

An Analytical study and conservation of bronze windows grilles in Sabil Al-Ahmadi, Tanta, Egypt

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دراسة تحليلية لعلاج وصيانة النوافذ البرونزية بسبيل الأحمدى بطنطا مصر

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Abstract

This research focuses on study the historical bronze window grilles of Sabil al-Ahmadi in Tanta city, in the Egyptian Delta region, which comprises three windows made of bronze. A comprehensive analysis was carried out for one of these windows using digital and metallographic microscopes, portable X-ray fluorescence (pXRF), scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS), and X-ray diffraction (XRD). These techniques were used to determine the composition of the alloy, its metallurgical properties, and the nature of its corrosion. The window grille was identified as being made of a quaternary bronze alloy (Cu, Zn, Sn, Pb), produced through a sand-casting process. The corrosion layers consisted primarily of cuprite and clinoatacamite, with dense layers of dust containing calcite, quartz, and gypsum. A series of mechanical cleaning processes were employed to remove tough incrustations and corrosion products, followed by the application of a protective coating, PUR-129, which has proven its effectiveness in experimental studies conducted to assess its efficiency. This coating was selected for its durability, strong adhesion, and ease of application, ensuring the long-term preservation of the bronze window.

Keywords: Quaternary bronze, Window grille, Corrosion, Analysis, Conservation.

المخلص

تركز هذه الدراسة على دراسة النوافذ البرونزية التاريخية لسبيل الأحمدى بمدينة طنطا في منطقة الدلتا المصرية، حيث يحتوي السبيل على ثلاث نوافذ مصنوعة من البرونز. تم إجراء فحص وتحليل شامل لأحد هذه النوافذ باستخدام الميكروسكوب الرقمي والميتالوجرافي، وجهاز تفلور الأشعة السينية المحمول، والميكروسكوب الإلكتروني الماسح مع مطيافية تشتت الطاقة، وكذلك حيود الأشعة السينية. تم استخدام هذه التقنيات لتحديد تركيبة السبائك وخصائصها المعدنية وطبيعة مركبات الصدأ. تم التعرف على سبيكة صنع النافذة، حيث تبين أنها مصنوعة من سبيكة برونز رباعية تتكون من النحاس، والزنك، والقصدير، والرصاص، وأنها صنعت بتقنية الصب في قالب الرمل. تتربط طبقات التآكل بشكل أساسي من الكوبريت والكلينواتكاميت، مع طبقات كثيفة من الغبار تحتوي على الكالسييت والكوارتز والجبس. تم استخدام سلسلة من عمليات التنظيف الميكانيكية لإزالة

الرواسب الصلبة ونواتج التآكل، تلا ذلك تطبيق طلاء واقٍ من مادة PUR-129، والذي أثبتت فعاليته في الدراسات التجريبية التي تمت لتقييم كفاءته. تم اختيار هذا الطلاء لمثابته، وقوة التصاقه، وسهولة تطبيقه، مما يضمن الحفاظ على استقرار حالة نافذة البرونز على المدى الطويل.

الكلمات الدالة: البرونز الرباعي، نافذة معدنية، الصدأ، التحليل، الصيانة.

1. Introduction

Across different historical eras, the bronze alloy has stood out as a key copper-based material, with copper as the dominant metal. It was widely used in creating numerous metal artworks^{1,2}. There are several types of bronze alloys, including binary alloys made of copper and tin, ternary alloys consisting of copper, tin, and lead. Quaternary bronze artifacts are composed primarily of copper, with the addition of tin, zinc, and lead beside Fe and S as main impurities³. This alloy was one of the major copper alloys known in antiquity, alongside arsenical copper, tin bronze, lead bronze, and brass^{4,5,6,7}. It is also known as historical bronze which has been extensively used for artistic casting designed for outdoor display^{8,9}. This alloy was used in the manufacturing of bronze windows grilles which were widely used in mosques or royal palaces for street-level, where ventilation was desired, and was utilized in the casting of statues and memorials in public squares in Egypt during the era of the Muhammad Ali family^{10,11}.

¹ Ogden, J., Metals (in:) *Ancient Egyptian Materials and Technology*, Cambridge University Press, U.K, 2000, p.151.

² Lucas, A., Harris J., *Ancient Egyptian Materials and Industries*, Dover Publications; 4th ed. Edition, 2011, p.319.

³ Chiavari, C., et al., *Composition and electrochemical properties of natural patinas of outdoor bronze monuments*, *Electrochimica Acta* 52 (2007) 7760–7769. doi:10.1016/j.electacta.2006.12.053

⁴ Weil, P.D., et al., *The corrosive deterioration of outdoor bronze sculpture*, *Studies in Conservation*, Vol. 27, 1982, p. 130.

⁵ Scott, D.A., *metallography and microstructure of ancient and historic metals*, Getty Conservation Institute in association with Archetype Books, 1991, p. 137.

⁶ Ogden, J., *Metals in ancient Egyptian materials and technology*, 151.

⁷ Almaviva, S., et al., *Use of ns and fs pulse excitation in laser-induced breakdown spectroscopy to improve its analytical performances: A case study on Quaternary bronze alloys*, *Spectrochimica Acta Part B*, Vol. 99, 2014, p. 186.

⁸ Bernardi, E. et al., *The atmospheric corrosion of quaternary bronzes: The leaching action of acid rain*, *Corrosion Science* 51, 2009, pp.159–170. doi:10.1016/j.corsci.2008.10.008

⁹ Alexander, S., et al., *Assessment of marine and urban-industrial environmental impact on stone acting as the base of a quaternary bronze sculpture*, *Microchemical Journal*, Vol. 204, 2024, p. 2.

¹⁰ Mohamed, W.A., et al., *Conservation of an outdoor historical bronze*, *Open Air Metal, Outdoor Metallic Sculpture: from the XIXth to the beginning of the XXth Century*, Paris, France, 2014, pp.176-185.

¹¹ Mohamed, W.A., et al., *Cairo University Memorial Statue: A historical, artistic and scientific study*, *CGUUA*, Vol. 22, 2021, pp. 770-797.

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Outdoors monumental and architectural items (sculptures, roofs and decorative objects, functional artifacts and industrial heritage) are mainly subject to weather conditions, pollution and climate change, which can lead to corrosion and degradation over time^{12,13,14,15,16}. When bronze artifacts are exposed to the atmosphere, they develop a thin corrosion layer, or patina, typically greenish-brown or bluish green in color. This patina acts as a protective barrier for the underlying metal, with its effectiveness determined by several factors, including its composition, adhesion to the metal, thickness, porosity, crystalline structure, and the varying weather conditions (such as relative humidity, temperature, light, ultraviolet (UV) radiation, and time of wetness). Additionally, the composition and concentration of atmospheric pollutants play a crucial role in influencing the patina's protective qualities^{17,18,19}.

Conservation and preservation of outdoor bronze window grilles are essential to preserve their aesthetic and structural integrity. Exposure to environmental elements such as moisture, pollutants, and temperature fluctuations can cause corrosion and tarnishing over time. Regular cleaning, protective coatings, and routine inspections are crucial to prevent deterioration, maintain their appearance, and ensure long-term durability. Proper maintenance not only safeguards the historical and artistic value of bronze grilles but also extends their lifespan in challenging outdoor conditions. The decision to choose a treatment method hinges on a comprehensive understanding of the artifact's condition, the nature of the degradation, and the environmental factors at play. A tailored approach that considers these elements will enhance the likelihood of successful conservation, ultimately preserving the artifact's integrity, historical value, and aesthetic appeal for future generations. This thoughtful, multi-faceted strategy underscores the importance of

¹² Mendoza, A.R., et al., *Outdoor and indoor atmospheric corrosion of non-ferrous metals*, Corrosion Science, Vol. 42, 2000, p. 1125.

¹³ Rocca, E., Mirambet, F., *Corrosion inhibitors for metallic artefacts: temporary protection*, In: Dillmann, P., et al., (eds.), *Corrosion of metallic heritage artifacts*, Cambridge: Woodhead publishing Ltd, England, 2007, p. 308.

¹⁴ Revie, R.W., Huhlig H.H., *Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering*, fourth edition, Wiley, Hoboken, 2008, p. 3.

¹⁵ Megahed, M., et al., *Selective Formula as a Corrosion Inhibitor to Protect the Surfaces of Antiquities Made of Leather-Composite Brass Alloy*, Egyptian Journal of Chemistry, Vol. 63, No. 12, 2020, p. 5269.

¹⁶ Letardi, P., *Testing new coatings for outdoor bronze monuments: A methodological overview*, Coatings, Vol. 11, 131, 2021, p. 5. <https://doi.org/10.3390/coatings11020131>

¹⁷ Scully, J.C., *The fundamentals of corrosion*, 3rd ed., Oxford, Pergamon Press, 1990, P. 103.

