

Fig. 1. Copper roof of Queen Ann's Summer Palace (Belvedere), built in 1558-1564; eastern ridge damaged part

Dagmar Knotková, Jiri Had, Katerina Kreislová

Restoration of Copper and Bronze Monuments in Prague

Corrosion Manifestations. Anticorrosion Measures

Introduction

The study of corrosion manifestations on copper and bronze monuments and cooperation with conservators was started by SVÚOM a. s. about eight years ago, when SVÚOM became a participant of the EU 316 Copal project. The solution conception is defined complexly in correspondence with the concept of an institute specialized in problems of atmospheric corrosion of metals and the selection of optimum anticorrosion measures in a long run.

Results of laboratory, site and other tests of copper and copper alloys with various types of patination, conservation and other measures for the restriction or modification of corrosion processes are dealt with in other individual publications.¹⁻⁴

This paper focuses on the generalization of results of pre-restoration research, and on the inspections and participation of restoration of selected copper and bronze monuments in and around Prague. An investigation of almost 100 objects was carried out; while in the case of about ten objects it was a systematic investigation followed by consultations during the restora-

tion process. Current research gives an outline of the types of corrosion manifestations on selected bronze and copper monuments in the area of the City of Prague.

Corrosivity of the Atmosphere in the Area of Prague

Those monuments included in our research have been exposed to the Prague atmosphere for several decades or even centuries (30-400 years). Obviously, corrosivity of the atmosphere has been changing during such a long period. The composition of patina changed in correspondence with these changes.

In conditions of exposure in the agglomeration of Prague, corrosivity reaches categories C 3-C 4, only occasionally C 5 (location of namesti Republiky) according to ISO 9223. However, in recent decades, the inner city of Prague, including the City Monument Reservation, has been exposed to the impact of atmosphere with corrosivity category C 4-C 5.

As far as copper and bronze monuments exposed for a long period are concerned, the last century brought first a gradual,

and then a rapid increase of corrosiveness of the atmosphere, and a consequent decrease in the last 3-5 years.

Although most assessed objects are located in the central part of Prague, objects in the suburbs that are not affected by gaseous and solid pollution to such an extent were assessed as well.

Observed Objects

Main attention was paid to bronze sculptures, but copper roofs and copper claddings of important historical buildings in Prague were assessed, too. Complex knowledge was gained through cooperation on the restoration of selected objects.

Methods of Evaluation, Solution Proposals

The methods of evaluation corresponded with the possibilities of a more widely framed research:

- inventorying of objects and determination of corrosivity of the exposure location,
- investigation of corrosion manifestations, photo documentation,
- measurements of residue thickness of copper roofs and cladding,
- complex analysis of patina from various exposure places on an object,
- analyses leading to determination of original technologies and conservation means.

Solution proposals involved:

- pre-selection of defective places and analysis of the cause of a defect,
- recommendation of a suitable technology and means for cleaning, patination and conservation of restored objects.

Examples of Solutions

Examples are selected in a way that they cover variability in a type of object, grade and way of corrosion damage and attitude to restoration.

Study of Argo stallion (final design of a horse for St. Wenceslas statue)

J. V. Myslbek

Made of bronze in 1953, placed in indoor spaces of the National Gallery, since 1993 placed in open atmosphere at a corrosivity category C3. Exposed with a dark patination, conserved with beeswax. Re-conservation is done in one-year periods to protect it against corrosion as much as possible. Parts of the statue have been experimentally conserved with modern conservation means on the basis of micro waxes. The effectiveness of thin conservation layers (even inhibited) is not sufficient. More exposed places turn to grey-green color, trickles made by precipitation are becoming visible, the horizontal surface of a pedestal shows a thin green coat. The object is interesting for our research, because assessment was started in the first year of open air exposure and it allows for an experimental verification of conservation products and technologies.

Equestrian statue of Jiri z Podebrad

J. Schnirch

Made of hammered copper in 1890, placed in open atmosphere at corrosivity category C3 for 100 years. During first 50 years, the statue was regularly checked and maintained, later the maintenance became irregular, often unprofessional. A complex restoration was done in 1995.

