An introduction to the history of metals conservation

The Metals Conservation Summer Institute May 27 - June 7, 2006, Worcester, MA, USA

Valentin Boissonnas, HEAA Arc, La Chaux-de-Fonds, Switzerland
An introduction to the history of metals conservation
An introduction to the history of metals conservation

1. Traditional techniques and materials
An introduction to the history of metals conservation

1. Traditional techniques and materials
2. The first conservation research centres
An introduction to the history of metals conservation

1. Traditional techniques and materials
2. The first conservation research centres
3. Chronological survey of concepts and techniques
An introduction to the history of metals conservation

1. Traditional techniques and materials
2. The first conservation research centres
3. Chronological survey of concepts and techniques
   • Corrosion, patina, original surface
An introduction to the history of metals conservation

1. Traditional techniques and materials
2. The first conservation research centres
3. Chronological survey of concepts and techniques
   • Corrosion, patina, original surface
   • Conservation treatments of bronzes
An introduction to the history of metals conservation

1. Traditional techniques and materials
2. The first conservation research centres
3. Chronological survey of concepts and techniques
   - Corrosion, patina, original surface
   - Conservation treatments of bronzes
   - Conservation treatments of iron
Traditional techniques and materials

Traditional products and techniques used on metal artefacts aimed at maintaining their function and preventing their deterioration
Traditional techniques and materials

Traditional products and techniques used on metal artefacts aimed at maintaining their function and preventing their deterioration

• Mechanical treatments: Riveting, soldering, polishing

• Chemical treatments: dissolution of corrosion products (vinegar, lemon juice, oxalic acid, etc.)

• Protective coatings: prevention of atmospheric corrosion after cleaning (paints, lacquers, resins, metallic coatings)
Traditional techniques and materials
Traditional techniques and materials

• **1000 BC:**
  Egyptians use excellent varnishes, heated combinations of oils and natural resins
Traditional techniques and materials

- **1000 BC:**
  Egyptians use excellent varnishes, heated combinations of oils and natural resins

- **Pliny, AD 75:**
  *Iron can be protected from rust by means of cerussa (lead oxide), gypsum and vegetable pitch. Bronze can be coated with turpentine and pitch.*
Traditional techniques and materials

• **1000 BC:**
  Egyptians use excellent varnishes, heated combinations of oils and natural resins

• **Pliny, AD 75:**
  *Iron can be protected from rust by means of cerussa (lead oxide), gypsum and vegetable pitch. Bronze can be coated with turpentine and pitch.*

• **Theophilius, 12th century:**
  *To protect iron, boil it in linseed oil and pitch*
Traditional techniques and materials

- **1000 BC:**
  Egyptians use excellent varnishes, heated combinations of oils and natural resins

- **Pliny, AD 75:**
  *Iron can be protected from rust by means of cerussa (lead oxide), gypsum and vegetable pitch. Bronze can be coated with turpentine and pitch.*

- **Theophilius, 12th century:**
  *To protect iron, boil it in linseed oil and pitch*

- **Cellini, 17th century:**
  First description of mechanical cleaning of archaeological bronzes with small chisels and hammers
Traditional techniques and materials

- **1000 BC:**
  Egyptians use excellent varnishes, heated combinations of oils and natural resins

- **Pliny, AD 75:**
  *Iron can be protected from rust by means of cerussa (lead oxide), gypsum and vegetable pitch. Bronze can be coated with turpentine and pitch.*

- **Theophilius, 12th century:**
  *To protect iron, boil it in linseed oil and pitch*

- **Cellini, 17th century:**
  First description of mechanical cleaning of archaeological bronzes with small chisels and hammers

- **Traditional recipe for knights armour, 1616:**
  *Pour olive oil in a heavy mortar, stir it well with a pestle until it warms itself, put white lead into it and rub it again until it becomes black. Pour a little oil of tartar into it and with Neat’s foot oil or old fat make a salve. Smear armour with the salve.*
Traditional techniques and materials

- **1000 BC:**
  Egyptians use excellent varnishes, heated combinations of oils and natural resins

- **Pliny, AD 75:**
  *Iron can be protected from rust by means of cerussa (lead oxide), gypsum and vegetable pitch. Bronze can be coated with turpentine and pitch.*