¹⁸ Fitzgerald K.P., et al., *The chemistry of copper patination*, Corrosion Science, Vol. 40, Issue. 12, 1998, p. 2030.

¹⁹ Nord, A.G., Boyce, A.J., *Atmospheric bronze and copper corrosion as an environmental indicator.*, Water, Air, and Soil Pollution, Vol. 127, 2001, p. 193.

expertise in conservation practices and materials science in the preservation of cultural heritage²⁰.

2. Materials and Methods

2.1 The window grille of sabil Al-Ahmadi (case study)

Sabil Al-Ahmadi, located in Tanta in Egypt's central Delta region, originally dates to the era of Ali Bey the Great, though none of his constructions have survived. The current structure was rebuilt by Muhammad Ali Pasha, the governor of Egypt, in 1825 AD^{21,22}. Named "Al-Ahmadi" due to its proximity to the Sayyid Ahmed Al-Badawi Mosque, the Sabil served as an essential public water source, a key element of any ancient city's infrastructure, providing water to nearby neighborhoods and playing a vital role in daily life²³ (Fig. 1.a). Sabil Al-Ahmadi was registered as an Islamic monument by Resolution No. 10375 in 1951 AD.

The external facade of Sabil Al-Ahmadi features three bronze windows that overlook the bustling market next to the Al-Sayyid Al-Badawi Mosque. Each window measures 3.12 meters in height and 1.74 meters in width. The window is distinguished by its symmetrical design, with the left and right sides mirroring each other. Its structure is divided into three sections:

Upper Section: This part features a semicircular shape adorned with intricate geometric and floral decorations. These designs converge around a small semicircular motif at the center of the base. At the center of the arch is a floral pattern, encircled by geometric decorations resembling intertwined rays, symbolizing the emblem of the Muhammad Ali family—a half sun disk. The entire upper section was crafted as a single unit using the casting method.

Middle Section: The middle of the window is a large square, filled with a repeating pattern of interwoven grids. Surrounding this square on all four sides are rectangles decorated with zigzag patterns, and at the intersection of these rectangles, a star motif appears at each corner.

²⁰ Scott, A.D., *Copper and bronze in Art, Corrosion, Colorants, Conservation*, Los Angeles, The Getty Conservation Institute, 2002, p.6.

²¹ Hanna, N., *Ottoman Egypt and the Emergence of the Modern World*, Cairo: The American University in Cairo Press, 1998, pp. 120-121.

²² Lotfy, A.A., *Al-Sayyid al-Badawi Mosque in Tanta City: A Documentary Architectural Study*, Master's Thesis, Faculty of Arts – Department of Archaeology – Division of Islamic Archaeology, Tanta University, 2014 AD, p. 36. (In Arabic)

²³ Levanoni, A., *Water Supply in Medieval Middle Eastern Cities: The Case of Cairo.*, Al-Masāq, Vol. 20. Issue 2., 2008, p.186.

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Lower Section: The lower portion is a rectangular form featuring repeated, symmetrical arches. These arches once served as openings to provide water to passersby. Between each pair of arches, there is a floral decorative motif, as illustrated in Fig. 1.b. Fig. 2 presents a two-dimensional drawing of the window, detailing its dimensions and the locations and sizes of its decorative elements²⁴.



a



b

Fig. 1. (a) Shows the exterior facade of the Sabil Al-Ahmadi, and (b) depicts the middle bronze window, the selected case study.

²⁴ *Records of Archaeological Documentation*, Gharbia Antiquities Area, Tanta Antiquities Inspection, 2023.

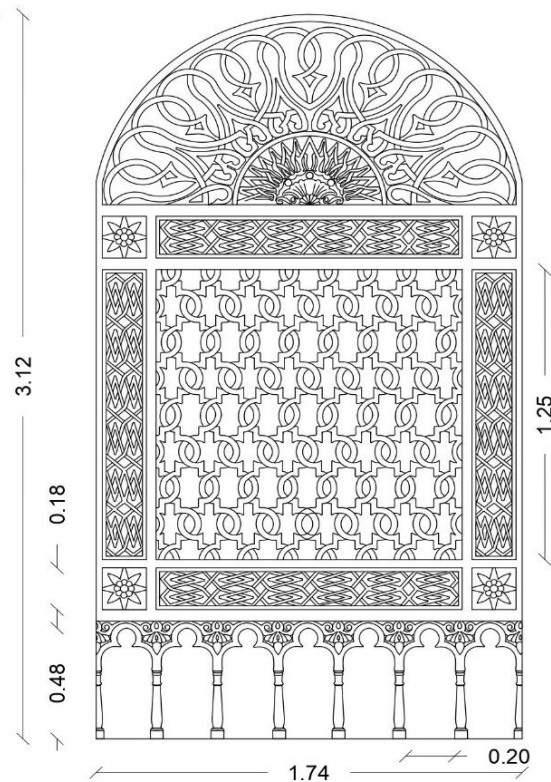


Fig. 2. Two-dimensional drawing of the Sabil Al-Ahmadi window, created using AutoCAD.

2.2 Examination and Analysis

Analytical techniques were carried to ensure a detailed understanding of the window's composition, manufacturing technique, the extent of damage, and the appropriate restoration methods to be employed.

2.2.1 Digital microscope

A RoHS USB Digital Microscope with a magnification of 200x was used in situ to identify the surface morphology of the window and to observe any surface irregularities, corrosion products, or signs of wear and deterioration. This allowed for a detailed examination of the window's condition without the need for removal or invasive techniques.

2.2.2 Portable X-ray fluorescence

A portable X-ray fluorescence device, specifically the NITON brand, was used for elemental analysis of the alloy. Multiple points on the window were analyzed, and these areas were sanded to remove dust, debris, and corrosion products before analysis. Dry cotton was then used to eliminate the remnants of the sanding process. This was followed by cleaning with cotton moistened with ethyl alcohol and then distilled water. This meticulous cleaning process was essential to prevent corrosion products from interfering

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with the X-ray fluorescence device, ensuring accurate results regarding the alloy's elemental composition.

2.2.3 Metallographic Microscope

For identify microstructure and manufacturing technique of the alloy, a small sample measuring 0.8 mm³ of the window was examined under an OLYMPUS BX41M-LED metallographic microscope to identify the microscopic structure of the alloy and manufacturing technique. The sample was fixed in cross-section and embedded in epoxy resin. The embedded sample underwent a series of grinding and polishing steps using sandpaper with grits ranging from 150 to 1200. Finally, the sample was impregnated with diamond paste to achieve a fine polish.

2.2.4 Scanning Electron Microscope with Energy Dispersive Spectroscopy (SEM-EDS)

SEM-EDS is crucial in analyzing bronze objects as it provides detailed information about both the microstructure and elemental composition. It allows for high-resolution imaging of the bronze's surface, revealing important features such as grain structure, corrosion layers, and inclusions. EDS complements this by identifying and quantifying the elements present in the alloy, such as copper, tin, zinc, and lead. This combined analysis helps in understanding the material's composition, corrosion processes, and the effectiveness of any conservation treatments. SEM/EDS analysis was conducted using a Jeol JSM 6510LV (Japan) to examine and analyze the same cross-section prepared for metallographic examination.

2.2.5 X-Ray Diffraction

Understanding the compounds present in an object is crucial for determining its stability and suitability for specific conservation treatments. Removing corrosion products without this knowledge could erase valuable historical information, damage fine surface features, or even alter the object's original shape and details. Corrosion products and encrustations were collected and ground in an agate crucible to obtain a fine powder. This powder was analyzed using a PANalytical Empyrean Series 3 X-ray diffraction instrument to determine the types of corrosion compounds, understand their formation mechanisms, and subsequently establish the restoration plan and the most appropriate maintenance procedures.

2.3 Cleaning and Protection Procedures

To clean and protect the bronze window, a series of mechanical cleaning steps were conducted to remove active corrosion products and thick layers of dust. Using brushes, scalpels, and a dental drilling machine, surface contaminants were meticulously eliminated without damaging the underlying material. After cleaning, the bronze surface

was treated with PUR-129, a clear polyurethane coating based on modified acrylic, produced by CMB-Egypt, and applied at the standard concentration recommended by the manufacturer. The coating consists primarily of polyurethane, which is created by the reaction between polyol (R-OH) and isocyanate (R'-NCO), resulting in a durable urethane bond structure. Additionally, acrylic is combined with polyurethane in the formulation to enhance properties such as drying speed and resistance to cracking. The coating includes ultraviolet stabilizers to prevent yellowing and degradation from sunlight, making it suitable for outdoor use. Its chemical composition imparts high resistance to weathering, chemical agents, and mechanical effects, while also providing flexibility and durability. This combination of polyurethane and acrylate offers protection against environmental factors, fast drying, and robust corrosion resistance, making PUR-129 ideal for safeguarding exposed metal surfaces in harsh outdoor conditions²⁵.

