

CHAPTER 4

Atmospheric corrosion and conservation of copper and bronze

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1 Introduction

Copper and its alloys are important technical metals both for use as construction materials and for special use, e.g. in electro-technical industry and crafts.

This chapter deals with the atmospheric corrosion of copper and bronze used for architectural purposes, constructions and objects of art, especially sculptures [1]. Such uses rely on a number of properties of copper and copper alloys such as high resistance to atmospheric corrosion or ability to form characteristic layers of corrosion products (patina) which not only protect objects, but also usually make objects look better. High resistance of copper and bronze corrosion product layers to corrosion allows for greater stability of objects in the atmospheric environment. Objects and elements made of these materials survive for centuries.

Copper and bronze objects or elements of construction (sculptures, roofs, cladding, artifacts of stone-made sculptural and architectural historical monuments) are affected by atmospheric environment. Its effect, especially with long-term exposure, causes gradual changes. The surface of objects is covered with corrosion products, dirt, biological contamination, etc.

The negative effect is seen mainly in outdoor atmospheric environments where along with natural climatic factors (changes of temperature, relative humidity, precipitation, snow, etc.), gaseous and solid pollutants released by industrial activities are also present. Aggressive components of pollution (gaseous, acid rain) are transported to long distances, which affect materials in a wider area.

Indoor atmospheres (museums, galleries, depositories, etc.) are less aggressive, although in closed spaces in depositories or storage unfavorable corrosion



conditions may be formed which can cause damage to the stored copper and bronze objects. This chapter does not specifically deal with this area.

Copper and its alloys also show specific corrosion manifestations in the form of inter-crystalline corrosion and corrosion cracking. Corrosion needs to be eliminated in bimetallic corrosion cells.

This chapter also focuses on studies of defects and disorders in copper and bronze objects exposed to atmospheric environment. Selected technological procedures of cleaning and conserving elements of construction objects namely, historical monuments are presented too.

2 Atmospheric corrosion of copper and its alloys

Copper

Copper is a suitable material for many constructions and architectural elements such as wall cladding, roof and copula roofing. Copper has good mechanical and metalwork properties and is therefore used for construction accessories such as gutters, window ledges, edging, troughs and chimney facing.

Properties of copper are significantly influenced by production technology. For centuries copper, like other metals, has been produced on a small scale by artisans. Metallurgically refined copper contains usually around 99.7% Cu, and silver or other precious metals are not taken out of it. It can be used directly for rolling. Electrolytic refinement produces purer copper containing 99.92%–99.97% Cu, 0.004%–0.02% O₂ and only 0.01%–0.015% of all metal admixtures, the rest being solved gases.

Sheets of rolled copper are used mainly for architectural and construction elements in atmospheric environment. Atmospheric exposure of copper sheets causes change of mechanical properties (strength, ductility) as corrosion spreads over the whole surface exposed to the corrosive environment. After 20 years of such exposure, tensile strength decreases by less than 5% and the change in length is 10% of the original values. Fatigue limit depends on the refinement of crystallization and can go down by one-third or more if crystallization gets significantly coarse.

Copper alloys

Historical monuments and objects of art are made mainly of bronze; brass is used only rarely. Bronze of various compositions is used. The differences among portions of individual alloy elements are big; these also depend on historical trends.

Traditional types of bronze used for making sculptures contain tin, lead and zinc, the share of each of these being approximately 5%. Modern types of bronze are represented by a wider variety of alloys containing approximately 90% copper and other metals such as tin, zinc, lead, aluminum, silver and others. Zinc and tin increase the breaking strength and hardness of an alloy; it improves castability and is cheaper than tin. Lead increases resistance to corrosion and improves the ease of processing and castability. Bronze used for sculptures also contains antimony and a small amount of iron and nickel (tenths of %). When an alloy is cooled slowly, it passes through different phases, each being different in crystalline composition and



content of individual elements. The resistance of the types of bronze used nowadays to corrosion does not significantly vary from the resistance of copper, evaluated in terms of corrosion loss. Surface manifestations of corrosion attack are more uneven: dips and corrosion on the grain edges are present.

Currently, bronze with a high level of resistance to corrosion is being developed to be used for making copies of valuable sculptures that should be stored in depositories. The increased resistance of newly developed alloys shall be achieved by additions of tin, silicon, or nickel.

A less-used group of modern bronze alloys is formed by alloys containing tin (10–14%). These materials are close to the historical types of bronze. Their resistance to corrosion is very good, and they are easy to process containing up to 10% of tin.

2.1 Corrosivity of atmospheres and guiding corrosion values for copper and copper alloys

Copper and bronze objects are exposed to atmospheric environment over a long term. It is important to know the conditions of the environment to estimate and evaluate the damage being caused and to select proper protective measures, that is, the means of conservation.

Corrosivity of atmospheres has been rising since the end of the 19th century together with atmospheric pollution, reaching maximum levels in the 1950s and 1960s. There has been a significant decrease during the last ten years as a consequence of various measures against atmospheric pollution and the change of industrial structure.

Standard ISO 9224 – Corrosion of metals and alloys – Corrosivity of atmospheres – Guiding values for the corrosivity categories provide guiding corrosion rates for copper for corrosivity categories according to ISO 9223 – Corrosion of metals and alloys – Corrosivity of atmospheres – Classification (see Table 1).

Corrosion of copper and bronze within Europe was evaluated as a part of the UN ECE International Co-operative Programme on *Effects on Materials including Historic and Cultural Monuments* for the period of eight years (1987–1995) [2].

Table 1: Guiding corrosion rates for copper.

Corrosivity category	Corrosion rate ($\mu\text{m/a}$)	
	First 10 years	Following years
C1	≤ 0.01	≤ 0.01
C2	$0.01 < 0.1$	$0.01 < 0.1$
C3	$0.1 < 1.5$	$0.1 < 1.0$
C4	$1.5 < 3.0$	$1.0 < 3.0$
C5	$3.0 < 5.0$	$3.0 < 5.0$



Table 2: Average mass loss (g/m^2) of copper and bronze on 20 European test sites [2].

Material	Exposure period	Time of exposure (years)		
		1	2	4
Copper	1987–95	10.1	16.4	27.8
	1997–2001	7.6	12.1	19.7
Bronze	1987–95	7.3	12.8	23.6
	1997–2001	4.2	7	12.8

Yearly corrosion loss of copper was between $0.2 \mu\text{m}/\text{year}$ (test site Toledo, Spain) and $1.6 \mu\text{m}/\text{year}$ (test site Kopisty, Czech Republic). Long-term exposure at the atmospheric station of SVUOM (1981–96) in the environment of C4 corrosivity category resulted in a corrosion rate of $2.6\text{--}2.8 \mu\text{m}/\text{year}$. Comparison of corrosion rates of copper and bronze exposed repeatedly in Europe in the first and second stages of the UN ECE International Co-operative Programme shows how the corrosivity of the observed territory has been changing during this time period (Table 2).

Decay of copper and bronze objects is highly influenced by environmental conditions, mainly by acidifying airborne pollutants. In the past ten years environmental conditions have changed in many European countries, the effect being a significant decrease of sulfur dioxide (-75%) and nitrogen dioxide (-40%) concentrations, whereas the amount of ozone remains nearly the same. Sulfur dioxide is still the main factor for corrosion processes but the presence and combinations of other pollutants are becoming more important. Repeated long-term exposure of copper (99% Cu) and bronze (81–85% Cu, 6–8% Sn, 3–5% Zn, 5–7% Pb) samples for 1, 2 and 4 years were carried out to prove and compare the corrosion effect under actual environmental conditions [2].

Compared to the exposure carried out between 1987 and 1991, reduced sulfur dioxide content in the environment seems to influence bronze surfaces more than copper surfaces. The mass loss of bronze reaches values lower by 45%, but copper's metal loss lower only by 24%. The most significant decrease of values can be seen in the weight change of bronze, which reaches values lower by 77% than ten years ago.

The results of the UN ECE International Co-operative Programme were used for the derivation of damage equations for copper and bronze, which help to calculate corrosion loss from environmental data. Besides the usual components of atmospheric pollution, the concentration of tropospheric ozone is considered for the calculation of the corrosion loss of copper and bronze [3].

Long-term corrosion tests of copper and its alloys and the following derivation of guiding corrosion rates are based mainly on corrosion tests using metal sheet samples. Casts made of copper alloys have different properties, which result in differences in the effect corrosion has on them.



Information about corrosion of copper in specific conditions was published in a study [4]. Copper is influenced even by a clear atmosphere at room temperature. A thin layer of invisible oxide is formed; no darkening appears. This layer provides some protection against low levels of pollution in indoor atmospheres.

