Casting a Healthier Future: Engineering Antimicrobial Alloys

Q1 Research Question and Hypothesis

•How do varying Zn and Al ratios in a Cu-based alloy (1% Sn) impact both corrosion resistance and E. coli kill

•Increasing the zinc and aluminum ratios of a Nordic Gold baseline will improve corrosion resistance and lower costs, while maintaining 60% copper will maintain antimicrobial efficacy

Q2 Methods

•Metal Casting

•Electrochemical testing

•SEM Characterization

•Antimicrobial Assay

Q3 Results

•Alloy 1, 3, 7: ~5 Log Kill

•High Efficacy Confirmed

•Alloy 1 has significant higher transfer charge resistance

•EBSD images show varying grain sizes

Q4 Conclusion

•Alloy 1: Most cost efficient for Corrosion and Antimicrobial properties

•Commercial Viability (Medical & Naval Applications)

The Motivation

Healthcare

•Prevent hospital infections & bacterial growth

•Cost-effective solution/alternative

Marine

•Lighter ship weight overall

•Fuel savings from weight reduction

Benefits for both

•Longer lasting

•Environmentally friendly

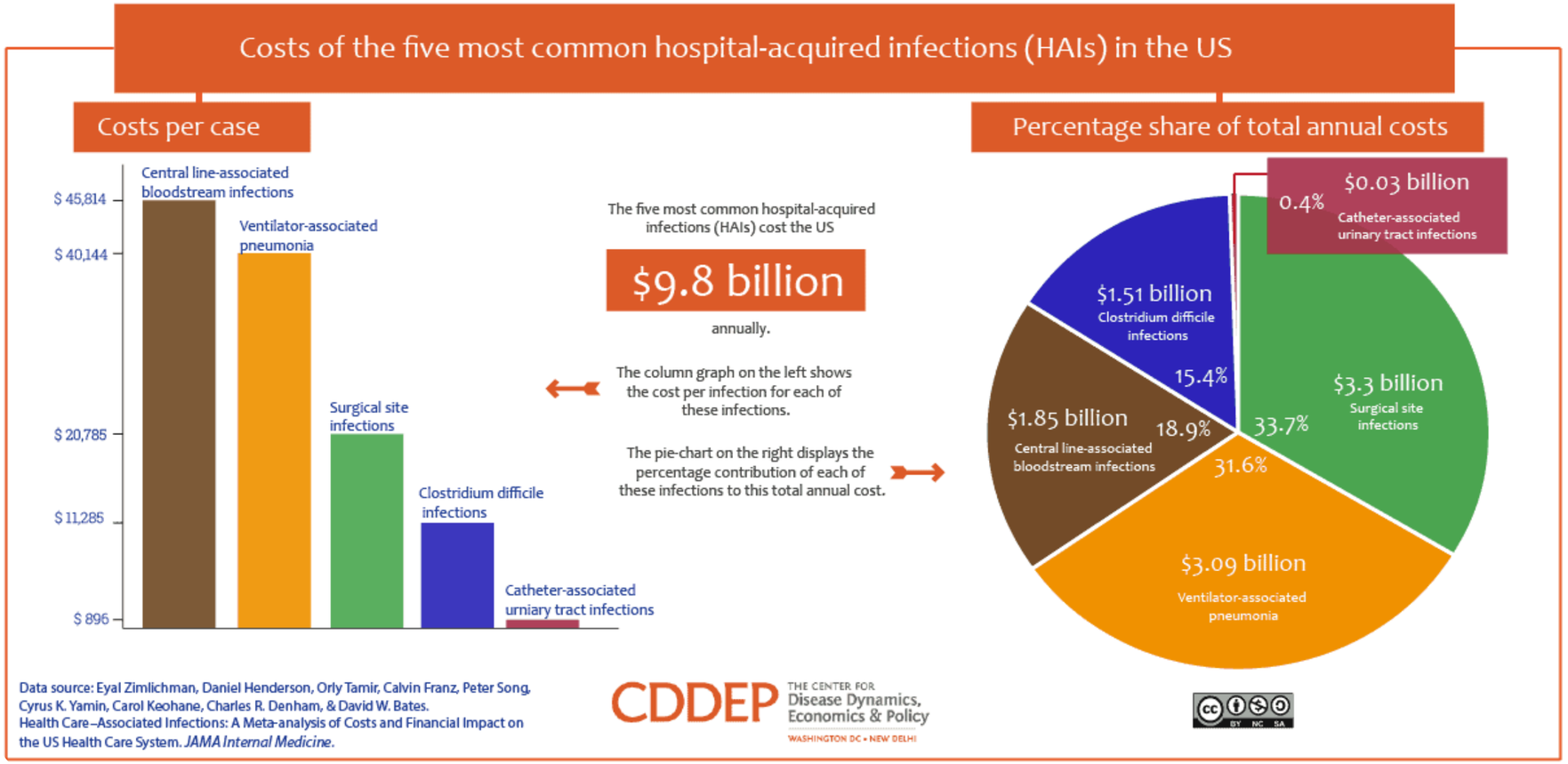


Fig. 1. Cost of five most common hospital acquired infections (HAIs) in the US from The Center for Disease Dynamics, Economics and Policy

Backround - Mechanism of Action against Bacteria

General Mechanisms

- **Membrane Damage**

Cu^{2+} ions bind and disrupt bacterial cell membrane, leading to a leakage of cellular contents

Zinc ions alters membrane permeability

- **Reactive Oxygen Species Production**

Copper participates in redox reactions that generates hydroxyl radicals which leads to oxidative damage to DNA, lipids and proteins.

