Characterization of some archaeological iron and bronze artifacts at king Farouk corner museum in Helwan

خصائص بعض المشغولات الأثرية الحديدية والبرونزية في متحف ركن الملك فاروق بحلوان

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Abstract

The Farouk Corner Museum in Helwan contains iron and bronze artifacts in its garden and marina. These artifacts are an iron table with decorative units and the royal crown with the name of King Farouk made of bronze. These artifacts were deteriorated by the impact of their presence near the Nile River as a permanent source of high humidity, as well as air pollution in the Helwan area, in addition to the absence of periodic maintenance. The heterogeneous surface layers were examined using a stereomicroscope and a scanning electron microscope, and it was found that they consist of rust products mixed with grains of quartz and dust. The analysis with the EDX unit attached to the scanning electron microscope revealed the presence of iron, chlorine and oxygen in the iron table samples. The elements copper, tin, oxygen, calcium, magnesium, chlorine and carbon also appeared in the samples of bronze works. The appearance of these elements is due to the components of iron and bronze works, and the contents of their surface layers of various rust products mixed with sand and dust grains. These results were confirmed by X-ray diffraction analysis of the presence of magnetite Fe_3O_4, lepidocrocite FeO (OH) and quartz SiO_2 minerals in the iron table samples. Also, the presence of cuprite Cu_2O, atacamite $Cu_2Cl(OH)_3$, paratacamite $Cu_2(OH)_3Cl$ and quartz SiO_2 in the samples of bronze works. Finally, the necessary treatment and maintenance operations were recommended for iron and bronze works after studying their condition to protect and preserve them from deterioration.

Keywords: King Farouk Corner Museum، Iron, Bronze, Antiquities, Deterioration, Conservation.

الملخص

يحتوي متحف ركن فاروق بحلوان على مشغولات حديدية وبرونزية في حديقته والمرسي النيلي الخاص به. هذه المشغولات عبارة عن منضدة حديدية بها وحدات زخرفية ومشغولات علي شكل تاج ملكي واسم الملك فاروق من البرونز. تعرضت هذه المشغولات الأثرية للتلف بتأثير وجودها بالقرب من نهر النيل كمصدر دائم للرطوبة العالية، فضلاً عن تلوث الهواء في منطقة حلوان ، بالإضافة إلى عدم وجود صيانة دورية. تم فحص الطبقات السطحية غير المتجانسة باستخدام الميكروسكوب المجسم

والميكروسكوب الإلكتروني الماسح ، ووجدت طبقات من مركبات الصدأ مختلطة بحبيبات الكوارتز والأتربة. أظهر التحليل بوحدة [EDX] (وحدة تشتيت الأشعة السينية الملحقة بالميكروسكوب الإلكتروني الماسح) وجود عناصر الحديد والكلور والأكسجين في عينات المنضدة الحديدية. كما ظهرت عناصر النحاس والقصدير والأكسجين والكالسيوم والماغنيسيوم والكلور والكربون في عينات المشغولات البرونزية. ويرجع ظهور هذه العناصر إلى مكونات مشغولات الحديد والبرونز ومحتويات طبقاتها السطحية من مركبات الصدأ المختلفة المختلطة بحبيبات الرمل والأتربة. تم تأكيد هذه النتائج من خلال تحليل حيود الأشعة السينية حيث أظهرت وجود معدني المجناتيت والكوارتز في عينات المنضدة الحديدية. أيضا أظهرت العينات وجود معادن الكوبريت والاتاكاميت والباراتاكاميت والكوارتز في المشغولات البرونزية. وأخيراً، تمت التوصية بعمليات العلاج والصيانة اللازمة للمشغولات الحديدية والبرونزية بعد دراسة حالتها لحمايتها والحفاظ عليها من التلف مرة آخرى .

الكلمات الدالة: متحف ركن الملك فاروق، آثار، حديد، برونز، تلف، صيانة.

1. Introduction

The Farouk Corner Museum and its Nile Marina site have iron and bronze artifacts. It includes two bronze artifacts at the entrance door to the museum, taking the shape of the royal crown and bearing the name of King Farouk Fig. (1), in addition to an iron table with geometric and floral motifs. Decorative ironwork was largely undertaken in wrought iron until the latter half of the 18th century, when cast iron became increasingly and the demand for mass-production. These bronze and iron artifacts suffer from deterioration due to their presence on the shore of the Nile, Figs. (2), (3), (4). As well as its presence in an open atmosphere that contains pollution gases and solid suspensions[1] resulting from the activity of factories in Helwan area such as, cement and petrochemical and various other industrial activities. These industrial activities lead to air pollution with the presence of a permanent source of moisture led to the formation of various corrosion compounds on the surfaces of iron and bronze artifacts [2] in the garden of Farouk Corner Museum. Besides, the effect of car exhaust due to heavy traffic near the museum, [3] in addition to the absence of continuous periodic conservation of these artifacts[4]. These circumstances have caused the iron and bronze artifacts to be deteriorated. This is evidenced by the formation of corrosion compounds in different colors on the surfaces of these artifacts[5]. The

1 Pan, C., et al., (2016), Atmospheric corrosion of copper exposed in a simulated coastal-industrial atmosphere. J Mater Sci Technol 33(6) ,P.12.
2 Oudbashi, O., (2016), Investigation on corrosion stratigraphy and morphology in some Iron Age bronze alloys vessels by OM, XRD and SEM–EDS methods, Applied Physics A,.P. 34.
3 Wang, Q., (2007), An investigation of Deterioration of Archaeological Iron, Studies in Conservation Journal. Vol, 52, P.20.
4 Sobhy D. R., (2014), "Study of corrosion mechanism of iron artifacts found in a chloride-rich environment and the methods of chloride removal; with application on selected objects", PhD, Conservation department, Faculty of Archaeology, Cairo University,P.43.
5 Badea G. E., (2011), "Corrosion studies in atmospheric environment", 17th Building Services, Mechanical and Building Industry Days" Urban Energy Conference, Hungary ,P.50.