If copper is exposed to air at high temperatures, a thin coating of interference colors is formed. If traces of sulfides or hydrogen sulfide are present in the atmosphere, copper darkens. Mixed layers of oxides and sulfides are very thin and adherent.

The initial corrosion effect in outdoor atmospheres is staining. It is typical for roofing and cladding and is not considered aesthetically valuable. Sometimes sharply demarcated stains and stripes are formed, especially at places where water is held up and dries out. Stains are dark, dark red or turning blue. This effect is accelerated even by the presence of mild hygroscopic salt deposits.

Stress corrosion cracking (SCC) is typical especially for brass, but is less for other copper alloys. The effect appears under tension stress above a certain limit in a polluted (industrial) atmospheric environment, especially when it contains ammonium compounds. SCC affects copper alloys containing 20% or more zinc, but only rarely the other alloys. Among the objects presented in this publication, brass screws connecting construction elements as window frames, metalwork details, etc. are affected by SCC. In sheltered exposures SCC can be accelerated by cumulating dust and other dirt.

2.2 Formation mechanism of surface layers

Atmospheric corrosion of copper and bronze results from the presence of air humidity and oxygen, while aggressive gaseous and solid components of atmospheric pollution are effective too [5–7]. The process, mainly in its initial stage, is of electro-chemical nature. Since layers of surface electrolytes are thin and dry out periodically, the reaction products are deposited in the form of solid surface layers which then take part in corrosion reactions, and the nature of the corrosion process becomes chemical too. Stability or solubility of surface layers components, especially the ability to bond aggressive atmospheric components into salts of limited solubility, have a fundamental influence on keeping corrosion rates of copper and its alloys low in atmospheric conditions. High resistance of copper and its alloys to corrosion in atmospheric conditions is then derived from the protective function of corrosion product layer usually called patina. Surface layers on bronze and copper are formed by periodically repeated processes during wetting and drop-out of basic salts from saturated electrolytes at a suitable but not too low pH.

Formation of patina is a long-term process going through a number of stages. Different mechanisms determine the speed of the process in individual stages. The corrosion product layer is subject to transformation in the formation period and eventually it gets into balance with the external environment affecting it. The natural, stable, green surface layer is formed in 10 to 20 years in atmospheric conditions, depending on the corrosivity of the atmosphere. At low levels of pollution in unsuitable climatic conditions (dry, low temperatures) the green surface layer is formed in a long time or could not be formed at all. Surfaces remain dark. Different local



Table 3: Stability of basic patina components in pH levels [7].

Compound	Formula	pH level
Cuprite	Cu_2O	>4
Brochantite	$\text{Cu}_4(\text{SO}_4)(\text{OH})_6$	3.5–6.5
Antlerite	$\text{Cu}_3\text{SO}_4(\text{OH})_4$	2.8–3.5
Atacamite	$\text{Cu}_2\text{Cl}(\text{OH})_3$	3.8–4.3
Gerhardite	$\text{Cu}_2(\text{NO}_3)(\text{OH})_3$	4.0–4.5
Malachite	$\text{Cu}_2(\text{CO}_2)(\text{OH})_2$	>3.3

degrees of wetness and other microclimatic effects cause uneven coloring of objects, e.g. roofing and sculptures. Typical properties of surface layers can be estimated after 3–5 years of exposure.

Primarily, a layer of cuprite is formed on newly exposed surfaces of copper and bronze after wetting. Surface electrolytes in the next corrosion stage contain sulfate ions corresponding with their dry and wet depositions from the atmosphere and ions of copper diffusing through the cuprite layer. Copper sulfates turn into basic sulfates, which are deposited on the cuprite surface in the form of solid layers.

Formation and composition of patina are significantly influenced by acidity of rain. Rain of high acidity dissolves the surface layer and washes it off. Rain of usual acidity influences the composition of patina in its pH, because the thermo-dynamical stability of minerals differs, e.g. antlerite is more stable in acid environments than brochantite (see Table 3).

Basic patina components are formed in the presence of surface water layer by the nucleation and deposition of solid phases in a row of reactions. Brochantite is said to need at least two weeks to crystallize. During this period insufficiently bonded copper and sulfate ions can be washed out by rain. Wash-out is effective especially for thin initial layers.

Relations between time required for the deposition of more stable components of patina and the occurrence of rain may influence the formation of layers of natural patina.

2.3 Influence of selected factors on quality of forming layers

Patina on copper or bronze object differs locally in thickness and composition in visually distinctive areas. The reason for this variety is the shape arrangement of objects, which creates differences in the access of individual environmental factors to the material in various parts either as a consequence of un/shelteredness from the factors or various speeds at which environmental components are transported to the surface. The surface layer formed manifests as various shades of green, can be blue and green, gray and green, brown or black. Results of X-ray diffraction analysis show that color (especially dark) does not provide sufficient information on composition of a layer. Color borders can be sharp or diffusive.



Occurrence of green stripes formed by streams of water flowing away on dark background is typical for sculpture surfaces. Dark, coarse and thick crusts on partial surfaces, mostly on soffits, usually differ in appearance too. These crusts contain many foreign matters – impurities and crystallized soluble fractions of corrosion products of copper. The protective function of such layers is limited.

Corrosion attack on bells 100–600 years old that was exposed in various atmospheric environments in the Czech Republic (countryside, cities, highly polluted industrial areas) was evaluated [1]. All bells were made of bronze containing a relatively high portion of tin (approx. 20%). Considering the massiveness of the bells, corrosion damage does not represent any threat to the function of the objects. Surfaces are covered with a relatively coherent but not compact layer of corrosion products. Corrosion attack on sides facing wind is usually more significant. No corrosion pits occur. Different manifestations of corrosion can be seen on the inner surfaces of the bells, especially in the bells exposed for long periods. The corrosion layer contains less impurities, is usually blue-and-green, and crusts are present locally. Condensation and wet corrosion probably take place inside the bells. Surface layers contain mainly antlerite, and a high portion of quartz, gypsum and calcite (dust). Also present is moolooite (copper oxalate) which proves biological pollution (birds). Brochantite was also found on a bell exposed since 1651.

Properties of layers, which then affect the corrosion rate of copper and its alloys in the long term, are formed according to conditions of pollution and temperature-humidity characteristics of an area, but also depend on the exposed surface.

The natural surface layer characteristic of current copper and bronze surface exposed for tens or hundreds of years in an open atmosphere contains mainly brochantite, antlerite and cuprite. Formation of antlerite or brochantite is subject to free access of precipitation. In atmospheres with natural or technological salinity, patina also contains atacamite and paratacamite – $\text{Cu}_2\text{Cl}(\text{OH})_3$. Patinas that have not reached a stabilized state contain posnjakite – $\text{CuSO}_4 \cdot \text{Cu}(\text{OH})_6 \cdot \text{H}_2\text{O}$. Gerhardite – $\text{Cu}_2(\text{NO}_3)(\text{OH})_3$ is found rarely. Patinas nowadays do not contain malachite – $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ which was present in analyses from the past years. Surface layers often contain admixtures of gypsum and siliceous sand, and patinas also contain portions of formates, acetates and oxalates which are formed in atmospheres polluted by anthropogenous and biological effects. These components have been identified only in the last few years by the use of ion chromatography in this field [8]. Salts of organic acids are reported to form a kind of binding agent in patina layers. Other substances can be formed in environments with specific effects. Soluble $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (chalcantite) cumulates in soffit areas. An overview of the occurrence of individual components and their properties is presented below.

Some papers refer to other types of components of patina in the initial stage of corrosion too.

2.4 Identification of individual corrosion products

An overview of the phases determined repeatedly in surface corrosion layers on copper and bronze objects in the Czech Republic is presented in Tables 4 and 5.



Table 4: Phases identified in patina in the atmospheric environment of the Czech Republic.

Name	Formula	Line
Antlerite	$\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$	7-407
Brochantite	$\text{CuSO}_4 \cdot \text{Cu}(\text{OH})_2$	13-398
Posnjakite	$\text{CuSO}_4 \cdot \text{Cu}(\text{OH})_6 \cdot \text{H}_2\text{O}$	20-364
Cuprite	Cu_2O	5-667
Tenorite	CuO	
Atacamite	$\text{Cu}_2(\text{OH})_3\text{Cl}$	25-269
Paratacamite	$\text{Cu}_2(\text{OH})_3\text{Cl}$	25-1427
Botallackite	$\text{Cu}_2(\text{OH})_3\text{Cl}$	8-88
Moolooite	$\text{C}_2\text{CuO}_4 \cdot n\text{H}_2\text{O}$	29-297
	$(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	11-660
Chalcantite	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	11-646
Gerhardite	$\text{Cu}_2(\text{OH})_3\text{NO}_3$	14-687
Melanothallite	Cu_2OCl_2	35-679
	$\beta\text{-Cu}_2\text{S}$	26-1169
	Cu_2S	23-959
Quartz	SiO_2	33-1161
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	33-311
Calcite	CaCO_3	5-586

Individual components were determined by a phase analysis of samples taken from objects in Prague and other places within the Czech Republic (approx. 300 samples) [9–10]. Components shown in Tables 4 and 5 are typical for urban and industrial atmospheres without any significant salinity effect.

