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ARTIFICIAL WEATHERING OF BRONZE PATINAS

Selection of test conditions

Work performed for the European Project ARTECH – Access,
Research and Technology for the conservation
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ARTIFICIAL WEATHERING OF BRONZE PATINAS

Selection of test conditions

In this report, results of a study carried out with the objective of establishing the conditions for artificial weathering practice adequate to patinated bronze with applied conservation treatments are presented. The work developed is part of the research activities that have been carried out in the Metallic Materials Division for the European project ARTECH, integrated in the working group *JRA1: Development and evaluation of new treatments for the conservation-restoration of outdoor stone and bronze monuments*.

ENVELHECIMENTO ARTIFICIAL DE BRONZE PATINADO

Seleção das condições de ensaio

Neste relatório apresentam-se os resultados de um estudo elaborado com o objectivo de estabelecer as condições de execução de ensaios de envelhecimento artificial adequadas a bronze patinado sujeito a tratamentos de conservação. O trabalho desenvolvido constitui parte das actividades de investigação que têm vindo a ser realizadas no Núcleo de Materiais Metálicos, no âmbito projecto europeu Eu-ARTECH, inseridas no grupo de trabalho *JRA1: Development and evaluation of new treatments for the conservation-restoration of outdoor stone and bronze monuments*.



Figure A3 – Visual aspect unpatinated bronze samples (BL_0 and BL_III) after cleaning in H₂SO₄ 10% solution for removal of the corrosion products

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Figure A1 – Visual aspect of MN64, UN(R)64 and UA6 bronze samples before exposure to the salt fog

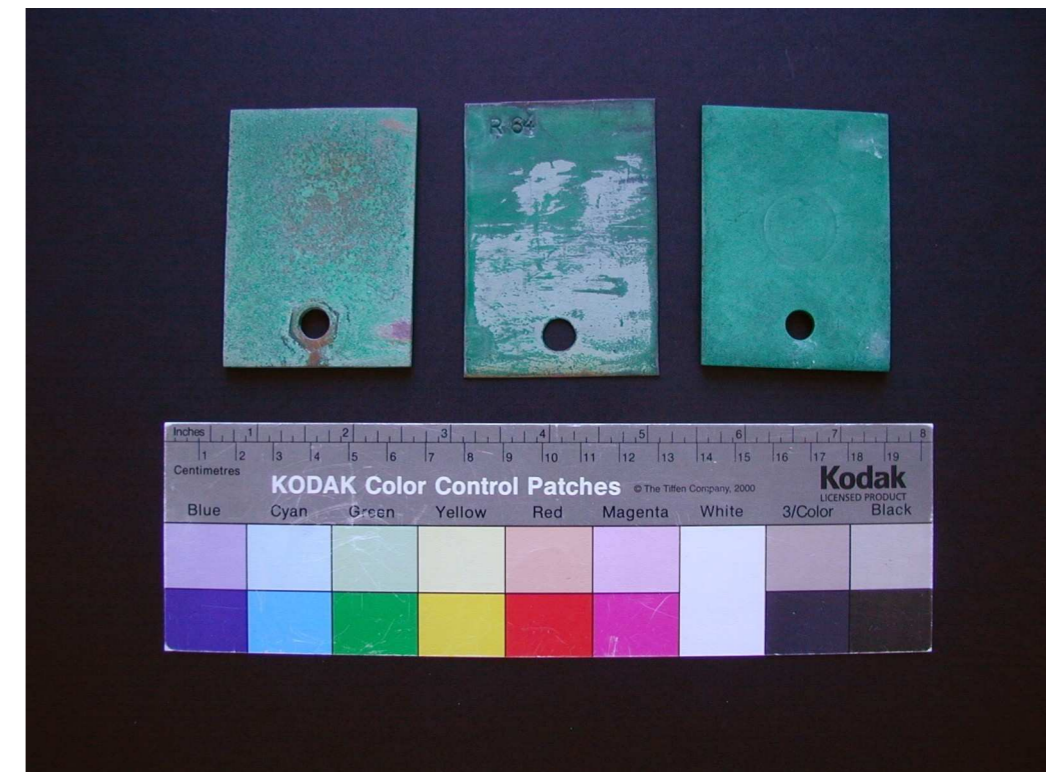


Figure A2 – Visual aspect of MN64, UN(R)64 and UA6 bronze samples after exposure 768 h to the salt fog

ARTIFICIAL WEATHERING OF BRONZE PATINAS.

Selection of test conditions

1. INTRODUCTION

The European project ARTECH - *Access, Research and Technology for the conservation of the European Cultural Heritage* - is a consortium among thirteen international European infrastructures operating in the field of artwork conservation, where LNEC is included. The objective of Eu-ARTECH is to achieve a permanent interoperability among the participating infrastructures, establishing cooperation and exchange of knowledge with the other infrastructures in the field, in the perspective of structuring a common European research area. This is a five-year project and its activity program is developed through the following activities: networking, access and joint research. The joint research activities, which are devoted to improve the performances of the participating infrastructures and the quality of the access offered to the scientific community, are divided in two parts [1]:

- JRA1: Development and evaluation of new treatments for the conservation-restoration of outdoor stone and bronze monuments;
- JRA2: New methods in diagnostics: Imaging and spectroscopy.

