Removal / blocking Chlorides Salts on Archaeological Bronzes

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Background

Bronze disease

Bronze disease: a progressive deterioration/corrosion of copper alloys caused by formation of cuprous chloride in presence of oxygen and moisture:

Anodic reaction: $Cu\ (s) = Cu^{+} + e^{-}$

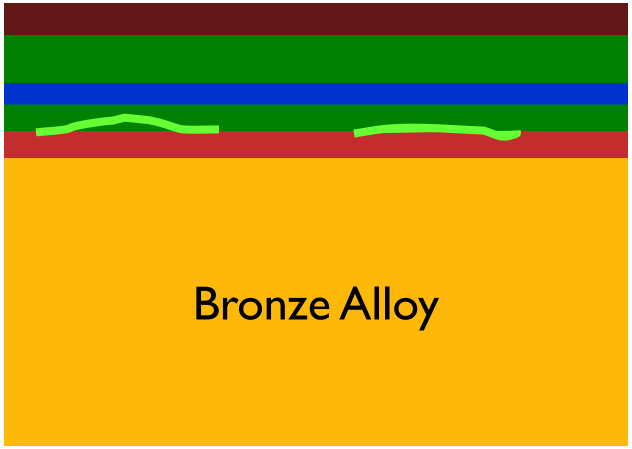
Cathodic reaction: $\frac{1}{2}\ O_2 + H_2O + 2e^{-} = 2OH^{-}$

$$Cu^{+} + Cl^{-} = CuCl(s) \qquad (1)$$

$$4CuCl + O_2 + 4H_2O = 2Cu_2(OH)_3Cl + 2H^{+} + 2Cl^{-} \qquad \Delta G = -360.9\ KJ/mol \quad (2)$$

Background

archaeological patina



Cuprite: Cu_2O
Nantochite: CuCl
Malachite: $CuCO_3 \cdot Cu(OH)_2$
Azurite : $2CuCO_3 \cdot Cu(OH)_2$
Ground

Background

archaeological patina

$$4CuCl + O_2 + 4H_2O = 2Cu_2(OH)_3Cl + 2H^+ + 2Cl^- \quad (2)$$

formation of copper hydroxychlorides isomers atacamite, paratacamite and botallackite

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Ground
Atacamite : $Cu_2(OH)_3Cl$
Paratacamite : $Cu_2(OH)_3Cl$
Botallackite : $Cu_2(OH)_3Cl$

Mazzeo R., *Patine su manufatti metallici, Le patine: genesi, significato e conservazione*, KermesQuaderni Nardini Editore, 2005, pp.29-43

Background

Copper hydroxychlorides

Name	Color	Chemical formula	Crystalline structure
Nantokite	pale green	$CuCl$	Cubic
Atacamite	vitreous green	$Cu_2 (OH)_3 Cl$	Orthorombic
Paratacamite	pale green	$Cu_2 (OH)_3 Cl$	Rhombohedral
Botallackite	pale bluish-green	$Cu_2 (OH)_3 Cl$	Monoclinic
clinoatacamite	pale green	$Cu_2 (OH)_3 Cl$	Monoclinic
Anarkite	Light green	$(CuZn_2)_2 (OH)_3 Cl$	Rhombohedral

Bronze disease: Why dangerous?

- Expand in volume on conversion to one of the copper trihydroxychlorides (cracking and fragmentation)
- Can reduce an apparently solid object into a heap of light green powder

Restoration steps of a bronze object

1. Disassembly
2. Cleaning ⇐
3. Washing treatments
4. Stabilization ⇐
5. Consolidation
6. Reassembly
7. Filling lacunae
8. New support
9. Protection

Removal or blocking Chlorides salts

Cleaning reagents

a. Rochelle salt

$$Cu_2(OH)_2Cl_2 + 2NaOH + 2C_4H_6O_6 \longrightarrow 2\ C_4H_5O_6Cu + 2NaOH + 4H_2O$$

b. Glyceryn or alkaline glycerol

$$Cu_2(OH)_2Cl_2 + 2C_3H_8O_3 \longrightarrow 2C_3H_6O_3Cu + 2H_2O + 2HCl$$

Removal or blocking Chlorides salts

Stabilization techniques

a. Chemical methods

1. Thouvenin method
2. Organ method (1961)
3. Sodium sesquicarbonate (1921)
4. Benzotriazole (BTA)
5. Sodium dithionite (1987)

b. Electrochemical/electrolytic methods

8. Rosemberg Method (1920-1970)
9. Na sesquicarbonate (1948)

1.Thouvenin Method

Treatment for diffuse corrosion

The treatment require the use of two solutions:

A. Complexing solution

$$CuCl_2 + 4NH_3 \cdot H_2O \rightarrow Cu(NH_3)_4Cl_2 + 4\ H_2O$$

blue color

B. Precipitating solutions

2. Organ method

<u>Treatment for small corroded areas</u>

Paste of Ag_2O in EtOH into the corrosion pit

$Ag_2O + 2CuCl = 2AgCl + Cu_2O$

3.Na sesquicarbonate

$NaHCO_3 \cdot Na_2CO_3$ (equimolar mixture)
5% solution in distilled water (pH10)

$$CO_3^{2-} + H_2O = HCO_3^- + OH^-$$

$$2CuCl + OH^- = Cu_2O + 2HCl$$
$$2HCl + Na_2CO_3 = NaCl + H_2O + CO_2$$

Drawback:

1. mineralogical changes of the patina
   $Cu_2O + H_2CO_3 + H_2O = CuCO_3 \cdot Cu(OH)_2 + H_2$
2. formation of chalconatronite(green/blue) $Na_2Cu(CO_3)_2 \cdot 3H_2O$ due to high conc of Na sesquicarbonate

4.Benzotriazole (BTA)

Benzotriazole (BTA) commonly used as an inhibitor

1% BTA solution in deionized water or 3-5% BTA in ethyl alcohol

When BTA reacts with cupric chloride, a cupric BTA derivative precipitates from solution; It has been assigned the formula Cu(BTA)Cl

5.Sodium dithionite

$$3Cu_2(OH)_3Cl + S_2O_4^{2-} + OH^- = 6[Cu(OH)] + 3Cl^- + 4H^+ + 2SO_4^{2-}$$

$$6Cu(OH) + S_2O_4^{2-} = 6Cu + 2SO_4^{2-} + 2H_2O + 2H^+$$

$$3Cu_2O + S_2O_4^{2-} + OH^- = 6Cu + 2SO_4^{2-} + H^+$$

8. Electrochemical method

Rosenberg method (galvanic cell method)

$$3CuCl + Al = 3Cu + AlCl_3$$

- The object is wrapped in aluminum foil and exposed to high humidity (>90% RH)
- A gel poultice of Agar-Agar water and glycerol is used as electrical connection between bronze and foil.

9.Electrolytic method

The artifact is the cathode

A mild steel electrode is the anode

5 % sodium sesquicarbonate can be used for the electrolyte

Applied potential difference: 0.10 V

Current density should not be allowed to fall below 0.02 A/cm^2

Cathodic reaction: $Cu^{2+} + 2e^- = Cu$

Secondary cathode reaction $2H_2O + 2e^- = H_2 + 2\ OH^-$

Anodic reaction: $4OH^- = O_2 + 2H_2O + 4\ e^-$

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Thank you for your attention