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INVESTIGATION AND CONSERVATION PROCESSES OF A PAINTED WOODEN COFFIN BASE EXCAVATED IN THE EASTERN SIDE OF TEBBET EL-GISH IN SAQQARA, EGYPT

BY

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ABSTRACT

[EN] The studied painted wooden coffin base, dated to the Late Period, was discovered in 2021 by the collaborative archaeological excavation conducted by the Supreme Council of Antiquities and Misr University for Science and Technology «MUST» on the eastern side of Tebbet El-Gish in Saqqara; it was registered N^o.TEE/B11/21. This study aims to assess the deterioration and the structure of the studied coffin base «identification of the wood species and characterization of the preparation layer and pigments» using multiple examination and analytical techniques to understand how it was made and to apply a suitable treatment method. The investigative study was conducted using visual examination, light optical microscopy «LOM», USB-digital microscope, scanning electron microscopy with energy dispersive X-ray spectroscopy «SEM-EDX», X-ray diffraction «XRD» and Fourier-transform infrared spectroscopy «FTIR». The findings indicated that the coffin base was constructed using *Tamarix sp*, with a preparation layer composed of a mixture of gypsum and calcite. In the painted layer, hematite «red color», malachite «green color», graphite «black color», and Egyptian blue «cuprorivaite» «blue color» were employed. Moreover, animal glue was used as the organic binding medium for the preparation layer and the pigments. These materials aligned with the data from the historical survey of the painted wooden coffins in ancient Egypt. The studied coffin base was in poor condition. It was highly affected by deterioration factors associated with the burial environment, such as subsurface water, soiling, salts, insects, and microorganisms, besides the effects of human damage, including excavation practices. It suffered from weakness and fragility, superficial solid deposits and muddy grime, stains, paint loss, holes, gaps, cracks, microcracks, detachments, and salts. Multiple treatments were applied with high accuracy to conserve the studied object, including preconsolidation, surface cleaning, fixation of detached and flaking paint layer, consolidation and treatment of cracks, missing parts and the preparation layer edges. Ultimately, the applied treatment procedures proved to be highly effective in stabilizing and reinforcing the coffin base, rendering it ready for display or storage.

KEYWORDS: Deterioration, Pigments, Preparation layer, SEM-EDX, Treatments, Wooden coffin base, XRD.

[AR] عمليات الفحص والصيانة لقاعدة تابوت خشبي ملون تم اكتشافها في الجانب الشرقي من تبة الجيش بسقارة، مصر. تم اكتشاف قاعدة التابوت الخشبية الملونة موضوع الدراسة والتي ترجع إلى العصر المتأخر في عام 2021 من خلال الحفائر الأثرية المشتركة التي أجراها المجلس الأعلى للآثار وجامعة مصر للعلوم والتكنولوجيا «MUST» على الجانب الشرقي من تبة الجيش في سقارة؛ وقد تم تسجيلها تحت رقم TEE / B11 / 21. تهدف هذه الدراسة إلى تقييم تدهور وبنية قاعدة التابوت «تحديد أنواع الخشب وتوصيف طبقة التحضير والألوان» باستخدام تقنيات فحص وتحليل متعددة لفهم كيفية صنعها بالإضافة إلى تطبيق منهجية العلاج المناسبة. أجريت عمليات التقييم باستخدام الفحص البصري والميكروسكوب الضوئي «LOM» والميكروسكوب الرقمي USB والميكروسكوب الإلكتروني الماسح مع مطيافية الأشعة السينية المشتتة للطاقة (SEM-EDX) وحيود الأشعة السينية «XRD» والأشعة تحت الحمراء «FTIR». وأشارت النتائج إلى أن قاعدة التابوت تم تنفيذها باستخدام خشب *Tamarix sp*، مع طبقة تحضير مكونة من خليط الجبس والكالسيت، وتم استخدام الهيماتيت «اللون الأحمر»، والملاكيت «اللون الأخضر»، والجرافيت «اللون الأسود»، والأزرق المصري «الكوبورفايت» «اللون الأزرق» كمواضع ملونة بطبقة التلوين، علاوة على

ذلك تم استخدام الغراء الحيواني كوسيط عضوي لربط طبقة التحضير والألوان. تتوافق هذه المواد مع بيانات المسح التاريخي للتوابيت الخشبية الملونة في مصر القديمة. كانت قاعدة التابوت في حالة سيئة، حيث تأثرت بشدة بعوامل التلف المرتبطة ببيئة الدفن، مثل المياه الأرضية، والأتساخات، والأملاح، والحشرات، والكائنات الحية الدقيقة، بالإضافة إلى آثار الأضرار البشرية، بما في ذلك ممارسات الحفر الخلسة. لقد عانت من الضعف والهشاشة، والرواسب الصلبة السطحية والأوساخ الموحلة، والبقع، وفقدت طبقة التلوين، والثقوب، والفجوات، والشروخ، والشروخ الدقيقة، والانفصالات، والأملاح. وقد تم تطبيق العديد من مراحل العلاج بدقة عالية للحفاظ على القطعة المدروسة، بما في ذلك التدعيم المسبق، وتنظيف السطح، وتثبيت طبقة التلوين المنفصلة والمتقشرة، والتقوية، ومعالجة الشروخ والأجزاء المفقودة وحواف طبقة التحضير. وفي النهاية، أثبتت إجراءات العلاج المنفذة فاعليتها العالية في تثبيت وتعزيز قاعدة التابوت، وجعلها جاهزة للعرض أو التخزين.

الكلمات الدالة: XRD، SEM-EDX، تلف، طبقة تحضير، قاعدة تابوت خشبية، معالجات، مواد ملونة.

I. INTRODUCTION

During the second season of the collaborative archaeological excavation conducted by the Supreme Council of Antiquities and *Misr* University for Science and Technology on the eastern side of Tebbet El-Gish in Saqqara, a painted wooden coffin base was discovered; it was registered under N^o.TEE/B11/21 [FIGURES 1/A-B]. Based on its design, the stratigraphic context in which it was discovered, and the associated archaeological finds, such as pottery, it was dated to the Late Period. It measures 174.1cm long, 47cm wide, and 5cm high. The structure consists of two wooden components; the larger component serves as the primary element, while a smaller piece interlocks with it at the upper section, resulting in an expanded upper area in relation to the lower section. Its inner surface is covered with a thin preparation layer of gesso, upon which is a colored drawing of Imentet, a goddess in ancient Egyptian religion symbolizing the necropolises west of the Nile, often referred to as the goddess of the west. Imentet wears a knitted garment, with the hieroglyph for «west» positioned on her head. The ancient Egyptians were accustomed to drawing her in a prevalent manner in the New Kingdom, extending into the depths of the coffins. She often extended her arms to receive the body of the deceased, which was placed above her image¹. Blue, red, and green were used in coloring, while black was used to outline the drawing. The base of the coffin lacks any inscriptions that would identify its owner. Its design suggests that the coffin was anthropoidal, a style that became prevalent during the Greco-Roman era, replacing the earlier common traditional coffin designs.

According to ancient Egyptian beliefs, the coffin was the most important element in the funerary furniture. Based on Egyptian mythology², the coffin was not only the container used to bury and protect the corpse from dangers or difficulties, but it was also considered a bridge to everlasting life. Moreover, it played an important role in protecting the deceased from evil spirits. On the other hand, it demonstrated the materials and techniques used by Egyptians and the development of religious concepts.

Numerous studies showed that coffins exhibited a wide range of designs, decorations, and types of wood utilized in their construction. Each of these elements provided insight into the historical context of the coffins, the social status of their

¹ TOSI *et Al.* 2008: 28; BILAL 2015: 170.

² For more information about coffin in ancient Egyptian beliefs, see: MOHSEN 2026: 95-126.

owners, and their religious convictions³. Therefore, many experimental and applied studies were conducted to demonstrate the effectiveness of multiple techniques and materials in the treatment and conservation of archaeological painted wooden coffins. Throughout history, wood has been recognized as one of the most ancient, strong and versatile materials, serving various purposes, from artistic endeavors to construction⁴.

During utilization, storage or burial, wood is subjected to various abiotic and biotic factors that degrade its physical and chemical properties⁵. One of the primary factors affecting wood deterioration is moisture fluctuation⁶. Wood can undergo various degradation processes as a biodegradable material, particularly when moisture levels in the burial environment are high. Excessive moisture is a key driver of the chemical and biological degradation processes of wood, leading to the degradation of cell wall macromolecules and the accumulation of inorganic substances during fossilization. The effectiveness of this process is significantly influenced by several factors, including the age and species of the wood, its intended application, and burial environment conditions «subsurface environment». Key aspects of the subsurface environment include soil composition, water presence and movement, soil pH, and salt concentration. Moreover, the duration the wood remains in these conditions, along with the stability or variability of the microclimate, is important⁷. Variations in chemical composition, particularly concerning wood-water relations, result in inconsistencies in its behavior⁸. Since conditions can differ from site to site, the chemical alterations in wood also fluctuate, contributing to the diverse chemical compositions observed in archaeological wood. Studies have shown that archaeological wood typically has lower cellulose content and a higher lignin content than recent wood. Although hydrolysis processes slowly deteriorate wood, biological factors, especially insects, also play a significant role in this degradation⁹. Furthermore, the biological decay of wood can commence prior to its burial in soil or water¹⁰. Effective preservation of archaeologically discovered wood is conditional on taking appropriate immediate measures at the site of discovery, which concerns the intact conservation of the object's state. These actions vary based on the microclimatic conditions, characteristics of the burial soil, its water content, and the discovered wooden objects. Without immediate intervention to prevent dehydration, the wood may suffer degradation, leading to increased fragility and the risk of collapse, shrinkage, or irreversible damage¹¹. The technical assessment of the studied wooden coffin base is a crucial phase in the diagnostic process. Therefore, it is essential to identify the wood species, evaluate its current condition, and understand any alterations in the structure of the woody cell walls. Moreover, assessing the surface

³ AFIFI *et Al.* 2011: 661-669; BRACCI *et Al.* 2015: 511-522; ABDRABOU *et Al.* 2015: 573-586; AFIFI *et Al.* 2019: 15-22.

⁴ NILSSON *et Al.* 2012: S5-S9; TIMAR *et Al.* 2014: 382-387.

⁵ KIM *et Al.* 2016: 233-257; KILIC *et Al.* 2019: 133-148.

⁶ Ghavidel *et Al.* 2021: 21-28.

⁷ FENGEL *et Al.* 1989: 613; FLORIAN 1999: 3-32; CREANGA 2009: 57-68; KILIC 2019: 133-148.

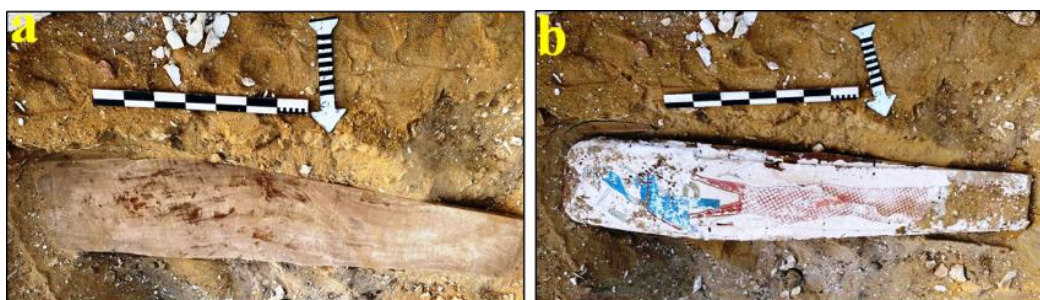
⁸ T. KOLAČAR *et Al.* 2014: 146-166.

⁹ ABD EL-KADER *et Al.* 2018: 35-41.

¹⁰ PASSIALIS 1997: 111-113.

¹¹ CHRISTENSEN *et Al.*: 2006: 1171-1178; CREANGA 2009: 57-68.

condition of «colored preparation layers» and the extent of any damage they have incurred is crucial. Such data play a significant role in determining all necessary aspects for effective treatment¹². Accordingly, the objectives of this research are to characterize the main materials used in the studied painted wooden coffin base «the wood, the painted preparation layer, and pigments», evaluate its current condition «conservation state», and select and apply the most effective treatment interventions to reveal its aesthetic, artistic significance, and enhance its historical value. Different examination and analytical methods were used, including visual examination, light optical microscopy «LOM», USB-digital microscope, scanning electron microscopy with energy dispersive X-ray spectroscopy «SEM-EDX», X-ray diffraction and Fourier-transform infrared spectroscopy «FTIR».



[FIGURES 1/A-B]: The studied painted wooden coffin base during the discovery © Photo taken by the researcher

II. MATERIALS AND METHODS

1. Samples

Tiny specimens «< 2×2×2 mm» were carefully collected from the deteriorated areas of the coffin base, encompassing pigments, preparation layer and wood. They underwent several investigations and analyses to obtain information about the painted and substrate layers.

2. Methods

A transmitted light OPTIKA microscopy «Italy», paired with an OPTIKA B 9 digital camera, was utilized to identify the wood species in the studied sample. The specimen was first prepared as thin section slides.

The VehoVMS-004 DELUXE portable USB-digital microscope was used to determine the stratigraphic structure and degradation features of the painted coffin base. It has a dynamic image sensor and eight super bright white LED lights. Offering magnification options from 20 to 500X, the microscope produces detailed images with a resolution of 1.3 MP. It allows for the examination of small details with high resolution without the need to extract samples from the object, as the images are directly projected onto a computer screen¹³.

The Quanta 250 environmental scanning electron microscope «SEM» was employed for the morphological studies of the archaeological collected samples.

¹² ABDEL-AZEEM *et Al.* 2019: 1-17.

¹³ ABDELMONIEMA *et Al.* 2022: 15- 26.

Furthermore, the attached EDX unit «energy dispersive X-ray analysis» was utilized for the microchemical analysis of the plaster and pigment samples¹⁴.

The mineralogical composition of the plaster and pigment samples was determined by a nondestructive mode without any sample preparation using XRD analysis, which was performed using an X-ray diffractometer system PW3040 – analytical equipment – PANalytical pro model with a Cu anode, working at 30mA/40kV. X'Pert high score data acquisition and interpretation software was used to determine the components of the samples.

The organic binder in the plaster and painted layers was identified by FTIR analysis, which revealed the organic functional groups present in the plaster sample after preparation. The analysis was performed using Bruker Vertex 80 «Germany» combined platinum diamond ATR, comprising a diamond disk that is like an internal reflector in the range of 4000- 400 cm⁻¹ with a resolution of 4 cm⁻¹ and a refraction index of 2.4¹⁵.

III.RESULTS AND DISCUSSION

1. Visual Assessment

The painted coffin base was discovered buried upside down within the soil stratigraphy, resulting in the painted surface being in direct contact with the soil beneath, while the wooden surface faced upward. Following its appropriate lifting, it was apparent that the coffin base suffered from multiple degradation processes due to the burial environment's deterioration factors, besides the effects of human damage, such as excavation practices. The optical observations [FIGURES 2-3] revealed that the painted surface had accumulated hard soil deposits and muddy grime.

The adhesion of these deposits was probably due to subsurface water and the pressure from the overlying soil layers¹⁶. Certain painted surface areas experienced paint loss, particularly the blue pigment. The coarse grains of the blue pigment could be a factor in the loss of the paint layer, as it demands a strong organic binder for stability.

The painted surface exhibited dark brown spots and color change, which could be attributed to chemical damage by moisture and the influence of microorganisms. Additionally, the preparation layer demonstrated considerable weakness and fragility, resulting in its transformation into a fine powder, especially in the peripheral regions. Some regions exhibited a loss of the preparation layer. Weakness, fragility, cracks, powdering of the wood surface, and tiny holes attributed to insect activity were observed in those regions. Cracks in the wood's surface enabled the infiltration of various weathering agents, especially moisture, into the inner layers. Furthermore, they are favorable areas for the growth and spread of fungi that cause wood decay¹⁷. Some parts had detachments of the painted layer or peeling, which may arise from the wood's natural expansion and contraction, as wood is a highly hygroscopic, heterogeneous, and anisotropic material. Fluctuations of temperature and humidity created stresses related

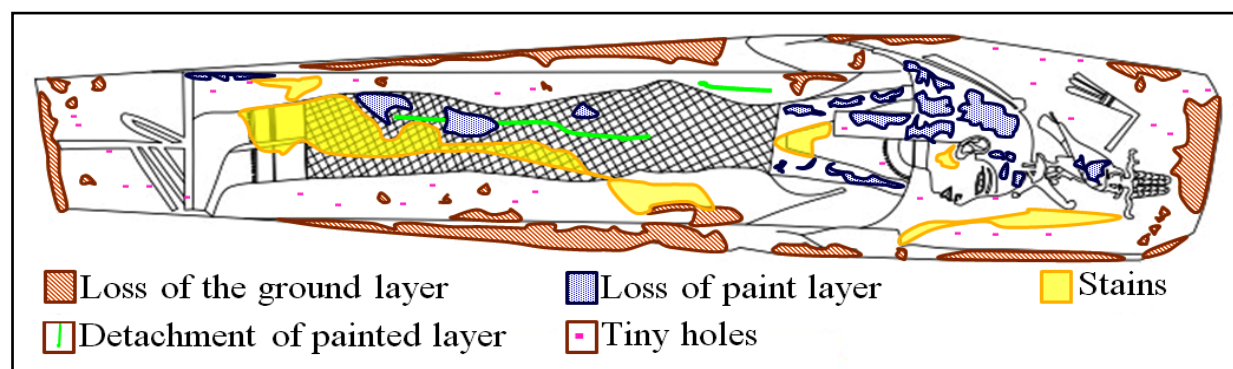
¹⁴ MARGARITI 2019: 1- 14; AFIFI *et Al.* 2020: 9- 23.

¹⁵ SCOTT *et Al.* 2003: 41-56.

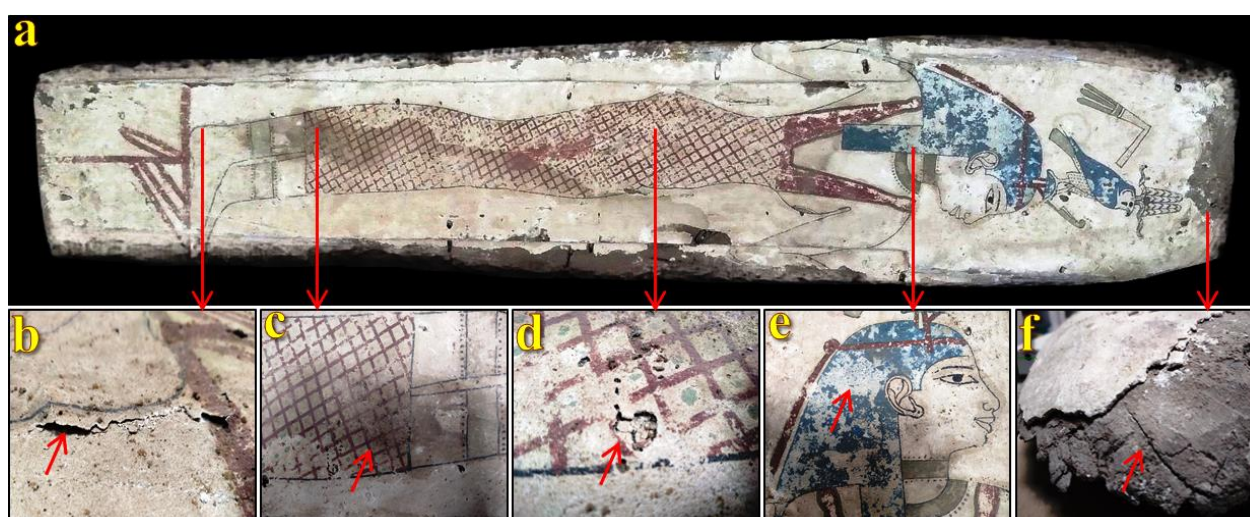
¹⁶ ALI 2020: 1-24.

¹⁷ SIVRIKAYA *et Al.* 2010: 72- 78; RAJKOVIĆ *et Al.* 2021: 1- 27.

to the water content of wood, leading to deformations, particularly in stratified wood works, in which the wood is a support for plaster or color layers. Consequently, the deformations in the wooden support could result in degradation patterns affecting them and the paint layers, causing losses and damage that diminish the aesthetic value of the artwork and increase its susceptibility to further damage¹⁸.



[FIGURE 2]: Schematic diagram of the studied painted coffin base showing the deterioration features by AutoCAD © Done by the researcher



[FIGURES 3/A-F]: A. Deterioration features of the studied painted coffin base; B. Detachment of the paint layer; C. Dark brown stains; D. Powdering and disintegration of the preparation layer; E. Loss of the paint layer; F. Loss of the preparation layer, cracks, powdering, and tiny holes of the wood © Photo taken by the researcher

2. Identification of Wooden Species

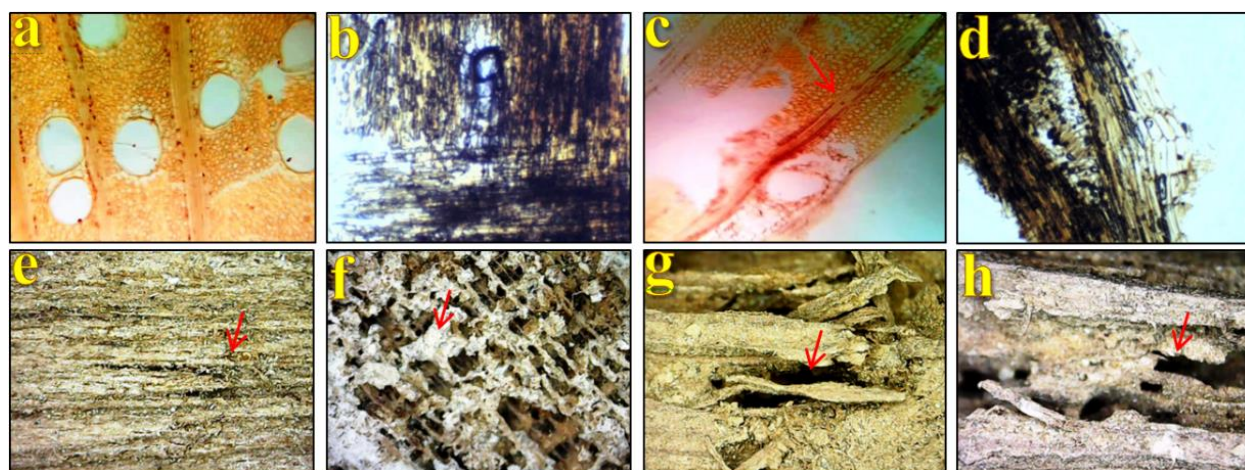
The microscopic examination of wood in the painted coffin base [FIGURE 4] was identified as *Tamarix* sp, as shown by the studied thin sections exhibiting distinct anatomical characteristics of *Tamarix* sp. The transverse section (TS) demonstrated that the wood is semirigid, with vessels solitary and in small clusters, and axial parenchyma scanty, paratracheal to vasicentric in [FIGURE 4/A]. The longitudinal section (LTS) exhibited large rays, often exceeding 10 seriates, storied axial parenchyma, and vessel elements arranged in a storied pattern [FIGURE 4/B]. Additionally, the tangential section

¹⁸ EATON *et Al.* 1993: 47; GENCO *et Al.* 2008: 217-221; SADEGH *et Al.* 2012: 369-373; BADER *et Al.* 2013: 397-412; SALEM *et Al.* 2016: 23-37, FEDERICA *et Al.* 2017: 77- 81.