iron table was also contains paints over the iron surface. It was deteriorated, eroded and peeled in different places on its surface. Relative humidity is one of the most important factors of deterioration as it interacts and causes physical and chemical changes; [6] in addition, it increases the effect of various deterioration[7]. The presence of ions and salts in different concentrations leads to the formation of corrosion compounds[8]. It is an electronic process where a very thin layer of corrosion products is formed that is not connected to the surface of the metal and the increase in humidity leads to an increase in the thickness of this layer formed of corrosion on the surface of the metal,[9] . This research aims to study the deterioration phenomena of the iron and bronze artifacts due to the impact of the surrounding environment containing air pollution and a permanent source of high humidity from the waters of the Nile River. This is done by carrying out various examinations and analyses to identify the components of the surface layers containing corrosion products to develop proposals for the conservation of these archaeological metal works and to preserve them from deterioration.

2. Materials and Methods

A cross section was made of a sample of bronze and another of iron artifacts. The samples were placed in araldite, allowed to dry, and their surfaces were polished. A polarizing microscope was used to examine the cross-section of the samples, as they contain corrosion products. Leica S9i, Stereozoom microscope was used for samples examinations (Stereozoom microscope with zoom magnification changer for incident light with integrated MC190 HD 10MP full HD digital video camera system). Samples were analyzed by Philips (XL30), Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray analysis (EDX). X-ray diffraction analysis carried out with Phillips X-ray diffraction equipment model pw/1840 with Ni filter, Cu radiation 1.54056 A° at 40 KV, 25mA, 0.05 /sec. Measurements were carried out on powders of the bronze and iron samples, in the range $0° < 2\theta < 60°$ with a step of 0.02°.

6 McCafferty E., (2010), “Introduction to corrosion science”, Springer: New York.P.21.
7 Shashoua Y. and Matthiesen H., (2010), “Protection of iron and steel in large outdoor industrial heritage objects”, Corrosion Engineering, Science and Technology, Vol 45, No 5, p.38.

8 Ingo G.M., (2019), Surface studies of patinas and metallurgical features of uncommon high-tin bronze artifacts from the Italic necropolises of ancient Abruzzo (Central Italy), Applied Surface Science, 470.p.231.

9 Oudbashi, O. (2015), From Excavation to Preservation: Preventive Conservation Approaches in Archaeological Bronze Collections, Wallon. P.257.

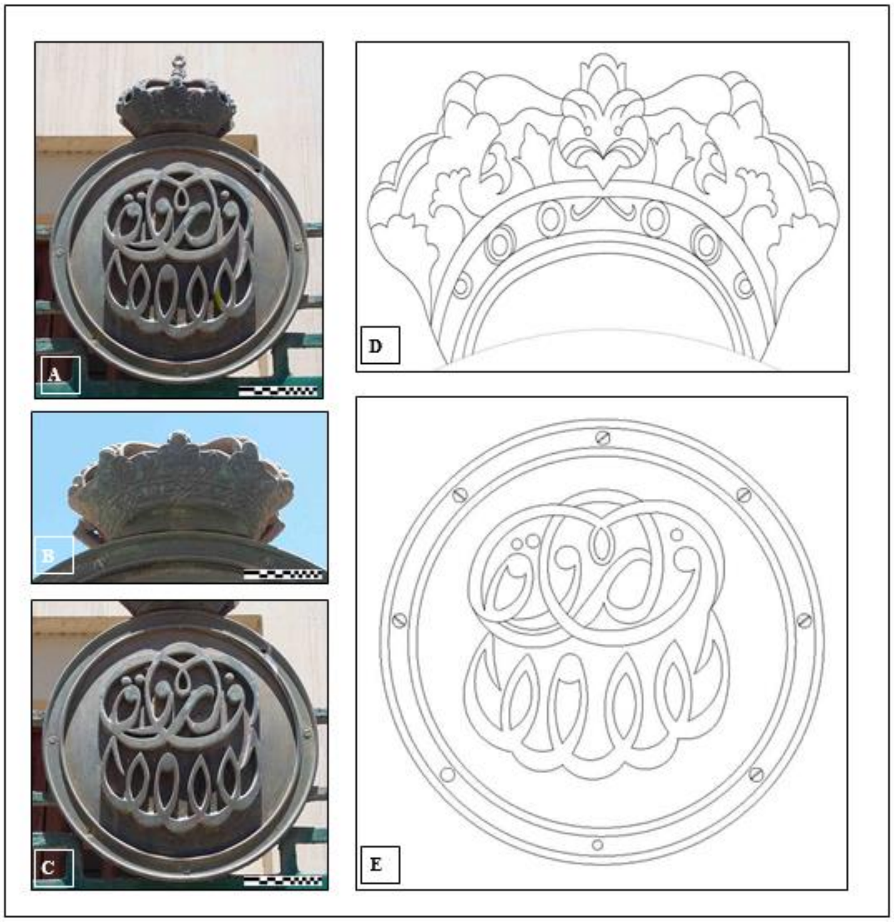


Fig. 1 A, B and C, The bronze artifacts at the entrance door of King Farouk corner museum, which take the shape of the royal crown and bear the name of King Farouk, D and E represent auto CAD recording of the bronze artifacts.

