Report on the outcomes of a Short-Term Scientific Mission[1]

Action number: IG16215

Grantee name: Nicola Ricotta, University of Florence, Italy

Details of the STSM

Title: "Optimisation of the use of Pleco® to locally and safely clean the tarnishing developing on sterling silver heritage artefacts"

Start and end date: 08/05/2023 to 12/05/2023

Location: Empa's Joining Technologies and Corrosion Laboratory, Dübendorf, Switzerland

Scientific support: Christian Degrigny (HE-Arc CR), Jorge Gonzalez Frutos (Empa) and Romain Jeanneret (HE-Arc CR & Abbey of Saint-Maurice)

Technical support: Empa's Joining Technologies and Corrosion Laboratory, Dübendorf, Switzerland: potentiostat, conventional electrolytic device, pumps and accessories; Opificio delle Pietre Dure, Florence, Italy: Pleco pencil.

General programme: implementation of Pleco pencil as an analytical tool of tarnished silver-based coupons; preparation of surface finish of metal coupons; methodologies for artificial tarnishing; performance of Linear Sweep Voltammetry - LSV measurement; protocols for pre-removal of copper-based corrosion products; performance of chronoamperometry measurements; discussion on final intervention after electrolytic cleaning.

Description of the work carried out during the STSM

The activities carried out involved optimizing the protocol for using Pleco (Fig. 1) as an analytical tool. Characterization of tarnishing of silver-based artifacts is critical to set up suitable electrolytic cleaning. Artifacts are rarely composed of pure silver and a percentage of copper in the alloy is always present. This can lead to inappropriate cleaning with reduced copper (black spots) depositing on the metal surface. Therefore, another important part of the work done involved optimizing a protocol for pre-removal of copper corrosion products.

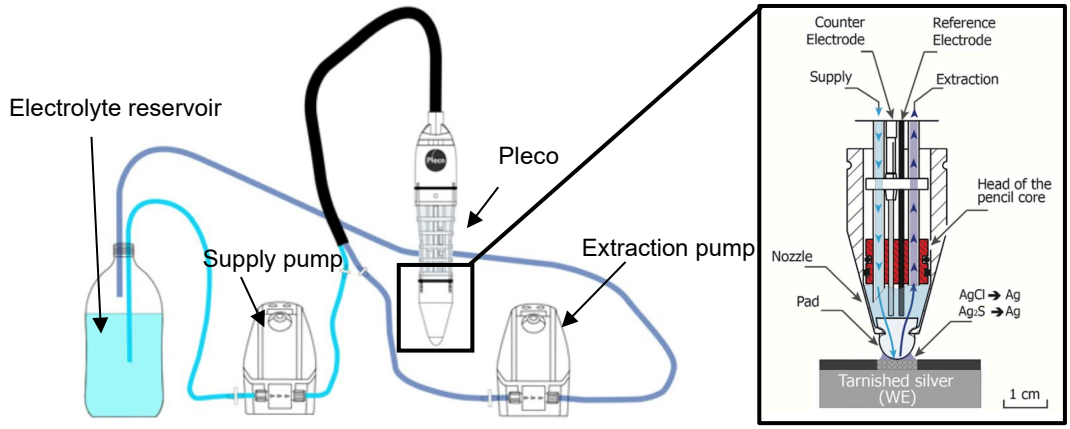

Figure 1. Setup (left) and cross-section of the Pleco electrolytic cell (right) with the pad in the nozzle that connects the electrolytic cell to the working electrode (WE), the glassy carbon rod (used as a reference electrode) and platinum rod (counter electrode), and the two hoses that supply and extract the electrolyte (1% (w/v) KNO_3) inside the cell. With this system, local electrolytic processes developing on the metal surface can be investigated, © Jeanneret Romain - HE-Arc CR.

[1] This report is submitted by the grantee to the Action MC for approval and for claiming payment of the awarded grant. The Grant Awarding Coordinator coordinates the evaluation of this report on behalf of the Action MC and instructs the GH for payment of the Grant.

