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Conservation purpose material testing of corrosion products on outdoor bronze statues

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Abstract. A detailed material testing was carried out before the conservation project of the János Arany statues of Garden of Hungarian National Museum. The scope of the testing to analyse the corrosion products on the surface and help to develop the best cleaning and protection practice. Samples were taken from more areas and the samples were analysed by SEM-EDS, XRD, FT-IR methods. This article introduces the results of the testing and the relevant effect to the conservation process.

1. Introduction

Outdoor sculptures, especially metal ones, are constantly exposed to atmospheric corrosion, that is the reason why their protection is extremely important. [1,2] Corrosion of copper and its alloys is slow process; however, it could be really harmful in large time scale. [3] On the other hand corrosion product can also destroy the aesthetic value of statues, furthermore, influence its further corrosion. [4] Bronze sculptures are widespread in the world. Investigation of its corrosion and corrosion products are particularly important in case of its conservation procedure.

Method of cleaning procedure is one of the biggest questions during the conservation. [5] Composition and structure of corrosion layers are also really valuable information in this case. [6]

Knowing of the exact composition and the stability of compounds are essential for the expected chemical reactions. It is useful to know that the corroded layer's chemical composition, looking for compounds which can damage the surface of the statue during the conservation process. The corroded layer's structure influences its stability: could removed from the surface easily or not, could cause any changes in adhesion as well as which parts should be removed or can be preserved. This information can help to figure out the appropriate cleaning method. [7]

Composition of corrosion products is also a crucial question of conservation: Could any other reaction appear which can influence not only the state of the sculpture but also its conservation? [8] According to these information plan of conservation can be prepared and perform the conservation progress. Using detailed material testing methods can answer these questions only.[9]

Statue of János Arany, who was one of the greatest Hungarian poets, is situated in the Garden of the Hungarian National Museum. Janos Arany's statue is surrounded by two other sculptures, Toldi and Piroska who are the main characters of his poetry. Conservation of outdoor sculptures was also completed during the renovation of Museum Garden. Restoration of Arany's statue group was a highlighted and greatest task of this project due to its extent and its national importance.

Figure 1. The statue of János Arany and Toldi at the front of the Hungarian National Museum.

Detailed investigation of corrosion products was performed before conservation because of the previously mentioned reasons. Chemical composition of corrosion product was compared to the composition of the sculpture's material. Its aim was to determine the chlorine compounds. Presence of chlorine on the surfaces was not so probable in Budapest but we wanted also to exclude this phenomenon. Renovation in the surrounding buildings as well as in the museum can cause the presence of gypsum in the corrosion layer, that is the reason why we investigated the presence of gypsum, furthermore organic compound. In this work results of material investigation as well as results and consequences for conservation are reported. Restoration of sculptures were carried out and Janos Arany's statue group is situated in the Garden of Hungarian National Museum again.

Figure 2. The different type of corrosion products on the surfaces of status. Right image shows a black and porous green layer, left image shows the continuous green and yellow-brown layer with a black covered area.

2. Materials and methods

Field portable X-ray fluorescence (pXRF) analysis was performed on the statues in several regions. The aim of this examination was to determine the elements and assumed chemical composition. Basically, four different corrosion product were identified on the surface: i, surface areas covered by black layer; ii, yellow-brown layer; iii, porous green layer on the surface; iv, continuous ductile green layer. The documentation wrote a bronze bas material. Measurements in different areas has been confirmed the documentation's copper and tin content. Silicon, aluminium and iron content also was detected in these areas. However, silicon and aluminium content were significantly higher in the black layer. Phosphorus was detected in the yellow-brown areas, which could be dangerous in terms of cleaning. Higher sulphur content was detected at the green layers, which originated to the patina first. Oxford XMET 8000 type pXRF analyser was used for the measurements. Powder samples were taken from the mentioned areas from more positions and statues. First energy dispersive X-ray spectroscopy (SEM_EDS) were made with a Hitachi –S4300 CFE to study the structure and the chemical composition of the different materials. XRD measurement were made with a Bruker D8 Advance to identify the different compounds. Only a small amount of samples could be collected, so the identification was hard. FTIR analysis was performed to find possible remains of a prior treatment with organic or polymeric materials. Samples were taken from the continuous green sample; which brittleness was tested by microhardness tests.

