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TNA PROJECT REPORT

1st Call of Proposals

12 January – 3 April, 2012

A) General Information

Proposal reference number(1)	CALL_1_6
Project Acronym (ID) (2)	SESAM
Title of the project(3)	Standardised Electrochemical in Situ Assessment of Metal Coatings
Host Research Infrastructure(4)	**MPL Genoa**
Starting date - End date(5)	01.07.2013-31.04.2015: - Access to MPL Genoa for task 1 - exposure of bare samples: from 05.11.2013 to 14.04.2014, and from 29.04.2014 to 20.11.2014, total 365 days - Access to MPL Genoa for task 2 ageing tests: from 01.10.2013 to 07.01.2014 - from 13.01.2014 to 14.04.2014 - from 29.04.2014 to 28.07.2014, and from 01.08.2014 to 31.10.2014, total 365 days
Name of Principal Investigator(6) **Home Laboratory** **E-mail address** **Telephone**	Edith Joseph Université de Neuchâtel, Laboratoire de Microbiologie, Rue Emile-Argand 11, CH-2000 Neuchâtel, Switzerland edith.joseph@unine.ch +41 32 718 22 35
Additional users (7)	Emilio Cano Ministerio de Economía y Competitividad-Centro Nacional de Investigaciones Metalúrgicas, Avda. Gregorio del Amo 8, 28040 Madrid, Spain ecano@cenim.csic.es +34 91 5538900 ext 309 Monica Albini Université de Neuchâtel, Laboratoire de Microbiologie, Rue Emile-Argand 11, CH-2000 Neuchâtel, Switzerland

B) Project objectives (max. 250 words) (8)

The main objectives of the project were 1) to perform electrochemical impedance measurements for assessing the effectiveness of innovative protective treatments in comparison with nowadays used ones and 2) to develop a standardized electrochemical methodology for in situ measurements. To a larger extent, this project will contribute to a better conservation-restoration of metallic artefacts based on the advances gained in the application of electrochemical techniques and to extend the knowledge on efficacy of biological interventions. To this end, the interaction with outdoor environment of several metals used in monuments and ornamentation is enlightened by taking advantage of a standard exposure site in a highly corrosive environment due to urban-marine atmosphere. Through this, the overall idea is, at long-term, to enhance research in the field of metal conservation-restoration by promoting a dialogue among conservators and scientists, to encourage the use of electrochemical techniques as well as new treatments based on clear scientific and ethical criteria (efficiency, harmless, respect of the aesthetic and historical values) and to enhance conservation activities in their social and

economical aspects with the development of ready-to-use conservation-restoration products.

C) Main achievements and difficulties encountered (max. 250 words) (9)

During the access allocated, our activities were accomplished according to the defined working plan that was overall respected. Meetings were organized at the beginning and end of the access time at the CNR MPL Genoa facility: Kick-off meeting on 1st July 2013 and Concluding meeting on 10th December 2014. Within Task 1, the samples were properly aged and presented a typical natural patina from an urban-marine environment. All data collected for the characterization of the patina formed are currently analysed in order to assess the corrosion behaviour of the different alloys exposed. Within Task 2, the efficiency of some protective treatments was evaluated and users paid regular visits in order to perform the foreseen *in situ* measurements: 01-05/07/2013, 08-09/07/2013, 02-04/09/2013, 23-24/09/2014, 07-10/01/2014, 14-17/04/2014, 28/07-01/08/2014, 03-10/11/2014 and 10-12/12/2014. Within Task 3, most of the measurements were performed in remote at the users' institutions and the obtained results were discussed by means of videoconferences. As outcomes, The project led to a better understanding of outdoor corrosion processes (Task 1), a validation of an innovative biological treatment for conservation-restoration (Task 2) and a definition of a protocol for *in situ* electrochemical measurements (Task 3). It's worth saying that thank to a cost-neutral extension to one year that was allocated to the initial 130-days TNA grant, the difficulties that may have been encountered in successfully achieving the foreseen tasks within a period of 130 days were hence overcome.