First, the working conditions of Pleco pencil, connected to the potentiostat (Metrohm Autolab PGSTAT204), and the electrolyte pumping system were checked. Among the preliminary steps it is essential to:

- measure the potential of the glassy carbon (GC) electrode employed as a reference electrode (RE). In fact the GC is not a real RE and it is important to check its potential before and after polarization. The potential of the GC was about 210 mV/Ag-AgCl (a value that is within the average of the values measured outside this STSM) (Fig. 2):

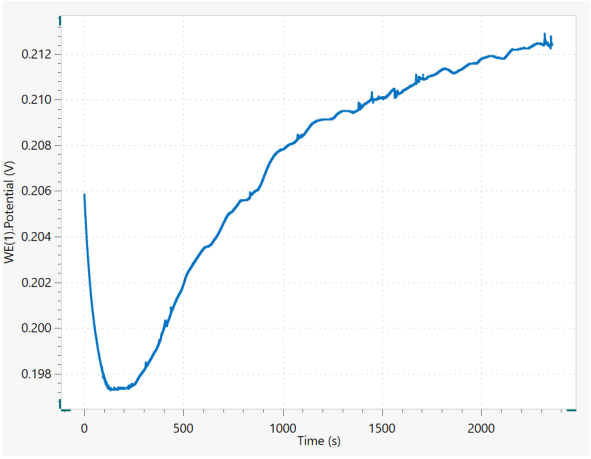

Figure 2. OCP of glassy carbon in KNO_3, 1% (w/v), pH 6; WE: GC; RE: Ag-AgCl 3M; CE: Pt wire, © Ricotta Nicola & Gonzalez Frutos Jorge.

- set measurement parameters so that current fluctuation in the plots (due to the change in contact area between the electrolyte and the metal surface being analysed) is minimized. Among the most important parameters are the sealing conditions of the Pleco electrolytic cell (10 cm of Teflon around the piston head and silicone hoses around the RE and CE), the electrolyte supply and extraction values (S 10 and E 45 mL/min.), and the shape and size of the pad (1.5 cm diameter and height and rounded tip) (Fig. 3). The above parameters were adjusted through the visual observation of the electrolytic cell (verifying that bubbles during pumping come from the pad and not from piston head, insuring then good sealing conditions) and of the pad (should not be too dry while preventing any leakage of electrolyte as drops); then by performing LSV measurements (on Ag925 coupons, from the ASTEC[2] project, tarnished by exposure during 48h to vapours produced by boiled eggs). At the end of each polarization, the pad was rinsed by stopping the extraction pump for about 1 min. The parameters remained unchanged for the rest of the experiments.

Figure 3. Shape and size of the pad, © Ricotta Nicola.

[2] Approaching the initial Surface appearance of Tarnished silver heritage objects by Electrolytic Cleaning: Definition of optimal treatment conditions, project funded by Haute Ecole Spécialisée de Suisse Occidentale – HES-SO.

All measurements were performed on sterling silver coupons (Ag925) but with different surface finishes: curved and mirror; flat, punched and mirror or matte from Nicola Ricotta's PhD project; flat and mirror from ASTEC's project (Fig. 4). In addition, to simulate the surfaces of the artistic artifacts, the coupons were tarnished by exposure to vapours produced by boiled eggs while still warm for durations of 1, 2, or 48h (to obtain different levels of tarnishing) inside an 11L desiccator and with the presence of a small fan to homogenize the concentration of H_2S (Figs. 5 and 6).

Figure 4. Coupons before artificial tarnishing, from left to right: curved and mirror; flat, punched and mirror; flat, punched and matte; flat and mirror, © Ricotta Nicola.

Figure 5. Jorge Gonzalez Frutos during the preparation of boiled eggs for tarnishing coupons, © Ricotta Nicola.

Figure 6. Coupons after tarnishing with boiled eggs for 2h, despite different surface finishes the level of tarnishing is equal among coupons, © Ricotta Nicola.