- **Protein Binding**

Cu binds to thiol groups in enzymes, deactivating enzymes

Zn^{2+} interferes with bacterial metabolic enzymes

- **DNA Damage**

Direct binding and oxidative strand break

- **Nutrient Uptake Inhibition**

Zinc ions competes with the essential metal ions inside cell

Sources: Horton et al. 2015, David 2011

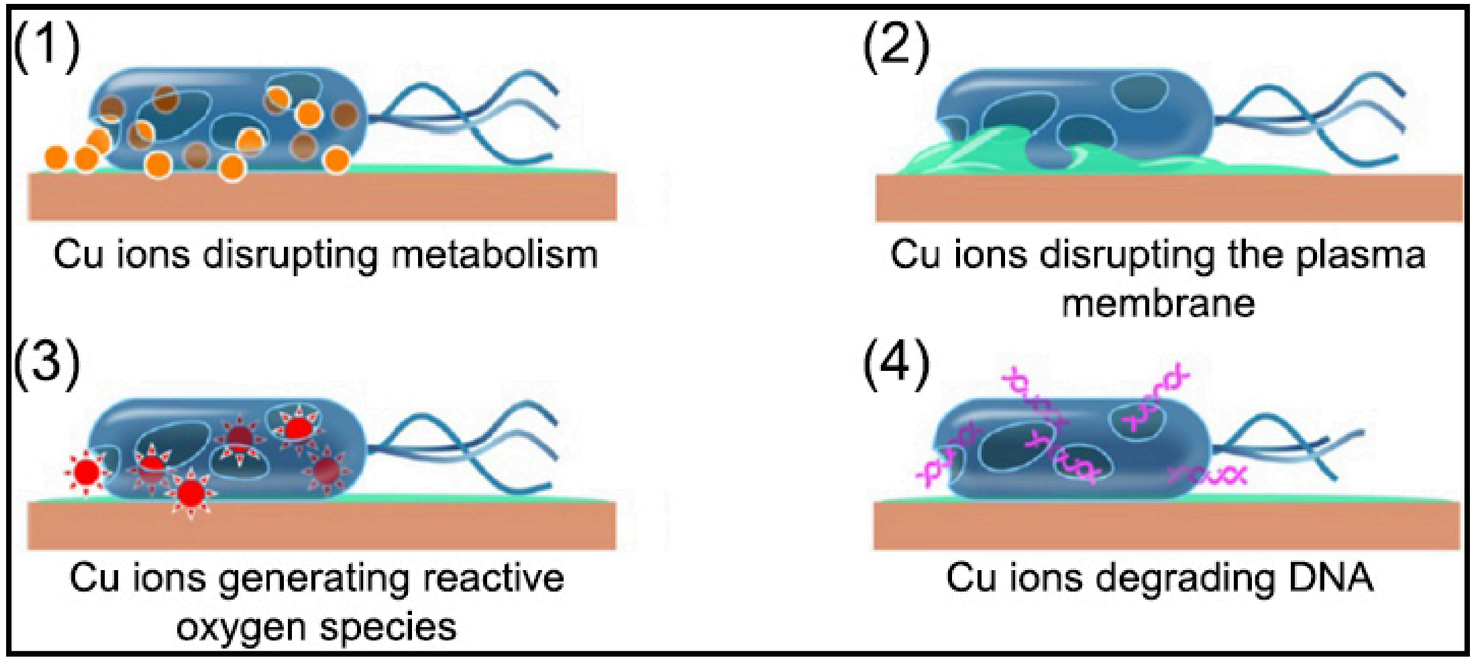


Fig.15 Image of depicting different kill mechanisms of copper to bacteria. Source: (https://cact.utoronto.ca/fields-of-research/anti-microbial-copper-based-alloys-coatings/anti-bacterial-coatings/)

Research Framework

Hypothesis

•Increasing the zinc and aluminum ratios of a Nordic Gold baseline will improve corrosion resistance and lower costs, while maintaining 60% will ,maintain antimicrobial efficacy.

Independent Variables

•Alloy Composition

•Cu-Zn-Al-Sn ratios; Sn held at 1%

Dependent Variables

•Bacterial Survival

•Corrosion Resistance

Control Variables

•Bare substrate on antimicrobial tests

•Cu-89-5Zn-5Al-Sn (existing research is on this alloy)