2.5 Composition of surface layers and patina components characteristics

- Brochantite $\text{CuSO}_4 \cdot \text{Cu}(\text{OH})_2$, antlerite $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$ – corrosion products of copper and bronze are mainly brochantite, antlerite or a mixture of both. Brochantite occurs mainly at places of direct impact of rain, snow and dew, while antlerite is formed mainly by condensed air humidity. Both products have protective properties and slow down further corrosion of metal surfaces. From the aesthetic point of view, they give patina blue-and-green coloring, which, however, can be devaluated by minimum amounts of darker components as carbon black, black oxides and sulfides.
- Cuprite Cu_2O , tenorite CuO – these represent an anchoring component on the metal-patina border. They form thin adhesive layers, mostly black, brown red or orange.
- Posnjakite $\text{CuSO}_4 \cdot \text{Cu}(\text{OH})_6 \cdot \text{H}_2\text{O}$ – it is a component of young sulfate patina and turns into antlerite or brochantite later on.



Table 5: Composition of patina layers.

Composition	Objects					
	Statues outside Prague (investigation in 1994) 18 samples		Statues, copper roofs in the center of Prague (investigation in 1994) 57 samples		Statues in the center of Prague (investigation in 1998) 33 samples	
	Abundance	Frequency (%)	Abundance	Frequency (%)	Abundance	Frequency (%)
Antlerite	9	50	18	31	10	30
Brochantite	6	33	43	75	17	52
Cuprite	3	17	16	28	8	24
Atacamite, paratacamite	0	0	3	0	1	3
Moolooite	0	0	0	0	1	3
$(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	0	0	4	7	4	12
Chalcantite	0	0	0	0	3	9
Quartz	12	67	33	58	18	55
Gypsum	4	22	2	4	13	40
Calcite	0	0	3	5	4	12
Entirely amorphous	2	11	1	2	0	0

- Atacamite, paratacamite $\text{Cu}_2(\text{OH})_3\text{Cl}$ – dominant component of patina in maritime environments. Only exceptional occurrence was identified within Czech Republic in cases of presence of chlorides (e.g. surfaces of fountains where chlorides are contained in water or on surfaces affected by de-frosting agents).
- Moolooite $\text{C}_2\text{CuO}_4 \cdot n\text{H}_2\text{O}$ – its occurrence is attributed to the effect of bird excrements on metal. It was identified at locations sheltered from a direct impact of precipitation.
- Ammonium copper sulfate $(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ – water-soluble corrosion product of copper which is contained in crusts. It was identified at locations affected by anthropogenic influences.
- Chalcantite $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ – was identified as a part of soffit crusts in highly polluted environments. This component is well soluble, has no protective effect and its presence indicates increased corrosion of metals.
- Quartz SiO_2 – most frequently occurring component of dust, chemically inert component of surface layers. It increases volume of patina at higher concentrations, decreases adhesion to surfaces and deteriorates the look of patina.
- Calcite CaCO_3 , gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ – calcite is often a part of dust, having a negative effect on it. It turns into gypsum by the effect of sulfate ions, causes expansion of volume and degradation of patina. High amounts of gypsum were identified in patinas from locations polluted with dust from neighboring lime works.

Besides copper, bronzes contain other alloy elements (lead, zinc, tin, iron). Corrosion products of these components occur in surface layers in small amounts that have no significant effect on the protective properties of these layers. Corrosion products of tin ($\text{SnO}_2 \cdot n\text{H}_2\text{O}$, SnO_2) used in bronze alloys in the past increase protective ability of surface layers.

Surface corrosion layers including the protective patina on copper and bronze do not have a simple composition, not even an unambiguous crystalline structure. Metallographic cuts document two- or three- layer construction of patina in most cases, in some cases foreign matters can be seen in the top green layer. Results [1, 11, 12] are related to the evaluation of layers on copper sheet; surface layers on bronze can be evaluated less frequently [13].

The closest zone to the metal on the cut is orange, red or dark layer, mostly made of copper oxides. The next layer is bright green and contains mainly brochantite, but also antlerite. In this sub-layer, dust and other impurities accumulate. However, siliceous particles can be in the bottom oxide layer too. Dark top layer, if present, is formed mainly by carbon black. Varying and atypical composition occurs in case of voluminous dark or gray and green crusts in soffit locations (high portion of dust particles, antlerite, various soluble corrosion products of copper).

Individual layers, even those that are relatively chemically homogenous, are formed by irregular crystalline formations. Besides impurities, cavities and other defects are also present in layers that allows for the transportation of ions through layers.



The thickness of green patina (green top sub-layer) formed in an open atmosphere in long term is between the range of 40–50 and 75 μm . The thickness of the black, red or dark sub-layer is approximately 10 μm . On the bottom side of the sheets, the dark sub-layer is thicker (approx. 20 μm), while the green sub-layer is only a few micrometers thick. The depth of pits (if they occur) on surfaces exposed in long term ranges from 50 to 70 μm , but also from 100 to 105 μm in some cases.

The thickness of crusts is higher (approx. 200 μm). The boundary of metal surface under these crusts is usually very uneven, broken, with corrosion penetrations of various depths. Penetrations have shapes rather different from those of shallow pits.

To sum up, the surface layer of copper is a system that may vary in chemical composition, composition in the layer cut, protective function and appearance.

3 Typical corrosion manifestations on copper and bronze objects

Copper and bronze objects or construction parts as roofing, cladding, doors or sculptures have been exposed to the atmospheric environment for centuries without any serious corrosion problems in most cases, except for the aesthetic problems caused by cumulating impurities and the formation of corrosion layers differing in color locally. In contrast to copper roofing and cladding, where corrosion damage may affect the service life of an object, damage in bronze sculptures is considered aesthetically desirable both for relatively higher thickness of the exposed material and for periodical maintenance and protection of some sculptures [1, 9, 14–16].

Standardization of defects and disorders and evaluation of causes of their occurrence are listed individually for sculptures (bronze and copper) and for roofing, cladding and metal work after general characterization, the reason being not only partial differences in causes but also differences in technical and aesthetic demands.

3.1 Sculptures and objects of art

Corrosion manifestations (described in more detail below), which may lead to defects in some cases, can be generally divided into the following groups:

- Manifestations of general corrosion differentiated by space arrangement of an object,
- uneven or local corrosion attack which may be resulting from space orientation of a surface but also from construction design (e.g. joints),
- mechanical damage (cracks, changes of shape),
- defects resulting from the way sculptures were made (connection lines, uncovered rivets),
- corrosion of carrying and supporting construction, even bimetallic,
- corrosion damage and formation of deposits resulting from the function of an object (fountains), and
- negative aesthetic manifestations resulting from previous conservation and various surface treatments (e.g. pigment coatings).



Main types of corrosion manifestations:

1. Formation of black and green layers of corrosion products. The composition of most samples of surface layers from various objects corresponds with the typical composition of patina formed nowadays in urban and industrial areas (brochantite, antlerite, cuprite, admixtures of quartz and calcite). The surface layer is bound firmly to the surface. The surface layer is protective, i.e. it decreases the corrosion rate of a metal.
2. Crusts that are formed mainly in sheltered locations are of usual composition (admixtures of gypsum, quartz, etc.). Specific components as ammonium copper sulfate $(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and copper formate $(\text{HCOO})_2\text{Cu}$ were found only in a small number of cases. Crusts on sculptures located in the center of Prague often contain chalcantite $(\text{CuSO}_4 \cdot 5\text{H}_2\text{O})$ and moolooite, i.e. copper oxalate $(\text{C}_2\text{CuO}_4 \cdot n\text{H}_2\text{O})$. These fractions do not have a protective function.
3. Turquoise areas are formed around little pits on surfaces of bronze sculptures where condensate from inside the sculpture reaches out.
4. Uneven corrosion along grains was observed in a limited number of cases on horizontal and less inclined surfaces of statues exposed in highly polluted environments.
5. An interesting finding was the occurrence of places with little pits in overlapping areas on sculptures made of hammered copper sheets (e.g. under coat overhang on a statue of a horse rider). These pits were under a layer of deposited dirt and corrosion products. It may be assumed that it is a case of crevice corrosion.
6. Bimetallic corrosion of steel joints and fixation elements and their surrounding was found on parts of sculptures that are not fully treated (back side). Corrosion of steel joints and voluminous corrosion products of iron may damage and open the joints.
7. Extensive corrosion damage was found on the inner steel supportive construction of sculptures made of hammered copper sheets. Bimetallic corrosion occurs at places where steel inner construction is in contact with copper surface. Corrosion attack on inner supporting construction reaches the degree of defective stability of an object in some cases, which even increases penetration of environment into the inner space of a sculpture.
8. Various joints and elements used during the treatment of a sculpture become visible (joint lines, matching of parts, overlaps of inner joints).
9. Soldered joints on sculptures made of copper sheets are being damaged and local corrosion manifestations occur around these joints. Dark dots and stains occur on soldered areas. This is also a case of soldered decorative parts of cladding and copulas.
10. Cracks in surfaces and deformations or fall-off of parts are rather rare.
11. Corrosion manifestations related to aging of sculpture coatings (conservation, patination, pigmented and transparent coatings) are aesthetically undesirable.