Afterwards, the coupons were analysed by LSV before and after treatment with different pH solutions and concentrations of EDTA, a chelating agent that is able to remove copper-based corrosion products without any expected effect on silver sulphide:

- 3% Na_4-EDTA at pH 10 (adjusted by the addition of HCl diluted to 37%) gelled by 4% agar-agar and applied on the coupons for 30'. Before and after gel application no particular difference is observed on the coupons (Fig. 7). The Na_4-EDTA solution and the time taken are not sufficient to achieve good chelating action and the Cu_2S peak is still present in the LSV plots (Fig. 8);

Figure 7. Left coupon tarnished for 1h and right coupon tarnished for 48h. Above black line: untreated area and below: Na_4-EDTA treated area, © Ricotta Nicola.

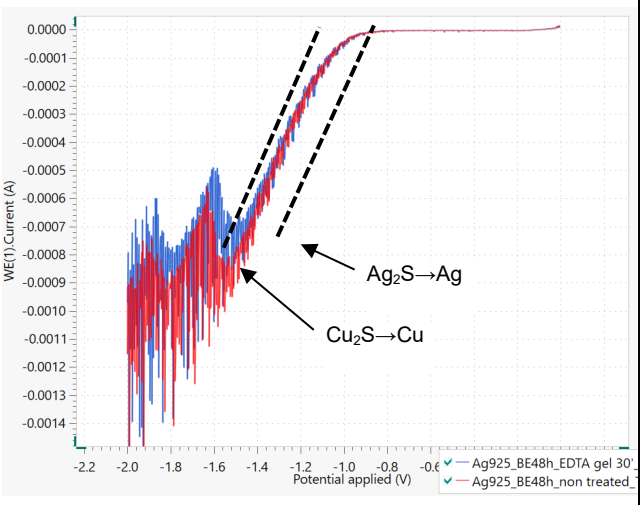

Figure 8. Red plot on an untreated area; blue plot on a Na_4-EDTA treated area, © Ricotta Nicola, Degrigny Christian, Gonzalez Frutos Jorge.

- 3% Na_4-EDTA at pH 10 (Na_2-EDTA adjusted by adding 5M NaOH) gelled with 4% agar-agar and applied on the coupons for 30' and 15h. As before and even after 15h, no difference is observed on the coupons, LSV plots are also the same before and after gel application;

- 5% Na_4-EDTA at pH 10 (Na_2-EDTA adjusted by addition of 5M NaOH) in free form and by coupon immersion for 15h (Fig. 9). Unlike the previous case, Na_2-EDTA made alkaline succeeds in chelating copper corrosion products (Fig. 10);