Corrosion manifestations: uneven patina layer, local crusts, repairs with pigmented paint, sporadic local corrosion-through of strongly hammered parts and galvanoplastic elements, non-uniform corrosion (small pits) on overlapping, significant corrosion damage or even destruction of inner iron skeleton (Colour Plate VI.3a, b), bimetallic corrosion at the connection of the inner skeleton with the copper coat, loosened and tattered soldered joints.

Patina was formed mainly by brochantite and antlerite (according to position) and the layer also contained quartz, gypsum, cuprite, sporadically also copper formate.

Restoration was done in cooperation with corrosion specialists and technologists (University of Chemistry and Technology, SVUOM, M-System and others). In the process of restoration, the statue was disassembled, individual parts were cleaned by blasting, the inner skeleton was made of stainless steel and complementary protected with paint, parts of the copper coat were completed by a girdler. After re-assembling, excluding the bimetallic joints, the statue was darkly patinated and conserved with beeswax. Gradual formation of green patina with a black toning is desired.

Copper roof of Queen Ann's Summer Palace (Letohradek kralovny Anny)

Built in 1558-1564, some parts replaced during the centuries. For many years, it was exposed to an environment of corrosivity category C3-C4-C3. Extensive measurements of the residue thickness of the sheets proved that the original thickness of about 0,8 mm of the most affected eastern ridge part has decreased to 0.35-0.50 mm with minimums of 0.30 mm. The residue thickness of other, less affected parts is about 0,6 mm. The formation of corrosive-mechanic cracks is caused also by an insufficient fixation of the sheets (Fig. 1 and 2). Numerous occurrences of black spots not only on the joints, but also on the surface of some sheets, cannot be derived from the orientation of a surface, or from the processing technology. Bound repaired joints are loosened.

The variety of colors and the composition of the patina correspond with the shape arrangement of a long-term exposed object (mainly brochantite, locally cuprite, sporadically antlerite). Compared to new objects, the brown surface layers of impurities (quartz, calcite) are more marked.

The eastern ridge part was recommended to be replaced with new roofing material patinated by a modern, rather industrial technology. The final proposal of reconstruction is being prepared.

Sculpture "Genius with a Lion" (Genius se lvem)

A. Popp

Made of copper sheet, partly of cast bronze in 1937. Placed on the roof of the Czech National Bank, corrosivity category of



△ 2a

2b ▽

Fig. 2a, b. Copper roof of Queen Ann's Summer Palace (Belveder), built in 1558-1564; sheet with corrosion-mechanical defects



atmosphere C5, increased weather effect. Maintenance was done unsystematically. The sculpture was taken down in 1997 and a complex restoration was started.

The sculpture is covered with a layer of green and black patina with repairs by a green-pigmented and graphite paint. The variety of colors is very uneven because of the lack of maintenance and repairs that was done. The inner part of the sculpture is covered with light-green and turquoise corrosion products. Crusts contain $(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

Soldered joints are of poor quality, often tattered, the inner skeleton is not markedly damaged by corrosion, non-uniform corrosion of the bronze parts.

A pre-restoration investigation is being carried out by SVÚOM (Colour Plate VI.2a, b). Cleaning and consequent patination will cause problems, because the authorities for the care of monuments require a combination of green and black surfaces.

Cupola of Town Hall (Obecni dum)

Built in 1906-1911

The cupola is covered with copper sheet and richly decorated with boxes and sculptures, partly gilt. Ventilation louvre-boards are installed. The object is exposed to an atmosphere of corrosivity category C5 with a significant influence of traffic and op-

eration effects (ventilation of restaurant and lounges). Locally dirtied by pigeon excrements on the upper border and at the box endings of the decorations.

The main corrosion manifestations occur on ventilation louvre-boards (crusts containing $(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) and on the boxes of decoration elements and in their vicinity: corrosion of the rivets of the joint with a supporting element leading to the destruction of a joint and deformation of an element, leakage of water with rust from boxes, loosening of soldered joints, formation of black spots in their vicinity (Colour Plate VI.1).

The restoration process involved local cleaning (under boxes, border with excrements), repair or replacement and anticorrosion protection of the inner elements in the boxes, repair and careful cleaning of the soldered joints, the installation of brass rivets, installation of copper grate to stop pigeon nesting.

