

News – SESAM setting-up and first experiments July 2013 - October 2013

End-users met on 1st July 2013 at the host facility, CNR-ISMAR, Genoa, Italy. This meeting was organized in order to set up the experiments foreseen in the JERICO TNA application form and perform preliminary tests (01-05 July 2013). The main objectives of the project are to define advantages and limits of an innovative biological treatment for conservation of metal artworks and to standardize a specially adapted electrochemical methodology for assessing its effectiveness in comparison with treatments of conservation-restoration nowadays used.

Task 1. Selection, preparation and characterization of samples to be used as standards.

It was decided to expose in Genoa during the 4 months of grant access 4 sets of bare samples made of copper, a ternary bronze (Cu90/Sn8/Pb2), a quaternary bronze alloy (Cu85/Sn5/Zn5/Pb5) and a weathering steel (such as CorTen steel), for a total amount of 60 samples. The goal is to obtain at the end of the task, samples properly aged with typical natural patina, which is fully characterized in order to have a start point before treatment and understand the eventual modifications which will occur during the following treatment and ageing. The samples were prepared by the end-users, sent to the host facility and the exposure of the bare samples started on 5th November 2013.

	number	acronym	dimension	alloy
Genoa Weathering Steel	16	GWS / gws	60x60x3	Similar to CorTen
Genoa Quaternary Bronze	16	GQB / gqb	60x60x3	Cu85/Sn5/Zn5/Pb5
Genoa Copper	16	GCU / gcu	60x60x1	Cu
Genoa Ternary Bronze	16	GTB / gtb	60x60x3	Cu90/Sn8/Pb2

Task 2. Evaluation of treatments' performance, efficiency and durability.

In parallel, the facility is planned to be used during the 4 months of grant access for evaluate the efficiency of a first selection of protective treatments on coupons (made of copper, ternary and quaternary bronzes) already available for a total amount of 27 samples.

Copper Urban Natural Neuchâtel	Genoa Marine natural Quaternary bronze	Genoa Marine natural Ternary bronze	
CUNN45	GMN 10	QQ 68	T0
CUNN50	GMN 2	QQ 51	
CUNN56			
CUNN61			
CUNN 67	GMN 3	QQ 66	T4
CUNN 68	GMN 12	QQ 82	
CUNN 69	GMN 11	QQ 34	
CUNN46	GMN 7	QQ 77	TR
CUNN47	GMN 5	QQ 28	
CUNN49	GMN 6	QQ 85	
CUNN58			

Sets of aged coupons used for evaluating the different treatments.

Part of the samples was leaved untreated (labeled T0) and others were treated with an innovative biological method based on the formation of copper oxalates patina (labeled T4). For comparison, wax Cosmolloid H80 used nowadays in bronze conservation was applied as reference treatment (labeled TR). The QQ and GMN samples were taken from the experimental marine station on 1st July.



Coupons exposed for evaluating the different treatments.

They have been brought in end-user institution in order to be treated together with CUNN samples during the month of August 2013. At the beginning of September, the treated samples were back in host facility for characterization. The performances of the different treatments before exposure were evaluated on the basis of their resistance, color, surface's morphology and protection behavior. During July and September 2013, a first campaign of analyses was conducted with a complement of analytical techniques: Fourier Transform InfraRed (FTIR) spectroscopy and Scanning Electron Microscope with Energy Dispersive X-Ray Spectroscopy (SEM-EDS) at the University of Neuchâtel; Documentation, colorimetric and Electrochemical Impedance Spectroscopy (EIS) measurements at the host facility. The ageing tests started on 1st October 2013 and the performance evolution of treatments will be now monitored during exposure.

In total 81 colorimetric data, 36 EIS measurements and 108 FTIR spectra were collected for characterizing the untreated patina and treatments at to. The data will be now better evaluated during the ageing period.

Task 3. Standardization of an electrochemical methodology for in situ assessment

In July, it was decided to perform some preliminary tests for standardizing an electrochemical methodology for in situ assessment. For this task, we used cupronickel samples with a natural patina obtained after 1 year exposure in the urban marine environment of the ISMAR SMS site (Genoa Harbour) from December 2011 to July 2013 (18 months). The samples (Cu75/Ni25, 58x58x3 mm) were taken from the experimental marine station on 1st July. A first photographic documentation was performed *in situ*. Samples were also documented in laboratory and the photographs calibrated using a X-Rite ColorChecker. Before measurements, all samples were washed with deionised water and dried under cold air. On 2nd July, thickness measurements were performed using a Phynix Surfex Pro[®]. Soaking cloths (commercial cleaning cloth Vileda n°9491) with a specific pattern for the EIS measurements with ST15 contact probe were prepared. All cloths were washed with a large amount of deionised water and immersed for 17h in 1L of deionised water. Then, deionised water was renewed and cloths immersed a second time for 6h. Afterwards, cloths were squeezed and left dried at room temperature. In the following days, 2 different designed contact probes (ST15 and a gel-polymer electrolyte -GPE- cell) together with 2 electrolyte solutions were used for the EIS measurements:

- Mineral water, electrical conductivity 316 μ S/cm, pH=7.9.
- Artificial rain water, electrical conductivity 118 μ S/cm, pH=5.9.

