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Preliminary Study of the Armored Door at Al-Zaher Barqūq's Mosque, Condition Assessment, and Previous Conservation Campaigns

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Abstract

Copper alloys-plaques used for the door of Barqūq's Mosque exhibited significant corrosion processes. Thorough chemical analyses revealed a diversity of metals and alloys in the plaques. This paper presents a case study related to the armored door's chemical structure and crafting techniques, along with its degradation and previous conservation campaigns. The surface morphology of the laminated door was examined by both stereomicroscope and scanning electron microscopy (SEM).
The microstructural analysis is done by scanning electron microscopy-energy dispersive X-ray spectrometry (EDXS). Copper-iron corrosion products collected from the surface were examined using Raman spectroscopy. Fourier-transform infrared spectroscopy (FTIR) was used to characterize of the adhesive material used to fix the inlaid silver. Results revealed that quaternary alloy (copper, tin, lead, and zinc) were mainly used to manufacture the armored door inlaid with gold, silver, and red copper. A disproportionate percentage of chloride and sulphur ions were detected in the active corroded products growth on copper-based alloys and inlays. These are the cause of morphological alterations. Recent routine techniques performed for conservation treatments of the plaques and inlaid silver. The protection system was done by benzotriazole, and incralack followed by a thin layer of Boston wax.
KEYWORDS: Al-Zaher Barqūq's Mosque, Armored Door, Copper-Alloy Sheet, Corrosion, Examination, Analyses, Conservation

Introduction

Islamic architecture's history is usually studied on the basis of religious architecture, because -apart from a few notable exceptions- later generations saw little need to preserve the secular buildings of their predecessors. They concentrated their efforts on maintaining mosques, madrasahs, and the like. With time, historical and archaeological building quickly fell into ruin.

Mamluk style can either be examined diachronically as one phase in the development of Islamic art in Egypt, or compared synchronically with contemporary artistic traditions in Islamic lands[1]. The first approach is privileged here. The architectural style in Mamluk Egypt depended on the local Egyptian heritage. Mamluk architecture initially relied on Fatimid and Ayyubid forms, developing into its distinct style [1], characterized by the large use of metal in decorating [2]. The Egyptian Mamluk dynasty produced some impressive Islamic patterns combining in copper-alloy plaques with wood [3]. In the 14th century, Barqūq was the first Circassian sultan of Egypt and the founder of the Mamluk dynasty (788 AH/ 1386 AD). The Sultan ordered to erect his mosque in the Coppersmith's Bazaar [4]. The Barqūq Complex[2] is located in the eastern area of modern Cairo [5], standing behind the Madrassa of Al-Nasir [4]. The main entrance is located on the west side of Al-Mu'izz Street, as shown in Fig.1.

1Bloom, J., Mamluk Art and Architectural History: Review Article, Middle East Documentation Center, The University of Chicago, 2012, p. 31.

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2 Registered as Monument No. 187 [3].

Fig. 1. Main entrance of Barqūq's Complex [6, 7]

The armored door installed at the entrance of the mosque is covered showing a large amount of silver, gold, red and yellow copper with entrance canopies. The inlay workers combined the metals, a popular craft in Egypt in Mamluk times [8]. The door and its window grilles match so well that it is likely that the production of metal fittings was standard. This contrasted the surface by creating multi-coloured patterns of metals [9]. The earliest remaining door is dated to 662AH/1262 AD [8]. Barqūq's door is similar in layout and style to Al-Muayyad [10] and Al-Tawil's doors [11].

The role of the huge door is to provide the interior parts with the needed lighting and ventilation. It also reduces the exterior noise reaching into the interior of the building [12]. The door was made of heavy wood planks joined together with tenons and adorned with metal plaques and inscription bands nailed supporting the protruding repousse designs.

This door is made of a wooden double-leaf, with twelve rectangular panels assembling on the battens. Two horizontal plaques with inscription running across the wings are made of engraved portions [13], inlaid with embossed silver, gold, and bronze units. The standard design of the star pattern on doors is composed of three elements: a large geometric central field of star designs, two rectangular inscription bands above and below, and a border frame surrounding the composition and demarcating the central geometric field from the epigraphic bands [8]. This décor was developed during Barqūq's reign [6]; the star patterned doors only appear in façades while another motif produced then, medallion or metal band doors, were used both as entrances and interiors [14].

Bundles made of zigzag patterns, guilloche bands, and fretwork were inlaid with gold and silver [8,14]. Barqūq's name adorns the center of the 18-pointed stars [15], as shown in Fig. 2. Various decorative elements are distinguished in this copper-alloy sheet as studs, star-pattern, and geometrical bands, as shown in Fig.3. Skilled manufacturers, such as blacksmiths, were present and produced decorative elements [8].

Fig. 2. Embossment of 18-pointed star pattern

Fig. 3. Details of decorated elements on the original

Six different materials (wood, copper-based alloys, silver, and gold) were used to make the Barqūq door. The endowment deed of Sultan Barqùq describes that walnut wood was used for the window shutters in the façade and for the six doors located inside the building. This type had an intrinsic value, as there was a dearth of quality wood. It might even be argued that to preserve valuable wood, door-makers in an earlier stage to cover the entire surface with metal to shield the costly support from the devastating effects of the sun and humidity. Wood is the support onto which thin copper-alloy plaques were applied as brass framing, especially when compared to the much thicker plaques that were attached to entrance door [10].

Most surviving Islamic metal objects are made of copper alloys [16]. Previous authors, such as Scott (2002), indicated that the armored doors were made of quarterly alloy composed of (Cu–Sn–Zn–Pb) [17]. Despite its remarkable properties, copper has insufficient mechanical strength properties, hence the use of copper alloys, especially in the manufacture of armored doors. Most elements are soluble in copper, and can constitute alloys with it. Copper alloys were widely used in precision works [18], due to their high resistance to corrosion, and their color varying depending upon the amount of zinc or other metals in the mixture. It has been suggested that Mamluk metalwork at the time (1360-1382) declined in quality [19], due to shortage of metal and experienced metal workers [20].

Silver, a precious metal frequently used for valuable decoration. To support this argument, Sultan Hasan’s complex’s multiple inlaid star patterned-doors were used as reference.

Techniques, such as casting, filling and sheet-cutting, were employed for the oblong inscribed bands on overall star pattern doors in variations inlaid with precious metals of gold, silver, and copper. The metalworkers prepared copper-alloy plaques by engraving the outline of the design. Repousse, the front of a metal sheet raised by hammering from the back, after the contours were refined through chasing, could be done by variously shaped punches, chisels, and tracers. The punches were stamps in the form of small bars with square, round, oval, or ring-shaped ends [16]. Different geometric shapes were repoussed into large plaques to be attached to the door’s exterior. The interior face of the door is undecorated [8]. The areas that were to be inlaid were roughened; silver wires were hammered deeply into the irregular lines made by the burin [16] shown in Fig.4.