Fig. 2 A, B show the corrosion products on the surface of the bronze objects, C, D, E show the corrosion compounds and details of the iron table at King Farouk corner museum.

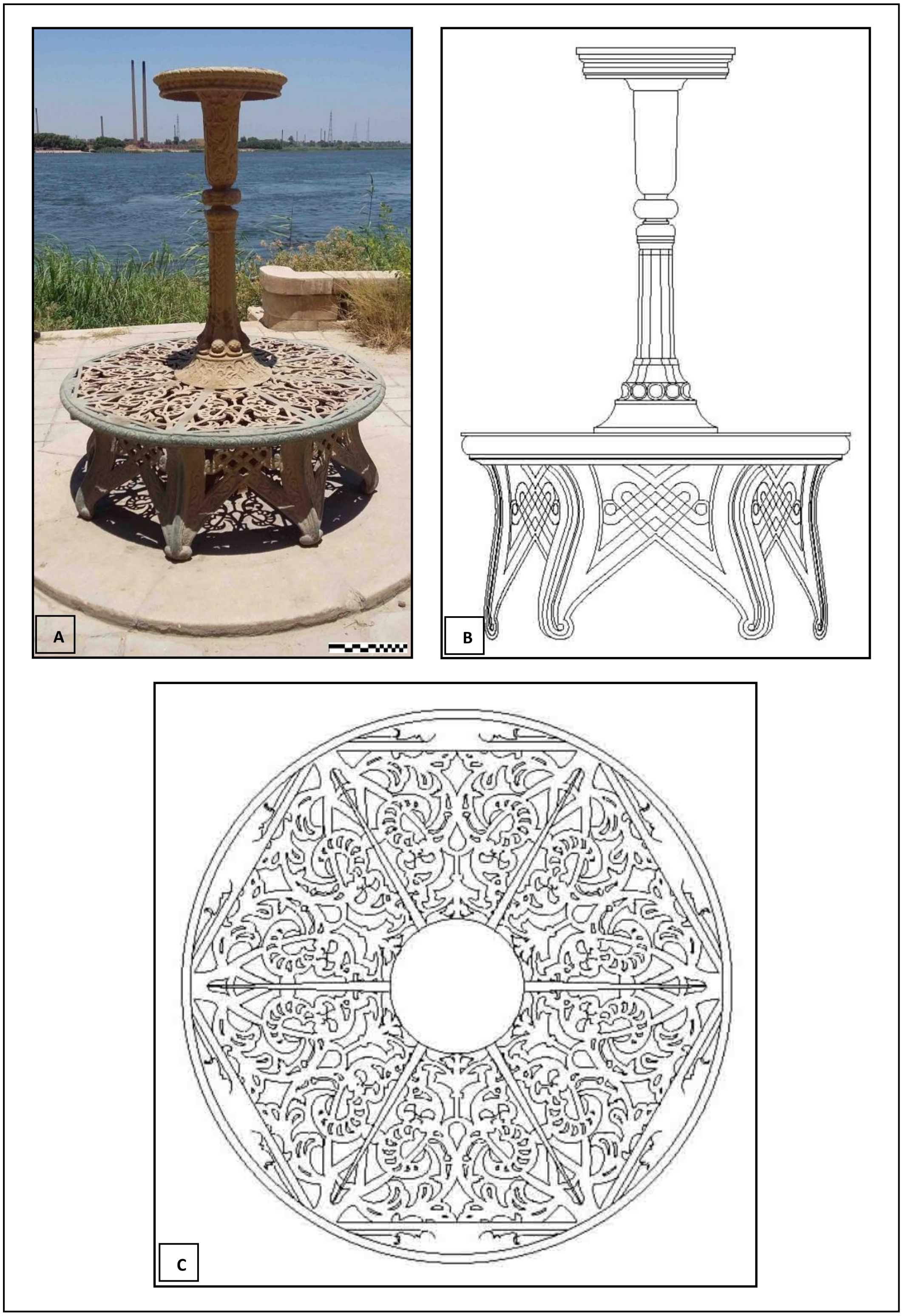


Fig. 3 A, The iron table at King Farouk corner museum, B and C recordings of the iron table using

auto CAD showing floral and geometric motifs of the table.

