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Conservation purpose material testing of corrosion products on outdoor bronze statues in Museum Park of Hungarian National Museum

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***Abstract* – A detailed material testing were made before the conservation project of the János Arany statues of Garden of Hungarian National Museum. The scope of the testing to analyse the corrosion layers, and help to develop the best cleaning and protection practice. Samples were taken from more positions and the samples were analyzed by SEM-EDS, XRD, FT-IR methods. This article introduces the results of the testing the relevant effect to the conservation process.**

I. INTRODUCTION

Outdoor sculptures, especially metal ones, are constantly exposed to atmospheric corrosion, that is the reason why their protection is extremly important. [1,2] Corrosion on 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 which element or compound in the corroded layer can damage the surface of the statue during the conservation process or which not. Structure of corrosion influences its stability: can be removed from the surface easily or not, could it 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 is also a critical 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 the conservation progress can be performed. Using detailed material testing can answer these questions.[9]

Statue of János Arany, who was one the greatest Hungarian poet, is situated in the park of Hungarian National Museum (Figure 1). János Arany (1817-1882) was a Hungarian journalist, writer, poet, and translator. He is often said to be the "Shakespeare of ballads" – he wrote more than 102 ballads which have been translated into over 50 languages, as well as the Toldi trilogy, to mention his most famous works. Arany was elected a member of the Hungarian Academy of Sciences in 1858. He was the secretary-general of the Academy from 1865. He participated in the Revolution 1848-49 as a solder called “nemzetőr” and then worked for the Ministry of the Interior led by Bertalan Szemere.

Janos Arany's statue in the Museum Garden is surrounded by two other sculptures Toldi and Piroska who are the main characters of his poetry (Figure 2). Conservation of outdoor sculptures were 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.

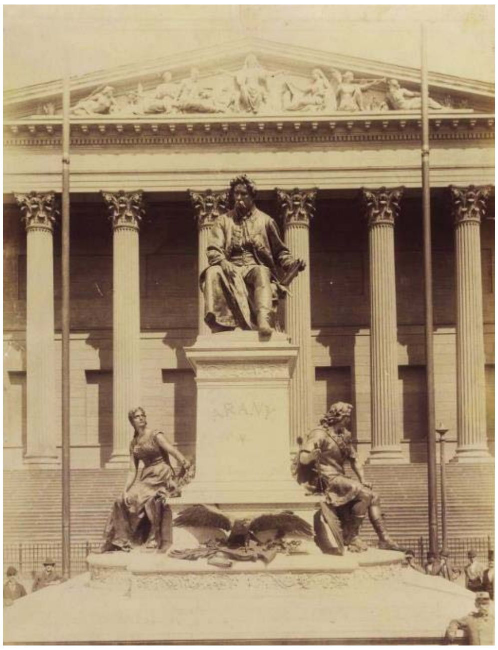

Fig. 1. The János Arany statue at the front of the Hungarian National Museum after the consecration at 1893.

Fig. 2. The status of the statues before the conservation work. The photograph shows the statues of János Arany (up) and Toldi (center). The statues covered by different corrosion layers.

Detailed investigation of corrosion products was performed before conservation because of the previously mentiond reasons. Chemical composition of corrosion product were compared to the composition of the sculpture's material. Its aim was to determine the chlorine compounds. Presence of chlorine compounds on the surfaces was not so probable in Budapest due to the continental atmosphere but this phenomenon was wanted to exclude. 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 content of gypsum, furthermore organic's content.

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 again in the park of Hungarian National Museum.

Fig. 3. The different type of layers on the surfaces of status. Upper image shows the black and porous green layer, lower image shows the continuous green and yellow-brown layer.

II. MATERIAL AND METHODS

pXRF survey was made on the statues in several positions. The aim of this survey was to study the elements and assumed chemical composition. Oxford XMET 8000 type pXRF was used in the survey.