3. Results and discussion

Just small amount of powder, and small parts were possible to collect from the different layers. So, a detailed SEM-EDS study was made to see the microstructure of the layer, and the local chemical compositions. SEM-EDS analysis show the structure of the different layers. The black and yellow-brown layer built-up from particle agglomerates, where different particles, dust sticked together (Figure 3. right) The green layer is really a continuous one, where particles are integrated to a matrix. It was observed during the sampling, the black and yellow-brown layers are brittle, and these are easily detached from the surface. It was suggested to remove it during the conservation process due to this property. Additionally, in the case of yellow-brown layer EDS analysis showed high iron content, the colour of thin layer originates to the iron-oxide content.
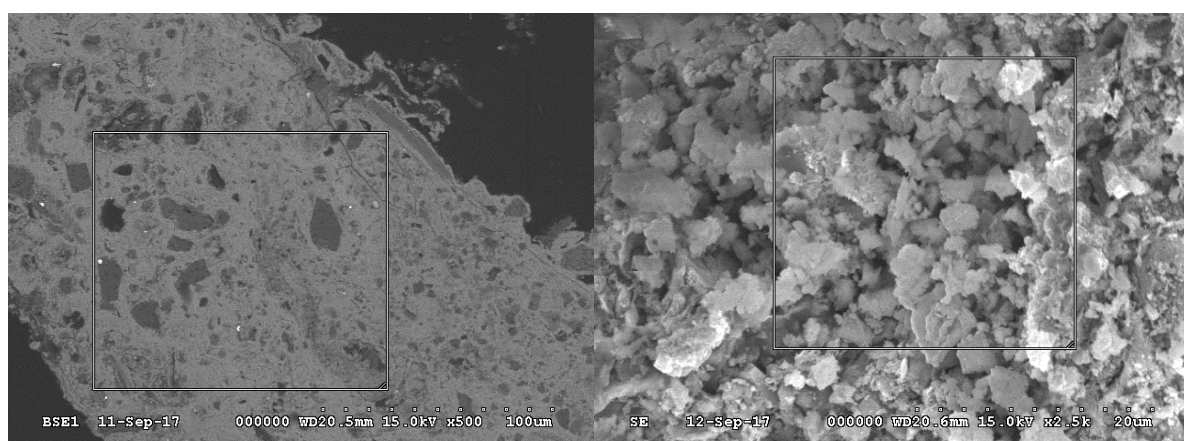