Sculpture "Embrace of Love and Death" (Objeti lasky a smrti)

B. Kafka

The second cast made in 1933, placed in the garden of the author's house, later on in the National Gallery park at corrosivity category C3 (with a possible effect of a cement factory). The sculpture was designed to be placed at a wall under arcades in a cemetery, where the first cast is placed, showing no particular effects. It is covered with a green patina of a shelter type from the front side. It is also covered with a layer of dust.

The second cast needs to be restored (Fig. 3). Corrosion manifestations: lengthwise hole on both upper and bottom sides of the right wing, where corrosion products of copper with rust leak from. Water is formed as a condensate and it also leaks in through joints and assembling hole at the back part. Impurities are being held up in a lap and voluminous patina containing gypsum forms. Marked corrosion or even destruction of the steel screw joints on the back untreated part of the sculpture. Loosened joint on a bronze plinth, bond washed off from the masonry plinth, broken compactness of masonry. Corrosion of the unprotected steel fixation rope.

SVÚOM elaborated a proposal for the restoration involving procedures for cleaning, closing the holes, local patina completion and complete anticorrosion treatment of the back part including the replacement of the screw joints.

Typization of Corrosion Manifestations on Copper and Bronze Monuments Exposed for Long Term Periods

Corrosion problems of copper roofs and cladding of buildings

Main types of corrosion manifestations:

1. The corrosion rates of copper determined from measurements of residue thickness by an ultrasound thickness gauge correspond with the corrosion rates determined in long-term testing programmes that are presented in standard documents, as e. g. ISO 9224 standard.
2. The color of patina and its composition accord with the properties of the surrounding environment and with the shape-design of the object. A more complicated design of roofs (cupola with decorative elements) and stylish cladding (rondel cubism) cause a higher variability of both color and composition of the patina.

- Pollution of the environment connected with human activity in the microclimate sense (ventilation of floor spaces, mainly kitchens and hygienic facilities) can cause, on surfaces affected by this pollution, formation of non-protective layers of corrosion products frequently containing $(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.
- Local corrosion effects are very rare and usually connected with either microclimatic corrosion factors, or, more often, with technological factors. They are mostly situated near the joints. Flat pits of 50 μm depth were observed.
- Corrosion-mechanical manifestations were evaluated on the roof of Queen Ann's Summer Palace (Letohradek kralovny Anny) on part of the surfaces with an increased combined stress connected with the shape-design of the roof and an insufficient fixation of the components. This defect limits the serviceability of the roof.
- Defects demanding a more extensive reconstruction were found on the cupola of the Town Hall (Obecni dum). An opened funnel of the decorative element in the upper part of the cupola brings water and impurities to a decorative box situated lower and connected to the cupola by steel stiffeners.
- Black projecting spots occur on old copper roofs. There was no correspondence found, neither with local metallurgical variousness, nor with local corrosion manifestations.
- Soldered joints of decorative elements get damaged. Black spots or even surfaces, locally even little pitting, occur in their vicinity.

Corrosion manifestations on copper and bronze sculptures

While, in the case of copper roofs and cladding, the corrosion effects can significantly influence the serviceability of the monument, manifestations on bronze statues are in most cases evaluated from the aesthetic points of view. However, serious problems arise when corrosion of the inner stiffeners and structures occurs.

Main types of corrosion manifestations:

- The composition of most of the collected patina samples from various surfaces of an object accords with the composition typical of patina forming nowadays in urban and industrial regions (brochantite, antlerite, cuprite, quartz, calcite).

Fig. 3a, b. Sculpture Embrace of Love and Death (Objeti lasky a smrti, B. Kafka, 1933); corrosion manifestation



△ 3a

3b ▽



- Crusts forming in partly sheltered locations are of the usual composition (addition of gypsum, quartz, carbon black, etc.). Specific components, as ammonium copper sulfate and formate, were determined. Chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and mooloite ($\text{Cu}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$) are typical constituents of crusts of bronze statues situated in the centre of Prague.

age of object (years)	typ of object		exposed in atmosphere ^a			defect		
	roof, cladding copper	statue, etc. (bronze, copper)	C3	C4	C5	aesthetic ^b	corrosion ^c	mechanical ^d
450-240	1	5	4	2	—	1	2	2
150-110	-	3	—	3	—	2	1	—
100-80	3	28	4	24	3	25	21	4
75-60	2	17	11	4	3	11	11	6
50-20	1	15	9	5	1	8	11	2
< 15	1	3	—	3	1	1	2	1
total	8	71	28	41	8	48	48	15

Table 1. Observed copper and bronze objects in Prague

^a derived according to ISO 9223

^b non-uniform patina, color differences

^c non-uniform corrosion, pits, crusts, etc.