Fig. 4. Gold and silver-inlaid on the decorative elements

By a series of these processes of hammering and re-embedding, followed by chasing, the metal attains its finished appearance. Longitudinal strips were applied in the center of the framing plaques of the star pattern, while patches of silver were used sparingly to accentuate the embossed stars. Epigraphy is an integral part of the decoration on Barquq's portal. Finally, the surface is smoothed using appropriate tools as file, before fixing them on the wooden panel.

The internal face of the copper-alloy sheet was painted by black coating identified as a mixture of hydrocarbons such as tar, bitumen and mastic (a brownish resin from the bark tree). The interior of the wood panels was painted by red material [10]. Hand-forged nails and screws were used for fastening both the stars and the surrounding bars to the underlying wood for support. They are of various lengths with heads in high relief. Mols mentions “cast brass plaques” in the description of the in-situ doors of the Barqūqiyya, but the knockers were made of cast and engraved bronze. Even today, the exact composition of Mamluk fittings is still unknown, as a scientific analysis of the composition of these base metals has yet to be conducted.

Metalworkers first gouged out longitudinal depressions in the framing plaques to accommodate the nails. After positioning the nails, they were covered with copper strips, hammered into the recess.

This method required a thick layer of copper designed for this usage [21]. The earlier and original decorative elements were affixed to the covering brass and bronze plaques by nails made of steel and brass (fourteenth century).

Comparison between Barquq's door and other similarity doors could be used to assess the authenticity, states of preservation, and the actual condition. The door in Kuwait was made with the intention that it should look like the main entrance door of the Barqūqiyya shown in Fig. 5 and 6.

Fig. 5. Laminated door of Barquq's Mosque

Fig.6. Armored door of Barquq preserved at Tareq's museum [11]

Fourier-Transform Infrared Spectroscopy

The detailed documentation of the components of this door would go a long way to clarify the original door's material and how much is restoration/replacement. These topics highlight the importance of this heritage spreading knowledge about the past.

There is no published paper about the corrosion mechanism and previous conservation campaigns of copper-alloy plaques at Barquq's Complex to the author's knowledge. This study of the armored door aims to characterize its chemical structure and corrosion in a polluted environment.

Experimental

Physical examination and analyses

Various investigations and analytical techniques were employed on separated metal samples, corrosion products, and pollutants. The morphology and the features of the decorative elements were investigated. The technical analysis contributed to understanding the manufacturing techniques of the armored door, characterizing the chemical structure and determining the corrosion products to develop the appropriate treatment plan.

Stereomicroscope investigation

A Zeiss stereomicroscope was used to characterize the morphology of the interface and external surface of the plaques in combination with magnification X40 objectives. Corrosion phases were observed in distinct regions.

Rapid Identification by Scanning Electron Microscope-Energy Dispersive X-Ray Spectrometry

Using a scanning electron microscopy-energy dispersive X-ray spectrometry (SEM+EDXS), geological survey XL301[1] was undertaken to study the microchemical structure and surface morphology of copper-alloy sheet/wood, the interface's nature with the base metals and their corrosion products. This method is a non-destructive technique used in investigation and analysis, which is carried out to characterize the crystallographic structure of the corrosion products. In particular, the combined use of surface and bulk techniques has been determined. The information is used to recognize technical aspects and provide data for the initial classification of copper-based alloys.

1 The XL-30 geological Scanning Electron Microscope is a state of the art high-resolution research instrument. It has a field emission electron gun (FEG) and can be operated in three vacuum modes, e.g., conventional high vacuum, low vacuum, and true environmental mode [25].

FT-IR measurements were performed using a Vacuum VERTEX 70V spectrometer with HYPERION 3000. Samples were prepared by grinding mixed with KBr. This powder mixture is then crushed in a mechanical die press to form a translucent pellet through which the spectrometer beams can pass. It is usually unnecessary to mark any of the bands in the fingerprint region (less than 1500 cm-1). The organic adhesive of silver inlays exhibits broad bands due to high degeneracy of the vibration, thermal broadening of the lattice dispersion and mechanical scattering from powdered samples [22].

Raman analyses

Raman scattering has been performed as a vibrational spectroscopy technique complementary to infrared spectroscopy for chemical analysis [23]. Obtained spectral signatures were used for the characterization of copper corrosion products and soil sediments. The basis of corrosion identification by Raman spectroscopy is done by comparing the spectra of an unknown material and reference.

The advantage of Raman spectroscopy is that the freshly cleaved surface can be used as the sample without any preparation [24]. Raman measurements were accomplished using a dispersive microscope made by Bruker Company (model Senterra spectrometer), equipped with an Olympus BH2 microscope.

Sampling

Different separate solid and powder specimens from the metal, corrosion products, and silver-inlaid were observed and analyzed, shown in Fig.6. The samples were prepared by embedding them in Araldite resin. Then they were ground using emery papers and polished by the use of fine α-alumina with water. Solid samples were examined as polished surfaces by stereomicroscope and scanning electron microscope coupled with energy dispersive X-ray spectrometry. Powder samples were analyzed by X-ray diffraction. The adhesive material of the inlaid area was collected for analysis by FT-IR.