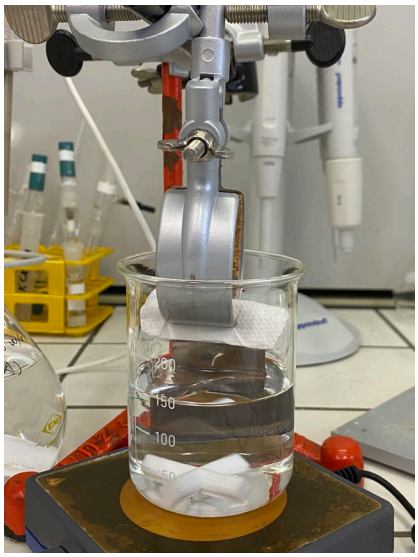

Figure 9. Coupon half immersed inside Na_2-EDTA made alkaline, © Ricotta Nicola

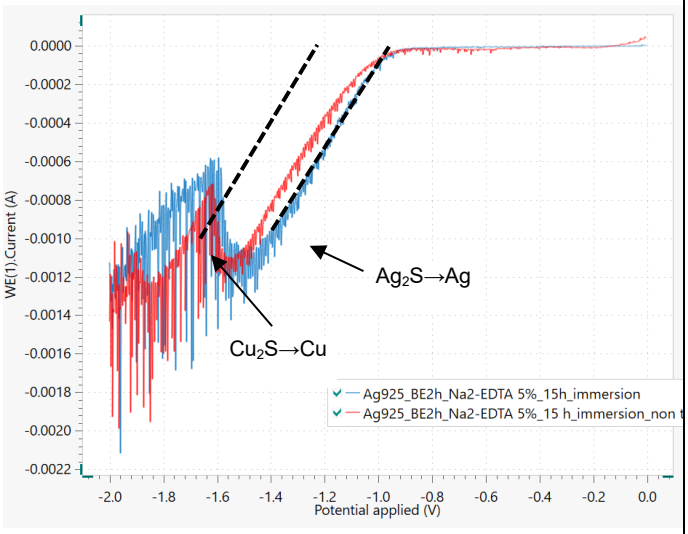

Figure 10. Red plot on an untreated area (with Cu_2S peak); blue plot on a Na_2-EDTA made alcaline treated area (without Cu_2S peak), © Ricotta Nicola, Degrigny Christian, Gonzalez Frutos Jorge.

- 5% Na_4-EDTA at pH 10 (Na_2-EDTA adjusted by addition of 5M NaOH) gelled with 4% agar-agar and applied on the coupons for 18, 20 and 38h (Fig. 11). Only after 38h was it possible to remove the copper-based corrosion products as in the previous case of the coupon immersed in solution (Fig. 12).

Figure 11. Coupon with Na_2-EDTA gel made alkaline, © Ricotta Nicola.

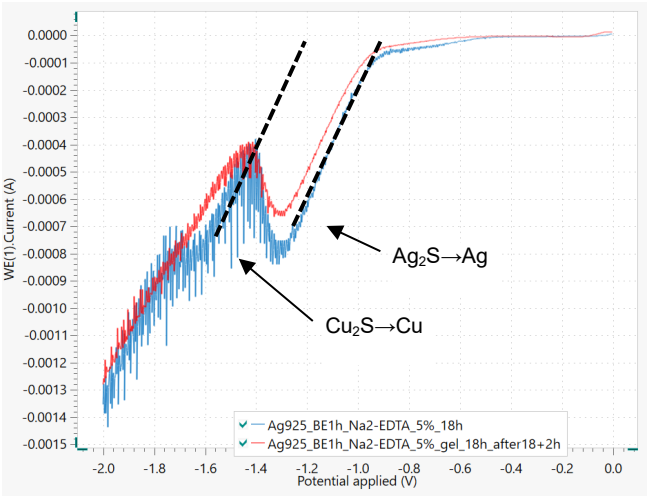

Figure 12. Blue plot on an area treated with gel for 18h (with Cu_2S peak); red plot on an area treated with gel for 38h (without Cu_2S peak), © Ricotta Nicola, Degrigny Christian, Gonzalez Frutos Jorge.

The preparation of the gelled EDTA solutions was possible thanks to the expertise of Romain Jeanneret, a member of the ENDLESS Metal project and Head of conservation of the treasure of the Abbey of St-Maurice (CH).

Another important analytical parameter investigated by chronoamperometry measurements was the time required for silver tarnish reduction, which also determines its thickness (Fig.13). The potential of -1.2 V/GC, in the specific case of the coupon analysed, corresponds to the middle of the Ag_2S reduction peak. This new cleaning protocol aims to limit the abrupt reduction of Ag_2S in Ag and the possible saturation of the pad with sulphur species that could create secondary effects on the metal surface (re-tarnishing, staining). As a result, the reduction is not immediate: there is a plateau after which the reduction is completed (visible after 120 seconds on figure 13).

