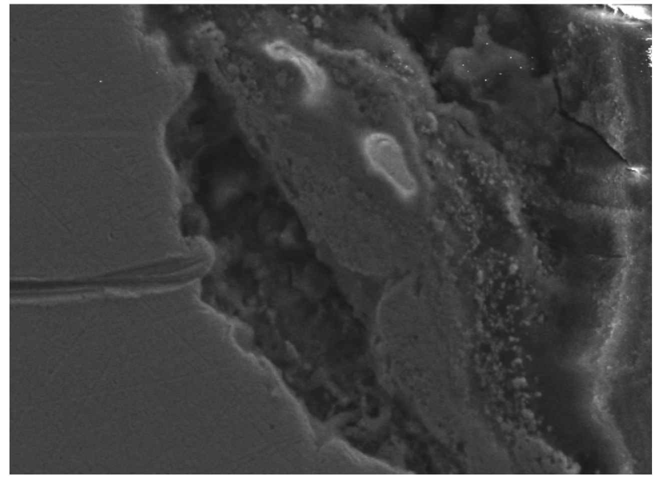
50 mg $[SO_4]$/L

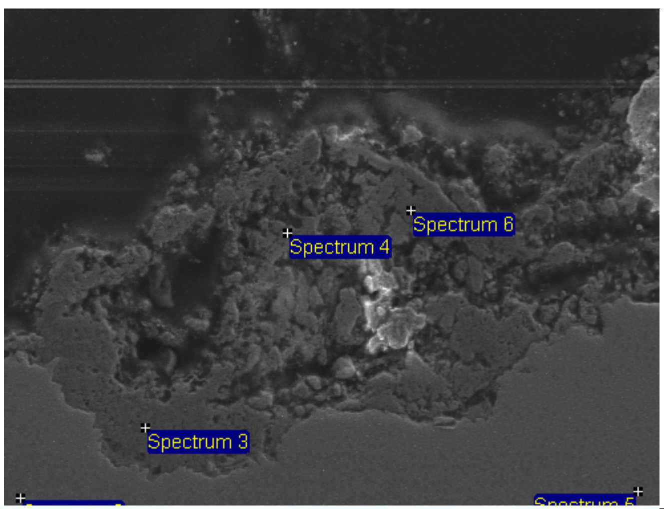
150 mg $[SO_4]$/L

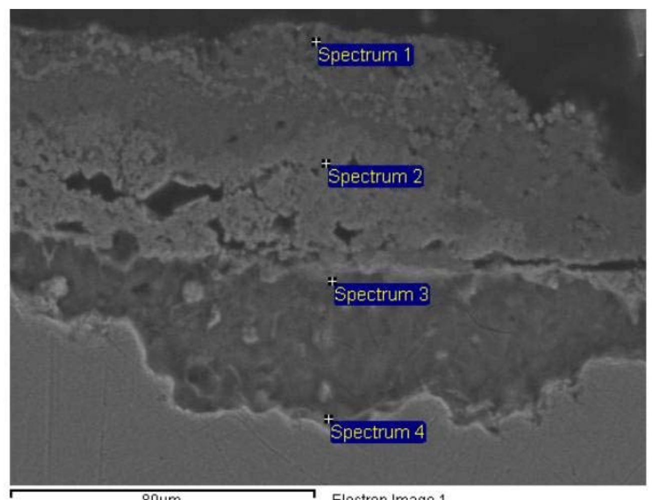
Pilot Study- Copper Recirc Study

SEM-EDS Evidence for Localized Corrosion





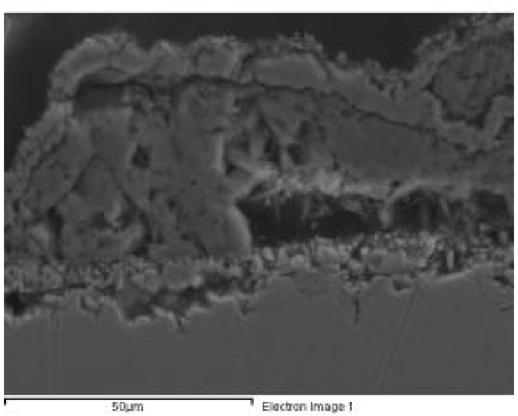




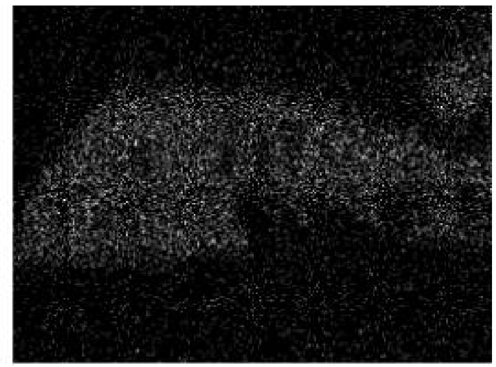
Pilot Study- Copper Recirc Study

SEM-EDS Evidence for Localized Corrosion

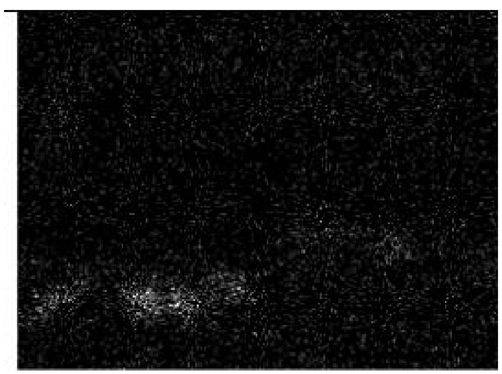
- pH 9, 50 mg SO_4/L, 28 mg Cl/L



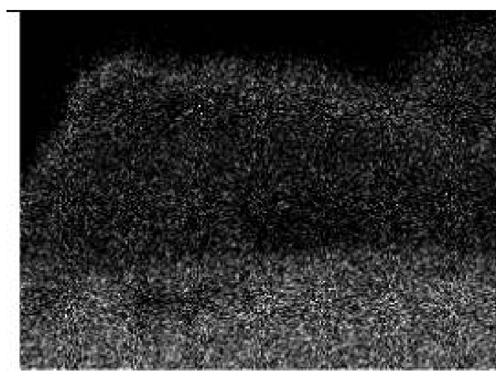
sulfur



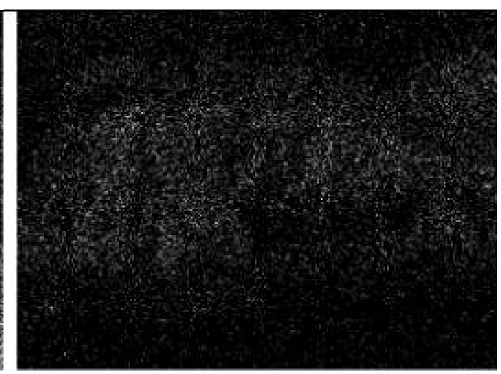
chlorine



copper

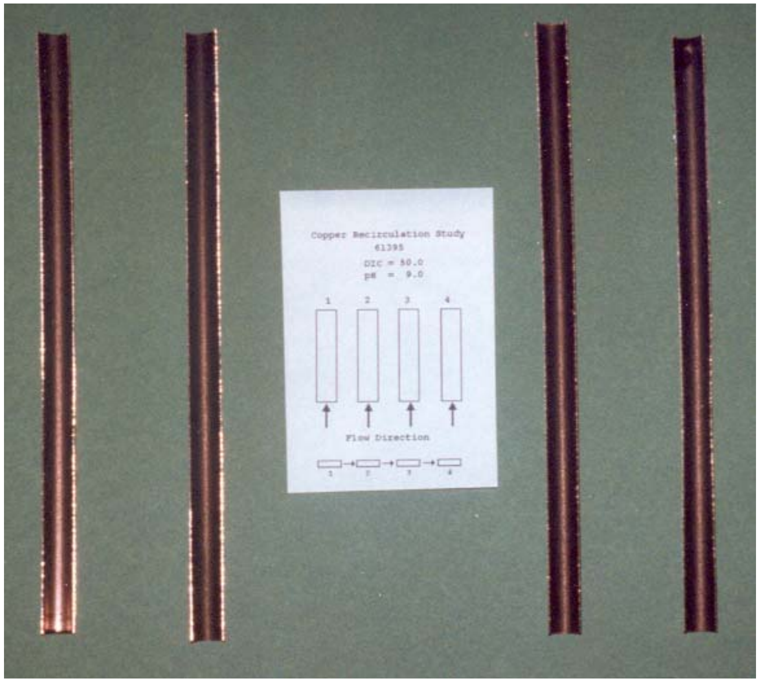


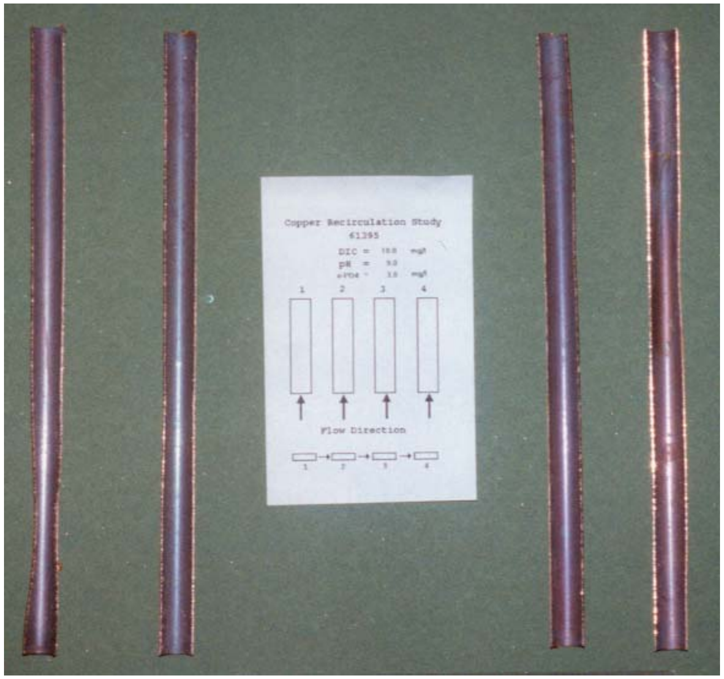
oxygen



Pilot Study- Copper Recirc Study

Role of DIC and phosphate at pH 9, chloride present