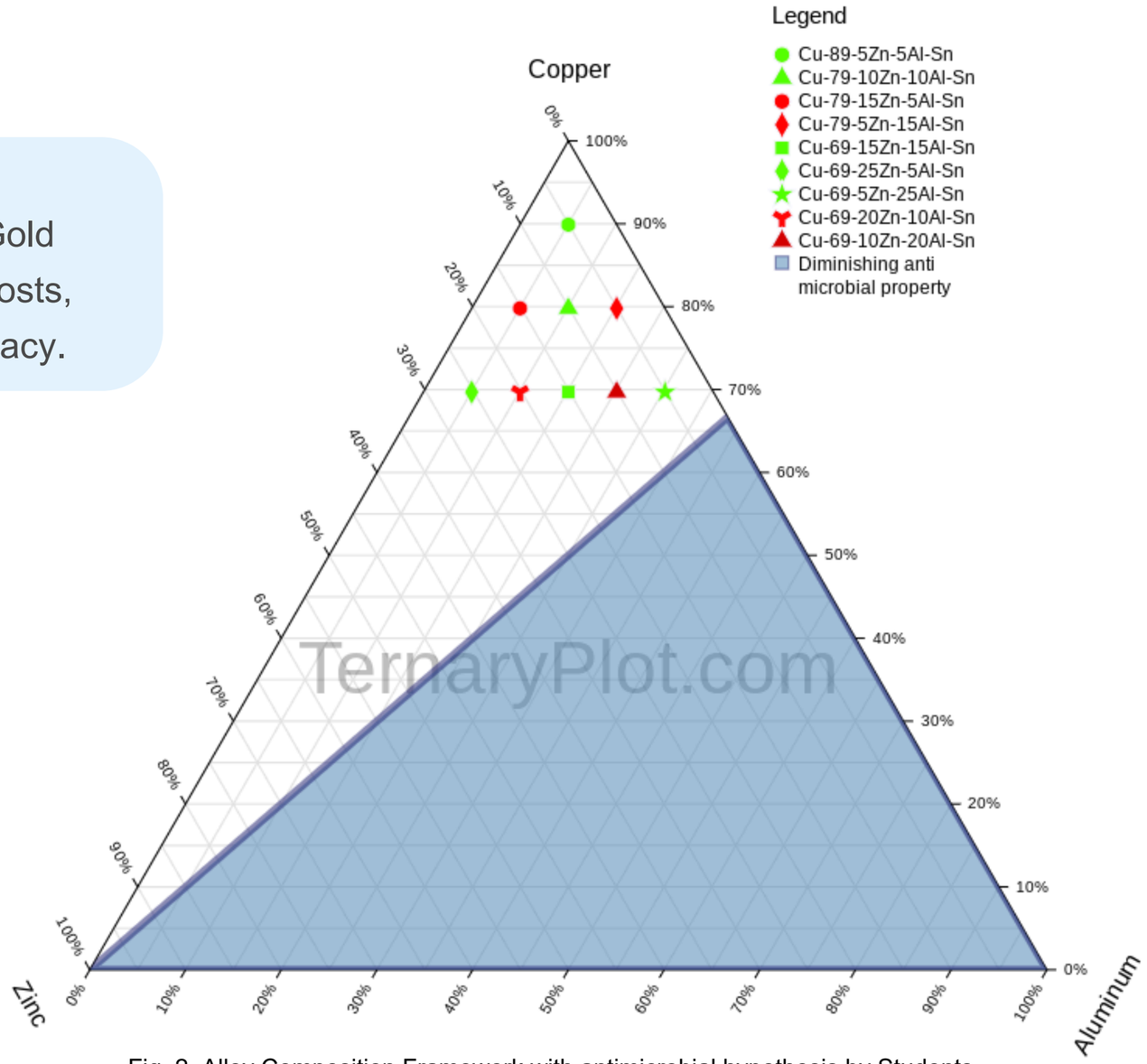


Fig. 2. Alloy Composition Framework with antimicrobial hypothesis by Students

Made with TernaryPlot.com

Methodology I - The Foundry

Melt Temperature

>1000°C

Protective Measures

Argon gas blanket

Safety

Full face Respirator, welding gloves, pants.

Fig. 3. The Foundry, Methodology 1 for Alloy Fabrication. Furnace used and casting of alloy 1 in progress.

Process Flow

Preheat Furnace to 1080C.

In order: Add Cu, Sn, Al, Zn.

Scrape off dross/oxidized metal.

Cast the metal into mold.

Methodology II - Electrochemistry

Test Solution

Artificial Sweat (5g/L NaCl)

Test 1: OCP

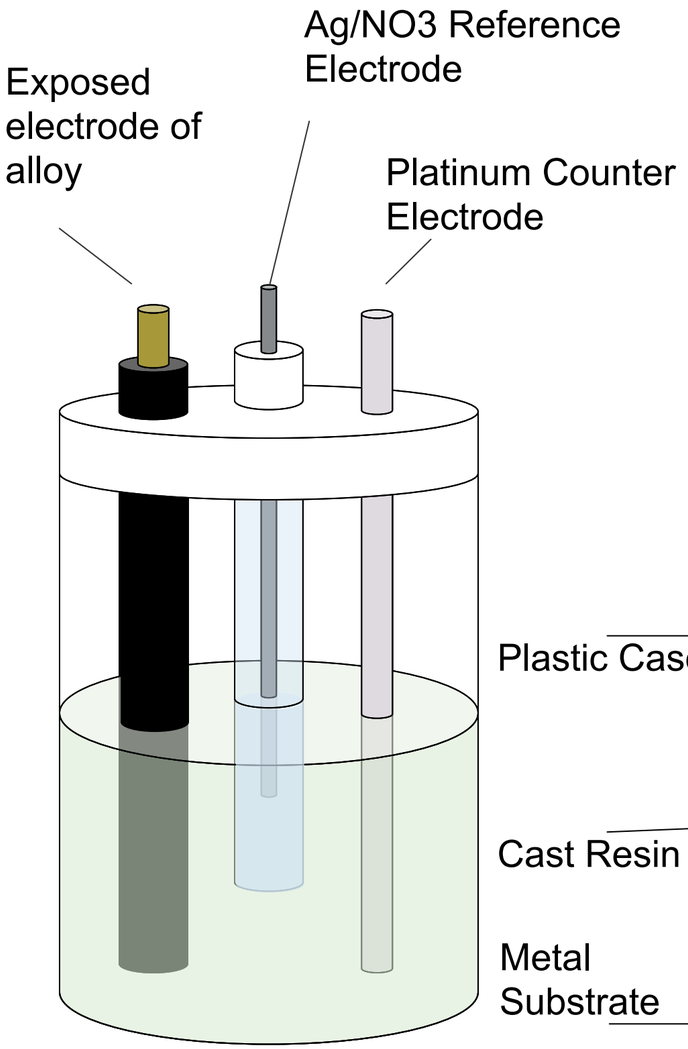
Voltage Potential (Volts)

•Gives quantitative information on chemical reactivity of alloy before corrosion tests begin.