3. Results and Discussion

To adapt the sand-casting process for producing bronze window grilles, the process remains largely similar, with adjustments primarily in the material used. Instead of iron, a bronze alloy (typically copper and tin) is melted and poured into a sand mold created using a wooden pattern. The mold is formed in two halves using green sand, known for its fine grain and ability to capture detail. Fine coal dust is added to prevent gas bubbles in the final product. After the molten bronze is poured into the mold through gates and risers, it is left to cool before the casting is removed, cleaned, and finished. Although the traditional green sand mold offers a high-quality finish, modern techniques use chemically set sand molds for reuse, though they may produce a rougher surface. This adapted process is suitable for crafting detailed and durable bronze window grilles^{26,27,28,29}.

3.1 Visual and microscopic examination

Visual inspection and examination using an USB digital microscope revealed the presence of green corrosion products, gaps, and pits on various areas of the window

²⁵ <https://www.cmbegypt.com/cmb/ar/product/kemapoxy-129-pur-matt/>

²⁶ Howell, J. S., *Architectural cast iron: design and restoration*, The Journal of the Association for Preservation Technology, Vol. 19, No. 3, 1987, p. 51.

²⁷ Gayle, M., et al., *Metals in America's Historic Buildings*. Washington, D.C.: U.S. Department of the Interior, National Park Service, Preservation Assistance Division, 1992, p.79.

²⁸ Donnelly, J., *Iron the repair of wrought and cast ironwork*, the stationery office, Duplin, Ireland, 2009, p 49.

²⁹ Megahed, M. M., et al., *Polyamide coating as a potential protective layer against corrosion of iron artifacts*, Egypt. J. Chem. 64(10), 2021, p5693.

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grille. Notably, these corrosion products were more concentrated at the edges compared to the rest of the bronze surface, as illustrated in Fig. (3). Additionally, layers of green corrosion products, calcified clay, and dirt obscured the decorative details of the window, cloth ties placed by visitors to the Sabil Al-Ahmadi, believed to bring blessings, were marked with red arrows. The decorations were covered with a green corrosion layer, which was further obscured by thick layers of dust, largely hiding the intricate details, as shown in Fig. (4), where the analyzed points by digital microscope were shown in Fig. 5.

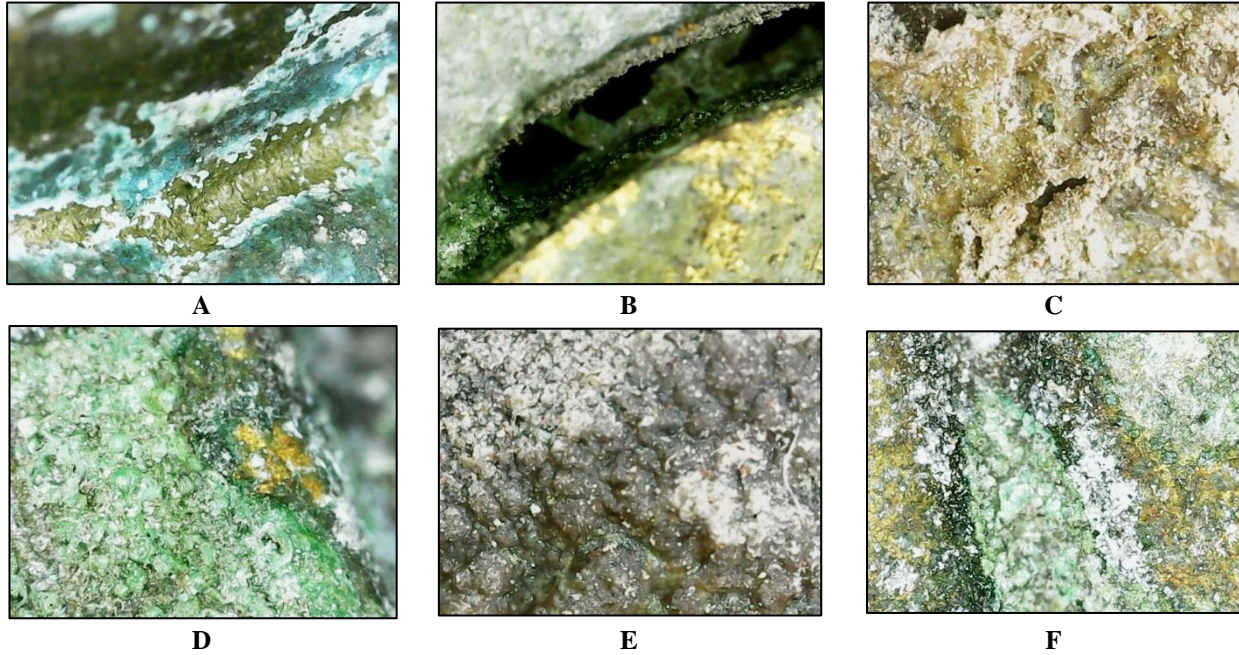
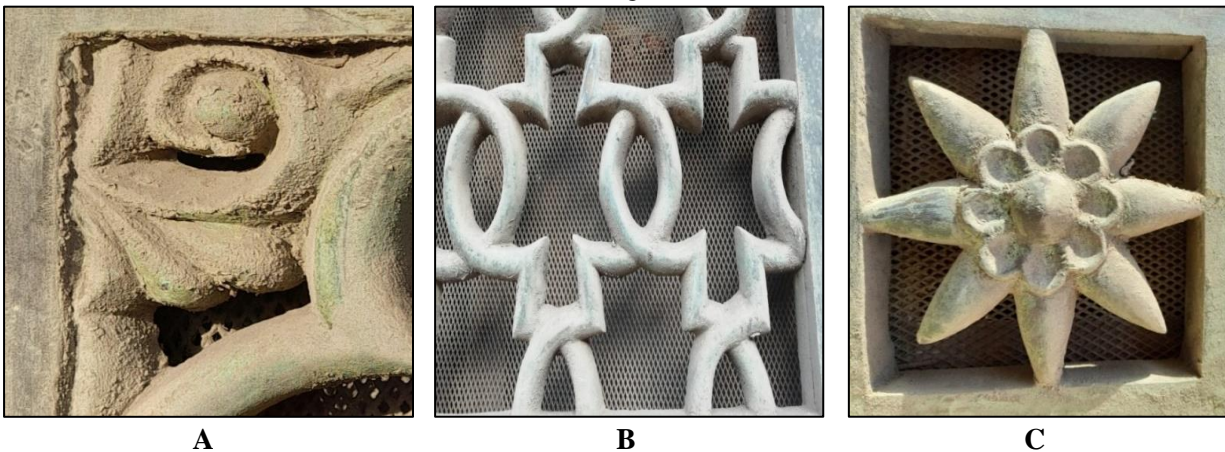


Fig. 3. (a - f) show green corrosion products, calcified layers, and dirt obscuring the decorative details of the window grille.



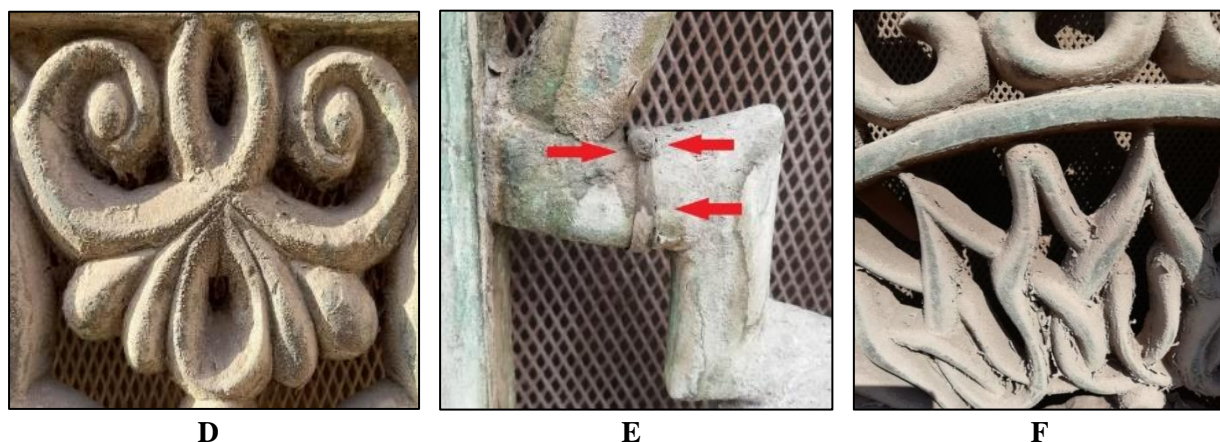


Fig. 4. (A, B, C) show the accumulation of dust covering the floral decorations. (D, F) show green corrosion products mixed with calcifications filling the gaps between the mesh grilles. (E) shows cloth ties placed by visitors to the Sabil Al-Ahmadi, marked with red arrows.

