9th International Conference on NDT of Art, Jerusalem Israel, 25-30 May 2008
For more papers of this publication click: www.ndt.net/search/docs.php3?MainSource=65

# RESTORATION AND CONSERVATION OF OUTDOOR BRONZE MONUMENTS: DIAGNOSIS AND NON-DESTRUCTIVE INVESTIGATIONS

Giorgio D'Ercoli[1], Maurizio Marabelli[3], Veniero Santin[1],
A. Buccolieri[2], G. Buccolieri[2], A. Castellano[2], G. Palamà[2]
[1]Istituto Centrale del Restauro, Roma, Italy
[2]Department of Material Science, University of Salento, Lecce, Italy
[3]Director of ICR Chemical Laboratory, retired

## ABSTRACT

*It is possible today to check bronze monuments in open air exposure and obtain experimental data for judging the state of conservation of corroded surfaces and analysing patina composition, controlling coating products available for restoration, and supporting the approval procedure after restoration and the maintenance program.*

*A monument has been studied, celebrating Garibaldi and his soldiers leaving from Quarto-Genua to Sicily: the bronze group, of the artist Eugenio Baroni, inaugurated in May 1915 and never restored, is positioned by the sea and has been heavily damaged, in some exposed porous areas, by marine particles rich of chlorides.*

*In October 2007 an ICR team has launched the restoration of the Garibaldi statue, in order to focus the methodology for treating the whole monument. In that occasion the following NDT have been previously adopted: measurements of wet corrosion rate of bronze surfaces and EDXRF analysis of patinas.*

*The results exhibit a good agreement and reciprocal synergy between the two techniques, and mark an improvement of the procedure for controlling bronze monuments outdoors, before, during and after restoration.*

## INRODUCTION

This paper collects results achieved during the study for conservation of the bronze Garibaldi's monument of the artist Eugenio Baroni, cast in 1914, located by the sea shore, facing south, Quarto, Genua (fig.1), utilizing two non-destructive techniques (Rp measurements, EDXRF analysis).

The main aims of the study have been:
1. To single out a standard easy protocol for characterizing corrosion and corrosion products of bronze monuments.
2. To measure the wet corrosion rate of the monument surfaces.
3. To check commercial coatings available for restoration of outdoor bronzes.

ICR research has started in 2001, supported financially at the beginning as a "Progetto Finalizzato" of CNR [note 1]. The research has been concluded in 2007, involving, during the last campaign, the University of Salento, Lecce.

## CHARACTERIZATION OF PATINAS – APPLICATION OF COATINGS

The patinas of bronzes outdoors grow depending on alloy components (for the Quarto bronze monument a copper/tin alloy with secondary components lead and zinc), on exposure or not to rain water (heavy showers and water drippings) and partially on deposition of air dispersed sea particles and pollution agents. At the very beginning a standard microdestructive analysis has been applied, XRD, on twenty one microsamples of patinas, choosing zones with different orientations (facing the sea side or a crowded country road behind), sheltered and not from rain water. The sampling has been carried out in depth, reaching almost always the bare metal surface. An extensive report on XRD analysis will be published from ICR in a general exhaustive paper.

The main components identified in patinas placed in sheltered position and also in dark green and black patinas and drippings (named a) are:

- In depth cuprite, frequently nantokite
- In the outer layer atacamite, or atacamite + some mushistonite.

Sometimes, as sediment on the top, quartz, gypsum, carbonaceous particles (not crystalline, but identified under the microscope) have been detected.

The components of green patinas exposed to heavy rain water, mainly green (named b) are:

- In depth cuprite, frequently nantokite
- In the outer layer mainly mushistonite and then atacamite.

In figure 2 results are summarized as % of the quoted above crystalline components, for the two types of patinas.

Six zones have been chosen on the monument surface:

- A, in sheltered position, under the legs of Garibaldi, facing the sea
- B, in exposed location, also in front of the sea
- BB, as above, with a very porous surface
- C, on the basement, restored probably in the past, also in front of the sea
- D, in almost sheltered exposure, but wetted, in the back
- E, in sheltered position, as A, in the back.

