Environmentally Benign Chemical Mechanical Planarization Slurries Aided by Amino Acids

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Outline

- Introduction: Cu CMP Process and Challenges
- Cu & Co Corrosion-Polishing with Inhibitors
- Degradation Methodology of Wastewater
- Conclusions
- Future work

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- Introduction: Cu CMP Process and Challenges
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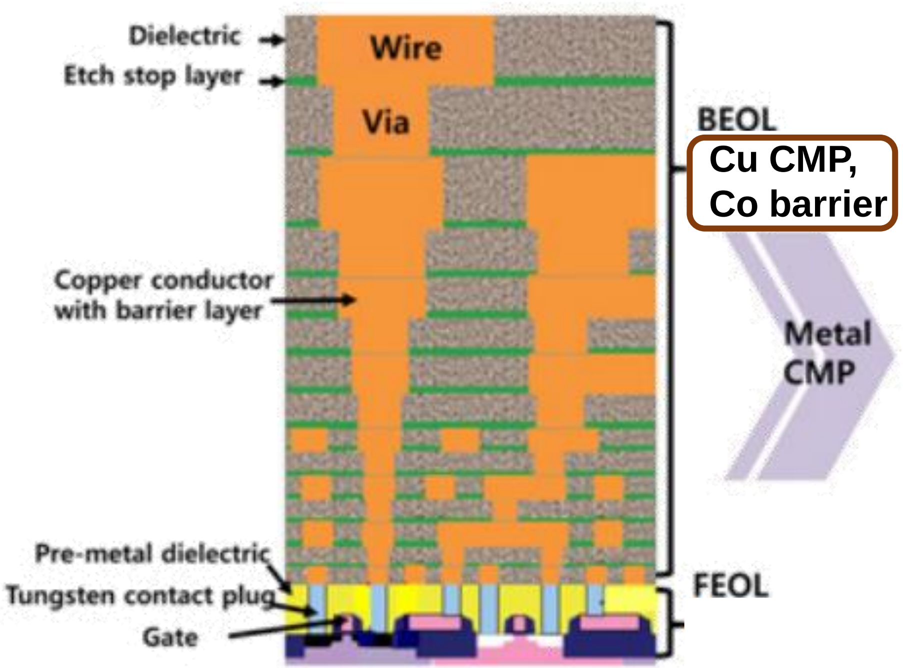
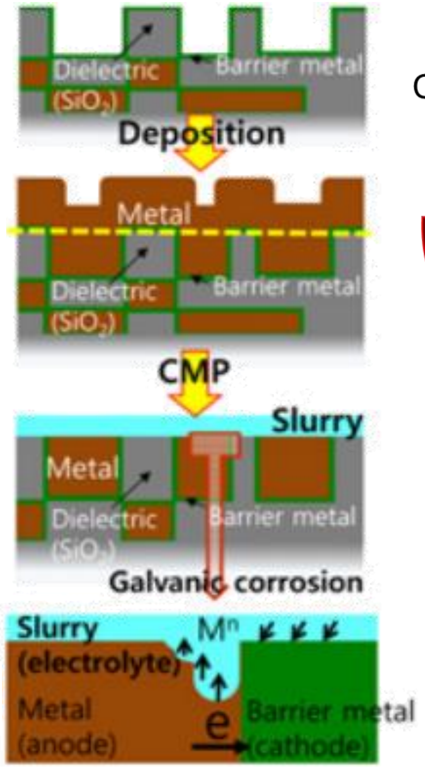
1. Introduction to Cu CMP

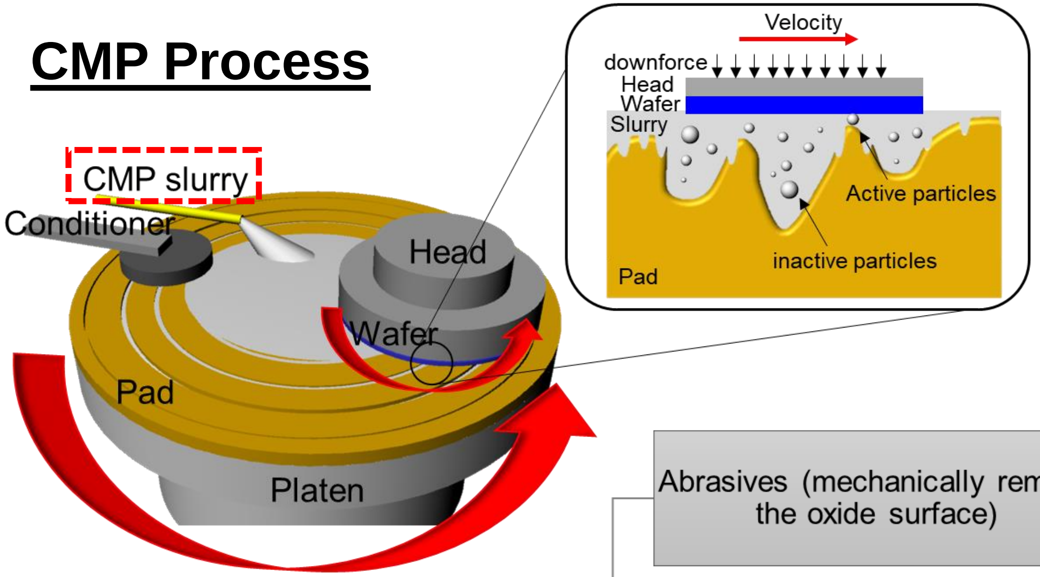
Cu CMP





Chemical mechanical planarization (CMP) is one of the most critical processes to planarize the surface of various materials (metal, dielectrics, and other thin films) using a combination of ***chemical*** and ***mechanical actions***.

CMP Process



Cu slurry

- Abrasives (mechanically remove the oxide surface)
- pH adjusting agents
- Oxidizer (form oxides)
- Corrosion inhibitors (reduce galvanic corrosion and pitting corrosion)
- Complexing agent (complex Cu, Co ions)

Suryadevara Babu, *Advances in Chemical Mechanical Planarization (CMP)*; Woodhead Publishing, 2021.
Journal of Materials Research volume 36, pages235–257 (2021)

