Investigating a bio-oxidant for adjustment of copper alloys' weather patina

Collaboration abstract for Queensborough Community College c/o Dr. R. Scal

February, 2011

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John Scott .
BA, MA, MBA, MA-CAS
NYC, USA.

President, New York Conservation Foundation, Inc.
New York State nfp organization, IRS 501 (c) 3

Principal, John Scott Conservator of Art and Architecture
Professional business

Atmospheric sources of corrosives

oxygen **O2 + 2 H20 > H2O2 + 2 OH-** dissolved oxygen is a very strong oxidant

carbon dioxide **CO2 + H2O > + 2 H+ + (CO3)2-** carbonic acid

sulfur dioxide **SO2 + 2 H2O > w/NOx > 2 H+ + SO4-** sulfuric acid

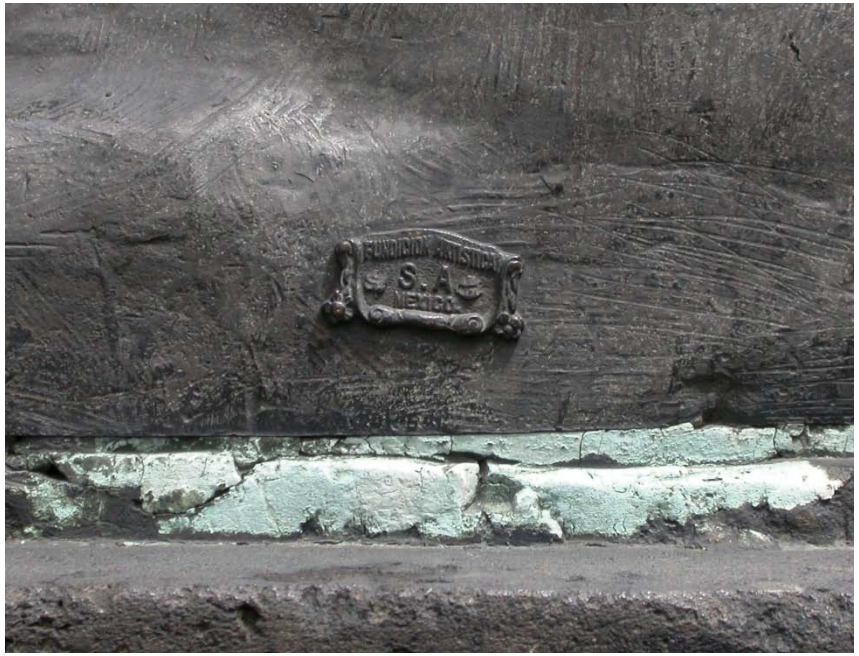
oxides of nitrogen **NOx + H2O .> > > 2H+ + +NO3-** nitric acid

salt **NaCl + H20 > Cl- + H+ + Na+ + OH--** chloride ion

Popocatepetl, a geological source

Weather patina near Popocatepetl

Most metal patina in Mexico City seems high in sulfur



Formation of bronze's weathered patina

Sn + O2 + 2 H2O > SnO2 + 2 H20 Stannite, tin oxide

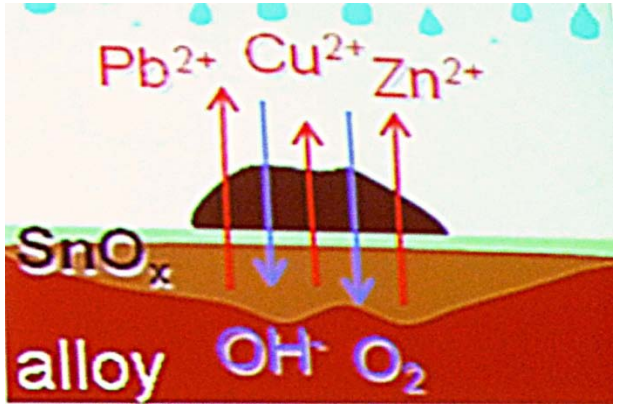
2 Cu + O2 + 2 H2O > 2 CuO + 2 H20 Cuprite, copper oxide