3.2 Alloy composition

The portable X-ray fluorescence (XRF) analysis is particularly valuable due to its non-destructive nature and ability to provide rapid, on-site elemental composition data without the need for sampling or invasive procedures. This is especially important in the context of cultural heritage preservation, where the integrity of historical objects, such as the Sabil window, must be maintained. By selecting flat surfaces for analysis, the risk of reflected X-ray leakage is minimized, ensuring more accurate results. The use of portable XRF allows for real-time decision-making regarding conservation strategies, as it enables a direct assessment of the alloy's composition across different areas of the window without damaging the artifact. This method is highly efficient, cost-effective, and ideal for analyzing delicate or immovable objects, preserving their historical and artistic value³⁰.

The portable X-ray fluorescence (XRF) analysis was conducted to determine the elemental composition of the alloy used in the net-making of the Sabil window. Analytical points of the window were chosen, focusing on flat surfaces to minimize the leakage of reflected X-rays to the detector, as illustrated in Fig. 6. The surface was sanded with sandpaper of grit size 1200 to remove corrosion layers and corrosion products to obtain more accurate results. The average results of the analysis of these points were taken, and the proportions of the elements that make up the Sabil window-making alloy were determined as quaternary alloys, consisting of the following basic elements: copper (Cu) 82.1%, tin (Sn) 5.9%, lead (Pb) 6%, and zinc (Zn) 4.3%, as illustrated in Table No. 1. Copper was alloyed with tin and zinc to enhance breaking

³⁰ Abdelbar, M., et al., *Conservation treatment and analytical study of Egyptian gilded bronze statue of seated Osiris*, International Journal of Conservation Science, 12:4, 2021, p. 1407.

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strength and hardness, while lead was added to improve castability and machinability^{31,32}. This alloy has been used in casting models and decorative elements to the present time³³. Quaternary bronze alloys (copper-tin-zinc-lead) tend to exhibit better corrosion resistance compared to binary alloys like copper-tin (bronze) and copper-zinc (brass) due to the combined benefits of the additional alloying elements. The combination of these elements in a quaternary alloy creates a material with a more complex and stable oxide layer, which is more resistant to various forms of corrosion, including general and localized corrosion³⁴.

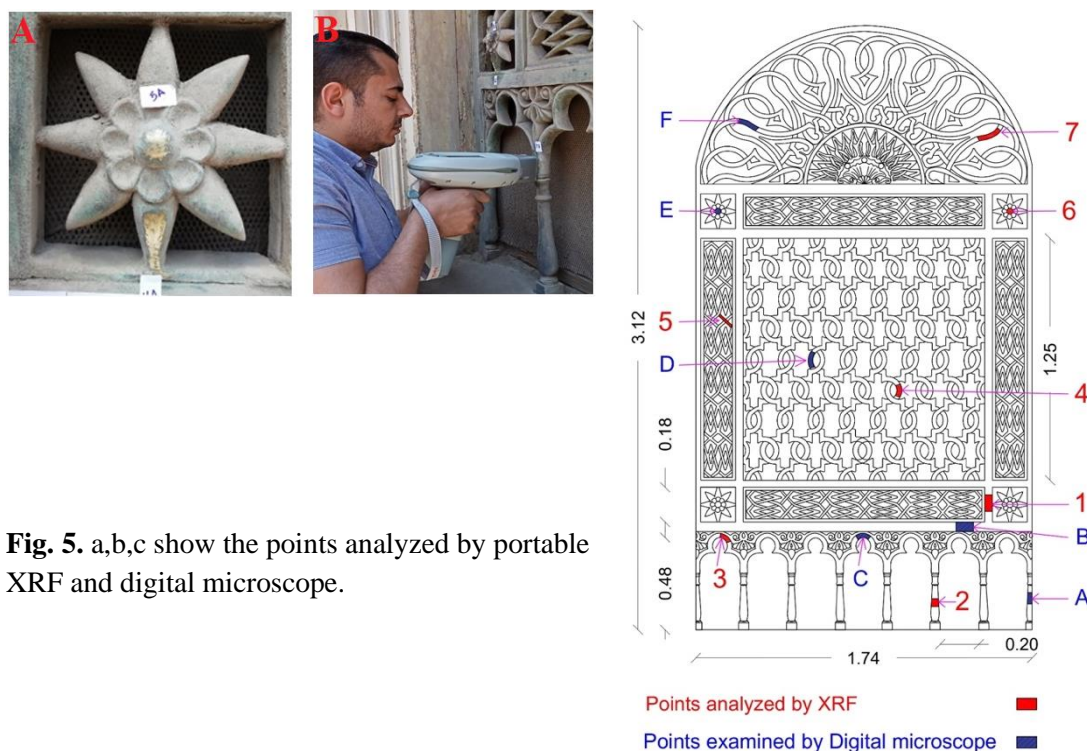


Fig. 5. a,b,c show the points analyzed by portable XRF and digital microscope.

³¹ Mayyas, A., et al., *Microstructural and compositional characterization of Roman bronze coins from khirbat edh-dharieh in Jordan*, ARQUEOLOGÍA IBEROAMERICANA, Vol 52, 2023, p 70.

³² Abdelbar, M., et al., *Understanding soil factors in corrosion and conservation of buried bronze statuettes: insights for preservation strategies*, Scientific Reports 14:19230., 2024, p 12.

³³ Scott, D.A., and Schwab, R., *Metallography in Archaeology and Art*, Springer International Publishing, Cham, Switzerland, 2019, p.153.

³⁴ Selwyn, L., *Metals and Corrosion: A Handbook for Conservation Professional*, Ottawa, Canadian Conservation Institute, 2004, p 53.

Table 1. Results of pXRF analysis at various locations on the Window of Sabil Al-Ahmadi.

Point No.	Main Elements Wt %				Traces Wt %					
	Cu	Sn	Zn	Pb	Fe	Se	Bi	Ag	Ni	Sb
1	77.88 ± 0.32	6.91 ± 0.14	11.83 ± 0.15	1.76 ± 0.06	0.55 ±0.06	0.41 ± 0.04	0.26 ± 0.02	0.19 ± 0.03	0.06 ±0.03	0.13 ± 0.12
2	77.18 ± 0.38	7.04 ± 0.17	12.32 ± 0.18	1.72 ± 0.12	0.56 ±0.07	0.49 ± 0.05	0.27 ± 0.03	0.21 ± 0.03	0.1 ±0.04	0.1 ± 0.14
3	78.45 ± 0.37	6.58 ± 0.16	11.9 ± 0.19	1.4 ± 0.17	0.62 ±0.07	0.47 ± 0.05	0.27 ± 0.03	0.2 ± 0.03	0.11 ±0.04	0.0 ± 0.14
4	76.4 ± 0.41	7.96 ± 0.18	11.88 ± 0.2	1.85 ± 0.11	0.69 ±0.08	0.45 ± 0.06	0.26 ± 0.04	0.19 ± 0.04	0.08 ±0.04	0.24 ± 0.16
5	78.02 ± 0.41	7.32 ± 0.2	10.21 ± 0.19	2.23 ± 0.09	1.04 ±0.09	0.58 ± 0.05	0.24 ± 0.04	0.27 ± 0.04	0.07 ±0.4	0.0 ± 0.17
6	75.4 ± 0.40	6.98 ± 0.16	12.24 ± 0.22	2.59 ± 0.14	1.56 ±0.09	0.35 ± 0.07	0.41 ± 0.04	0.24 ± 0.04	0.12 ±0.04	0.11 ± 0.16
7	76.14 ± 0.42	5.97 ± 0.15	12.87 ± 0.22	2.15 ± 0.12	1.54 ± 0.10	0.72 ± 0.06	0.38 ± 0.03	0.19 ± 0.04	0.04 ±0.04	0.0 ± 0.16

By study the cross-section of quaternary bronze alloy using SEM, we can observe distinct microstructural features (Figs 6,7). Lead typically appears as black or dark globules due to its immiscibility in copper and its lower electron scattering properties. On the other hand, tin and zinc are primarily integrated into the copper matrix as part of the alpha phase, forming a homogeneous solid solution. These phases tend to appear in lighter or white colors because of their higher electron density and scattering in comparison to lead. This allows us to understand the distribution of elements within the alloy and how they affect its overall structure and properties. In the provided SEM image (Fig. 7) of a quaternary bronze alloy cross-section at 500x magnification, shows the locations where EDS analysis was performed (Fig. 8) and Table 2. The selected points highlight areas within the bronze matrix and near lead inclusions. EDS analysis at these points provides quantitative data on the elemental composition, confirming the presence of copper, tin, zinc, and lead in specific regions. The lead-rich areas, correlating with the black inclusions, further validate the distribution of the elements within the alloy, as observed through SEM. The EDS analysis results, showing copper at 79.93%, zinc at 14.30%, tin at 2.34%, and lead at 2.81%, align with the pXRF analysis, which identified the Sabil

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window-making alloy as a quaternary bronze consisting of copper (82.1%), tin (5.9%), lead (6%), and zinc (4.3%). Both analyses confirm that the alloy is a quaternary bronze, with tin and zinc primarily incorporated into the copper matrix as part of the alpha phase, as demonstrated by the metallographic examination. This consistent elemental distribution across different analytical techniques highlights the alloy's complex composition and structural integrity.