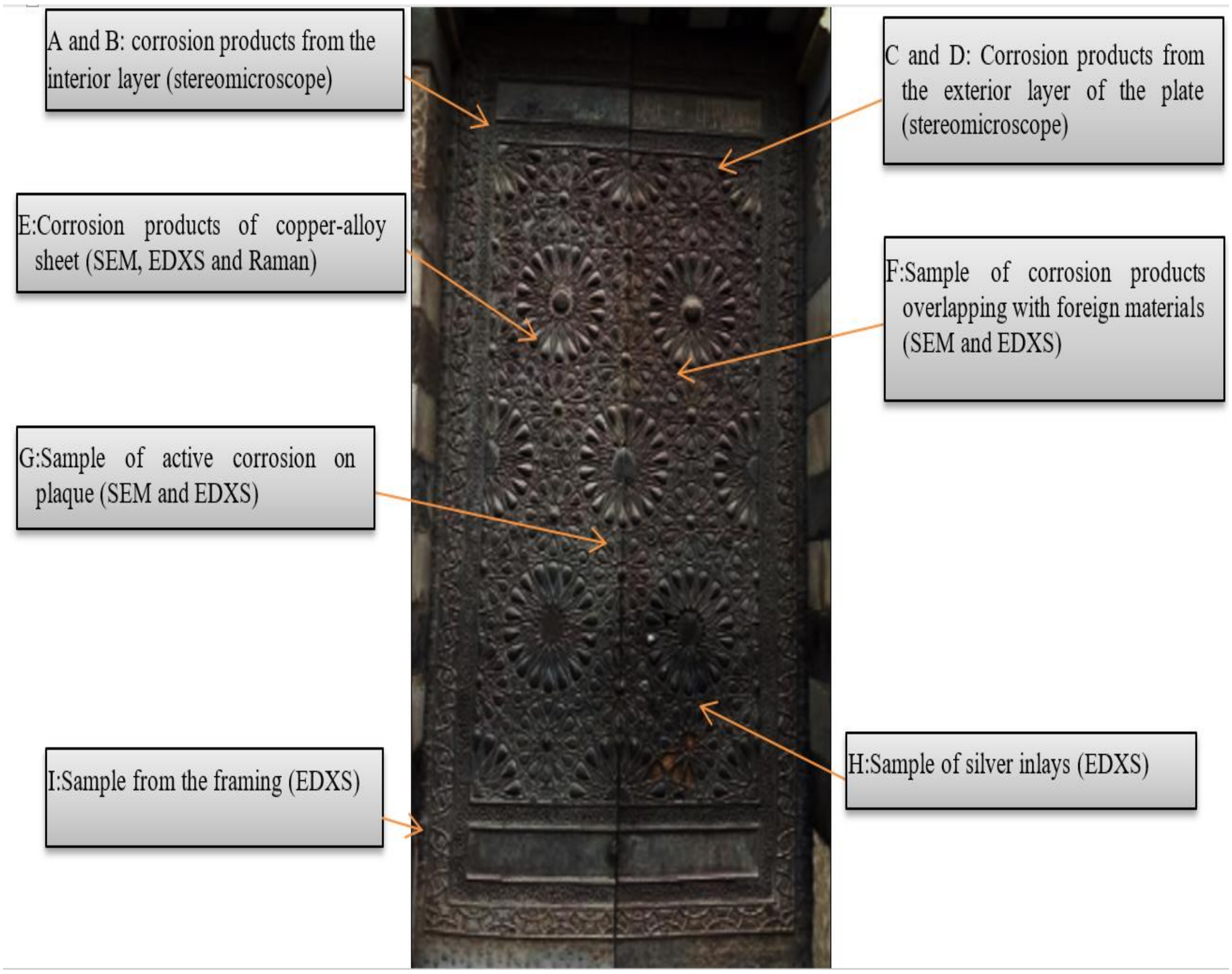

Fig. 7. Selected sampling sites for investigation and analyses of the copper alloy sheet/wood

Results

Visual Examination of the Exterior and Interior Surface of a Copper-alloy Sheet

Traces of inlays with gold remain. Different samples were investigated by stereomicroscope to reveal the distribution of corrosion products adjacent to the characterized the rate of corrosion reactions on the armored door. The panel surface appeared in pinkish-red color, seen with a natural green patina shown in Fig. 8.

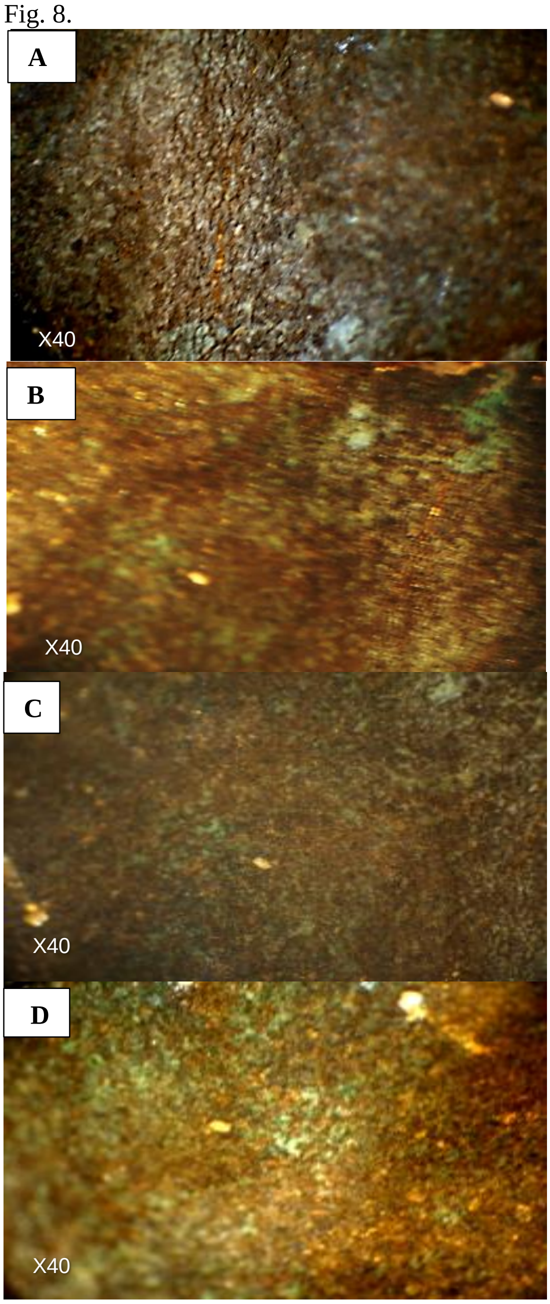

Fig. 8. Stereomicroscope results of the plaques patina. (A and B) Investigation result of the interface of the planks/wood. (C and D) Investigation result of the exterior layer

Scanning Electron Microscope-Energy Dispersive X-Ray Spectrometry

The morphology of copper alloy plaques and silver-inlaid decorative elements was investigated using a Scanning electron microscope (SEM) to monitor changes. Detailed observation and analysis results of the selected samples by SEM-EDXS are shown in figure 12 and Table 1.