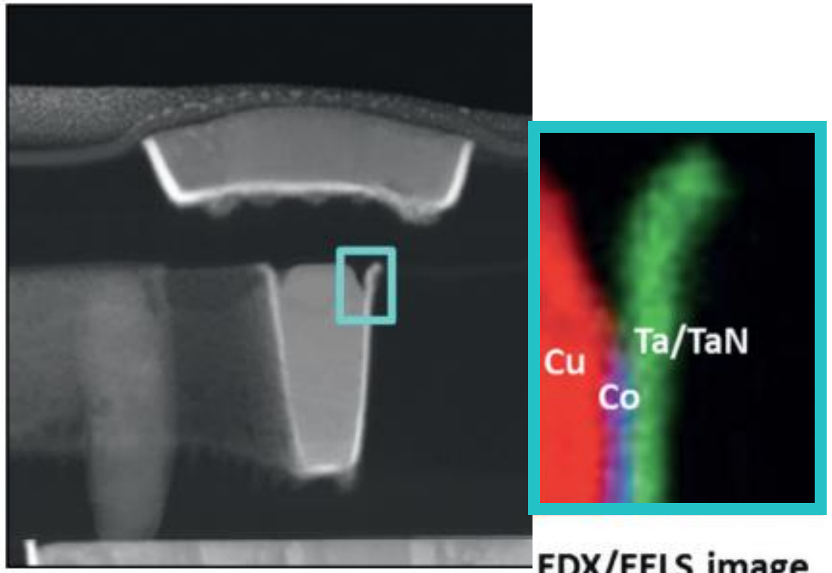
Cu/Co CMP Process and Challenges

Cu/Co Barrier CMP

Our focus

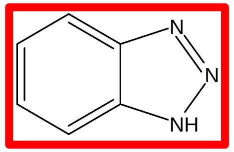
Cu-Co corrosion

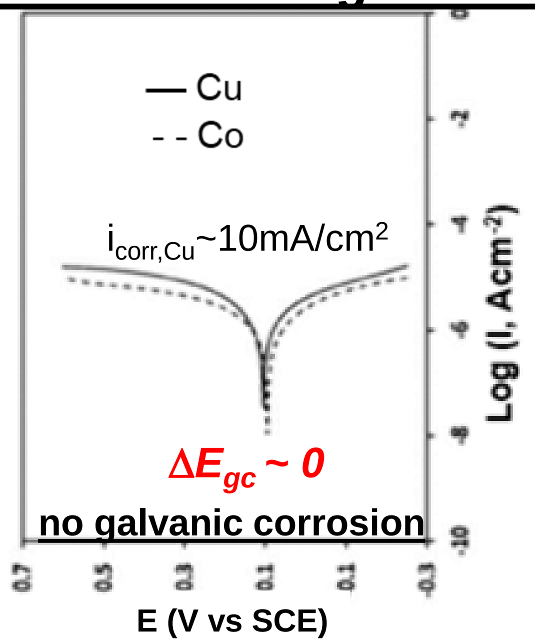
Possible Galvanic Corrosion Defects



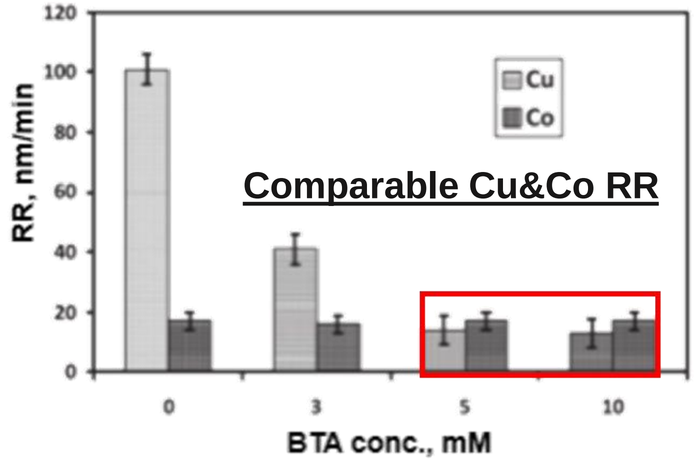
EDX/EELS image

BTA controls Cu/Co galvanic corrosion





Slurry conditions: 1 wt% H_2O_2, pH 10, silica particles, 0.5 wt % arginine, & 5 mM **BTA**



T. Nogami et al., IEEE International Interconnect Technology Conference, pp. 1–3 (2013).
B.C. Peethala et al., J. Electrochem. Soc, 159(6), H582-H588, 2012

Concerns with Azoles (e.g., BTA)

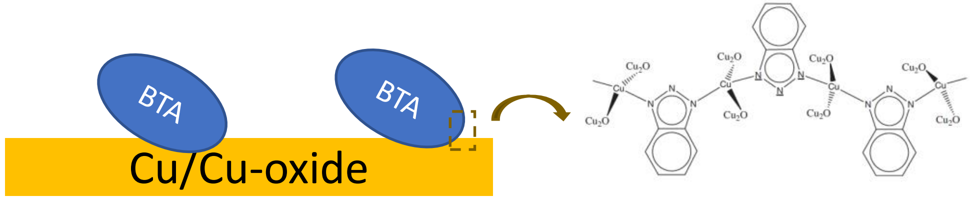
Environment

- Azoles are poorly biodegradable during wastewater treatment
- Toxicity to plants, invertebrates, microorganisms
- In 2008, BTA was classified as emerging organic pollutants (EPs) by the United States Environmental Protection Agency

Need more benign CMP slurry!

CMP Process

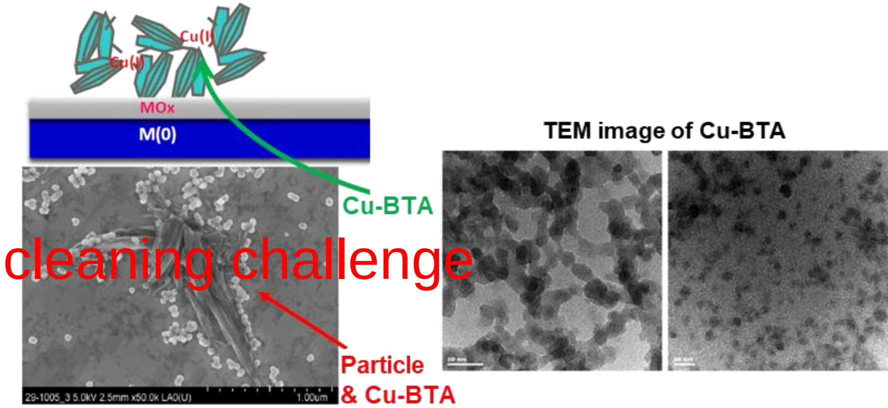
- Removing BTA residue can be problematic



Involves Cu-N bonds

R.F. Roberts, *J. Electron. Spectrosc.* **4** 273 (1974).
M. Finsgar, ,I. Milosev, *Corros. Sci*. **52** 2737 (2010).

- In the presence of cupric ions in the slurry BTA can precipitate as nanoparticles which are difficult to remove (although can be minimized by complexants)

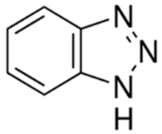
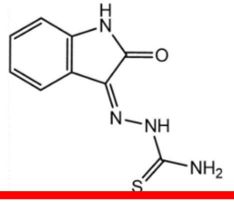
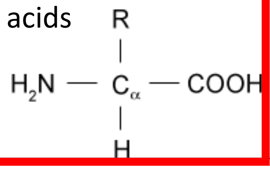
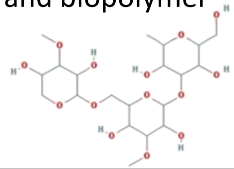
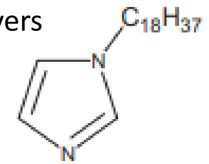


Post-CMP cleaning challenge

Z.-Q. Shi, Y.-S. Liu, Q. Xiong, W-W. Cai, G.-G. Ying, *Sci.Total Environ.* **661**, 407 (2019)
S. D. Richardson, Anal. Chem. 80, 4373 (2008)
https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NHEERL&dirEntryId=307075