LNEC has an active part in JRA1 activities, which have started in the end of 2004 and will go on till the end of the project in 2009.

In this report, part of the work carried out by the Metallic Materials Division, in 2007, for the JRA1 activities - bronze working group – of Eu-ARTECH , concerning a specific task, is presented. This task had the objective of establishing the exposure conditions to a salt solution adequate to patinated bronze, to perform the artificial weathering of conservation treatments applied in this material foreseen in the JRA1 working plan.

Patinated bronze is a unique material consisting in the alloy covered by a thin layer of corrosion products (patina), usually very stable and adherent, protecting the metal underneath against corrosion. In a simplified manner, the bronze patina can be considered as a coating on the metal, of inorganic nature. The experimental study carried out was needed because there is almost no information available in literature about weathering procedures specific for patinated bronze materials. Also the existing standardized tests procedures for conducting accelerated corrosion tests were developed for testing paints and varnishes (organic coatings) or for metals and alloys in general.

2. MATERIALS AND EXPERIMENTAL PROGRAM

In the research work that has been carried on by the ARTECH - JRA1 partners, several treatments to be applied in the conservation-restoration of outdoor bronze monuments were developed. To evaluate their (potential) efficacy, they should be applied in representative test specimens and subjected to an accelerated weathering.

Outdoor bronze monuments usually present their surface covered by a patina, as a result of the atmospheric corrosion of the metallic alloy elements, specially of copper. The patina's composition and thickness depend on the time of exposure and on nature of the exposure



environment, namely, on the type of pollutants present, for example: SO₂ gases are typical of urban and industrial atmospheres, while marine atmospheres are rich in chlorides. Consequently, bronze (old) urban patinas are usually constituted mainly by copper sulphates, and bronze marine patinas by copper chlorides. These type of corrosion products are green, being responsible for the green surface acquired by these type of monuments with time (Figure 1). More complete information on bronze patina formation could be read in another LNEC report [2] and in several scientific publications referenced in it.

Figure 1 – The equestrian statue of King D. José I (Séc. XVIII)

So for application and testing of treatments, three types of patinated test specimens were “prepared”. The description of patinas properties and its genesis, and type of substrate is presented in Table 1.

Table 1 – Patinated test specimens: patina and substrate characteristics

Name	Patina characteristics				Substrate type
	Type	Process of formation	Average thickness	Composition (main product)	
UN (R)	Urban	Natural exposure for 80 years in Munich (Germany)	19 µm	<i>brochantite</i> Cu ₄ (SO ₄)(OH) ₆	Copper sheet
UA	Urban	Artificial process	79 µm	<i>brochantite</i> Cu ₄ (SO ₄)(OH) ₆	Bronze plate
MN	Marine	Natural exposure for 1 year in Cabo Raso (Portugal)	29 µm	<i>paracatamite</i> (Cu ₂ (OH) ₃ Cl)	

ANNEX A

REFERENCES

- [1] <http://www.eu-artech.org/>
- [2] Fontinha, I. R.; Salta, M. M., "Metodologia para o diagnóstico da corrosão em estátuas de ligas de cobre", Relatório nº16/2000 - NQ, LNEC, Janeiro de 2000.
- [3] Salta, M. M.; Fontinha, I. R., "Diagnóstico da corrosão da estátua de D. José I em Lisboa", Relatório nº313/98 - NQ, LNEC, Novembro de 1998.
- [4] EN ISO 11341:2004 - Paints and varnishes - Artificial weathering and exposure to artificial radiation - Exposure to filtered xenon-arc radiation (ISO 11341:2004)
- [5] NF EN ISO 11997-2:2006 - Paints and varnishes - Determination of resistance to cyclic corrosion conditions - Part 2 : wet (salt fog)/dry/humidity/UV light
- [6] ASTM D5894-05 Standard Practice for Cyclic Salt Fog/UV Exposure of Painted Metal, (Alternating Exposures in a Fog/Dry Cabinet and a UV/Condensation Cabinet)
- [7] EN ISO 2360:2004 - Non-conductive coatings on non-magnetic electrically conductive basis materials - Measurement of coating thickness - Amplitude-sensitive eddy current method (ISO 2360:2003)
- [8] L.Morselli; E. Bernardi; C. Chiavari; G. Brunoro, Appl. Phys. A 79, 363-367 (2004)

The conservation-restoration treatments object of ARTECH study to be weathered by LNEC are of different nature: silane type (two products); cuprite layer (inorganic), incralac (organic) - to be used as reference for the comparison with the silanes; 5% limewater solution (inorganic) as passivation agent to be compared with the traditional corrosion inhibitor benzotriazole (organic).

For testing the treatments applied in the marine patinated (MN) bronze samples, it was decided to expose it in the high corrosive marine site Cabo Raso for one year, maximum 18 months. This exposition started in April of 2007 and it is going on.