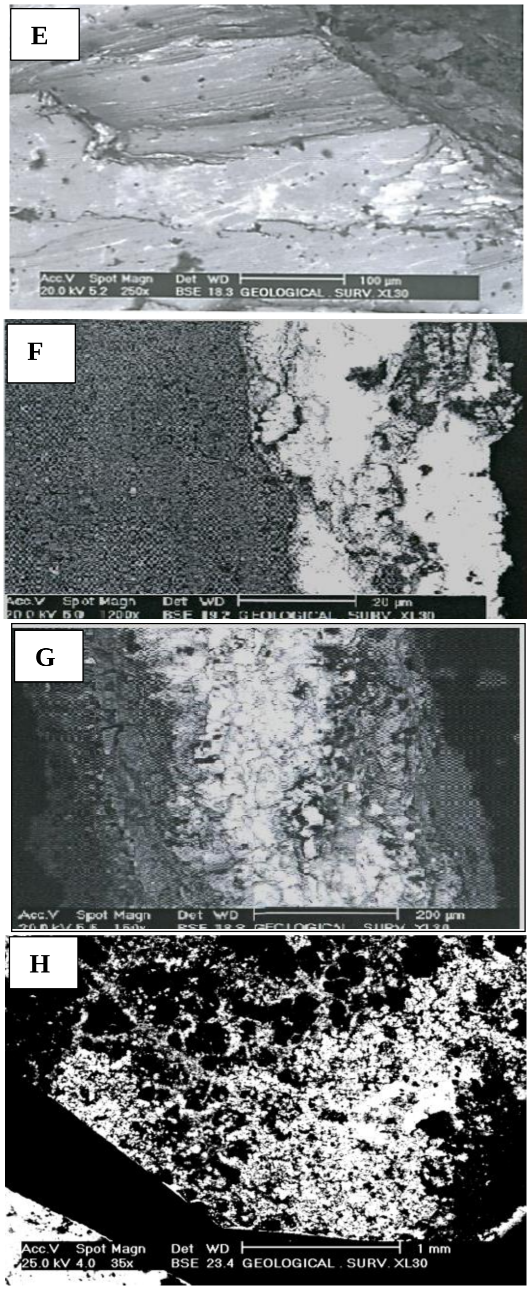

Fig.9. SEM images of different samples representing the morphology of the plaque surface. E: Sample of corrosion products of bronze alloy. F: Sample of corrosion products mixed with foreign materials made up of the bronze patina. G: Sample of active corrosion on the brass alloy. H: Sample of silver inlays on the surface adherent to its corrosion products [26].

Fig. 9, E: The Scanning electron microscope image of the bulk sample revealed the morphological characteristic of bronze with zinc and lead, as deep cracks on the surface. Distribution pits were caused by segregation of the insoluble lead grains. **F:** The Scanning electron microscope image shows surface fretting damage and cracking caused by chloride and sulphide ions associated with salts. **G:** The Scanning electron microscope image shows stress layered and intergranular corrosion forms on decorative elements. **H:** The Scanning electron microscope image shows surface degradation of inlays resulting from active corroded areas.

There is a relationship between the chemical structure of copper-alloy plaques and the surface morphology shown in the following table (1). The crystal structure information of copper alloy sheet inlaid with silver and their corrosion products was identified by Energy Dispersive X-Ray Spectrometry (EDXS).

Table (1). EDXS results of the quantitative reporting of elemental concentrations of patina and foreign elements on copper-based alloys and silver inlaid [26]

Sample	Cu	Sn	Ag	Zn	Pb	Cl	Na	Ca	S	Fe	Al	Si	k	Mg
E	75.77	2.35	-----	8.29	9.20	0.65	----	----	-----	0.74	1.20	1.79	-----	----
F	11.54	-----	----	----	----	4.48	1.58	32.9	26.7	3.70	4.31	11.8	1.26	1.54
G	55.85	----	------	13.01	----	11.7	6.53	2.74	5.81	-----	1.16	1.86	0.64	0.68
H	0.82	-----	80.64	-----	----	8.22	-----	-----	9.55	0.77	-----	-----	-----	-----
I	88.14	-----	------	10.98	----	-----	-----	-----	-----	0.88	-----	-----	------	-----

According to the EDXS results of sample **(E)**, central decorative elements are made of quarterly alloy (Cu 75.77 wt.%, Sn 2.35 wt.%, Zn 8.29 wt.%, Pb 9.20 wt.%). The copper alloy plaques have zinc and lead as major alloying elements. Tin was detected at more than 2% in the microstructure of the corroded surface. Other elements were identified in low percentages as iron and chloride ions. Pitting corrosion is the main form in this area; chloride ions were detected in the surface pits.

EDXS results of sample (**F**) show that copper was detected in a small proportion overlapping with white stains caused by gypsum salts initiated by dusting. They are likely due to gap-filling with stucco during earlier conservation works. Aluminum and silicon were detected in a high percentage, likely caused by surface contamination with copper corrosion products. In addition, decuprification occurred by selective Cu dissolution of this area.

Sample (**G**) appears to be a brass deterioration with bronze disease; sulphur and chloride ions were detected in high proportions in the silver inlays, as well as seen in sample (**H**), revealed by a discoloration in those areas. Also, gypsum salts were detected in this area. Pure silver is the main component for inlaid inscriptions; electrum alloy was not used. EDXS results of sample (**I**) demonstrate that the purity of copper used in forming brass alloy was composed of more than 88 wt.%, with zinc added for the remaining 12 wt.% for the framing. Na^{+} is accompanied by the presence of Ca^{2+} and K^{+}, in samples (**F**) and (**G**) were detected, but in samples (**E**), (**H**), and (**I**), and were not detected. They are alkaline elements which were affected by the surrounding environment.

Raman spectroscopy

Laser power gives high energy without burning the sample for observation, as seen in fig. 10.

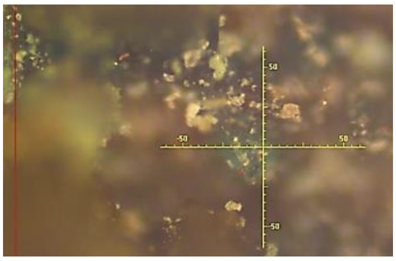

Fig.10. Optical microphotographs of corrosion products on the plaques

Raman spectroscopy to the surface provided a sensitive in situ probe of copper and iron corrosion products in the rusty-brown area. The peak shift was concluded with smoothing. The results show that the corroded surface samples were in contact with iron nails (Figure 11).

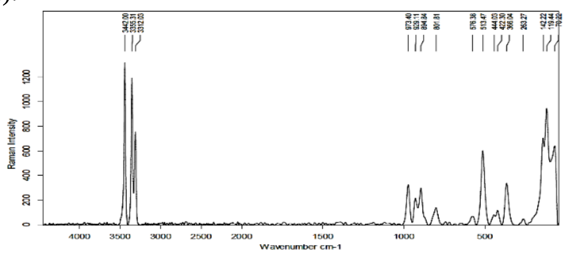

Figure 11. Raman shift of corrosion products of copper-alloy sheet

Regarding the spectrum of the plated-door, there is a crowding of bands in the 70-973 cm^{-1} and 3312-3442 cm^{-1} regions caused by different copper corrosion products, but there are no peaks in the region 1000-3311cm^{-1}.