M. White, *CMPUG meeting*, U.S.A., 2016; H.S. Lu et al., *J. Electrochem. Soc.*, 159 (9), C383-C387, 2012;

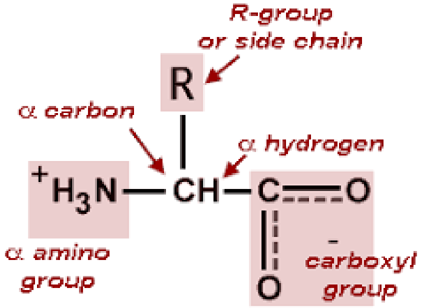
Cu & Co Corrosion Inhibitors

Corrosion inhibitor	Non-toxicity, Biodegradability	Reducing corrosion	Water-Solubility	Notes	References
Azoles 	X	✓	✓	Non-biodegradability	S. D. Richardson, Anal. Chem. 80, 4373 (2008), (2)
Schiff bases 	X	✓	✓	Require complicated synthesis method ($R_2C=NR$)	Y.N. Sudhakar,D. Krishna Bhat, in Biopolymer Electrolytes, 2018, Ahmed A. Al-Amiery et al. Scientific Reports | (2022)
Amino acids 	**Our focus** ✓	✓	✓	Natural origin	Kohsuke_Hayamizu, Sustained Energy for Enhanced Human Functions and Activity, 2017
Polymer and biopolymer 	✓/X	✓	X	Require modifying structures, thick passivation	Mohammad Mobin et al., ACS Omega2017, 2, 3997–4008 Desai et al., 1986, Shokry et al., 1998
Self-assembled Monolayers  1-octadecyl-1H-imidazole	X	✓	✓	Require highly ordered molecular assemblies	B.V. Appa Rao, M. Narsihma Reddy, Arabian Journal of Chemistry, 2014

Corrosion Inhibitors examined

Amino Acid are of interest due to:

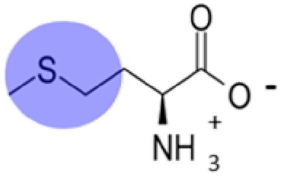
- ❖ Highly soluble in CMP slurries
- ❖ More easily degradable with less toxicity



$-NH^{+}_{3}$: electron donation

$-COO^{-}$: electron-withdrawing

1. Electron donation capability at R (heteroatoms S>O>n-alkyl favoring chemisorption)



Methionine

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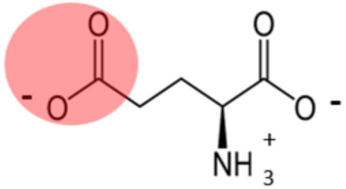

Glutamic acid

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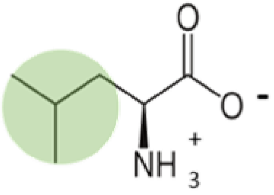
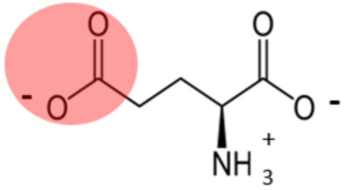


Leucine

2. Charge at alkaline medium (pH 8): (Physisorption)



Glutamic acid

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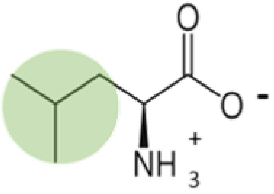

Leucine

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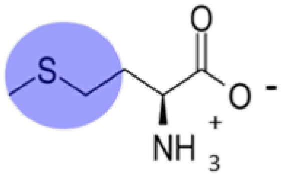
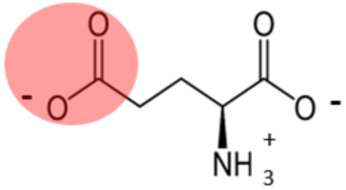


Methionine

3. Chemical structure, chain length (physisorption):



Glutamic acid

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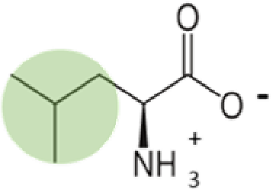

Leucine

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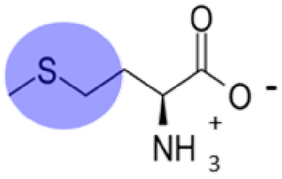

Methionine

*Since different functional groups on the amino acids provide **different electron-donating abilities** that promote chemisorption, physisorption, would corrosion inhibition & polishing follow this trend?*

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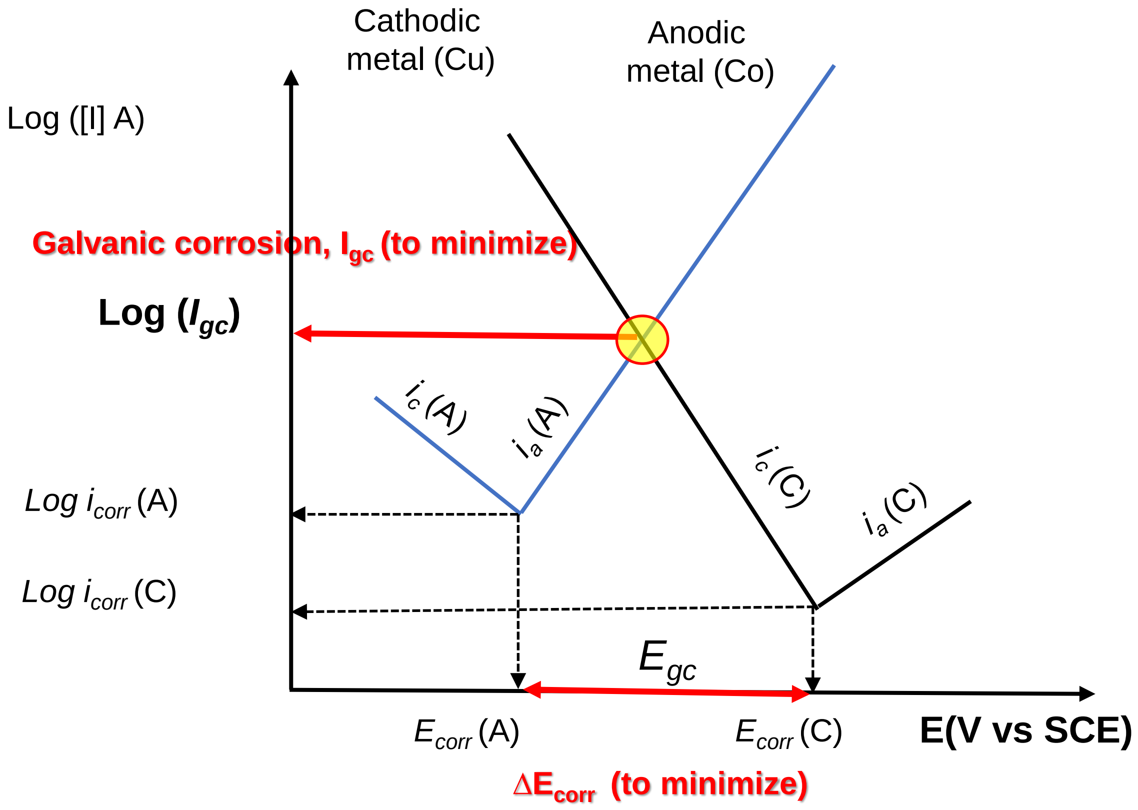
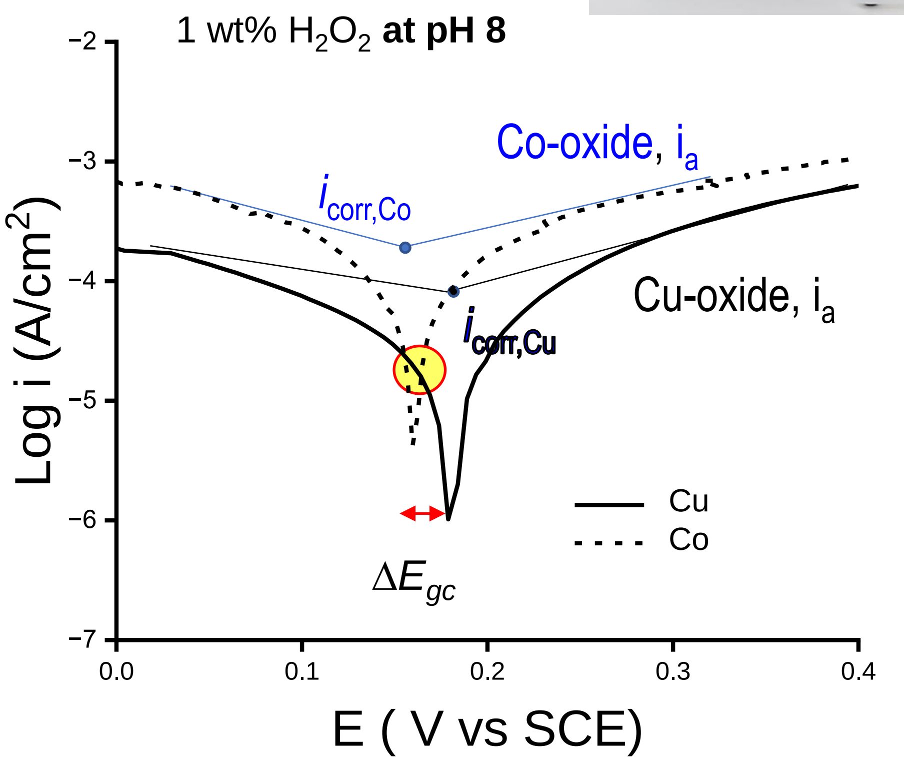
2. Cu/Co corrosion, galvanic corrosion