Coatings change in color, wash away, grow through corrosion products or are gradually separated from the base.

12. Water deposits in fountains.
13. Corrosion manifestations on bells are significantly influenced by the manner of exposure (tower spaces) and shape (inner and outer surface). Pollution by bird excrements is an important factor. Serious damage occurs after mechanical wear-out on the inner surface and corrosion damage on steel parts of bell hangers.

3.2 Copper roofs, cladding and metalwork elements

Copper sheets and metalwork elements were used in the past only for roofing and other parts of important buildings (churches, palaces). During the last ten years there has been a growth in the use of copper for a wider range of purposes (family houses, business objects).

Both the types of use differ in the material used, construction design and technological treatment which is reflected by differences in the tendencies for formation of defects and damages. Material and technological differences of both types of use are also reflected in the mode of maintenance and repairs.

A great deal of attention has to be paid to the designing and making of copper roofs or claddings of a modern object. Designing copper (and also titan-zinc) roofing and cladding is a specialized technical work nowadays. Producers of materials and elements elaborate extensive manuals setting construction designs and technological treatment of elements, their connections and making them into an object, especially in relation to its temperature-wetness regime and material composition in combination with copper parts.

There are four main causes of defects and damages of copper roofs and metalwork elements – mechanical damage, corrosion impact of the outdoor environment, corrosion impact derived from the construction design of a building and specific corrosion impact derived from its indoor regime. The degree of stress caused by individual effects may differ, and causes are often combined. The method of repair is chosen according to the type of defect.

Mechanical damage

- parts loosen by wind,
- extensive heat stress, changes of temperature,
- obstacles to compensate movement during heat stress,
- operation stress (walking areas),
- accidental damage (falling objects, perforations).

Corrosion attack (environmental effect and design)

- impact of surrounding local atmospheric environment,
- local effect of smoke,



Table 6: Types of defects on bronze and copper objects in Prague.

Age of objects (years)	Type of object		Defect		
	Roof, cladding (copper)	Sculpture (bronze, copper)	Aesthetic ^a	Corrosion ^b	Mechanic ^c
450–240	1	5	3	3	2
150–110	–	4	2	1	1
100–80	3	28	25	21	4
75–60	3	17	13	13	6
50–15	1	39	24	24	6
<15	2	4	3	5	1
Total	10	97	70	66	20

^aNonuniform patina, differences in color.

^bPitting, crusts, etc.

^cHoles, damaged joints and supporting constructions.

- corrosion effects caused by contact with unsuitable materials (bimetallic corrosion, soldering),
- corrosion effect of rinsing of surrounding materials (acidic fractions and others),
- corrosive and other negative effects of nesting birds, mainly pigeons,
- pitting on roofing overlaps and board welts (depth to 50 μm),
- formation of non-protective surface layers (ammonium copper sulfate contained) around ventilation inlets where exhalations from residential and operation spaces of buildings leave,
- rusty areas on roofs surrounding steel elements (e.g. lightning-conductor connections).

Damages caused by indoor effects

- condensation,
- indoor exhalations,
- damaged base or inner construction as a result of decay or insect attack.

Table 6 gives an overview of the different types of defects on copper and bronze objects in Prague [1, 14].

4 Selected methods of cleaning and conserving copper and bronze objects

This section lists methodical knowledge, conditions of use and properties of treated surfaces for these technologies:



- physical (mechanical) and chemical cleaning methods,
- patination and properties of artificial patina including their transformation after exposure in atmospheric environment,
- conservation.

The main benefit is quantification of changes caused by selected technologies of cleaning on surfaces of objects [1].

4.1 Cleaning of copper and bronze objects, namely sculptures

Techniques of cleaning and removal of corrosion products [1] can be divided into three groups:

- cleaning by water under pressure,
- mechanical or abrasive cleaning (blasting),
- chemical cleaning – ‘draw-off’ and pickling.

4.1.1 Cleaning by water under pressure

Removal of corrosion products and dirt by water under pressure is often used in combination with abrasive techniques or chemical cleaning. Pressures between 50 and 1000 psi are used for water cleaning. Particles that fall off or are not fixed to the surface and soluble parts of corrosion crusts and layers are removed or redistributed on the surface by pressure washing. The effectiveness of washing depends mainly on the conditions and configuration of a surface and the abilities and experience of staff.

4.1.2 Mechanic (abrasive) cleaning

Various methods of mechanical cleaning such as different types of abrasive and polishing agents, pastes, metal wool and brushes made of various materials including mechanical brushes, scalpel, special abrasive steel wool, etc. are used by conservators. Cleaning using hand-operated mechanical equipment is difficult and time-consuming. These methods can remove crusts, deposits and growth from a surface and keep a thin layer of patina. Whether it is possible and desirable to maintain a thin layer of patina depends on the degree of pollution of a sculpture, previous surface treatment, shape of an object, etc. Usually not all parts of a sculpture can be cleaned in this way, especially those with no access.

A big problem during the mechanical cleaning of sculptures is the removal of a layer of previous improper ‘conservation’ by various coatings and waxes or the removal of the remnants of partially deteriorated previous conservation.

Mechanical cleaning using abrasives – blasting – is used on historical objects rather rarely, but there are cases when this method is the one to be used (e.g. inner surface of fountains, bell surfaces). Blasting is a process during which solid particles of metals, minerals, synthetic resins or plants, sometimes combined with water, are thrown at high speed against objects in order to clean, reduce or harden



Table 7: Material loss of copper with a thin brown layer of corrosion products after blasting by various abrasive agents (blasting normal to the surface).

Abrasive agent	Pressure (MPa)	Nozzle diameter (mm)	Material loss			
			Copper		Brass	
			(g/m ²)	(μm)	(g/m ²)	(μm)
Corundum 120	0.4	1	1.5	0.18	1.8	0.22
		2	4.5	0.55	3.5	0.43
	0.2	1	1.1	0.13	0.7	0.09
		2	2.1	0.26	2.9	0.36
Black corundum 180	0.2	1	1.0	0.12	2.2	0.26
Balotine 60	0.2	2	0.5	0.06	0.1	0.02

their surfaces. Compressed air (pressure between 140 and 550 kPa) and abrasives of different sizes, usually between 175 and 1000 μm, are used for blasting. Different combinations of speed, distance from surface and angle of incidence are used. The selection of these parameters is determined by the character of the surface to be cleaned, especially by its coarseness, hardness and thickness of crusts and corrosion layers. These methods have a great impact on the topography of a surface, its deformation and the deformation of microstructure, etc., although very soft abrasives are used, e.g. glass balls, sodium carbonate, aluminum oxide, olivine sand, plastic with different hardness and size of particles, some natural products such as ground walnut shells or crushed corn.

Blasting gives rise to unstable surfaces sensitive to humidity, which makes corrosion processes continue. These methods remove neither the active centers of chlorides or the sulfates from deep surface pits. The blasting process can leave parts of abrasives on a surface, which can negatively affect it after exposure to environment. Aggressive abrasive techniques can uncover more active pits and centers on surfaces than less aggressive procedures. The impact of blasting on surfaces of copper and its alloys was evaluated on samples of copper sheet at a different degree of corrosion attack (Tables 7 and 8).

Surfaces are changed after blasting in a way resulting from the technology used:

- Blasting agents significantly increase the coarseness of cleaned surfaces depending on the hardness of the agent and the shape of its particles.
- Bigger changes of macrostructure are caused by corundum, but the surface is cleaned more efficiently; blasting by balotine leaves remnants of surface layers.
- Blasting contaminates surfaces with elements or impurities contained in the blasting agent. Higher portion of trace amounts of impurities occurs when balotine is used.

Table 8: Weight and thickness loss of copper with natural green patina exposed for 60 years after blasting by various abrasive agents (blasting normal to the surface).