D) Dissemination of the results (10)

Preliminary results were disseminated through conferences:

- EUROCORR 2014 congress, 8-12 September 2014, Pisa, Italy
- Open Air metal workshop, 4-5 December 2014, Paris, France

In total, 2 publications related to the MAIA project were published or are in preparation in 2 books and 2 peer-reviewed journals:

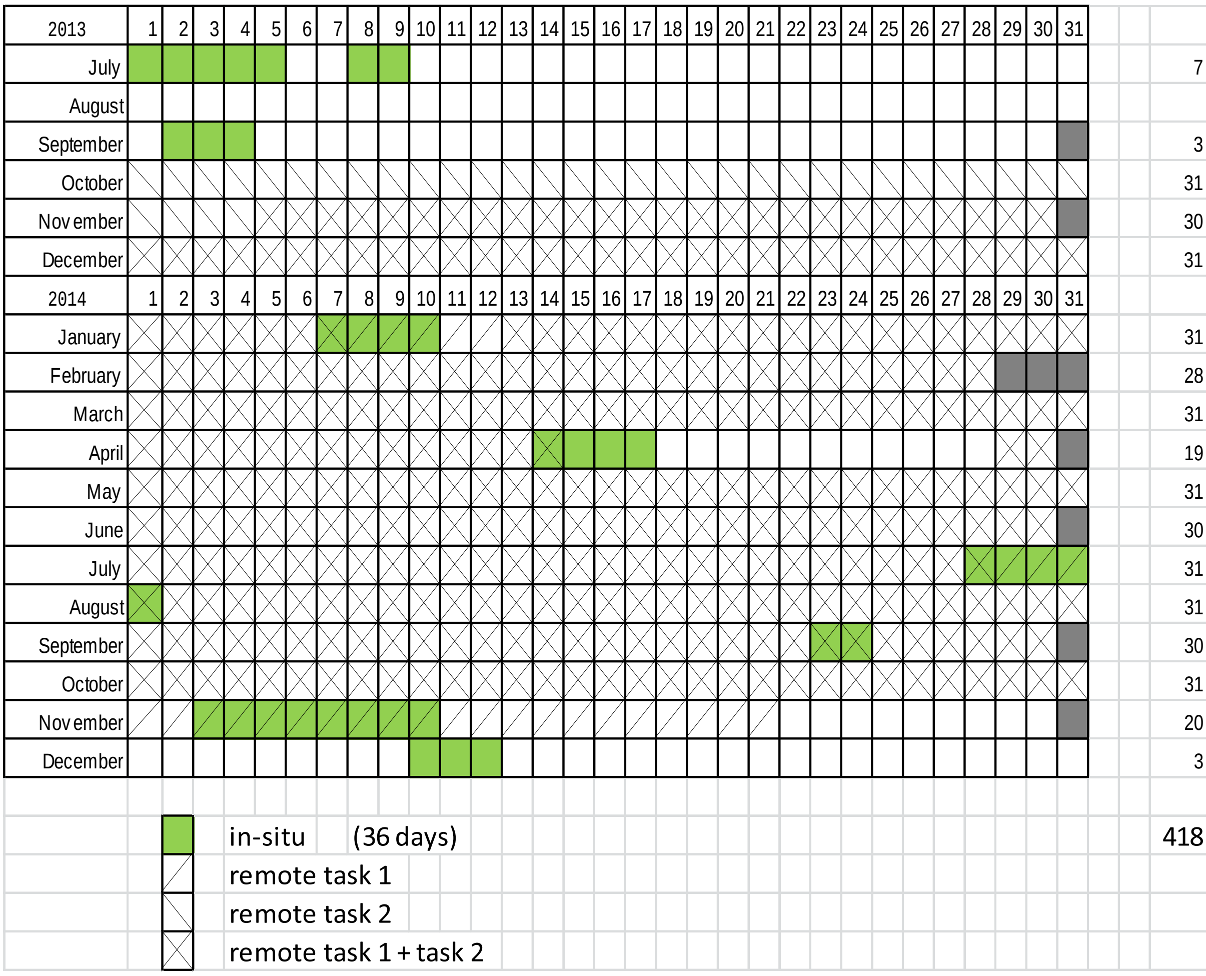
- E. Joseph et al. Innovative biological approaches for metal conservation. In Conference Proceedings of EUROCORR 2014, European Corrosion Congress. Pisa, Italy. 8th-12th September 2014. DECHEMA e.V., Frankfurt and AIM – Associazione Italiana di Metallurgia, Milano, 2014; ISBN 9783897461598, 1-10.
- E. Joseph et al. BIOPATINAS: Innovative biological patinas for copper-based artefacts. In Conference Proceedings of Outdoor Metallic Sculpture from the XIXth to the Beginning of the XXth Century: Identification, Conservation, Restoration. Paris, France. 4th-5th December 2014. ICOMOS France, Paris, 2014; ISBN 9782905430182, 154-162.
- E. Joseph et al. BIOPATINAS: Innovative biological approaches for metal conservation. Special issue of the Eurocorr WP21, *Materials and Corrosion, submitted.*
- All data are currently completed in order to be integrated within a publication in *Corrosion science*.