Table (2). List of the copper-iron corrosion products collected from the laminated door

Compounds	Formula	Characteristic Wavelength Cm^{-1}	References
Natokite	**CuCl**	**263.27**	**24, 27**
Cuprite	**Cu_2O**	**513, 576**	**28**
Botalchite	**$Cu_2(OH)_3Cl$**	**894**	**28**
Brochantite	**$Cu_4(OH)_6.SO_4$**	**142.22-422.30-444.03-973.40**	**28**
Iron hydroxychloride	**$\beta.Fe_2(OH)_3Cl$**	**422.30**	**26, 29**
Hematite	**$\alpha.Fe_2O_3$**	**283.27**	**26, 30, 31**
Clinoatacamite	**$Cu(OH)_3Cl$**	**139-513-894-973-3312**	**32**
parataacamite	**$Cu(OH)_3Cl$**	**283.27-366-513-894,148**	**28, 33**
Atachamite	**$Cu(OH)_3Cl$**	**119-283.27-366.04-422.30-513.74-972.40-3442-3355.31**	**28, 34**
Gerhardtite	**$Cu(OH)_3NO_3$**	**261-929**	**34**
Cu-nitrate	**$Cu(NO_3)2.H_2O$**	**119.44-142.22-801.81**	**34**
Limonite	**FeO (OH) nH_2O**	**894-366**	**28**

As illustrated in Table 2, chloride-rich patina products, such as nantokite, atacamite and botalkite were mostly in the corroded parts of the plaques. Cuprite and tenorite were also detected in the deteriorated structure. Copper corrosion products were associated with iron rust (limonite and hematite).

FT-IR results

A different phenomenon is distinguished in the FT-IR spectra of ancient adhesive of silver inlays. Spectral ranges from 600-3400cm^{-1} collected these results. After comparison with a referenced database, wavenumbers of the ancient adhesive material match with the wavenumber of Alcohol-based Mixtion adhesive of polyvinyl acetate (Figure 12).

According to previous literature, the difference between the FTIR results and the standard sample of the adhesive material is caused by aging and degradation mechanisms altering the chemical groups.

Condition Assessment

The plaque condition is assessed from the perspectives of its chemical structure, its residual properties, and its environment. Al-Mu'izz Street is a crowded tourist destination with human made-deterioration lead to increase the corrosion rate of the Islamic metal works. Careless and uninformed treatments represent the major problem facing Al-Mu'izz Street heritage, because of the quick expansion of the urban network. Construction damage to the stone gate initiated the destruction of the building elements, and became dilapidated and partially in ruins by the second half of the 19th century (Figure 13).

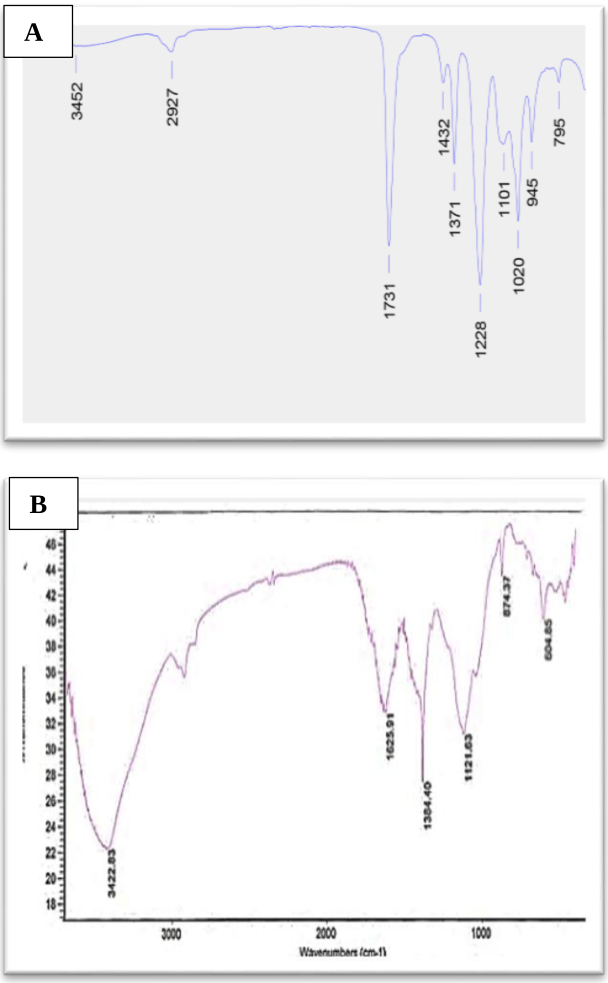

Fig. 12. FT-IR spectra of the adhesive material, (a) Polyvinyl acetate standard; (b) Studied sample [25]

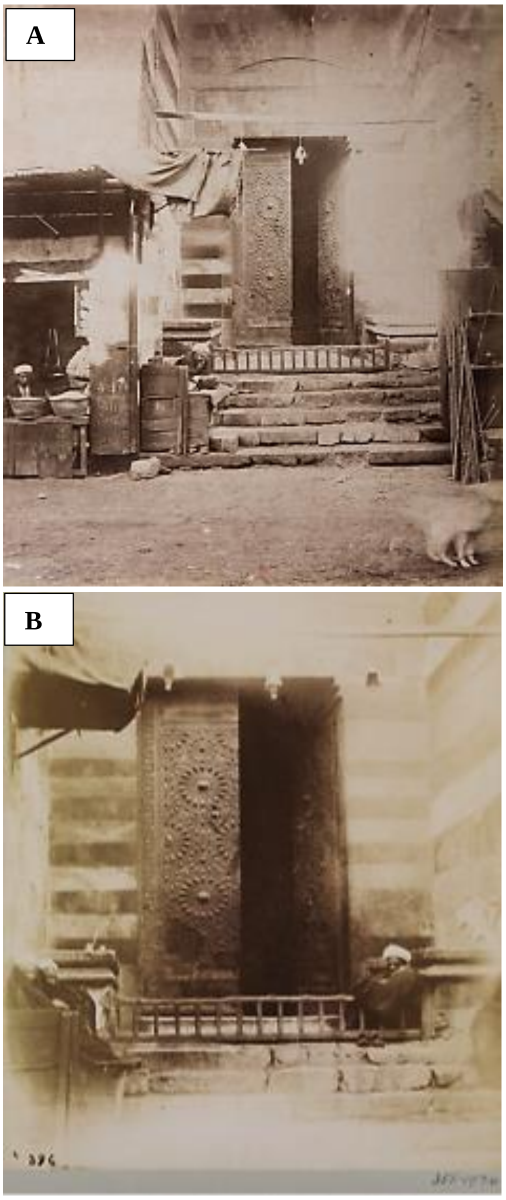

Fig.13. Old photos show serious damage of the entrance door at the funerary madrasa of Barquq before the refurbishment [20]

The wooden panel below the copper-alloy plaques was separated, nails and decorative elements detached due to hygroscopic construction materials with temperature excess and relative humidity. Humid air oxidation and moisture content of wood represent an electrolyte of the interface constituents (wood-metal corrosion) taking place in electrochemical cells consisting of different metals or corrosion products [35].