Abrasive agent	Pressure (MPa)	Nozzle diameter (mm)	Material loss	
			(g/m ²)	(μm)
Corundum 120	0.4	2	1.2	0.15
	0.2	1	11.2	1.38
		2	1.0	0.13
Black corundum 180	0.2	1	11.2	1.37
Balotine 60	0.4	2	1.2	0.15
	0.2	2	1.0	0.13
Balotine 134	0.2	1	10.7	1.31

4.1.3 Chemical cleaning

Methods of chemical cleaning include mainly drawing-off and pickling using different chemical solutions. The difference between drawing-off and pickling is that pickling removes all layers of corrosion products down to pure metal.

Drawing-off is a method that can be carried out in standardly equipped workshops or even in the field. It is not quite possible to achieve the defined and even effect of agents on a sculpture surface. Corrosion products are removed only partly and locally which however might be suitable for some purposes.

Chelation or complex-forming solutions or pastes are used for drawing off, e.g. [17]:

- alkaline Rochelle salt (sodium potassium tartrate) removes corrosion products without affecting the base metal;
- applications based on EDTA (ethylenediaminetetraacetic acid) selectively remove unadhesive or active corrosion products from bronze surfaces, leaving them enriched with copper oxides allowing for future repatination;
- application of ammonium hydroxide solution and simultaneous brushing with wool removes unadhesive layers of corrosion products,
- application of a solution of water and ammonium hydroxide (1:1) and simultaneous brushing with a metal brush or pumice removes thick incrustations;
- application of a paste containing 1 volume part of powder soda, 5 volume parts of calcium hydroxide and 2 volume parts of sawdust removes corrosion products for strongly deteriorated and corroded surfaces.

Pickling is a process used in technical practice especially as a pre-treatment before the application of various types of protective coatings. Cleaning is thorough but surfaces are often more affected. Loss of base metal during chemical cleaning processes equals to 2.5–9.0 years of exposure in an urban atmosphere. For technical purposes, pickling is defined in ISO 8407 Corrosion of metals and



Table 9: Mass loss of copper with thin layer of oxides after pickling in various solutions (temperature 20°C).

Pickling solution	Concentration (M)	Time (min)	Total mass loss of copper	
			(g/m ²)	(μm)
Citric acid	0.10	5 × 3	0.45	0.05
Chelatone 3	0.20	4 × 20	0.40	0.04
Sodium hexametaphosphate	0.50	4 × 3	0.28	0.03
Sulfuric acid	0.10	5 × 2	0.43	0.05
Sulfamidic acid	0.05	5 × 2	0.85	0.10
Phosphoric acid	5.00	4 × 2	0.73	0.08
Sodium hydroxide ^a	0.25	4 × 10	0.48	0.05

^aTemperature of solution 70°C.

alloys – Removal of corrosion products from corrosion test specimens. The standard includes recommended solutions for individual metals and alloys. According to this standard, pickling periods differ for different pickling solutions, metals or degrees of corrosion. When pickling is used on historical objects it is recommended to apply pickling solution repeatedly, thoroughly wash the objects after each application and remove loosened corrosion products and dirt, mechanically.

Comparison of pickling agents and procedures for copper and brass was carried out both from the point of view of corrosion loss and morphology of surfaces after pickling in solutions (citric acid, Chelatone 3, sodium hexametaphosphate, sulfuric acid, sulfamidic acid, sodium hydroxide, phosphoric acid) [18]. Pickling procedures were verified on copper and brass samples with thin layer of corrosion products formed in indoor environment (Table 9), and copper samples with thick layer of green corrosion products formed after exposure in condensation chamber with SO₂ and salt spray (layer of approx. 0.7 g/m² – Table 10) [1]. It is important that during pickling undesirable layers of corrosion products are removed and the base metal is affected to the minimum.

Intermediate loss of copper after individual intervals of pickling by Chelatone 3, sulfuric acid and sodium hydroxide are shown in Fig. 1. Intervals of pickling are defined in Table 9. It is obvious that after pickling in Chelatone 3 solution and sulfuric acid was finished, all corrosion products were removed from the surface (curve gradually turns into straight line). In the case of pickling in sodium hydroxide solution, not all corrosion products were removed after four intervals. All corrosion products were removed by pickling in sulfuric acid already after three intervals (6 min); the base metal has been slightly dissolved in the following intervals. Chelatone 3 solution dissolved corrosion products more slowly, but after four intervals (80 min) all corrosion products were removed.



Table 10: Mass loss of copper with relatively thick layer of corrosion products after pickling in various solutions (temperature 20°C).

Pickling solution	Concentration (M)	Time (min)	Mass loss of copper	
			(g/m ²)	(μm)
Citric acid	0.1	5 × 3	22.9	2.6
Chelatone 3	0.2	4 × 20	36.5	4.1
Sodium hexametaphosphate	0.5	4 × 3	56.3	6.3
Sulfuric acid	0.1	5 × 2	4.0	0.4

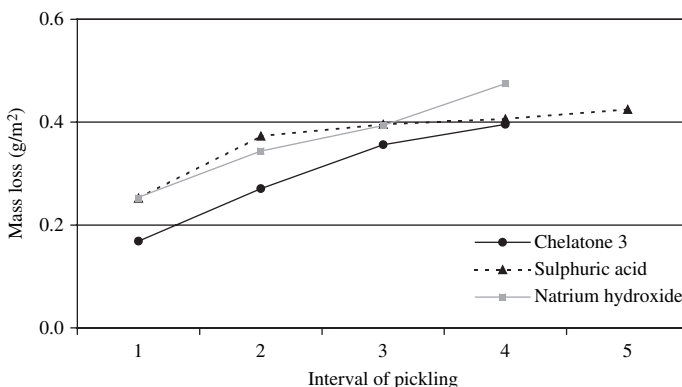


Figure 1: Corrosion loss of copper during pickling.

In the case of the samples covered with a thick layer of corrosion products, the course of pickling is similar: only the absolute values of material loss are higher. Chelatone 3 solution acts more strongly in the first interval, but after the second interval the intensity of dissolving corrosion products is similar to that of the sulfuric acid solution. The total material loss after pickling in Chelatone 3 solution is lower than in the case of pickling in the sulfuric acid solution, while the degree of cleaning the surface is the same (Table 11).

Surfaces are changed after pickling in a way resulting from the technology used:

- etching of surfaces after pickling does not increase the coarseness of surfaces, but the structure of metals is more marked, and
- trace amounts of elements contained in pickling solutions (Na, P) can be found on pickled surfaces even after proper wash-off in some cases.

4.1.4 Other cleaning technologies

Other options are use of high-pressure steam or blasting with little dry ice balls. Electrolytic methods are suitable for cleaning copper and bronze objects, especially

Table 11: Condition of copper surface after pickling in various solutions.

Pickling solution	Condition of copper surface after pickling
Chelatone 3	Original corrosion products removed, products of reaction with the pickling solution present, their occurrence is related to crystallographic orientation of grains of the base metal
Sodium hexametaphosphate	Areal removal, grain borders slightly marked, occurrence of undefinable stains which can be a result of selective pickling or products formed during pickling or material impurities
Sulfuric acid	Original products removed, course of pickling and also formation of new products depends on crystallographic orientation of grains of the base metal
Citric acid	Original products removed, course of pickling and also formation of new products depends on crystallographic orientation of grains of the base metal, less marked than in case of sulfuric acid pickling

archeological findings. The aim of cleaning is to remove aggressive ion fractions (chlorides) from surface layers. These methods allow to keep the layer of patina and other components on a treated object.

4.2 Artificial patination

Artificial patination is an important step in the process of creating and restoring bronze and copper historical objects and objects of art [19]. Artificial patination is not suitable for big outdoor surfaces as copper roofs or copper parts of cladding of buildings. Because of the long time it takes for a natural green patina to form there is a need to create patina artificially. Artificial patination is used mainly when a desired look of a surface needs to be reached quickly. Protective properties or the resistance to corrosion of created layers vary; in most cases they are not known or considered.

4.2.1 Creation, composition and properties of artificial patinas

Natural and artificial patinations are processes differing in principle and so they need to be understood and evaluated. Possibility of use of artificial patina needs to be assessed case by case.

There are a number of formulas for patination containing various components. Most of them are complex procedures, and their success is conditioned by experience and practice. The effect of chemical components is completed by other procedures that mechanically remove unadhesive portions of patina, mechanically



increase the homogeneity of remaining layers or cause secondary reactions at raised temperature. The process of creation of artificial patina is fairly difficult. Development of methods of artificial patination is supported by the need for fast formation of relatively evenly green or differently colored surfaces. Requirements for artificial patinas, especially aesthetic ones, are highly specific; treated surfaces are usually not very big and various craft procedures may be used to finish the surfaces. Data on composition of artificial patina are limited, especially data mentioning the patination process together with the final composition of a layer of artificially created products.