Various studies have classified alloys composed of copper, tin, zinc, and lead as "quaternary bronze" rather than brass, even when zinc content surpasses that of tin. Robbiola et al. (2008) analyzed a bronze alloy from the statue of King Louis XIV, which contained significant zinc but was still termed "quaternary bronze" due to its outdoor use and resistance to environmental degradation³⁵. Polikreti et al. (2009) similarly described the alloy in a Greek statue as quaternary bronze based on its historical context³⁶. Chiavari et al. (2007) further supported this classification, noting that such alloys are commonly used in artworks and architectural elements exposed to outdoor environments³⁷. Also, Mohamed et al. (2021) analyzed the alloy in the Cairo University Martyrs Memorial, finding it to contain copper (78.92%), tin (6.41%), zinc (9.71%), and lead (1.7%). Despite the higher zinc content compared to tin, this alloy was classified as "quaternary bronze" due to the historical practice of combining these elements for outdoor artworks, common from the 18th to the 19th century³⁸. Their classifications emphasize that the presence of both tin and lead, in conjunction with zinc, aligns these alloys more closely with historical bronze types than with brass. Therefore, despite the variable zinc and tin ratios, the alloy in this study aligns with the historical "quaternary bronze" categorization used in conservation and historical studies.

³⁵ Robbiola, L., Rahmouni K., Vermaut P., New insight into the nature and properties of pale green surfaces of outdoor bronze monuments, *Appl. Phys. A* 92, 161–169 (2008).

³⁶ Polikreti, K., et al., *Tracing correlations of corrosion products and microclimate data on outdoor bronze monuments by Principal Component Analysis*, *Corrosion Science* 51 (2009) 2416–2422.

³⁷ Chiavari, C., et al., *Composition and electrochemical properties of natural patinas of outdoor bronze monuments*, *Electrochimica Acta* 52 (2007) 7760–7769.

³⁸ Mohamed, W.A., et al., *Cairo University Memorial Statue: A historical, artistic and scientific study*, CGUUA, Vol. 22, 2021, pp. 770-797.

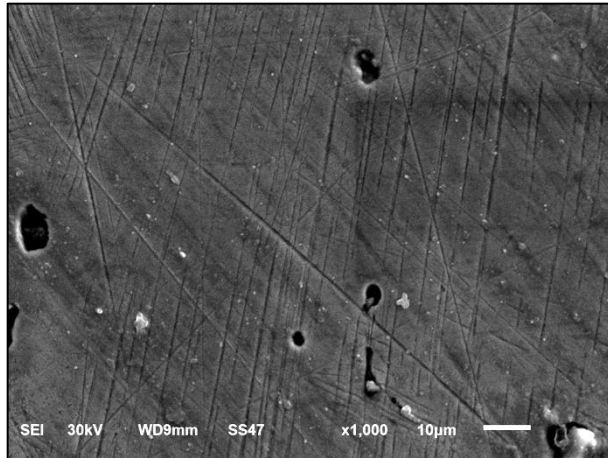


Fig. 6. shows SEM image of a cross-section of a quaternary bronze alloy at 1000x magnification, showing black lead globules.

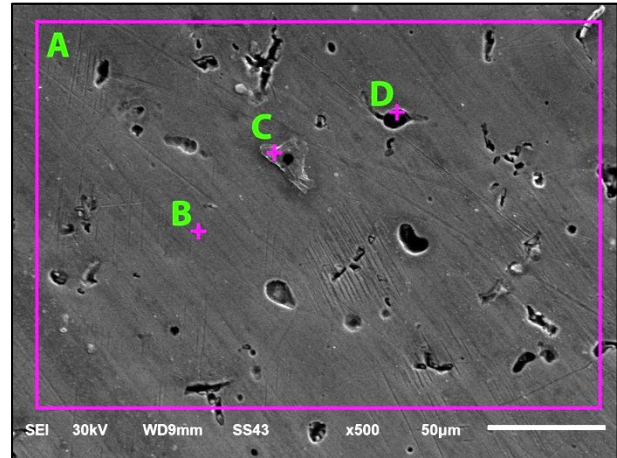


Fig. 7. shows SEM image at 500x magnification showing the locations of EDS analysis.

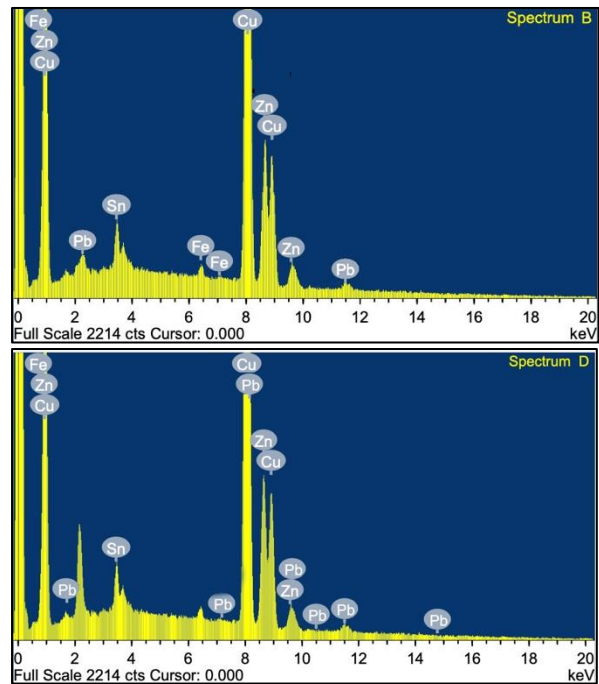
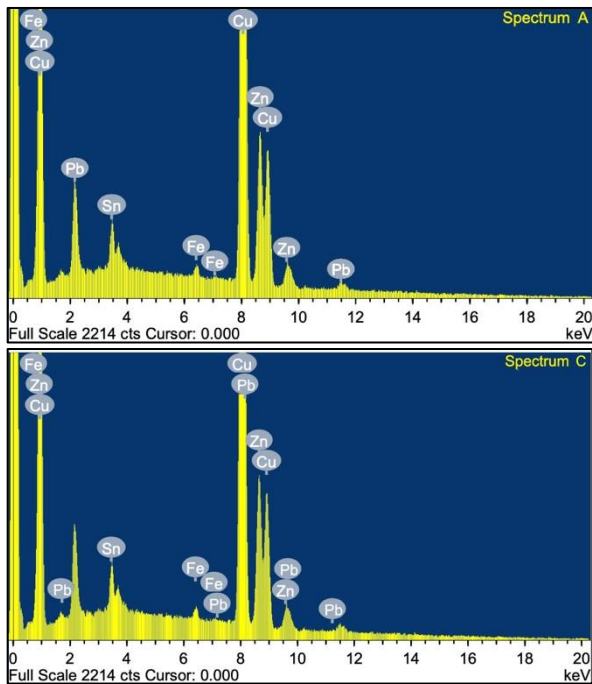


Fig. 8. A-B EDS spectra of different points within the bronze matrix and near lead inclusions.