(TLS) revealed rays typically ranging from 2 to 7 seriate, alongside storied axial parenchyma, simple perforation plates, and alternate inter-vessel pits [FIGURES 4/C-D].

USB-digital microscope micrographs revealed significant deterioration in tissue and cells of the wood surface. Fragility and disintegration of surface wood fibers (a breakdown in the bonding between fibers) and microcracks were evident in certain tracheids and tissue, with remnants of preparation layer particles on the wood tissue [FIGURE 4/E]. These particles penetrated the wood cells, leading to the degradation of the prismatic crystals of superficial parenchyma cells [FIGURE 4/F]. Biological attacks were evident in the form of insect holes and fraying of the wood fibers, particularly in areas where the preparation layer was lost [FIGURES 4/G-H].

Tamarix «tamarisk» species grow in salty locations, along riversides, or valleys where water flows occasionally. Two notable species of *Tamarix* are indigenous to Egypt: *Tamarix aphylla*, which exhibits very broad rays sometimes reaching as much as 20 cells, and *Tamarix tetragyna*, distinguished by its narrower rays. This wood is characterized by its light color, medium bending, compression strength, medium density, moderate hardness, and a coarse, fibrous texture. These attributes contributed to its popularity in ancient Egypt, where it was frequently used alongside sycamore and cedar in coffins, sculptures, bows, and other artifacts¹⁹.



[FIGURES 4/A-H]: *Tamarix* sp; A. Transverse section (TS) (100X); B. Longitudinal section (TLS) (200X); C. Tangential section (100X); D. Details of the tangential section (200X); E-H. USB-digital microscope micrographs of the deterioration manifestations to the painted wooden coffin base; E. Fragility, microcracks, and disintegration of surface wood fibers; F. Remnants of the preparation layer particles on the wood tissue, G & H. Insect holes and fraying of the wood fibers © Done by the author

3. Preparation Layer

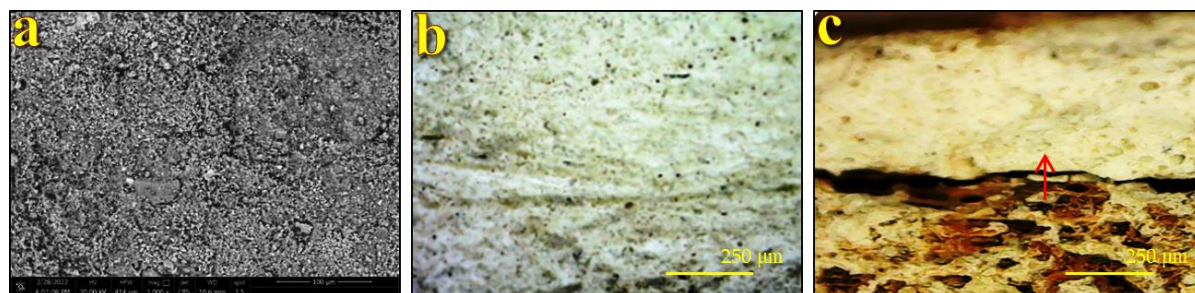
SEM and USB digital microscope examinations revealed that the preparation layer consisted of fine, homogeneous grains, with scattered gradient quartz particles within the groundmass. In cross-section, this layer appeared as a single layer with a thickness ranging from 335 μm to 450 μm , covering the wooden support [FIGURES 5/A-C].

The XRD analysis of the preparation layer sample [FIGURE 6/A] indicated that it consisted of gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and calcite CaCO_3 . The EDX spectrum [FIGURE 6/B] showed calcium Ca (33.59 %), carbon C (1.11 %), oxygen O (40.16 %), and sulfur S

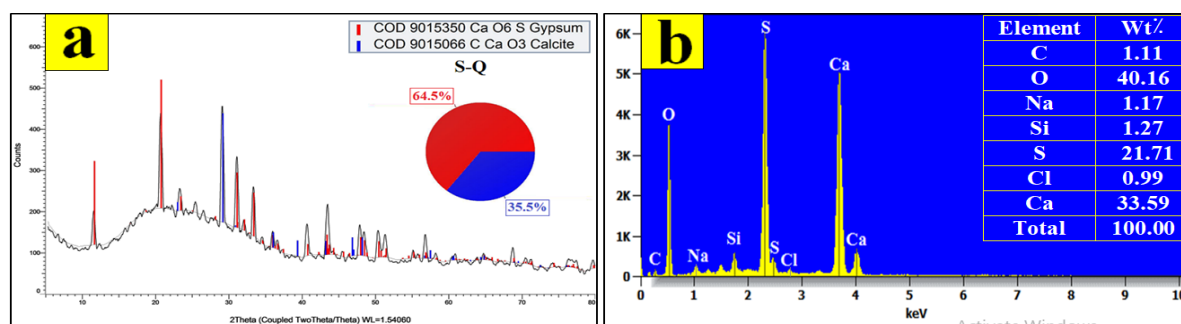
¹⁹ ABDRABOU *et Al.* 2015: 573-586; ABDRABOU *et Al.* 2017: 49-62; BADR *et Al.* 2018: 11-24; ABDRABOU *et Al.* 2021: 12-19; GEWEELY *et Al.* 2022: 1-19.

(21.71 %), indicating that the preparation layer was a blend of gypsum and calcite. Furthermore, the presence of halite (NaCl) was confirmed by peaks of chlorine Cl (14.29 %) and Na (13.24%), while the peak of Si (2.20 %) was attributed to quartz.

These findings aligned with prior research, demonstrating that a preparation layer can be applied as either a thin mono-structured layer or multiple layers. This method effectively fills gaps between boards of wooden artifacts, suppresses wood defects, smooths the surface for drawing and painting, and reduces the detrimental effect of wood's natural movement. In ancient Egypt, calcium carbonate, calcium sulfate hydrate, or both, mixed with an organic binder, were widely used for this purpose²⁰.



[FIGURES 5/A-C]: A-B. SEM and USB digital micrographs, respectively, show the preparation layer with homogeneous fine to very fine grains by SEM and USB digital microscope, respectively; C. A cross-section of the preparation layer by USB digital microscope shows it as a saturated and homogenous very thin layer © Done by the researcher



[FIGURES 6/A-B]: A. XRD pattern of the preparation layer sample; B. EDX pattern of the same sample © Done by the researcher

4. Red Pigment

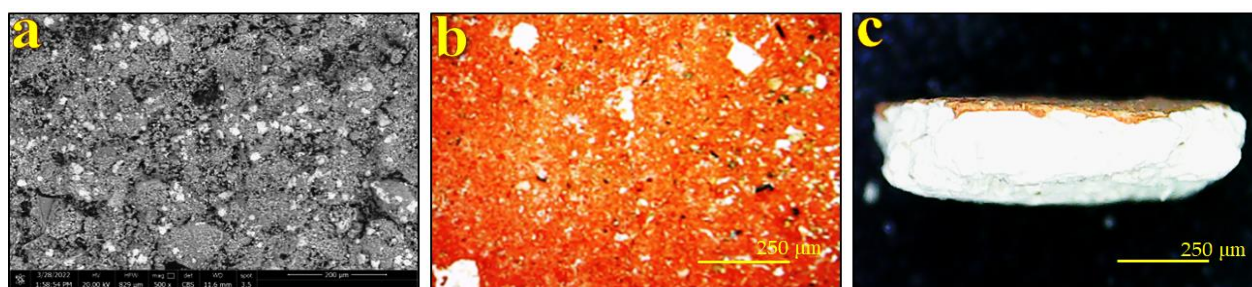
The SEM and USB microscopy examinations of the red pigment layer [FIGURES 7/A-B] revealed a coarse surface morphology characterized by a homogeneous distribution of fine to very fine dark red grains. A significant size contrast was evident between the quartz grains and the scattered dark grains in the groundmass. This pigment appeared as a saturated, homogenous, and very thin layer, with a thickness ranging from 6 µm to 15.3 µm, as observed in the cross-section under the USB microscope [FIGURE 7/C].

The XRD analysis of the red pigment [FIGURE 8/A] revealed that it consisted mainly of hematite Fe_2O_3 and calcite CaCO_3 . Calcite appeared to be related to the composition of the preparation layer. The EDX spectrum of the same sample [FIGURE 8/B] displayed significant peaks of Fe (20.56 %) and oxygen (40.25 %), which

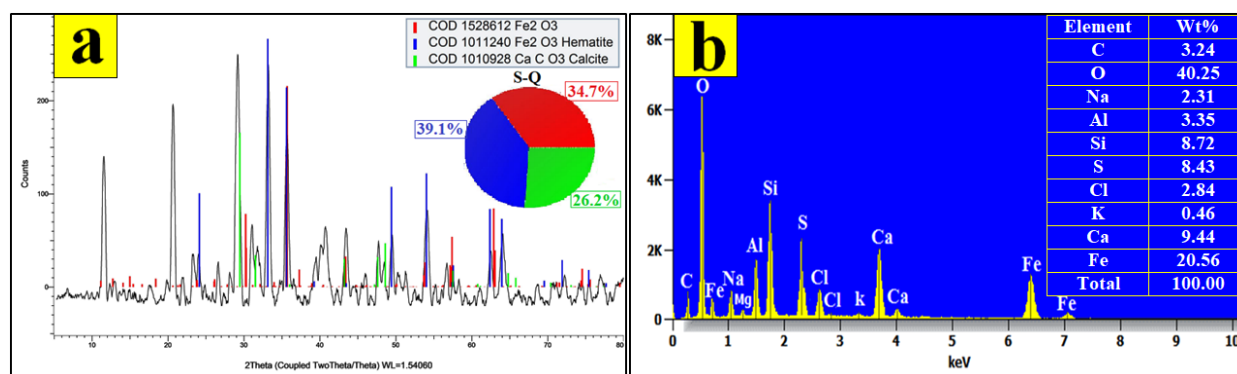
²⁰ RIFAI *et al.* 2010: 16-24; ABDRABOU *et al.* 2015: 573-586; ABDALLAH *et al.* 2016: 1047-1064; DAWSON *et al.* 2016: 75-111; SALEM *et al.* 2016: 23-37; AFIFI *et al.* 2019: 15-22.

confirmed the presence of iron oxides (probably hematite Fe_2O_3) as the main material for red pigment. Furthermore, the peaks of calcium Ca (9.44 %), carbon C (3.24 %), oxygen O (40.25 %), and sulfur S (8.43 %) were associated with gypsum and calcite, the main components of the preparation layer. The presence of Si (8.72%) and Al (3.35%) suggests the existence of aluminosilicate materials, possibly originating from clay minerals linked to red/yellow ochres and commonly found in earth pigments²¹. The peaks of Na (2.31%) and Cl (2.84 %) further confirm the presence of (NaCl).

Hematite was the predominant red pigment in ancient Egypt, from the Predynastic era throughout its history. It naturally occurs in the Oases of the Western Desert and near Aswan. It is characterized by longer lasting and more light-fast than others and is sometimes of astonishing brilliance²².



[FIGURES 7/A- C]: A-B. SEM and USB digital micrographs, respectively, show the red pigment layer is characterized by a coarse surface morphology; C. A cross-section by USB digital microscope shows the preparation layer as a saturated and homogenous, very thin layer © Done by the researcher



[FIGURES 8/A-B]: A. XRD pattern of the red pigment sample; B. EDX pattern of the same sample © Done by the researcher

5. Green Pigment

On the microscopic examination of this green-painted layer [FIGURES 9/A-B], the surface exhibited rough and grainy morphology characterized by homogeneous distribution. In addition, blue and black pigment particles were scattered in the groundmass. It probably suggests potential accidental impurities resulting from the use of an unclear brush in coloring²³. In a cross-section [FIGURE 9/C], the green pigment appeared as a thin single layer, with a thickness ranging from 7 µm to 13.8 µm. XRD pattern [FIGURE 10/A] declared the presence of quartz SiO_2 , malachite $\text{CuCO}_3\text{Cu}(\text{OH})_2$, and calcite CaCO_3 as the main components of the green pigment. EDX spectrum

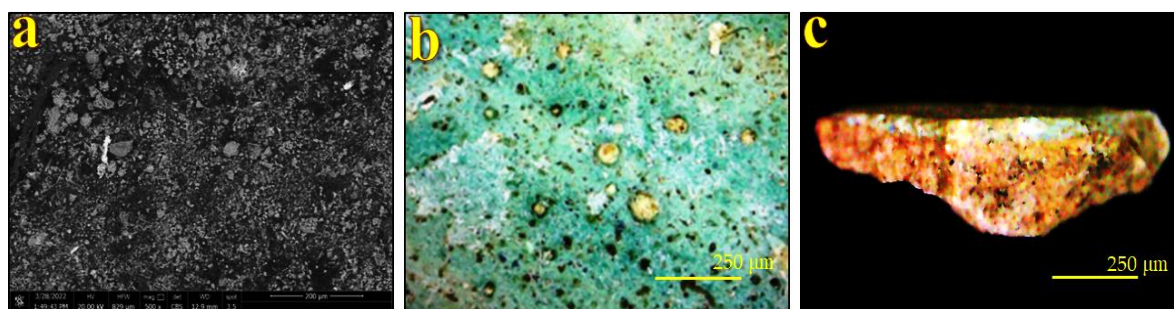
²¹ HANESCH 2009: 941- 948; MANCI *et Al.* 2023: 27-46.

²² MOTAWEA *et Al.* 2023: 75-90; MANCI *et Al.* 2020: 1535-1554.

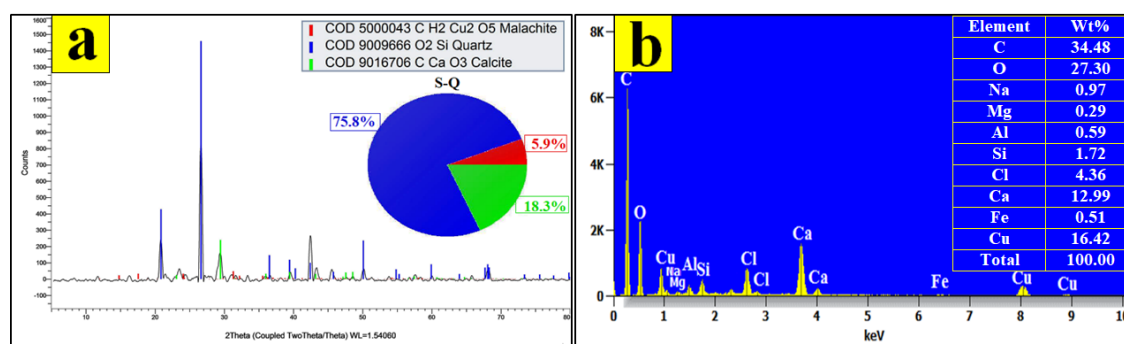
²³ ABDRABOU *et Al.* 2018: 39-54.

[FIGURE 10/B] showed a significant percentage of Ca (12.99 %), C (34.48 %), O (27.30 %), and Cu (16.42 %). This result proved the presence of malachite $\text{CuCO}_3\text{Cu}(\text{OH})_2$ as the main material of green pigment. The presence of traces of Si (1.72 %), Al (0.59 %), Mg (0.29 %), and Fe (0.51 %) is probably related to the dust or soil materials at the excavation site. The peaks of Na (0.97 %) and Cl (4.36 %) demonstrated the presence of halite.

In ancient Egypt, the green color symbolized vitality, growth, fertility, new beginnings, and the resurrection of Osiris. Malachite, one of the oldest green pigments known, was utilized in Egypt for painting since the Pre-dynastic era and has been discovered on tomb paintings dating back to the 4th Dynasty. It was particularly prominent in female coffins, characterized by distinctive green faces during the 26th Dynasty, known as the Saite Period, around the 7th century BC. Malachite is a basic copper carbonate and shares characteristics similar to azurite. It is common to find aggregates of these two minerals together. Natural malachite deposits occur in Sinai and the Eastern Desert in Egypt²⁴.



[FIGURES 9/A-C]: A-B. SEM and USB digital micrographs, respectively, show the green pigment layer is characterized by rough, grainy, and homogeneous morphology; C. A cross-section of the green pigment by USB digital microscope shows that the pigment is formed as a thin single layer © Done by the researcher



[FIGURES 10/A-B]: A. XRD pattern of the green pigment sample; B. EDX pattern of the same sample © Done by the a researcher

6. Black Pigment

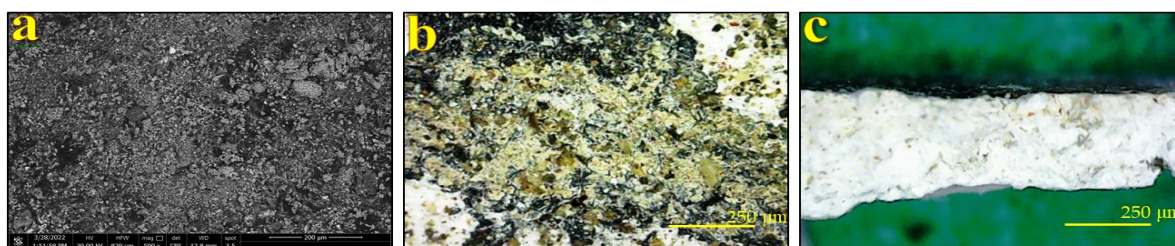
The microscopic investigation [FIGURES 11/A-B] demonstrated that the black pigment formed a very thin, dark black layer. Its thickness varied between 5.73µm and 15.91µm [FIGURE 11/C]. It consisted of very fine granules distributed homogeneously, characterized by fineness, uniformity, and consistency. XRD pattern [FIGURE 12/A]

²⁴ AFIFI *et al.* 2020: 69-83; MANCI *et al.* 2023: 27-46.

confirmed the presence of a crystalline phase related to graphite with calcite and anhydrite in the black pigment sample. The presence of calcite and anhydrite was associated with the ground layer. EDX spectrum [FIGURE 12/B] showed a significant percentage of O (42.52 %), S (8.53 %), and Ca (14.82 %) associated with calcite and gypsum in the ground layer. The presence of carbon black (graphite) in the sample was identified by the prominent C peak (10.69). The concentrations of Na (0.48 %) and Cl (7.22 %) indicated the presence of halite.

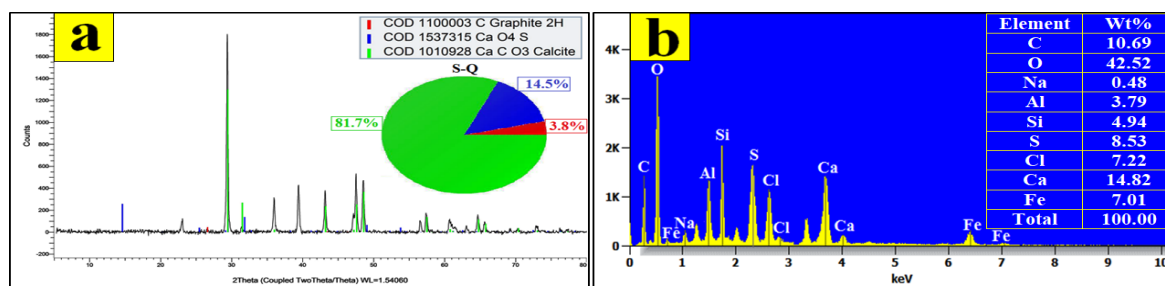
In ancient Egyptian culture, the black color was intrinsically linked to death and the afterlife, denoting a profound psychological significance that represented immortality and rebirth. Thus, it played a crucial role in their funerary practices. Also, it symbolized the darkness, the primordial water of the first ocean, absence, modernity, malevolence, sorrow, night, underworld, resurrection, and fertility. It represented the opposite ideas (power, humility, rebellion, harmony, affluence, and destitution). It was used to write texts on walls, papyri, coffins, color wigs, beards, women's hair and eyeliner, as well as to outline the drawings. The ancient Egyptians designated it as km and became a symbol of the black soil of Egypt, which was called the «black earth».

Carbon is the primary coloring material of black. There are two primary forms of carbon: crystallized carbon and amorphous carbon. Graphite is the sole type of crystallized carbon used for coloring. Amorphous carbon is not pure, as it contains mineral impurities, hydrocarbons, and tar. It is produced by burning or carbonizing various materials, such as oils and wood. Carbon black has many names, including lamp black (soot), vegetable black, and animal (bone black and ivory black). In rare cases, the black color is from mineral oxides, such as magnetic iron oxides magnetite (Fe_3O_4) and manganese oxide pyrolusite (MnO_2)²⁵.



[FIGURES 11/A- C]: A & B. SEM and USB digital micrographs, respectively, show that the black pigment layer is characterized by very fine granules distributed homogeneously; C. A cross-section of the black pigment layer by USB digital microscope shows it is formed as a very thin single layer ©

Done by the author



[FIGURES 12/A-B]: A. XRD pattern of the black pigment sample; B. EDX pattern of the same sample

© Done by the author

²⁵ LEE *et Al.* 2000: 111-121; LESKO 2002: 174; GREEN 2011: 43-48; SCOTT 2016: 185-202.

7. Blue Pigment

The microscopic examination of the blue pigment revealed a rough surface morphology characterized by saturated and very coarse blue grains, rectangular, sharp edges, and that are homogeneously dispersed throughout the matrix in layered formations. In addition, chromatic alteration of the blue pigment in specific areas was observed [FIGURES 13/A-B]. In a cross-section, the pigment was observed as a thin single layer, with a thickness ranging from 9 μm to 16.9 μm [FIGURE 13/C]. The XRD pattern of the blue pigment [FIGURE 14/A] revealed that it consisted mainly of Egyptian blue «cuprorivaite ($\text{CaCuSi}_4\text{O}_{10}$) and quartz (SiO_2). The presence of quartz was attributed to contamination from the burial environment in Saqqara. The EDX spectrum of the same sample [FIGURE 14/B] confirmed this result, as the atomic percentage ratio of Ca (14.77 %), Si (22.41 %), and Cu (14.47 %) aligned with the chemical formula of cuprorivaite. Traces of Al (0.95 %), Mg (0.86 %), K (0.43 %), and Fe (0.69 %) were also observed, likely to originate from dust or soiling materials at the excavation site. Furthermore, the presence of Na (0.41%) and Cl (0.95%) peaks indicated the existence of halite (NaCl).

Numerous prior studies attributed the color change of Egyptian blue to the influence of halite salt. Additionally, the presence of sodium chloride salt during the manufacture of Egyptian blue prevented the formation of cuprorivaite, which, in turn, affected the color of the pigment produced. This implied that a cleaning step was undertaken prior to the pigment's manufacturing²⁶. Recent studies revealed an additional factor contributing to the color change of Egyptian blue, which was linked to the growth of fungal and bacterial species that depend on these copper-based pigments for nutrition, serving as a primary source of carbon and energy²⁷. Egyptian blue was the dominant blue pigment in ancient Egypt since the 3rd millennium BC. It is the earliest known synthetic pigment. The Egyptians designated it as *hsbd iryt*, meaning artificial lapis lazuli²⁸. It is known as the most iconic synthetic pigment throughout history. It was produced by mixing and heating quartz, copper, calcite, and flux, which could be either alkali flux or plant ashes, at temperatures between 850 and 950 °C²⁹. It is crucial to understand that Egyptian blue, produced outside Egypt, was not imported in its final form; only the raw materials were brought from Egypt and then processed locally. It was widely believed to have vanished from Western Europe after the catastrophic fall of the Roman Empire. However, in several recent studies, this hypothesis proved partially erroneous. It was detected in the paint layers of Robert Falk's 1907 painting «Birch Spring» and sketches on the reverse side of the canvas, potentially representing the first instance of Egyptian blue found in a 20th-century artwork³⁰.