E) Use of the Infrastructure/Installation (11)

	In situ	By remote
Nr. of Users involved	3	3
Access units (days/months/etc)	days	days
In situ stay day / Remote Access duration	36	418

F) User project scientific field

Main field [(12)]	Material Sciences
Scientific description [(13)]	Other - Material Sciences

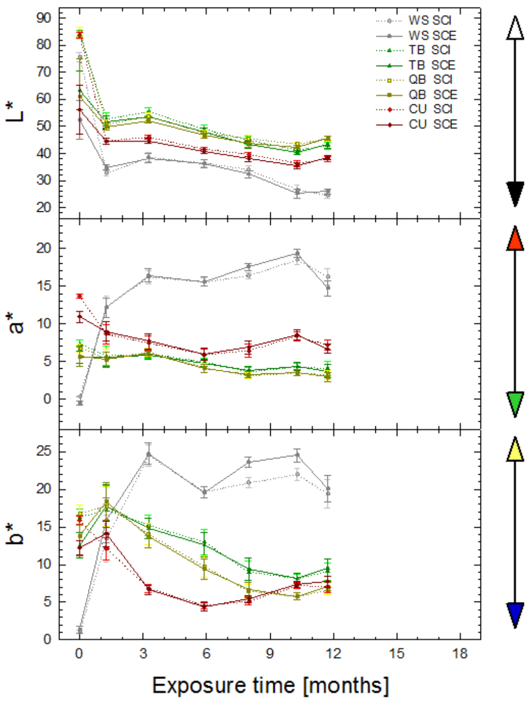


H) Technical and Scientific preliminary Outcomes (max. 2 pages) [14]

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

We exposed 16 (6x6cm-large) and 12 (3x3cm-small) coupons for each of the four alloys considered (Ternary bronze TB, Quaternary bronze QB, Copper CU and Weathering steel WS).

For each alloy, subsets of 3 larges samples and 3 small samples were monitored *in situ* for color variation at regular interval. In order to characterize the different alloys and their relative weathering behavior, a couple of small samples was also removed at regular interval (1-3-6-12 months) and characterized in terms of weight, color, patina thickness and composition (by X-Ray Diffraction-XRD). As reference, unexposed samples were also characterized with the same complement of analytical techniques.



exposure [days]	DP [mg] TB	QB	CU	WS
38	1,6 ± 0,2	2,1 ± 0,1	1,0 ± 0,5	57,9 ± 0,9
98	0,45 ± 0,05	0,4 ± 0,1	0,8 ± 0,2	92 ± 3
177	-0,1 ± 0,0	-0,1 ± 0,0	1,2 ± 0,0	99 ± 3
352	1,9 ± 0,0	2,2 ± 0,6	1,4 ± 0,6	114,7 ± 0,2

Figure 1 - Variation of the colorimetric data according to the exposure time. Weight changes observed on the different alloys.

Weight change on CU, TB and QB samples was less important than on WS coupons. On this latter, a constant and significant increase of weight was observed.

For TB and QB alloys, the color variation was quite similar but with slightly higher b* values (tendency to yellow) for TB; CU samples and in a larger extent WS samples showed the most important chromatic variation; as expected for all alloys, the L* coordinates presented a significant variation after the first month of exposure.

The patina thickness of WS samples increased rapidly in the first months of exposure and is still not fully stabilized after 12 months of exposure; on CU, TB and QB samples, the patina seemed to develop slower and started increasing only after 6 months (this aspect is observed for the first time, on contrary to previous ageing tests performed at MGL Genoa and need further investigation).

For CU, TB and QB coupons, XRD data demonstrated firstly the formation of Cuprite followed by the increase of $Cu_2Cl(OH)_3$ polymorphs (Atacamite, Botallackite, Anatacamite); Some sulphates were identified for longer exposure. In particular Brochantite was identified on CU while on TB and QB alloys, Anglesite and possibly Ramsbeckite were present. On WS, peaks from the underlying metal disappeared after 1month of exposure confirming that a thicker patina mainly composed of Lepidocrocite with traces of Akaganeite was developing here. All these data need deeper investigation, in particular a correlation with the meteorological data of the exposure time will be considered.

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

Coupons were prepared from two copper alloys with a marine natural patina and from a copper roof with an urban patina for evaluating the efficiency of selected treatments. Part of the coupons 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).