Evans Plot



Tafel curve for Cu and Co



- For metals, there is a driving force for Co corrosion in the presence of Cu
  $E^0_{Cu/Cu^{2+}} > E^0_{Co/Co^{2+}}$ (0.34 V > -0.28 V vs NHE)
- But oxides have different equilibrium E^0
  $E^0_{Cu/Cu2O} < E^0_{Co(OH)2/Co3O4}$ (-0.02 V < +0.1 V vs NHE, pH 10)

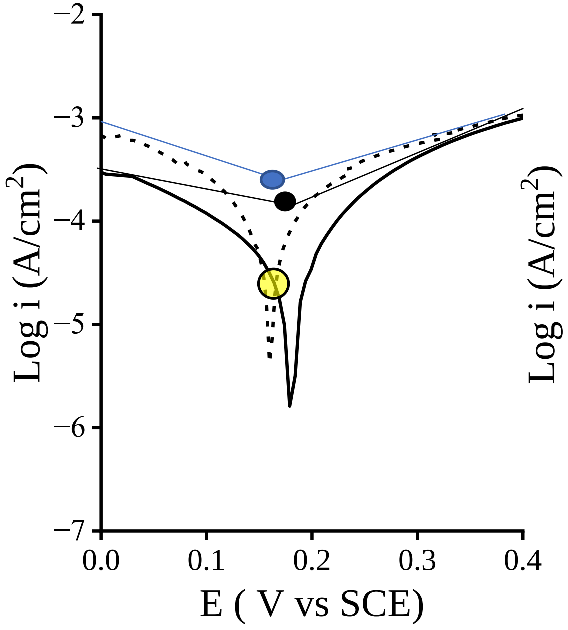
Significant Co corrosion, galvanic corrosion of Co, i_{gc} ~ 63 μA/cm², $i_{corr,\ Co}$ ~ 76 μA/cm², $i_{corr,cu}$ ~ 43 μA/cm², ΔE_{gc} ~ 40 mV

2. Cu/Co corrosion with inhibitors, pH 8

Electrolyte: 1wt % H_2O_2, 10 mM corrosion inhibitors (amino acids), 900 rpm, pH 8, RT.