In the six zones some areas 6x8 (height) $cm^2$ have been selected, mechanically cleaned, controlled as patina thickness with the Eddy Current procedure (table 1), and then treated with six different commercial formulations, listed in table 2. Average thickness of coatings was about 10 μm [6]. Thin layers of coatings have been adopted for two reasons:

- for avoiding a glossy or waxy looking of the monument after restoration
- for testing the effective sheltering power of the system patina + coating, as normally adopted by restorers.

Areas untouched and other ones mechanically cleaned, but not treated with coatings, have been also included for comparison. Areas of zones A and BB are shown in fig. 3 and 4. Surfaces have been ready in June 2001.

## NON-DESTRUCTIVE INVESTIGATIONS AND RESULTS

Stability and efficiency of coatings have been tested with a non-destructive methodology in October 2001, at the beginning of the research, and then in September-October 2002 and in September 2007. For these campaigns a portable equipment has been adopted, in order to measure Rp (Resistance of polarization), i.e. the ratio $\Delta E/\Delta I = Rp$; in a few words a current impulse is transmitted into the bronze through the head of the instrument in contact with the surface, up to produce a shift of the equilibrium potential of the surface not greater than +10 mV. From 1/Rp it is possible, multiplying by a constant K, to obtain the rate of wet corrosion of the alloy in μm/year. Details of the methodology are reported in bibliography [1-5, 7-9].

Obviously, the best performances of coatings are signalled by a low corrosion rate. The characteristics of the portable Rp equipment are: MP 110 Rp model ATEL, stainless steel AISI 304 counter electrode, bronze reference electrode, potential shift +10 mV, lowest appreciable corrosion rate 0.01 μm/year, specific conductivity of water 114 microS/cm, pH

7.8. As an example, the results referring to a sheltered zone (A) and to an exposed one (BB) are summarized for comparison in table 3.

From results the following conclusions can be drawn.

- In the sheltered non porous areas of the zone A corrosion rate is very low for all coatings; the lowest values are exhibited by Incralac + Soter. Also corrosion rate of not coated areas is very low.
- For the exposed and porous zone BB, Soter (blend of microcrystalline waxes + an inhibitor, fluid and easy to apply, with a melting point lower than the other microcrystalline wax R 21), Incralac and Incralac + Soter result after 6 years to be very efficient, with Id lower than 1 for Soter.
  The BB surfaces not treated have a very high corrosion rate (from 200 to 700 times greater than the c.r. of the coated areas).
- As far as it concerns all results of the six zones (only partially listed here), the double layers and also Soter and Incralac exhibit a good performance.

Another non-destructive technique has been applied at the end of the research in 2007 (in collaboration with the University of Salento), in order to carry out EDXRF analysis of chlorine and sulphur superficial content in correspondence of:

- Not treated or simply cleaned patinas of the zones tested with the Rp procedure (the six zones previously cited).
- Other new untouched patinas, dark green, less spoiled by heavy rain (type 1), in comparison with other new untouched green patinas, heavily washed by rain water (type 2).

The following equipment has been utilized [10]:

- X-ray tube MOXTEC, Be window 0.25 mm, d. 2 mm, Pd anode, 4-40 kV, 0-100 μA; experimental conditions : 5 kV, 30 μA, time counts 60 sec.; 15 kV, 3 μA, t.c. 60 sec.
- SiLi counter AMPTEK XR-100CR, resolution. 190 eV at 5.0 keV.

The results are summarized in tables 4 and 5. Also corrosion rates are listed.

It is evident that patinas of zones A, and E , sheltered, D partially sheltered but wetted, and C (in the basement, cleaned and protected in the past) contain superficially only chlorine; on the contrary patinas of the zones B and BB, spoiled by rain water, exhibit an high content of superficial tin (mushistonite), in addition to chlorine (copper chlorides).

As it regards the other patinas, type 1 dark green patinas N1/2/3/4 have a higher content of superficial chlorine and a lower one of tin, in comparison with type 2 green patinas N1/2/3/4. Tin is quite absent in the sheltered patinas of the A zone N5/6/7/8.