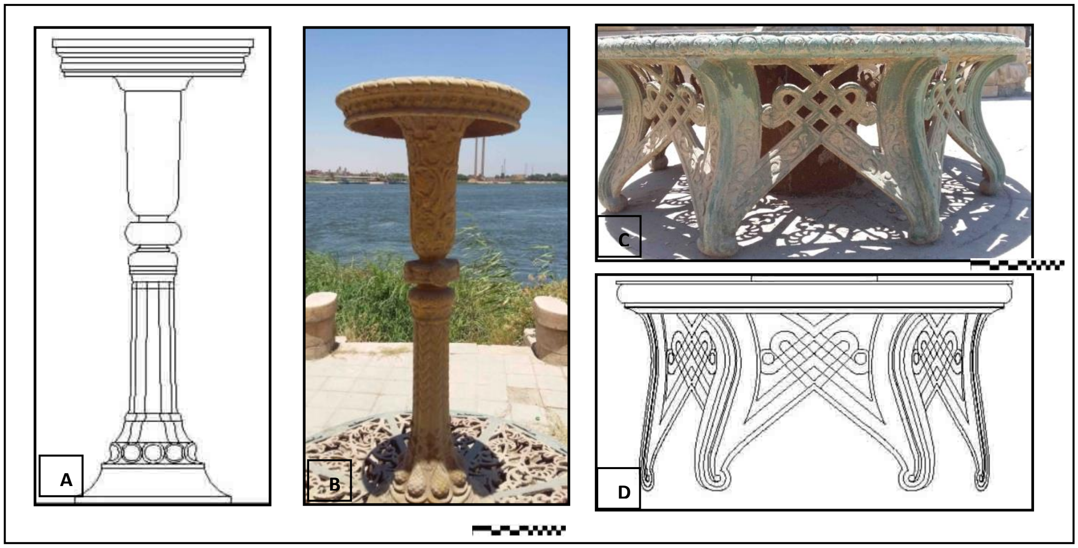


Fig. 4 A and D, Details of the iron with auto CAD recording, B and C, details of the iron table at King Farouk corner museum.

Results 3.

3. 1 Examination by Stereo microscope

The bronze and iron artifacts suffer from damage due to their presence on the shore of the Nile. It is also present in the air pollution in the Helwan region. This led to the formation of various rust compounds on the surface of the iron artifacts. Examination shows that, there are different layers of corrosion in the iron table and bronze works and cracks, especially in the areas of welding between the different parts of the table. The corrosion compounds appeared in green in its degrees in the bronze sample, fig. (5). Rust compounds appeared in green and yellowish brown color, interspersed with cracks and separations with an overlap between the layers of rust and sand grains, fig. (6).

3 .2 Examination by Scanning Electron Microscope (SEM)

Examination with a scanning electron microscope revealed the presence of cracks, separations and corrosion in the surface layers in some parts of the iron table sample, in addition to the presence of rust layers. Micro cracks, corrosion, separations between the grains and metal components also appeared in the bronze works, figs. (7), (8).

3. 3 Analysis by (EDX) unit equipped with (SEM)

Energy-dispersive spectrometry (EDX), which equipped with Scanning electron microscopy (SEM), was used to study the component of the surface layers which represent the corrosion products. The analysis for the iron sample shows that it contains Fe, O and Cl elements. On the other hand, the analysis for the bronze sample shows that it contains Cu, Sn, O, Ca, Mg, C and Cl elements, figs. (9), (10).

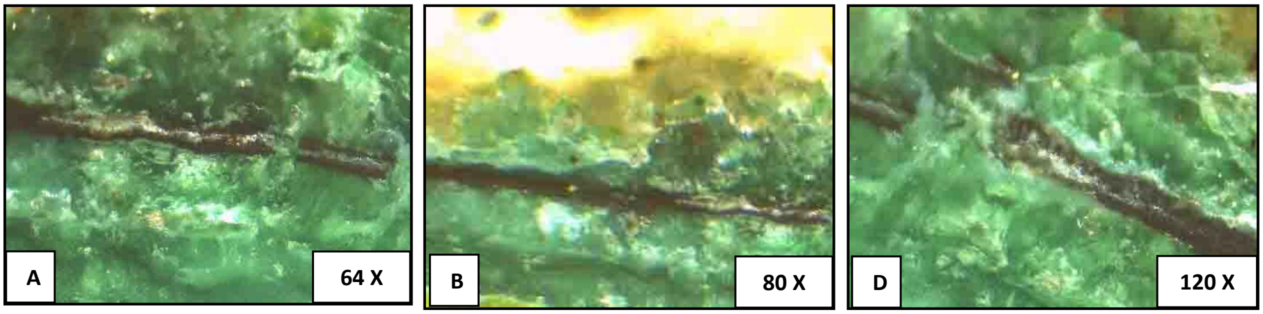


Fig. 5 A, B, C, shows the layers of corrosion products with the bronze alloy through the stereo microscope examination of the bronze artifact's samples.