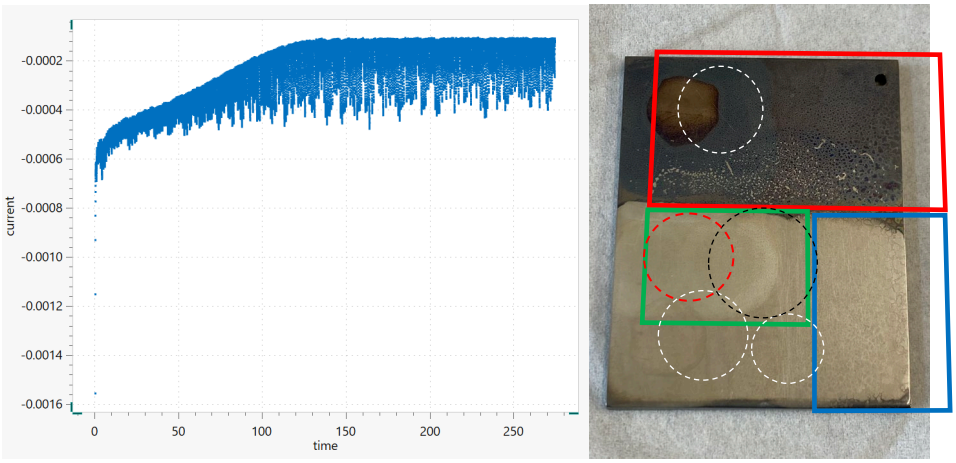

Figure 13. Chronoamperometry on a Ag925 coupon treated with 5% Na_4-EDTA pH 10 in immersion for 15h. After polarisation at -1.2 V/GC and during 120s, it was possible to reduce the tarnish on the coupon as is highlighted by the blue rectangle. In addition, an untreated area (highlighted in red) and an area treated with a potential of -1.8 V/GC (highlighted in green) can be seen on the coupon. The -1.8 V/GC potential corresponds to a value that goes beyond the Ag_2S reduction peak to test the overcleaning effect (the surface indeed looks cleaner than the area treated with a -1.2 V/GC potential). The spots that can be observed on the coupons are due to LSV measurements with a potential scan down to -2 V/GC (white circles) and to chronoamperometries at a potential of -1.6 V/GC (red circle) and -1.8 V/GC (black circle), © Ricotta Nicola, Degrigny Christian, Gonzalez Frutos Jorge.

<u>Other activities performed included:</u>

- optimization of the pad production protocol using abrasive paper (Fig. 14) as suggested by Jorge Gonzalez Frutos. The size, shape, and physical integrity of the pad are critical in order to make LSV measurements reproducible. After cutting the wet PVFM pad using a hole puncher for rubber stopper (to create a cylinder with a constant diameter and no imperfections), the resulting pad is left to dry and the tip is shaped with abrasive paper.

Figure 14. Dry pad worked by abrasive paper, © Ricotta Nicola.

- testing tarnishing protocols using 80% pure albumen powder (Fig. 15). By means of boiled eggs, a blue surface tarnish is obtained quickly (one hour); conversely, with liquid and pure albumen, many more hours are required before a thick level of tarnish is obtained even though this better reflects tarnishing on a real object. The aim of these experiments was to speed up the process of tarnishing by means of albumen powder which is less expensive than pure liquid albumen.