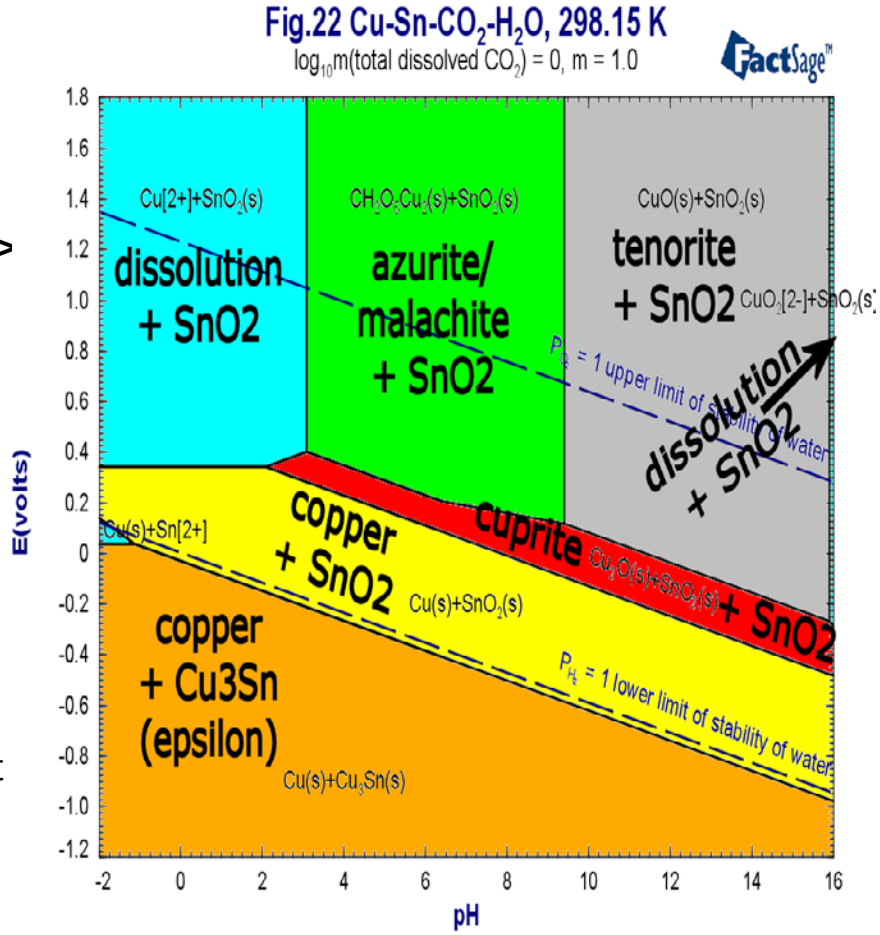
4 CuO +3 H20 + SO2 + ½ O2 > CUSO4 . 3 (Cu(OH)2)
Brochantite, an hydroxysulfarte of copper

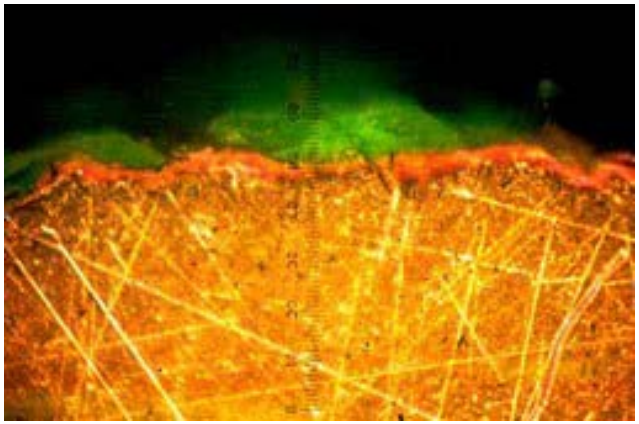
2Cu + CO2 + O2 + 2 H2O > CuCO3 + Cu(OH)2 + H2O > CuCO3 . Cu(OH)2
Copper carbonates

Seldom present:

Cu + 4 HNO3 > Cu(NO3)2 + 2 H2O + 2 NO3 // NaCl + H20 > Cl- + H+ + Na+ + OH--
Copper nitrate, usually lost in runoff, as it crystallizes wit difficulty in most outdoor conditions







Weather patina developing on bronze outdoors

Weather patina on bronze, cross section, top rt.