Test 2: EIS

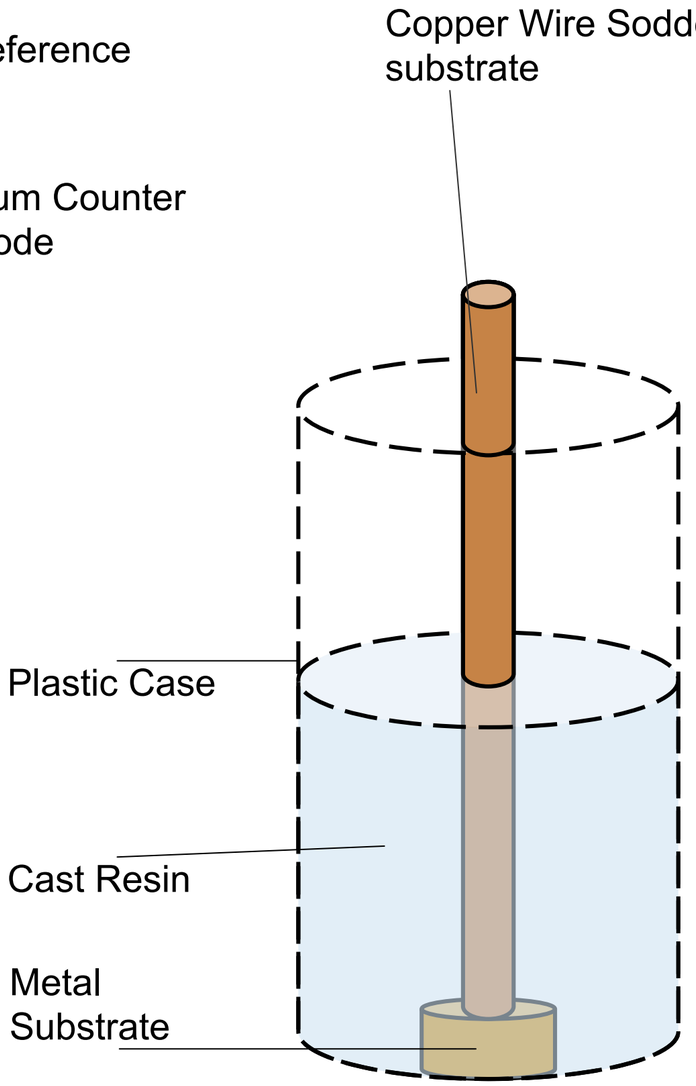
Impedance / Durability (Ohm*cm^2)

•Actual corrosion rate happening in real time. Measures how resistive the alloy is to electron movement (electron movement dictates reactions).



Electrochemical Cell

Fig. 4 Student made representation of 3 electrode electrochemical cell.



Custom-made working electrode

Fig. 5 Student made diagram of how working electrode was created.

Methodology III - Microbiology

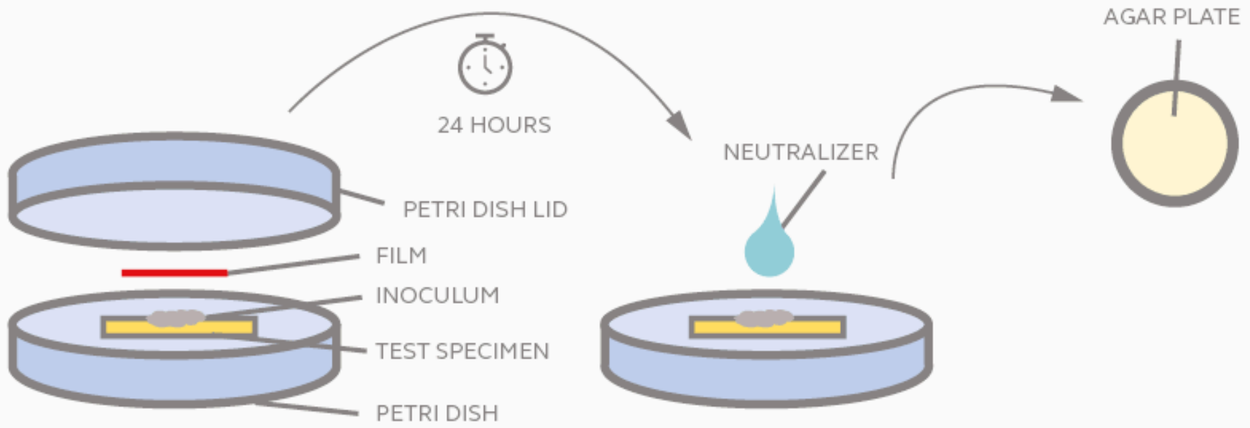
> **Antimicrobial Testing Standard**
>
> Modified ISO 22196

Model Bacteria

Bacteria: *E. coli* HB101 strain

1:10 dilution of Phosphate Buffer solution

Diagram 1: ISO 22196 test method



https://www.viroxylabs.com/microbiological-testing-services/disinfectant-efficacy-testing/iso-221962011/

Fig. 6. ISO 22196 Testing Method by Viroxy Labs

Modified ISO 22196 Process

Inoculate 30µl of *E.Coli* Innoculum onto alloy coupon.

Incubate for desired contact time.

Recover bacteria by washing with 5ml PBS solution.

Plate 100µm for 24 to then compare to no treatment.