Table 2 . EDS analysis of different spots in the bronze cross sections (wt.%)

Spot	Cu	Zn	Sn	Pb	Fe
A	80.55	14.30	2.33	2.01	0.81
B	81.98	15.05	1.80	0.60	0.57
C	81.79	14.12	2.52	1.34	0.23
D	86.28	4.12	0.15	8.71	0.74

3.3 Alloy microstructure

The microstructure of cast bronze alloys is critical to understanding their mechanical properties, corrosion behavior, and overall performance. Bronze, primarily composed of copper with varying amounts of tin, zinc, lead, and sometimes other elements, forms a complex microstructure that is influenced by factors such as alloy composition and the casting process. In a typical cast bronze alloy, the primary phase is the copper-rich alpha phase, where elements like tin and zinc are integrated into the copper matrix, forming a solid solution. Lead, being immiscible with copper, often appears as discrete globular inclusions, providing some degree of lubrication and enhancing machinability. During the solidification process, the distribution of these elements within the alloy plays a key role in determining the final microstructure. Variations in cooling rates and alloying element concentrations can result in the formation of dendritic structures, grain boundaries, and segregation of phases. These microstructural features directly impact the mechanical strength, ductility, and corrosion resistance of the alloy, which are critical considerations in both historical and modern applications of bronze^{39,40}.

Typical quaternary cast alloys (Cu-Zn-Sn-Pb), often referred to as gunmetal or, in modern terms, leaded red brasses, exhibit eutectoid structures and lead particles within the α Cu-solid solution. These alloys have been commonly used for casting items up to the present day. Although composed of four primary elements, these alloys can be considered a ternary mixture of copper, zinc, and tin because the lead forms immiscible droplets visible in the microstructure. The core areas of each grain are richer in copper, while the peripheries are richer in zinc and tin^{41,42,43}. Metallographic examination reveals that with 5.9% tin, the primary phase of the alloy is the alpha (α) phase. Additionally, with 4.3% zinc, the alloy stays within the alpha phase of brass, as shown in Fig. 9. Both tin and zinc are primarily accommodated in the copper matrix as part of the alpha phase. Due to lead's very limited solubility in copper, it predominantly forms separate phases or inclusions within the copper matrix^{44,45,46}. Copper was alloyed with tin and zinc to enhance breaking strength and hardness, while lead was added to improve castability and machinability⁴⁷.

³⁹ Scott, D.A., *metallography and microstructure of ancient and historic metals*, p. 137.

⁴⁰ Scott, D.A., Schwab, R., *Metallography in Archaeology and Art*, p.157.

⁴¹ Goffer, Z., *Archaeological Chemistry A source book on the applications of chemistry to archaeology*, John Wiley & Sons, New York, 1980, pp.195-197.

⁴² Scott, D.A., and Schwab, R., *Metallography in Archaeology and Art*, p.158.

⁴³ Abdelbar, M., Ahmed S., *Conservation treatment and analytical study of Egyptian gilded bronze statue of seated Osiris*, p.1407-1420.

⁴⁴ Scott, D.A., *metallography and microstructure of ancient and historic metals*, p 137.

⁴⁵ Constantinides, I., et al., *Microstructural characterisation of five simulated archaeological copper alloys using light microscopy, scanning electron microscopy, energy dispersive X-ray*

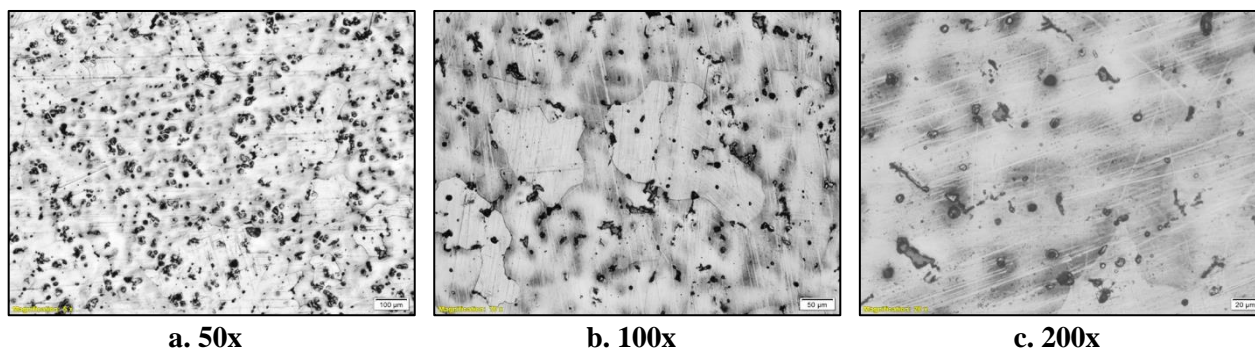


Fig. 9. a-c. Show the microstructure of the quaternary bronze. Both tin and zinc are primarily accommodated in the copper matrix as part of the alpha phase, while lead forms immiscible inclusions.

For the SEM/EDS analysis, the results revealed the elemental composition of the bronze alloy, with copper at 79.93%, zinc at 14.30%, tin at 2.34%, and lead at 2.81%. These findings correlate with the metallographic examination, which confirmed that both tin and zinc are predominantly integrated into the copper matrix, forming part of the alpha phase. This indicates that the alloy's microstructure supports the distribution of these elements within the solid solution, contributing to the alloy's overall properties and stability.

3.4 Corrosion and degradation

The corrosion degradation of outdoor bronze is a significant concern, particularly for historical artifacts and architectural elements exposed to varying environmental conditions. Bronze, an alloy primarily composed of copper with tin, zinc, and lead, is vulnerable to a range of corrosion processes when exposed to outdoor environments. The combination of moisture, pollutants, salts, and oxygen accelerates the formation of corrosion products on the bronze surface, leading to both aesthetic and structural deterioration. The primary corrosion mechanisms in outdoor bronze involve the formation of cuprite (Cu_2O), a protective oxide layer that can slow down further oxidation under controlled conditions. However, in aggressive environments, such as coastal areas or polluted urban settings, harmful compounds like chlorides and sulfates can penetrate the protective oxide layer, forming more damaging corrosion products such as clinoatacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$) and brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$). These compounds lead

microanalysis and secondary ion mass spectrometry, *Analytica Chimica Acta*, Vol 440, 2001, p 189.

⁴⁶ Scott, D.A., and Schwab, R., *Metallography in Archaeology and Art*, p.159.

⁴⁷ Mayyas, A., et al., *Microstructural and compositional characterization of Roman bronze coins from khirbat edh-dharikh in Jordan*, p. 70.

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to the development of patinas and pitting corrosion, which can severely compromise the integrity of the bronze. Moreover, environmental pollutants, including sulfur dioxide (SO₂) and carbon dioxide (CO₂), contribute to the formation of sulfuric acid and carbonic acid on the surface, resulting in the deposition of gypsum (CaSO₄·2H₂O) and calcite (CaCO₃), further accelerating degradation. Dust, biological growth, and fluctuating humidity levels exacerbate the corrosion process, leading to mechanical weakening, surface roughness, and loss of intricate details in bronze artifacts. Effective conservation and protective strategies are necessary to mitigate these corrosion processes and preserve the longevity of outdoor bronze objects^{48,49,50}.

The X-ray diffraction (XRD) analysis identified several compounds on the surface of the alloy, including clinoatacamite (Cu₂(OH)₃Cl), cuprite (Cu₂O), calcite (CaCO₃), quartz (SiO₂), and gypsum (CaSO₄·2H₂O), as illustrated in Fig. 10 and detailed in Table 3. These compounds signify various stages and types of corrosion processes affecting the Sabil window, which has been exposed to outdoor environmental conditions. The initial corrosion product formed on copper artifacts in the atmosphere is cuprite, which gradually reacts with oxygen and airborne pollutants like SO₂, Cl⁻, and CO₂ to form basic salts. The moisture content and concentration of air pollutants are critical factors influencing the rate of corrosion, which occurs through a wet corrosion mechanism due to water adsorbed on the metal surface. The thickness of this moisture layer varies about 100 microns from rain, 10 microns from condensation, and approximately one micron at 100% relative humidity. The rate of corrosion is closely linked to the duration of this moisture layer on the metal, which is influenced by atmospheric humidity, temperature, rainfall, sunlight, and air pollution levels. Given that copper, the primary component of quaternary bronze, is an electropositive metal, the predominant corrosion mechanism involves electrochemical reactions where copper oxidizes and forms cupric salts in the presence of anions such as sulfates, hydroxides, and phosphates^{51,52,53,54,55,56}.

⁴⁸ Cronyn, J. M., *The Elements of Archaeological Conservation*, London Routledge, 1990, p. 216.

⁴⁹ Scott, A.D., *Copper compounds in metals and colorants: oxides and hydroxides*, Studies in Conservation, Vol. 42, No. 2, 1997, PP. 93-100.

⁵⁰ Novák, P., *Environmental deterioration of metals*, in Moncmanová A.(eds), Environmental Deterioration of Materials, WIT Press, UK, 2007, p. 47.

⁵¹ Scully, J. C., *The fundamentals of corrosion*, p. 103.