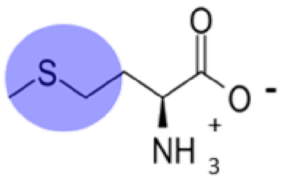
No inhibitor

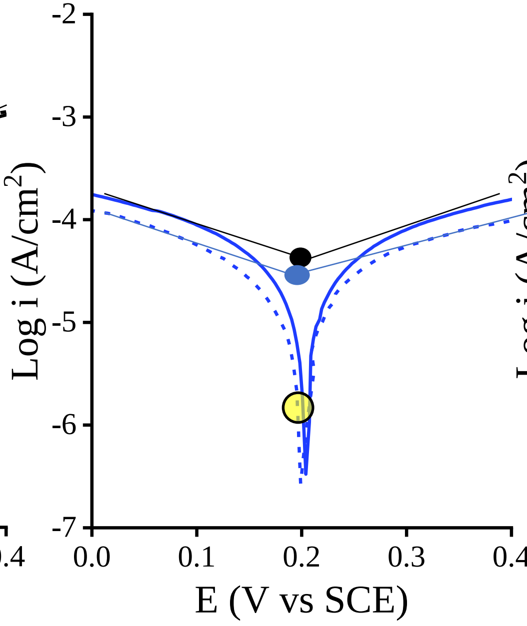
Cu: solid line
Co: dash line



- Co Galvanic corrosion
- High Co corrosion

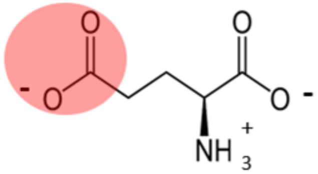
Methionine

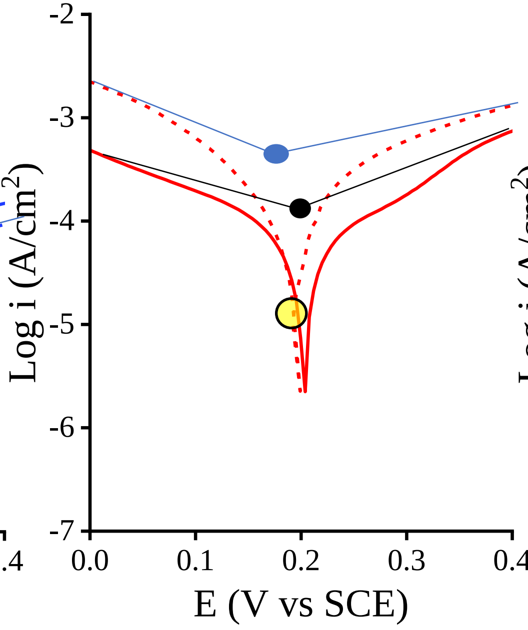




- No Co Galvanic Corrosion
- Cu,Co Corrosion Inhibition

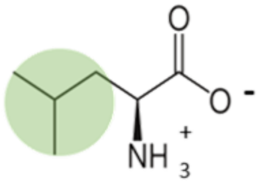
Glutamic acid

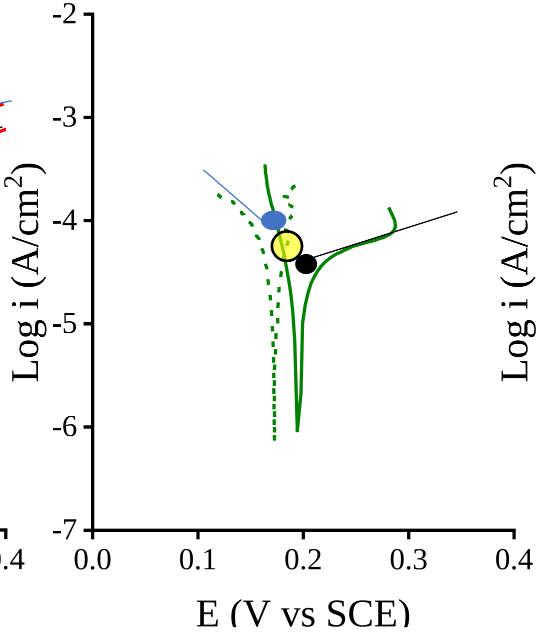




- No Co Galvanic Corrosion
- Accelerates Cu, Co Corrosion

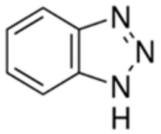
Leucine

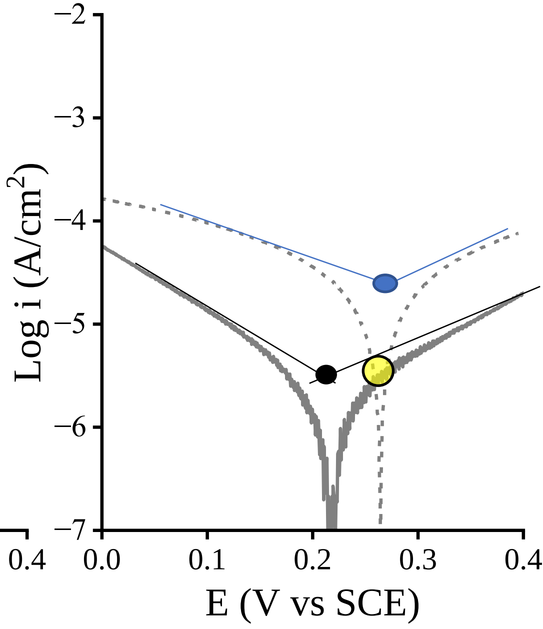




- Co Galvanic Corrosion
- Cu Corrosion Inhibition

BTA





- Cu Galvanic Corrosion
- Cu,Co Corrosion Inhibition

Galvanic corrosion current density

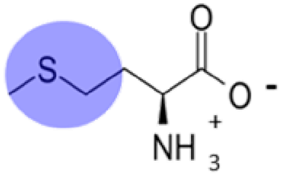
Cu/Co corrosion with inhibitors, pH 8

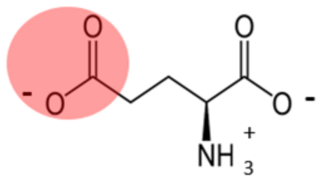
Electrolyte: 1wt % H_2O_2, 10 mM corrosion inhibitors (amino acids), 900 rpm, pH 8, RT.

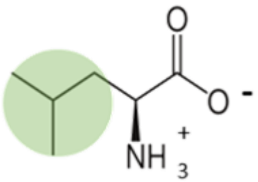
No inhibitor | Methionine | Glutamic acid | Leucine