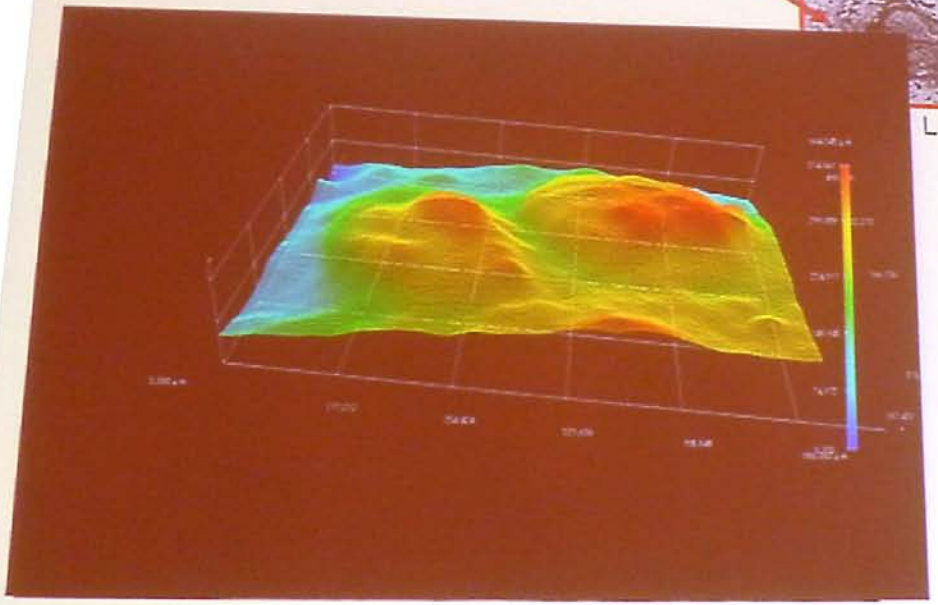
Standard patina development chronology, lower rt.

Study source of following images

Results / Unsheltered areas: pale green patina-black islet

PG (pale green patina)
BI (black islet)