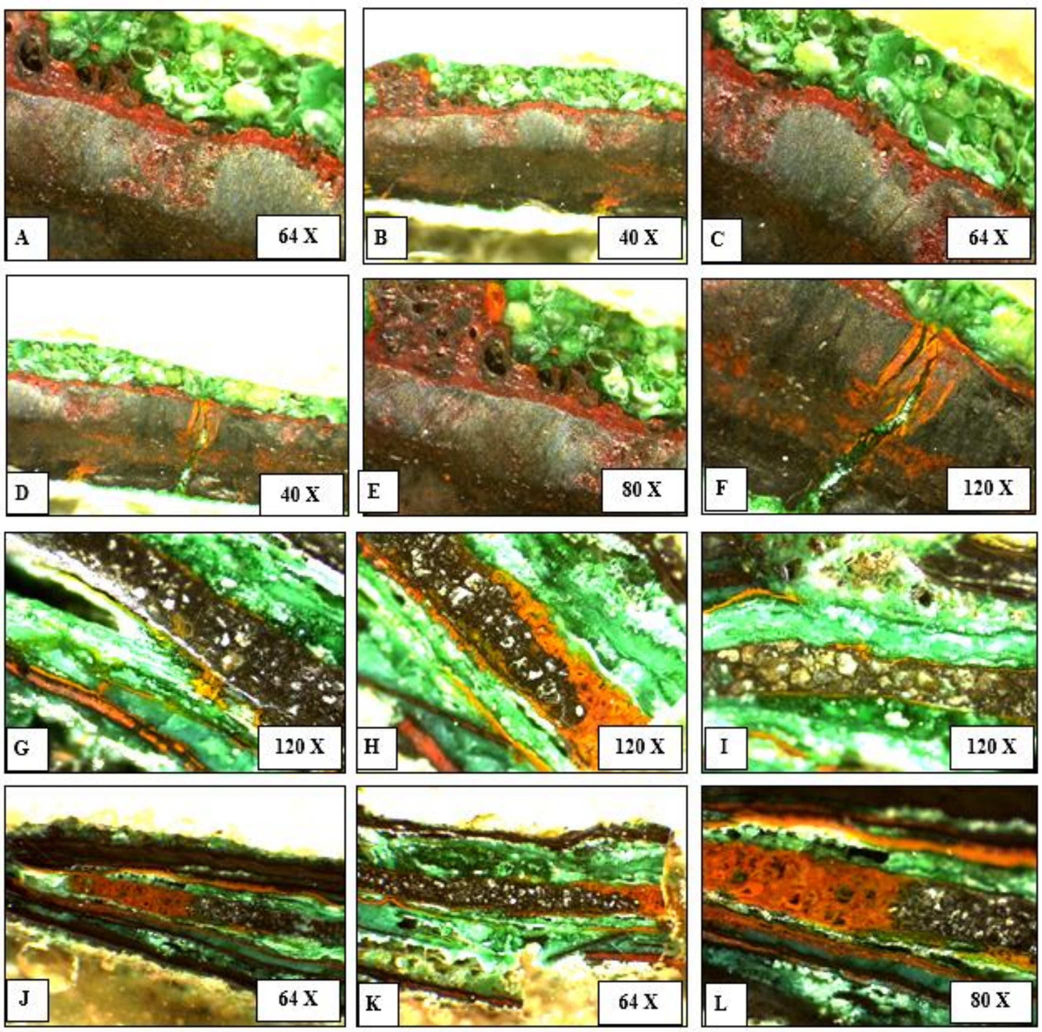


Fig. 6 A-L, shows cracks, erosion and layers of corrosion products in different colors with iron through the stereoscopic examination of the iron table samples.

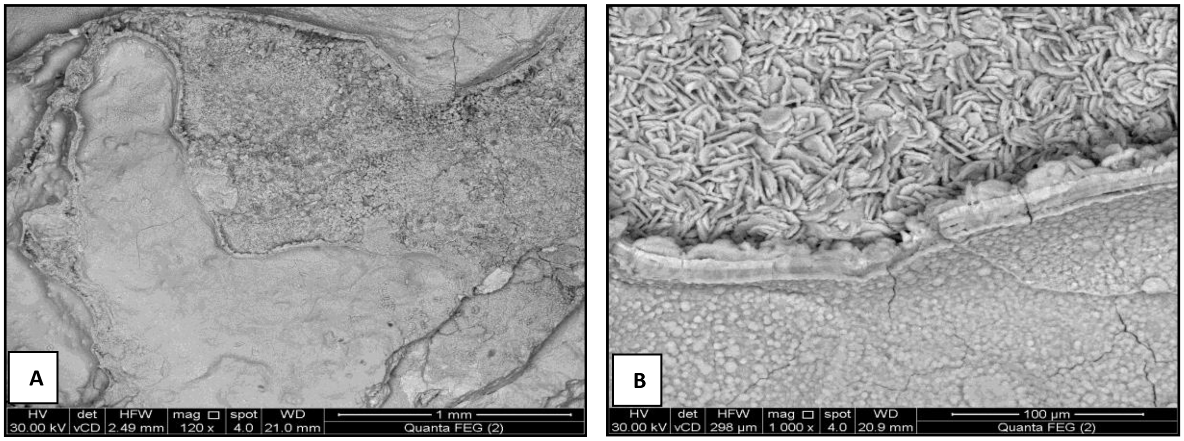


Fig. 7 A, B, shows cracks, breaks, erosion and layers of rust from the microscopic images of the scanning electron microscope of the iron table.