²⁶ MOUSSA *et Al.* 2013: 261-274; GIMENEZ *et Al.* 2017: 174-180.

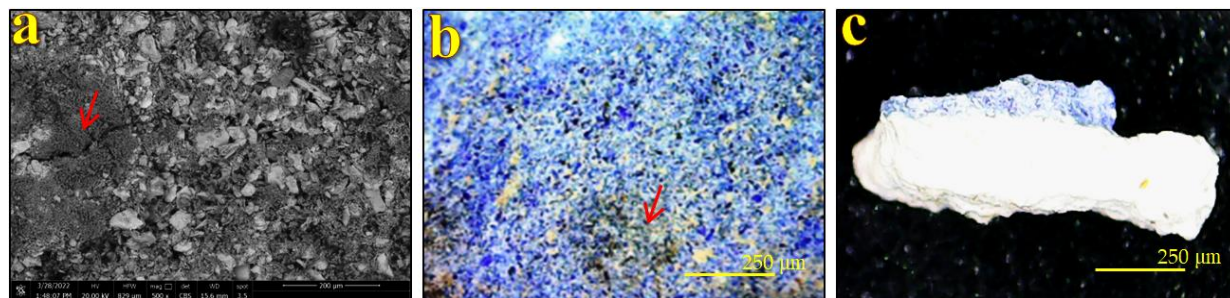
²⁷ MOUSSA *et Al.* 2021: 1–15.

²⁸ NICOLA *et Al.* 2019: 5377–5392.

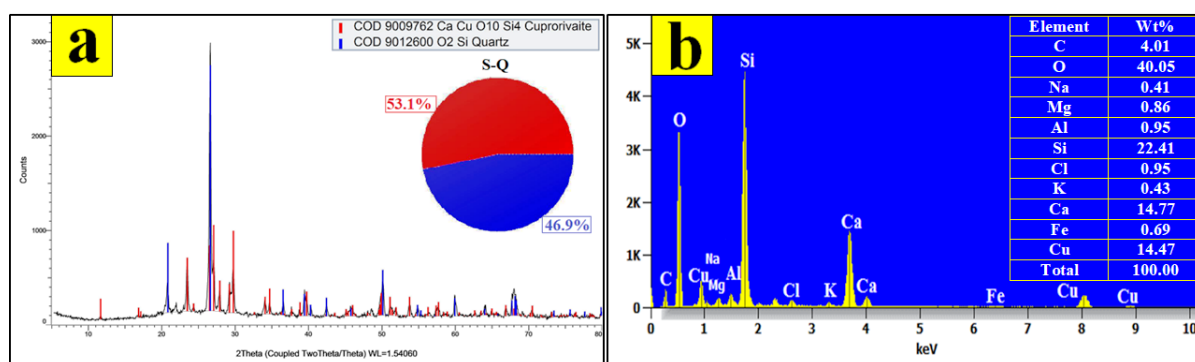
²⁹ SCOTT 2016: 185-202.

³⁰ ALI *et Al.* 2022: 63-79.

The presence of sodium chloride in all samples, as indicated by EDX analysis, may be associated with the materials used in the preparation layer and the surrounding burial soil in contact with the painted wooden coffin base³¹.



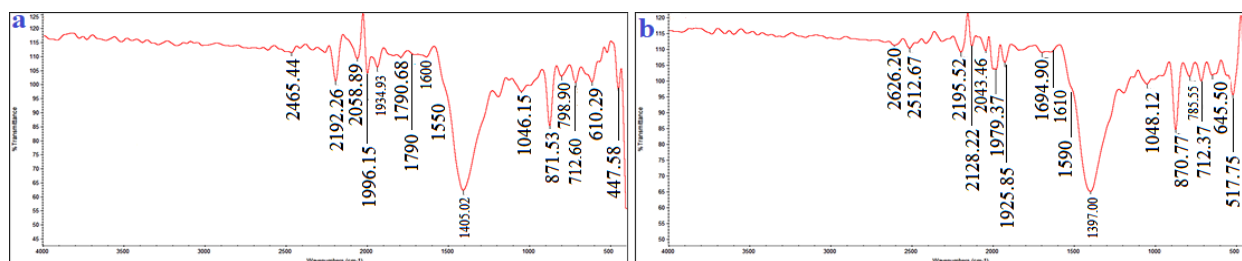
[FIGURES 13/A- C]: A-B. Blue pigment with coarse morphology by SEM and USB digital microscope, respectively; C. A cross-section of the blue pigment by USB digital microscope showing that the pigment formed a thin layer © Done by the researcher



[FIGURES 14/A-B]: A. XRD pattern of the blue pigment sample; B. The EDX pattern of the same sample ©Done by the researcher

8. Identification of Binding Media

Two samples were subjected to FTIR analysis, the first from the preparation layer and the second from the painting layer, to identify the binding media [FIGURE 15]. The analysis of the preparation layer sample indicated the presence of characteristic bands of a proteinaceous binder (animal glue) used to bind the particles. Similarly, the analysis result of the painting layer sample corroborated the presence of the same binder (animal glue), which was commonly utilized as a binding medium in both the gesso and paint layers since the early ancient Egypt³². The characteristic bands of animal glue are elucidated in [TABLE 1].



[FIGURES 15/A-B]: A. FTIR spectra of the sample taken from the ground layer; B. FTIR spectra of the sample taken from the painting layer © Done by the author

³¹ BADER *et Al.* 2013: 397-412; ABDRABOU *et Al.* 2017: 49-62; BADR *et Al.* 2018: 11-24.

³² NEWMAN *et Al.* 2001: 22-32; ABDRABOU *et Al.* 2019: 9-19.

Functional Group	Wave Number(cm ⁻¹)	
Animal Glue	Sample (1)	Sample (2)
The broad O-H stretching band overlaps the N-H stretching of animal glue.	3100 – 3400	3104– 3420
CH stretching band of the aliphatic group	2465.44	2606.20
C=O stretching band of CO ₃ ²⁻ of calcite	1790.68	–
Combination of: - Carbonyl stretching band (amide I) of animal glue - CN stretching band + NH bending band (amide II) of animal glue	1790 1600 + 1550	1694.90 1590 + 1610
Asymmetric SO ₄ ²⁻ stretching band	1140 – 1080	–
Broad band due to the combination of the C-H bending vibration of animal glue and the (CO ₃) ²⁻ stretching band of calcium carbonate	1405.02	1397.00
C – O stretching	1180.22 – 1046	1048.12 – 1076
O-C-O bending band of carbonate group of calcite	871.53	870.77
SO ₄ ²⁻ bending band	610.29	645.50

[TABLE 1]: FTIR spectra results of the preparation layer and the painting layer samples © Done by the researcher

IV. TREATMENTS

1. Pre-Consolidation

The painted coffin base displayed considerable weakness and fragility, which required an initial consolidation with a consolidant capable of deep penetration to enhance its structural integrity. Therefore, Klucel G «hydroxypropyl cellulose» was dissolved in ethyl alcohol at a concentration of 0.5 %. To secure the detached parts and support heavily cracked areas, temporary strips of Japanese tissue were installed using 3% Klucel G on the edges of the detached parts of the painted ground layer and wooden support. These steps were essential to ensure the safe transportation of the coffin base from the excavation site, preventing any potential damage during its handling³³ [FIGURE 16/A].

2. Surface Cleaning

The cleaning process entails the removal of harmful and undesired materials from the surfaces of the painted coffin base, including dust, hard soil deposits, grime, stains, and salts, that could adversely affect their aesthetic and artistic values. It commenced with mechanical cleaning, utilizing fine brushes, fiberglass brushes, and a manual air pump to effectively remove solid particles, such as dust, sand, salts, and soil deposits [FIGURE 16/B]. Following mechanical cleaning, chemical cleaning was conducted to remove any remaining dirt and stains. Solubility tests revealed that a mixture of acetone with trichloroethanol was the optimal solvent for removing dirt and stains while preserving the integrity of the original materials. Dirt was removed effortlessly using cotton swabs dipped in the solvent. The swabs were checked periodically during the cleaning to verify whether there was any pigment residue from the painted coffin base³⁴.

³³ DAVIS *et Al.* 2021: 254-274.

³⁴ HAMED *et Al.* 2013: 153-160; AHMAD *et Al.* 2018: 1-13; ALI 2020: 167–180.

3. Fixation of the Detached and Flaked Paint Layer

The paint layer exhibited significant loss of adhesion to the wooden base of the coffin in several areas in the form of flakes, given the extreme fragility of those detached flakes. The initial treatment involved chemical consolidation, as the lifting flakes on the wooden support were slightly softened using Klucel G dissolved in 0.5% ethyl alcohol applied with a fine paintbrush. Subsequently, a 3% Klucel G solution was injected between the separated parts of the ground layer and the wooden support using a thin syringe. Finally, a polyethylene sheet was placed over these areas, applying gentle pressure to ensure they were properly attached and well in place until the adhesive was fully set [FIGURE 16/C].

4. Consolidation

Due to the general weakness and fragility of the painted layer and wooden support, it was affected by various chemical, mechanical, and biological deterioration factors. To ensure effective treatment, a consolidant that can penetrate deeply should be used to enhance the mechanical properties of both layers and improve the cohesion of the painted surface particles and their adhesion to the support, all while preserving the overall appearance with minimal color change³⁵. Therefore, Klucel G was selected to consolidate the painted wooden coffin base based on the results of the literature on the consolidation of archaeological painted wood³⁶. The solutions of 0.5, 1 and 1.5%w/v Klucel G in ethyl alcohol were applied by pipette to consolidate the painted layer and wood support, particularly in areas where paint loss occurred. This process was repeated several times until its strength was satisfactorily improved [FIGURE 16/D].

5. Treatment of the Cracks, Missing Parts and the Ground Layer Edges

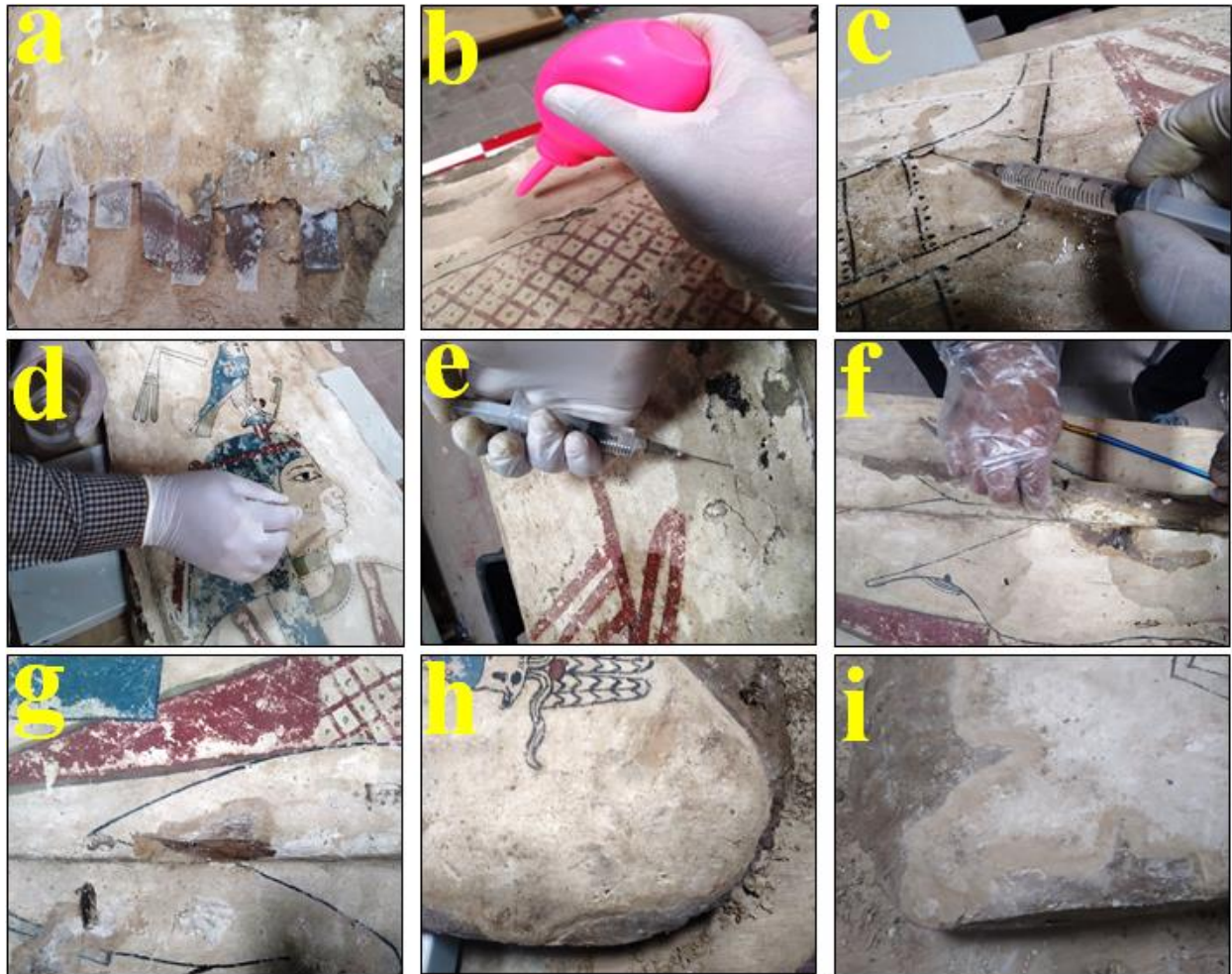
Addressing the cracks and voids in this painted coffin base relied heavily on the gap-filling materials that must have a set of properties, including reversibility, good adhesive properties, being strong yet weaker than the archaeological object, exhibiting minimal shrinkage, being easy to carve, ensuring long-term flexibility, providing excellent light fastness, suitability for in painting or coloring and manipulating with a spatula and sanded³⁷. To fill cracks and missing parts of the painted ground layer and close its external edges, a fine putty was prepared consisting of 15% w/v Paraloid B72 in acetone, glass micro balloons and earth pigments that matched the original colors of the parts to be treated. This putty was prepared in accordance with contemporary literature on gap-filling materials. It was applied and finished in the cracks and missing parts using fine spatulas so that its level was lower than the original ground layer³⁸. Then, the prepared putty was spread obliquely to effectively seal the ground layer edges and connect them with the wooden holder [FIGURES 16/E-I].

³⁵ BADER *et Al.* 2013: 397-412; EL HADIDI *et Al.* 2014: 1-11.

³⁶ ABDALLAH *et Al.* 2016: 1047-1064; ABDELMONIEM *et Al.* 2023: 1485-1506.

³⁷ ABDRABOU *et Al.* 2015: 573-586.

³⁸ AFIFI *et Al.* 2011: 661-669; ISMAIL *et Al.* 2016: 15-28; SALEM *et Al.* 2016: 23-37; NABIL 2020: 9-21.



[FIGURES 16/A-I]: The conservation processes of the painted wooden coffin base: A. Pre-consolidation; B. Surface cleaning; C. Fixation of the detached and flaked paint layer; D. Consolidation of the delicate and fragile painting layer; E. Treatment of cracks; F- I. Treatment of the missing parts and the ground layer edges © Photos taken by the researcher



[FIGURE 17] The painted wooden coffin base after treatments © Photo taken by the researcher

CONCLUSION

Various analytical and investigative techniques, including visual examination, SEM, portable USB digital microscope, optical microscope, XRD, EDX, and FTIR, were employed to identify the materials utilized in the painted wooden coffin base No. TEE/B11/21, which was discovered by the collaborative archaeological excavation conducted by the Supreme Council of Antiquities and Misr University for Science and Technology (MUST) in the eastern side of Tebbet El-Gish in Saqqara in 2021. Wood identification results revealed that the coffin base was crafted from *Tamarix sp.*, a local wood and was carved in an anthropoidal style. This design was commonly seen during the Greco-Roman era. A thin mono-preparation layer was observed on the surface of the coffin base and directly beneath the painted layer. Analyses revealed that it was composed of a mixture of gypsum and calcite. Pigment analysis confirmed that the ancient Egyptian artist used hematite to obtain the red pigment, Egyptian blue to obtain the blue pigment, malachite to obtain the green pigment, and graphite to obtain the black pigment. Animal glue was used as a binding medium for the components of the preparation layer and the pigments. As a result, due to the influence of the deterioration factors associated with the burial environments and the human-induced damage, including excavation practices, the painted coffin base suffered considerable deterioration, e.g., superficial solid deposits, muddy grime, stains, paint loss, holes, gaps, cracks, microcracks, detachments, salts, and a general state of weakness and fragility. Various treatment and preservation procedures for the painted coffin base were executed successfully, both upon its discovery and after its transfer to the restoration and conservation lab, which became ready for display or storage. The findings will be useful for identifying the materials used in manufacturing wooden coffins in ancient Egypt, especially those covered with colored preparation layers, as well as the methods for their treatment and conservation, particularly those discovered at excavation sites.

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DISCLOSURE STATEMENT

No Potential conflict of interest was reported by the author

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ENHANCING THE PHYSICAL AND MECHANICAL PROPERTIES OF MUD BRICKS USING NATURAL, SYNTHETIC AND CHEMICAL ADDITIVES: AN EXPERIMENTAL APPROACH

BY

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ABSTRACT

[EN] This study focuses on the earthen structures found in the archaeological cemetery of Quesna, Menoufia Governorate, Egypt. The primary aim is to enhance the physical and mechanical properties of both archaeological mud bricks and newly manufactured mud bricks intended for conservation purposes by applying natural, synthetic additives and chemical composites. A sieve analysis was conducted to identify the coarse and fine components of the archaeological mud bricks. The natural and synthetic additives used in the study included: straw, fiberglass, ceramic powder, hydrated lime and natural hydraulic lime «NHL 3.5». Chemical treatments involved the application of Sika Gard 710, Estel 1100, nano-silica and nano-lime. Each of these chemicals was mixed at a concentration of 10% with Paraloid B-72 dissolved in 3% acetone. The resulting chemical composites were added to the mixing water at approximately 15% concentration, used in the production of conservation mud bricks. Additionally, direct consolidation with these chemical composites «excluding Paraloid B-72/nano-lime» was applied to archaeological mud brick samples using a brush. To evaluate the effectiveness of these treatments, the samples underwent a series of laboratory tests to assess their physical and mechanical properties. Examination and diagnosis were also carried out using scanning electron microscopy «SEM», along with measurements of color change and water contact angle on the treated samples. The results demonstrated that the addition of fiberglass significantly reduced water absorption and improved the mechanical strength of the manufactured mud bricks. Furthermore, the nanocomposites consisting of Paraloid B-72/ nano-silica (10%) and Paraloid B-72/ nano-lime (10%) enhanced water absorption behavior and mechanical durability. The composite of Paraloid B-72/ Estel 1100 (10%) exhibited effective water repellency on treated mud brick samples.

KEYWORDS: Apparent porosity, chemical additives, compressive strength, mud brick, nano composites, natural additives, water absorption.

[AR] تحسين الخصائص الفيزيائية والميكانيكية للطوب اللبن باستخدام إضافات طبيعية واصطناعية وكيميائية: دراسة تجريبية
تلقي هذه الدراسة الضوء على المباني الطينية المستخدمة في جبانة قويسنا الأثرية بمحافظة المنوفية بمصر. وتهدف إلى تحسين الخواص الفيزيائية والميكانيكية للطوب اللبن الأثري، والطوب اللبن المصنع لأغراض الترميم، عن طريق استخدام بعض الإضافات الطبيعية والمواد المركبة الاصطناعية والمركبات الكيميائية. تم عمل تحليل منخلي للتعرف على المكونات الخشنة والدقيقة للطوب اللبن الأثري. وقد تضمنت الإضافات الطبيعية والمواد المركبة الاصطناعية المستخدمة في هذه الدراسة: التبن، والألياف الزجاجية، ومسحوق السيراميك، والجير المطفي، والجير الهيدروليكي الطبيعي (3.5). كما تضمنت المعالجات الكيميائية، استخدام المواد الكيميائية: سیکا جارد 710، وإستيل 1100، ونانو السيليكا، ونانو الجير؛ حيث تم استخدام كل مادة من المواد السابقة ممزوجة بتركيز 10% في البارالويد ب-72 المذاب في الأسيتون بتركيز 3%، وأضيفت هذه المركبات الكيميائية بنسبة 15% تقريباً إلى ماء الخلط المستخدم في صناعة الطوب اللبن المعد لأغراض الترميم. كما تم تطبيق التقوية المباشرة بالمركبات الكيميائية السابقة «ما عدا البارالويد ب-72/ نانو الجير» على عينات الطوب اللبن الأثري باستخدام الفرشاة. ولتقييم كفاءة المعالجات المستخدمة، تم إخضاع عينات الدراسة لمجموعة من الاختبارات المعملية لقياس الخواص الفيزيائية والميكانيكية، كما تم الفحص والتشخيص باستخدام الميكروسكوب الإلكتروني الماسح، بالإضافة إلى قياس درجة التغير اللوني، وزاوية اتصال الماء للعينات الأثرية المعالجة. أكدت النتائج أن إضافة الألياف الزجاجية تخفف من امتصاص الطوب اللبن للماء، كما تحسن القوة الميكانيكية للطوب اللبن المصنع. كما حسنت إضافة كل من المتراكبات النانوية «بارالويد ب-

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72/نانو سيليكات 10%» والمركبات النانوية «بارالويد ب 27/ نانو الجير 10%» من معدلات امتصاص الماء، وقوة التحمل الميكانيكي للطوب اللبن، كما أثبتت المركبات الكيميائية «بارالويد ب 72/إستيل 1100» قدرة على طرد الماء في العينات الطينية المعالجة. الكلمات الدالة: الإضافات الطبيعية، الإضافات الكيميائية، امتصاص الماء، الطوب اللبن، قوة الضغط، المركبات النانوية، المسامية الظاهرية.

I. INTRODUCTION

Earth is one of the earliest known building materials and all earthen constructions share the same fundamental ingredients: soil and water. Various techniques exist for forming earthen structures, often incorporating additional materials to facilitate mud brick production or enhance their mechanical properties¹. Mud bricks—a traditional construction material—are typically composed of a mixture of soil «containing clay, silt and sand», water and often organic additives, such as straw. Raw earth, as a building material, offers several advantages: it is locally available, requires low processing energy during construction and is highly recyclable². The essential properties of earthen construction materials depend largely on the nature and composition of the soil, as well as water content and compaction level. These properties can be modified and improved using various additives, which allow for the use of earthen materials in a wide range of structural and non-structural elements³. Earthen construction offers notable advantages in terms of thermal and environmental performance. Adobe bricks, one of the most well-known forms of earthen construction, exhibit favorable hygrothermal characteristics, including water absorption capacity, a high equilibrium moisture content, excellent water vapor permeability, a high specific heat capacity and lower thermal conductivity compared to conventional building materials⁴. These properties have contributed to the widespread historical use of mud bricks and their continued application. However, mud bricks are highly susceptible to mechanical damage and environmental degradation caused by factors, such as temperature fluctuations from solar radiation or water exposure due to rainfall or changes in groundwater levels. The low resistance of mud bricks to atmospheric conditions often accelerates the deterioration of mud brick structures, necessitating ongoing conservation interventions⁵. Given the widespread use of this traditional material, particularly in the restoration of heritage buildings, further research should be conducted to improve its mechanical performance. Enhancing the mechanical properties of adobe bricks can significantly increase the load-bearing capacity of structural elements, thereby improving the overall stability and durability of earthen architecture⁶. One of the most prominent ancient Egyptian archaeological adobe sites in Lower Egypt, which has suffered from climatic and environmental changes, as well as inconsistent conservation efforts, is the Quesna archaeological cemetery [FIGURES 1/A-B]. This site stands as a living testament to ancient civilization, with its mud brick structures offering valuable insights into past

¹ LINGLE 2019: 18.