For testing the treatments applied in the urban patinated (UN and UA) samples, it was decided to carry out an artificial weathering in laboratory, because in a natural urban environment the corrosion would be too slow. Due to the different nature of the treatments under study, the weathering procedure should include exposure both to UV radiation and to an acidic solution. Considering this, after consulting some scientific articles and standards for corrosion testing of metallic materials and paints and varnishes, several possible alternative procedures were selected and analyzed by the JRA1- bronze working group during the ARTECH meeting held in Munich this year. Then it was accorded to carry out the artificial weathering with a cyclic procedure involving alternate exposure to filtered Xenon-arc radiation (Table 2) followed by exposure in a salt fog chamber (Table 3), based in standard procedures. The salt solution should contain both chlorides and sulphates in low content in order to be approximated to the urban rain water composition.

Table 2 - Exposure conditions for artificial weathering of conservation treatments – Part I: UV radiation exposure.

Designation of test	Exposure conditions	Bibliog. Reference
<i>Exposure to filtered Xenon-arc radiation</i>	38°C 18 min 100%RH; 102 min 50%RH	EN ISO 11341 [4]

Table 3 - Exposure conditions for artificial weathering of conservation treatments – Part II: Salt solution exposure.

Designation of test	Exposure conditions	Bibliog. Reference
<i>Wet (salt fog) / dry cycle</i>	Salt fog, (23°C or 35 °C) ±2°C, 100%RH Dry atmosphere , 35°C ±2°C. Salt fog: NaCl (0,5 g/L) + (NH ₄) ₂ SO ₄ (3,5 g/L)	EN ISO 11997-2 [5] ASTM D5894-05 [6]

However, due to the fact that the standard procedures consulted for the establishment of these salt solution exposure conditions were developed for testing of paints and varnishes, it was raised the question of how the patina of the bronze samples would behave, namely, if the salt fog would be too aggressive to them. So, it was decided to carry out a preliminary test of the salt fog chamber with patinated (MN, UN, UA) bronze samples without protective treatments to assess the salt fog corrosivity to patinas. Additionally, some unpatinated bronze samples (extra ARTECH) were also exposed along with the patinated ones in the salt fog chamber to evaluate its corrosivity to the bronze metal. The alloy composition of the unpatinated bronze samples is presented in Table 4 and its similar to the ARTECH bronze samples, then should be representative of these.

Table 4 - Alloy composition (%) of unpatinated bronze samples (BL)

Alloy type	Cu	Sn	Pb	Zn	Minor elements
CB1 (ISO 1338)	80,94	7,58	6,48	4,31	P, Ni, Fe, Sb, S, Al, Si

For the preliminary test of the salt fog chamber the most aggressive exposure conditions were selected: the higher temperature (35°C) without a dry period (100%Rh continuously), in this case, for operating the salt fog chamber the ISO 9227 guidelines should be followed.

Two sets of bronze samples were exposed in the previous conditions for a period of around 4 weeks. The second set started exposition one week after the first one. Measurements of some patinas properties and weight changes of the samples were carried out before and during the test according to the scheme described in .

Table 5 - Tests performed on bronze samples and respective time schedule

Set	Bronze samples	Thickness EN ISO 2360	Mass change	EIS	Total duration of exposure
I	UN(R)63 , MN63	24h, 168h and weekly till the end	1h, 24h, 72h, 168h and weekly till the end of test		672 h (4 weeks)
	BL_0 , BL_III	-	1h, 24h, 72h, 168h and weekly till the end of test		
II	UN(R)64 , MN64 , UA6	weekly till 504h and at end of test	1h, 24h, 72h, 168h and weekly till 504h and at end of test		768 h (4 weeks+4d)
	BL_I , BL_II	-	1, 2, 4 weeks	-	672 h

UN(R) – Urban natural patina; MN – Marine natural patina; UA – Urban artificial patina;
BL – unpatinated bronze; EIS – Electrochemical impedance spectroscopy

In relation to the duration of the exposure to the salt fog, when testing the treated bronze samples, the results obtained pointed out this should be at least 168 h (one week). This period is what is generally recommended for each part of an alternating weathering procedure like the one is intended to do. In this case, evaluation of the exposed treated bronze specimens shall be performed every 336 h, after a complete exposure cycle (UV + salt solution). Usually, for these type of tests a total of around 1000h of exposure is each part is enough to render differences between the performance of products applied.

Collaborations: This work had the collaboration of Nuno Garcia in the experimental part.

Lisboa, Laboratório Nacional de Engenharia Civil, February of 2008

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reflect the effect of the corrosion products layer formed in the surface of these samples with the exposure, that was visually observed.