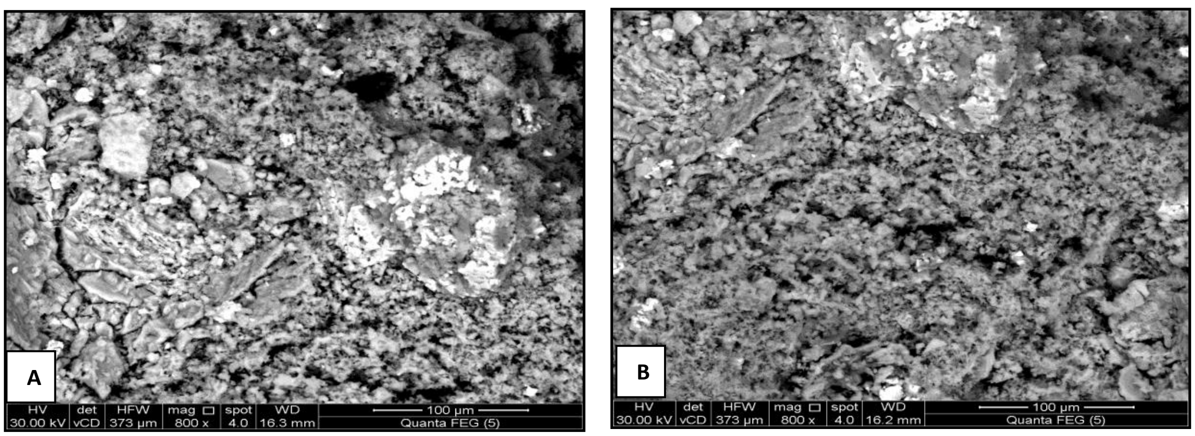
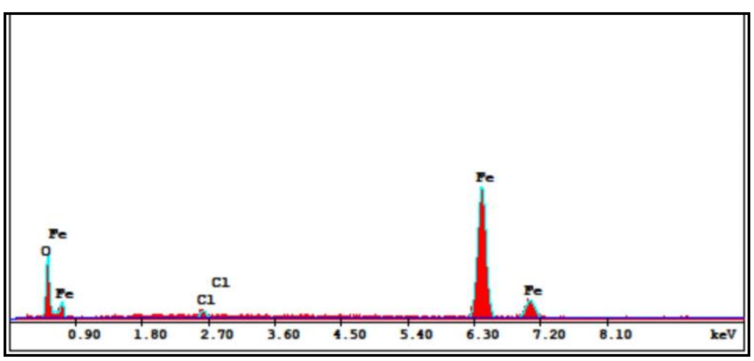
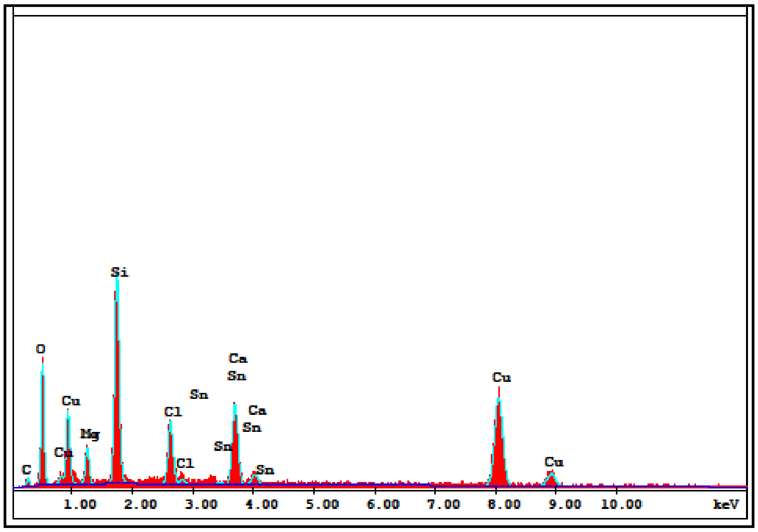


Fig. 8 A, B, Shows the layers of corrosion compounds, cracks and mineral grains through the microscopic images of the scanning electron microscope for bronze artifacts



Element	Wt %
Fe K	73.69
O K	24.55
Cl K	1.76
Total	100.00

Fig. 9 Shows EDX pattern of corrosion products sample of the iron table.



Element	Wt %
C K	4.89
O K	25.34
Mg K	5.21
Si K	38.56
Cl K	16.74
Sn K	4.25
Ca K	21.49
Cu K	19.16
Total	100.00

Fig. 10 Shows EDX pattern of corrosion products sample for bronze artefacts.

<u>3.4 X-Ray Diffraction Analysis</u>

The XRD data of the bronze samples consist of Cuprite (Cu_2O) , Atacamite $Cu_2Cl(OH)_3$, Paratacamite $Cu_2(OH)_3Cl$, and Quartz SiO_2, Fig. (10). The XRD analysis result of the iron shows that, it consists of Magnetite Fe_3O_4, Lepidocroctie [Fe O (OH)] and Quartz (SiO_2), Fig. (11).

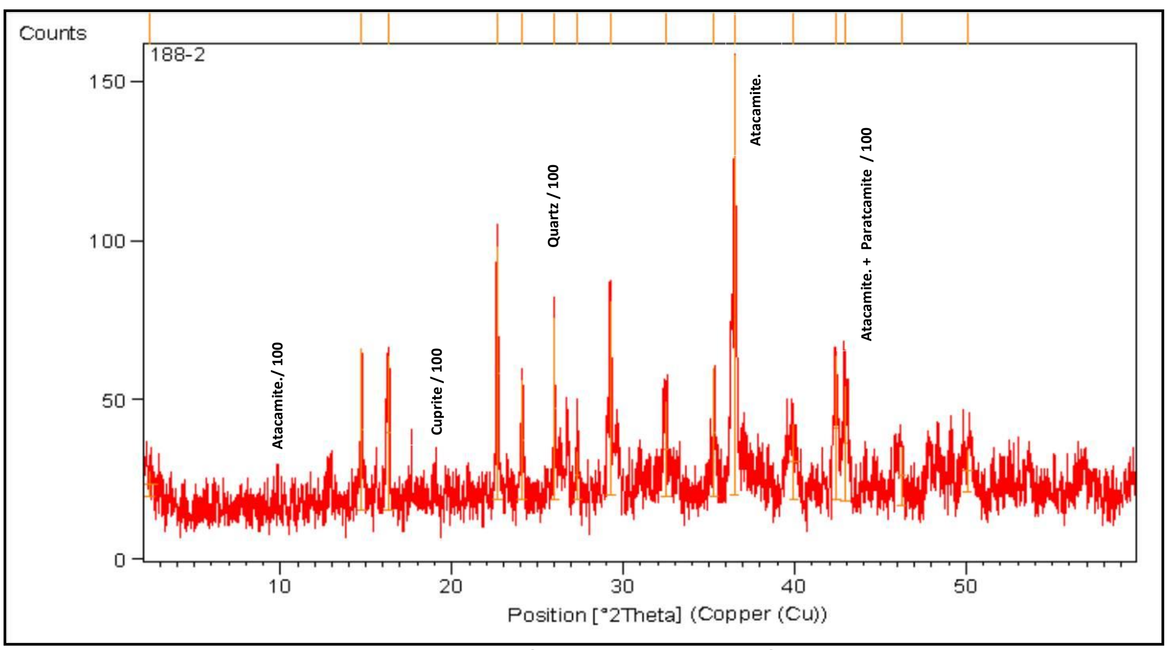


Fig. 10 Shows XRD pattern of corrosion sample for bronze works.