Figure 3. The structure of the continuous green layer (left micrograph) and the yellow-brown layer (rignt micrograph).
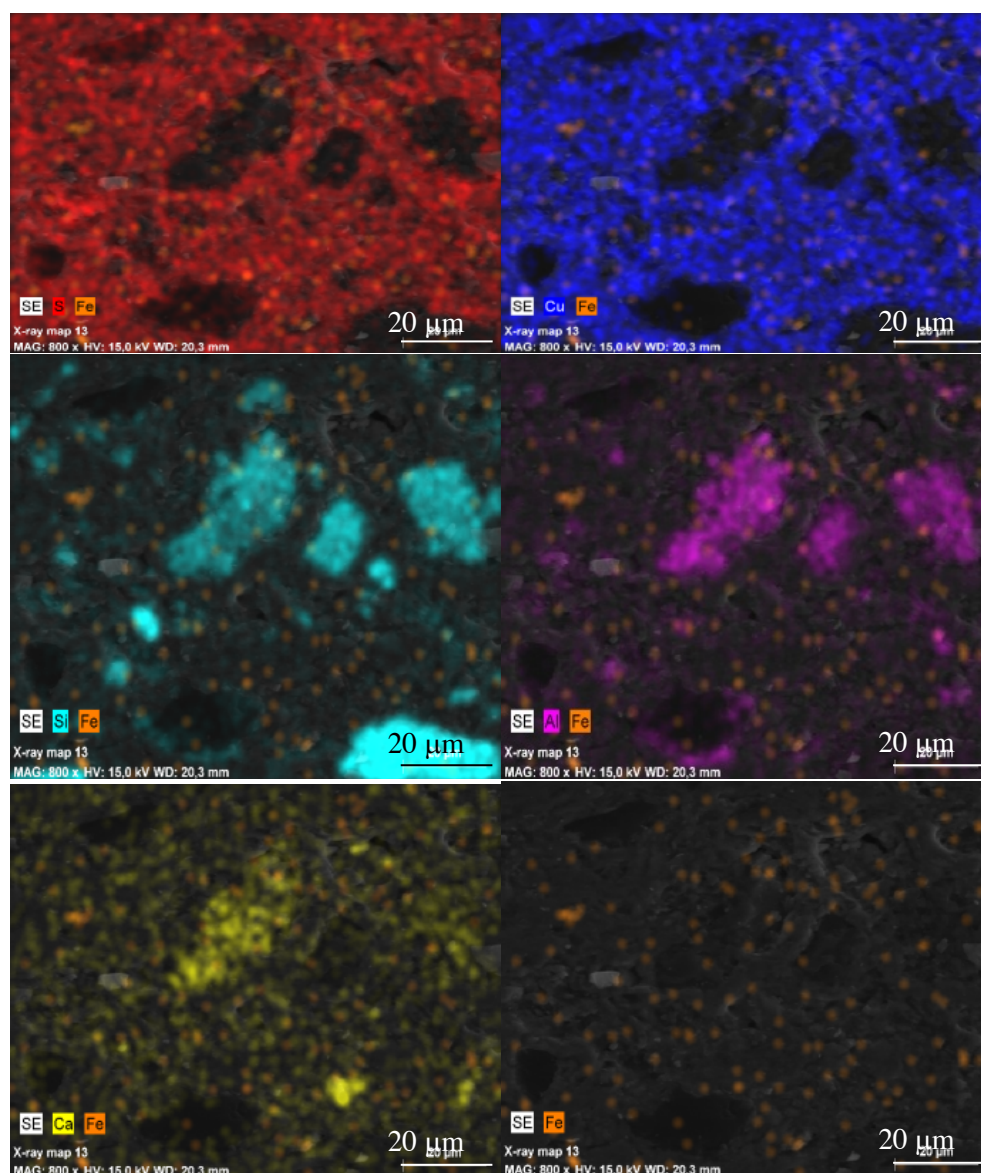
Figure 4. Element distribution map of the surface of the continuous green layer. The matrix is the patina the particles are from dust.

The green layer seems compact and it was hard to remove from the surface during the sampling. It was also analyzed, and high copper and sulfur content were measured, so this assumed as the patina layer. Figure 4 shows the distribution of different elements in a typical cross section of this layer. It reveals that the particles have a high aluminum and silicon content. These elements clearly distinguish the particles and the matrix. Calcium content detected in the particles only, which did not contain sulfur. This shows that the layer either contains calcium, but not in gypsum form, it come from the dust. An interesting observation is that the iron distribution is nearly uniform, and small particles can be seen mainly in the matrix material. Chlorine did not detect, so chlorides or other substances which contains chlorine did not exists on the surface of the statutes.

These results show that the particles are also from dust, which deposited to the surface. The matrix is the real corrosion product, the patina which growth continuously during the corrosion process. The patina layer involved the dust particles with its growth process. The results of the EDS analysis and the suggestions will compare to an XRD phase analysis later.