- surface



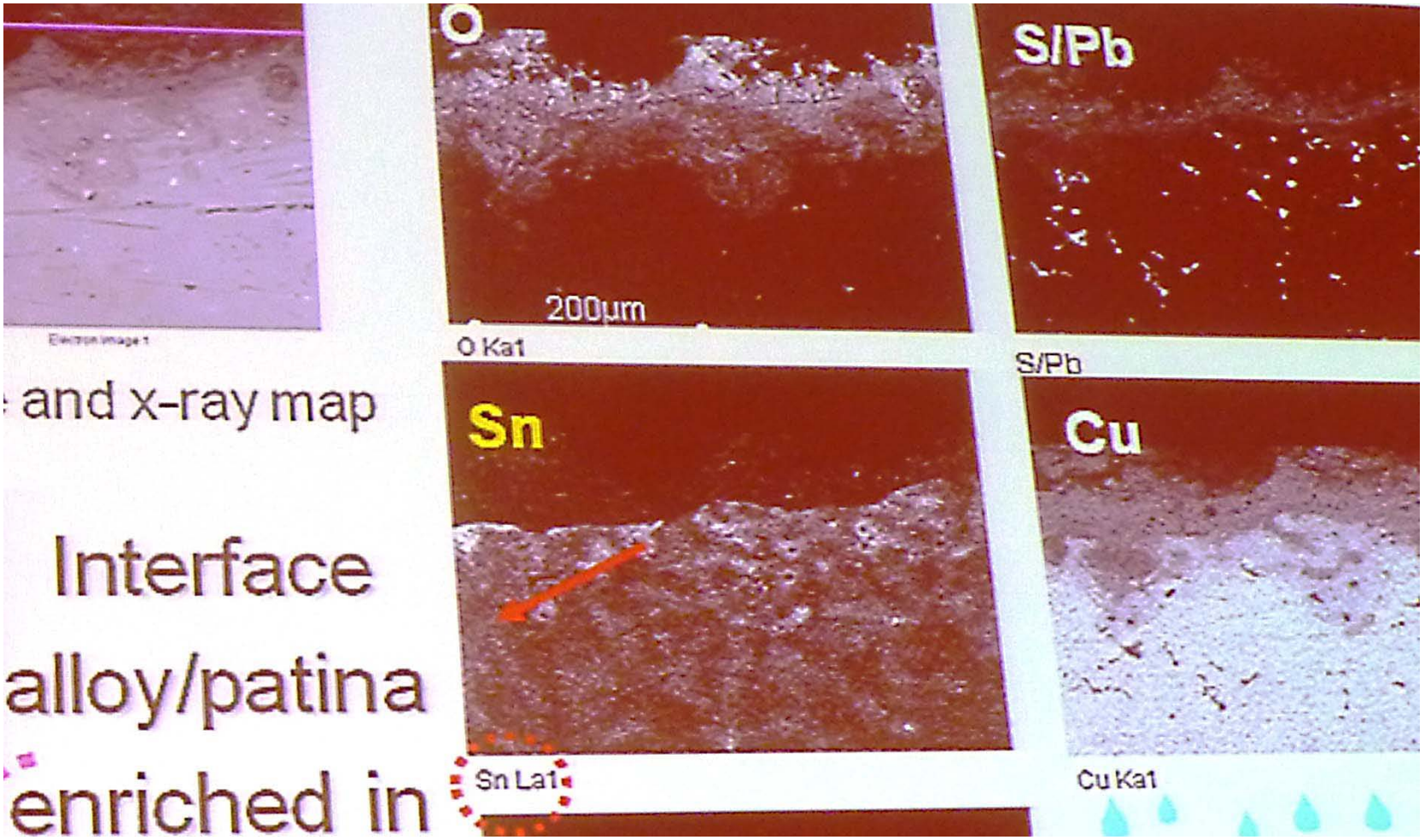
L.Robbiola *et al.*, Applied Physics A 92 (2008) 161-169.

Louis XIV (1836, Versailles)

Weather patina: its stratified structure and components

(Robbiola et al, 2008)

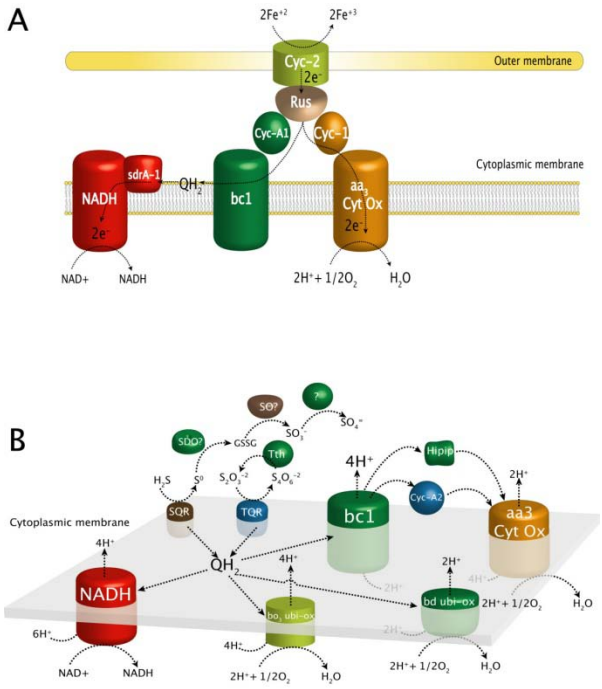
BSE image X-ray elemental maps .