Copper-based alloys (bronze and brass) and silver lose their physical properties due to atmospheric pollutants. The inferior structure at Al-Mu'izz, Barquq complex increases the relative humidity with pollutants which increases the oxidation. Cuprite, copper receives another natural coating of black oxide (tenorite, CuO) [36] which transform copper and cuprite into the green patina formed by copper carbonate mixed with basic copper sulphate and basic cupric chloride (atacamite). Silver tarnishes rapidly in a polluted urban environment. Both chloride and sulphur in the environment cause rapid blackening of the surface.

Reactions of the plaques can be catalyzed by iron nailed corrosion products, which cause degradation of the cellulose in the wood [37]. In the converse, the presence of tannins, cellulose, and polycyclic compounds usually enhance the film formation over the metal surface, thus producing a layer inhibiting and retarding the corrosion of steel nails [35].

Aqueous extracts from wood change the pH around 4-5 because of the effect of their organic acids. Lead alloyed with copper can be attacked by organic acid vapors and pollutants emitted from wooden planks and organic adhesive (Figure 14) [38].

EDXS results point to sulphur being detected in a high percentage. Hydrogen sulphide, in this case, can be the consequence of the bio-deterioration of sulphur-containing polymeric materials, producing acanthite or argentite, representing anti-friction alloys [39].

The interface (wood/metal) consists of copper corrosion products covering with a noble patina; the exterior layer is formed by green corrosion products of activated corrosion area and other salts [40]. Copper-alloy plaques were covered by mixed encrustations of grayish-green patina compact with dust. EDXS results revealed that sulphur and chloride ions were detected in high content with copper and silver corroded products. Pitting corrosion deeply is observed which lead to weight loss and surface pits [41] (Fig. 14).

Fig. 14. Accelerated corrosion voids

Lead as an alloy component is stable in wet conditions as it is covered by a protective coating of $Pb(OH)_2.PbCO_3$. In the presence of high quantity of carbon dioxide, corrosion is likely to occur due to the formation of the more soluble lead bicarbonate $Pb(HCO_3)_2$ [42]. For lead, this large variation has to be ascribed to Pb globules that are not miscible in the Cu matrix [43], because lead does not alloy with the copper other ground salts, it forms discrete droplets as globules randomly throughout the metal that range from a few microns to 30-200µm in diameter [17] such as in the latticework.

Lead and tin have similar corrosion potentials to produce a lamellar wart-infested surface with powdery corrosion products [44]. Galvanic deposits have been reported to occur mostly in bimetallic couples (copper and steel). Also, it is being identified in many situations (e.g., galvanic corrosion of metals occurs in metal-reinforced polymer matrix composites and metal matrix composites. It has been found that minerals, in general, exhibit potentials more noble than most metals and, therefore, may cause galvanic corrosion [45].

Galvanic corrosion occurs between copper and steel. They can change positions in the galvanic series depending on alloy elements and relative humidity. Cu/Fe couples (µAcm-2) are six times greater at 100% relative humidity as compared to 75% [42].

Higher fatigue corrosion appears on the star-pattern area, especially where the distance between the decorative units widened due to edges cracking. An initial strain was led by repousse and hammering techniques. Disruptive expansion heating is likely to be a factor of cracking caused by the variations in the concentration of tin, lead, and zinc, soluble copper solid solution.

Some decorative elements were replaced and moved from their original places during conservation procedures, resulting in cracking (Fig.15).

Many studs and nails were absent, leading a bundle and four decorative elements to be lost (Fig. 16, 17 and 18). Intricate arabesque door knockers/ hammers with pointed tips that touched the panel are missing (Fig. 19). Those preserved in the David Collection in Copenhagen coordinate with the door design [9]

Fig. 15**.** Edge cracking of the placement of the decorative elements

Fig.16. Lost bundle and nails

Fig.17.Missing decorative units on the right wing of the planks

Fig.18. Nail holes along its borders

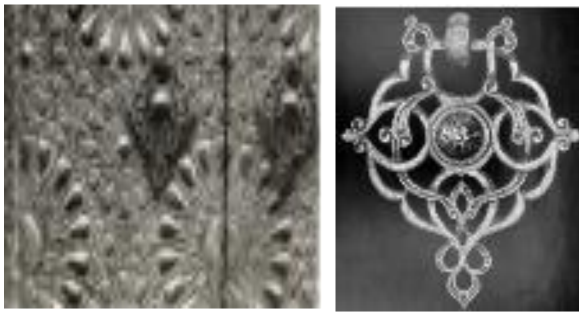

Fig.19. Missing artistic door knocker embossed star unit

Increased damage is seen on the lower section of the door, near its edge, due to the high ground moisture and salts, as well as the friction of the moving door (Fig. 20).

Fig.20. Erosion in the lower parts of the plaques

Recently, significant destructions were human-made vandalism. Precious metals such as brass, gold, and silver were an obvious target for looting. Both door leaves do not match, as one side was reworked and redecorated after revival works (Fig. 21).

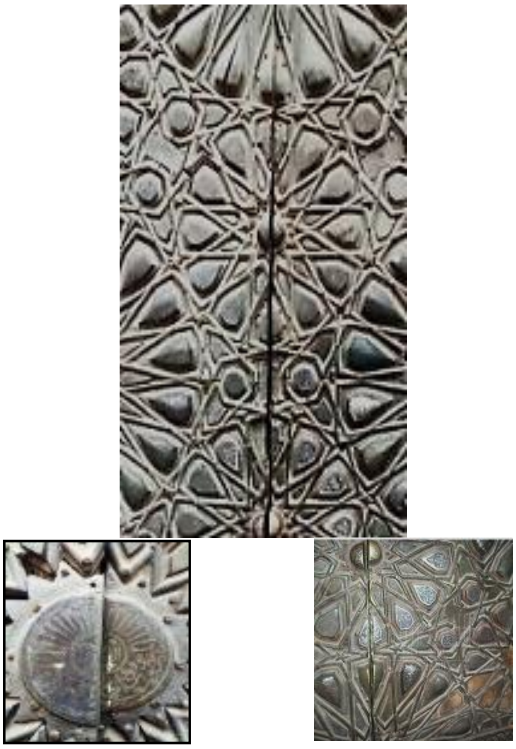

Fig. 21. Two leaves of the planks not matching

The presence of geometric patterns filing the openwork plaques' interiors or decorating the actual surface is almost negligible [11]. Ancient organic matter used in the adhesion of silver and gold wires deteriorated; they went missing or were fragmentary.