Powder samples were taken from the mentioned areas from different positions and statues. Firstly SEM-EDS analysis were made to study the structure and the chemical composition of the different materials. (Hitachi –S4300 CFE). XRD measurement is made by Siemens (Cu K Alfa) to identify the different compounds. Only small number 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.

III. RESULTS AND DISCUSSION

Basically, four different surface elements were identified (Figure 3):

- surface areas covered by black layer;
- yellow-brown layer;
- porous green layer on the surface;
- continuous green layer on the surface.

The documentation wrote a bronze raw material. There were metallic surface areas where it was measured with 9,0w/w% tin content. According to the composition of the raw material copper and tin content was measured all the mentioned position. Silicon, aluminum and iron content also was detected in all position. However, silicon and aluminum content were significantly larger in the black layer. Phosphorus content was found in the yellow-brown areas, which could be dangerous in terms of cleaning. This layer contained the largest amount of silicon, iron and aluminum. Higher sulfur content was detected at the green layers, which originated to the patina first (Table 1).

Table 1. The results of the pXRF analysis. The table shows the chemical composition in w/w%.

place	color	Cu	Sn	Pb	Si	Al	Fe	S	P
sword	green (a2)	rem.	23.85	3.77	5.77	2.53	1.41	1.6	1.23
helmet	green (a3)	rem.	24.63	3.01	4.87	1.44	2.71	2.42	1.35
helmet	yellow-brown	rem.	10.72	1.31	10.73	4.02	11.28	1.87	2.24
helmet	black (a6)	rem.	4.33	0.61	7.71	3.07	1.18	0.18	0.39
wreath	green	rem.	24.69	1.37	2.35	1.13	0.30	3.53	-
wreath	metallic	rem.	9.0	0.23	0.88	-	-	0.72	0.09
wreath	black	rem.	7.16	0.12	6.59	1.33	1.7	-	-

SEM-EDS analysis was performed on selected samples as it was mentioned above. SEM-EDS analysis show the structure of the different layers. The black and yellow-brown layer are particle agglomeration, where different particles have stuck each other from dust (Figure 4). This layer had not had a solid nature.

The green layer is solid, continuous one, where particles are incorporated to a matrix. The black and yellow-brown layers are brittle, and these could easily detach from the surface. It was suggested to remove it during the conservation process. Additionally, in the case of yellow-brown layer EDS analysis showed high iron content, the color of thin layer come from the iron-oxide content.

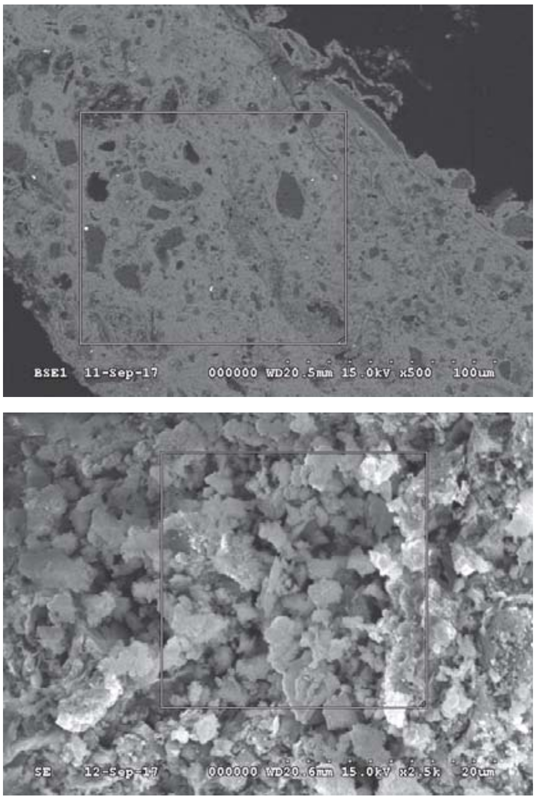

Fig. 4. The structure of the continuous green layer (upper micrograph) and the yellow-brown layer (lower micrograph).