⁵² Fitzgerald, K. P., et al., *The chemistry of copper patination*, p. 2032.

⁵³ Nord, A. G., Boyce, A. J., *Atmospheric bronze and copper corrosion as an environmental indicator*, P 198.

⁵⁴ Picciochi, R., Ramos, A. C., Mendonça, M. H., Fonseca, I. T E., *Influence of the environment on the atmospheric corrosion of bronze*, Journal of Applied Electrochemistry, Vol. 34, 2004, pp. 989.

Clinoatacamite forms in the presence of chloride ions common in marine or urban environments. Its presence suggests chloride ions have reacted with the copper, forming a green corrosion product. Chloride corrosion compounds on the Sabil window were due to air pollutants and the use of tap water containing chlorine ions for periodic washing^{57,58}. The facade of the Sabil is completely covered with marble tiles, and workers have regularly washed the facade and windows with tap water. Calcite forms from calcium ions in rainwater or dust reacting with carbon dioxide. Quartz, common in dust and dirt, and gypsum, from sulfur dioxide reacting with calcium compounds, suggest significant deposition of environmental particulates and pollutants. These compounds trap moisture and pollutants against the metal surface, exacerbating corrosion. Exposure to outdoor conditions subjects the window to rain, humidity, and temperature fluctuations. Urban environments with higher pollutants like chlorides and sulfur compounds exacerbate corrosion. Rainwater and humidity provide electrolytes for electrochemical corrosion, dissolving airborne pollutants and forming acidic solutions that accelerate corrosion. Variations in temperature cause the metal to expand and contract, leading to microcracks in the protective oxide layer and further ingress of corrosive agents⁵⁹.

⁵⁵ Ahmed, S., et al., *Experimental study of gap-filling of ancient completely corroded copper bowl via nano-polymers*. International Journal of Conservation Science, Vol 11, Issue 1, 2020, p.97.

⁵⁶ Elashery, N.H., et al., *Archaeometric characterization and conservation of bronze patina on archaeological axe head in military museum, Cairo*, Journal of Archaeology and Tourism-Must, Vol 2, Issue (1), 2023, p. 23.

⁵⁷ Scott, A.D., *Copper and bronze in Art, Corrosion, Colorants, Conservation*, p.14

⁵⁸ Selwyn, L., *Metals and Corrosion: A Handbook for Conservation Professional*, p. 53.

⁵⁹ Knotkova, D., Kreislova K., *Atmospheric corrosion and conservation of copper and bronze*, in Moncmanová A.(eds), *Environmental Deterioration of Materials*, WIT Press, UK, 2007, p. 111.

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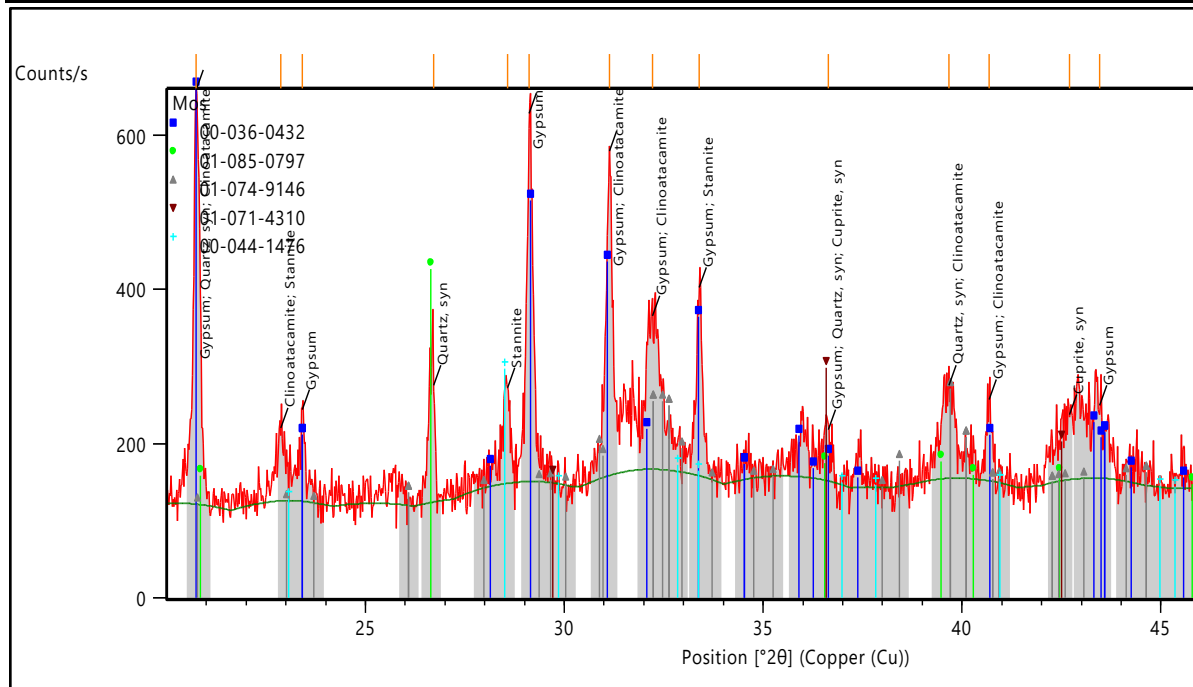


Fig. 10. shows XRD spectrum of corrosion products and dust accumulated on the window surface.

Table 3. Corrosion products and dust accumulated on the window grille of Sabil Al-Ahmadi.

Sample	Crystalline Component	Compound Name	Chemical Formula	Ref.Code	Semi-quantitative %
Corrosion Products with accumulated dust	Cuprite	Copper Oxide	Cu ₂ O	01-071-4310	11
	Clinoatacamite	Copper Hydroxide Chloride	Cu ₂ (OH) ₃ Cl	01-074-9146	13
	Calcite	Calcium Carbonate	CaCO ₃	01-083-4629	27
	Quartz	Silicon Oxide	SiO ₂	01-085-0794	9
	Gypsum	Calcium Sulfate Hydrate	CaSO ₄ .2H ₂ O	01-070-0982	40

3.5 Treatment and Conservation

The decision to treat and clean a window exposed to the elements, particularly one that has accumulated layers of rust and dense dust, is critical for both aesthetic and conservation reasons. Over time, these layers can obscure the intricate artistic details and decorations, diminishing the historical and cultural significance of the window. Cleaning is essential to reveal these features, allowing for a better appreciation of the craftsmanship and artistry involved in its creation. Moreover, the presence of rust not only detracts from the visual appeal but can also lead to further deterioration of the material if left untreated. Effective cleaning methods must be carefully chosen to avoid damaging the original surfaces. Non-invasive techniques, such as mechanical cleaning with appropriate tools or gentle chemical treatments, should be prioritized to preserve the

integrity of the window. The goal is to remove harmful corrosion products and dust while safeguarding the underlying materials and decorations. Additionally, once cleaned, protective coatings can be applied to prevent future corrosion and dust accumulation, ensuring the window's longevity and preserving its artistic value for future generations. This holistic approach balances immediate aesthetic improvement with long-term conservation objectives.

The importance of the treatment and maintenance process for the Al-Sabil Al-Ahmadi window is not limited to revealing the decorative details that were obscured by dust and corrosion layers. It also plays a crucial role in stabilizing the alloy and removing potential causes of future damage. The choice of cleaning method depends on the intended role to be highlighted for the antique piece, the kind of its manufacturing materials, the surrounding conditions, the materials used in its creation, and the type of deterioration products on the surface⁶⁰. The treatment and conservation strategy developed for the Sabil Al-Ahmadi window employs a graduated approach to cleaning procedures and the application of protective coatings.

3.5.1 Cleaning Techniques

The choice between mechanical cleaning (using brushes, abrasives, or ultrasonic cleaners) and chemical cleaning (using solvents or acids) depends on the artifact's condition and the type of contaminants present. Mechanical cleaning may be effective for removing thick corrosion layers but risks damaging the surface. Chemical methods can be more selective but require careful handling to avoid adverse reactions⁶¹. This method involves creating directed stress to disintegrate corrosion products and dust accumulations. It is used if there is a layer of corrosion products with poor adhesion to the metal surface or if it is not homogeneous, as observed in some parts of the window. Dust and corrosion are removed using scalpels, which are then used to remove calcified dust firmly attached to the window surface due to exposure to rainwater and improper cleaning methods. Brushes of various shapes and roughness levels are used to match the details of the specific window section being cleaned, as shown in Figure 11.