² LOSINI *et Al.* 2021: 3.

³ MYOAYE *et Al.* 2020: 241.

⁴ AZALAM *et Al.* 2024: 145.

⁵ ZAREMBA *et Al.* 2021: 68.

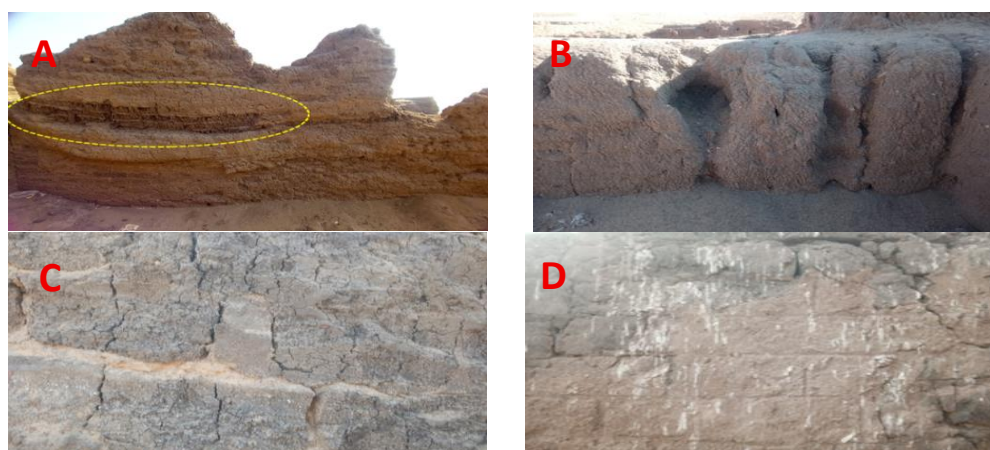
⁶ MOHAMMADI *et Al.* 2022: 465.

cultures. Located in the Governorate of Menoufia, The Quesna site was discovered in the mid-1990s during sand extraction operations. Its historical and archaeological significance stems from its status as one of the key heritage sites in the Nile Delta. The cemetery features mud brick-built tombs dating to the Late and Ptolemaic Periods⁷. The mud bricks used at the site were composed primarily of Nile silt mixed with sand and a small amount of plant material⁸.



[FIGURES 1/A-B]: The Quesna archaeological cemetery, with evident adobe architecture patterns © Photos taken by BASSEM MANSOUR

Regarding the current condition of the archaeological cemetery in Quesna, the earthen structures exhibit significant deterioration and structural weakness caused by multiple deterioration factors, most notably climate change. The extreme fluctuations in temperature, combined with seasonal rainfall, wind erosion, biological factors and inadequate regular conservation, have collectively contributed to the degradation of the site. Visible manifestations of deterioration include the collapse of some walls, cracks and fissures, the loss of mud brick blocks, salt efflorescence and staining of the walls with organic residues⁹ [FIGURES 2/A-D].



[FIGURES 2/A-D]: Selected deterioration features observed at the Quesna archaeological cemetery: A. Disintegration and loss of mud brick units due to prolonged weathering; B. Surface erosion, vertical channels and deep cavities in the earthen walls caused by rainwater; C. Cracks and fissures in the mud plaster due to alternating effects of moisture and extreme temperature fluctuations; D. Wall surface distortion resulting from bird droppings and biological deposits © Photo taken by BASSEM MANSOUR

⁷ ROWLAND *et Al.* 2011: 333.

⁸ ROWLAND *et Al.* 2018: 372.

⁹ ADAM 2023: 33-53.

II. MATERIALS AND METHODS

The research utilizes natural, synthetic and chemical components to enhance the physical and mechanical properties of archaeological mud bricks through direct consolidation with chemical composites or to improve the properties of mud bricks manufactured for restoration purposes by incorporating natural, synthetic and chemical materials during the mud brick manufacturing process¹⁰.

1. Materials

A. Preparation of Experimental Adobe Samples with Different Additives

Experimental cubic samples of mud brick (adobe) were prepared using some natural, synthetic and chemical additives [TABLE 1]. Natural and synthetic additives included: straw, fiberglass, ceramic powder, slaked lime and natural hydraulic lime (NHL 3.5), which were added at a rate of 10% to the dry mud mixture consisting of clay/silt at a rate of 40% and sand at a rate of 60%¹¹. Chemical additives included Sika Gard 701, Estel 1100, nano-silica and nano-lime. Each chemical was added in a ratio of 10% to a solution of Paraloid B72 dissolved in acetone at a concentration of 3%. The chemical composites were added to the mixing water at a ratio of approximately 15%. On the other hand, the chemical composites Paraloid B72 3%/ Sika Gard 701, Paraloid B72 3%/ Estel 1100 and Paraloid B72 3%/ nano-silica were applied by direct consolidation to archaeological mud brick samples, measuring 5×5×5 cm, using a brush¹².

Material	Source
Clay	Clay formations near the archaeological site «most likely used in the construction work of the archaeological Quesna cemetery»
Fiberglass	Fox Construction Chemicals Industry, New Cairo, Egypt Website: https://shop.foxccs.com , accessed on (10-06-2025)
Natural Hydraulic Lime (NHL 3.5)	CTS Egypt Company, Cairo «info@cts-egy.com», accessed on (10-06-2025)
Slaked Lime	Arts Conservation Agency, Egypt « www.acaegy.com », accessed on (10-06-2025)
Ceramic Powder	Milano Ceramic Company, Egypt « www.milanoceramic.com », accessed on (10-06-2025)
Sika Gard 701	Sika Egypt Company « https://egy.sika.com/ », accessed on (10-06-2025)
Estel 1100	CTS Egypt Company, Cairo «info@cts-egy.com», accessed on (10-06-2025)
Nano-Silica	Faculty of Postgraduate Studies for Advanced Sciences, Beni-Suef University «central.lab@psas.bsu.edu.eg», accessed on (10-06-2025)
Nano-Lime	Al-Sadiq Factory for Restoration Materials « https://sadiqsons.com/ », accessed on (10-06-2025)

[TABLE 1]: Natural, synthetic and chemical additives used in the study and their sources © Done by the researchers

¹⁰ ADAM 2024 1397–1428.

¹¹ ADAM 2023: 33-53.

¹² HAGAGI KHAMIS *et Al.* 2023: 1107-1083.

The concentrations of the substances were selected based on previous studies and preliminary laboratory experiments conducted by the researchers until optimal concentrations were determined. Moreover, the study considered the use of similar concentrations of the substances to ensure a more realistic evaluation from a practical perspective. [TABLES 2-3] describe the clay mixtures, chemical composites and concentration ratios used in the study.

Natural and synthetic additives	Percentage	Mixture Components
Straw	10%	Clay + Sand + Straw
Fiberglass	10%	Clay + Sand + Fiberglass
Hydraulic Lime	10%	Clay + Sand + Hydraulic lime
Slaked Lime	10%	Clay + Sand + Slaked lime
Ceramic Powder	10%	Clay + Sand + Ceramic powder

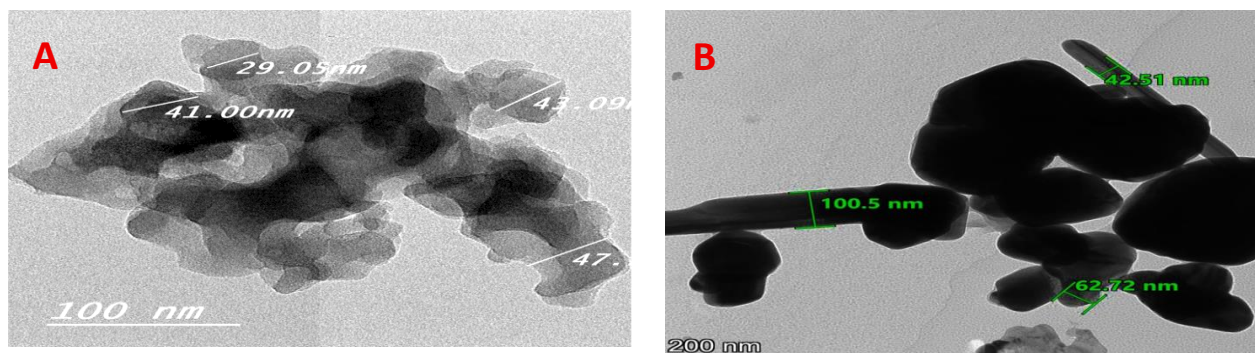
[TABLE 2]: Natural and synthetic additives used in the study to improve the physical and mechanical properties of manufactured mud bricks © Done by the researchers

Chemical Additives	Percentage	Mixture Components
Sika Gard 701	10%	Clay + Sand + Paraloid B72 3%/ Sika Gard 701
Estell 1100	10%	Clay + Sand + Paraloid B72 3%/ Estell 1100
Nano-silica	10%	Clay + Sand + Paraloid B72 3%/ Nano-silica
Nano-lime	10%	Clay + Sand + Paraloid B72 3%/ Nano-lime

[TABLE 3]: Chemical additives used in the study to improve the physical and mechanical properties of archaeological mud bricks © Done by the researchers

B. Preparation of Nano-Silica and Nano-Lime with Polymer

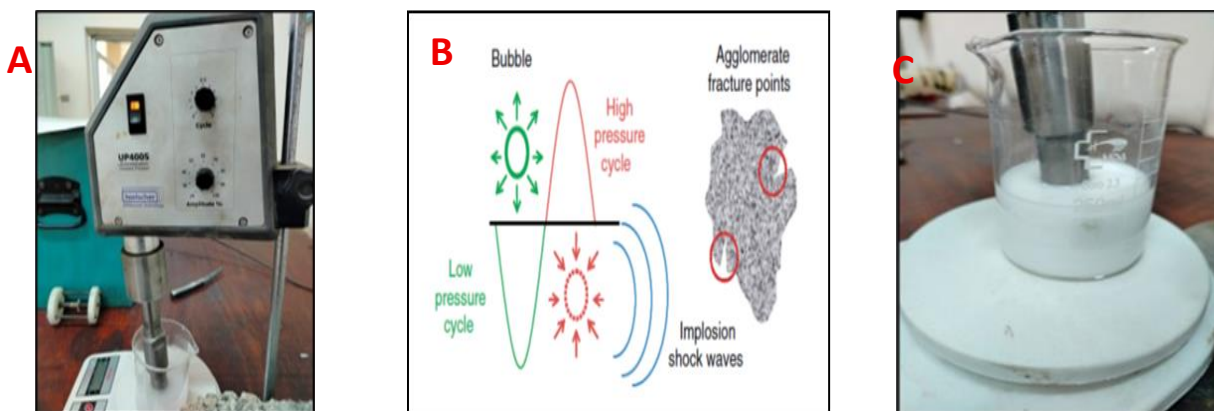
In this study, silica nanoparticles and calcium hydroxide nanoparticles «nano-lime» were used [FIGURES 3/A-B]. Each nanoparticle was mixed separately at a concentration of 10% with a solution of Paraloid B72 dissolved in acetone at a concentration of 3%. The nanocomposites, i.e., Paraloid B72 3%/ nano silica and Paraloid B72 3%/ nano lime, were prepared by dispersing the nanoparticles in Paraloid B72. Dispersion systems are commonly used in conservation practice¹³.



[FIGURES 3/A-B]: A. TEM photomicrograph of the silica nanoparticles (< 50 nm); B. TEM photomicrograph of the calcium hydroxide nanoparticles (nano lime) ranging from 42.5 to 100.5 nm © Done by the researchers

¹³ ALDOASRI *et Al.* 2017: 1–17.

The sonicator probe, commonly called the horn, serves as the acoustic component that transmits sound energy from the transducer to the liquid mixture. The acoustic energy delivered to the mixture relies on the design and size of the probe, along with how deeply it is submerged in the liquid. The vibrational intensity of the probe at a specific power level is influenced by the taper of the probe. Typically, more significant tapers result in larger vibrational intensities; consequently, a greater amount of power is delivered¹⁴. This sonication technique is frequently utilized for breaking apart and distributing nanomaterials within polymer-based substances, which is essential for enhancing the uniformity and stability of the mixture. A direct sonicator model up to 400s was used for this purpose¹⁵ [FIGURE 4/A]. Ultrasonic waves can be generated in liquid suspensions through direct sonication using a submerged transducer horn. During the process of ultrasonic disruption, sound waves propagate through the liquid medium in alternating high- and low-pressure cycles at frequencies typically in the 20–40 kHz range¹⁶. During the low-pressure cycle (rarefaction), microscopic vapor bubbles are formed in a process known as cavitation¹⁷[FIGURE 4/B]. The nanomaterials used in the study were mixed in the Materials Laboratory, Department of Electrical Engineering, Faculty of Engineering/Menoufia University. The blends were prepared by directly mixing polymer and nanoparticles (10% W/V). Dispersions were stirred vigorously for 30 minutes by an ultrasonic model UP400S. After the mixing process, the mixture became homogeneous, as the nanoparticles were distributed regularly within the carrier polymer particles [FIGURE 4/C].



[FIGURES 4/A-C]: A. Direct sonicator model UP400S; B. Ultrasonic wave induced cavitation of the suspension. TAUROZZI *et Al.* 2011; C. Homogeneity and stability of the nanocomposite © Photos A & C taken by BASSEM MANSOUR

¹⁴ TAUROZZI *et Al.* 2012: 8.

¹⁵ KAUR *et Al.* 2017: 1.

¹⁶ SAWAWI 2015: 31.

¹⁷ MANSOUR 2022: 126.

2. Methods

This section presents the standard methods used for examining, analyzing and testing clay samples before and after treatments aimed at improving their physical and mechanical properties.

A. X-ray Diffraction Analysis (XRD)

The analysis was conducted in the Environmental Studies and Research Institute/ University of Sadat City, using an X-ray diffractometer, model N^o.D2 Phaser 2nd Gen. The test method used an in-house method «ESRI/EGL/test p/01», based on BRUKER AXS, a laboratory manual for X-ray powder diffraction, as specified in ISO 17025:2017. XRD was performed on archaeological clay samples collected from the fallen parts of the cemetery buildings to determine their mineral composition. Then, experimental clay mixtures similar in mineral composition to the original mixtures were employed to ensure the accuracy of the results and the consistency with the archaeological materials¹⁸.

B. Sieve Analysis Test

The grain size distribution test of clay samples is an important test for determining the mechanical properties of adobe blocks and, consequently, the overall structural behavior of the building. It was conducted using a modern sieve analysis method that relied on laser technology. The test was conducted at the Housing and Building National Research Center using the Horiba LA-950 device, a laser diffraction/scattering particle size distribution analyzer that utilizes light scattering phenomena as its measuring principle. The maximum particle diameter that can be measured by this analyzer is 3 mm; 1.5 times that of a conventional analyzer¹⁹.

C. Scanning Electron Microscopy «SEM»

Scanning electron microscopy «SEM» examination of archaeological mud brick samples from the study site is an effective tool for characterizing the building material, describing its mineral grains, identifying precipitated salts and the degree of cohesion of the internal structure of the mud brick material, in addition to the mechanical deformations of the mud brick components, such as quartz grains and clay minerals.

Moreover, it is important for evaluating the physical and chemical treatments that aim to improve the physical and mechanical properties of mud bricks²⁰. The analysis was conducted in the Grand Egyptian Museum by using a FEI Quanta 3D 200i scanning electron microscope. The accelerating voltage was 20 kV in the magnification range of 100 to 3000x.

D. Physical Properties of Mud Brick Samples

Studying the physical properties of experimental samples mixed with natural, synthetic and chemical additives is an important test to evaluate the effectiveness of these

¹⁸ ABD EL-HAFEZ 2018: 1–13.

¹⁹ ALYOUSIF *et Al.* 2015: 1– 11.

²⁰ MANCI 2023: 121–146.

additives in enhancing the properties of mud bricks. Furthermore, it is essential to compare the different additives and select the best ones for the strengthening processes of the lab-made samples. The tested physical properties included density, apparent porosity and water absorption rate, according to the American specification «ASTM C20-00-2015»²¹.

The values of density, water absorption and porosity were calculated using the following equations:

1. **Density** = $\frac{W}{V}$ (gm/cm³)

2. **Porosity** (%) = $\frac{W2-W1}{V}$

3. **Water absorption** (%) = $\frac{W2-W1}{W1}$

Where W is the sample weight, V is the sample volume, W1 is the sample weight before immersion in water for 24 h and W2 is the weight after immersion in water²².

E. Mechanical Properties of Mud Brick Samples

Mechanical resistance is the most important factor in determining the functionality of construction materials²³. The compressive strength is one of the main engineering parameters that gives an indicator of the quality of the construction materials²⁴. The compressive strength test is one of the methods used to study the mechanical properties of building materials. The compressive strength of mud brick samples, including those with natural and industrial additives, was measured in samples to which polymeric and nano materials were added, to determine the extent of the effect of these additives on improving the mechanical properties of mud bricks. The mechanical characteristics of the compressive strength of the clay brick samples were determined in accordance with «ASTM C 67 – 03a»²⁵.

F. Colorimetric Measurement

The appearance of treated sample surfaces is a critical factor when applying consolidants to archaeological building materials in general. Treatments should produce minimal discoloration and chemical treatments should never cause visual distortion or noticeable discoloration of treated surfaces²⁶. The colorimetric test was performed to determine the aesthetic color change before and after application. The change in color using the CIE L*a*b* was calculated with the following equation:

²¹ ASTM C20-00 2015: 2.

²² ABD EL HAFEZ *et Al.* 2023: 403 – 414.

²³ EL-YAHYAOU *et Al.* 2023:13.

²⁴ MORSY *et Al.* 2024: 173.

²⁵ ASTM C 67 – 03a 2017: 2.

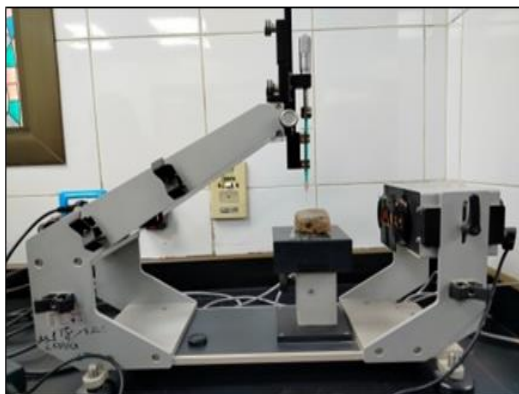
²⁶ MANCI 2023: 802.

$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$, where, ΔL^* , Δa^* and Δb^* are the differences in the L^* , a^* and b^* coordinates (according to CIEL AB color space) of the treated and untreated mud brick samples²⁷.

G. Water Contact Angle Measurement

Any porous substance can absorb water in its liquid form through capillary action, which is driven by surface tension and the adsorption forces of the pore walls. High surface tension reflects strong intermolecular forces²⁸, i.e., high cohesive forces. The size of the pores and the arrangement of the pore structure significantly influence the capillary water uptake process²⁹. To evaluate the impact of water on a surface treated with reinforcing materials, the water contact angle is measured, which indicates the interaction between the water droplet and the surface: a contact angle of less than 90° suggests that the surface is hydrophilic and tends to attract water, while an angle greater than 90° indicates a hydrophobic, water-repellent surface³⁰. Water contact angle measurements were carried out to assess the change in surface hydrophobicity resulting from the applied coatings³¹.

The contact angle is defined as the internal angle formed between the substrate and a tangent to the water droplet at the point of contact. This method helps evaluate the effectiveness of consolidating materials in repelling water and in determining the surface's susceptibility to wetting. Measurements were conducted using a Krüss device³² [FIGURE 5].



[FIGURE 5]: Krüss device used to measure the water contact angle of treated mud brick samples © Photo taken by BASSEM MANSOUR

III.RESULTS AND DISCUSSION

1. X-ray Diffraction Analysis (XRD)

[FIGURE 6] shows the X-ray diffraction pattern of an archaeological mud brick sample from the Quesna cemetery, a standard sample for mud brick compositions at the

²⁷ AL-DOSARI, MOHAMMAD *et Al.* 2016: 192 – 204.

²⁸ ANDERSSON 2018: 6.

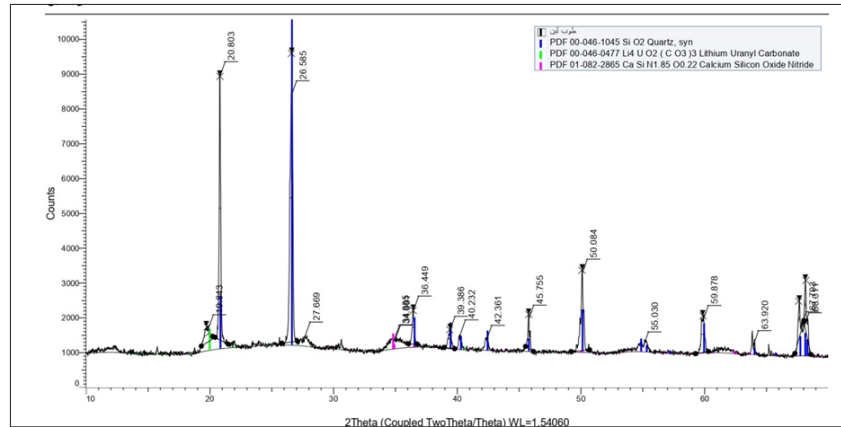
²⁹ DONG FENG *et Al.* 2018: 8.

³⁰ EL KADY *et Al.* 2023:110.

³¹ RIBEIRO 2021: 134.

³² ASTM D7490–13 2022: 2.

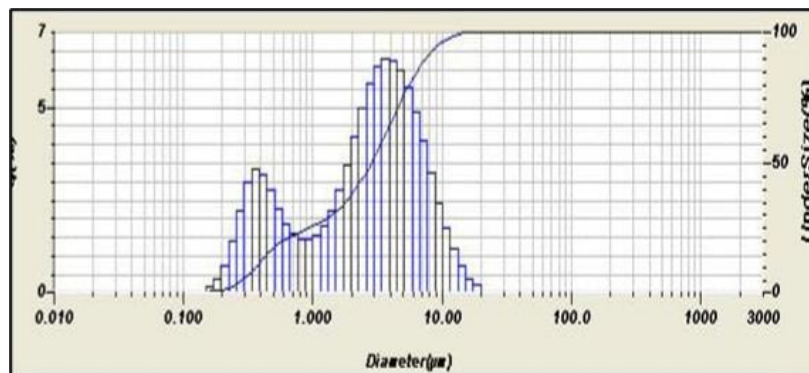
archaeological site in general. The mud bricks contain a high percentage of quartz minerals, indicating a high sand content.