^d holes, damaged joint elements and supporting structures

- Non-uniform corrosion was observed in a limited number of cases on horizontal and less sloping surfaces of statues exposed to the heavily polluted environment of the center of Prague.
- An interesting finding is the occurrence of surfaces with little pits in the zone of transition between open and sheltered exposure in the case of a statue made of hammered copper sheet (under an overlapping coat of a rider on a horse). These pits were under a crust of sedimented impurities and corrosion products. It can be assumed that in the crevice of overlapping corrosion stimulation pollution is accumulated and the time of wetness is longer.
- Galvanic corrosion of steel connection elements on the back side of a bronze statue designed to be situated against the wall.

- Extensive surface and local galvanic corrosion on the inner steel construction supporting a statue made of hammered copper sheet, showing many leakages.
- Higher corrosion effects on entry of the metallic structural elements into the masonry plinths, marked corrosion damage up to destruction of the subsidiary internal structures of the hollow masonry plinths.

An overview of the assessed objects, their location and observed defects is worked into Table 1.

The variability of the composition of the corrosion products' layers is evident from Table 2. The effect of the shape and sheltering is decisive.

Exposure 100 years at corrosivity category C4-C 5.

Position on sculpture	Appearance of sample	Crystalline compounds (in order of strongest XRD reflection)
External surfaces (Fig. 4)		
a – upper border (fully exposed)	light green	brochantite
b – head of lion (convex parts)	light green	brochantite
c – surface of the eyes (partly sheltered)	light turquoise	brochantite, antlerite
d – oral hollow	gray-green	antlerite, quartz, gypsum
e – upper perpetual part of border	dark gray	cuprite, antlerite
f – lower perpetual part of border	turquoise and dark gray	antlerite, gypsum, quartz
g – attachments of sculpture	dark gray-green	antlerite, cuprite, quartz, mooloite
h – attachment of sculpture (lower part)	dark brown	antlerite, cuprite
i – lower dark border	brown-red	cuprite, antlerite
Internal surfaces (Fig. 5)		
a – lower part with dirt and crusts (semi-sheltered exposure)	dark gray - green	antlerite, chalcantite, gypsum, $(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$
b – lower part with crusts (semi-sheltered exposure)	light turquoise with gray parts	chalcantite, antlerite, $(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$
c – lower part (semi-sheltered exposure)	turquoise, gray parts	chalcantite, antlerite, brochantite, gypsum
d – lower part (semi-sheltered exposure)	turquoise	chalcantite, gypsum, $(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$
e – upper part (fully sheltered by mantle of the sculpture)	dark gray, light parts	antlerite, quartz
f – upper part (fully sheltered by mantle of the sculpture)	green-gray	antlerite
g – head of lion (inner surface)	dark green	antlerite
h – head of lion (inner surface)	light brown, gray-green	cuprite, quartz, antlerite
i – lower part at border of sculpture	turquoise, light brown parts	quartz, brochantite, gypsum

Table 2. Analysis of the layers on the copper sculpture on the roof of the Decorative Arts Museum in Prague