Acidithiobacillus ferrooxidans

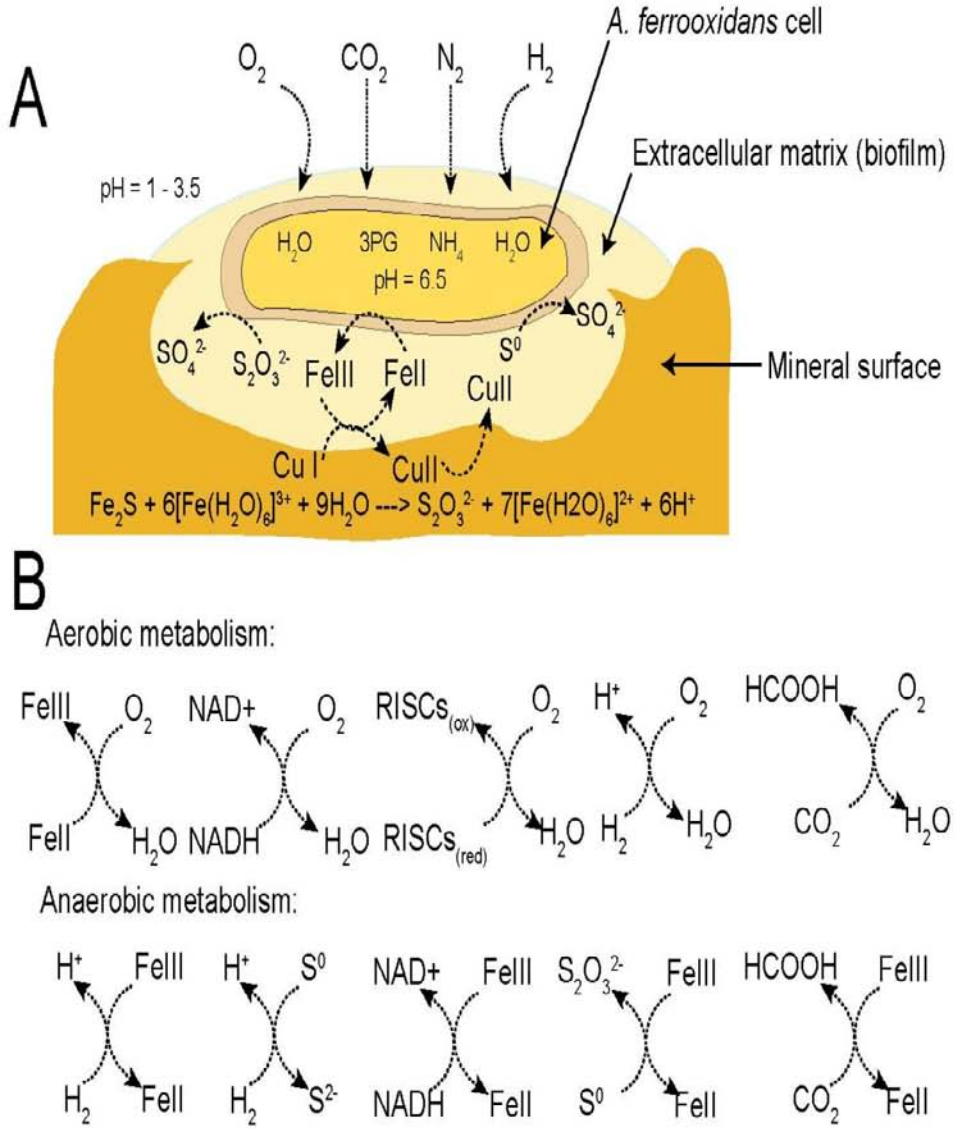
TEM image **X30000 (Lundgren)**

Metabolism iron oxidizing and water oxidizing metabolisms, in media ca. pH 2.8 (Valdez, et al 2009)



Microbial attack on patina's outer hydrosulfate stratum

(diagrams from Valdes, et al 2009)



Media for Cultivating *Acidithiobacillus ferrooxidans*

Ingredient	Quantity of Ingredients (g L^{-1})			
	9K[a]	T&K[b]	L[c]	T and C[d]
$(NH_4)_2SO_4$	3.0	0.4	0.15	0.5
KCl	0.1	—	—	—
K_2HPO_4	0.5	0.4	0.05	—
$MgSO_4 \cdot 7H_2O$	0.5	0.4	0.5	1.0
$Ca(NO_3)_2$	0.01	—	0.01	—
$FeSO4 \cdot 7H_2O$	44.22	33.3	1.0	129.1

H20, HNH3, SO4-2, Fe+2, pH ca 1 – 3.5

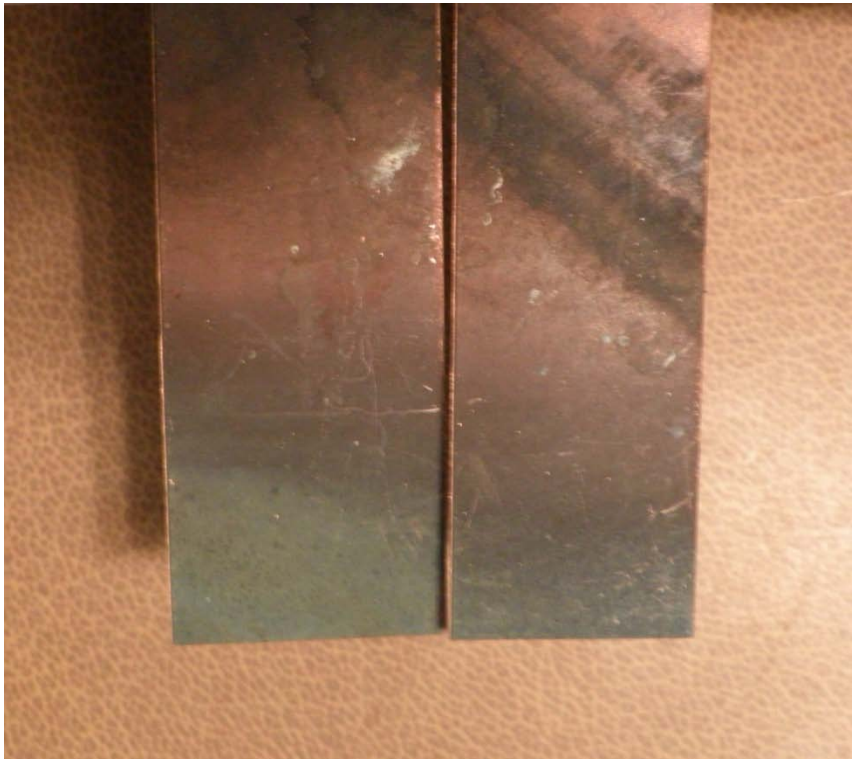
Orange juice pH is ca 2.8

Experimental

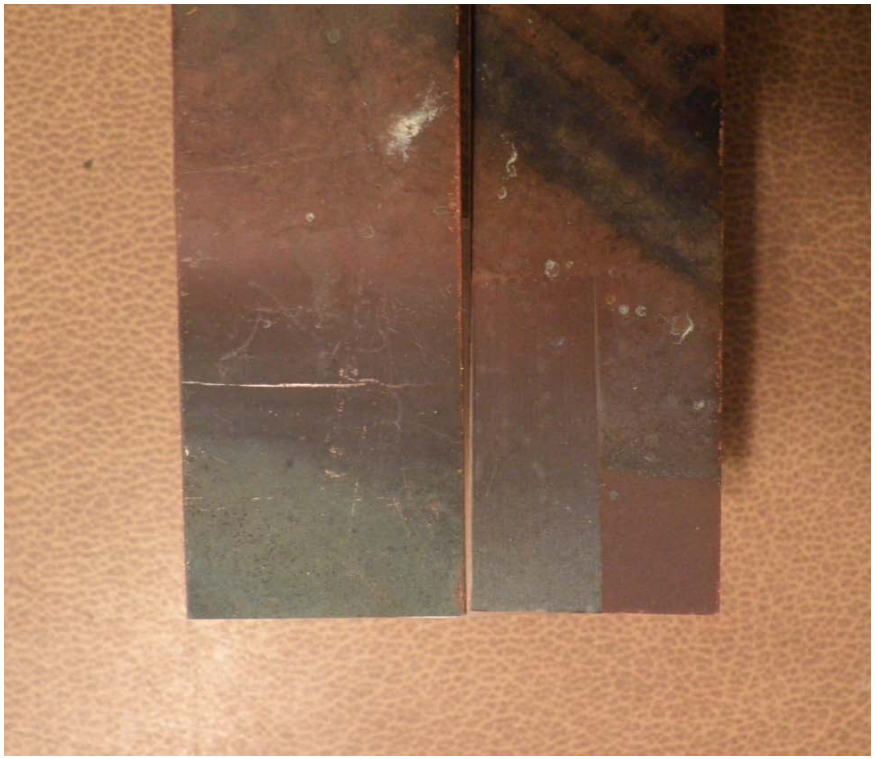
Macro and micro effects of bio-oxidant gel

Two coupons of roofing copper, surfaces corroded outdoors
control coupon left, test coupon right, test area lower right

macro, before test



macro, after test



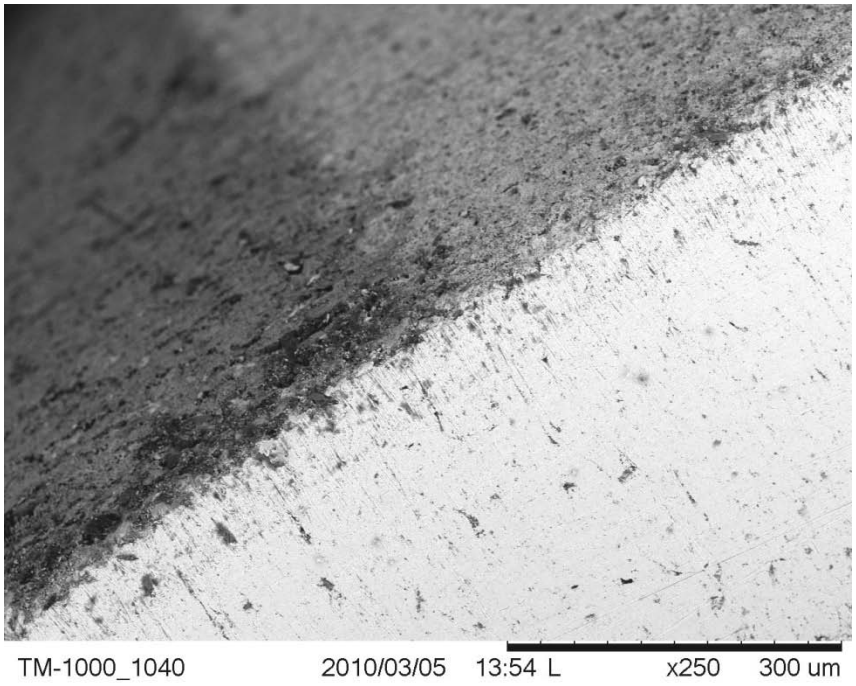
SEM, EDS in collaboration with Queens Community College

Micro (SEM) views of test area

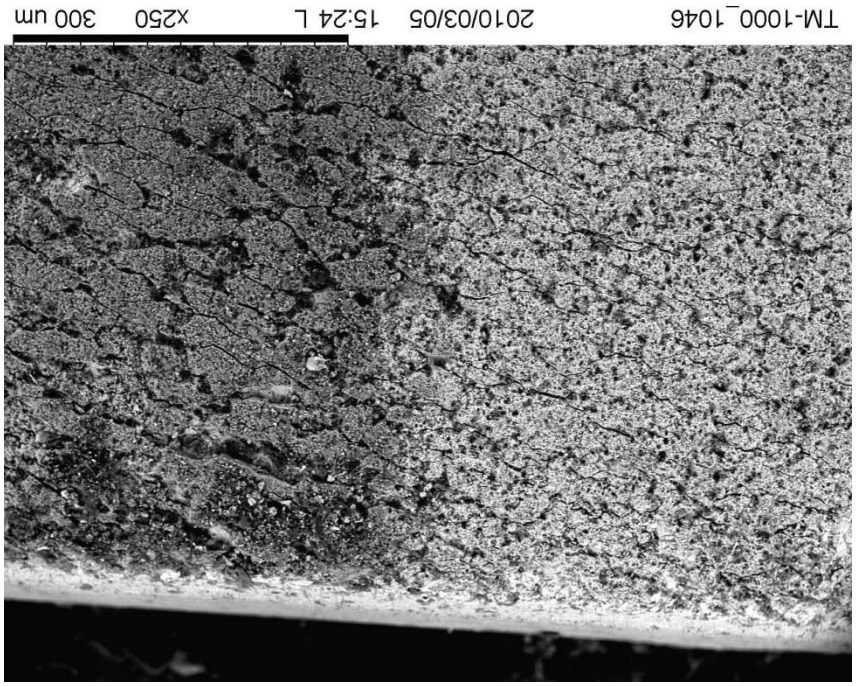
Surface at right was exposed to the method

Surface at left was shielded from the method

inclined view , test surfaces upper left
x-sectn lower rt



perpendicular view of test surfaces .

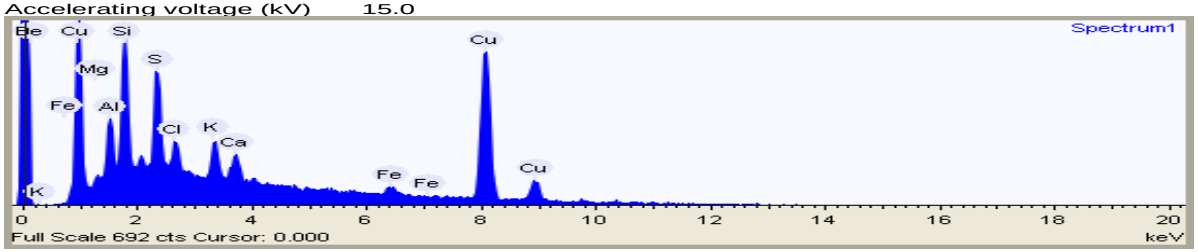


SEM-EDS analysis of the test surfaces

Spectrum 1 is of the surface not subjected to the method
Spectrum 5 is of the surface subjected to the method

Note that S5 shows neither sulfur nor many other elements that appear in S1

Spectrum name	**Spectrum1 outdoor weathered copper coupon**
Location	flat non-method-exposed surface very near transition 10000 b.ipj
Acquisition time (s)	120.0
Process time	4
Accelerating voltage (kV)	15.0

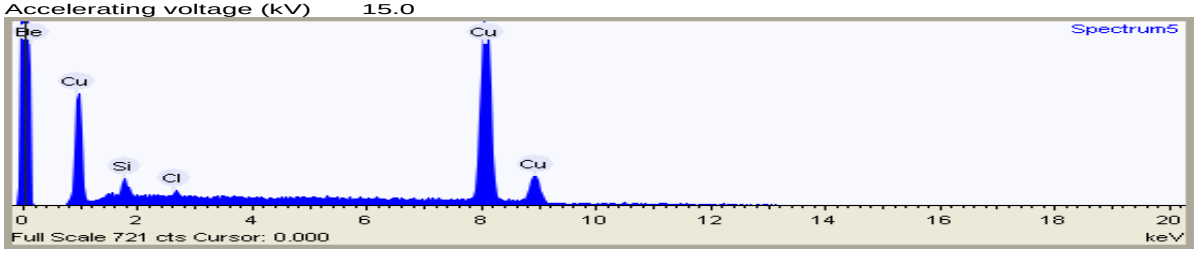


Quantification method All elements (normalised)

Summary results

Element	Weight %
Magnesium	1.4
Aluminum	5.2
Silicon	11.4
Sulfur	8.6
Chlorine	3.0
Potassium	3.9
Calcium	2.7
Iron	2.7
Copper	61.1

Spectrum name	**Spectrum5 outdoor weathered copper coupon**
Location	flat method-exposed surface very near transition 10000 b.ipj
Acquisition time (s)	120.0
Process time	4
Accelerating voltage (kV)	15.0



Quantification method All elements (normalised)

Summary results

Element	Weight %
Silicon	5.1
Chlorine	1.5
Copper	93.4