[FIGURE 6]: X-ray diffraction pattern of the archaeological mud brick sample taken from the archaeological Quesna cemetery. It shows that quartz is the major mineral © Done by the researchers

2. Sieve Analysis Test

Standard methods for characterizing earthen building materials include the grain size analysis test, which is performed to determine the percentage of each particle size in a soil (mud brick) sample. Particle size distribution is a fundamental property that defines soil structure and texture³³. It is determined by sieve analysis [FIGURE 7], which is also used to evaluate the practical size distribution of soil. The analysis results showed that the sample consists of 35% clay/silt and 65% sand.



[FIGURE 7]: Grain size distribution test of mud brick sample taken from archaeological Quesna cemetery © Done by the researchers

3. Scanning Electron Microscopy «SEM»

The scanning electron microscopy «SEM» examination is performed to analyze the crystal structure, surface topography, electrical behavior and chemical composition of approximately one micrometer of the upper part of the sample³⁴. SEM can study the surface of a sample without sample preparation, offering magnification capabilities of up

³³ ALYOUSIF *et Al.* 2015: 1–11.

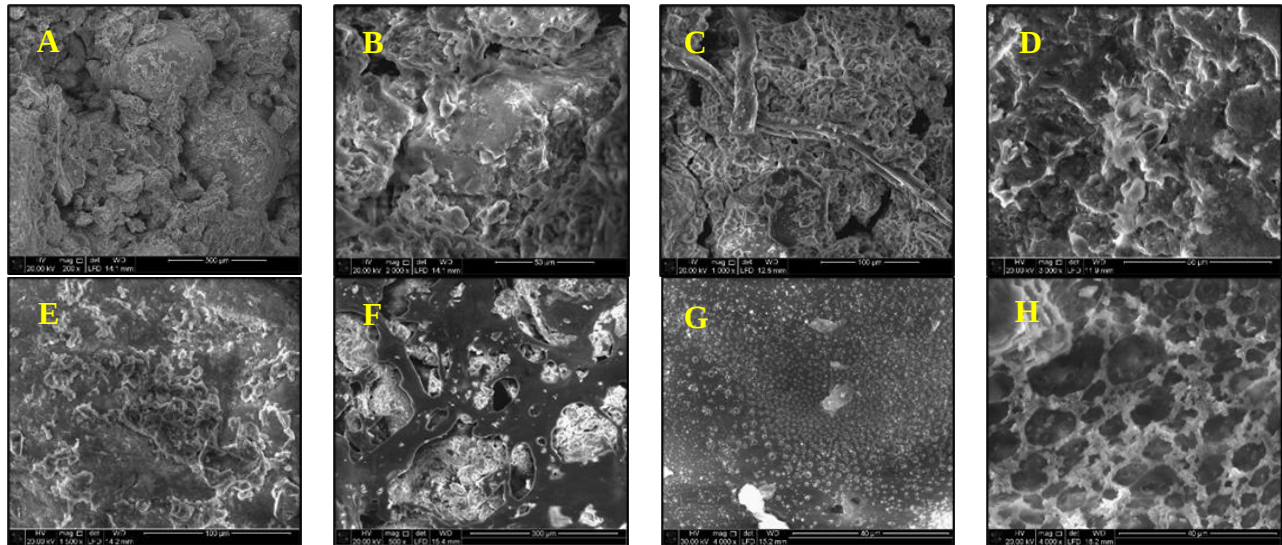
³⁴ ALI *et Al.* 2023: 2.

to 1 million times and generating high-resolution three-dimensional images³⁵. In the current study, SEM aimed to determine the extent to which the addition of polymeric and nanomaterials improves the physical and mechanical properties of archaeological mud bricks or the manufactured mud bricks for restoration and reinforcement purposes. It was performed on samples treated with chemical composites, either by adding them to the mixing water to produce modern mud bricks for restoration purposes or by directly consolidating the archaeological mud brick samples using a brush. The first chemical treatment «adding the chemical compounds to the mixing water» included Paraloid B72 3%/ Sika Gard 701, Paraloid B72 3%/ Estell 1100, Paraloid B72 3%/ nano-silica and Paraloid B72 3%/ nano-lime. The second chemical treatment (direct consolidation of the archaeological mud brick samples) included Paraloid B72 3%/ Sika Gard 701, Paraloid B72 3%/ Estell 1100 and Paraloid B72 3%/ nano-silica.

[FIGURES 8/A-E] show the results of the microscopic examination of the standard mud brick sample and mud brick samples manufactured with the addition of the chemical composites Paraloid B72 3%/ Sika Gard 701, Paraloid B72 3%/ Estell 1100, Paraloid B72 3%/ nano-silica and Paraloid B72 3%/ nano-lime. The results indicated that the chemical composite Paraloid B72 3%/ Sika Gard 701 failed to improve the physical and mechanical properties of the manufactured mud brick, as it was unable to bind the grains and fill the voids uniformly and homogeneously. In comparison, the chemical composites Paraloid B72 3%/ Estell 1100, Paraloid B72 3%/ nano-silica and Paraloid B72 3%/ nano-lime successfully spread homogeneously throughout the mud brick components and coated the mineral grains effectively.

Furthermore, [FIGURES 8/F- H] show the results of the microscopic examination of the archaeological mud brick samples treated with the chemical composites Paraloid B72 3%/ Sika Gard 701, Paraloid B72 3%/ Estell 1100 and Paraloid B72 3%/ nano-silica. The results indicated that the chemical composite Paraloid B72 3%/ Sika Gard 701 failed for the second time to improve the physical and mechanical properties of the manufactured mud brick when applied by brush, as it was unable to bind the grains and did not fill the voids well and homogeneously. In contrast, the chemical composites Paraloid B72 3%/ Estell 1100 and Paraloid B72 3%/ nano-silica successfully spread homogeneously throughout the mud brick components and coated the mineral grains effectively. This finding confirmed the results of the first treatment and demonstrated the effectiveness of these chemicals and nanocomposites, whether added to the mixing water to manufacture modern mud bricks for restoration and reinforcement purposes or applied directly to consolidate archaeological mud bricks at the indicated concentrations.

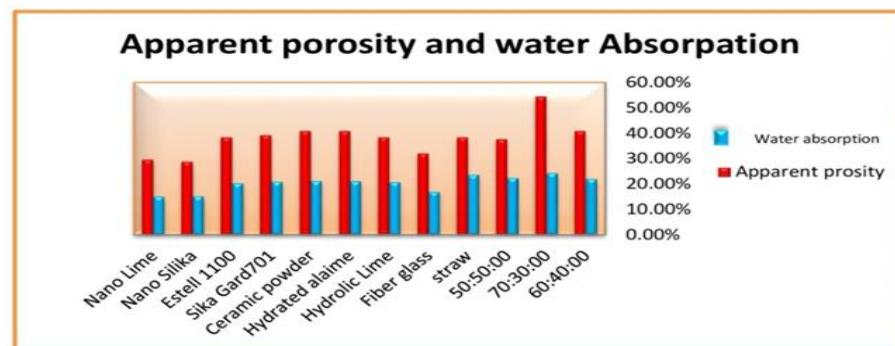
³⁵ ROHAYEM *et Al.* 2018: 94.



[FIGURES 8/A-H]: A. Standard mud brick sample showing clay particles and quartz grains; B. Mud brick sample manufactured by adding the chemical composite Paraloid B72 3%/ Sika Gard 701; C. Mud brick sample manufactured by adding the chemical composite Paraloid B72 3%/ Estell 1100; D. Mud brick sample manufactured by adding the nano composite Paraloid B72 3%/ nano-silica; E. Mud brick sample manufactured by adding the nano composite Paraloid B72 3%/ nano-lime; F. Archaeological mud brick sample treated with the chemical composite Paraloid B72 3%/ Sika Gard 701; G. Archaeological mud brick sample treated with the chemical composite Paraloid B72 3%/ Estell 1100; H. Archaeological mud brick sample treated with the nano composite Paraloid B72 3%/ nano-silica © Done by the authors

4. The Physical Properties of the Mud Brick Samples

The results showed that the use of fiberglass in the clay mixture or Paraloid B72 3%/ nano-silica and Paraloid B72 3%/ nano-lime, either in direct consolidation or added to the mixing water, significantly reduced the water absorption of the adobe bricks. Moreover, it reduced the porosity of mud bricks, thereby enhancing their durability and resistance to deterioration. In contrast, the other additives showed similar results in terms of porosity and water absorption, which are fairly average. Furthermore, it was proven that porosity increases with increasing sand content in the clay mixture. The results of physical properties are shown in [FIGURE 9].

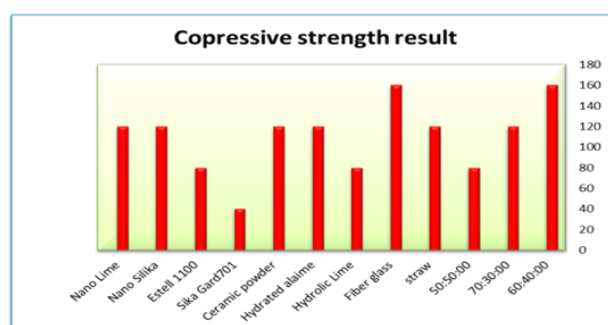


[FIGURE 9]: Results of the physical properties of manufactured and chemically treated mud brick samples © Done by the researchers

5. The Mechanical Properties of the Mud Brick Samples

The results showed that the samples enhanced with fiberglass achieved the highest compressive strength, followed by the samples treated with the composites Paraloid B72 3%/ nano-silica and Paraloid B72 3%/ nano-lime and samples enhanced with straw, slaked lime and ceramic powder, which achieved relatively high compressive strength.

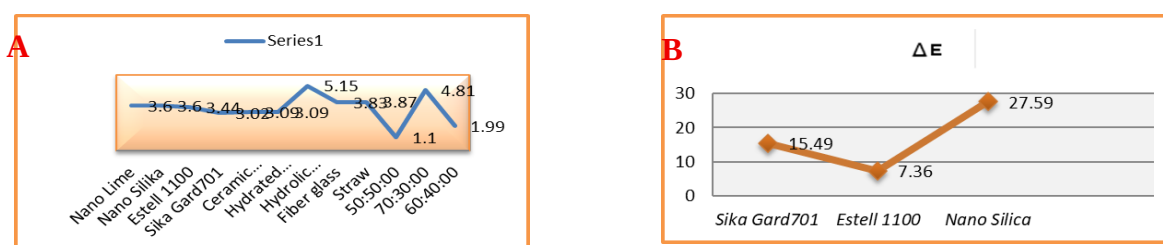
Furthermore, the test results demonstrated that the compressive strength of the clay samples achieved the best results when the clay mixture ratio was 60% sand: 40% clay/silt. This finding is consistent with several relevant scientific studies. The efficiency of this mixture may be attributed to the balance achieved between the sand component, which imparts strength and durability to the mud brick and the fine-grained materials (silt and clay), which act as binding materials for the mud brick constituents. The results of compressive strength are shown in [FIGURE 10].



[FIGURE 10]: Results of compressive strength of manufactured and chemically treated mud brick samples

6. Colorimetric Measurement

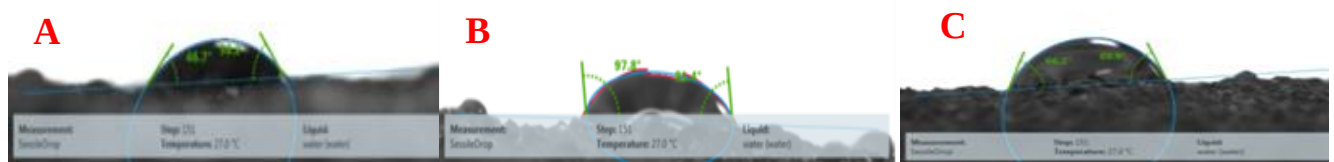
Colorimetric measurements showed that the clay samples manufactured for restoration purposes, whose properties were enhanced with natural, synthetic and chemical additives, all fell within the safe limits in terms of surface color change, with $\Delta E < 5$. Other archaeological mud brick samples consolidated with chemical composites showed varying color changes, although the chemical composite Paraloid B72 3%/ Estell 1100 was the least color-changing ($\Delta E = 7.36$). The color change in the consolidated samples may be due to testing before the polymer was completely dry, or possibly to an increase in concentration, which requires further future testing to achieve optimal results. The results of colorimetric measurement are shown in [FIGURES 11/A-B].



[FIGURES 11/A-B]: A. Results of colorimetric measurement of the manufactured mud brick samples; B. Results of colorimetric measurement of the chemically consolidated mud brick samples © Done by the researchers

7. Water Contact Angle Measurement

The water contact angle test was performed on archaeological mud brick samples consolidated with the chemical composites: Paraloid B72 3%/ Sika Gard 701, Paraloid B72 3%/ Estell 1100 and Paraloid B72 3%/ nano-silica. The results shown in [FIGURES 12/A, B & C] indicated that the chemical composite Paraloid B72 3%/ Estell 1100 was able to repel water, as the water contact angle was greater than 90°. The chemical composites Paraloid B72 3%/ Sika Gard 701 and Paraloid B72 3%/ nano-silica failed to repel water from the treated samples, as the water contact angle was less than 90°. The test results were as follows: Paraloid B72 3%/ Sika Gard 701 (angle = 56°), B. Paraloid B72 3%/ Estell 1100 (angle = 97°) and C. Paraloid B72 3%/ nano-silica (angle = 69°).



[FIGURES 12/A- C]: Results of the water contact angle test of the samples treated with: A. Paraloid B72 3%/ Sika Gard 701 (angle = 56°); B. Paraloid B72 3%/ Estell 1100 (angle = 97°); C. Paraloid B72 3%/ nano-silica (angle = 69°) © Done by researchers

IV. CONCLUSION

This paper presented an experimental study on mud brick (adobe) structures from the archaeological cemetery of Quesna, Menoufia Governorate, Egypt. It aimed to identify the components of archaeological mud bricks and enhance their physical and mechanical properties through consolidation using various chemical composites, including Paraloid B72 3%/ Sika Gard 701, Paraloid B72 3%/ Estell 1100 and Paraloid B72 3%/ nano-silica.

Additionally, it aimed to enhance the properties of newly manufactured mud bricks for restoration and reinforcement purposes by incorporating natural, synthetic and chemical additives. The natural and synthetic additives tested were straw, fiberglass, ceramic powder, slaked lime and natural hydraulic lime (NHL 3.5). The chemical additives included Sika Gard 710, Estel 1100, nano-silica and nano-lime. Each chemical material was used at a concentration of 10%, mixed with Paraloid B72 dissolved in acetone at 3% and added to the mud brick mix water at a proportion of approximately 15%. Evaluation involved a range of analytical methods, including physical and mechanical property testing, SEM, colorimetric analysis and water contact angle measurements. Sieve analysis of the archaeological samples revealed a composition of 35% clay/silt and 65% sand. The findings showed that the use of fiberglass significantly reduced water absorption and improved the mechanical strength of the mud bricks. The inclusion of nanocomposites, specifically Paraloid B72 3%/ nano-silica or Paraloid B72 3%/ nano-lime, enhanced water resistance and strength. However, Paraloid B72 3%/ nano-silica caused some color change, which could be mitigated in future studies by adjusting the concentration while maintaining its performance benefits. Its water-repellent capacity is also expected to

improve. Among the composites tested, Paraloid B72 3%/Estel 1100 demonstrated good water-repellent behavior in treated samples, although it had a limited effect on improving other physical and mechanical properties. The use of Paraloid B72 3%/Sika Gard 701 for the direct consolidation of archaeological mud bricks in Quesna cemetery is not recommended. Overall, the study encourages the use of natural additives, such as straw and slaked lime and synthetic materials, e.g., fiberglass, to enhance newly manufactured mud bricks intended for conservation. Positive improvements in the physical and mechanical properties of mud bricks were achieved by adding Paraloid B72-based composites «with Sika Gard 701, Estel 1100, nano-silica and nano-lime» to the mud brick mix water in defined proportions. The direct consolidation of archaeological mud bricks can be safely achieved using Paraloid B72 (3%) combined with either Estel 1100 or nano-silica at low concentrations. In addition to improving physical and mechanical properties, the treated samples also suggested potential resistance to thermal stresses under preliminary testing conditions. However, the long-term performance of these chemical composites under environmental stressors remains to be fully evaluated. Further research, including extended artificial aging experiments, is recommended to assess their overall effectiveness in resisting climatic fluctuations.

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DISCLOSURE STATEMENT

No Potential conflict of interest was reported by the author

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THE ROLE OF ARTIFICIAL INTELLIGENCE IN THE PRESERVATION OF MURAL PAINTINGS UNDER CLIMATE CHANGE: OPPORTUNITIES, CHALLENGES AND EMERGING FRAMEWORKS

BY

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ABSTRACT

[EN] This study provides a structured analytical framework to elucidate how AI-driven methodologies can fundamentally shift preventive conservation strategies from a paradigm of reactive repair to a proactive, sustainable stewardship approach under climatic stress. By conducting a systematic examination of the integration of Machine Learning (ML), Deep Learning (DL) and the Internet of Things (IoT), the research paper critically evaluates the efficacy of these technologies within real-world heritage scenarios. The analytical results highlight the transformative capability of Convolutional Neural Networks (CNNs) for identifying microcracks and surface defects within controlled environments with remarkable precision, achieving accuracy rates of 94%. Concurrently, it explores the potential of digital twins in simulating non-invasive restoration interventions, thereby minimizing physical risks to the artwork. Findings demonstrate that adopting AI-driven predictive maintenance strategies offers significant economic benefits, potentially reducing long-term conservation costs by approximately 35% through the implementation of early warning systems. However, the practical application of AI is not without impediments, including data scarcity, the absence of standardized datasets and the prevailing technical gap between data scientists and heritage conservators. Consequently, this paper establishes a strategic roadmap for integrating AI into heritage management, emphasizing the need to adopt «Green AI» principles and establish ethical governance frameworks. It concludes that fostering interdisciplinary collaboration is essential for building resilient, climate-adaptive systems capable of safeguarding cultural heritage for future generations.

KEYWORDS: Artificial intelligence, climate change, CNNs, digital twins, mural conservation, predictive maintenance, sustainability.

[AR] دور الذكاء الاصطناعي في حفظ الصور الجدارية في ظل التغير المناخي: الفرص، والتحديات، والأطر الناشئة تساهم هذه الدراسة بتقديم إطار تحليلي منظم يهدف إلى توضيح كيف يمكن للمنهجيات القائمة على الذكاء الاصطناعي أن تحدث تحولاً جذرياً في استراتيجيات الحفاظ الوقائي، منتقلة بها من «نهج الإصلاح التفاعلي» إلى «نهج الصيانة المستدامة الاستباقية» في ظل الضغوط المناخية. ومن خلال إجراء فحص منهجي لتكامل تقنيات تعلم الآلة (ML) والتعلم العميق (DL) وإنترنت الأشياء (IoT)، يقيم البحث تقيماً نقدياً فعالية هذه التقنيات داخل سيناريوهات التراث الواقعية. تسلط النتائج التحليلية الضوء على القدرة الفائقة للشبكات العصبية الالتفافية (CNNs) في تحديد الشروخ الدقيقة وعيوب السطح داخل بيئات خاضعة للتحكم محققة معدلات دقة تصل إلى 94%. وفي الوقت ذاته، تستكشف الدراسة إمكانات التوائم الرقمية (Digital Twins) في محاكاة تدخلات الترميم غير المتلفة، مما يقلل المخاطر المادية التي قد تلحق بالعمل الفني. وتوضح النتائج أن تبني استراتيجيات الصيانة التنبؤية المدعومة بالذكاء الاصطناعي يوفر فوائد اقتصادية ملموسة، حيث يمكن أن يقلل تكاليف الحفاظ على المدى الطويل بنسبة تقارب 35% من خلال تطبيق أنظمة الإنذار المبكر. على الرغم من هذه النتائج الواعدة، يواجه التطبيق العملي للذكاء الاصطناعي بعض التحديات، مثل ندرة البيانات وغياب مجموعات البيانات القياسية الموحدة والفجوة التقنية بين علماء البيانات ومرمي التراث. وبناءً عليه، تضع هذه الورقة خارطة طريق استراتيجية لدمج الذكاء الاصطناعي في إدارة التراث، مع التشديد على ضرورة

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تبني مبادئ «الذكاء الاصطناعي الأخضر» وإرساء أطر للحوكمة الأخلاقية. وفي الختام، تخلص الدراسة إلى أن تعزيز التعاون البيئي هو ركيزة أساسية لبناء أنظمة مرنة ومتكيفة مناخياً قادرة على حماية التراث الثقافي للأجيال القادمة. الكلمات الدالة: الاستدامة، التغير المناخي، التوائم الرقمية، حفظ الجداريات، الذكاء الاصطناعي، الشبكات العصبية CNNs، الصيانة التنبؤية.

I. INTRODUCTION

Climate change is a major threat to cultural heritage globally¹. Mural paintings in desert regions are especially at risk because they are sensitive to the environment². They are directly affected by changes in temperature and humidity, as well as extreme events, e.g., heavy rain or sandstorms, which cause serious damage, such as surface cracking, fading colors and paint layer detachment³.

Concurrently, Artificial Intelligence (AI) has grown rapidly in fields like medicine and industry⁴. Heritage conservation is also using these advanced tools⁵. Technologies, such as machine learning, computer vision and big data analysis, offer new ways to protect murals. They facilitate the monitoring of climate patterns, the prediction of future damage and the suggestion of better restoration plans without needing to touch the artwork⁶.

According to UNESCO, climate change now threatens more than 10% of World Heritage Sites⁷. Recent studies show that AI solutions can cut maintenance costs by up to 35% by detecting problems early. This use has been seen in projects like the digital documentation of Pompeii's murals using computer vision and temple restoration in Cambodia via machine learning analysis⁸.

This research paper connects two critical fields: AI and heritage conservation. It aims to present a vision for protecting murals from the effects of climate change. It also aims to bridge the gap between these two fields by addressing the following primary research questions:

- How can AI mitigate climate-induced deterioration of mural paintings?
- What technological and ethical constraints limit its application?
- How can AI support sustainable conservation strategies?

II. CLIMATE CHANGE AND DETERIORATION MECHANISMS OF MURAL PAINTINGS

Mural paintings are integral parts of the buildings they decorate. Thus, they are directly affected by the surrounding microclimate. The literature confirms that Relative Humidity (RH) is the most critical factor driving deterioration in these artworks⁹. The

¹ CASSAR 2005: 11; El Hagrassy 2022:166.

² CAMUFFO 2019: 45.

³ BINDA & TIRABOSCHI 1999: 47.

⁴ KUMAR 2017: 5.

⁵ XU *et Al.* 2022: 221.

⁶ FIORUCCI *et Al.* 2020: 103.

⁷ UNESCO 2022: 5.

⁸ LEISSNER *et Al.* 2015: 6.

⁹ CAMUFFO 2019: 4.

interaction between moisture and mural, as a complex, multi-layered system, triggers a chain of damage¹⁰.

1. Mechanical Stress and Cracking

Murals function as a complex, multi-layered system «support, plaster and paint». Each layer reacts differently to moisture, which infiltrates these layers primarily through capillary action and condensation cycles, creating differential stress zones¹¹.