Results - Composition Verification

Analysis Method

XRF Spectroscopy (X-ray Fluorescence)

Result

Castings matched target ratios

Notes

- Aluminum loss due oxidation
- Zinc loss due to vaporization
- Impurities due to aluminum source (melted cans)

Target Composition				
Name	Cu%	Zn%	Al%	Sn%
Pure Copper	100			
Alloy 1	69	20	10	1
Alloy 2	79	7.5	7.5	1
Alloy 3	79	10	10	1
Alloy 4	69	15	15	1
Alloy 5	69	25	5	1
Alloy 7	89	5	5	1
Alloy 8	79	5	15	1

Fig. 7 Student made Table of target compositon of each alloy made.

Actual Composition Sourced Via XRF					
Name	Cu%	Zn%	Al%	Sn%	% Impurity
Pure Copper	1				
Alloy 1	68.72	19.44	8.42	1.53	1.89
Alloy 2	83.84	5.46	9.2	1.27	0.23
Alloy 3	78.99	8.94	9.72	1.54	0.81
Alloy 4	68.46	12.69	11.95	1.265	5.635
Alloy 5	69.2	25.1	4.2	1.17	0.33
Alloy 7	87.18	5.72	4.91	1.3	0.89
Alloy 8	79.86	4.97	12.16	1.47	1.54

Fig. 8 Student made Table of actual compositon of each alloy made.

Results - Electrochemical Data

Alloy 1

Highest Impedance (Most Durable).

Alloy 3

Most Noble Metal (Least Chemically reactive).

Charge Transfer Resistance

•Only alloy 1 had significant p value when comparing to any other alloy.

Open Circut Potential

•Alloy 3 is the most noble metal, would be best used on ships to prevent dezincification.

Circuit Fit Used (R1 + Q2/R2)

R1 = Solution Q2=Alloy Surface

R2 = Alloy

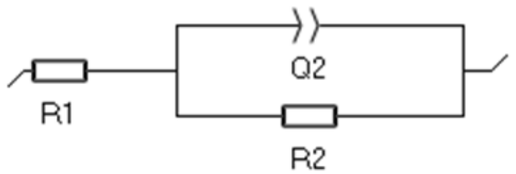


Fig 18. Equivelant Randles Circuit (R1 + Q2/R2). Sourced via EC-Circuit Lab.

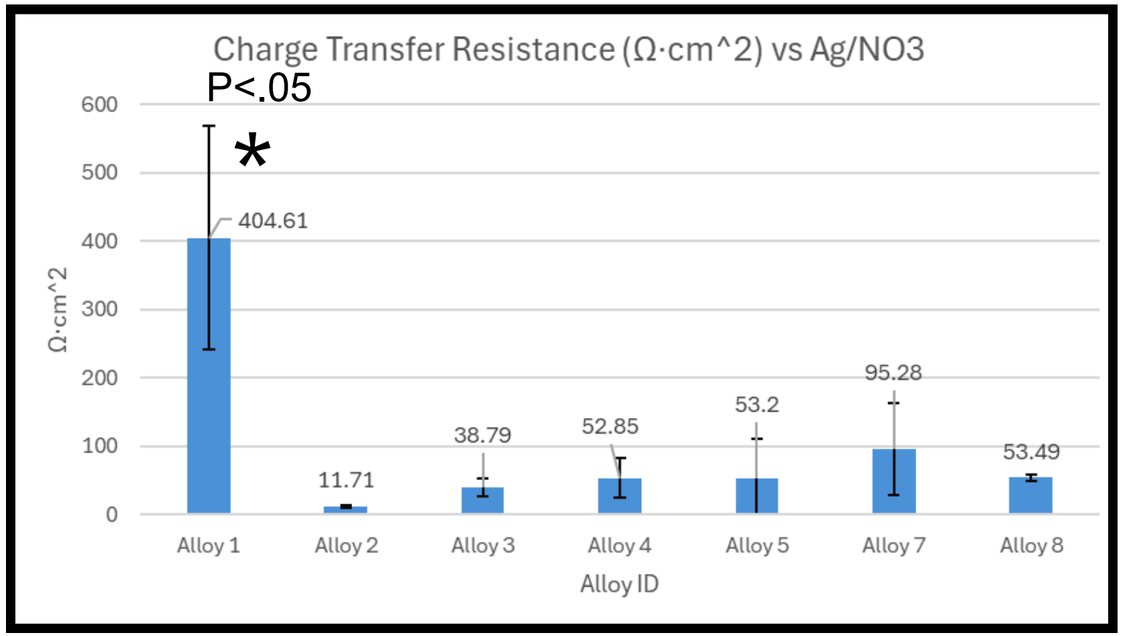


Fig. 9 Student made graph of aquired Rct values.