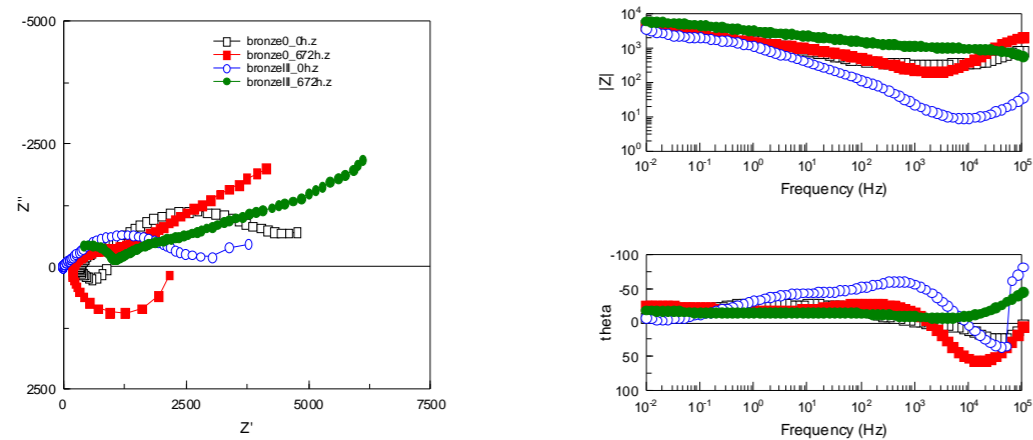


Figure 13 - EIS results for unpatinated bronze samples BL_0 and BL_III before and after exposure in the salt fog. It fog.

4. CONCLUSIONS

From the observations done and the results of the tests performed, it figured that the exposure conditions used for perform the part II (salt fog exposition) of the weathering procedure to be applied to the bronze conservation treatments, are not too aggressive to the urban patinas UN(R) and UA, which constitute the subtract where the treatments are applied.

The exposure of also MN bronze samples and unpatinated bronze allowed to gathered more data for characterizing the corrosive effect of the salt fog and to verify its ability to represent an urban environment.

Based on the nature of the corrosion products formed in the unpatinated bronze samples and on the composition of the exposed patinas, it can be stated that the salt fog exposure conditions can simulate an urban corrosive environment as it was pretended. Furthermore, it was found that these exposure conditions although not too aggressive to the bronze patinas, indeed accelerate bronze corrosion, thus promoting weathering as it was intended. This constitutes an additional reason to consider it adequate for testing the protective action of the treatments applied to the patinated bronze samples.

3. EXPERIMENTAL RESULTS

3.1 Visual aspect

The exposure to the salt fog caused some changes in the aspect of the patinas (Figure 2 and Figure 3): the UN(R) bronze samples surface became darker in some zones (dark green) and lighter in the remaining surface; the NM bronze samples surface became lighter and in the spots where the bronze surface was visible (this is a uneven patina not covering all the bronze surface) it became dark brown; the UA bronze sample became slightly lighter. (In the Annex A UN(R)64, MN64 and UA6 bronze samples photos are presented). The unpatinated bronze samples became generally reddish brown and a with a lot of green corrosion products deposited (Figure 3).

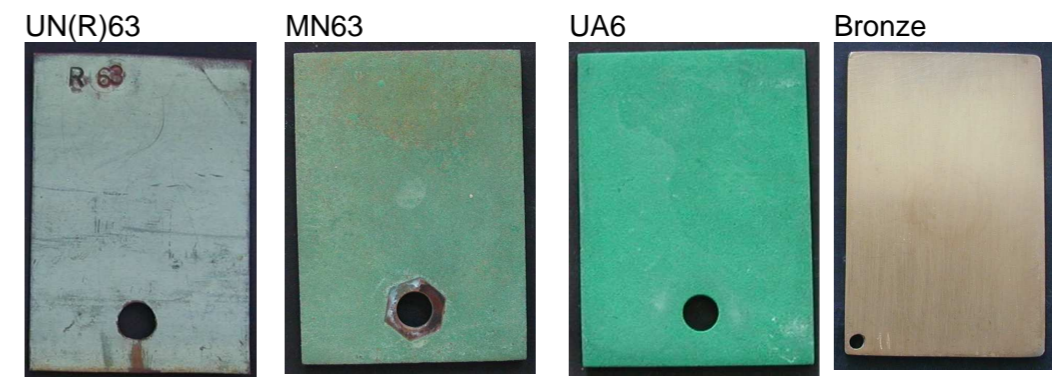


Figure 2 - Visual aspect of testing samples before exposure.