- **Theophilius, 12th century:**
  *To protect iron, boil it in linseed oil and pitch*

- **Cellini, 17th century:**
  First description of mechanical cleaning of archaeological bronzes with small chisels and hammers

- **Traditional recipe for knights armour, 1616:**
  *Pour olive oil in a heavy mortar, stir it well with a pestle until it warms itself, put white lead into it and rub it again until it becomes black. Pour a little oil of tartar into it and with Neat’s foot oil or old fat make a salve. Smear armour with the salve.*

- **Far East:**
  Lacquers are used well before the Christian area, mainly made from *Rhus vernicifera*
The first major conservation research centres

Königliches Museum Berlin
inaugurated in 1888.

Otto Olhausen (1840-1922) establishes the first scientific conservation lab and hires Friedrich Rathgen (1862-1942) as assistant.
Rathgen soon becomes head of the research department and will stay there for 40 years doing pioneering work.

‘Die Konservierung von Alterthumsfunden’ (1898)
The first major conservation research centres

National Museum of Denmark in Copenhagen (1855)

Gustav Rosenberg (1878-1941), heads the conservation department.

‘Antiquités en fer et en bronze. Leur transformation et leur conservation’ (1917)

Works mainly with electrolytic reduction techniques to stabilize bronze and iron finds.
The first major conservation research centres

The British Museum London

1920 the conservation research department is opened by Dr. Alexander Scott after many objects were damaged because of bad storage conditions during the 1st World War.

‘The Cleaning and Restoration of Museum Exhibits’ (first report 1921, second 1923, third 1926)
The first major conservation research centres

The British Museum London

1926 Harold Plenderleith is appointed conservation-scientist and heads the conservation & research department.

‘The Conservation of antiquities and works of art’ (1956, 1971)

Robert Organ, a physicist, joins the research lab in 1951 where he works for 14 years before heading for the Royal Ontario Museum and later for the Smithsonian Institution in Washington.
The first major conservation research centres

Columbia University
Professor Colin Fink and his assistant Charles Eldridge are working at Columbia University in the electro-chemical department. They publish in 1925 a manual on the conservation of bronze antiquities.

The Metropolitan Museum of Art installs its first conservation laboratories at Columbia University following the example of the British Museum.
The first major conservation research centres

Rutherford Gettens, chemist and metallurgist, works at the Freer Gallery of Art in Washington on the technology of Chinese bronzes.


After the war museums scientists will found in 1950 the International Institute for Conservation (IIC).

‘Studies in Conservation’ first appears in 1952
The first major conservation research centres

**France-Lanord** (1915-1993)
A founding member of the *Laboratoire d’Archéologie des métaux de Nancy* in France.

Helps developing major concepts such as the integrity of the object and the location of the ‘primitive surface’ or ‘skin’.
1850-1900 Digging up problems
1850-1900 Digging up problems
1850-1900 Digging up problems

‘During the 1860's it was possible to "excavate" as many as sixty-six grave barrows from an Iron Age graveyard in Ringerike, Norway, in ten days, amassing thousands of iron objects in need of treatment once removed from the soil (Hansen 2001).’
1850-1900 Digging up problems

**Corrosion**: First interpretations are rather confused. Some call only nicely preserved green surfaces **Edelrost** or **Patina** (Krause, Vanino / Seitter), others accept a variety of colours, as long as the surface is uniform and smooth (Hausding).

Various attempts are made to chemically describe the variations in colour from green to blue to red with the burial context and the composition of the artefacts.
Corrosion: Many bronzes are excavated from peat bogs and preserve a metallic surface. Others, from lake dwellings, just have calcareous deposits. The acceptance of metallic surfaces and the application of stripping techniques might well have been influenced by those early finds from Northern Europe.
1850-1900 Digging up problems

*Active Corrosion on copper alloys* is first described by Mond and Cuboni (1893) and then by Frazer and Nicols in 1898. **Bacteria** discovered on such items lead to the suspicion that they are responsible for this ‘bronze disease’.