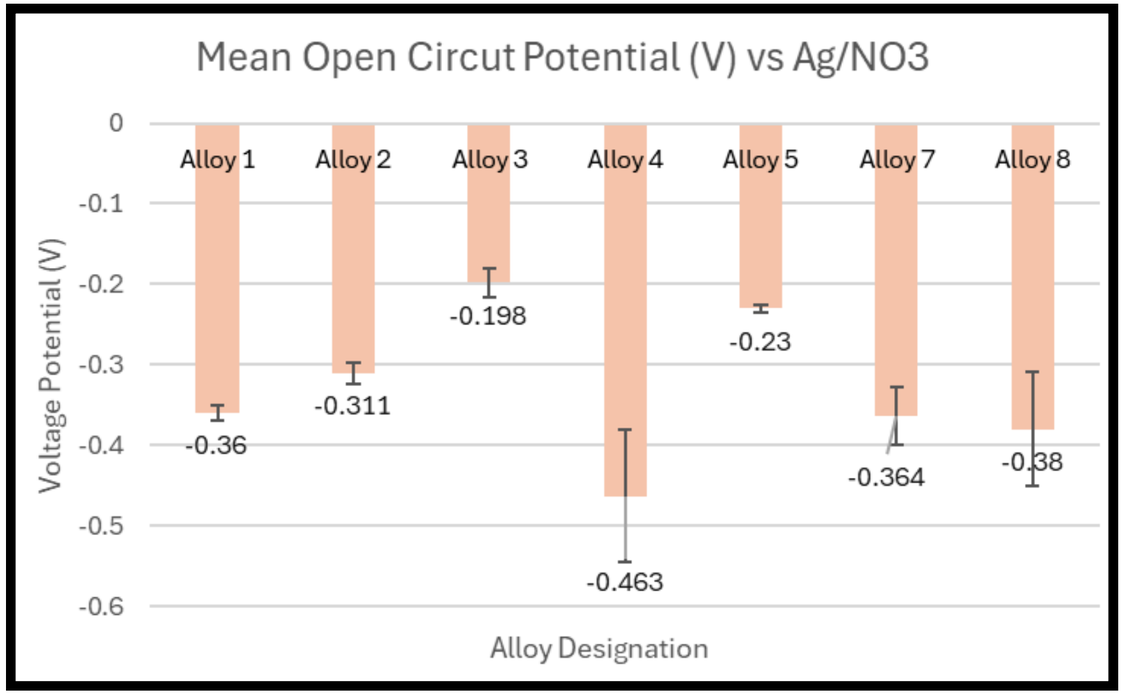


Fig. 10 Student made graph of aquired OCP valuesvalues.

Results - Microstructure

Alloy 1

Homegenous structure means uniform attack

Alloy 8

Heterogeneous structure allows for corrosion hotspots

XRD

Alloy1: α-brass

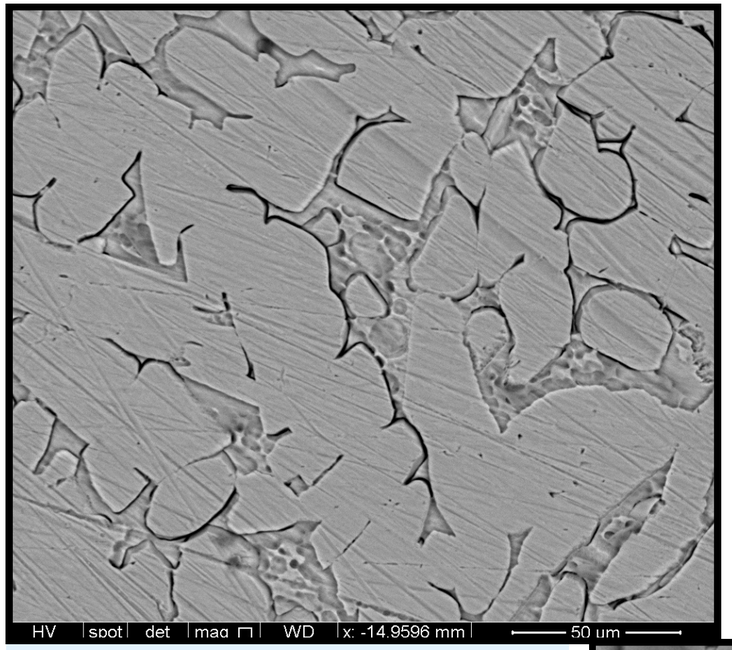
Alloy 3: α- and ß-brass mix

Alloy 4: ß- brass

Alloy 8: ß- and γ-brass

Analysis

Uniformity and phase determine corrosion



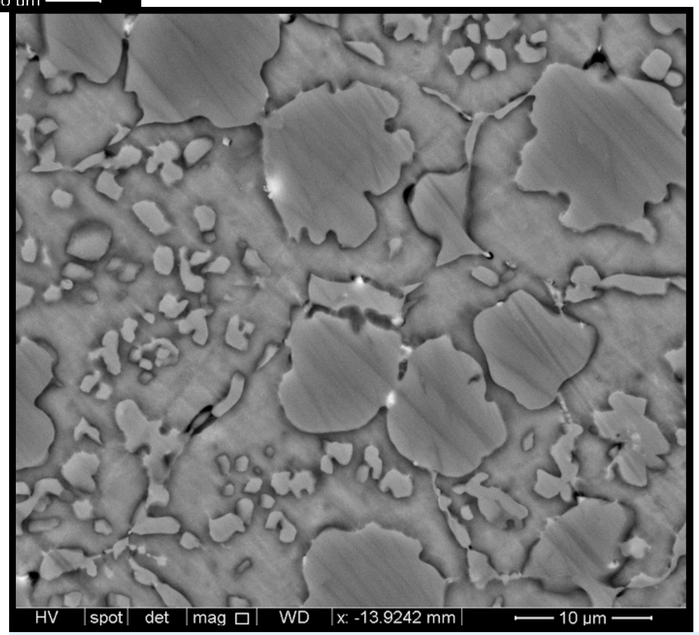
BSED of Alloy 1

Alloy 1 shows α-brass distrubition with preciptates of non incoporated elements. Larger grain size increases corrosion resistance and workability.

Fig.11 Student aquired image of BSED image of alloy 1.

Alloy 8 shows non uniform grain size and crystals. Smaller grain sizes makes it more susceptible to corrosion.

Fig.12 Student aquired image of BSED image of alloy 1.



BSED of Alloy 8

Results - Bacterial Efficacy

Alloys 1, 2, 3, 7

~5 Log Reduction

Alloy 1 and 3 Tested Further

Mean log reduction at T=~30 min meets EPA standard.