Fig.19. Missing of artistic motifs on the embossed star unit of central field

Most deteriorations of the plaques occurred during revival works. The front of the plaques shows more wear than the interface.
Humid pollutants at Al-Muizz Street decreased in recent years, but the environmental conditions of the armored door do not remain stable.

Conservation strategies applied on Armored Door

In parallel to the scientific investigations, corrosion removal was carried out to reveal hidden decoration. The conservation of the armored door and silver inlays required skill and experience. It is considered a composite object with wood and metal. Based on the visual observation and results of conducted analyses, the treatment of the plaques was accomplished using a variety of copper alloys.

Previous Conservation Campaigns

Many conservation interventions were attempted for the Islamic architectural style at Al-Mu'izz Street lead to disappear the original look of the armored door. Indeed, governments prioritized devotion places in conservation projects to welcome people's prayers. Metalworkers and artists performed this conservation work with luxurious finishing according to the economic state.
The first conservation intervention of the entrance door was performed by metalworkers who appropriated the door and substantially reworked and redecorated.
Rogers's suggests that two doors might have been produced out of the main entrance door of the Barqūqiyya during its complete restoration around 1890. Therefore Herz installed a simple wooden door in 1898; he confirmed that this door was executed in 1893. This forgery misled competent judges and provoked an inquiry.
Maladroit restorations were carried before the outbreak of World War I in 1914. Up to this date, there is no mention of the removal or replacement of this door. According to expert Ḥasan ʿAbd al-Wahhāb (1945), the door was of excellent quality, but certainly a fake, because the Sultan's titles were mixing old and modern parts. Bronze might date to the 18th century, but the brass sheet is later, dating to the 19th or beginning of 20^{th} century. He suspects that nails and framing are not medieval due to their high zinc content, being later than the original date of the door.
Instead of the sheet inlay typical in Mamluk times, the inlay of silver wire also points to a later date. Abdel Wahāb (1945) restored the entrance door when he substantially reworked and redecorated the smaller doors [11]. Treatments of decorative and inscribed plaques were done through previous conservation campaigns, as illustrated in Fig.22. It remains challenging to determine all the replaced parts.

Fig.22. A diagrammatic description of the orientation and method of attachment

All plaques and decorative elements are structured with parts from the revival works. The creation of new parts of the plaques was carried out in the early Ottoman period by metalworkers during the construction of the entire assemblage [10].

In the 1890s and 1900s, two doors might have been produced out of the main entrance of the Barqūqiyya during the complete restoration of its panels and decorative plaques [4]. Conservation works were carried out on seven doors, the main entrance and six doors opening into the ṣaḥn [10]. Copper and iron were not regarded as a noble metal in conservation. Gap-filling the spaces and cracks was performed by placing strips inside the hollows or a piece of metal and wood parallel to the edge, as shown in Fig. 23. Sometimes, artists used oxidized copper to fill the voids on the plaques.

Past conservation interventions and replacements were probably performed by metalworkers and artists who made the pieces without much supervision. The style and decorative repertoire are evidence that the artisans experienced in producing portable objects were responsible for these doors [10]. Green oil-based coatings were used to polish and add shimmer in many spots of the plaques (Fig. 24).

Fig.23. Gap-filling of missing parts and hollows loosen by corrosion

Fig. (24) Green paint as artificial patina on some parts of the plaques

(a)Yellow framing supported by the presence folded edges. (b)The bundle with green paint as artificial patina [49]

The striped decorative elements' replacement was difficult to achieve; however, turtle geometry was the best method [46]. Conservation treatment of this door was not accomplished using welding between the plaques during revival works; instead, nailing was the main technique used in the fixation.

Recent Intervention conservation

Many attempts were made for the conservation interventions of the Islamic architectural style at Al-Mu'izz Street during the renovation project of Fatimid Cairo. Those works were conducted by a private company called Abnaa A'laam Company under the supervision of Professor Dr. Atef Abdel Alattif, 2002. According to his report, conservation was performed as follows:

Multilayers of corrosion deposits overlapping dust were removed via mechanical ablation using brushes, scalpels, dry air-blasting, and bronze wool. Removal of metallic gold varnish, red oxide metal (primer/build) and layers of over paint was undertaken carefully using 99% alcohol mixed with distilled water.

Active corrosion areas were not easily cured; the green powder was cleaned mechanically and then desalinated by placing compresses of 2% NaOH. It was effective to remove both the active centers of chlorides and the sulphates from deep surface pits [47]. For neutralization, plaques were washed by distilled water for removing the chemical remains on the treated areas. After removing the chloride ions, the exposed plaques were restored to a bright surface.

Alcohol-based mixtion adhesive of polyvinyl acetate was used for gluing the new silver leaves on the plaques by brushing. Missing nails, studs, heavily rusted nails and about thirty small decorative elements were replaced with new ones that looked exactly like the original. Two broken and loose units were replaced with new ones and re-attached with common nails and screws.

Heavily corroded decorative elements were detached for cleaning and re-secured using new common nails with a rosetta head shape similar to the original ones. Structural stabilization of the corroded parts was consolidated using paraloid B72. Also, an acrylic resin was used to assemble the ancient silver inlays by impregnation. Copper-alloy plaques were brushed by benzotriazole (BTA), and nails were brushed by tannic acid. The final protection of the planks was undertaken by incralac. Then, conservation and consolidation of wood panels were performed before fixing the bronze plaques to restore the interface. Butchers Boston wax was used to protect the wood/metal interface and to render the surface smooth with its semi-matt appearance. Fig. 25 shows the final state of the armored door before its treatment and after.

Recommendations

The condition of the pairs of double doors in the Barquq Mosque Complex calls for continuous conservation. Indeed, monitoring the interface must be constant in order to avoid biocorrosion of the plaque. This section is designed for conservators in charge of preserving this monument and other copper alloy armored doors. The protection afforded to the brass may lie in its ability to eliminate the formic acid vapour before it can react to form the pale blue corrosion product [48].

Before conservation of the armored door, the environment of work should be prepared. It is better to detach the plaques during conservation treatment of copper-alloy sheet from wood to undertake all interventions. Nailing, replacing the decorative elements, re-silvering and re-gilding should all be documented by chemical analysis. For this reason, the study of the history of restoration techniques would be of great interest to decide whether to preserve or remove past elements.

Fig.25. Details of the access door on the eastern facade of the Barquq Mosque [43]

Discussion

The visual inspection identified unusual growth features on the armored surface as cracks and pits, evidence for the corrosion mechanism and corrosion rate developed. Stress corrosion was likely caused by hammering, and work hardening led to techno-corrosion, and nails act as an area of weakness on the wall of the decorative elements.