Contaminated objects are systematically sterilized at 120-150°C.
1850-1900 Digging up problems

Cleaning of copper alloys:

The total removal of corrosion products is considered important by certain to regain the aesthetically pleasing metallic shine of the metal (Bibra 1869).

Others are less convinced, as many objects are first stripped and then patinated to satisfy an esthetical look (Petrie 1888).
1850-1900 Digging up problems

**Mechanical Cleaning of copper alloys**: All traditional mechanical methods were in use, such as *wire brushes, abrasive papers, grinding tools, hammers, heating and quenching*. Fragments were regularly *soft soldered* as no adhesives existed that had the necessary strength to hold load bearing metal pieces.

*Animal glue* (fish bladder) was mostly used for smaller parts, *drilling* and *doweling* were standard operations.
Electrochemical cleaning of copper alloys:

Finkener (1886) advocates electrolytic reduction in potassium cyanide (Cyankalium) baths and stripping by hydrogen evolution before thorough washing. Removal of all accessible core material! After brushing with wire brush objects are coated with nitrocellulose lacquer in order to ‘give back a metallic look’.
1850-1900 Digging up problems

**Electrochemical cleaning of copper alloys:**

Axel Krefting (1883), suggests to remove all corrosion layers, preventing further rusting. Bronzes are stripped for 24h by immersion in sodium hydroxide with zinc granules without external electrical source.

Other obscure methods exist at the time, such as dipping coins in liquid lead (Pb), followed by quenching in cold water and leaving over night in milk. Is supposed to give a beautiful olive coloured patina.
Protective coatings for copper alloys:

Protective coatings are already used to protect, consolidate, but also to improve the look of bronzes. Mostly **linseed oil, bees wax** or **shellac**.

The invention of **cellulose nitrate** coatings (Celluloid or Zapon lacquers) is considered a major step in improving surface coatings and is immediately adopted by many conservators.

**Paraffin wax** will replace bees wax and improve long term protection.
1850-1900 Digging up problems

Cleaning & stabilization methods for iron:

Peter Petersen (pre 1870): boiling in linseed oil and coating with hot beeswax (later replaced with Copal varnish).

Axel Krefting (1883): electrolytic stripping techniques. Coating with paraffin wax. Other coatings such as stearin, shellac, linseed oil are frequently used.
1900-1920 Towards a better understanding
1900-1920 Towards a better understanding

Corrosion & mechanical cleaning of copper alloys:

1905 Corrosion that contains detail is defined by Rathgen as a noble patina.

1917 Rosenberg is the first to talk of an original surface and how it can be replaced by corrosion products. He also suggests that it is possible to find it by mechanical means.
1900-1920 Towards a better understanding

**Mechanical cleaning of copper alloys:**

An interesting method is described by *Springer* who coats bronzes with hot and liquid *animal glue*. While drying it shrinks and pulls off mostly external corrosion products.
1900-1920 Towards a better understanding

Active Corrosion on copper alloys:

The debate about what influences the corrosion of copper alloys continues. Sometimes even chlorides are attributed to the good preservation of bronze surfaces!

It is Rathgen (1889), Krefting (1892) and then Petrie (1904) who suggest that chlorides are the reason for actively corroding bronzes. From then onwards chlorides are acknowledged by most to be the source of active corrosion.

Conservation treatments now aim at removing chlorides from objects in order to stabilize them. This has priority over the growing concept of preserved information within corrosion products.
1900-1920 Towards a better understanding

**Stabilization of copper alloys**:

*Rosenberg* advocates a localized stabilization method by using *aluminium foil* and an *Agar Agar / Glycerol* electrolyte to electro-chemically reduce copper chlorides into stable cuprite or tenorite.
1900-1920 Towards a better understanding

**Stabilization of iron**: 

1904 *William Flinders Petrie* uses on-site washing of iron in water, oven drying, waxing.

1905 *Rathgen & Finkener* propose boiling iron in molten potassium cyanide.

1917 *Rosenberg* suggests heating iron up to 800 °C, quenching in potassium carbonate. Subsequent boiling in frequent changes of distilled water until no more chlorides. Boiling in paraffin or microcrystalline wax.