Used coupons	Electrolyte solution	
	Mineral water	Artificial rain
Electrochemical cell	Mineral water	Artificial rain
Contact probe ST15	QN19 + QN11	QN11 + QN19
GPE cell	QN11 + QN19	QN11 + QN19

The artificial rain water was prepared according to the following procedure:

- on 4th and 5th July preparation of 1000x and 10x concentrated artificial rain solution according to the literature (Goidanich Arkos 2011, Bernardi AppliedPhysicsA 2008):

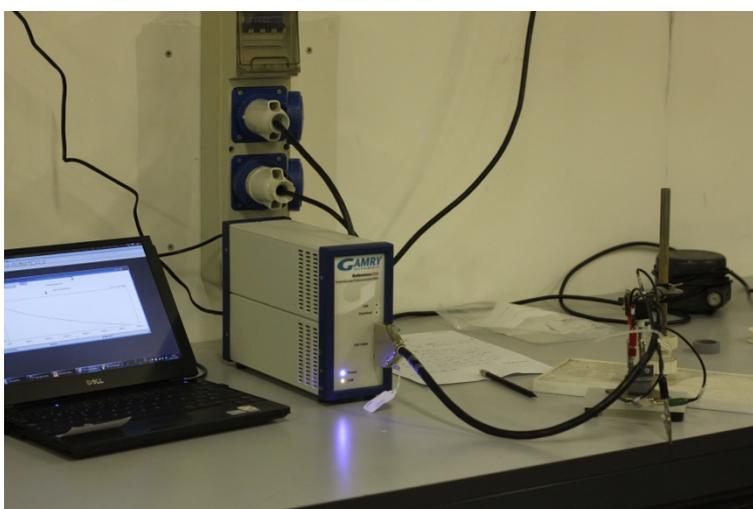
Salt	Concentration mg/L
CaSO ₄ ·2H ₂ O	1.443
(NH ₄) ₂ SO ₄	1.504
NH ₄ Cl	1.915
NaNO ₃	1.513
CH ₃ COONa	0.319
HNO ₃ 65%	Some drops of 50% solution diluted in water to adjust pH to 5

Regarding the ST15 contact probe, the nominal area is 1.77 cm². A commercial cleaning-cloth soaked with an electrolyte solution is fixed to the contact cell, and the system obtained is then leant on the surface to be measured. The cloth was immersed in the electrolyte solution for 120 min before being fixed to the contact cell. The EIS spectra acquisition was started after a time to around 30 min after the cell is leant on the measurement area, in order to stabilize the open circuit potential.



Setting with ST15 contact probe

Regarding the GPE cell, the nominal area is 5,72 cm². The design is based on a traditional 3 electrode cell, in which the electrolyte has been gelified, allowing precisely positioning and holding it over the sample. The positioning and stabilization is the same as with the ST15 contact probe.



Setting with agar contact probe

EIS measurements were made with a Gamry REF600, with Framework/EIS300 V5.3 software[©]2007, Gamry Instruments, Inc. Spectra with 10 points per decade were acquired in potentiostatic mode with 10mV AC signal level at open circuit potential. Measurements were acquired in the frequency range 100 KHz - 10 mHz. For each system under examination, two spectra were measured, in order to check homogeneity and repeatability of results. After each measurement a digital photograph of the wet footprint of the EIS contact probe was recorded with a VEHO[®] VMS-004 usb Microscope. In order to calibrate the photographs, samples were photographed on graph paper using MicroCapture software. The results are summarized in the table below. Data will be now carefully evaluated.

Coatings	sample	label	pnt	file foto setup		filename date	Starting time [s]	Eoc [mV]	Φ10mHz	Z 10mHz [KW]	A [cm ²]
				ft usb yes	ft usb no						
mineral water	QN19	QNT0G1	C	103-5018		QN19CT0NQ1-1STG 04.07.2013	1978	-38.16	-14.54	19.51	1.79
				X							
	QN11	QNT0G2	C	103-5021		QN11CT0NQ1-1STG 04.07.2013	1980	-57.75	-17.47	17.17	2.44
				X							
	QN19	QNT0AR1	C	103-5028		QN19CT0NQ2-1STAR 05.07.2013	2500	-58.33	-19.73	18.61	2.28
				X							
artificial rain	QN19	QNT0AR1	C	103-5029		QN11CT0NQ2-1STAR 05.07.2013	1760	89.98	-16.79	15.88	3.11
				X							
	QN11	QNT0AR2	C	103-5029		QN11CT0NQ2-1STAR 05.07.2013	1760	89.98	-16.79	15.88	3.11
				X							
				X		QN11-GEL-RAI 05.07.2013	2101	77.32	-19.29	10.1	6.01

In order to define the specific methodology for applying electrochemical methods and testing protective treatments in situ, in particular during ageing, an experimental design has been established. EIS measurements will be performed on 4 different types of systems:

- alloys (A)
- coated alloys (CA) – a microcrystalline wax such as cosmoloïd H80 will be used.
- patinated alloys (PA)- natural urban marine 17-months aged coupons available in host facility will be used.
- coating on patinated alloys (CPA).

Some coupons (QN11, QN17 and QN24) are now at the premise of the end-users (CSIC-CENIM) in order to be prepared and coated with wax. This experiment will be performed during next stay of end-users at the host facility.

It's worth saying that this 4-month access grant is too short to truly determine the long-term behavior of treatments but it will give us some tendency. Therefore end-users planned to apply to a further JERICO TNA grant in order to extend the ageing tests and assess with precision the performances of the different treatments.