Patination is a process of controlled corrosion followed by further treatment of the corroded surfaces. Patination causes loss of the base material; all types of patination cause corrosion loss of bronze several times higher than the average corrosion loss in urban atmosphere (3 to 10 times higher). The highest corrosion loss is caused by two-step procedure (e.g. black patina created by solution of sulfurated potash, green patina created by solution of copper nitrate). However, corrosion loss of 3–10 μm is not important for loss in the thickness of either sculptures or sheets of objects of art on an object.

Mixtures of different chemical substances are used for patination, and creation of aesthetically desired even surface layers of artificial patina is very complicated. Brown and black patina is created in water solutions of sulfurated potash and ammonium sulfide (amorphous mixture of polysulfides). A thin layer of copper sulfide is formed on surfaces of bronze objects. Green patina is usually created in water solutions of copper nitrate or chloride together with other oxidants and complex-forming agents. There are also industrial processes of patination of monuments or semiproducts (sheets).

Longer service life of layers created this way is reached by consequent application of waxes, microcrystalline waxes or transparent coatings. Regular maintenance must be carried out to preserve the final aesthetical effect. However, repeated conservation causes changes in color.

Artificial patinas are more porous and less compact than natural patinas. Layers of artificial patina cannot be sufficiently bound to the copper or bronze base of an object. That is reached gradually by the repeated impact of climatic conditions, especially precipitation and dry-out. Uneven impact of outdoor environment also creates color tones typical for natural patina.

Artificially created green patinas on restored historical objects have a number of disadvantages:

- insufficient adhesion,
- partial wash-out by precipitation (artificial patinas contain more water-soluble components), and
- undesired changes of look during the process of transformation of artificial patina into patina the composition of which is closer to natural patina.

Artificial patinas vary in composition, and the contained components depend on the composition of patination solutions or pastes used and the manner of consequent surface treatment (mechanical treatment – brushing, washing, raised temperature).



4.2.2 Artificial patinas produced in workshops

Several techniques are used for application of artificial patinas [20]:

- Direct patination – direct application of chemical solutions on surfaces of objects using moistened cloths, soft brushes, etc. so that a thin coating is formed on a surface,
- Patination in vapors – objects are exposed to impact of chemical vapors in a closed environment. Areas differing in color can be formed during patination on surfaces of different orientation where gaseous vapors are condensed.
- Dipping patination – the whole object is dipped into chemical solution, often at higher temperatures. Solutions contain oxidizing substances, copper compounds and also acids or alkaline substances in some cases. On big objects, solution can be applied by pouring; however this method does not produce sufficiently homogeneous and even-in-color patina layers.
- Patination at higher temperatures – a wide variety of mainly dark colors of copper and bronze can be produced by the use of heat only. Patina layer is relatively thin. Such dark layer is often used as preparation treatment before further patination to green color.

Surfaces of objects can also be sprayed with suspension of basic copper salts. Suspended particles are then fixed to a surface by wax-binding agents applied after the suspension dries out.

The biggest problems occur in the case of patinating only parts of objects after repairs, exchanges of damaged parts, etc. Even if the color of artificial patina is the same as the color of natural patina, the new layer becomes visible due to the transformation of artificial patina.

4.2.3 Industrially produced artificial patina (examples)

Producers of copper sheets offer sheets with a layer of artificial patination – dark and green – too. Patinas are made continually on a production line by mechanical-chemical heat process or by application of gel containing copper nitrate and basic sulfates or copper chlorides. Extensive changes of patina composition can be expected to occur during its aging.

TECU®-Patina made by KM company (Germany) was used for cladding and roofing on both modern and historical buildings in Europe [21]. Sheets with Nordic Green patina made by Outocumpu company (Finland) were used on many historical and modern buildings around Scandinavia [19]. In the Czech Republic, both types of artificial patinas has been used on private or commercial buildings; artificial patina Nordic Green was used in roofing of Belveder (Queen Anna's summer palace) in Prague.

Sheets of artificial patina Nordic Green have been exposed for a long term at the atmospheric test sites of SVUOM and the changes of patina layer are being observed. A gradual wash-out occurred during the exposure but after approximately four years the green surface began to spread again. There is a gradual formation of natural patina, which grows through the layer of artificial patina. Computer picture



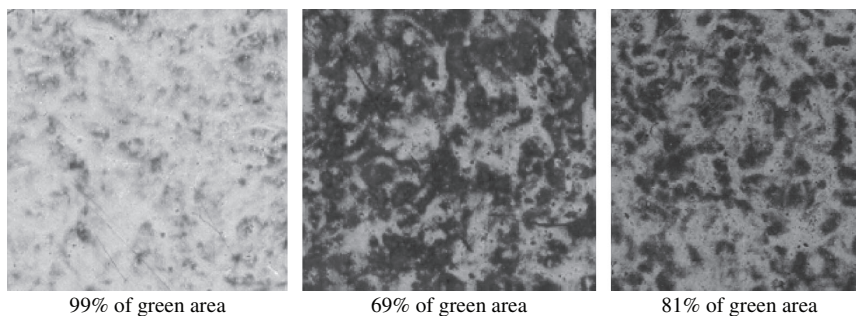


Figure 2: Changes of the layer of artificial green patina Nordic Green.

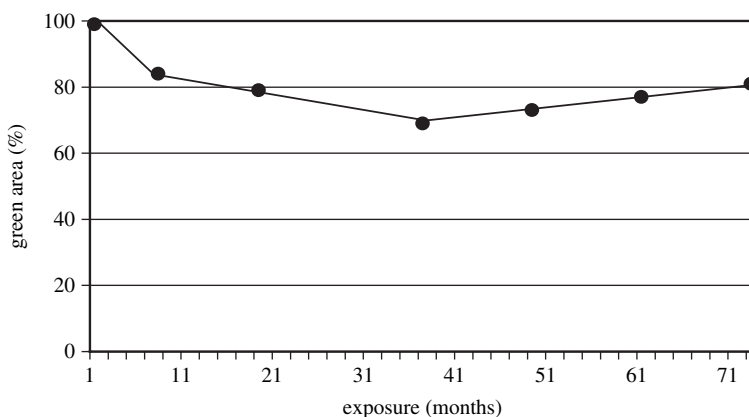


Figure 3: Changes of the layer artificial green patina Nordic Green during long-term exposure at a field test site Prague.

Table 12: X-ray diffraction analysis of patina layers.

Exposure	Time (years)				
	0	1	2	3	5
Composition of layer	Brochantite Posnjakite	Brochantite Posnjakite Cuprite	Brochantite Posnjakite Cuprite	Brochantite Posnjakite Cuprite	Brochantite Cuprite

analysis was used to evaluate these changes which allow for exact objective evaluation of the decreasing portion of the surface covered with green patina and the expression of gradual changes by numerical values (Figs 2 and 3). Transformation of the patina layer was observed at the same time (Table 12).

Table 13: Transformation of artificial patinas in various environments [13].

Patination agent	Composition of patina before exposure	Composition of patina after 2 years of exposure		
		Stockholm	Göteborg	Kopisty
Mixture of polysulfides	Very thin layer–unidentified	Cuprite Gerhardite	Cuprite Atacamite	Cuprite Posnjakite Brochantite
Mixture of polysulfides + Cu(NO ₃) ₂	Gerhardite	Gerhardite	Cuprite Atacamite Posnjakite Brochantite	Cuprite Posnjakite Brochantite Antlerite
Cu(NO ₃) ₂	Gerhardite	Cuprite Gerhardite	Cuprite Atacamite	Antlerite

Stockholm – low-pollution urban atmosphere influenced by traffic; Göteborg – urban atmosphere partially influenced by sea; Kopisty – industrial atmosphere, prevailing influence of SO₂.

4.2.4 Transformation of artificial patinas

Results of long-term tests prove that artificial patinas (produced in workshops or industrially) are transformed into natural patinas, which are in balance with the surrounding environment. The rate and degree of transformation depends on the type of atmosphere, its corrosivity and access of outdoor environmental impacts (Table 13) [22].

4.3 Conservation

Conservation of copper and bronze is used on historical objects and objects of art; it is used only rarely on construction elements (objects of arts on buildings). Conservation decreases the negative effect of outdoor atmosphere on copper and bronze surfaces and reduces the speed of deterioration of historical monuments. Conservation in the case of bronze and copper historical monuments means mainly treatment of surfaces by various types of waxes. Conservation should produce water-proof, hydrophobic, chemically stable, solid, elastic and even protective layer. Regular re-conservation at 1-2 years intervals can significantly reduce formation of patina on bronze and preserve original look of the material. Conservation agents are applied on objects covered with artificial green patina to protect it from wash-out and transformation.