The unstable and polluted condition at the environment of Al-Mu'izz Street increased the corrosion rate of copper-alloy plaques, as observed on the surface and interface. Daily activities and long-term behaviours of visitors constitute a significant deterioration factor, more prevalent than the effects of the corrosion process.

Investigation techniques used to identify issues was undertaken by stereomicroscope images revealing the agglomerates of corrosion products are randomly dispersed. Lead segregation was observable in highly leaded bronzes. SEM/EDS results confirmed Raman spectroscopy and stereomicroscope results. Raman results demonstrate that iron corrosion products were detected overlapping with copper corrosion products. Iron was detected in high value caused by galvanic corrosion of iron nails, which led to a high tendency to oxidation and low corrosion resistance.

The separation of decorative elements was caused by techno-corrosion cracking of the frame and the plates and the absence of nails. Many parts on the plate are missing, due to accelerated corrosion without superimposed stress. Pits act as notches which produce a reduction in fatigue strength [49]. EDSX determined high chloride contents in both copper-alloy plaques and the area of the inlay. Raman results demonstrate that the grayish-green color was due to basic copper chloride (nantocite, atacamite and paratacamite). Atacamite $Cu_2(OH)_3Cl$ was detected on the armored door on both sides; active corrosion goes away by converting to paratacamite. EDXS identified in Sample (G), sodium, and chloride elements. Sodium chloride is the main reason for the accelerated aging of copper-based alloy.

The outdoor pollution with the selective dissolution of Cu and Zn had a high impact of the dezincification involved the suspension of Zn from brass and bronze alloys, as reported in the EDXS results of Sample (F). Tin corrosion products are loosened by diffusion during chemical reactions on the exterior layer [45]. Copper and zinc concentrations steeply migrate from the internal layer to the external ones due to dissolution lead proportions increase due to the thickness of the patina [36].

EDXS results demonstrate that sulphur and chloride were detected in high content, which made the silver inlays gray. Silver chloride (ceragyrite AgCl, chlorargyrite), and silver sulphite (Ag_2SO_4) are the most commonly found during silver corrosion [56]. Calcium and sulphur were identified in high content, associated with the detection of gypsum ($CaSO_4.2H_2O$), which covers the surface, being airborne in the environment, and owing to the lack of continuous cleaning.

The gilding on the surface was identified as gold chloride ($AuCl_3$), differing from gold paints coating the plaques. The gold leaf appears as a solid surface, whereas the paint appears granular, streaky, and dull in appearance by comparison. Gold leaf does not tarnish, but paint oxidizes and consequently ages into a green-brown. Genuine gilding retains its characteristic metallic sheen long after the paint has lost its original shine [50].

Recently, conservation treatments were used as mechanical tools and chemical treatments as alcohol removed thick layers of gold paint. They restored the surface to their original state. Also, air blasting was rarely used to remove the foreign materials; it made the unstable surfaces sensitive to humidity, furthering the corrosion process.

To inhibit further corrosion, the copper-alloy plaques were brushed with benzotriazole (3% BTA). The repeated application of protective coating with incralack increased its protection; it was a barrier to humid pollutants for long-term.

To bring the door back to integrity, conservation works were carried out. Strengthening conservation of the gaps between decorative units was made mechanically by applying wooden or metallic strips. Nailing was the main technique used in the fixation rather than welding to be alike the original technique. Some decorative elements and nails have been replaced, which were difficult to distinguish. FTIR results demonstrate that mixtion or missione adhesive was used to fix the silver wires again into the surface. Decorative elements were supported by metallic or wooden fillers.

Sections of decorated elements that are easily detached from their context may be treated and preserved before reapplying for its revival.

The plaques on the wooden doors of the Barquq Complex and their decorative elements were made with quaternary alloy of Cu-Sn-Zn-Pb. Edge plaques and nails were made of brass during the 14th century due to their physical properties and corrosion resistance. Bronze was used in several trade names when tin is present more than 2% [7], the absolute tin content of these bronzes was unchanged during corrosion and that no arsenic or antimony was lost [51]. Two types of nails were used in fastening the decorative elements manufactured from steel and brass to play a visual role with their fluted heads standing out in relief. The restored new pieces were affixed using screws [11]. However, in instances, original brass and steel nails have been reused [10]. There are several types of silver inlaid, each suitable for a particular type of leaf and basecoat fixed using both hammering and adhesive material.

In the eighteenth and nineteenth centuries what is now bronze was often referred to as brass (yellow copper alloy). The Islamic artifacts did not was not

manufactured by bronze so stick with brass, leaded brass and gunmetal composed of 88% copper, 10% tin, and 2% zinc.
Tin was detected in low percentage; it was lost by diffusion and movement of moisture, associated with rainfalls, which produce insoluble oxides and hydroxides. The oxides of tin are amphoteric and react with alkalis to form soluble salts [52]. This destabilized the copper-alloy patina formation.
The extent of previous conservation works is not known at present; cast brass and bronze portions are difficult to date and locate, because of local variations in concentrations of alloyed elements as "bosses" and lack of conservation.

8. Conclusion

The entrance door at Barqūq's Mosque is the original, but three generations of plaques, decorative elements and nails were manufactured in the traditional technology. EDXS results demonstrate that the armored door and its decorative elements were made with a quarterly alloy composed of copper, lead, zinc and tin inlaid with silver and gold. Some decorative elements and nails are not original caused by previous human alterations.
Variations of copper-based alloys used in manufacturing the plaques reflect that the metalwork is a mix of original pieces and replacement ones at a later date. Decorative elements were lost by vandalism and abuse.
The two leaves of the armored door do not match because the left door was repaired and redecorated.
Visual inspection revealed surface defects, gaps, irregularity, and corrosion forms due to the bronze disease and the behavior of lead in the alloy. Cuprite mixed with vivid green has formed on the surface since the active corrosion led to decuprification. Pitting corrosion was detected on the cast bronze alloy caused by the reaction of sulphur and chloride ions with copper alloys. The corrosion of lead perforated plaques structure. The iron detected in high content represents the victim metal, influencing the metal dissolution process. FT-IR results revealed that Matixon was the adhesive used in fixating silver wires in previous conservation works. Opinions differ about whether to reform the missing decorative elements, which would increase the artistic appearance of the door. For some, these unique doors should go into the museum. These questions are heritage-related and can only be asked once the doors have been fully restored and the corrosion neutralized.
Much remains relatively unclear, whether the history of previous conservation, the original style of the inscription and the decorative elements' form. Both of these would help establish an exact chronology for the doors

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