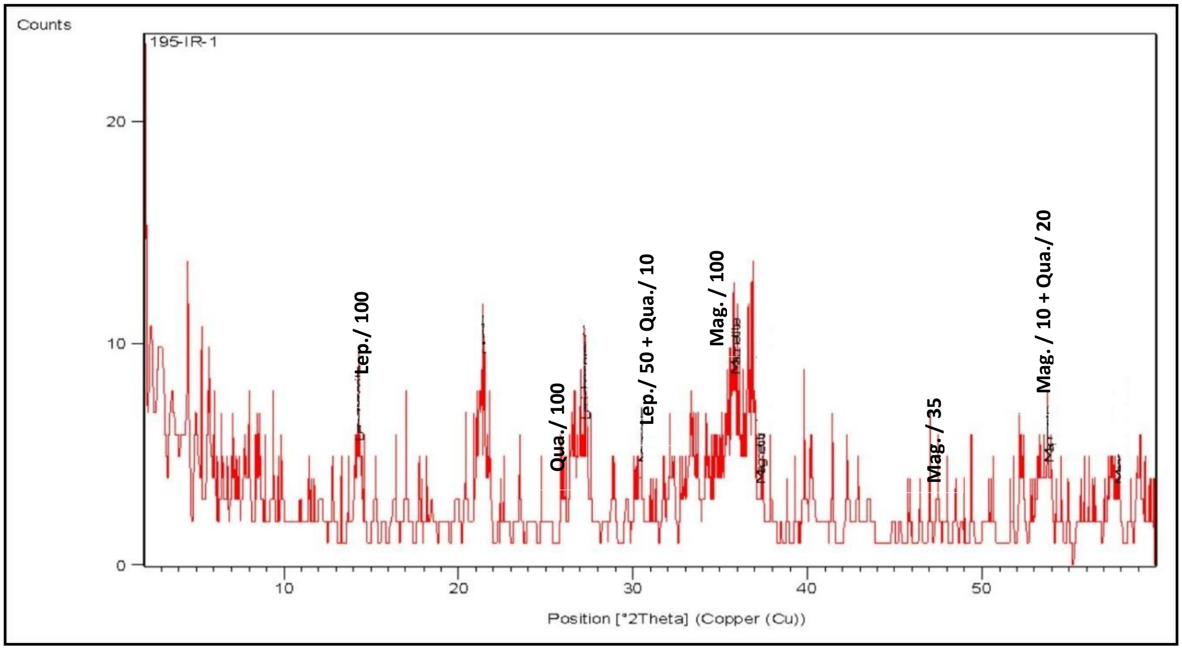


Fig. 11 Shows XRD pattern of corrosion sample of the iron table.

4. Discussion

Through the study, examination and analysis of bronze and iron artifacts at Farouk Corner Museum, it was found that they were deteriorated, which led to the formation of various corrosion compounds by the influence of the surrounding environment. The environment surrounding these bronze and iron artifacts contained various air pollution gases, [10] as well as solid aerosols due to the presence of factories and various industrial activities[11] in the Helwan city. In addition to the presence of these bronze and iron artifacts in the Farouk Corner Museum in Helwan on the Nile shore, this led to a permanent source of high humidity, [12] These surrounding factors led to the formation of various corrosion compounds on its surface [13]. These

10Dillmann, P., Mazaudier F. and Hoerle S., (2004), "Advances in understanding atmospheric corrosion of iron I - Rust characterisation of ancient ferrous artefacts exposed to indoor atmospheric corrosion", Corrosion Science 46(6) ,p.35

11 Monnier, J., Burger E., Berger P., Neff D., Guillot I. and Dillmann Ph., (2011), "Localisation of oxygen reduction sites in the case of iron long term atmospheric corrosion", Corrosion Science, Vol. 53,98,p.27.

12Selwyn L., (2004), "Overview of archaeological iron: the corrosion problem, key factors affecting treatment, and gaps in current knowledge", In: Ashton, J. and Hallam D. (eds) Metal 2004: Proceedings of interim meeting of the ICOM-CC Metal WG, National Museum of Australia Canberra,p.65.
13 Hoerle S., Mazaudie F., Dillmann Ph. and Santarini G., (2004), "Advances in understanding atmospheric corrosion of iron. II. Mechanistic modelling of wet–dry cycles", Corrosion Science, Vol. 46,p.29.

compounds appeared in green and brown colors and were mixed with bronze alloy as well as iron metal. It led to the presence of erosion and roughness on the surface, loss of the surface layers, peeling and cracks that appeared clearly in the iron table[14]. It was examined using a stereo microscope and a scanning electron microscope. It was also found that the presence of dust and sand grains adhered to the surfaces of the artifacts and mixed with corrosion compounds, and this was evident on the bronze artifacts that were also examined by stereo and scanning electron microscope. It was clear from the analysis by EDX unit attached to the scanning electron microscope the presence of iron, oxygen and chlorine elements in the samples analyzed from the corrosion layers of the iron table. This explains the appearance of the minerals magnetite and lepidocrocite [15] from X-ray diffraction analysis of the corrosion layer samples [16]. On the other hand, it appeared from the analysis by EDX unit of the surface layer samples for the bronze artifacts, the presence of copper and tin elements, which shows that the alloy used is a bronze alloy[17] . In addition to the presence of silicon, oxygen, chlorine, calcium and magnesium elements, which are consistent with the results of the analysis by X-ray diffraction, which show the presence of the minerals quartz, cuprite and atacamite. It is clear from this that the surface layers on the bronze artifacts are corrosion compounds of bronze mixed with grains of sand and dust [18]. The presence of these iron and bronze artifacts in the open environment caused the presence of pollutants and high humidity whose permanent source is the presence of the Nile River, with the lack of maintenance for these bronze and iron artifacts, which led to the obliteration and disappearance of the original archaeological surface under the layers of rust mixed with dust, sand and surface dirt[19] . It was found from the case study of these metal artifacts that they need to carry out treatment and conservation processes.