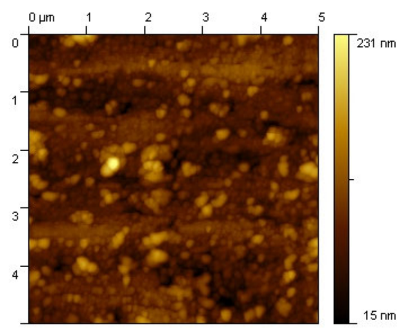
TIC=50 mg C/L

TIC= 10 mg C/L, 3 mg PO_4/L

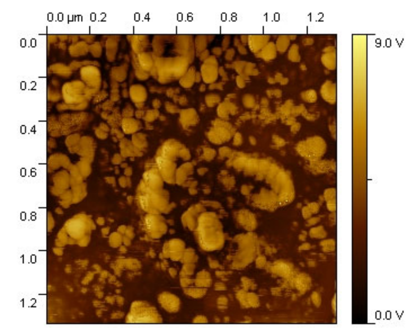
Current Research Topics

- Corrosion Mechanisms/Fundamentals
  - *Field pilot studies*
  - *Electrochemistry/solids analysis studies (UC)*
  - *Atomic Force Microscopy (AFM)*

AFM imaging



Topography and roughness

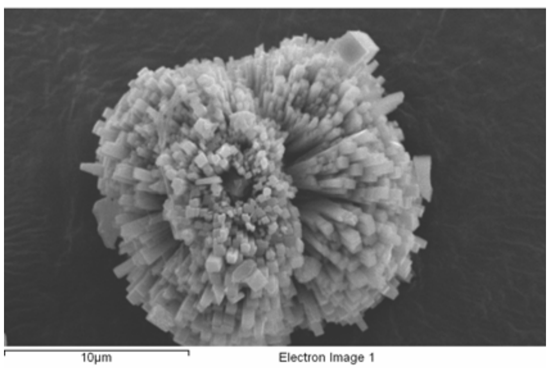


Phase

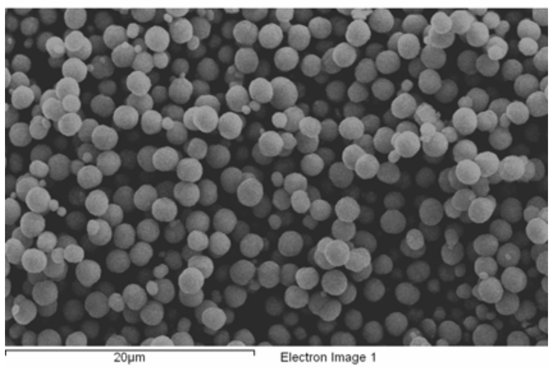
From the work of Brian Lewandowski, Ph.D. student, U.S. EPA/LSU (2007)

Current Research Topics

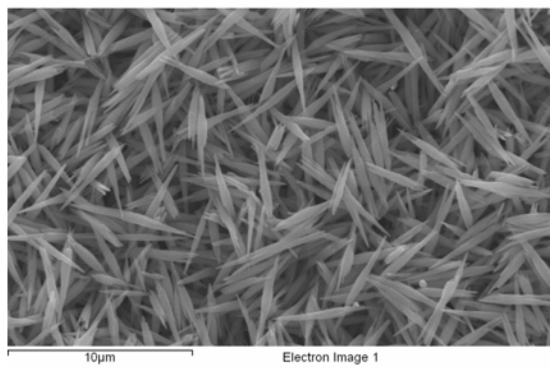
- Copper solids synthesis research
  - *Solids associated with localized corrosion*
  - *Solubility of solids as a function of water chemistry*
  - *Particle properties*



Copper carbonates



Copper oxides



Copper sulfates

From the work of Lisa Melton, M.S. student, U.S. EPA/Univ. of Dayton (2007)

Conclusions

- Copper solubility of "fresh" copper (II) solids increases with increasing DIC and decreasing pH
- Thermodynamic models nicely predict observed copper (II) solubility
- Orthophosphate reduces the solubility of copper
- Orthophosphate addition is a treatment option for high DIC waters with copper problems
- Phosphates increases the charge in a negative magnitude of copper particles
- Jar testing reasonably predicts copper solubility in some field applications
- Low DIC, high pH water with chloride (and sulfate) was conducive to pitting corrosion
- Phosphates tended to reduce pitting corrosion

Thank-you

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