When humidity rises, organic binders and salts absorb water and expand. When it drops, they shrink. This cycle of swelling and shrinking creates internal stress driven by the mismatch in expansion coefficients between layers, leading to delamination¹². Over time, this mechanical fatigue causes serious structural damage, such as cracking, cupping and paint layer flaking¹³.

2. Salt Crystallization

Climate change causes extreme fluctuations in temperature and humidity¹⁴, which control the movement of soluble salts within the walls. At high humidity, salts dissolve. When the air becomes dry, these salts turn into crystals. The pressure from crystallization inside the pores is powerful enough to break the plaster and push the pigment off the surface¹⁵. Consequently, recent extreme weather events accelerate these crystallization cycles, causing rapid pulverization of the pigment layer¹⁶.

3. Biological Deterioration

Moisture also brings life to the wall. Sustained high humidity levels «usually above 65-70%» create the perfect environment for fungi and bacteria to grow. These microorganisms produce acids and colored stains that disfigure the artwork and digest the organic materials used in the paint¹⁷. This microscopic growth is often difficult to detect by the naked eye in early stages, necessitating the use of computer vision and spectral imaging for early diagnosis¹⁸.

III. CHALLENGES AND ETHICAL CONSIDERATIONS

While technology is promising, its application faces significant hurdles that this study highlights:

1. Data Limitations: AI models require massive datasets of annotated images to learn.

However, the heritage sector lacks standardized databases for deterioration patterns¹⁹.

¹⁰ MECKLENBURG *et Al.* 1998: 465.

¹¹ CAMUFFO 2019: 23.

¹² MECKLENBURG *et Al.* 1998: 468; CALIFANO *et Al.* 2025: 2.

¹³ BRATASZ 2013: 68; PERLES *et Al.* 2024: 3.

¹⁴ SABBIONI *et Al.* 2010: 15.

¹⁵ ARNOLD & ZEHNDER 1991: 110 ; ARCE-NAZARIO *et Al.* 2024: 4.

¹⁶ SABBIONI *et Al.* 2010: 15.

¹⁷ STERFLINGER 2010: 49.

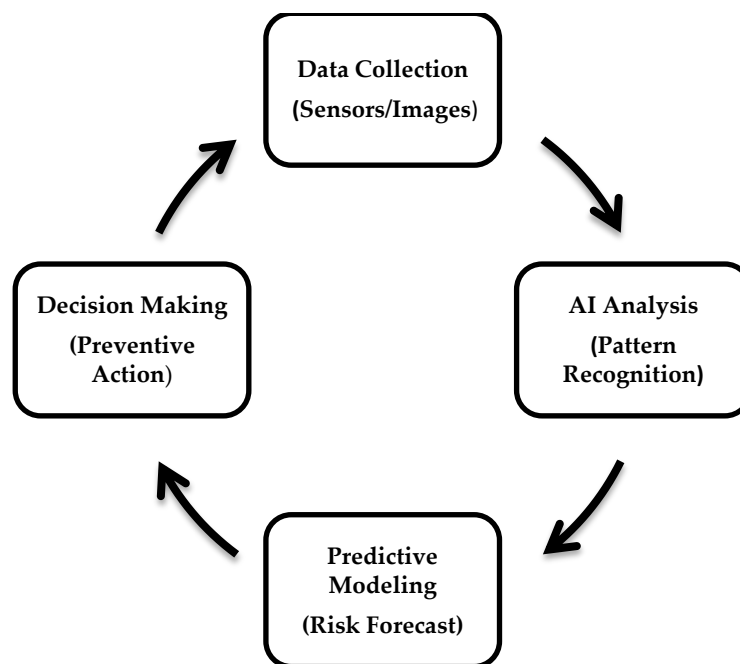
¹⁸ FIORUCCI *et Al.* 2020: 104.

¹⁹ CORNELIS *et Al.* 2013: 5; FIORUCCI *et Al.* 2020: 107.

2. **Skill Gap:** There is a shortage of professionals who combine expertise in both conservation science and data engineering²⁰.
3. **Ethical Concerns:** The use of generative AI to reconstruct missing parts of a mural raises questions about authenticity. Does the AI «hallucinate» details that never existed? Thus, it requires strict ethical guidelines to ensure the historical integrity of the artwork²¹.

IV. APPLICATIONS OF ARTIFICIAL INTELLIGENCE IN MURAL CONSERVATION

Artificial intelligence is not just a theoretical concept; it has become a practical tool in various heritage sites globally. This section reviews the most notable technologies used in mural conservation. To visualize how these technologies function within a systematic framework, [FIGURE 1] illustrates the integrated workflow from data collection to decision making.



[FIGURE 1]: The integrated workflow of AI technologies in mural conservation © Done by the researchers

1. Automated Image Analysis and Computer Vision

Computer vision algorithms, particularly Convolutional Neural Networks (CNNs), have revolutionized damage detection. Recent models like YOLOv8 and Vision Transformers (ViT) have demonstrated remarkable precision, achieving experimental accuracy rates exceeding 94% in identifying microcracks on heritage surfaces²².

The recent Segment Anything Model (SAM) developed by Meta represents a leap forward. It enables automatic identification of damaged areas without extensive prior training. This technology has been successfully tested in projects, such as MapSAM, paving the way for precise damage mapping on complex mural surfaces. While SAM excels in segmentation, it requires integration with classification algorithms to

²⁰ GHAITH 2025: 4.

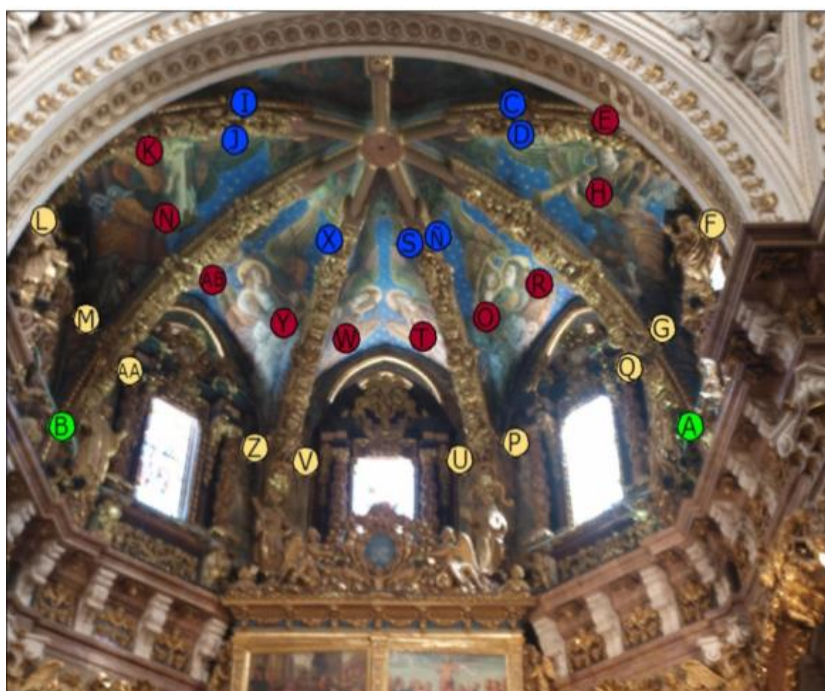
²¹ RODRÍGUEZ MIRANDA & REINOSO 2023: 88.

²² HUANG *et Al.* 2025: 7898.

distinguish between cracks and biological growth²³. To address the issue of data scarcity in heritage datasets, techniques such as data augmentation and transfer learning are increasingly employed to train models on limited numbers of images²⁴.

2. Smart Monitoring Systems «IoT»

To counter the fluctuations in humidity and temperature, conservationists are now using AI-powered Internet of Things (IoT) systems. For instance, LoRaWAN-based sensors can be embedded within the plaster layers of murals. These sensors transmit real-time environmental data to a central platform, allowing for immediate intervention. Its application was demonstrated in the monitoring of frescoes in the Cathedral of Valencia, where sensors helped correlate microclimatic changes with surface deterioration²⁵. Furthermore, the deployment of Micro-Electro-Mechanical Systems (MEMS) ensures that these sensors are non-invasive and have minimal visual impact on the artwork²⁶. Data collected are then processed using Recurrent Neural Networks (RNNs) or Long Short-Term Memory (LSTM) for time-series forecasting, predicting risks like salt crystallization hours before occurrence²⁷. To visualize this practical implementation, [FIGURE 2] shows the distribution of these wireless sensors installed directly on the Renaissance frescoes to monitor microclimatic conditions.



[FIGURE 2]: Distribution of wireless sensors on the Renaissance frescoes at the Cathedral of Valencia for microclimatic monitoring. ZARZO *et Al.* 2011: 8690

3. Predictive Modeling and Climate Simulation

AI is not limited to monitoring; it predicts the future. By integrating historical climate data «such as the CMIP6 dataset» with machine learning, researchers can

²³ KIRILLOV *et Al.* 2023: 5.

²⁴ FIORUCCI *et Al.* 2020: 106.

²⁵ ZARZO *et Al.* 2011: 8685; GHAITH 2025: 4.

²⁶ BERTOLIN & FERNÁNDEZ-NAVAJAS 2020: 2.

²⁷ FIORUCCI *et Al.* 2020: 106.

simulate future deterioration scenarios. A notable case study was the Nasca World Heritage Site in Peru, where AI-driven predictive modeling was used to estimate the impact of climate-induced floods and human threats, enabling the development of preventive strategies before disaster strikes²⁸. Furthermore, adopting AI-driven predictive maintenance strategies has proven to be economically beneficial, potentially reducing long-term conservation costs by approximately 35% by preventing catastrophic damage before it occurs²⁹. Algorithms, such as LSTM and Random Forest, are particularly effective for time-series forecasting to predict environmental risks³⁰. AI techniques are also essential for downscaling global climate models (CMIP6) to predict site-specific microclimatic risks³¹.

4. Digital Twins and Virtual Restoration

The concept of «digital twins» allows for the creation of a virtual replica of the mural. This involves multiphysics simulations to model moisture transport virtually, ensuring minimum intervention and preventing irreversible human errors³². This digital copy can be used to test restoration materials virtually before applying them to the real artwork. An inspiring example is the Digital Twin project of Saint. Peter's Basilica in the Vatican. This AI-driven model allows for precise monitoring of the structure. It has reduced the need for physical on-site inspections by up to 75%, significantly minimizing the risk of accidental damage³³.

To summarize the transformative impact of these technologies [TABLE 1] compares traditional conservation methods and AI-driven approaches.

Feature	Traditional Conservation	AI-Driven Conservation
Methodology	Reactive «fixing damage after it occurs»	Proactive «predicting damage before it happens»
Inspection Speed	Slow «manual inspection by eye»	Real-time «automated monitoring via sensors»
Accuracy	Subjective «depends on human experience»	Objective «micro-level detection and data-driven»
Intervention	Physical / Invasive	Non-invasive «virtual restoration and digital twins»
Data Management	Fragmented records	Integrated digital databases
Cost Efficiency	Low initial cost but, high long-term maintenance	High initial investment but, low long-term cost

[TABLE 1]: Comparison between traditional conservation methods and AI-driven approaches © Done by the researchers

²⁸ ARCE-NAZARIO *et Al.* 2024: 5.

²⁹ LEISSNER *et Al.* 2015: 6.

³⁰ FIORUCCI *et Al.* 2020: 106.

³¹ LEISSNER *et Al.* 2015: 6.

³² CALIFANO *et Al.* 2025: 914–935 .

³³ BARNI *et Al.* 2021: 8.

V. ADVANCED OPPORTUNITIES FOR SUSTAINABLE CONSERVATION

AI offers more than just technical tools; it provides a strategic framework for decision-making. This section explores how intelligent systems can transform conservation management.

1. Intelligent Decision Support Systems «IDSS»

One of the most significant opportunities is the use of Case-Based Reasoning (CBR). It allows conservators to compare the current condition of a mural with a database of similar past cases to propose the best treatment. Additionally, Multi-Criteria Decision Analysis (MCDA) helps balance conflicting factors, such as cost, sustainability and historical value, when choosing a restoration material. This approach has been successfully applied in adaptive reuse strategies for historic buildings in Italy, ensuring outcomes that are both economically and culturally viable. Moreover, both systems assist experts by reducing cognitive bias, especially when selecting between traditional and green materials³⁴.

2. Big Data and Bayesian Networks

By analyzing global conservation data, AI can find hidden patterns. For example, Bayesian networks are used to identify probabilistic relationships, demonstrating high robustness even in cases of missing data, a common challenge in archaeological sites³⁵.

Furthermore, projects like Linked Conservation Data provide a unified repository for restoration knowledge, helping researchers access standardized terminology and material properties instantly³⁶.

3. Remote Sensing and Satellite Monitoring

For large-scale heritage sites, AI analyzes satellite imagery to detect the surrounding environmental changes. This macro-scale monitoring serves as a first line of defense, guiding the precise placement of micro-scale sensors inside the building. The integration of Sentinel-2 satellite imagery with multispectral indices (e.g., NDVI) has proven effective in detecting soil marks and potential threats to archaeological sites without the need for physical excavation, as demonstrated in arid heritage sites in North Africa and the Middle East³⁷.

4. Critical Perspectives: Authenticity and AI

While AI offers precision, it raises critical questions regarding authenticity and technological determinism. Does AI-generated reconstruction of missing mural parts compromise the historical integrity of the artwork? It is crucial to ensure that AI remains a supportive tool for the conservator's judgment rather than a replacement, maintaining the human-centric approach to heritage stewardship. This aligns with the principles of the Venice Charter, ensuring that AI acts as an IDS, not a decision maker³⁸.

³⁴ GIRARD *et Al.* 2020: 256.

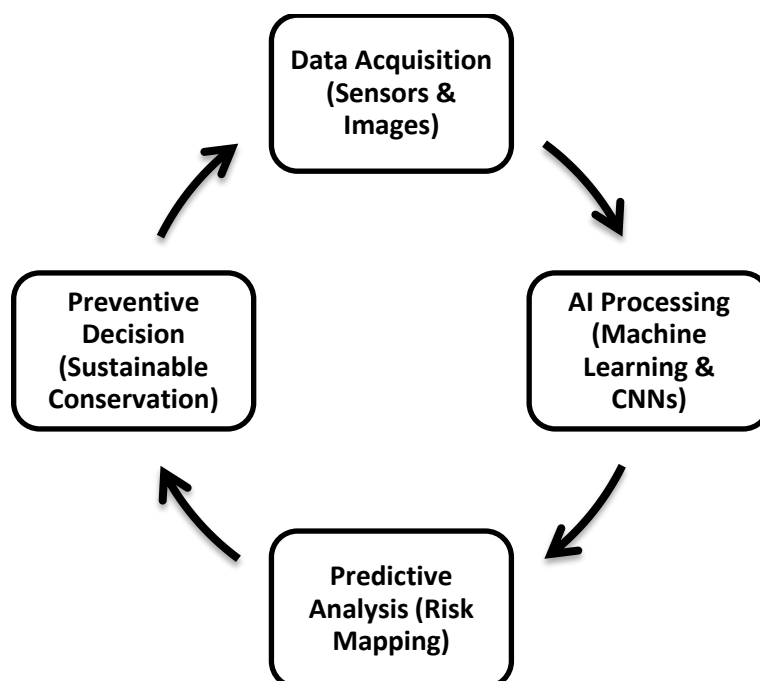
³⁵ FIORUCCI *et Al.* 2020: 107.

³⁶ VELIOS & JOHN 2021: 285.

³⁷ ABATE & LASAPONARA 2023: 104188.

³⁸ MIRANDA & REINOSO 2023: 88.

In alignment with these ethical considerations, the following strategic roadmap [FIGURE 3] outlines the proposed framework for integrating AI technologies into a cohesive, sustainable conservation workflow.



[FIGURE 3]: A strategic roadmap integrating AI technologies for sustainable mural conservation
© Done by the researchers

VI.CONCLUSION

This study concludes that the cumulative impact of climate fluctuations accelerates the erosion rate of mural layers. The findings establish a robust correlation between AI-driven predictive modeling and the long-term structural integrity of mural paintings. However, the integration of AI has demonstrated a capability to mitigate these risks. Predictive AI models have achieved detection accuracy rates of 94% compared to traditional methods and have reduced maintenance costs by approximately 35% through targeted interventions. The study demonstrates that AI is not a replacement for the conservator but, a powerful ally that enhances precision and sustainability. Ultimately, the integration of AI into mural conservation must be guided not only by technical efficiency but, by critical awareness of cultural meaning, ethical responsibility and long-term heritage stewardship.

Based on the analysis, the research proposes the following roadmap:

Standardization and National Databases: Establish a national standardized database for damage patterns, adopting international standards, such as CIDOC-CRM, to ensure data interoperability.

Educational Reform: Integrate specialized modules on AI-Heritage Informatics into archaeology curricula, alongside launching joint training programs to bridge the gap between data engineers and conservators.

Green AI: Prioritize energy-efficient algorithms «Green AI» to align digital preservation with environmental sustainability goals³⁹.

Ethical Governance: Establish technical-ethical committees within cultural ministries to oversee the implementation of generative AI in restoration.

Economic Viability: Allocate dedicated budgets for digital innovation, emphasizing that this initial investment will lead to a 35% reduction in long-term maintenance costs, ensuring economic sustainability.

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³⁹ D'AGOSTINO *et Al.* 2017: 692.

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EXAMINATION AND SPECTROSCOPIC EVALUATION OF VINTAGE MONOCHROME AND HAND-COLORED TINTYPES FROM PRIVATE COLLECTIONS

By

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ABSTRACT

[EN] Tintypes, a popular photograph medium of the late 19th century, consist of multiple layers that include a collodion-based silver image, varnish for protection and a japanned metallic support, some with hand-applied color. Their multi-layered composition makes them highly prone to degradation such as varnish yellowing, metallic support rusting, image loss and cracking of the structure. This study analyzed two samples from private collections: a monochrome tintype and a hand-colored tintype. The following analytical techniques were employed to assess condition and material composition: digital and stereomicroscopy, SEM, ATR-FTIR, micro-Raman and XRD. The findings revealed signs of degradation, including scratches, cracks, rust and peeling of the image layers. Conservation treatments were carried out, including mechanical and chemical cleaning, loss compensation and the application of an atmospheric pressure plasma jet (APPJ) with Ar/TEOS to provide rust protection. Better storage conditions were also recommended for long-term preservation.

KEYWORDS: Conservation, FTIR, Hand-coloring, Monochrome, Raman, SEM/EDS, Tintype.

[AR] التشخيص والتحليل الطيفي لصور التينتايب الفوتوغرافية أحادية اللون والملونة يدويا من المجموعات الخاصة
تُعدّ صور التينتايب من الوسائط التصويرية الشائعة في القرن التاسع عشر، وهي تتكون من عدة طبقات تشمل طبقة الصورة المكوّنة من جسيمات
الفضة في وسط رابط من الكولوديون، وطبقة من الورنيش الواقي، إضافةً إلى دعامة معدنية مدهونة بالورنيش الأسود «الجابان». وفي بعض النماذج
أضيف التلوين اليدوي ليكون جزءاً أصيلاً من التكوين أو أضيف لاحقاً. وبسبب طبيعتها متعددة الطبقات، تُعاني هذه الصور من مظاهر تدهور
متنوعة مثل اصفرار طبقة الورنيش، وصدأ الدعامة المعدنية، وفقدان أجزاء من الصورة، وتشققات أو خدوش في البنية. تناولت هذه الدراسة
صورتين من مجموعات فوتوغرافية خاصة: الأولى أحادية اللون، والثانية ملونة يدوياً. وقد استُخدمت عدة تقنيات فحص وتحليل مثل المجهر الرقعي
المحمول، والمجهر الاستيريوسكوبي، والمجهر الإلكتروني الماسح (SEM)، والتحليل الطيفي بالأشعة تحت الحمراء (ATR-FTIR)، والمطيافية الميكرو-
رامان، وحيود الأشعة السينية (XRD). أظهرت النتائج وجود تشققات وخدوش وصدأ وسقوط في بعض طبقات الصورة. وبُنيت على ذلك إجراءات
الترميم المقترحة، والتي شملت التنظيف الميكانيكي والكيميائي، وتعويض الفاقد، وتطبيق طبقة واقية على الدعامة باستخدام بلازما الضغط الجوي
(APPJ) مع غاز الأرجون ومركب TEOS للحد من الصدأ، بالإضافة إلى تحسين ظروف الحفظ والتخزين لضمان صونها على المدى الطويل.
الكلمات الدالة: أحادي اللون، التحليل الطيفي بالأشعة تحت الحمراء، التلوين اليدوي، التينتايب، الرامان، الصيانة، الميكروسكوب الإلكتروني الماسح
المزود بوحدة تشتت الأشعة السينية.

I. INTRODUCTION

Historical photographs are powerful documentary tools that offer visual records of influential individuals, critical events, values, social changes, cultural traditions, technological progress and even cherished family memories. The tintype, also known as the ferrotype or melainotype, is one of the earliest photographic processes that has mostly captured the existence of the average person. It is produced by making a direct positive on a metal sheet. The name is deceptive, ironically, since the photographs were typically developed on thin iron plates rather than using tin to make the images¹. The procedure was established in 1851 by FREDERICK SCOTT ARCHER but, because he neglected to file for a patent, many people have since copied it. Unfortunately, ARCHER's invention did not bring in any money during his lifetime and he passed away penniless. ARCHER's creation outlasted him. Tintypes were extensively utilized throughout the world from the 1850s until the early 20th century². Tintypes were a popular photographic process in the West at the time since they offered some advantages over other conventional methods. Unlike daguerreotypes, another widely used type of photography, their images were devoid of reflections. The processing of tintypes required approximately fifteen minutes, resulting in the formation of positive images within a similar duration. As a result, they gained considerable popularity for portrait photography. As with daguerreotypes and ambrotypes, tintypes were hand-colored using several different techniques, such as oil-based paint, crayon, colored chalk and pastel; however, due to their metallic foundation, watercolor was not a suitable medium. In order to preserve the Loring, colorful chalk or pastels used to color the tintype was typically sealed beneath glass³. Horace M. Hedden developed a method for producing a colored tintype plate to provide a fuller, warmer tintype image⁴ described his method as applying a mixture of linseed and Indian red oil on iron plates.

Tintype plates were colored in yellow, blue and chocolate. The brown plate was commonly used, while the blue and yellow plates were costly and extremely rare⁵. The tintype is a multilayered photograph consisting of a black japanning layer, an iron or steel plate, a collodion or nitrocellulose binder that retains the particles of the silver image and a varnish coating for protection [FIGURE 1].