Visuals below show antimicrobial plates after 2 hrs show great antimicrobial activity.

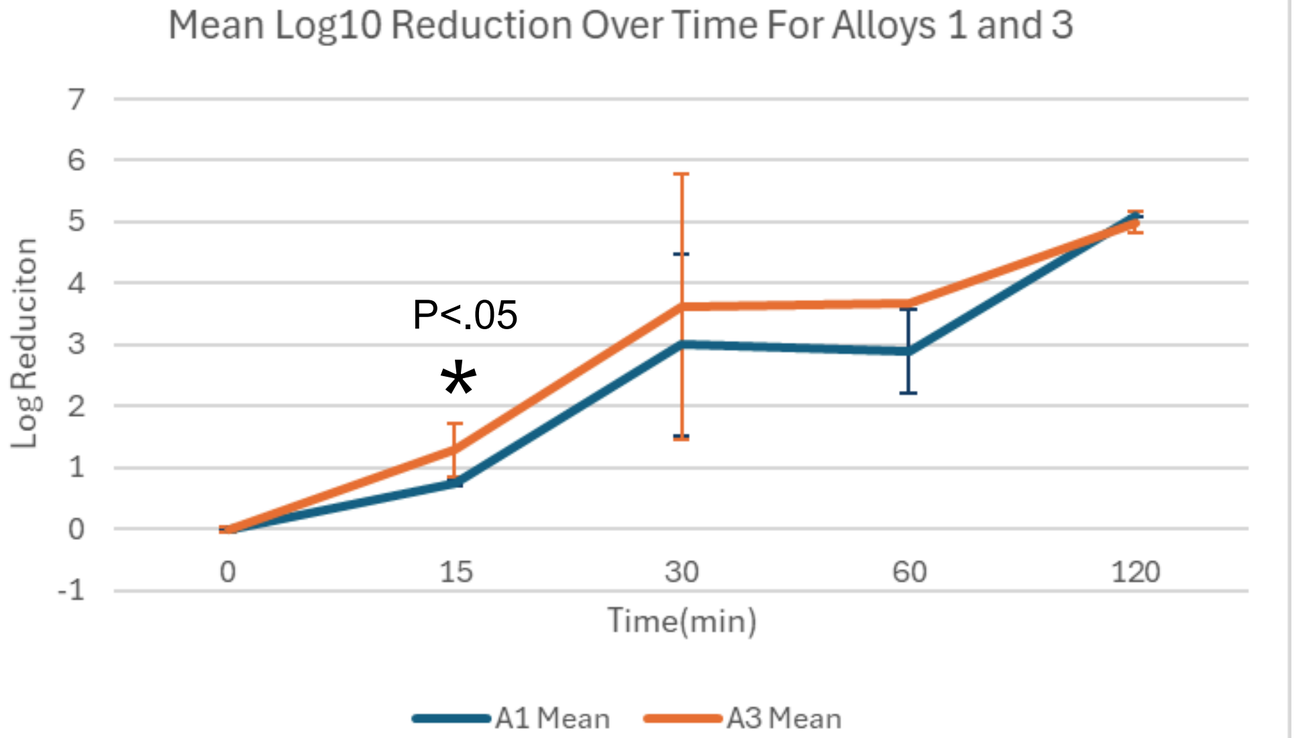


Fig.13 Student made graph of log reduction of alloys 1 and 3.

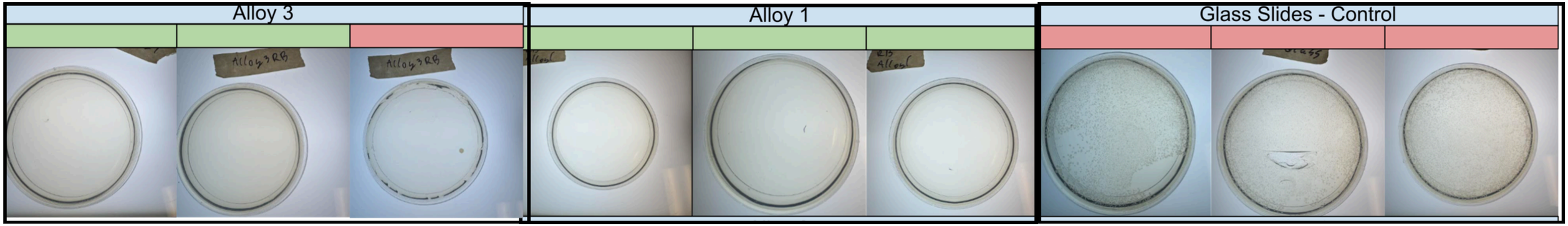


Fig.14 Student made image of select assayed plates at t=2 hrs.

Conclusion - The Verdict

Winner: Alloy 1 (Cu69%)

- High Antimicrobial Power
- High Corrosion Resistance
- Lower Cost (Less Copper)

Fig.16 Student made image of aliquot of alloy 1.

Discussion - What We learned from this Alloy system

- **There is a suggestion for inverse relationship between Rct and Antimicrobial activity**
  - Follows a thermodynamic logic that the less chemically resistant metals output more ions.
  - Was not followed by other timestamps due to the assays nearing our limit of detection.
- **The effect of impurities.**
  - Magnesium and other impurities on antimicrobial tested alloys did not hinder antimicrobial ability to meet 2 hour log reduction goal.

- **The addition of Aluminum lowers the threshold for Gamma Phase formation of %wt Zn.**
  - Alloys 4 and 8 showed γ-brass formation at lower concentrations of zinc due to aluminum acting as a substituting atom in crystal structure.