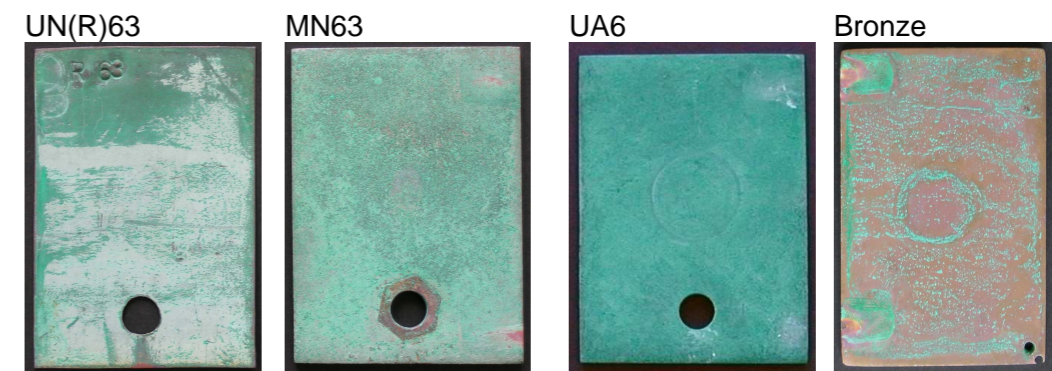


Figure 3 - Visual aspect of testing samples aspect after salt fog exposure

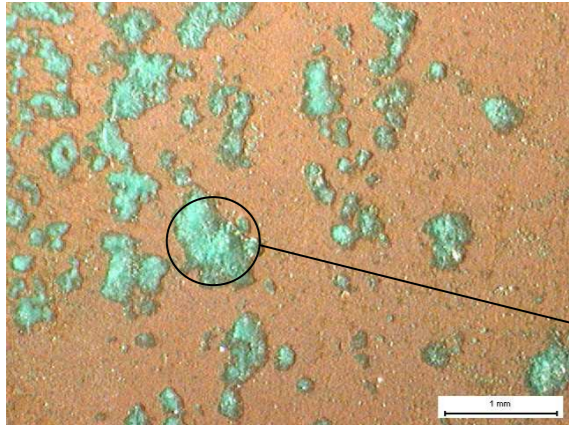


Figure 4 - Detail of the of bronze surface after exposure to the salt fog (Optical micrograph).

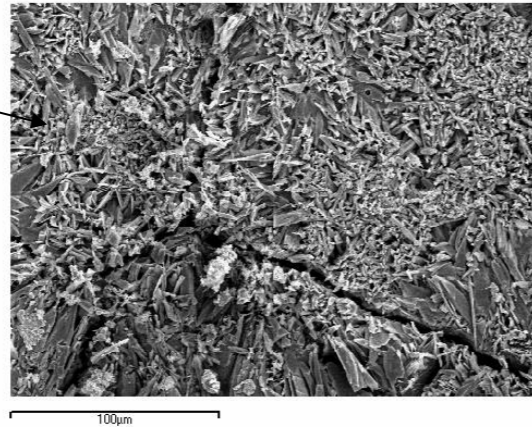


Figure 5 - SEM micrograph of the green deposits taken from the bronze surface.

3.2 Analysis of surface products

The analysis of the elemental composition of the green corrosion products scrapped from bronze surface and observed at SEM (Figure 5) was done using the EDS system coupled to the SEM. The semi-quantitative results obtained and respective EDS spectrum are shown below. The results obtained revealed the presence of sulphur (S), along with cooper and oxygen. This indicates that these products should be mainly copper sulphate (green) and there should be also some copper oxides.

Table 6 - SEM-EDS semi-quantitative analysis of bronze green products

Copper (Cu)	Sulfur (S)	Oxygen (O)
49%	8%	43%

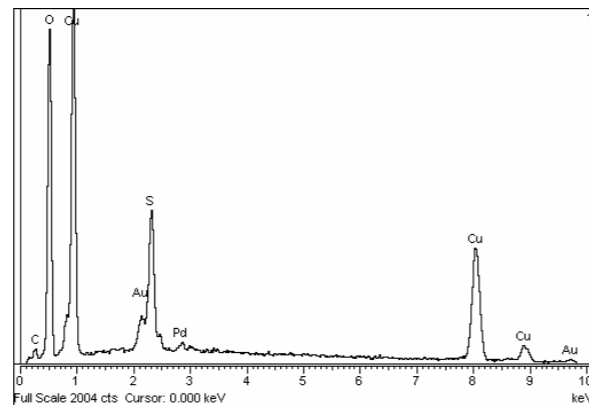


Figure 6 - SEM-EDS spectrum obtained in the surface area of Figure 5.

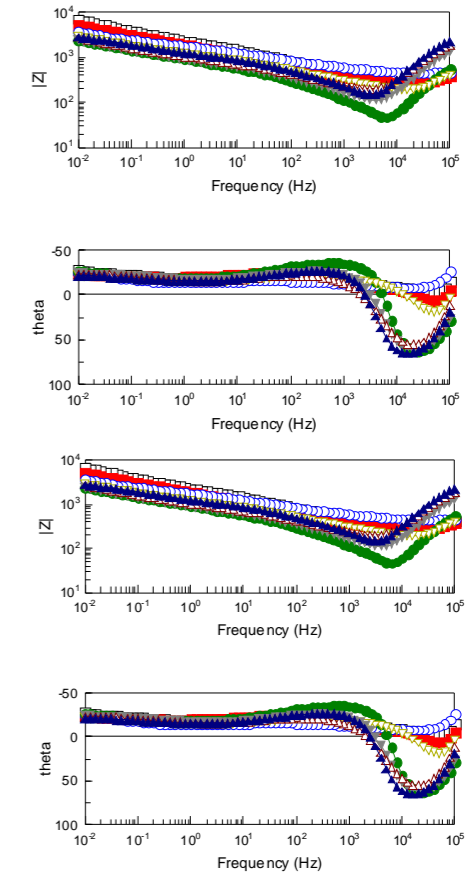
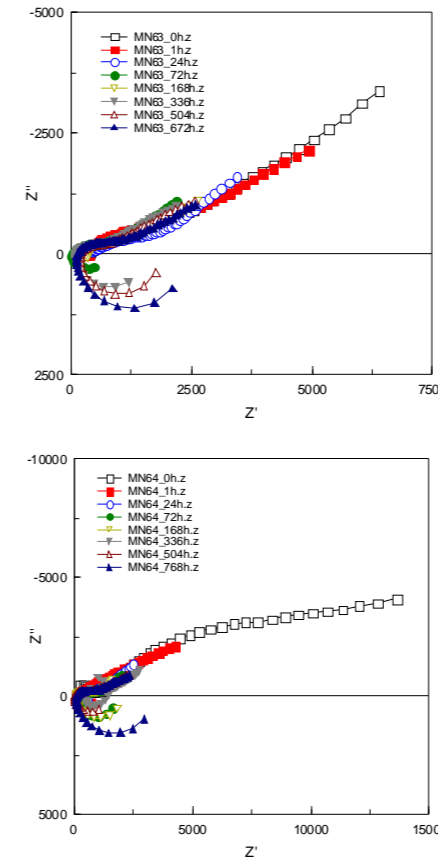