Other impregnation methods use water glass, natural rubber, dammar resin, linseed oil, and animal fats.
1920-1950 New concepts and old recipes
1920-1950 New concepts and old recipes

**Corrosion:**
Total removal of corrosion products is being seriously questioned by *Rathgen* in his reedited book (1924) and *Scott* (1926), who now considers a corroded surface far more important than a shiny surface of bare metal.

With the introduction of the Rosenberg method there is an alternative to stripping actively corroding bronzes.

However, the loss of such surfaces observed with some treatments is still accepted in order to stabilize objects.
1920-1950 New concepts and old recipes

Cleaning copper alloys:

Vigorous chemical cleaning methods are still used such as electrochemical cleaning, boiling in sodium phosphate, Alkaline Rochelle salt and citric and sulphuric acid.
1920-1950 New concepts and old recipes

**Stabilizing copper alloys**

Scott (1921) suggests long immersion in sodium sesquicarbonate, sometimes combined with Alkaline Rochelle salt.

Nichols (British Museum 1924) uses localized stabilization treatments such as silver nitrate (later modified to silver oxide, then zinc powder).

**Protective coatings**

come from the automobile and aircraft industry. Cellulose acetates and Perspex are replacing traditional natural waxes.
1920-1950 New concepts and old recipes

Stabilizing iron:

Scott (1921) suggests to use long soaking in sodium sesquicarbonate. Dammar varnish as surface protection.

In 1933 he tries natural rubber in solution and advocates the use of chlorinated rubber to consolidate fragile metals. Soon abandoned, as unstable and most irreversible.
1920-1950 New concepts and old recipes

**Stabilizing iron:**

For both bronzes and iron finds the use of **controlled storage** in sealed cases with buffering materials (silica gel) are beginning to be used after Rathgens 1924 publication. The use of nitrogen filled storage containers are first used for finds of the Sutton Hoo treasure in 1946.
1950-Today
Corrosion:

Increasing awareness of corrosion crusts and the concept of original surface. For France-Lanord and Eichhorn preservation of original surface has priority over stabilization.

But only in 1990ies the original surface is defined as the surface that represents the object when abandoned. Bertholon (2000) defines the original surface more precisely as limitos, that can be located with the help of markers.
1950-Today

Electrolytic treatments of copper alloys:

1956 Plenderleith still recommends the use of electrolytic reduction in sodium hydroxide.

Most unfortunately this harsh method is still used today on some excavations and in labs that lack trained personnel.
1950-Today

**Electrolytic treatments of copper alloys:**

In the 70ies *France-Lanord* proposes electrolytic reduction with low current. Increases removal of chlorides without stripping corrosion products. EDF pushes technique further for treating marine bronzes under cathodic protection in *sodium sesquicarbonate*. This treatment has been adapted as standard treatment for marine bronzes. The measurement of the corrosion potential of the object with a reference electrode allows a precise and controlled reduction of only unwanted corrosion products (chlorides).
1950-Today

Electrolytic treatments of lead and silver alloys:

Consolidative reduction of very corroded lead also uses a low current, preventing hydrogen bubbling and reducing acidifies corrosion products to metallic lead. In the 90ies potentiostatic reduction helps refining this technique.

After 2nd World War, mineralized silver is also converted into metallic particles by electrolytic reduction.
Chemical cleaning of copper alloys:

Various complexing agents and acids were used, such as Alcaline Rochelle salt, Calgon, ammonium hydroxide, EDTA, sodium hydroxide, citric acid, formic acid and sulfuric acid.

All these products can etch copper alloys and if not properly used. Most research went into improving these existing recipes and changing to less aggressive chemicals.

Sodium tripolyphosphate (replaced Calgon), EDTA, alcaline dithionite (for chlorinated marine bronzes), sodium dithiolate (for copper sulfates), formic acid.
1950-Today

**Stabilization of copper alloys:**

1967 *Madsen* introduces **Benzotriazole** (BTA), a *corrosion inhibitor* developed for the copper industry. Widely adopted by the conservation community. The most recent studies use it in combination with another corrosion inhibitor, AMT.
Protective coatings for copper alloys:

New protective coatings appeared after the 2nd World War such as Frigilene and Ercalene (nitrocellulose lacquers). Bedacryl (butyral methacrylate) and soluble nylon both proved insoluble after a while.