The green layer was also analyzed, and high copper and sulfur content were measured, so this assumed as the patina layer. Figure 5 shows the distribution of different elements, and it reveals that the particles has a large 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 content was not detected. So, chlorides or other compounds which contains chlorine did not exists on the surface of the statues, or just so minor concentration that won't react during the conservation work. XRD phase analysis was also performed.

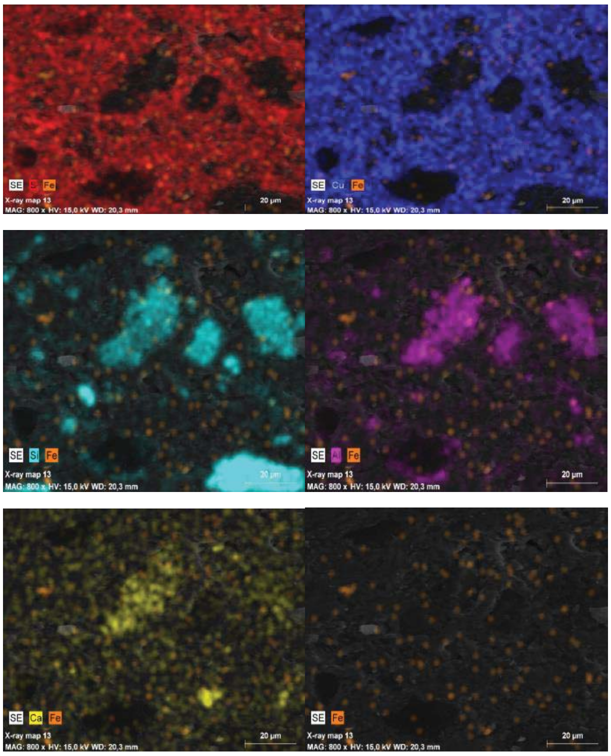

Fig. 5. Chemical composition map of the continuous green layer. The matrix is the patina the particles are from dust.

XRD and FTIR tests were made on other powder samples. Samples are taken from the previously analyzed positions. The samples were named by a2, a3, and a6. Figure 6 shows the position of the sampling.

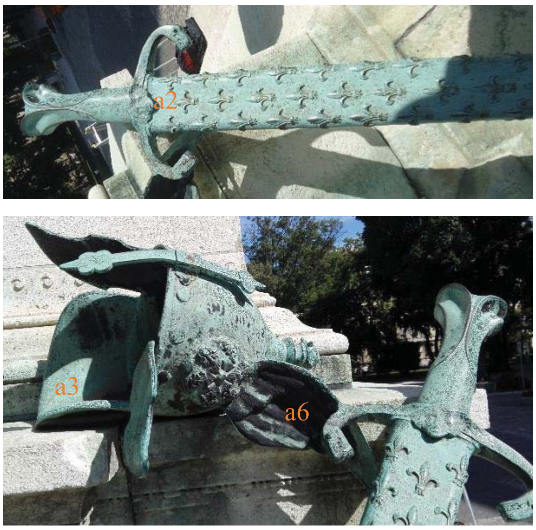

Fig. 6. The position of the sampling. Sample a2 was taken from the green layer of the Toldi's sword. Samples a3 and a6 taken from the surface of Toldi's helmet. Sample a3 represented the green, while a6 taken from the black layer.

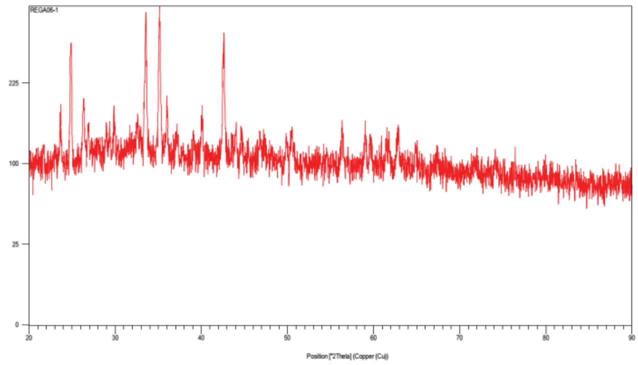

Fig. 7. The XRD spectrum of the green layer a2. This green layer formed on the Toldi's sword. This layer had a solid nature and a similar microstructure as it was shown on Figure 4.