**CONCLUSION**

From the experimental data some observations can be drawn.

1. Analysis of patinas has highlighted that their growth and composition depend mainly on exposure/not exposure to heavy rain water, on deposition of marine particles and air dispersed pollutants and not on orientation to the sea shore or to the road traffic. Deposition of marine particles affects the whole monument; heavy rain removes partially chlorides from the outer surface, which on the contrary concentrate more and more in zones not or less spoiled by rain water. In washed areas mushistonite, a copper/tin compound, is often present, as a main component: it has been found in patinas of outdoor bronzes here for the first time (card 20-0369). No sulphates have been detected;

carbonaceous particles from dust and suspended particulate matter (from road traffic and perhaps other domestic and industrial sources) are present in sheltered or less washed areas (dark green, black).
2. Data from EDXRF superficial analysis show a lower content or absence of superficial chlorine in areas spoiled by rain water, while on the contrary chlorine % is higher in dark patinas and overall in sheltered ones; in these last areas superficial tin is absent.
3. The adopted Rp methodology has allowed to measure the wet corrosion rate in areas representative of the monument. In general not only the sheltered and the treated areas but also the exposed ones – without coatings, cleaned and not cleaned - reveal no very remarkable corrosion rate but the BB not coated ones, exhibiting a porous superficial structure.
4. As it regards the testing of commercial coatings, it has been possible to identify the most efficient products for the six areas, after six years of outdoor exposure: the best one is the double layer Incralac + Soter, followed by d.l. Incralac + R21, Soter and Incralac. Furthermore, from examination of Id values of all the coatings for all the areas (only partially here reported) the need of a maintenance program, after restoration of the monument, has been put in evidence.
5. At the end of this research a useful synergy has been demonstrated between the two adopted NDI, suggesting a standard procedure for checking bronzes in outdoor exposure.

**ACKNOWLEDGMENTS**
Many thanks to L. Arceri, D. Artioli, G. Guida, M. Mercalli of ICR, P. Letardi of CNR-ISMAR and I. Reindell private restorer, for their collaboration.
Many thanks also to the ICR restoration team: S. Federico, E. Huber, I. Marcelli, M. Prunas, E. Senatore.

**ENDNOTE**
1. Since 2002 two parallel researches have been carried out: one by P. Letardi of the CNR Institute ISMAR of Genua, checking surfaces of the bronze monument and also of standard samples exposed outdoors with an EIS equipment, and the second, exclusively on the monument, with the aforesaid investigations, by ICR, Rome, and finally in 2007 by the University of Salento .

**BIBLIOGRAPHY**
1. C. Bartuli, R. Cigna, B. Colombo, M. Marabelli. Valutazione dei fenomeni corrosivi in corso sulla superficie del Marco Aurelio. Materiali e Strutture,VI , 3 (1996) 127-136.
2. G. D'Ercoli, M. Marabelli, V. Santin. Monumenti bronzei: valutazione dello stato conservativo mediante la resistenza di polarizzazione, in Atti della LXIV riunione SIPS "La Scienza per i Beni Culturali". Roma 16-18 Ottobre 1997, pp, 225-233.
3. C. Bartuli, S, Angelucci, S. Lanuti. Polarization resistance measurements for the monitoring of protected copper alloy structures, in Proceedings of the "6th International Conference ART 99", edited by ICR and AIPnD. Roma 17-20 May 1999, pp. 1343-1360.
4. M. Bartolini, R. Cigna, B. Colombo, G. D'Ercoli, M. Marabelli, A. Marano. Misure di microcondensazione capillare e controlli elettrochimici per il restauro dei bronzi di Riace , in "I bronzi di Riace – Restauro come Conoscenza", vol. 1, A. Melucco Vaccaro e G. De Palma ed., Artemide Edizioni. Roma 2003, pp. 203-214.
5. S. Angelucci, C. Bartuli. Le sculture moderne in lega di rame della collezione Peggy Guggenheim: un piano conservativo assistito da metodi elettrochimici, in "Monumenti in Bronzo all'Aperto – Esperienze di Conservazione a Confronto", P. Letardi, I. Trentin, G. Cutugno ed., Nardini editore . Firenze 2004, pp. 195-200.