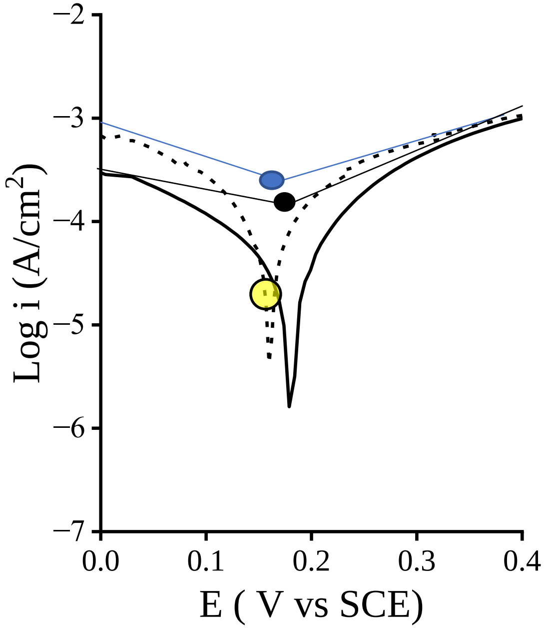
Cu: solid line
Co: dash line

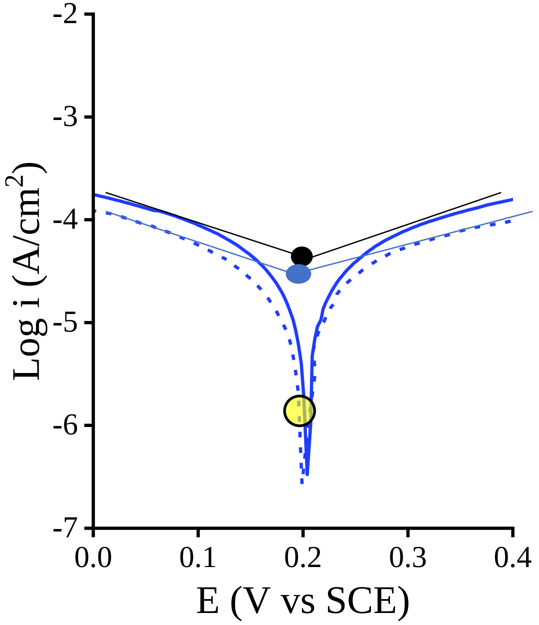
Galvanic corrosion current density

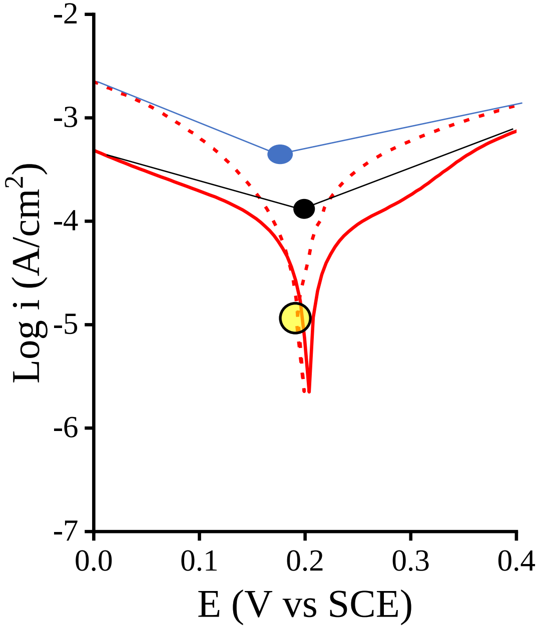


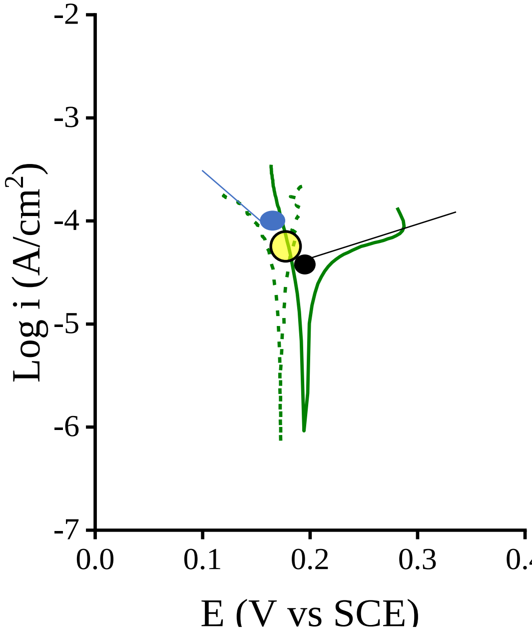












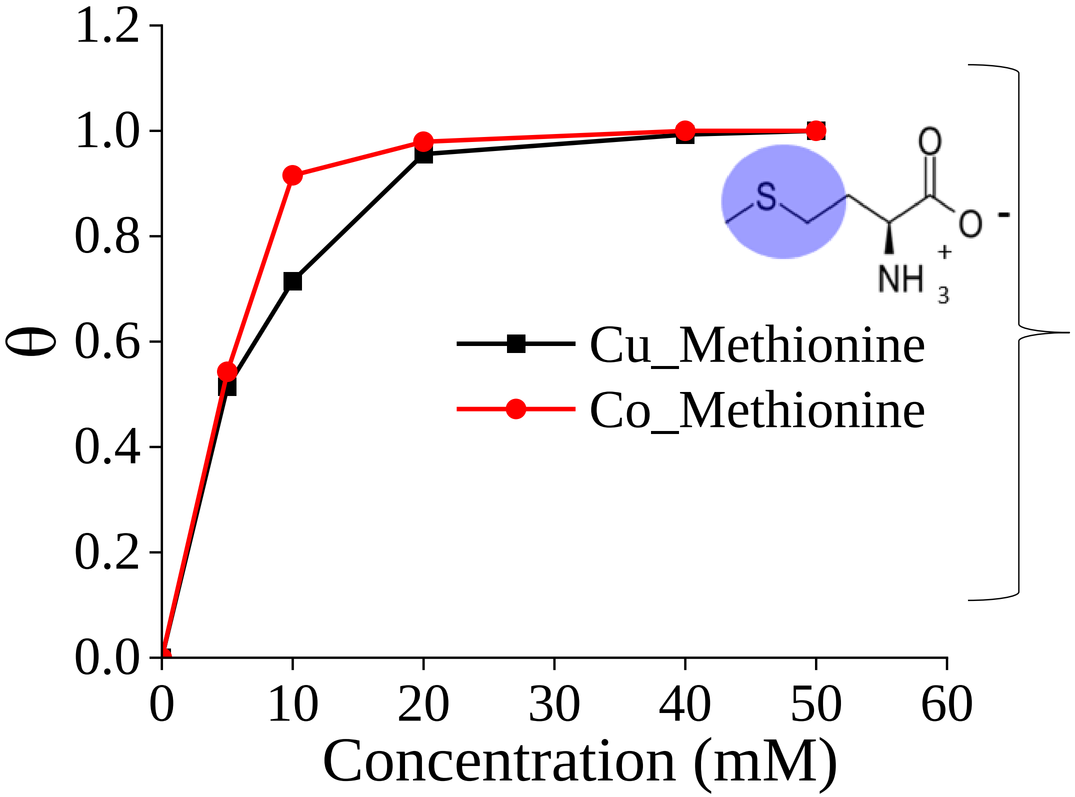
Increasing the electron-donating ability of the side chain (S>O>n-akyl, C=O withdrawing group) increases the corrosion inhibition:

Methionine ← Leucine ← Glutamic acid

Determining Adsorption Energy

Fractional adsorption

$$\theta = \left[\frac{i_{corr,o} - i_{corr}}{i_{,corr,o} - i_{corr,sat}}\right]$$



Assuming a Langmuir Adsorption

$$\theta = \frac{KC}{1 + KC}$$

Rearrange Langmuir

$$\frac{C}{\theta} = \frac{1}{K} + C$$

Re-plot, $\frac{C}{\theta}$ vs C

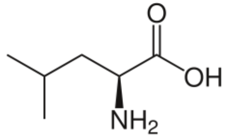
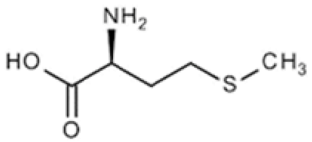
find intercept, 1/K

Finding the adsorption energy from K

$$\mathrm{K} = \frac{1}{55.5} \exp\left(-\frac{\Delta G^0_{ads}}{RT}\right)$$

Adsorption Energy, ΔG^0_{ads}

Physisorption $-\Delta G^0_{ads} \leq 20$ (kJ/mol)
Chemisorption $-\Delta G^0_{ads} > 40$ (kJ/mol)

		Cu	Co
Leucine 	K (L/mol)	76.8	No inhibition with higher concentration
	$-\Delta G^0_{ads,25℃}(\frac{kJ}{mol})$	20.5	
Methionine 	K (L/mol)	276.5	1092
	$-\Delta G^0_{ads,25℃}(\frac{kJ}{mol})$	23.9	27.3

Largely physisorbed

More chemisorbed
ΔG_{ads},Co > ΔG_{ads},Cu

vs. BTA $-\Delta G^0_{ads,BTA/Cu} = 31\,\frac{\text{kJ}}{\text{mol}}\,(*), -\Delta G^0_{ads,BTA/Co} = 29\,\frac{\text{kJ}}{\text{mol}}$ (**)

$|\Delta G^0_{ads\ of\ leucine,\ methionine}| < |\Delta G^0_{ads\ of\ BTA}|$

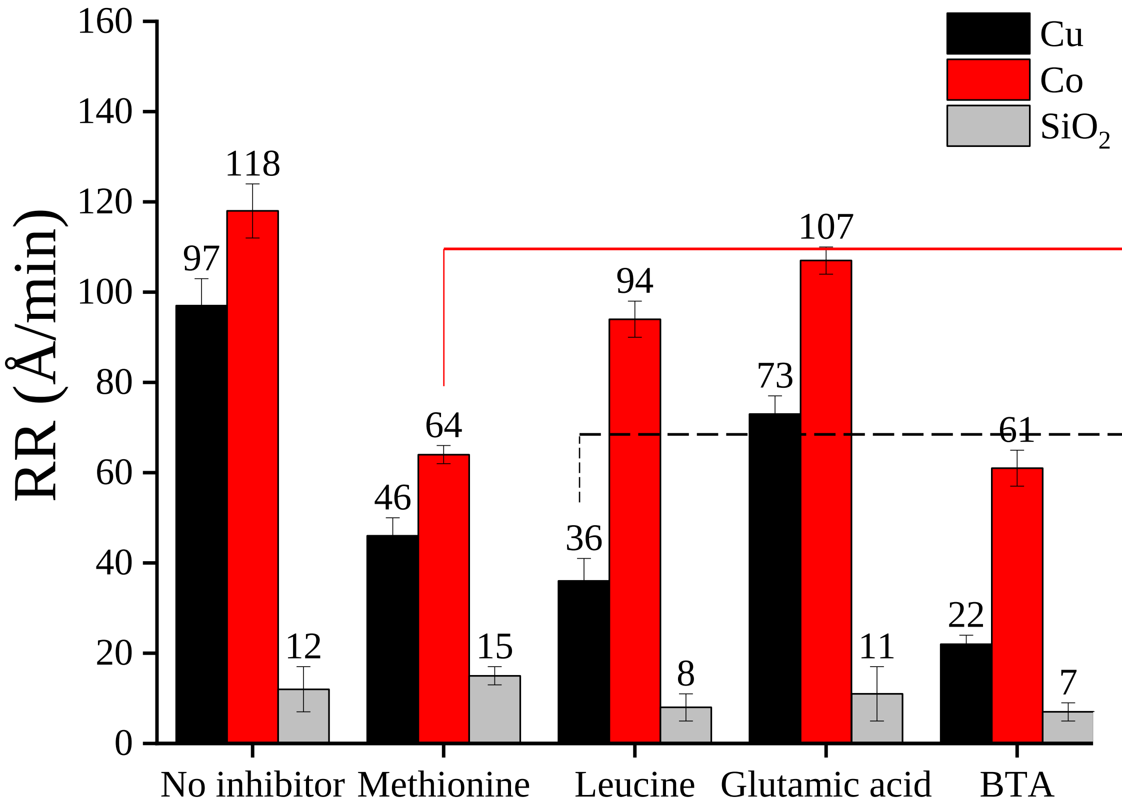
Leucine & methionine may be easier to clean off the surface