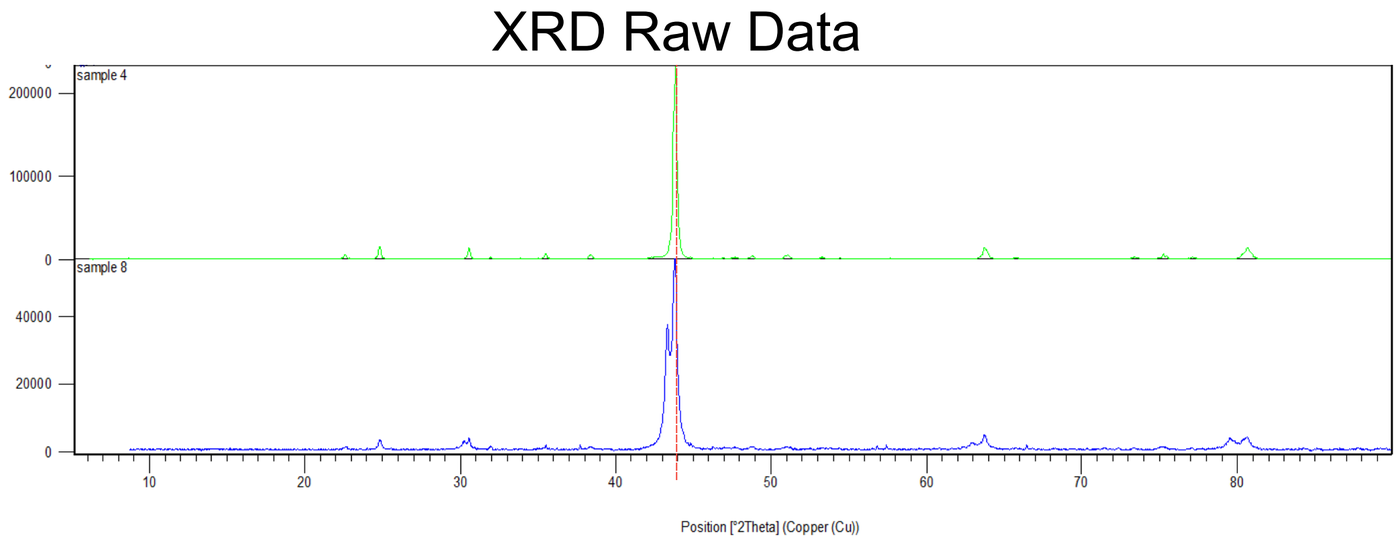


Fig.17 Figure of XRD results with line to indicate gamma phase peak. Sourced by students.

Future Applications

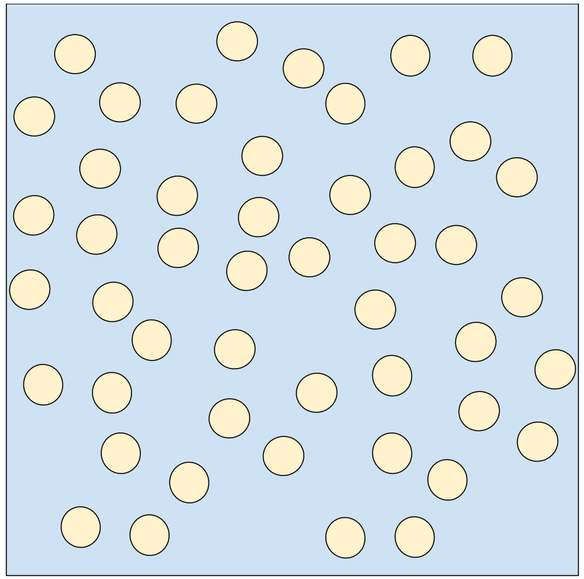
Future models to test

- MRSA
- Cupriavidus metallidurans – Bacteria that thrives on metals.
- Virus denaturing.

Future Research Ideas

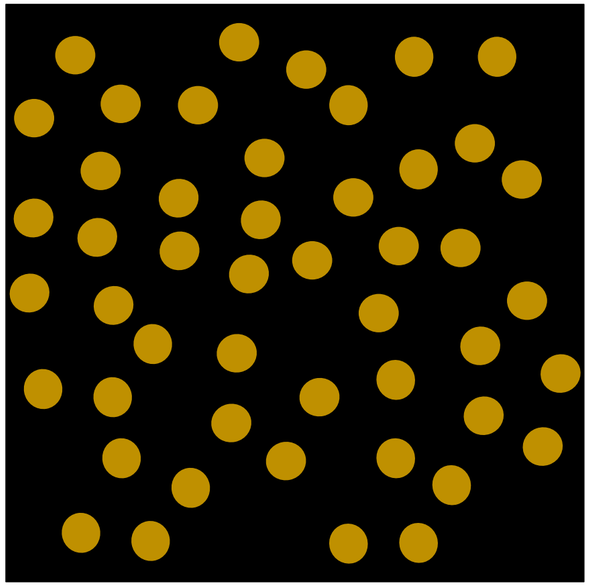
- Resistance to Biofilm Formation
- Tested properties after oxidation.
- Kinetics of ion release.
- Test Mechanical Properties

Proposed Hospital Paint



- Powdered with alloy 1.
- Possibly survive the harsh chemical treatments.
- Use latex paint base.

Proposed Marine Paint



- Powdered with alloy 3.
- Chemical reactivity means limits dezincification.
- Use oil alkyd paint base.

References

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https://cact.utoronto.ca/fields-of-research/anti-microbial-copper-based-alloys-coatings/anti-bacterial-coatings/