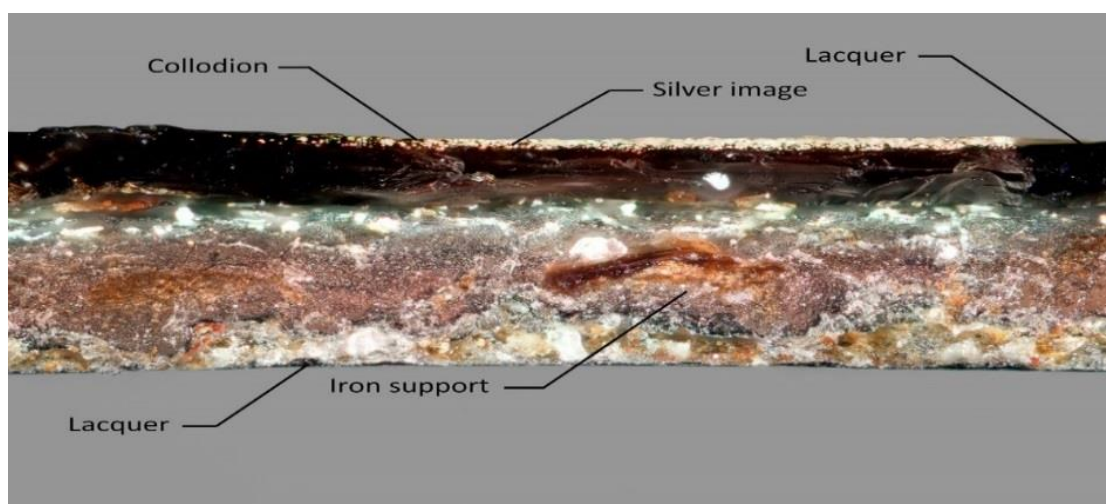
¹ BURNS 1995; HEWGLEY 1999: 78-87.

² LAVÉDRINE & GANDOLFO 2009: 34; ELSHAMY 2019: 39-48.

³ CHIPMAN *et Al.* 2011: 168-185

⁴ SCHIMMELMAN 2000: 1-24.

⁵ MAURICE 1995: 10-19; WHITE 1997: 9-10.



[FIGURE 1]: Cross-section of a complete tintype showing the iron support, manufacturer applied verso varnish and japanning layer and the artist-applied Collodion image layer and recto varnish. ROGGE 2018: 169-188

Photographs, especially tintypes, have a complicated layered structure that makes them prone to damage. Degradation is divided into three types: physical, chemical and biological. Physical degradation involves structural and mechanical damage forms and is usually caused by poor handling, storage or display⁶. Chemical degradation is frequently caused by either the materials used to make the photograph or things in the air or nearby items that are not part of the shot⁷. Additionally, damage may occur if the fixing time is too short, the fixing solution is exhausted, or the image is improperly washed, leaving fixer residues behind. These residues can cause the image tone to shift toward yellow or brown and lead to fading. Biological degradation can be active or inert, depending on the makeup of the material. It is caused by animals, fungi, or bacteria⁸.

Rust may occur on both the recto and verso surfaces of the tintype. Preliminary microscopic analysis suggests that the predominant corrosion products are hydrous ferric oxides, primarily goethite–limonite assemblies, frequently exhibiting adsorbed water. These rust layers are often associated with remnants of Japanese lacquer on the reverse side or lacquer, photosensitive compounds and protective varnish on the image side. The filiform rust separates the two layers by expanding and migrating between the Japanese lacquers and the metal plate. The iron plate is altered by exposure to air, moisture, carbonic or organic acids, glues and the paper components of the holders themselves, which results in all these oxides of secondary origin. Under the right circumstances, calcium-based papers might theoretically aid in the production of rust.

High humidity levels cause collodion to become unstable, which makes it possible for free nitrogen oxides to target the cellulose chain and the silver imaging particles, causing damage to the collodion layer.

⁶ LAVÉDRINE 2003: 32-64.

⁷ HILL 2018: 1-42; YOSRI *et Al.* 2020: 39-50.

⁸ BORREGO *et AL* 2015: 109-120; ELDEEB *et Al.* 2022: 105632.

Eventually, this causes the collodion to crumble and turn yellow⁹. Reticulation of the collodion layer is another characteristic observed in these images. It is defined by the contraction and increased brittleness of the collodion layer, leading to the formation of capillary fissures. Additionally, it may also cause material loss, chipping, abrasion, or layer separation. Among the techniques employed in this study, which present various benefits as highlighted in earlier research, Atmospheric pressure plasma jets (APPJ) provide the opportunity to create coatings and surface modifications applicable in areas ranging from biomedical sensors to opto-electronic devices, eliminating the requirement for costly vacuum systems and allowing operation in an open environment¹⁰. The initial application of plasma treatment in cultural heritage involved the conservation of historic metallic artifacts. Plasma was utilized in the processing of daguerreotypes, namely, a photographic representation on a metallic base¹¹. Its disinfecting effect on paper has also shown positive results in tests. Additionally, plasma treatment trials were conducted on smoke-damaged artworks to eliminate grime and different organic pollutants from their surfaces¹². From this point forward, the aim of this research paper was to perform an analytical study of the composition of both monochrome and hand-colored tintypes.

The study also aimed to document and assess the deterioration condition of the selected photographs using a portable digital microscope, a stereomicroscope and a scanning electron microscope (SEM) and to analyze the selected tintypes using ATR-FTIR to identify the binding material and the type of lacquer used, Raman to identify the pigments and X-ray diffraction analysis (XRD) to identify the rust compounds for the primary supports.

II. MATERIAL AND METHODS

1. Vintage Monochrome and Hand-Colored Tintypes

The study was carried out on two tintypes from private collections. The first tintype is a monochromatic image with colored frills, obtained from Dr. MARK OSTERMAN'S studio (Scully & Osterman, from the United States of America) [FIGURES 2/A-B]. The second is a hand-colored tintype from the private collection of Francis Amin [FIGURES 2/C-D], an Italian tour guide and photo collector who was awarded the Knight's Medal by the Italian president. An analytical study was conducted on each photograph to determine their composition and the extent of damage that has occurred.

The monochrome tintype measures approximately 6.8 cm in length and 5.1 cm in width, while the hand-colored tintype measures about 8.8 cm by 6 cm. Photographic documentation revealed various forms of deterioration, including rust spots, tonal variations and areas of image layer loss, as shown in [FIGURES 2/A-D].

⁹ COSTA 2016: 1-24.

¹⁰ DEMAUDE *et Al.* 2019: 77-83; RIZA *et Al.* 2024: 130648.

¹¹ BOSELLI *et Al.* 2017:1600027.

¹² ELATTAR *et Al.* 2023: 91-104.



[FIGURES 2/A-D]: Shows the current condition of the photographs under examination. A-B. The monochrome tintype; C-D. The hand-colored tintype, presented in recto and verso views, exhibiting various forms of deterioration © Done by the researchers

2. Methods:

A. USB Microscope

A Super Eyes PZ01 500X USB digital microscope was utilized to document the surface characteristics of both monochrome and hand-colored tintypes, as well as to examine deterioration forms not visible to the naked eye, such as cracks in the binder layer of both photos, fingerprints, erosion in the image layer and substrate rust and finally, scratches in the varnish layer. This procedure was carried out at the faculty of archeology, Cairo university¹³.

B. Stereomicroscope

A stereomicroscope was employed to examine the photographs at elevated magnifications, enabling the observation of morphological characteristics not discernible to the naked eye. This examination provided a deeper understanding of the objects' intrinsic characteristics, reflecting both their overall structure and manufacturing techniques, as well as existing forms of deterioration. Image-forming particles were given special attention in order to gain insight into their morphology.

Additionally, portions exhibiting the object's most pertinent deterioration patterns were detected. The LEICA M165C was used at the Faculty of Nanotechnology, Cairo University, Sheikh Zayed Branch.

¹³ ELDEEB *et Al.* 2022: 41-52.

C. SEM/EDS

A variable pressure SEM «FEL Quanta 3D 200i EDX/thermo fisher pathfinder» at the Grand Egyptian Museum (GEM) was employed to examine the photographs without applying a conductive coating. It was run in low vacuum for acceleration voltages between 20.0 and 30.0 kv using a wide field detector at a working distance of 15 to 17 mm. Since the SEM microscope has a sizable chamber where tiny items can be inserted, the analyses were performed directly on the samples without any prior preparation. The variable pressure mode was selected to accommodate the presence of organic coatings on the surface of the objects.

D. ATR-FTIR Spectroscopy

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy «ATR-FTIR» was employed to investigate the molecular structure of the binder of both hand-colored and monochromatic tintype images, as well as the composition of the darkened varnished or «japanned» metal surface «lacquer structure». A vertex 70, Bruker was used to record the IR spectra of the images using a zinc selenide crystal in attenuation total reflection (ATR) mode at a wavelength of 400–4000 cm^{-1} . This analysis was performed at the Projects Sector, Ministry of Antiquities in Cairo, Egypt, the samples' IR transmittance frequencies were measured using an average of 128 scans and a resolution of roughly 4 cm^{-1} .

E. 2.2.5 μ -Raman Spectroscopy

Micro-Raman spectroscopy « μ -Raman» was used to identify the substances used to color the photos, as well as the silver degradation products. Placing the tintype directly on the microscope stage allowed for an in-situ examination of the area. This analysis was carried out using a BRUKER «SENTERRA II» Raman spectrometer, a high-stability OLYMPUS BX41TF optical microscope and an Ivac CCD detector. Data was collected using a diode laser at 785 nm. A neutral density filter «10% optical density» was used to modify the laser's strength. The samples were scanned for 1000–3000 MS at 10% laser power., with ten cycles per sample. The longer acquisition interval was employed to lower the signal-to-noise ratio. Measurements were carried out at room temperature and ambient humidity. Analytical points were selected as follows: colored regions to identify the type of material used; at least one point to determine photographic compounds such as silver halides and degradation products and visibly deteriorated areas to characterize rust and the composition of other degradation products. In other instances, the designated areas experienced high activity, probably, likely resulting from bathtub cleaning and repairs. μ -Raman spectroscopy can also induce fluorescence by eliminating residual silver salts, leaving only the organic binder, which may explain the fluorescence originating from the organic varnish layer overlaying the emulsion.

F. XRD Analysis

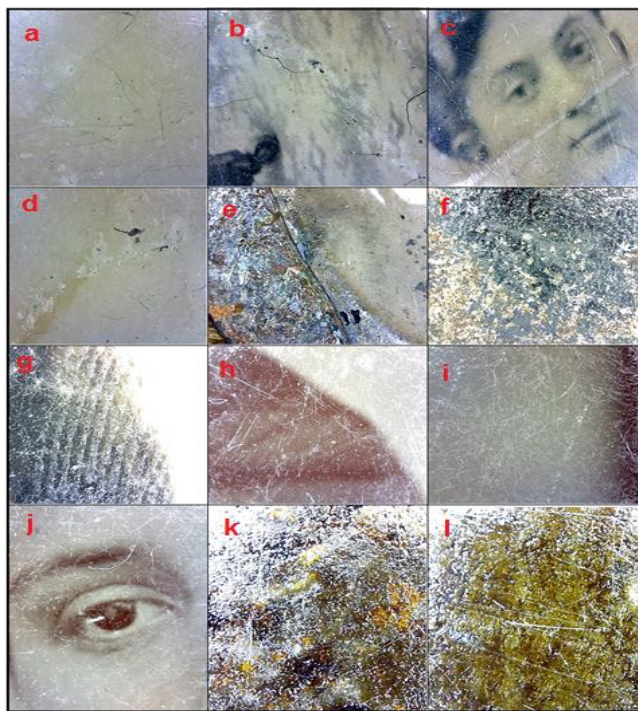
X-ray diffraction analysis (XRD) was conducted to identify the rust components present in the primary support of both tintype images. The analysis was performed directly on the samples using a PANalytical X'Pert PRO Diffractometer equipped with a

secondary monochromator and a Cu-K α_1 radiation source « $\lambda = 0.1542$ nm», operating at 45 kV and 40 mA. Scanning parameters included a 2θ range of 70° , a step size of 0.02° and a scan rate of $0.05^\circ/\text{s}$. The resulting diffraction patterns were used to determine the 2θ values and relative intensities (I/I_0) of the detected phases. The analysis was carried out at the Faculty of Nanotechnology/Cairo University, Sheikh Zayed branch.

III.RESULTS AND DISCUSSION

1. USB Microscope

The portable digital microscope revealed that both the monochromatic and hand-colored tintype images suffer from multiple forms of damage. The monochrome image showed pronounced scratching of the varnish layer [FIGURE 3/A], black stains on the varnish surface [FIGURE 3/B], cracking of the photographic binder layer and scratching of the red pigment applied to the cheeks [FIGURE 3/C]. Additionally, several portions of the varnish layer were found to have detached, accompanied by noticeable yellowing [FIGURE 3/D]. The detached parts of the image layer were examined [FIGURE 3/E]. Further observations indicated partial loss of the lacquer layer, rusting of the metal support [FIGURE 3/F] and the presence of fingerprint marks [FIGURE 3/G]. Similarly, the hand-colored tintype displayed extensive surface scratches on the varnish layer [FIGURE 3/H], cracks within the binder layer [FIGURE 3/I], localized losses at the image corners [FIGURE 3/J], corrosion stains with yellow to orange discoloration [FIGURE 3/K] and finally scratches within the lacquer layer [FIGURE 3/L].

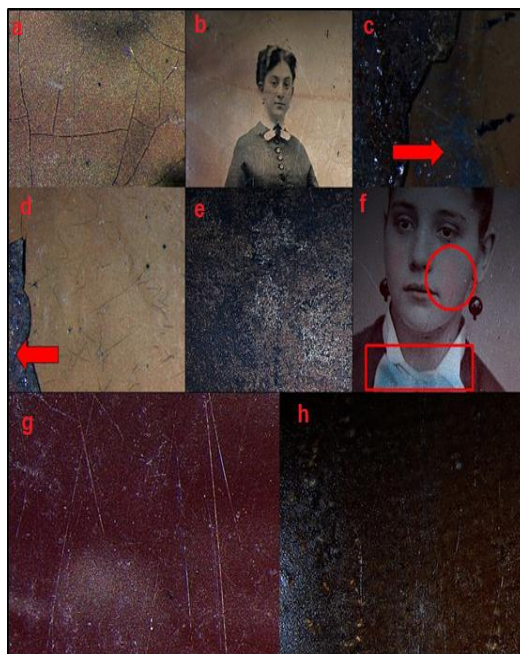


[FIGURES 3/A-I]: Damage forms of monochromatic and hand colored tintype. A. Scratching of the varnish layer. B. Black stains on the varnish layer. C. Cracking of the binder later. D. yellowing. E. Detached parts of the image layer. F. Rusting of the primary support. G. Fingerprints. H. Scratching of the varnish layer in the hand-colored tintype. I. Cracking of the binder layer. J. Loss in the corner of the photograph. K. Corrosion stains. L. Scratching of the lacquer

© Done by the researchers

2. Stereomicroscope

Stereomicroscopic examination revealed several deterioration forms, including cracks within the binder layer [FIGURE 4/A], scratches on the varnish layer [FIGURE 4/B], stains of varying colors, silver degradation appearing as bluish discoloration [FIGURE 4/C], losses in the image layer [FIGURE 4/D] and rust of the primary support [FIGURE 4/E]. In the case of the hand-colored tintype, the analysis identified areas containing colored frills [FIGURE 4/F], scratches on the surface of the image [FIGURE 4/G] and rust formation on the primary support [FIGURE 4/H].



[FIGURES 4/A-H]: Different forms of damage on monochromatic and hand-colored tintypes. A. Cracks in the binder layer. B. Scratches in the varnish layer. C. Staining and image silver decay. D. LOoss of the image layer; E. Rusting of the primary support. F. Color frills in the hand-colored image. G. Scratching of the image surface. H. Rusting of the primary support © Done by the researchers

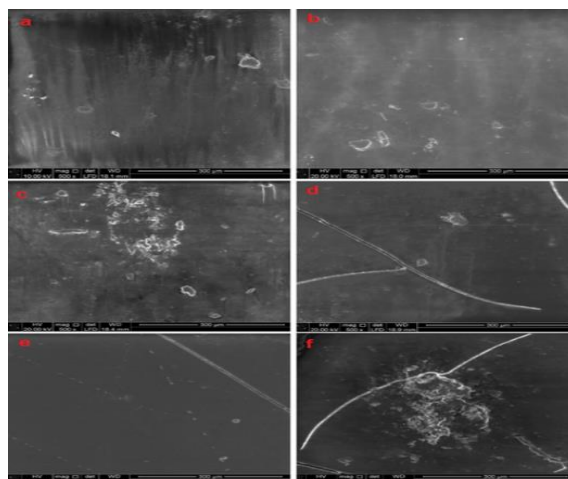
3. SEM/EDS Analysis

SEM/EDS analysis revealed that the primary constituent of the image material in both photographs is metallic silver (Ag). The presence of chlorine (Cl) is likely attributed either to insufficient washing or to deterioration of the image silver. Inadequate washing prevents the complete removal of residual processing chemicals and light-sensitive materials, including silver halides, which subsequently contribute to image degradation. In addition, atmospheric pollutants may interact with the silver particles within the image, leading to the formation of silver chloride and further deterioration¹⁴. Carbon (C) was also detected which is attributed to the binding material, collodion¹⁵. For the hand-colored tintype, three analytical points were selected. The first point aimed to identify the basic components of the image, including the final imaging material, the binding medium and

¹⁴ GLASER 2013: 222-238.

¹⁵ ROGGE 2014: 57-63.

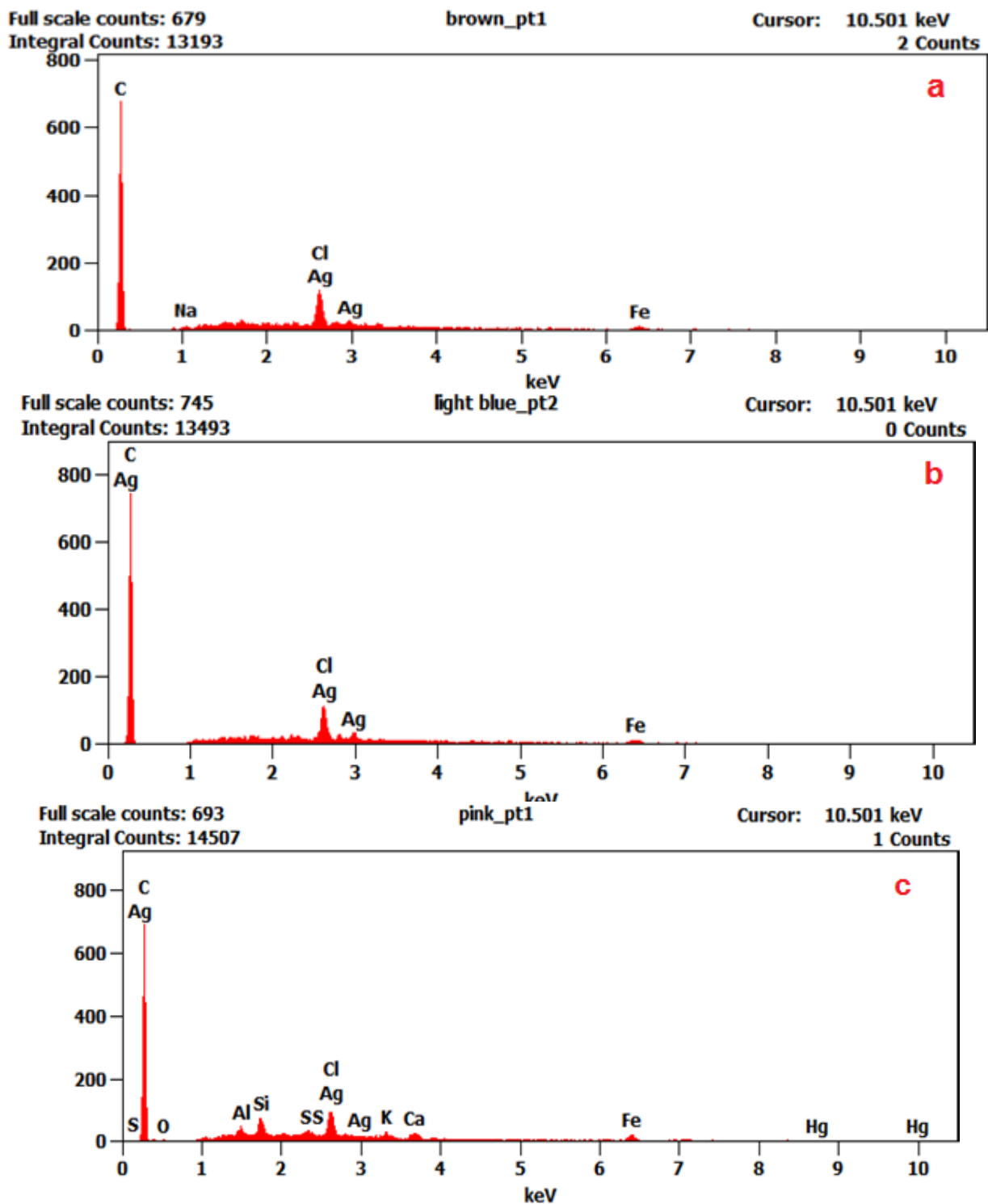
the primary support [FIGURE 5/A]. The results indicated the presence of sodium (Na), suggesting the use of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) as the fixing agent, iron (Fe) from the iron-based support and carbon (C) from the binder [FIGURE 6/B]. The second point was selected from the blue-colored region to determine the pigment used for hand-coloring [FIGURE 5/B]. Results detected silver, the material used to create the final image; carbon, the binder layer; and iron, which indicates the use of Prussian blue for the blue color [FIGURE 6/B]. The analysis detected silver, corresponding to the final image material; carbon, representing the binder layer; and iron, indicative of Prussian blue pigment. This result is consistent with¹⁶. The third analytical point was taken from the red cheek area, which exhibited a dense accumulation of pigment and visible cracks within the binder layer [FIGURE 5/C]. Elemental analysis revealed that the red pigment consisted primarily of iron oxide, as indicated by the presence of iron (Fe) and oxygen (O). The presence of sulfur (S) is associated with silver deterioration through the formation of silver sulfide (Ag_2S). Aluminum (Al) and silica (Si) have been identified as impurities¹⁷ [FIGURE 6/C]. Similarly, three points were analyzed on the monochromatic tintype—corresponding to a dark region, a highlight area and the cheek—to identify the pigment used. Observations revealed the presence of cracks [FIGURE 5/D], varnish with a smooth surface [FIGURE 5/E] and a color mass [FIGURE 5/F]. In the dark region, silver was identified as the primary image material, while sulfur was detected as a major cause of silver degradation and iron was confirmed as the main component of the support material [FIGURE 7/A]. The analysis of the highlight area confirmed the presence of silver as the final image material, along with chlorine and sulfur related to image deterioration and carbon which is attributed to the binder material [FIGURE 7/B]. Analysis of the third area «i.e., the cheeks» revealed that the red pigment used is vermilion (HgS) as indicated by the presence of sulfur (S) and mercury (Hg). Iron and silver were also present in this area [FIGURE 7/C].