FTIR analysis of the samples performed to look for organic material or polymers from a possible previous treatment. Without any treatment the samples examined and neither organic nor polymeric materials were found (Figure 6.). The curves on Figure 6 cannot show any radicals or organic substances. Three samples were tested: a2, a3 and a6. Samples a2 and a3 are taken from green layer. Sample a2 was taken from Toldi's sword, sample a3 take from Toldi's helmet. sample a6 is a sample from the black layer and it was taken from Toldi's helmet. There is no significant difference in the FTIR spectra. Just a small amount of carbonates could be identify.
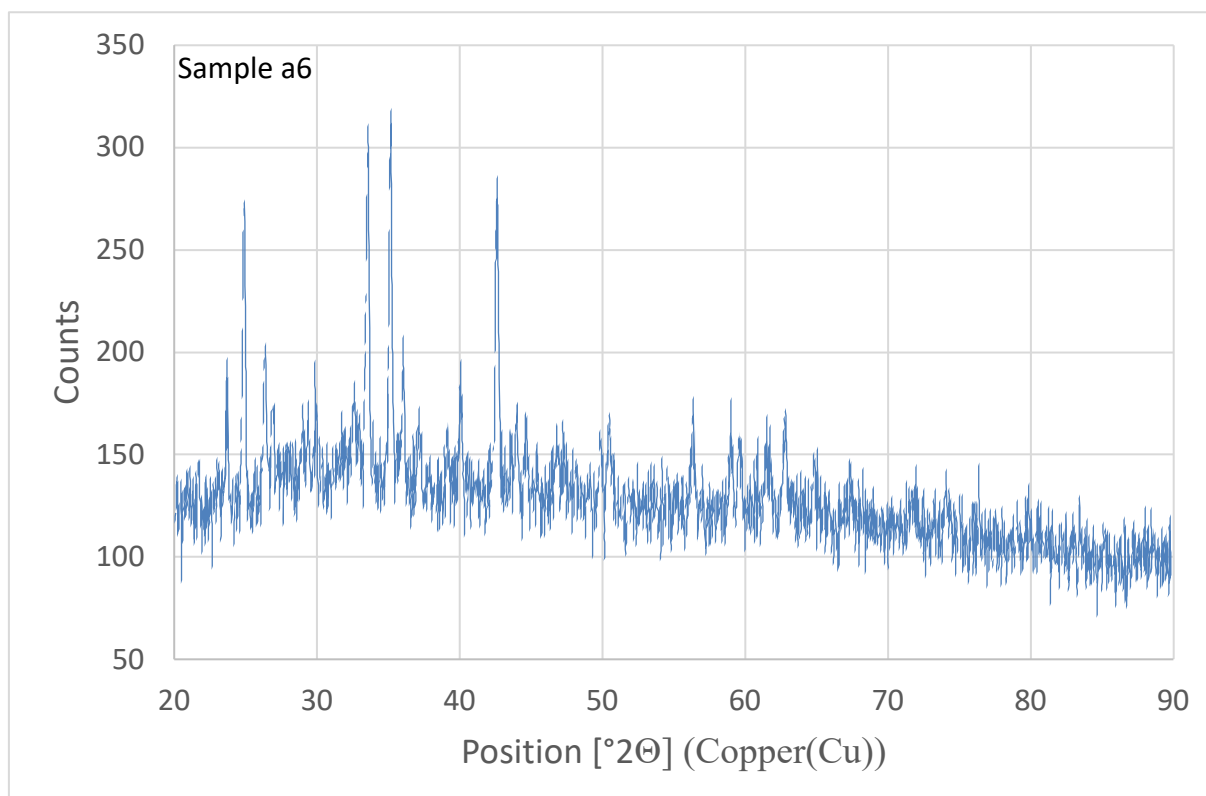

Figure 5. The XRD spectrum of the green layer.