6. P. Letardi. Laboratory and field tests on patinas and protective coating systems for outdoor bronze monuments, in Proceedings of "Metal 2004", National Museum of Australia, Canberra ACT. J. Ashton, D. Hallam Editors, Canberra 2004, pp. 379-387.
7. G. D'Ercoli, G. Guida, M. Marabelli, V. Santin. Non destructive testing by the Rp method of bronze monuments: three case studies, in Proceedings of the "7th International Conference ART 2002", published as "Cultural Heritage Conservation and Environmental Impact Assessment by Non-Destructive Testing and Micro-Analysis", edited by R. Van Grieken and K. Janssen, Antwerp University, A.A. Balkema Publishers. Leiden 2005, pp. 19-25.
8. G. D'Ercoli, P. Letardi, M. Marabelli. Non-destructive investigations for the conservation of the bronze "Il Cristo degli Abissi", in Proceedings of the "8$^{th}$ International Conference ART 2005". Lecce 15-19 Maggio 2005, p.166 of The Book of Abstract.
9. G. D'Ercoli, M. Marabelli, V. Santin. Controllo elettrochimico della corrosione del Satiro Danzante di Mazara del Vallo, in "Il Satiro Danzante di Mazara del Vallo – Il Restauro e l'Immagine", R. Petriaggi ed., Electa . Napoli 2005, pp. 63-76.
10. Analisi EDXRF su monumenti in bronzo esposti ad agenti inquinanti. University thesis of L. Miccoli, 2003/2004, University of Salento, G. Buccolieri, M. Marabelli proposers.

| *Table 1 – Thickness of patinas before and after the mechanical cleaning* | | | |
|---|---|---|---|
| Zone | Before cleaning<br>µm | After cleaning<br>µm | Difference<br>µm |
| A | 132 ± 14<br>133 ± 38 | 76 ± 14<br>75 ± 27 | 56<br>58 |
| B | 82 ± 25<br>114 ± 30 | 78 ± 30<br>105 ± 33 | 4<br>9 |
| BB | 119 ± 34<br>98 ± 25 | 90 ± 33<br>89 ± 17 | 29<br>10 |
| C | 85 ± 27<br>96 ± 24 | 75 ± 33<br>73 ± 17 | 10<br>23 |
| D | 116 ± 31<br>109 ± 24 | 112 ± 26<br>94 ± 22 | 4<br>15 |
| E | 93 ± 37<br>78 ± 30 | 61 ± 14<br>49 ± 11 | 32<br>29 |

| *Table 2 - Tested coatings* | |
|---|---|
| Soter 201 LC | Dispersion of microcrystalline waxes and benzotriazole in organic solvents - esters and terpenic components, solid content 20-24% . Produced by Baraldi Lubrificanti s.r.l., Osteria Grande (Bologna). |
| R21 | Dispersion of microcrystalline waxes in white spirit, solid content 20%. Supplied by Phase , Bologna. |
| TeCe 3534F | Dispersion of microcrystalline waxes in white spirit, solid content 33%. Produced by TROMM Gmbh , Colonia (Germania). |
| Incralac | Main component acrylic resin (Paraloid B-44) + benzotriazole in organic solvents. Supplied by Bresciani s.r.l., Milano. |
| Incralac+Soter 201LC | Double layer, primer Incralac and Soter 201 LC on the top. |
| Incralac+R21 | Double layer, primer Incralac and R21 on the top. |