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14 Stratmann, M., (1990), "The atmospheric corrosion of iron and steel", Metallurgica I Odlewnictwo, 16(1),p.13.

15 Barrero C.A., Morales A.L., Mejia M.I., Arroyave C.E., (2001), "On Magnetite Formation as a Corrosion Product of Steel", Hyperfine Interactions (C), In: Thomas M.F., Williams J.M., Gibb T.C. (eds), Proceedings of the International Conference on the Applications of the Mössbauer Effect, (ICAME 2001) Oxford, U.K,p.11.

16 Petiti, C. et al, (2020), Effects of cleaning procedures on the long-term corrosion behavior of bronze artifacts of the cultural heritage in outdoor environment, Environmental Science and Pollution Research,p.86.

17 Sik, P. J., (2020), The technological and social implication of the discriminated use of tin and arsenic noted in EIA copper-based objects of Central Kazakhstan, Archaeological and Anthropological Sciences,p.96.

18 Park, J., et al, (2020), The implication of diachronic changes reflected in LBA bronze assemblages of Central Kazakhstan. ArchaeolAnthropol Sci,p.54.

19 Degrigny C., Vella D., Golfomitsou S. and Crawford J., (2007), "Characterisation of Corrosion Product Layers on Atmospherically Corroded Historic Ferrous Objects: Application to the Armour of the Palace Armoury, Valletta, Malta", In: Argyropoulos V, Hein A, Abdel Harith M (eds) Strategies for

5. Recommendations for Conservation and protection against corrosion

It was found from the examinations and analyzes of the metal artifacts in the King Farouk Corner Museum that, metal artifacts need to carry out treatment and conservation processes that will include mechanical and chemical cleaning to clean surfaces and remove layers of corrosion products mixed with soil and quartz grains[20] .Mechanical cleaning will be done using appropriate hand tools such as fine brushes and scalpels[21]. Rochelle salt solutions and sodium carbonate can be used to remove bronze corrosion products, and ethylene di-amine tetra-acetic acid (EDTA) can be used to remove iron table rust products [22] after mechanical cleaning processes are completed to remove thick rust products and layers of modern paints that are damaged and existing on the surface. The surface treatment of metal artifacts of chloride compounds (bronze disease) will be done using benzotriazole solution at a concentration of 3%. Finally, a layer of protective coatings will be made on the surface using a suitable compound, and it is suggested to

use Paralloid B-82 at a concentration of 3% for bronze artifacts [23], and Permalac (N-Butyl acetate-14.0) for the iron table.[24]

6. Conclusion

From the study of the current state of bronze and iron artifacts at Farouk Corner Museum in Helwan, through examinations and analyzes, it became clear that the surrounding environment of these artifacts has an important role in the damage that occurred. There is air pollution in the surrounding environment with various polluting gases resulting from industrial activities in

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Saving our Cultural Heritage. Proceedings of the International Conference on Conservation Strategies for Saving Indoor Metallic Collections, Cairo. TEI of Athens,p34.

20 Blackney, K. and Martin, B., (1998), "Development and long-term testing of methods to clean and coat architectural wrought ironwork located in a marine environment", In: Research and case studies in architectural conservation, Metals, Vol.1,p.76.
21 Degrigny C., (2008), "The search for new and safe materials for protecting metal objects", In: Argyropoulos V. (eds), Metals and Museums in the Mediterranean, Protection, Preserving and Interpreting, PROMET Project, Athens (Greece), p.37.
22 Davey A., (2013), "Maintenance and repair techniques for traditional cast ironwork", Historic Scotland,p31.
23 Hammouch H. Dermaj A., Goursa M., Hajjaji N. and Srhiri A., (2007), "New Corrosion Inhibitor Containing Opuntia ficus indica Seed Extract For Bronze and Iron-based Artefacts", In: Argyropoulos V, Hein A, Abdel Harith M (eds) Strategies for Saving our Cultural Heritage. Proceedings of the International Conference on Conservation Strategies for Saving Indoor Metallic Collections, Cairo. TEI of Athens,p.76.

24 Donnelly J., (2009), "Iron: the repair of wrought and cast ironwork", Department of the Arts, Heritage and the Gaeltacht,p65.

Helwan area. In addition to the impact of the Nile River water as a source of permanent moisture near these artifacts. Examinations and analyses conducted on these artifacts confirmed the formation of various bronze and iron corrosion compounds, where the minerals quartz, cuprite and atacamite appeared in the bronze artifacts. Quartz, magnetite and lepidocrocite appeared in the iron table. This shows the role of the surrounding environment in the deterioration of these artifacts, as corrosion compounds mixed with dust and surface calcifications as a result of their presence in the open air, where these artifacts are located in the garden and marina of Farouk Corner Museum. It was also found from the study that these bronze and iron works need to carry out treatment and conservation processes to keep them from being deteriorated again.

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