Protective effect of waxes is the result of a barrier effect of the layer, mainly its low permeability for humidity and gaseous pollutants. Waxes provide only short-term protection (depending on type of wax, thickness of coating and corrosivity of atmosphere – 2 years at the maximum) and gradually grow old and loose elasticity

and flexibility. They then need to be removed, and the surfaces must be re-conserved or treated with another protective system. Although very diluted waxes are used and the coatings formed are very thin, solvents and mechanical treatment have to be used to remove them.

Application of waxes and similar conservation agents changes the color of surfaces – mainly those covered with green patina, but partially also those covered with dark patina. Smallest changes of color are caused by beeswax.

Beeswax is the most often used traditional protective agent for copper and bronze sculptures. For application on historical objects beeswax is diluted with technical petrol. Beeswax applied by this way forms thin transparent coatings of 50–100 μm . Protective effect of beeswax results mainly from the barrier effect of its layer.

A very important property of beeswax for its use in conserving historical monuments is its water-repellent ability (hydrophobicity). Beeswax has a number of other advantages for protection of bronze monuments:

- very little changes of look, color and character of surfaces and patinas are observed;
- can be easily removed;
- does not change its look during gradual degradation and has no influence on the look of a monument;
- its protective effect is well known and verified by long-term use in practice.

The disadvantage of beeswax is a relatively short protective effect in outdoor atmospheres. The effectiveness of beeswax, especially its hydrophobic properties, is lowered by the impact of light (esteric bonds are being destroyed).

Microcrystalline waxes are mixtures of carbohydrates with linear, branched or cyclic chains. Waxes are esters of aliphatic acids C_{20} – C_{30} with high-order mono-function alcohols. Waxes are produced by cooling melted waxes in suitable solvents to form a structure of very small crystals, close to amorphous structure. These microcrystalline waxes can be applied in thin layers and produce smooth and bright coatings after polishing. Microcrystalline waxes are not as hydrophobic as beeswax. The protective effect of microcrystalline wax itself does not last longer than one year. Re-conservation is more difficult than in the case of beeswax layers. Gradual degradation creates an ugly-looking layer that should be removed before re-conservation. A number of commercially produced conservation waxes is based on microcrystalline waxes. Higher effectiveness of commercially produced conservation waxes is a result of the corrosion inhibitors contained by them.

Application of waxes coated at high temperatures is preferred and tested in Germany [23] and Sweden. Wax applied at high temperatures was also used in the Czech Republic during last three years. The protective effect of the conservation layer after approximately two years is satisfactory. Waxes applied in this way penetrate surface layers more easily and form thicker coatings in most cases.

Application of organic coatings with prevailing barrier effect seems to be effective only in few cases, one of the reasons being less suitable aesthetic effect after application on bronze monuments. General repair of old coatings, especially removing them, is hard and almost impossible in case of applying coatings over patina.



The problem of coatings is tried to solve them by new hybrid organic-inorganic coatings, which are applied in very thin layers. International task EUR 16637 EN to develop Ormocer coating was finished in 1995 [24]. The coating has not been sufficiently tested in practice so far. The aesthetic effect of the new coating may not be the most suitable one in all cases (high brightness, change of color of the base when applying the coating over green patina).

Fixation and anti-graffiti coatings on copper sheet semiproducts covered with industrially produced artificial patina can also be put into this category of protective measures of temporary effect.

5 Economic impacts

The process of atmospheric corrosion causes permanent damage in materials and objects. Considerable sums have to be spent on the maintenance or replacement of elements or damaged parts of objects. Economic considerations are highly influenced by the relation between the price and service life of materials/elements. Costs related to replacements need to be considered too.

It is very difficult to give statements about the economy of maintenance and conservation or restoration of sculptures, historical objects and objects of art. Prices differ a lot; they are often set individually; their service life is considered in time periods of centuries; and there are also specific relations between service life expressed as stability and service life considered in different aspects. The process of atmospheric deterioration of an object is often stopped by making a copy of an object and placing the original in a depository.

There are, therefore, only present examples of direct costs for repairs of copper elements of buildings. Data need to be understood rather in their relations than in terms of direct values, which differ both in time and place (Tables 14 and 15). Prices shown below include costs for categories other than direct material costs:

- price of material/element,
- design and technological preparation,
- amount of work, including its organization, and
- storage and transport of waste.

Comparing data in both tables leads to the conclusion that using copper for constructional and architectural purposes is economical. Although the material is relatively expensive, the service life of elements is long and the requirements for maintenance are small. Long service life is supported also by the fact that copper elements and bigger areas (roofing) are used mainly for offices, banks or important city buildings where professional treatment and proper maintenance can be expected.

If maintenance and replacement of copper elements is carried out on historical objects, costs are higher, usually by multiples of ten times.

Transfer of copper into the environment as a result of atmospheric corrosion, which is an ecological burden especially for water and soil, is considered a negative effect having economic consequences. Green corrosion products of copper and its



Table 14: Prices for repair and maintenance of roofing materials in the CR (in 1996) [25, 26].

Materials	Repair type	Repair cost (€/m ²)
Galvanized steel	Replacement	14.1
	Removal	0.5
Aluminum	Replacement	12.9
	Removal	0.7
Copper	Replacement	74.6
	Removal	0.5
Concrete tiles	Replacement	18.9
	Removal	2.3
Clay tiles	Replacement	12.6
	Removal	1.1
Special clay tiles	Replacement	24.6
	Removal	1.8
Slate	Replacement	46.0
	Removal	2.0

alloys are washed away damage also neighboring areas of construction materials. It is very difficult and expensive to remove traces of this effect and so it is carried out only exceptionally.

6 Impact of atmospheric corrosion of copper and its alloys on the environment

As a result of weathering of roofs, facades and other parts of constructions, which is accelerated due to acidifying pollutants, a significant part of metals is emitted to the biosphere. The main accumulation of metals occurs in urban areas where the influx of metals is the greatest. Elevated levels of heavy metals in the sludge used as fertilizers, in bottom sediments or in potable water may in the long run have adverse effects on biological systems and human health. Gravimetric measurement of exposed samples was the methodology used for assessment of release of heavy metals due to corrosion of materials within the UN ECE International Co-operative Programme on *Effect on Materials including Historic and Cultural Monuments* [27].

A layer of corrosion products is formed on surfaces of metals and thickness of metal or metallic layer goes on decreasing. Part of the corrosion product remains on the surface and other parts are washed away by precipitation or flown into the environment by wind as soluble salts or particles. Results of copper exposure show that a significant part of the corroded metal remains on the surface as a part of corrosion products: for example, as green-colored patina on copper roofs or



Table 15: Material corrosion costs by type of building [25] in thousands NOK06 (1995).

Type of building	Material										Total	Percentage
	Galvanized steel					Other						
	Untreated	Wire, profile	Treated	Aluminum	Copper	Wood	Plaster	Concrete	Roofing felt	Brick		
Small house	2616	0	3663	136	63	27030	3896	2869	2060	317	42650	21.6
Apartment block	5169	0	9434	547	97	4636	16994	7307	2319	597	47101	23.8
Manufacture	1055	0	1260	109	31	326	321	387	1212	71	4771	2.4
Office	10620	0	10042	463	103	11240	4169	2148	7175	415	46375	23.5
Hotels	91	0	98	5	1	110	41	42	70	8	465	0.2
Services	1457	0	1430	66	14	1600	594	474	1021	91	6748	3.4
Agriculture	2267	0	2219	123	0	5850	116	163	23	40	10803	5.5
Other	1711	0	1433	65	23	2760	1212	827	701	84	8815	4.5
Infrastructure	0	3452	26552	0	0	0	0	0	0	0	30005	15.2
Total	24983	3452	56133	1515	332	53552	27342	14216	14581	1623	197732	100.0
Percentage	12.6	1.8	28.3	0.8	0.2	27.1	13.8	7.2	7.4	0.8	100.0	



Table 16: Ranges of copper corrosion rates and metal release rates based on results on corrosion attack from ICP Materials during the period 1987–95.

Exposure time	Corrosion rate ^a (g/m ² a)	Metal release rate ^a (g/m ² a)	Metal release (%)
1	6.7–13.4	0.3–1.2	3–21
2	5.2–10.3	0.5–1.6	7–33
4	5.0–9.3	0.7–1.8	10–33
8	3.8–6.8	0.8–2.0	20–42

^aAverage yearly value during the measuring period.