| *Table 3 - Corrosion rate values and Id for the three campaigns for areas of A and BB zones* | | | | |
|---|---|---|---|---|
| Zone A<br>Area coating | c.r. min÷max/average values<br>µm/year<br>campaign<br>October 2001 | c.r.<br>min÷max/average v.<br>µm/year<br>campaign August-September 2002 | c.r.<br>min÷max/average v.<br>µm/year<br>campaingn<br>September 2007 | Id<br>Index of deterioration |
| Soter | 0.04 ÷ 0.08 / 0.06 | 0.60 ÷ 5.0 /2.1 | 1.2 ÷ 2.6 / 1.6 | 27 |
| R21 | 0.06 ÷ 0.42 / 0.22 | 0.60 ÷ 2.4 / 1.42 | 1.2 ÷ 2.6 / 1.9 | 8.6 |
| TeCe | 0.08 ÷ 0.40 / 0.22 | 0.20 ÷ 0.40 / 0.26 | 0.20 ÷ 1.6 / 0.62 | 2.8 |
| Incralac | 0.40 ÷ 1.0 / 0.56 | 0.40 ÷ 3.4 / 1.1 | 2.0 ÷ 6.0 / 4.5 | 8.0 |
| Incralac + Soter | < 0.02 / < 0.02 | 0.02 ÷ 0.06 / 0.02 | 0.16 ÷ 0.38 / 0.20 | 10 |
| Incralac + R21 | 0.02 ÷ 0.08 / 0.04 | 0.06÷ 0.28 / 0.16 | 1.6 ÷ 3.8 / 1.3 | 32 |
| Cleaned 1 | 6.0 / 6.0 | 2.0 ÷ 7.0 / 4.3 | 2.0 ÷ 6.0 / 4.5 | 0.7 |
| Cleaned 2 | 2.0 ÷ 4.0 / 2.9 | 2.0 ÷ 4.0 / 3.0 | 6.0 ÷ 10 / 8.0 | 2.8 |
| Untouched | 0.60 ÷ 2.8 / 1.8 | 2.0 ÷ 4.4 / 3.1 | 2.0 ÷ 2.2 / 1.1 | 0.6 |
| Zone BB<br>Area coating | as above | as above | as above | as above |
| Soter | 0.60 ÷ 18 / 5.0 | 0.08 ÷ 3.4 / 1.0 | 0.40 ÷ 1.0 / 0.56 | 0.1 |
| R21 | 0.20 ÷ 8.0 / 2.2 | 0.16 ÷ 0.76 / 0.70 | 0.32 ÷ 6.0 / 2.8 | 1.3 |
| TeCe | 0.80 ÷ 1.0 / 0.86 | 0.08 ÷ 2.0 / 0.90 | 12 ÷ 48/ 34 | 39 |
| Incralac | 0.08 ÷ 0.26 / 0.12 | 0.20 ÷ 1.1 / 0.50 | 0.10 ÷ 1.0 / 0.40 | 3.3 |
| Incralac + Soter | < 0.02 / < 0.02 | 0.02 ÷ 0.06 / 0.04 | 0.26 ÷ 1.8 / 0.84 | 42 |
| Incralac + R21 | < 0.02 / < 0.02 | 0.02 ÷ 0.36 / 0.04 | 0.40 ÷ 3.4 / 1.4 | 70 |
| Cleaned 1 | 80 ÷ 360 / 210 | 100 ÷ 720 / 468 | 140 ÷ 440 / 314 | 1.5 |
| Cleaned 2 | 360 ÷ 660 / 488 | 380 ÷ 1160 / 666 | 260 ÷ 520 / 378 | 0.8 |
| Untouched | 260 ÷ 520 / 400 | 260 ÷ 780 / 474 | 140 ÷ 320 / 230 | 0.6 |