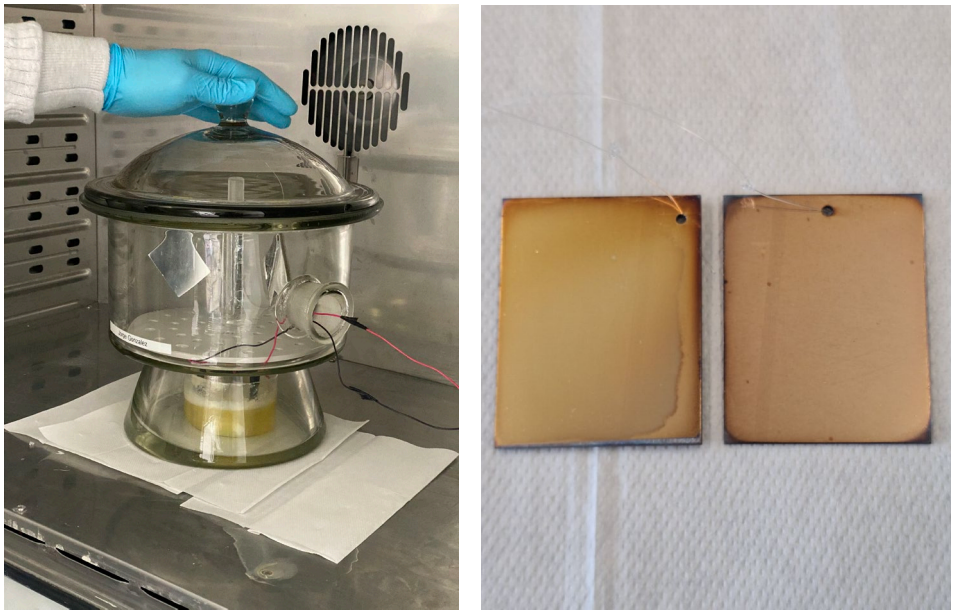

Figure 15. 11L desiccator with two coupons (Ag999-Ag925), albumen powder (Apollo Scientific) diluted to 20% in 100 mL of Milli-Q H_2O and a fan placed in an oven at a temperature of 70 °C. At right is a photo of the coupons after 1h of tarnishing: it is possible to obtain a yellow-brown tarnish that is a middle ground between the blue tarnish that is obtained with boiled eggs and the light-yellow tarnish obtained with pure liquid albumen, © Ricotta Nicola.

- burnishing of the surface after electrolytic cleaning (Fig. 16). The reduction of tarnish in metallic silver may result in surface whitening and matting. This undesirable effect can be corrected by mechanical action with cotton cloths until the desired effect is achieved. In this specific case, we did not manage to remove entirely the whitening phenomenon. It has to be noted that if it systematically occurs on electrolytically cleaned tarnished mirror-polished coupons, we observed it less on real objects.

Figure 16. Burnishing the coupon with cotton cloth, © Degrigny Christian.

Description of the STSM main achievements and planned follow-up activities

With the protocols studied and optimized Pleco currently represents one of the most valuable tools for the analysis and cleaning of silver-based artifacts. In particular, the following achievements have been reached:

- protocol of use of Pleco electrolytic pencil for analytical purposes. Starting with the measurement of the GC reference electrode potential by OCP, to the setting of parameters to minimize current fluctuation, and following with the characterization of tarnishing by LSV and up to the determination of the time of tarnish reduction by chronoamperometry. During chronoamperometry measurements, it is possible to evaluate the cleaning level that is achieved at different values of potentials characteristic of the silver tarnish present;
- protocol for pre-removal of copper-based corrosion products using 5% EDTA at pH 10. For the same tarnish level and Na_4-EDTA solution, copper-based corrosion products on a coupon immersed are removed faster than in gel application (15h for immersion and around double time with gel);
- optimised protocols for producing reproducible coupons in terms of artificial tarnishing levels. By means of 80% pure albumen powder, it is possible to tarnish silver more slowly than boiled eggs and faster than liquid albumen. This solution is a middle ground to control the tarnishing processes and make them more reproducible than with boiled eggs but at the same time faster than with liquid albumen. In addition, with albumen there is a slow tarnishing process and the typical reduction peaks present on real objects (Cu_2O, Ag_2S and Cu_2S) appear. With boiled eggs, Cu_2O does not appear;
- optimised protocols for pad production. By means of a hole puncher it is possible to cut the pad while it is still wet to define its final diameter and heigh. The pad is the left to dry and shaped with abrasive paper according to the desired shape.

This STSM was an opportunity to strengthen the collaboration between several Italian and Swiss institutes: the University of Florence and the Opificio delle Pietre Dure in Florence, the Haute Ecole Arc Conservation-restauration in Neuchâtel, the Conservation lab of the abbey of St-Maurice and the Empa's Joining Technologies and Corrosion Laboratory in Dübendorf. These institutes are already collaborating within the ASTEC project which aims to develop protocols to safely electrolytically clean silver tarnishing. and/or the Endless Metal Innovators Grant project which aims to disseminate the use of low-cost, portable and easily accessible analytical tools developed at HE-Arc CR such as Pleco.

These results form the basis for the development of the investigation and restoration phases of silver-based alloy artifacts. The first objects on which the protocols studied so far will be applied will be a Valadier cooler (Fig. 17) and a bas-relief with the Last Supper (Fig. 18) from the Tesoro dei Granduchi, Gallerie degli Uffizi, Florence.

Figure 17. Valadier cooler, XIX century, © Ricotta Nicola.

Figure 18. Last supper, Matthias Walbaum, XVI century, © Ricotta Nicola.