(*) P. G. Fox, G. Lewis, and P. J. Boden, *Corros. Sci*. **19**, 457 (1979).
(**) D. Yin, et al. Colloids and Surfaces A 591 (2020) 124516

2. Cu-Co removal rate with variable AAs

Cu/Co removal rate with inhibitors (P= 2 psi)

Slurry: **1wt% Silica particles**, 1 wt % H_2O_2 , 10mM corrosion inhibitors, pH 8

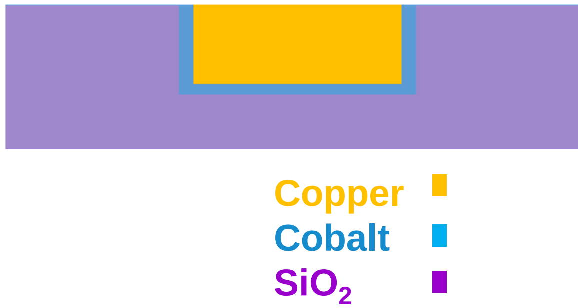


Methionine (S): inhibitor for Co, Cu

Leucine (n-alkyl chain): inhibitor for Cu

►Down pressure, Head /Platen, flow rate: **2psi**, 93/87 rpm, 120 ml/min

Cu/Co Barrier CMP



	No inhibitor	Methionine	Glutamic acid	Leucine	BTA
Cu:Co:SiO_2 RR selectivity	8:9:1	3:4:1	7:10:1	4.5:12:1	3:9:1

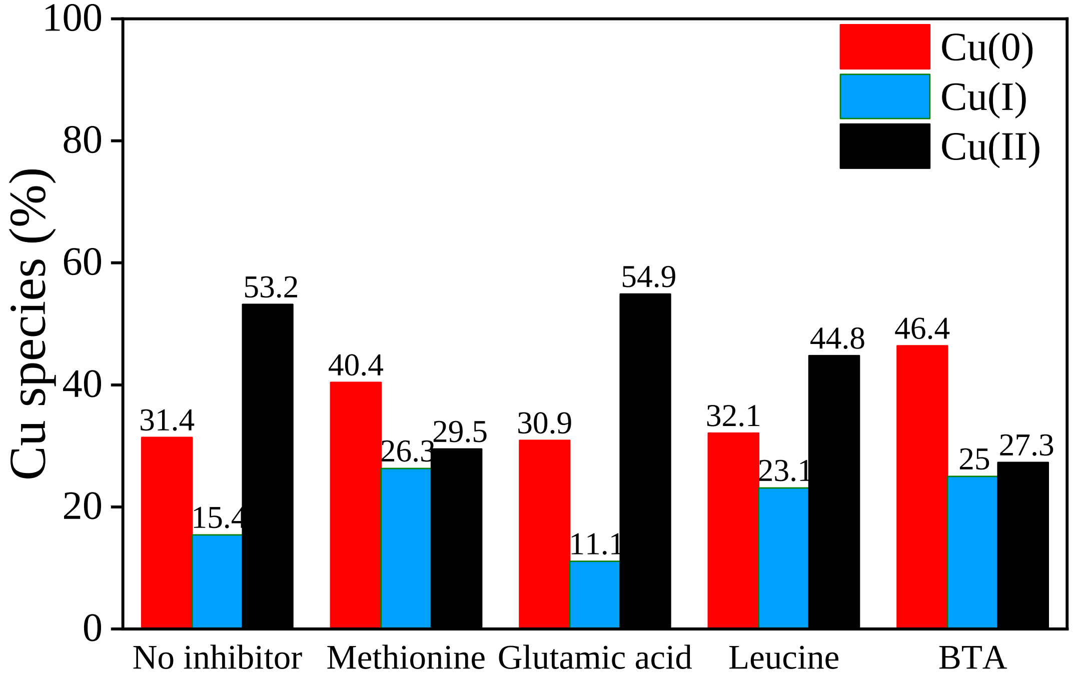
MRR with the amino acid inhibitors follow the same trend with the corrosion results with:

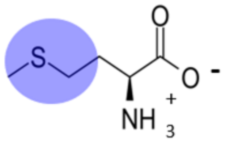
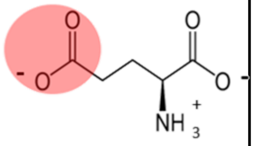
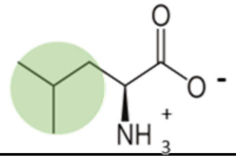
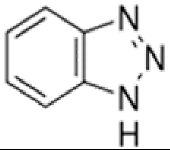
- Methionine having more comparable Cu:Co removal rates
- Leucine inhibiting Cu, but not Co

Cu species with H_2O_2, inhibitor at pH8

<u>Aim to</u>: Understand Cu species

- Cu species observed by XPS $Cu2p_{3/2}$



Additives	Cu species	Corrosion current reduction
No additive	Cu(II) > Cu(I),Cu(0)	No
Methionine 	Cu(0) > Cu(I) ≈ Cu(II)	Better
Glutamic acid 	Cu(II) > Cu(I),Cu(0)	No
Leucine 	Cu(II) > Cu(0)>Cu(I)	Less
BTA 	Cu(0) > Cu(I) ≈ Cu(II)	Better

AAs change the Cu surface oxides differently

Outline

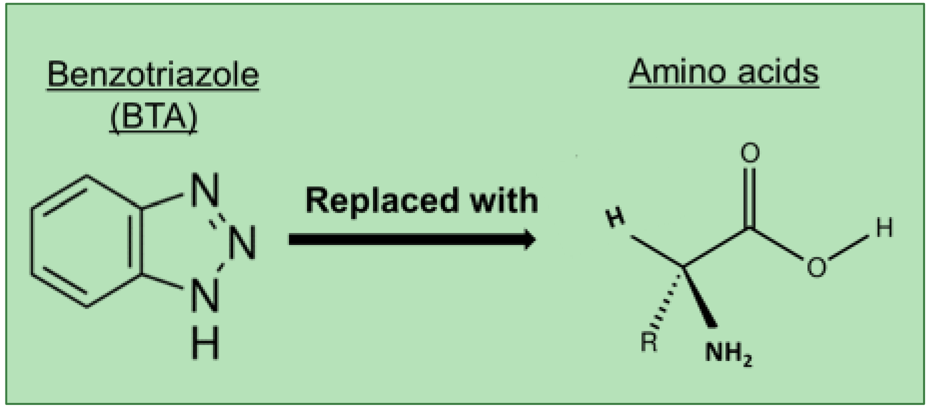
- Introduction: Cu CMP Process and Challenges
- Cu & Co Corrosion-Polishing with Inhibitors
- Degradation Methodology of Wastewater
- Conclusions
- Future work

Concerns with Azoles (e.g., BTA)

Environment

- Azoles are poorly biodegradable during wastewater treatment
- Toxicity to plants, invertebrates, microorganisms
- In 2008, BTA was classified as emerging organic pollutants (EPs) by the United States Environmental Protection Agency

Can amino acids be easier to degrade after their use?