The XRD analysis of the green layers were performed (Figure 5. sample a3). The intensity in the XRD spectra was low due to the small amount of samples but $CuSO_4 \cdot 2Cu(OH)_2$ and $CuSO_4 \cdot Cu(OH)_2$ were clearly identified as the components of the patina layer. The SEM-EDS observations helped to identify the different compounds. $Al_3Fe_5O_{12}+SiO_2$ identified as dust particles. Next to these SnO, CuO_2 and Fe_2O_3 oxides were found in the sample. Tin and copper oxides are also a corrosion product of the raw material. The SEM micrograph revealed the distribution of the iron-oxide particles. The XRD analysis told nothing about the status of calcium due it's small concentration.
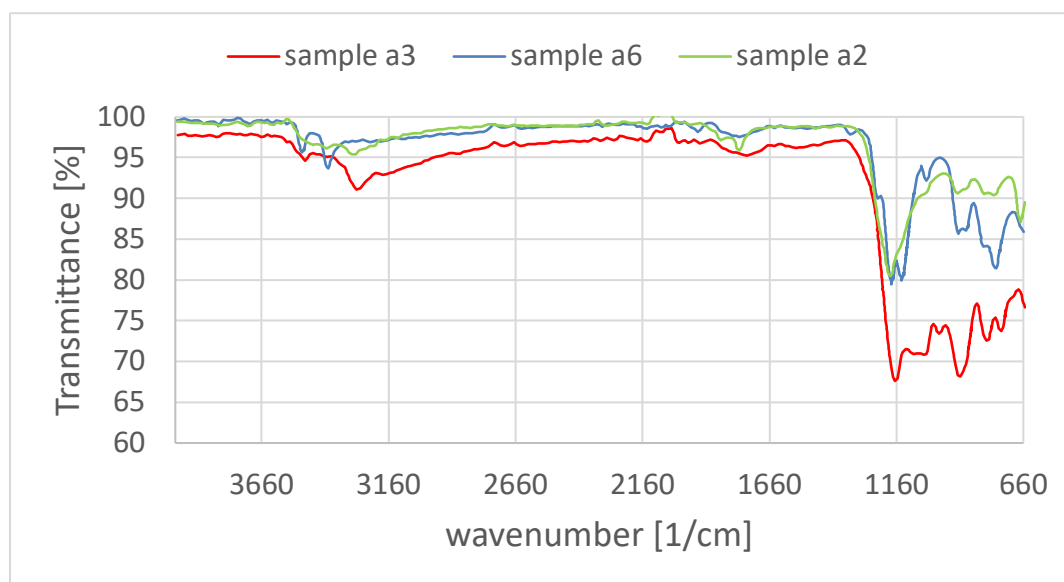
Figure 6. The FTIR spectra of three different samples of green layer.

The FTIR spectra identified only carbonates which either could be a copper compound in the patina layer or calcium-carbonate content of the dust particles. These results show another evidence the absence of gypsum in the layer.

The results suggest that it was necessary to remove the black and the yellow-brown layer from the surface of the statue. The green layers could be left over the surface and could be used a patinating process to equalize the outlook of the surface. The black and yellow-brown layers are brittle layers and easily detached from the statue, so a mechanical cleaning process (blasting) can be used. Neither polymeric nor other organic substances were found which makes necessary a special chemical treating during the cleaning. Chlorine or other substances also did not find which could cause problem during the patinating process.

Figure 7. The Toldi's shield after the claning experiment.

Based on this information cleaning probes were made to choose the best cleaning, blasting agent. The results of a $NaHCO_3$ particles blasting is showed by figure 7.

The chosen cleaning process removes all undesired material from the surface, therefore other chemical treatment was not necessary just the patinating process (Figure 8.). After the patinating process a protective thin resin layer also applied which did not change the outlook of the statues just gives an additional protection.

Figure 8. The cleaned and patinated shield.

Currently the statues can be seen at the original place and the treatment gives the original beauty of the statues. These again a great sight of the Museum Garden and of the Hungarian National Museum.

4. Conclusions

The statues of János Arany (The Poet and two main character of His poetry: Toldi and Piroska) from the Garden of the Hungarian National Museum were conserved. Before the conservation process a detailed material testing of the corrosion products were made. Different layers were identified: green layer, yellow-brown and black. Green layer was a patina, which contains silicate particles. It is a continuous intact layer, and it is hard to remove it from the surface. The other layers mainly formed by dust. These layers mainly particle agglomerates. Therefore, these are brittle and easily detach from the surface. The colour of the yellow-brown layer originates to its iron-oxide content. Detailed analysis was made to define the chemical composition, the microstructure of the layer and identify the different compounds. The main question was the existence of dangerous materials as chlorine, gypsum or organic compounds which could have a harmful effect to the conservation process or the lifetime of the conservation. Chlorine or other organic or inorganic compound did not find in the corrosion layers which can damaged the bronze material or can make reaction with the materials used by cleaning and patinating. Calcium content was detected, but in small amount. The tests show that the calcium presence as carbonate. The patina layer contains copper-sulphate and copper-hydroxide. This contains small silicate particles. The green layer is a ductile layer and sticks to the bronze material well, but the other layers are brittle. During the conservation the process the patinating chosen with the removal of the mentioned black and yellow-brown layers. $NaCO_3$ particle blasting was chosen for cleaning.

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