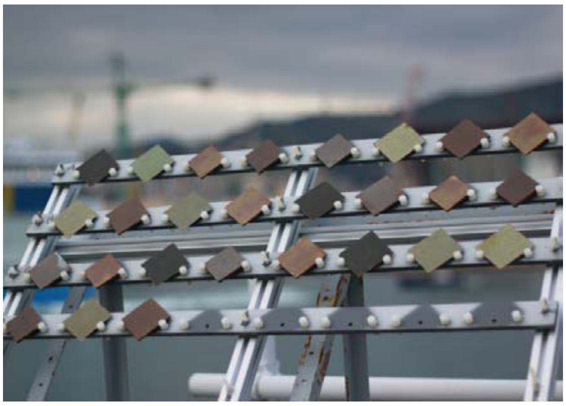


Figure 2 - Sets of aged coupons used for evaluating the different treatments.

A characterization of the patinas was achieved before treatment and the performances of the different treatments were evaluated before exposure on the basis of their resistance, color, surface's morphology and protection behavior. Several analytical methods were used: Fourier Transform infrared Spectroscopy (FTIR), colorimetry, Scanning Electron Microscope and Energy Dispersive X-ray spectroscopy (SEM-EDS) and Electrochemical Impedance Spectroscopy (EIS). The ageing tests were initiated on 2nd October 2013 and ended after 12 months of exposure on 20th November 2014. The treatments' behaviors were monitored every three months during exposure.

T4 coupons presented a general behavior similar to a natural patina, as indicated by colorimetric and electrochemical measurements comparable with those obtained on T0 coupons. Indeed, the biological treatment studied here does not produce an extra coating layer, as wax can do, but a layer of copper oxalates that is forming from the underneath patina. These results demonstrate the chemical and physical compatibility of biopatina treatment with corroded copper-based surfaces. On the contrary, TR coupons had their own behavior, typical of organic coating. However, the coating's performance was not constant over time and drastically decreased after 12 months of exposure. The wax film showed failure and presented colorimetric and electrochemical measurements reaching the values of the untreated coupons.

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

Task 3 dealt with the standardization of an electrochemical methodology for *in situ* assessment of coatings and patinas. A comparison was made between two electrochemical cells: the contact probe (CP) developed by P. Letardi and a gel-polymer electrolyte cell (GPE) developed by E. Cano; and two low-aggressiveness electrolytes: mineral water and concentrated artificial rain. First tests were made using cupronickel samples exposed 17 months in MPL Genoa.

The data were fitted to a two time-constant equivalent circuit (EC) model (Figure 3). In this model, the first R-CPE couple corresponds to the properties of the patina or coating, and the second to the corrosion process of the base metal. The values of the different elements of the EC indicated that the electrolyte did not have a significant influence on the measurements and the results were very similar for the Q11 and Q19 samples presented here. On the contrary, the used cell seemed to have a minor influence on the results (Figure 4). The processes involved are similar, so the EC is similar, but the values of the elements differed slightly: for the GPE, resistance values were lower and (pseudo)capacitances higher. Agar used in the GPE seemed to increase the anodic dissolution of copper, what would explain the decrease in R, probably acting as an anodic depolarizer.

Comparison of the cells will be completed by measuring aged and coated samples from Task 2.

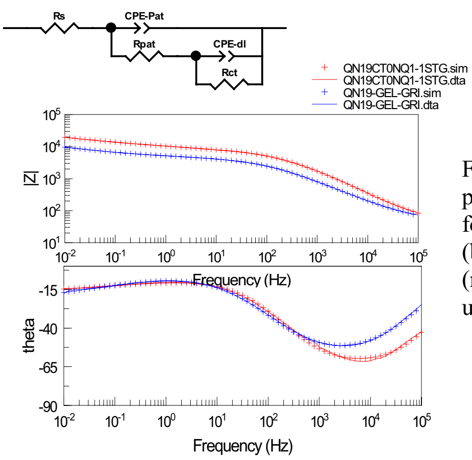


Figure 3 - Bode plot of EIS data for the GPE (blue) and CP (red) and EC used for fitting.