| *Table 4 - EDXRF measurements for superficial Cl and Sn and corrosion rate values for not treated (untouched) and only cleaned areas of zones A – B – BB – C – D – E* | | | | |
|---|---|---|---|---|
| Zone | Area | Cl % | Sn % | corrosion rate min-max (µm/year) |
| A | not treated | 13 | - | 2.0 ÷ 2.2 |
| | “ | 14 | - | |
| | cleaned | 15 | - | 2.0 ÷ 6.0 |
| | “ | 15 | - | 6.0 ÷ 10 |
| B | not treated | 3.5 | 20 | 4.0 ÷ 8.0 |
| | “ | 3.4 | 19 | |
| | cleaned | 7.0 | 11 | 6.0 ÷ 34 |
| | “ | 6.0 | 10 | 2.0 ÷ 18 |
| BB | not treated | 3.2 | 33 | 140 ÷ 320 |
| | “ | 3.3 | 33 | |
| | “ | 3.3 | 33 | |
| | cleaned | 6.0 | 25 | 140 ÷ 440 |
| | “ | 6.0 | 21 | 260 ÷ 520 |
| | “ | 5.0 | 27 | |
| C | not treated | 9.0 | - | 2.4 ÷ 8.0 |
| | “ | 7.6 | - | |
| | cleaned | 8.7 | - | 1.4 ÷ 3.8 |
| | “ | 8.3 | - | 1.4 ÷ 3.8 |
| D | not treated | 11 | - | 5.8 ÷ 7.8 |
| | “ | 10 | - | |
| | cleaned | 12 | - | 3.4 ÷ 9.0 |
| | “ | 12 | - | |
| E | not treated | 9.1 | - | 2.4 ÷ 4.2 |
| | “ | 8.0 | - | |

| *Table 5 - EDXRF measurements for superficial Cl and Sn and corrosion rate values for eight new areas: comparison between green , dark green and sheltered patinas* | | | | |
|---|---|---|---|---|
| Zone | Area | Cl % | Sn % | c.r. (µm/year) |
| N1, Garibaldi's left arm, surface upwards | green 1<br>green 2 | 3.0<br>2.4 | 31<br>30 | middle - high values highest v. 66 |
| | dark green 1<br>dark green 2 | 7.3<br>5.7 | 4.0<br>9.0 | middle - low values lowest v. 4.0 |
| N2, Garibaldi's left arm, surface upwards | green 1<br>green 2 | 3.2<br>3.3 | 38<br>39 | middle -high values highest v. 24 |
| | dark green 1<br>dark green 2 | 3.7<br>4.7 | 26<br>4.0 | middle - low values lowest v. 2.8 |
| N3, Garibaldi's left arm, surface downwards | green 1<br>green 2 | 3.2<br>3.2 | 35<br>39 | middle -high values highest v. 156 |
| | dark green 1<br>dark green 2 | 4.6<br>6.4 | 27<br>25 | middle - low values lowest v. 6.0 |
| N4, Garibaldi's left arm, surface downwards | green 1<br>green 2 | 5.0<br>3.1 | 28<br>36 | middle -high values highest v. 124 |
| | dark green 1<br>dark green 2 | 10<br>8.3 | 4.0<br>20 | middle -low values lowest v. 8.0 |
| N5/1,2,3, zone A | green sheltered | 9.0 | - | 2.0 ÷ 10 |
| | ,, | 13 | - | |
| | ,, | 15 | - | |
| N6/1,2,3 , zone A | ,, | 10 | - | 2.0 ÷ 4.0 |
| | ,, | 15 | - | |
| | ,, | 14 | - | |
| N7/1,2,3, zone A | ,, | 14 | - | 1.4 ÷ 2.0 |
| | ,, | 13 | - | |
| | ,, | 12 | - | |
| N8/1,2,3, zone A | ,, | 13 | - | 0.8 ÷ 3.0 |
| | ,, | 14 | - | |
| | ,, | 9.0 | - | |