Figure 11 - EIS results for MN63 and MN64 samples before and during exposure in the salt fog.

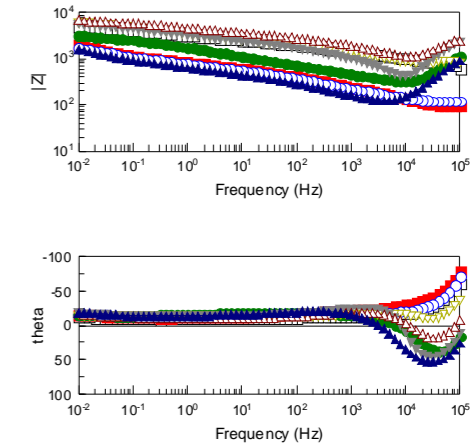
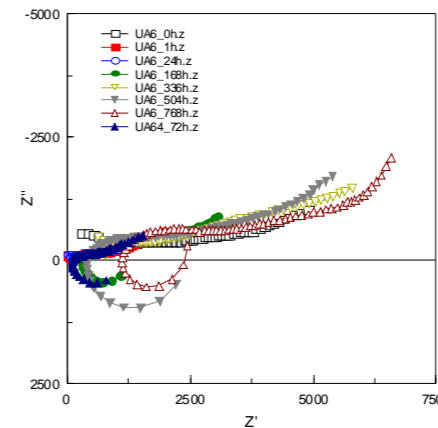


Figure 12 - EIS results for UA6 and UA6 sample before and during exposure in the salt fog.

A plot from the impedance response of o unpatinated bronze samples before and after exposure to the salt fog is also presented in the next figure. The EIS results for this material

3.5 Electrochemical Impedance Spectroscopy (EIS)

AC impedance measurements were performed in all the patinated bronze samples and also in one set of the unpatinated bronze samples before, during and after the exposure to the salt fog (Table 5). Measurements were carried out after 30 min in distilled water, using a three-electrode configuration with a saturated calomel electrode (SCE) as reference electrode. Impedance diagrams were made over the frequency range 100 kHz to 10mHz under controlled potentiostatic conditions, at the open-circuit potential. A Frequency Response Analyser (FRA, Solartron 1255) and a potentiostat (Solartron 1287) were used for these measurements.

In the next figures, Nyquist and Bode plots are presented to represent the behaviour during the exposure period observed for each patina type (UN(R), MN and UA). Without going further in the analysis of the EIS results for the patinated bronze samples, what can be stated by observation of these diagrams is that no great changes of patina electrochemical properties have occurred in the salt fog and that those more significant have happened within the first week of exposure.