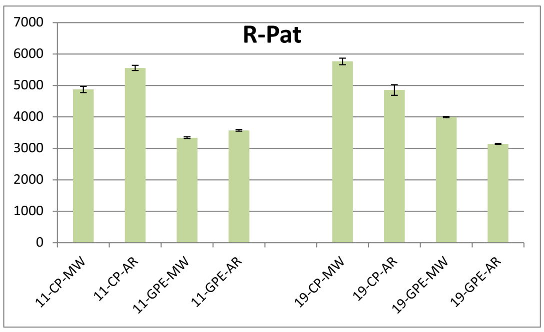


Figure 4 - Comparison of values for patina resistance (R-Pat) obtained by EC fitting of data of two samples (11 and 19), using the GPE and CP cells and two different electrolytes, mineral water (MW) and artificial rain (AR).

Guidelines for the TNA Project Preliminary Report

This report is due within one month after the completion of the JERICO TNA project by the User Group Leader (P.I.) and should be submitted to the **JERICO TNA Office** (**jerico.tna@ismar.cnr.it**) and the **Scientific Site Coordinator** at the hosting facility with a copy to the **JERICO Coordinator** (**jerico@ifremer.fr**).

An online "user group questionnaire" has also to be completed by each **Group Leader** of a user-project supported under JERICO as soon as an experiment has come to an end - you will find it here: **http://cordis.europa.eu/fp7/capacities/questionnaire_en.html#fnote**.

NOTES:

Refunding of the TA reimbursement will be processed as soon as the JERICO TNA Office, the Scientific Site Coordinator and the JERICO Coordinator will received this report.

Part of the information collected with this report will be used to fill in the European Commission MS Access database. Following article 4.4.2, the User Group PI will be asked by the JERICO Coordinator to update it at the reporting deadlines.

Notes for the compilation

(1) It is the reference number assigned to the proposal by the TNA-Office.
(2) It is the user-project identifier and must be unique under the grant agreement and for its lifetime. The length cannot exceed 20 characters.
(3) Specify a title for the approved proposal. The length cannot exceed 255 characters.
(4) Name of the installation/infrastructure accessed with this project. If more than one. installations/infrastructures are used by the same project; please list them in the box.
(5) Specify starting and end date of the project (including eventual preparatory phase before the access).
(6) Fill with the full contact of the Principal Investigator (user group leader).
(7) List the full users team (name and affiliation) that made direct use (physically or remotely - please specify) of the installation/infrastructure under the direction of the group leader.
(8) Write the short-term, medium and long-term objectives of project. Use no more than 250 words.
(9) Describe briefly the main achievements obtained and possible impacts, as well as possible difficulties encountered during the execution of the project. Use no more than 250 words.
(10) Describe any plan you have to disseminate and publish the results resulting from work carried out under the Transnational Access activity in JERICO: scientific articles, books - or part of them -, patents, as well as reports and communication to scientific conferences, meetings and workshops. Highlight peer-reviewed publications. Users supported under the transnational access activity are encouraged, as far as possible, to make available on open repositories their publications. Acknowledgement to EC and JERICO is requested following article 4.5 of the “End-User“ Agreement.
(11) Indicate the number of users involved in the activity (the P.I. plus the users described at point 6), the amount of access to the installation/infrastructure and the length of in-person stay at the installation or the operator laboratory (e.g. for preparing the experiment).
(12) See Annex, First column.
(13) See Annex, Second column.
(14) Describe in detail results and main findings of your experiment at the present stage.

Annex of the TNA Project Preliminary Report - User-Project Scientific fields

Main field	**Scientific description**
Physics	Astronomy/Astrophysics/Astroparticles Atomic & molecular physics Condensed matter physics High energy and particle physics Nuclear physics Plasma physics Quantum electronics & optics Other - Physics
Chemistry	Chemistry
Life Sciences & Biotech	Food quality & safety Agriculture & Fisheries Medicine Veterinary sciences Molecular & cellular biology Other - Life Sciences & Biotech
Earth Sciences & Environment	Global Change & Climate Observation Ecosystems & Biodiversity Natural Disaster & Desertification Marine Science/Oceanography Water Science Hydrology Other – Earth Science Other – Environment
Engineering & Technology	Aeronautics Space New production processes Nanotechnology & Nanosciences Transport Other - Engineering & Technology
Mathematics	Mathematics
Information & Communication Technologies	IST for citizens, businesses & organizations Trust & Security Communication & Networks Computing & software technologies Components & Micro-systems Knowledge & interface technologies Other - ICT
Material Sciences	Knowledge based multifunctional materials Other - Material Sciences
Energy	Sustainable energy systems Fusion Other - Energy
Social Sciences	Economics Political Sciences Educational sciences Law Demography Other - Social Sciences
Humanities	Arts Hystory Languages Other - Humanities