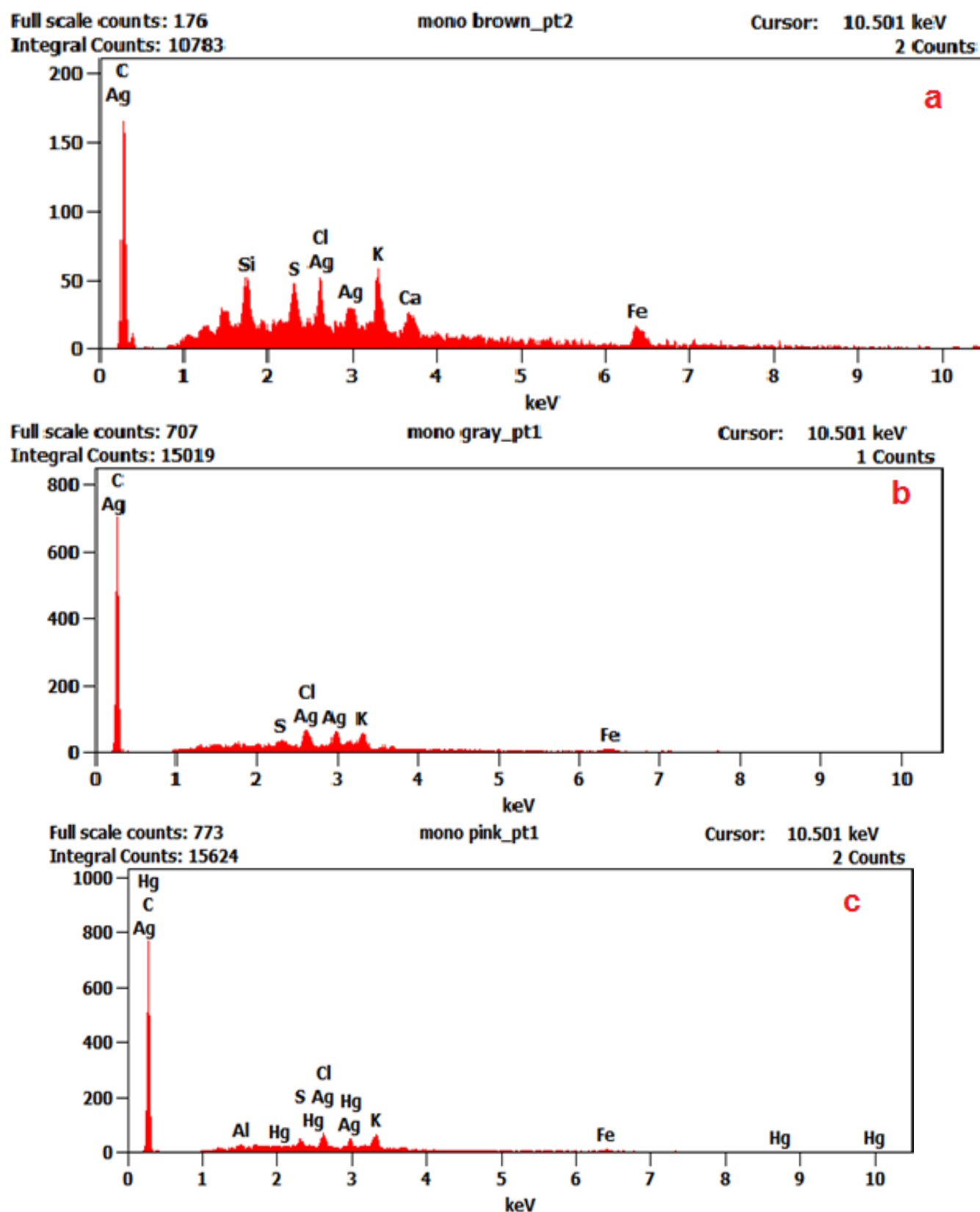
[FIGURES 5/A-F]: SEM images for both tintype «i.e., monochromatic and hand-colored». A. The surface of the image. B. The blue color. C. The red color. D. The dark area. E. The light area. F. The red color for the cheeks © Done by the researchers

¹⁶ FARAH *et Al.* 2013: 12132-12146.

¹⁷ SHAHEEN *et Al.* 2020: 1093-1102.



[FIGURE 6]: EDS analysis of the hand-colored tintype. A. Surface of the photo. B. The blue color. C. The red color © Done by the researchers



[FIGURE 7]: EDS analysis of the monochrome tintype. A. The dark area. B. The highlight area of the same photo. C. The red color of cheeks © Done by the researchers

4. ATR-FTIR Spectroscopy

The ATR-FTIR analysis detected the existence of collodion and determined the sources of varnish¹⁸. The appearance of nitrocellulose's characteristic absorption bands «C₆H₇(NO₂)₃O₅» at 1632-1641 cm⁻¹, 1059 cm⁻¹, 1268-1273 cm⁻¹ and 824-833 cm⁻¹ indicates the presence of collodion¹⁵. Several distinct absorption bands are required to identify the varnish. Varnishes derived from proteins, tree resins, insect resins or oils exhibit a carbonyl band within the 1630–1750 cm⁻¹ region, while wax- or gum-based varnishes are characterized by C–H stretching vibrations between 2850–2960 cm⁻¹. These spectral features allow for a more precise differentiation of the materials used in varnish production. FTIR spectra was collected from both the recto and verso of the monochrome and hand-colored tintypes. In both cases, absorption bands characteristic of collodion was observed. For the monochrome tintype, these appeared at 1648 cm⁻¹, 1234 cm⁻¹, 1033 cm⁻¹ and 779 cm⁻¹, while for the hand-colored tintype, they were detected at 1656 cm⁻¹, 1251 cm⁻¹, 1035 cm⁻¹ and 725 cm⁻¹ [FIGURE 8]. Regarding the varnishes, the monochrome tintype exhibited absorption bands at 2927 cm⁻¹, 2858 cm⁻¹, 1377 cm⁻¹, 1166 cm⁻¹ and 723 cm⁻¹, consistent with the presence of shellac. Additional bands at 1710 cm⁻¹¹⁸, 1461 cm⁻¹ and 1166 cm⁻¹ suggest the presence of mastic, indicating that a mixture of both natural resins was likely used [FIGURE 8]. For the hand-colored tintype, shellac is indicated by absorption bands at 2929 cm⁻¹, 2856 cm⁻¹, 1375 cm⁻¹ and 1035 cm⁻¹^{5,18}, while mastic is evidenced by peaks at 1463 cm⁻¹ and 1710 cm⁻¹ [FIGURE 8].

Carbon black was identified as the black lacquer applied to the verso to enhance image contrast¹⁹. Carbon black has a structure like crystalline graphite, consisting of stacked graphene sheets, with the exception that it is less ordered and three-dimensional, suggesting a mix of crystalline and amorphous carbon substructures.

There are concentric inner layers as a result of the carbon black graphene sheets being parallel to one another but, not arranged in order²⁰. This structural complexity results in multiple functional groups. For carbon black (lamp black), the peaks at 2921 cm⁻¹ and 2860 cm⁻¹ represent the antisymmetric and symmetric stretching vibrations of the C–H₂ group. The peak at 1702 cm⁻¹ corresponds to the C=O stretching vibration of carbonyl and carboxylic groups. Peaks at 1378 cm⁻¹ and 1579 cm⁻¹ are associated with amorphous carbon. In the monochrome tintype, a peak at 1203 cm⁻¹ corresponds to C–C stretching, while the band at 1029 cm⁻¹ is related to C–H aromatic stretching²¹ [FIGURE 9]. For the hand-colored tintype, the peak at 2933 cm⁻¹ and 2858 cm⁻¹ are the antisymmetric and symmetric stretching vibration peak of C–H₂ band, the peak at 1708 cm⁻¹ is associated to the C=O stretching vibration corresponding to carbonyl and carboxylic group, 1384 cm⁻¹ corresponds to amorphous carbon and the peak at 1166 cm⁻¹ corresponding to C–H in

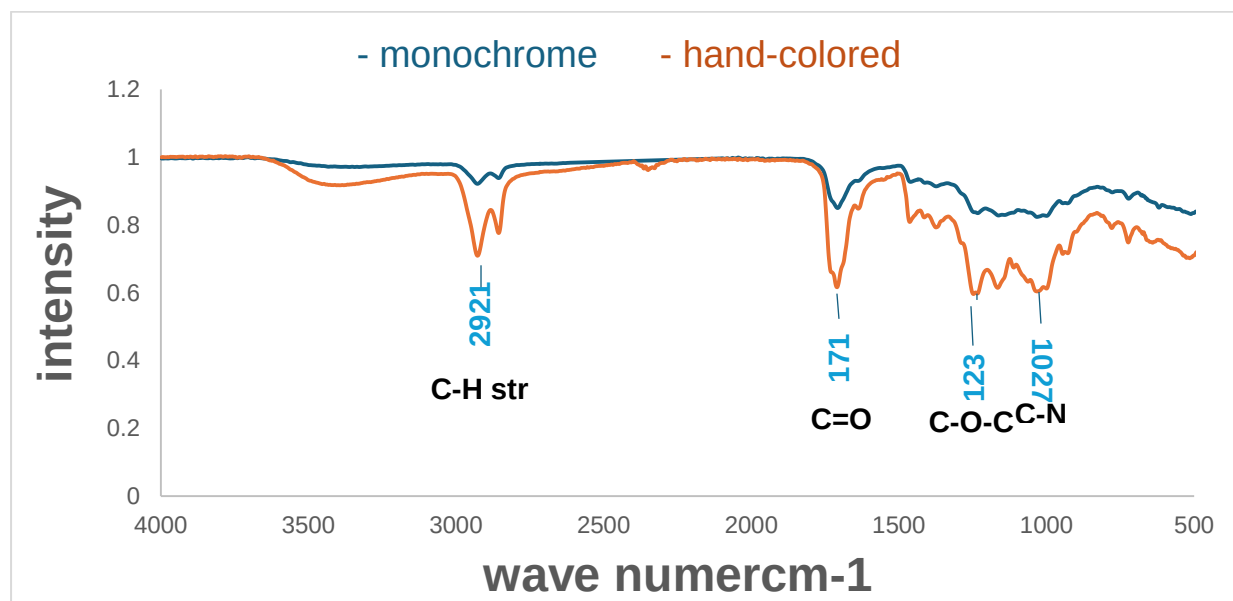
¹⁸ ABDEL-GHANI 2015: 23-37.

¹⁹ PFAFF 2022: 109-125.

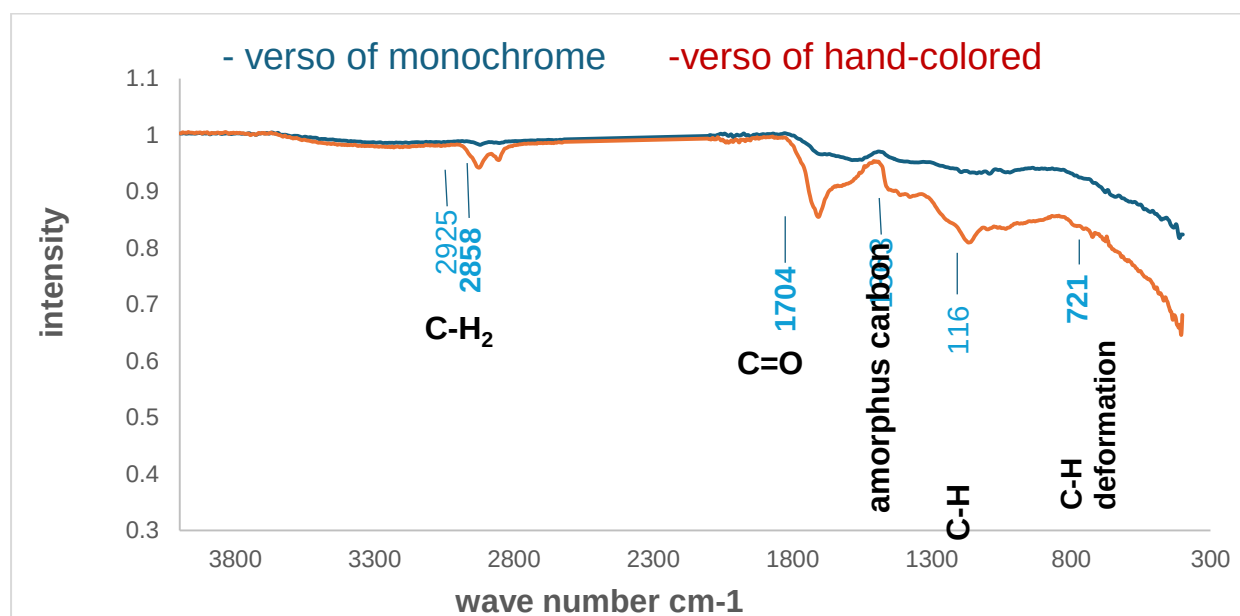
²⁰ SHIN 2023: 122829.

²¹ ZHENG *et Al.* 2023: 583.

aromatic stretching group [FIGURE 9]; however, there is a peak at 723 cm^{-1} which indicates the deformation of C-H stretching group²².



[FIGURE 8]: ATR- FTIR spectrum of the surface of the monochrome tinte and the surface of the hand-colored tinte © Done by the author

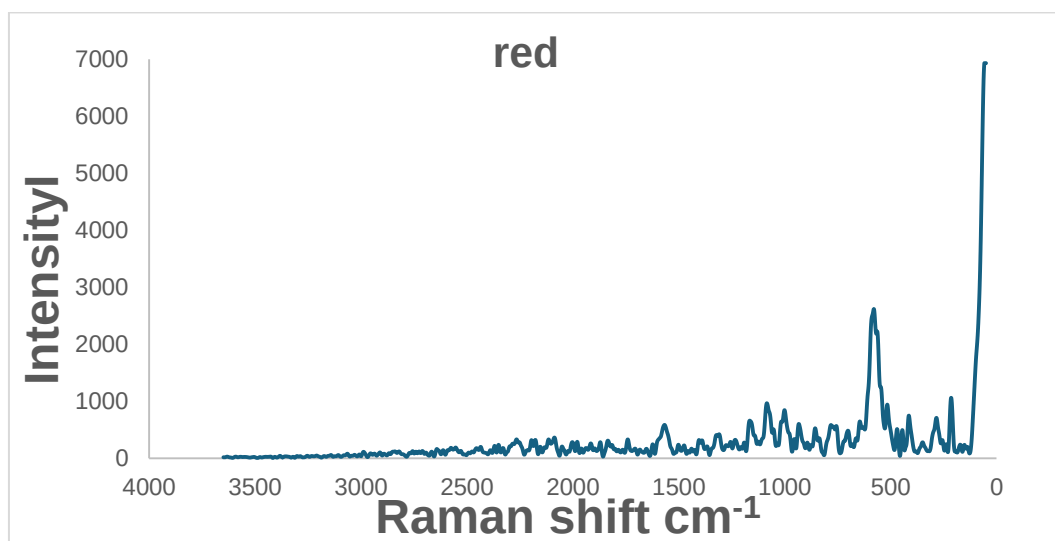


[FIGURE 9]: ATR- FTIR spectrum of the verso of the monochrome tinte and the verso of the hand-colored tinte © Done by the researchers

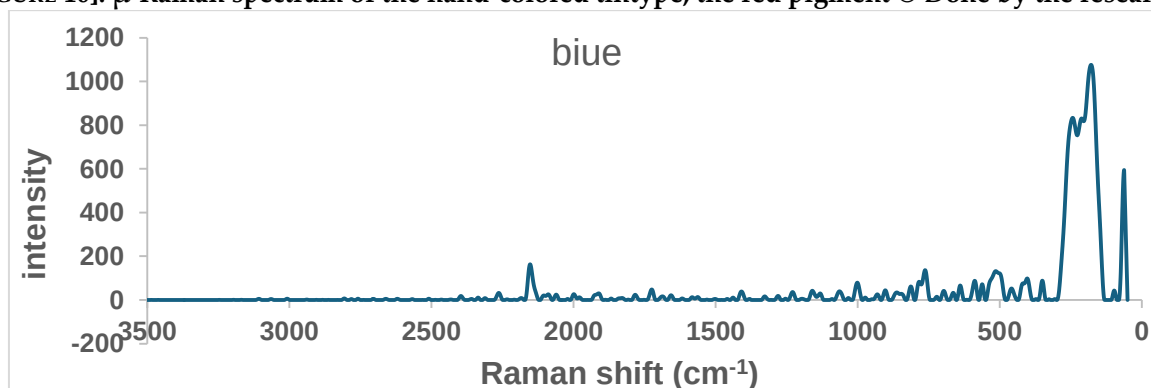
²² SIRINWARANON *et Al.* 2023: 106139.

5. μ -Raman Spectroscopy

Raman analysis was employed to identify the coloring materials applied to the hand-colored tintype photographs. Two areas were analyzed: the red region (cheeks) and the blue region (bow). The spectrum obtained from the red area exhibited six characteristic bands at 1322 cm^{-1} , 579 cm^{-1} , 414 cm^{-1} , 284 cm^{-1} , 214 cm^{-1} and 144 cm^{-1} [FIGURE 10], corresponding to synthetic iron oxide (Fe_2O_3), commonly used as a red pigment²³. The spectrum from the blue area displayed five bands at 2152 cm^{-1} , 1224 cm^{-1} , 520 cm^{-1} , 237 cm^{-1} , 204 cm^{-1} and 175 cm^{-1} [FIGURE 11], characteristic of synthetic Prussian blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$)²⁴. For the monochrome tintype, two analytical points were examined. The first point produced a two-band spectrum at 230 cm^{-1} and 127 cm^{-1} [FIGURE 12], corresponding to silver chloride (AgCl), which typically exhibits peaks near 128 cm^{-1} and 224 cm^{-1} . The second point showed a single band at 110 cm^{-1} , suggesting the possible presence of Ag^3 [FIGURE 13].



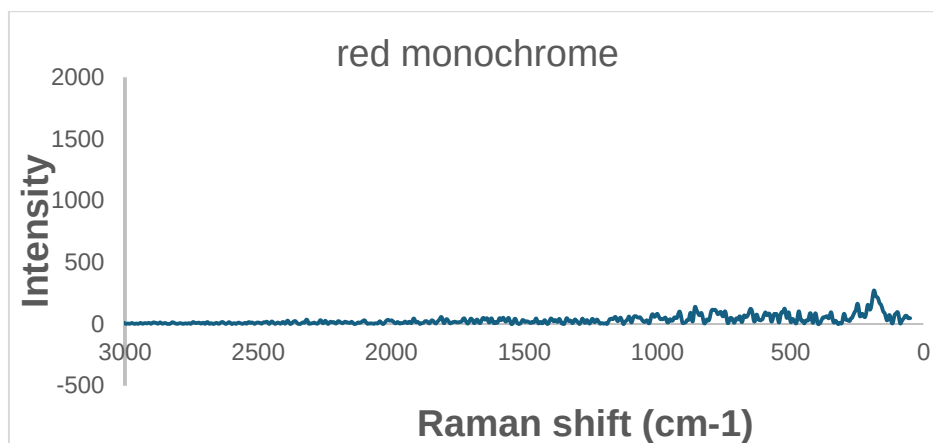
[FIGURE 10]: μ -Raman spectrum of the hand-colored tintype, the red pigment © Done by the researchers



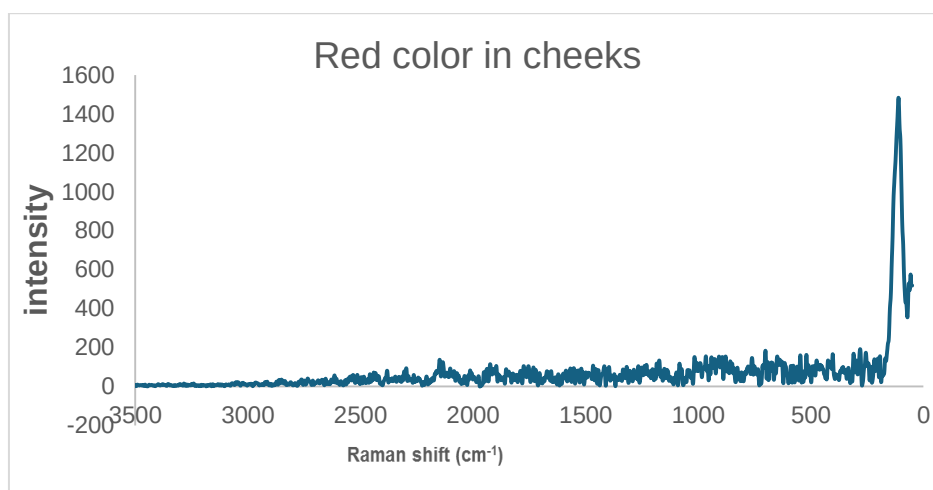
[FIGURE 11]: μ -Raman spectrum of the hand-colored tintype, the blue pigment © Done by the researchers

²³ HOPPE 2010: 1-116

²⁴ MORETTI & GERVAIS 2018: 1198-1204.



[FIGURE 12]: μ -Raman spectrum of the monochrome tintype, the red pigment © Done by the researchers



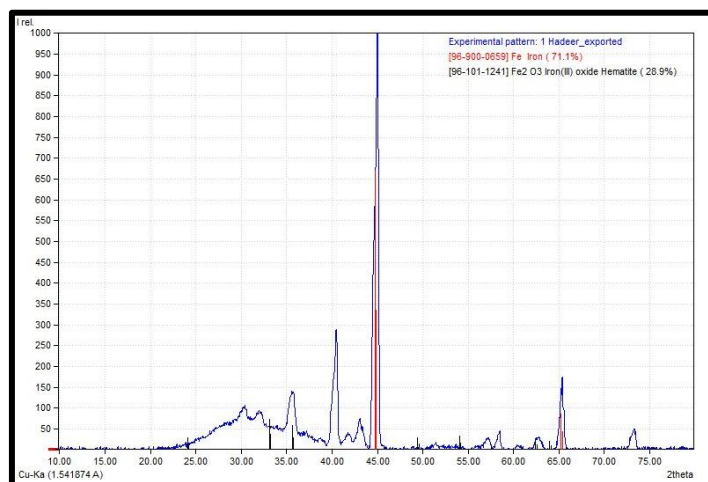
[FIGURE 13]: μ -Raman spectrum of the monochrome tintype for the red color, point 2 © Done by the researchers

6. XRD Analysis

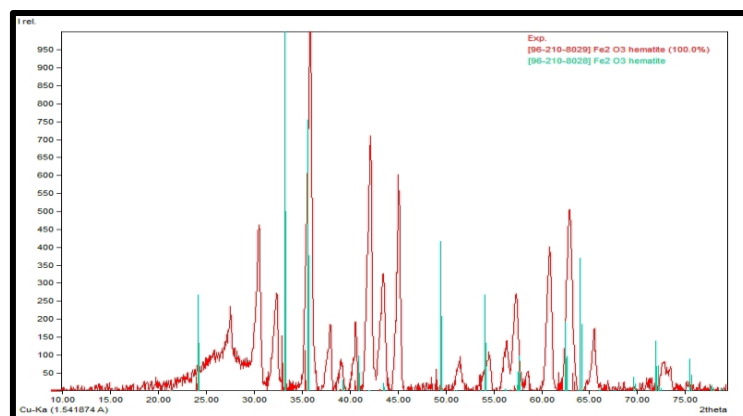
The XRD was the most effective method for identifying the crystalline structure of corrosion products²⁵. Accordingly, this analysis was used to identify the rust compounds formed on the metal support of the tintypes. Two points were selected for this study. Results revealed that iron is the primary constituent of the support, comprising approximately 71%. Hematite (Fe_2O_3) was also, accounting for about 28.9% [FIGURE 14]. Hematite, an iron oxide, is the frequent byproduct of iron corrosion, or rust²⁶. During iron corrosion, in order to create the original complex, the energy needed to transform iron ore into metallic iron is recovered. The XRD analysis of the second point on the hand-colored tintype confirmed that the corrosion product present on the support consisted exclusively of hematite, with a composition of 100% [FIGURE 15].

²⁵ NEFF *et Al.* 2004: 739-745.; MI *et Al.* 2016: 9728-9735.

²⁶ RATNANI *et Al.* 2024: e3003.



[FIGURE 14]: XRD diffractogram for the support of monochrome tintype © