

A New Method for Conserving Weathered Surfaces of Copper and Bronze

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Conservators often need to mitigate unsightly patina on bronze or copper forms. Most conservation of weathered outdoor sculpture blocks up hues of weather patina by washing and waxing, or removes some metal during repatination. Textures change as we erode or reform metallic surfaces, and if corrosion products have pseudomorphically replaced metal surface, their removal is loss. With a new method developed using bioactive media which can be independently produced but are readily available, unsightly mottled greenish to black patinas give way to more pleasing reddish browns, with minimal or no loss of form.

The Method in Practice

1. Apply gel or immerse in liquid treatment medium, allow time for action (time based on pretests and observation).
2. Remove medium and rinse well.
3. Keep surface wet while removing softened matter.
4. Rinse well and allow to dry.
5. After treatment, apply coating(s) as needed. Greenish to black colors are replaced by reddish browns (fig. 1 - 6).

Weather Patina on Bronze and Copper

Weather patina covering bronze and copper corroded over time in outdoor moisture and

air, generally at first comprises only metal oxides such as cuprite (oxidized copper), in a dense reddish stratum directly integrated with underlying metal at an interpenetrating interface. Over long periods these patinas usually also comprise copper hydroxysulfates such as brochantite, in a less dense greenish outer layer directly interfaced with the underlying oxides (fig. 7). Weather patinas always entrain diverse matter deposited from air. Many investigators over many years have studied outdoor corrosion of cultural heritage and other metal surfaces, often with some attention to patinas.

Experimental

Hypothesis: Treatment removes greenish sulfates strata, exposes reddish oxides strata, without exposing metallic surface. Experimental: Our treatment method was applied to part of the surface of a coupon cut from weathered copper flashing (fig. 8), while adjacent surface was protected from treatment by waterproof adhesive tape masking, which was removed after treatment. Finally, the surface's resulting adjacent untreated and treated areas were imaged using SEM, and analyzed using EDS. Results support the hypothesis (see fig. 10 a & 10 b).

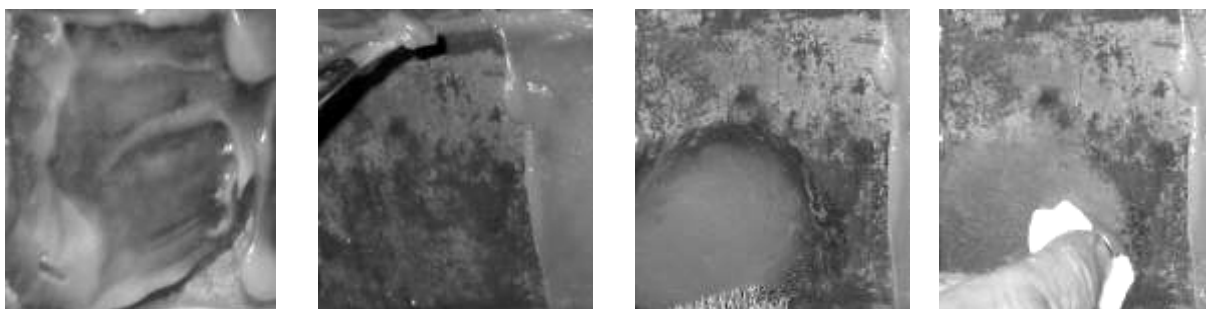
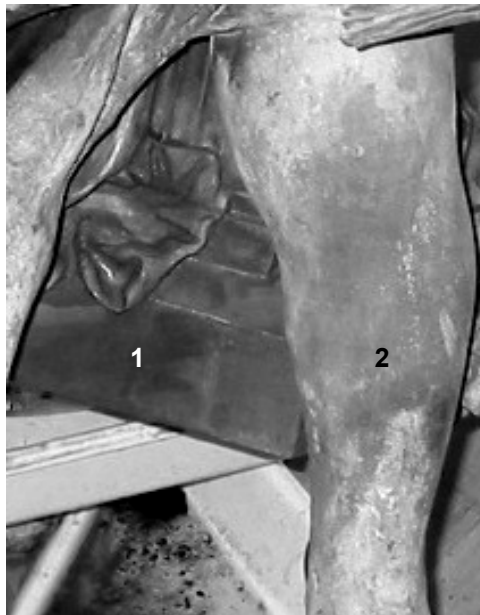
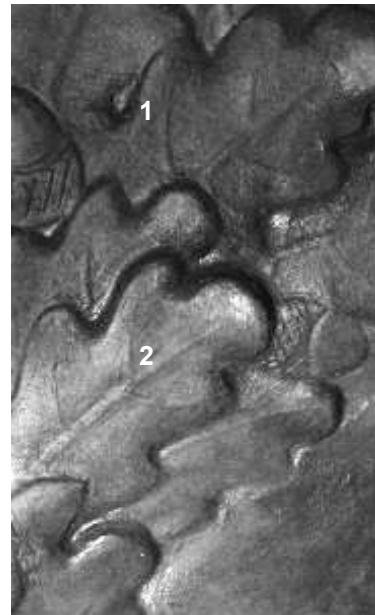


Fig. 1-4 Steps in treatment method.
Photos: J. Heinonen & J. Scott, at NYCF, NYC, USA



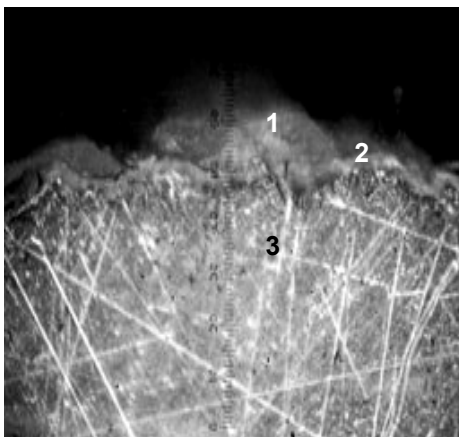
1 before
2 after

Fig. 5 Before/after, detail of Figure. Photo: J. H. & J. S., at NYCF



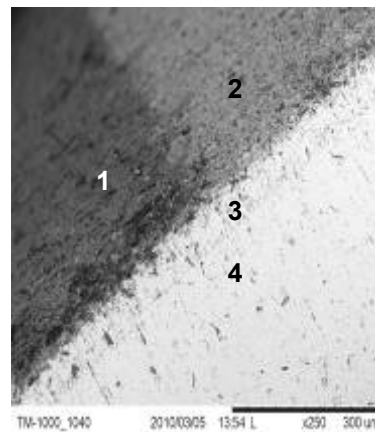
1 after
2 before

Fig 6 Before/after, close detail of plaque Photos: J. H. & J. S., at NYCF



1 sulfates
2 oxides
3 bronze

Fig. 7 Weather patina structure magnified cross section. Photo: R. Lodge, Oberlin, OH, USA



1 untreated
2 treated
3 *CuO₂&Cu*
4 Cu

Fig. 8 Patina coupon surface. Photo: J. Scott

Biochemical process

Literature and observation indicate a sulfates-oxidizing biochemistry enables our treatment, with treatment media adapted from biohydrometallurgy. In bioleaching and biomining, metals are recovered from leach solutions, after ore minerals have been digested via aqueous redox reactions catalyzed metabolically by bacteria such as *Acidithiobacillus ferrooxidans* (fig. 9).

Biooxidation is already used in removing corrosion products from objects made from silver, copper, iron, aluminum and their alloys. Our biooxidative treatment works too quickly for the acidic treatment medium to

erode the patina's oxides layer or underlying metal, and under acidic conditions *A. ferrooxidans*' respiration does not engage copper oxides. Weather patina's layered structure, its layers' distinct compositions of reduced

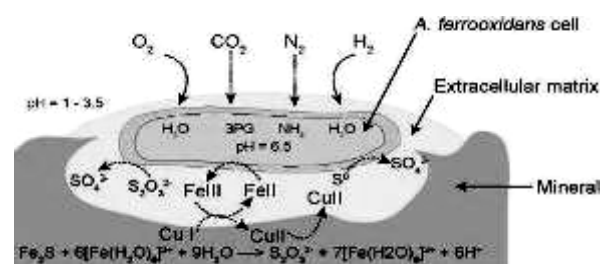


Fig. 9: *Acidithiobacillus ferrooxidans* catalysis of oxidation. Diagram: Valdes, et.al.

copper and oxidized copper, *A. Ferrooxidans*' oxidative respiration in aerobic acidic media, and conservator skill, are all key in this biooxidative treatment for outdoor patinas of copper and bronze. They allow us to soften and remove weather patina's outer sulfates layer, in order to exchange unsightly mottled greenish to black patinas for more pleasing reddish browns, with little or no alteration of texture.

References

Chiavari, C., K. Rahmouni, H. Takenouti, S. Joiret, P. Vermaut, and L. Robbiola, 2007: 'Composition and electrochemical properties of natural patinas of outdoor bronze monuments', *Electrochimica Acta* **52/27**, 7760-7769.

Graedel, T.E., K. Nassau, and J.P. Franey, 1987: 'Copper patinas formed in the atmosphere - I. Introduction', *Corrosion Science* **27/7**, 639-657.

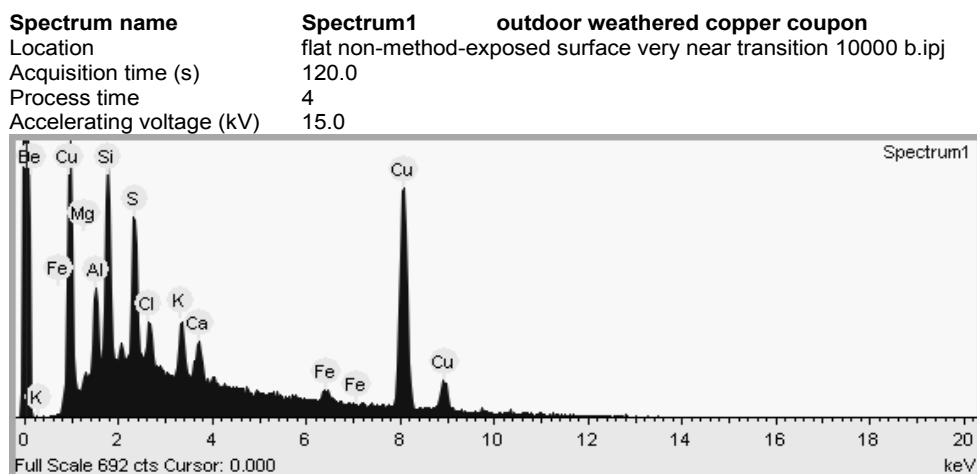
Strandberg, H., 1997: *Perspectives on bronze sculpture conservation: modelling copper and bronze corrosion*. Göteborg: Göteborgs Universitet, AfOK

Valdés J, I. Pedroso, R. Quatrini, R.J. Dodson, H. Tettelin, R. Blake, J.A. Eisen, and D.S. Holmes, 2008: 'Acidithiobacillus ferrooxidans metabolism: from genome sequence to industrial applications'. *BMC Genomics* **9**, 597.
www.ncbi.nlm.nih.gov/pubmed/19077236

Vernon, W.H.J., 1931: 'A laboratory study of the atmospheric corrosion of metals', *Transactions of the Faraday Society* **27**, 255-277.

Vernon, W.H.J., and L. Whitby, 1929: 'The Open-Air Corrosion of Copper. A Chemical Study of the Surface Patina', *Journal Institute of Metals* **24(2)**, 181-195.

Vernon, W.H.J., and L. Whitby, 1930: 'The Open-Air Corrosion of Copper, Part II, The Mineralogical Relationships of Corrosion Products', *Journal Institute of Metals* **44(2)**, 389-96.



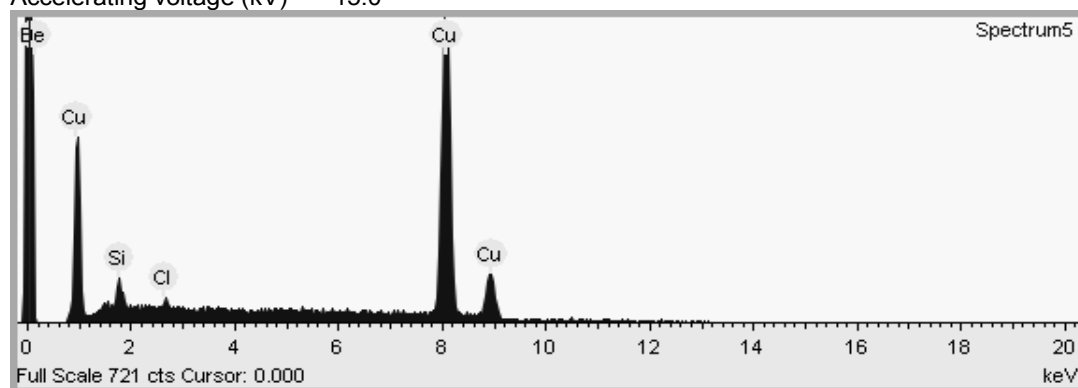
Quantification method All elements (normalised)

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

Fig. 10a EDS spectra of Fig. 5 patina surface: Spectrum 1 untreated. Spectra: J. Scott

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

Fig. 10b EDS spectra of Fig. 5 patina surface: Spectrum 5 treated. Spectra: J. Scott

Acknowledgements

Thanks to Alicia F. Boan and Jari Heinonen.