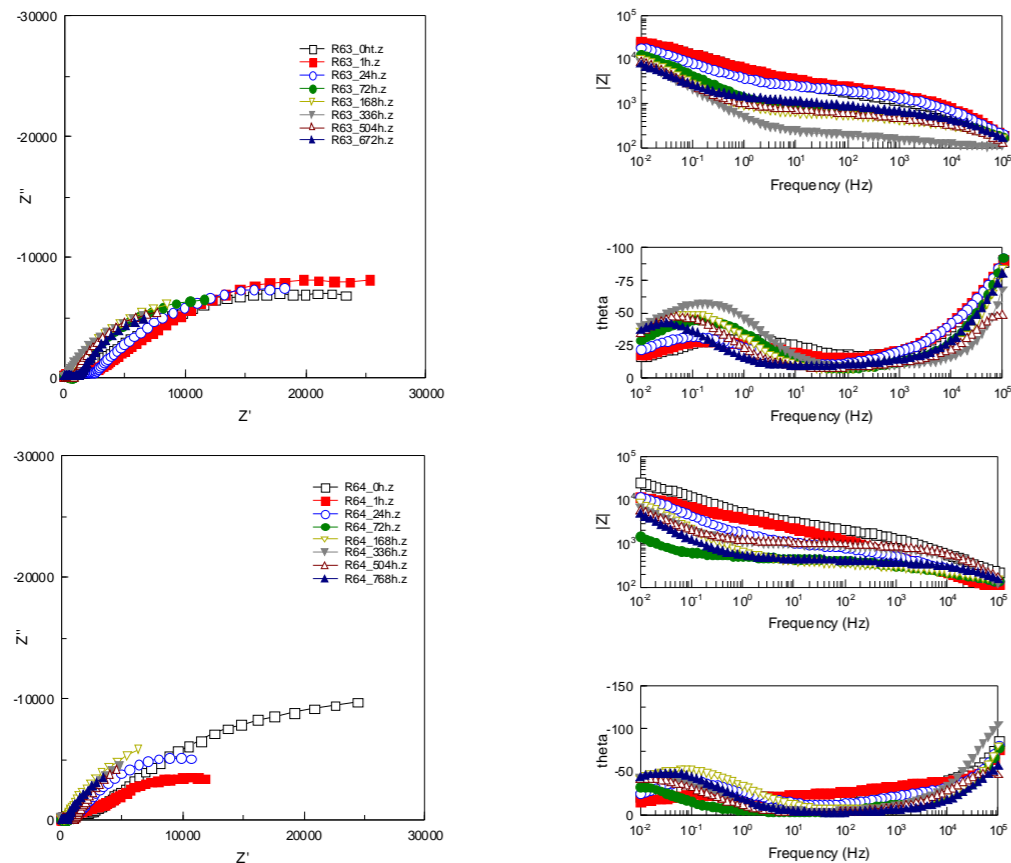


Figure 10 - EIS results for UN(R)63 and UN(R)64 samples before and during exposure in the salt fog.

X-Ray diffraction analysis (XRD) of the products scrapped from the superficial patina layers of UN(R), MN and UA bronze samples was also done. The results obtained indicated that the main product in all the three types of patina is *brochantite* ($\text{Cu}_4(\text{SO}_4)(\text{OH})_6$). In the patina of the MN bronze sample it was also found vestiges of *paracatamite* ($\text{Cu}_2(\text{OH})_3\text{Cl}$) and *cuprite* (Cu_2O), and in the patina of the UA bronze sample it was also found *antlerite* ($\text{Cu}_3(\text{SO}_4)(\text{OH})_6$).

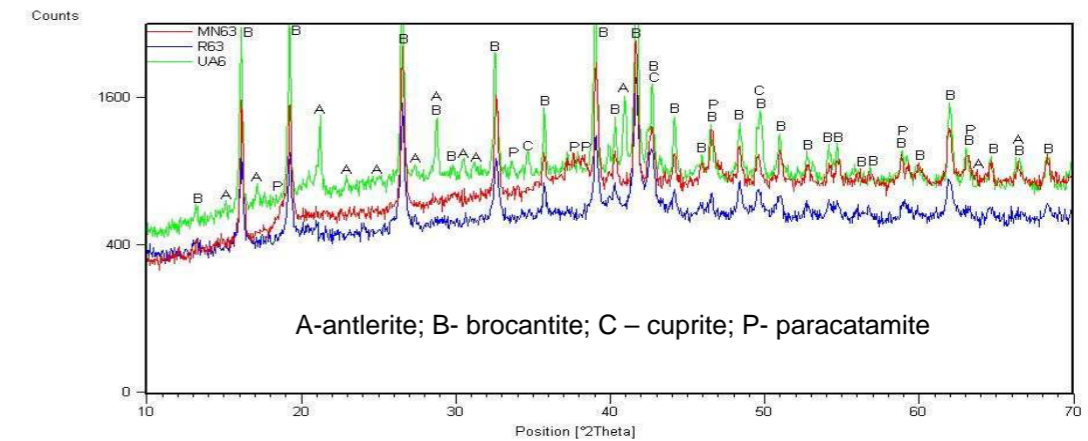


Figure 7 - XRD spectra of MN63, UN(R)63 and UA6 bronze samples patina.

The presence of *brochantite* was expected in the case of UN(R) and UA patinas according to their nature (Table 1), because this is the main constituent of these patinas, but in the case of the MN patina, more copper chlorides were expected. Probably during the exposition to the salt fog some chemical transformation of the copper chlorides into copper sulphates should have occurred. This process should be thermodynamically favourable in the presence of high sulphate content, also in natural marine atmospheres with high SO_2 pollution it was found that copper alloy patinas can be predominantly constituted by sulphated instead of chlorides. The presence on *antlerite* in the UA patina should have resulted from a partial transformation of the existing brochantite in this compound, this type of sulphate could be found in patinas of copper alloy statues exposed to atmospheres with high level of SO_2 pollution.

3.3 Thickness changes

Measurement of the patina thickness were carried out at different times of exposure (Table 5) by a non destructive method (Eddy current) based in the EN ISO 2360 [7]. The results obtained are presented in Figure 8.