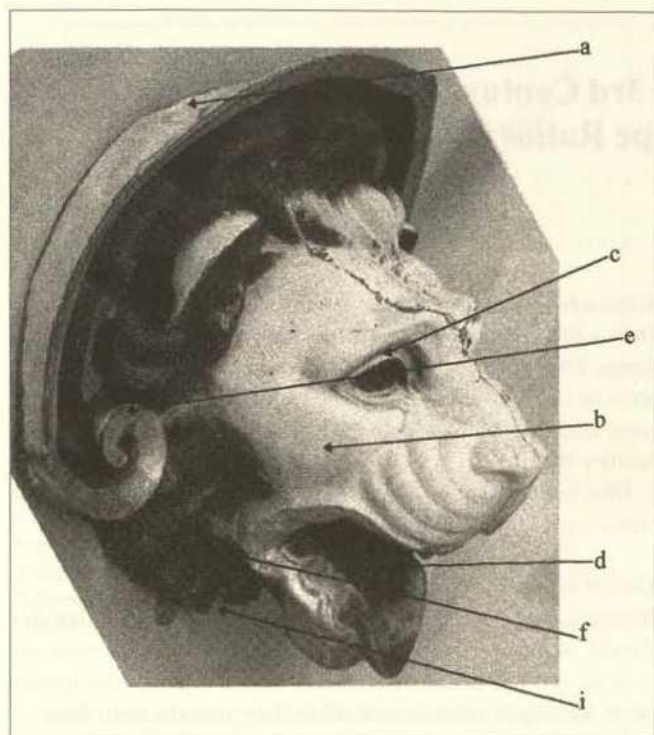
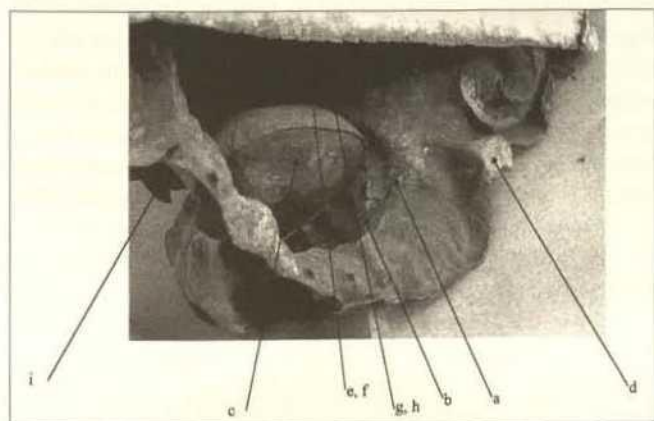


Fig. 4. Copper sculpture (external surface) from roof of The Decorative Arts Museum in Prague with marked position of sampling (cf. Tab. 2)

Fig. 5. Copper sculpture (internal surface) from roof of The Decorative Arts Museums in Prague with marked position of sampling (cf. Tab. 2)



Conclusion

The results of the extensive investigation, which is documented by several examples, are gradually being elaborated into a database. The approach to the restoration of copper and bronze monuments cannot be unified since there are many viewpoints (aesthetic, cultural, technological, kind of use, economical, etc.). There are also local differences of understanding and evaluation of these objects.

The typization of defects resulting from our investigation clearly shows that the field has got enough space for the assertion of specialists in the field of corrosion and anticorrosion protection.

SVÚOM has started cooperating with the National Gallery in Prague, The Gallery of the City of Prague and authorities in the care of monuments and tries to bring a certain system into the restoration process. The system issues from the knowledge of corrosion processes and effects and uses a rational attitude for the selection of measures, including anticorrosion protection.

Good results are acquired in cooperation with several restoration workshops which support an interdisciplinary communication.

Citations

- 1 DAGMAR KNOTKOVÁ/JAROSLAVÁ VLČKOVÁ/KATERINA KREISLOVÁ/JIRI HAD, *Atmospheric Corrosion of Bronze and Copper Statues, Roofs and Cladding of Prague's Monuments*, in: Art 96, Budapest, p. 391-406.
- 2 DAGMAR KNOTKOVÁ/KATERINA KREISLOVÁ, *Contribution to the Problem of Conservation of Outdoor Bronze Sculptures*, in: COPAL Proceedings, Wien, 1996.
- 3 DAGMAR KNOTKOVÁ/KATERINA KREISLOVÁ, *Patinace a konzervace medených a bronzových historických a umeleckých objektů*, Metodický list, Brno, 1996 in Czech.
- 4 DAGMAR KNOTKOVÁ/KATERINA KREISLOVÁ, *Chemické postupy čištění medených a mosazných povrchů*, Metodický list, Brno, 1997 in Czech.

Photo Credits

All photographs by Dagmar Knotková, 1994-1997