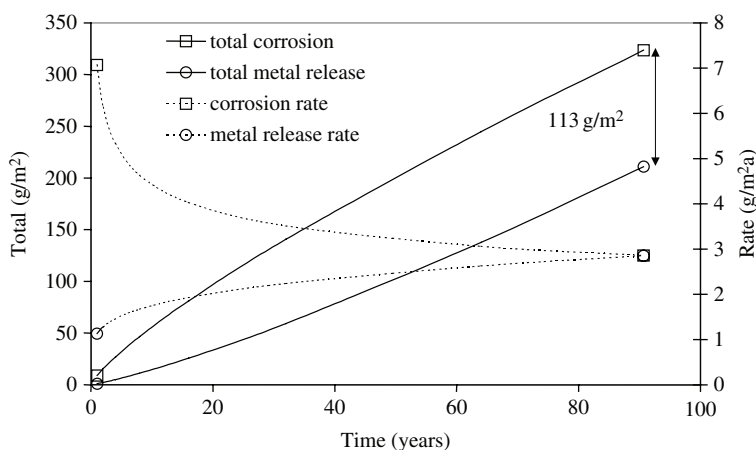


Figure 4: Calculated copper corrosion and metal release amounts and rates.

bronze sculptures. Results of average corrosion rates and metal release rates are shown in Table 16 after 1, 2, 4 and 8 years of exposure. Metal release rate is always lower than corrosion rate and the proportion increases with time due to decreasing corrosion rates and increasing metal release rates.

In constant environmental conditions, corrosion rate and metal release rate eventually reach the same value, corresponding to the so-called steady state where the composition and amount of corrosion products do not change with time. In Fig. 4 calculated copper corrosion and metal release amounts and rates as a function of exposure time based on dose-response functions and constant environmental conditions ($[\text{SO}_2] = 10 \mu\text{g}/\text{m}^3$, $[\text{O}_3] = 40 \mu\text{g}/\text{m}^3$, $\text{RH} = 75\%$, $T = 10^\circ\text{C}$, $\text{Rain} = 700 \text{ mm}/\text{a}$, and $\text{pH} = 4.5$) are illustrated. The difference between the amounts of corrosion and metal release ($113 \text{ g}/\text{m}^2$ at steady state) corresponds to the amount of metal retained on the surface in corrosion products.

7 Case studies

During the period 1992–98 in compliance with EU 316 COPAL, inspections on about 200 copper and bronze objects have been performed by SVUOM specialists. Results are summarized in a database. Following are three examples:

- Copper decoration element from the roof of Museum of Applied Arts, Prague,
- Bronze statue of St. John of Nepomuk, Charles bridge, Prague, and
- Copper roof of Queen Anna's Summer Palace, Royal Garden, Prague.

All examples document the stage of non-treated copper and bronze cultural objects exposed over a very long period in very polluted urban areas.

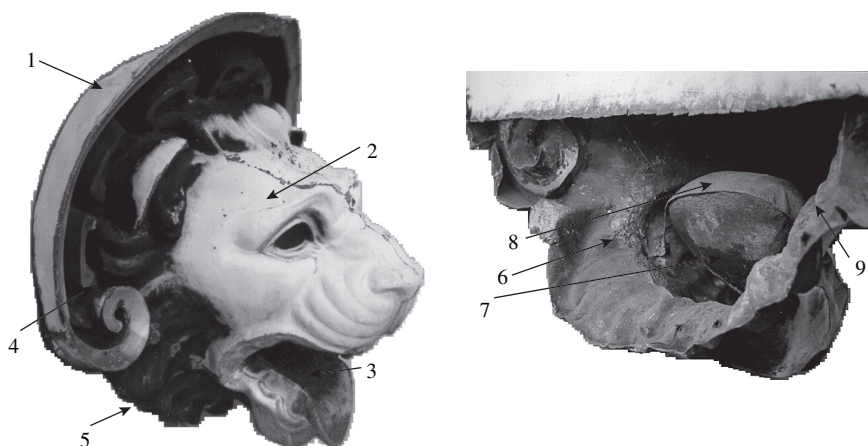
7.1 Case study 1 – Decoration element on the roof of Museum of Applied Arts in Prague

Material: copper sheet, partly gilded, sheet remaining thickness 0.43–0.60 mm

Exposure: 100 years in urban atmosphere with corrosivity C4–C5

Defects:

- isolated cracks in area of forming and joints
- release of joints, non-functional joining by steel nails
- bimetallic corrosion
- occurrence of black spots in the area of soldered joints
- occurrence of crusts
- degradation of gilded surface



X-ray analysis of surface layer

Area of removal of samples	Appearance of layer	Composition
1 Upper hem	Bright green, turquoise	Brochantite
2 Upper edge of eye	Bright turquoise	Brochantite, antlerite
3 Mouth	Grey and green	Antlerite, quartz, gypsum
4 Profiled part of hem	Dark gray	Cuprite, antlerite
5 Lower dark hem	Red and brown	Cuprite, antlerite
6 Lower part of inside surface with dust and crusts	Bright turquoise with gray parts to dark gray and green	Antlerite, chalcantite, gypsum, (NH ₄) ₂ Cu(SO ₄) ₂ · 6H ₂ O
7 Lower part of inside surface	Turquoise, gray parts	Chalcantite, antlerite, brochantite, gypsum
8 Upper part of inside surface	Grey-and-green to dark green, dark gray	Antlerite, quartz
9 Inside surface of hem	Brown, gray and green	Cuprite, quartz, antlerite

Microprobe analysis: chlorides in surface layers (samples 4 and 5)

Metallography cross: uniform microstructure of copper with patina layer

7.2 Case study 2 – Sculpture of St. John of Nepomuk on the Charles bridge in Prague

Material: bronze alloy, gilded steel decorative elements

Exposure: 300 years in urban atmosphere with corrosivity C4

Defects:

- small holes on the most open areas (forehead, cap)
- dark surface with dust deposits in shelter position
- corrosion on the borders of grain of alloy
- application of lead as filling material for holes and openings





X-ray analysis of surface layer

Area of removal of samples	Appearance of layer	Composition
Upper surface of cap	Green-and gray	Brochantite, cuprite
Lower part of coat, shelter	Black	$(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, graffite
Open surface of body	Green	Brochantite, quartz, cuprite, anglesite (PbSO_4)

7.3 Case study 3 – Roof of Queen Anne’s Summer Palace in Royal Garden in Prague

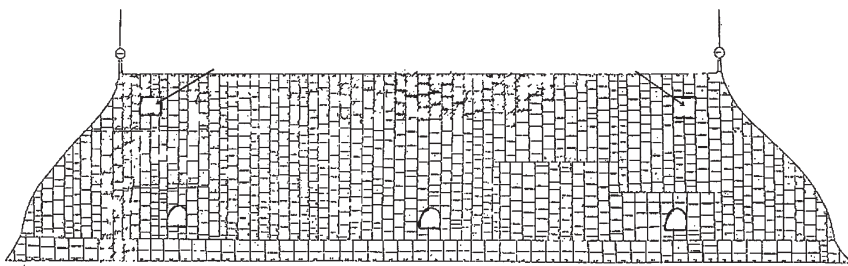
Material: copper sheet, sheet remaining thickness 0.80 mm on the most of roof sheet remaining thickness 0.35–0.40 mm on the east saddle part

Exposure: 100–400 years in urban atmosphere with corrosivity C4–C5

Defects:

- cracks and perforations on the sheets with minimum thickness
- occurrence of black spots on sheets

East side of roof

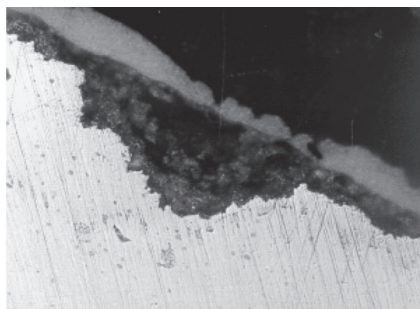
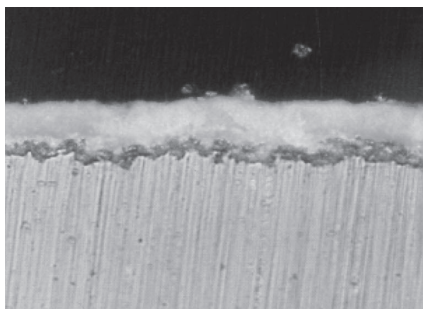


X-ray analysis of surface layer

Area of removal of samples	Appearance of layer	Composition
1 Cover of window	Middle green	Brochantite
2 Sheets on east side	Yellow and green	Brochantite, quartz, gypsum
3 Area with black spots	Black	Cuprite

Microprobe analysis of spots: high amount of Fe

Metallography cross: layered patina – lower layer cuprite; upper layer brochantite, antlerite pits



200×

Reconstruction:

- realized in 2000–03
- replacing of damaged sheets by new copper sheets
- application of artificial green patina on replaced sheets



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