3.5.2 Protective Coatings

The selected protective materials must be compatible with the artifact to avoid adverse chemical reactions. For example, certain coatings may contain solvents that could harm sensitive surfaces. It should also be selected for their long-term effectiveness in the specific environmental conditions. Coatings for external artifacts must be able to withstand UV exposure, moisture, and temperature fluctuations. After completing the

⁶⁰ Cronyn, J. M., *The Elements of Archaeological Conservation*, p. 224.

⁶¹ Scott, A.D., *Copper and bronze in Art, Corrosion, Colorants, Conservation*, 2002, p.122.

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cleaning steps and removing dust, calcifications, and corrosion products, the surface is thoroughly cleaned using distilled water to eliminate any remaining dust and dirt. It is then dried using ethyl alcohol in preparation for applying the insulating material. Additionally, the marble base at the bottom of the window (the lower part of the facade of the Sabil building) was covered with polyethylene wraps to ensure it remained unaffected by the protective coatings during their application to the bronze window. Three layers of the polyurethane-acrylic based protective coating PUR-129 were applied, selected for its proven effectiveness in experimental studies. Known for its high resistance to harsh environmental conditions and chemicals, PUR-129 offers robust protection for exposed metal surfaces in uncontrolled outdoor settings⁶².

The selection of PUR 129 coat was driven by its superior properties, including high durability, flexibility, corrosion resistance, and excellent adhesion to surfaces, making it ideal for outdoor artistic metal works. While it has a longer drying time (1-2 hours), this is a characteristic of its chemical composition, which is based on acrylic and polyurethane, designed to enhance durability and resistance to corrosion and chemicals. To mitigate drying time, we optimized application conditions by choosing dry, sunny days with minimal air traffic. Ventilation was improved by setting up a protective cover two meters away from the window to shield it from dust while allowing good airflow. This approach ensured that each layer dried in less than 30 minutes. Ultimately, the advantages of PUR 129, particularly its long-lasting protective qualities, outweigh the drying time, which is secondary to its performance. Thus, the balance between drying time and durability aligns with the research objectives, emphasizing that the drying time should not be viewed as a significant drawback given the coat's overall benefits.

The application was carried out using a brush, starting from top to bottom. The protective coatings were applied to both the inner and outer sides of the window, where three perpendicular layers of the PUR-129 protective coating were applied with a 12-hour drying period between each layer to ensure complete drying, as shown in Figure 12 and 13. Once treatment has been applied, regular monitoring is essential to assess the effectiveness of the conservation efforts and to identify any emerging issues. This might involve routine inspections and potentially reapplying protective coatings, or cleaning as needed.

⁶² Reda, Y., Abdelbar, M., Elshamy, A.M., *Fortification performance of polyurethane coating in outdoor historical ironworks*, Bull Natl Res Cent. Vol. 45(69), 2016, p. 13.

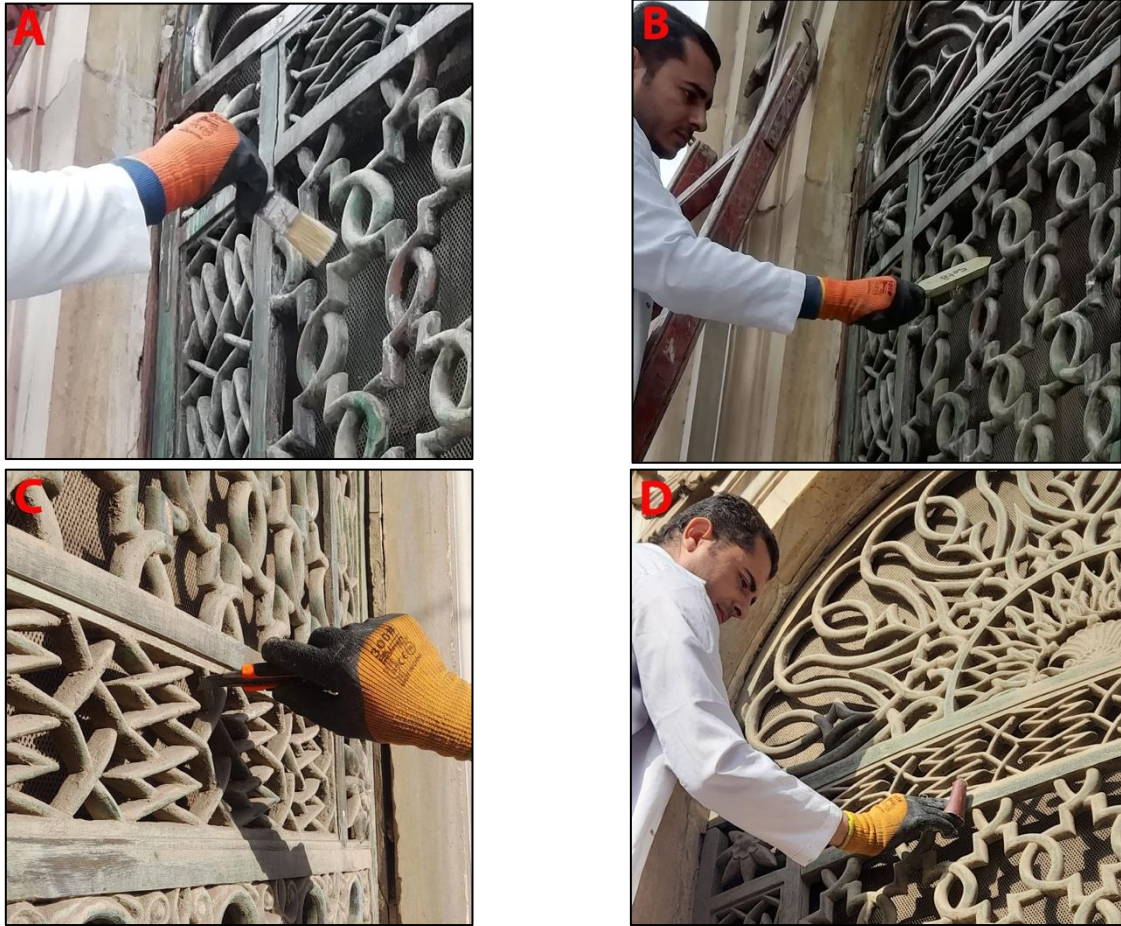


Fig. 11. A-D; Mechanical cleaning using hand tools like brushes and scalpels to remove calcified dust and thick corrosion products.

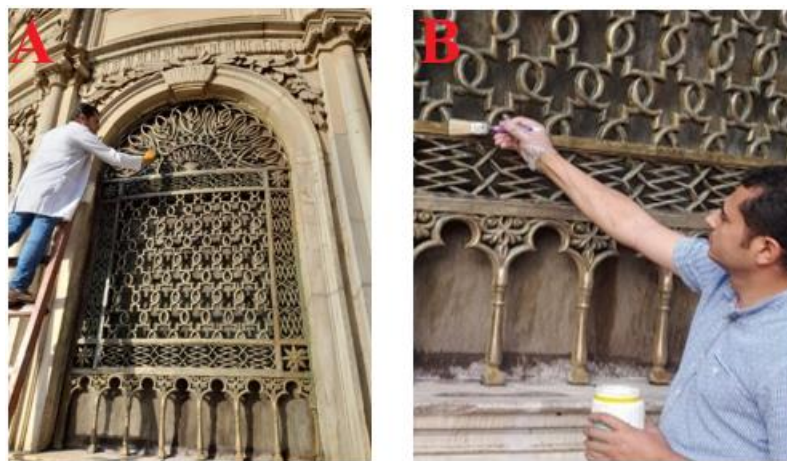


Fig. 12. A,B; show application of protective coating (multi-layer Pur-129).

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Fig. 13. shows the window grille after cleaning and protection.

4. Conclusion

The analysis revealed that the alloy used in the net-making of the Sabil window is a quaternary bronze consisting of 82.1% copper (Cu), 5.9% tin (Sn), 6% lead (Pb), and 4.3% zinc (Zn). This quaternary alloy exhibits better corrosion resistance compared to binary alloys. The combination of these elements creates a stable oxide layer that is more resistant to various forms of corrosion. Metallographic examination revealed that the alloy predominantly consists of the alpha (α) phase, with lead forming separate phases or inclusions within the copper matrix, contributing to its overall durability and suitability for decorative and structural applications. The XRD analysis reveals a complex interaction of various corrosion processes on the Sabil window. The combination of oxidative corrosion, chloride-induced pitting, and the deposition of environmental particulates and pollutants suggests that the window is undergoing significant corrosion due to its exposure to the outdoor environment. The comprehensive treatment method for the Sabil Al-Ahmadi window involved meticulous cleaning and the application of a multi-layered protective coating of PUR-129, ensuring both the preservation of its decorative details and the stabilization of its alloy.

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