Bronze samples thickness change during salt spray test
(weekly and global after 4 weeks exposure)

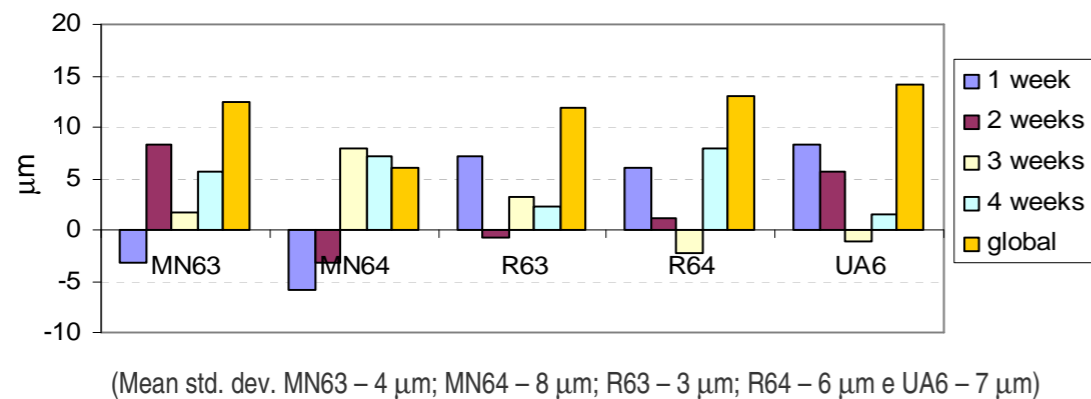


Figure 8 - Average thickness changes for untreated patinated bronze samples measured during salt fog test.

It can be seen from the previous figure that although most of the weekly thickness variations fall within the value of the standard deviation, because most of them are positive, it could be assumed that there is a trend to increase the patinas thickness with the exposure time. This effect could be expected owing to the deposition of salts from the fog solution and eventually to the transformation of pre-existing compounds in hydrated and more voluminous products. In the case of the MN bronze samples, there is a initial decrease of thickness that could be due to the powdered nature of this type of patina, which would have led to the removal of a superficial layer of this patina from the surface with manipulation or by washing in the chamber by the fog condensates.

3.4 Mass changes

The weighting the bronze samples was carried out at different times of exposure (Table 5) without washing them. The results obtained are shown in the Figure 9. It can be seen that there is a general trend to mass gains during the exposure which should be caused mainly by the deposition of salts from the fog. The significant initial mass losses of the MN bronze samples could be attributed to a partial loss of patina surface by the reasons pointed previously in the thickness measurements analysis.

To, in a certain way, assess the corrosivity of the chamber to the bronze metal, the four unpatinated bronze samples exposed to de salt fog were additionally cleaned in a 10% H₂SO₄ solution, to remove the corrosion products formed and then reweighed (a photo of one

of these samples after cleaning is presented in Annex A). This allowed to evaluate the mass loss due to corrosion and calculate bronze corrosion rate. The values obtained are presented in the Table 7.

Bronze samples mass change during salt spray test
(weekly and global after 4 weeks exposure)

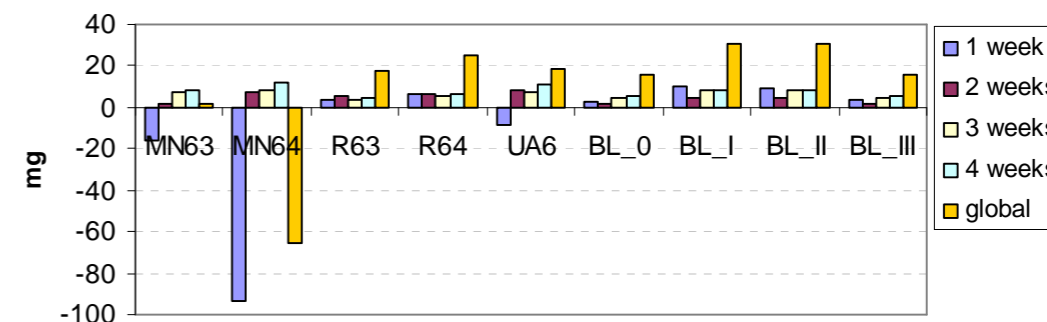


Figure 9 - Mass changes for untreated patinated bronze samples and for bronze without patina (BL samples) measured during salt fog test.

Table 7 - Mass loss by unpatinated bronze samples (BL) after 4 weeks exposure in the salt spray chamber (0,5 g/L NaCl + 3,5 g/L (NH₄)₂SO₄ ; pH ≈ 4,3)

BL_0	BL_I	BL_II	BL_III	Mean
89,6 mg	109,4 mg	101,2 mg	93,4 mg	98,4 mg
Corrosion rate (averaged – 4 weeks)				≈ 11 mg.dm ⁻² .d ⁻¹ ≈ 0,125 µm/d ≈ 45 µm/y

Only for comparison, according to ISO 9223, an atmosphere with a corrosivity class of C5 (the highest class) would have an average copper corrosion rate of 2,8 – 5,6 µm/y. For Cabo Raso exposure site that has a corrosivity class higher than C5, it was measured an average copper corrosion rate of 6,8 µm/y. Morselli et al [8], have measured for bronze alloy G85, an average corrosion rate of 2,73 mg.dm⁻².d⁻¹ after 15 days wet-dry cyclic test involving immersion in natural rain water (pH≈4,3).

The comparison of the corrosion rates stated above with the corrosion rate yielded by the bronze samples in the salt fog chamber reveals that the exposure conditions selected for conducting the test are aggressive enough to accelerate corrosion of a copper alloy.