*Fig.1. The bronze monument.*

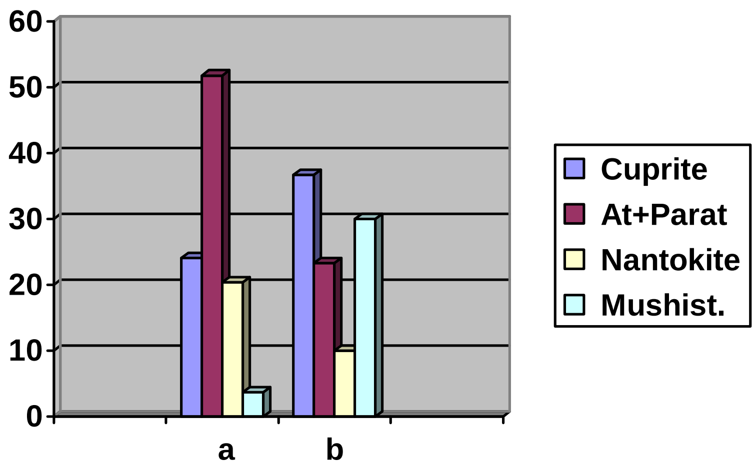
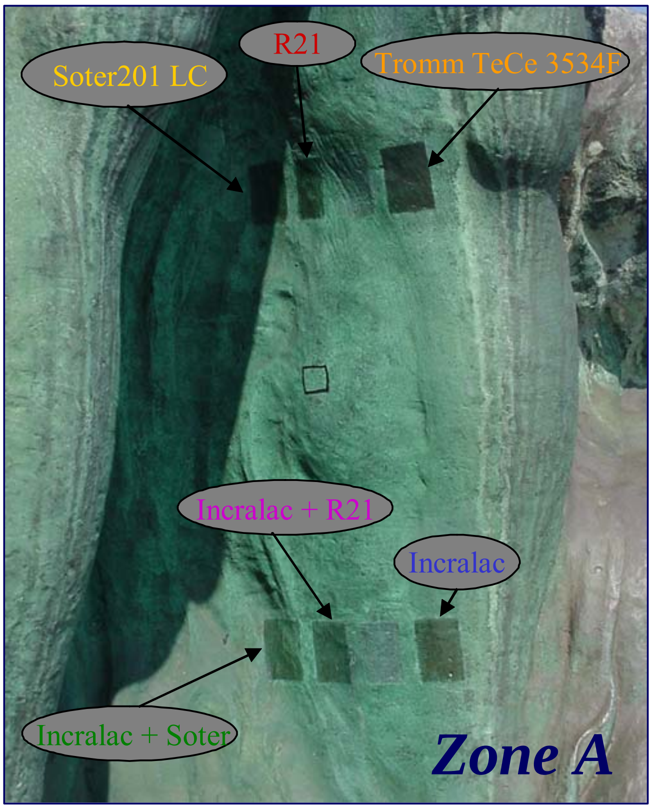



*Fig.2. % of copper and tin crystalline compounds in black and sheltered patinas (type a) and in heavily rain washed ones (type b).*




*Fig,3. Areas of zone A.*

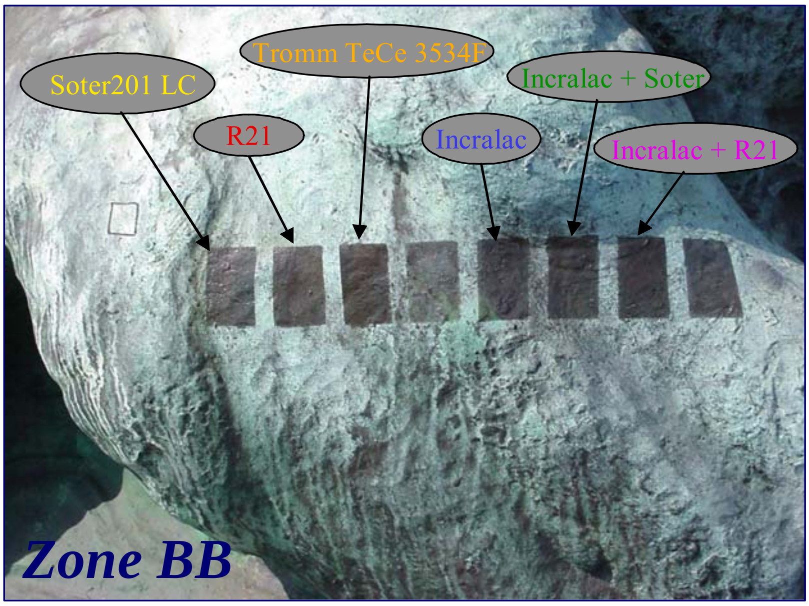



*Fig.4. Areas of zone BB.*

Back to Top