Removal / blocking Chlorides Salts on Archaeological Bronzes

Emilio Catelli
Norwegian University of Science and Technology (NTNU)
Department of Chemistry
Trondheim, Norway
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**: \( \text{Cu} (s) = \text{Cu}^+ + e^- \)
- **Cathodic reaction**: \( \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e^- = 2\text{OH}^- \)

\[
\text{Cu}^+ + \text{Cl}^- = \text{CuCl}(s) \tag{1}
\]

\[
4\text{CuCl} + \text{O}_2 + 4\text{H}_2\text{O} = 2\text{Cu}_2(\text{OH})_3\text{Cl} + 2\text{H}^+ + 2\text{Cl}^- \quad \Delta G = -360.9 \text{ KJ/mol} \tag{2}
\]
Background
archaeological patina

Cuprite: $\text{Cu}_2\text{O}$
Nantochite: CuCl
Malachite: $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$
Azurite: $2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$
Ground

Bronze Alloy
Background
archeological patina

$$4\text{CuCl} + \text{O}_2 + 4\text{H}_2\text{O} = 2\text{Cu}_2(\text{OH})_3\text{Cl} + 2\text{H}^+ + 2\text{Cl}^-$$

(2) formation of copper hydroxychlorides isomers atacamite, paratacamite and botallackite

Cuprite: Cu$_2$O  
Nantokite: CuCl  
Malachite: CuCO$_3$ • Cu(OH)$_2$  
Azurite: 2CuCO$_3$ • Cu(OH)$_2$  
Ground  
Atacamite: Cu$_2$ (OH)$_3$ Cl  
Paratacamite: Cu$_2$ (OH)$_3$ Cl  
Botallackite: Cu$_2$ (OH)$_3$ Cl

## Background

### Copper hydroxychlorides

<table>
<thead>
<tr>
<th>Name</th>
<th>Color</th>
<th>Chemical formula</th>
<th>Crystalline structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nantokite</td>
<td>pale green</td>
<td>CuCl</td>
<td>Cubic</td>
</tr>
<tr>
<td>Atacamite</td>
<td>vitreous green</td>
<td>Cu$_2$ (OH)$_3$ Cl</td>
<td>Orthorombic</td>
</tr>
<tr>
<td>Paratacamite</td>
<td>pale green</td>
<td>Cu$_2$ (OH)$_3$ Cl</td>
<td>Rhombohedral</td>
</tr>
<tr>
<td>Botallackite</td>
<td>pale bluish-green</td>
<td>Cu$_2$ (OH)$_3$ Cl</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>clinoatacamite</td>
<td>pale green</td>
<td>Cu$_2$ (OH)$_3$ Cl</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Anarkite</td>
<td>Light green</td>
<td>(CuZn$_2$)$_2$ (OH)$_3$ Cl</td>
<td>Rhombohedral</td>
</tr>
</tbody>
</table>
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

\[ \text{Cu}_2(\text{OH})_2\text{Cl}_2 + 2\text{NaOH} + 2\text{C}_4\text{H}_6\text{O}_6 \rightarrow 2\text{C}_4\text{H}_5\text{O}_6\text{Cu} + 2\text{NaOH} + 4\text{H}_2\text{O} \]

b. Glyceryn or alkaline glycerol

\[ \text{Cu}_2(\text{OH})_2\text{Cl}_2 + 2\text{C}_3\text{H}_8\text{O}_3 \rightarrow 2\text{C}_3\text{H}_6\text{O}_3\text{Cu} + 2\text{H}_2\text{O} + 2\text{HCl} \]
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
   9. Na sesquicarbonate (1948)
I. Thouverenin Method

**Treatment for diffuse corrosion**

The treatment require the use of two solutions:

A. Complexing solution

\[ \text{CuCl}_2 + 4\text{NH}_3 \cdot \text{H}_2\text{O} \rightarrow \text{Cu(NH}_3)_4\text{Cl}_2 + 4\text{H}_2\text{O} \]

blue color

B. Precipitating solutions
2. Organ method

Treatment for small corroded areas

Paste of Ag$_2$O in EtOH into the corrosion pit

$\text{Ag}_2\text{O} + 2\text{CuCl} = 2\text{AgCl} + \text{Cu}_2\text{O}$
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

\[3\text{Cu}_2\text{(OH)}_3\text{Cl} + \text{S}_2\text{O}_4^{2-} + \text{OH}^- = 6[\text{Cu(OH)}] + 3\text{Cl}^- + 4\text{H}^+ + 2\text{SO}_4^{2-}\]

\[6\text{Cu(OH)} + \text{S}_2\text{O}_4^{2-} = 6\text{Cu} + 2\text{SO}_4^{2-} + 2\text{H}_2\text{O} + 2\text{H}^+\]

\[3\text{Cu}_2\text{O} + \text{S}_2\text{O}_4^{2-} + \text{OH}^- = 6\text{Cu} + 2\text{SO}_4^{2-} + \text{H}^+\]
8. Electrochemical method

Rosenberg method (galvanic cell method)

\[ 3\text{CuCl} + \text{Al} = 3\text{Cu} + \text{AlCl}_3 \]

- 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/cm²

Cathodic reaction: \( \text{Cu}^{2+} + 2\text{e}^- = \text{Cu} \)
Secondary cathode reaction: \( 2\text{H}_2\text{O} + 2\text{e}^- = \text{H}_2 + 2\text{OH}^- \)

Anodic reaction: \( 4\text{OH}^- = \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \)
References

- Schott D., Bronze and copper in Art, Getty publication, 2002
- Schott D., JAIC 29(1990): 193-206
- Organ R.M, Studies in Conservation (1962)
- Mazzeo R., KermesQuaderni Nardini Editore, 2005, pp.29-43
Thank you for your attention