Z.-Q. Shi, Y.-S. Liu, Q. Xiong, W-W. Cai, G.-G. Ying, *Sci.Total Environ.* **661**, 407 (2019)
S. D. Richardson, Anal. Chem. 80, 4373 (2008)
https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NHEERL&dirEntryId=307075

Need more benign CMP slurry!

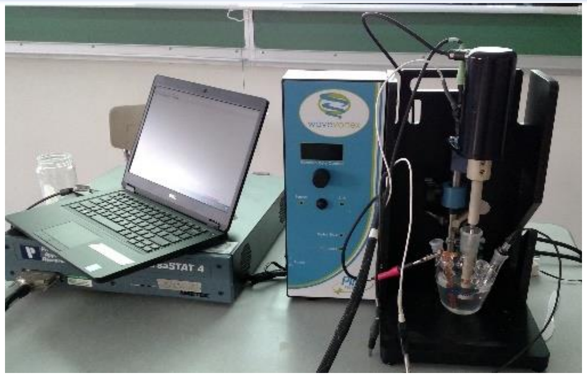
3. Degradation of amino acids and BTA

Fenton-based advanced oxidation process (AOP)

- $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$
- Fe^{3+} regeneration to Fe^{2+} at the cathode: $Fe^{3+} + e^- \rightarrow Fe^{2+}$
- Water oxidation at the anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
- OH* + Organics → $CO_2 + H_2O + N_2$ + (degraded by-products)
- Organic compounds in our case: amino acids and BTA

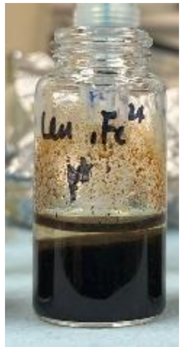
C_0 = 10 mM Methionine, Leucine or BTA, at pH 2.5

C_t/C_0 = ? , $E_{applied}$ = 2 V vs SCE



By-products ← ^{1}HNMR LC-MS ESI-MS

← filtration



Fe^{3+}, Fe^{2+} precipitation

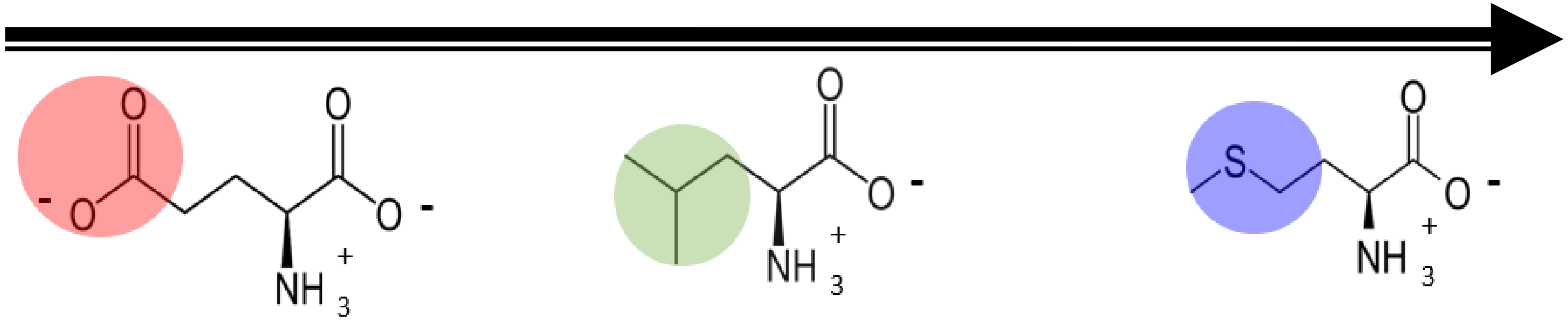
← KOH

Electrolyte

D.B. Miklos et al. A critical review. Water Research 139 (2018) 118-131.
F.C.Moreira et al./ Applied Catalysis B: Environmental 202(2017) 217–261

Conclusions

(1) Increasing the electron-donating ability of the side chain (S>O>n-akyl, C=O withdrawing group) increases the corrosion inhibition:



L-glutamic acid L-leucine L-methionine

(2) Cu $2p_{3/2}$: Methionine treated is more Cu(0)/Cu(I) with better Cu corrosion resistance, leucine has similar Cu(0)/Cu(I)/Cu(II) with less Cu corrosion resistance and no Cu corrosion resistance with glutamic acid the surface has more $Cu(OH)_2$.

(3) The $\Delta \boldsymbol{G}_{ads}$ values for leucine and methionine indicate weaker adsorption compared to BTA (possibly better for post-cleaning)

(4) MRR follows similar trends consistent with the corrosion studies

(5) There is no methionine, or leucine presence after t = 30min, but BTA presents even after t=30min.

The degraded products are found by ESI-MS.

(6) More methionine and leucine reacted than BTA, showing that it is more easily decomposed.

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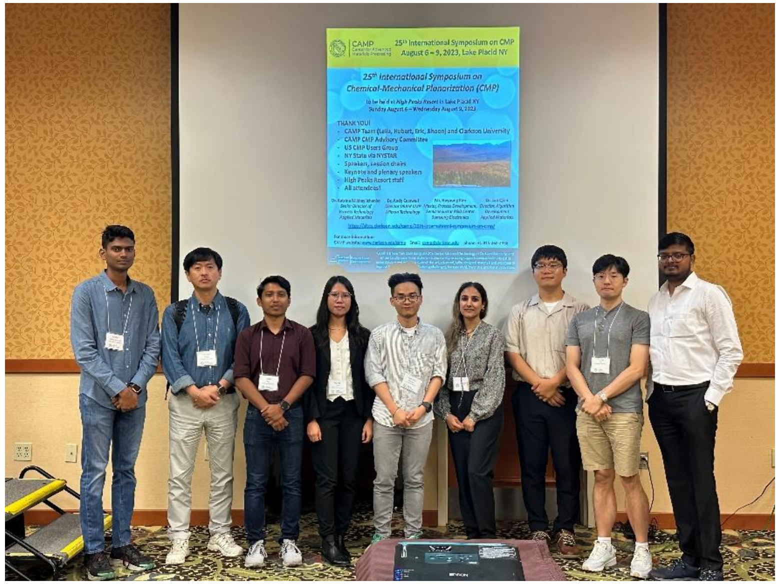
- **Clarkson CMP Group**



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-Thank you for your attention-

And question?