All these polymers were replaced by acrylic resins such as Paraloid (in US Arcyloid) as well as combined with stabilizing agents (Incralac).

On outdoor bronzes microcrystalline waxes are still used today.
1950-Today

Cleaning of iron

The introduction and adaptation of air abrasive cleaning with various abrasive powders (aluminium oxide, sodium bicarbonate, walnut shells etc.) improved cleaning techniques tremendously.

X-ray radiography and tomography greatly improved assessing and cleaning of corroded iron.
Stabilization of iron

1964 **Hydrogen reduction** is first used for the conservation of iron finds from the *Vasa*. These heat treatment involves temperatures of up to 850°C.

Successful for stabilization of cast iron artefacts, but much metallurgical information is destroyed. Replaced by controlled electrolytic reduction techniques.
Stabilization of iron

Hydrogen gas plasma emerges in the 80ies as the ideal treatment for large amounts of artefacts. The created hydrogen plasma is highly reactive and reduces iron oxides.

Proved not effective enough to reduce all chlorides. Today it is still used in some labs as a pre-treatment before desalination and mechanical cleaning.
1950-Today

**Stabilization of iron**

1984 EDF sets up a research programme advocating electrolytic techniques. Cast and wrought iron is treated, but also non-conducting materials such as leather, wood, paper or porcelain.

1987 The Titanic is discovered and 1800 items are conserved at EDF using innovative electrolytic techniques.
1950-Today

**Stabilization of iron**

Electrolytic techniques have greatly improved and the use of reference electrodes has given us safe tools to work with. They are currently also used *in situ* to monitor and stabilize submerged iron artefacts.
1950-Today

**Stabilization of iron**

A new desalination method using alcaline sulfite baths was introduced in the late 70ies and has been widely adapted for chloride contaminated archaeological iron.

This method breaks down insoluble chloride containing products, such as akaganéite.
1950-Today

**Adhesives & protective coatings for iron**

After 2nd World War, **epoxy resins** are widely used in conservation of all materials due to their strength and durability. They *replace traditional soldering methods* that often damaged the patina and were highly irreversible. However, epoxy resins once cured, cannot be dissolved.

Much iron was consolidated and glued with epoxies such as *Araldite*. Today we struggle with such objects that have not undergone desalination, as they continue to break up, but cannot be retreated.

Lacquers are still in use, mostly **acrylic polymers** such as Paraloid (Acryloid) for indoor iron artefacts. Outdoors **epoxy resins** or **polyurethane resins** are used for their durability.
1950-Today

*Preventive conservation of metals*
1950-Today

Preventive conservation of metals

Dessicants and barrier films:
Silica gel, ESCAL foils
1950-Today

*Preventive conservation of metals*

**Dessicants and barrier films:**
Silica gel, ESCAL foils

**Oxygen scavengers:**
Ageless, RP System
1950-Today

**Preventive conservation of metals**

**Dessicants and barrier films:**
Silica gel, ESCAL foils

**Oxygen scavengers:**
Ageless, RP System

**Pollution scavengers:**
Activated charcoal, impregnated textiles,
1950-Today

Preventive conservation of metals

Dessicants and barrier films:
Silica gel, ESCAL foils

Oxygen scavengers:
Ageless, RP System

Pollution scavengers:
Activated charcoal, impregnated textiles,

Pollutant identification:
Oddy test, Beilstein test, ….
Tomorrow?
Tomorrow?

• Achieve better understanding of corrosion mechanisms
Tomorrow?

• Achieve better understanding of corrosion mechanisms

• Achieve better understanding of current treatments, develop new and safer methods
Tomorrow?

• Achieve better understanding of corrosion mechanisms

• Achieve better understanding of current treatments, develop new and safer methods

• Deal with an ever increasing mass of previously conserved and freshly excavated objects
Tomorrow?

• Achieve better understanding of corrosion mechanisms

• Achieve better understanding of current treatments, develop new and safer methods

• Deal with an ever increasing mass of previously conserved and freshly excavated objects

• Improve standards and facilitate access to education and training in conservation
Bibliography