The intensities in the XRD spectrum 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 main components of the patina layer. $Al_3Fe_5O_{12}$+SiO_2 identified as dust particles in the matrix at Figure 5. Next to these compounds SnO, CuO_2 and Fe_2O_3 oxides were identified in the sample. Tin and copper oxides are a corrosion product of the raw material. The SEM micrographs revealed the uniform distribution of the iron-oxide particles. The XRD analysis told nothing about the calcium due it's small concentration.

FTIR analysis of the samples (Figure 7) were performed to look for organic material or polymers which could be on the surface probably from an earlier treatment. Without any treatment before the FTIR analysis the samples were examined and neither organic nor polymeric materials were found (Figure 8)

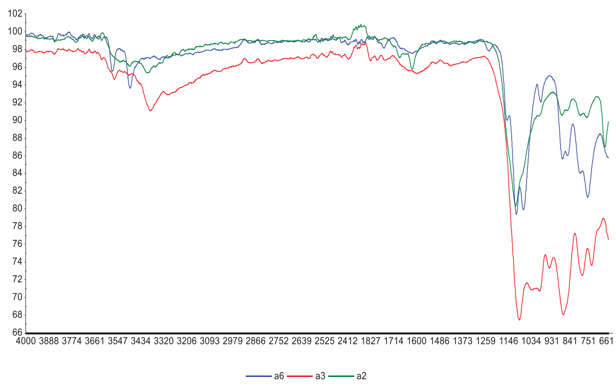

Fig. 8. The FTIR spectra of three different samples of green and black layers. Figure 6 shows the position of the sampling, and Table 1 contains the chemical composition of the samples measured by pXRF.

The FTIR spectra only identified 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 can easily detach from the statue, so a mechanical cleaning process (blasting) can be used. Neither polymeric nor other substances were found which makes necessary a special chemical treating during the cleaning. Chlorine or other substances also did not found which could have cause problem during the patinating process.

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 9.

The chosen cleaning process removes all undesired material from the surface, therefore other chemical treatment was not necessary just the patinating process (Figure 10). After the patinating process a protective thin resin layer was also applied which did not change the outlook of the statues just gives an additional protection.

Fig. 9. The Toldi's shield after the claning experiment. The left side of the shield was cleaned by particle blasting. The right side of the shield shows the original outlook of the object.

Fig 10. The cleaned and patinated shield. The leaf symbols revealed after the cleaning and patinating process which were hidden by the removed corrosion layers.

Currently the Statues can be seen at its original position and the treatment gives the original beauty of the statues. Several fine hidden features of the statues became visible which were under the corrosion layers. These sculptures are again a great sight of the Museum Park and the Hungarian National Museum.

IV. CONCLUSION

The statues of János Arany from the park of the Hungarian National Museum were conserved. Before the conservation process a material testing of the corrosion products were carried out. Different layers were identified. Green layer was a patina, which contains silicate particles. The other layers mainly formed by dust. Chlorine or other organic or inorganic compound, which can damage the bronze material, or can make reaction with the materials during the cleaning and patinating process, did not found in the corrosion layers. Calcium content was detected, but only in small amount. The tests show that the calcium exists as carbonate. The patina layer contains copper-sulfate and copper-hydroxide. These parts of the corrosion layers contain 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 process patinating was carried out with the removal of the mentioned layers. The chosen cleaning process before patinating was a blasting with $NaCO_3$ particles.

V. ACKNOWLEDGEMENTS

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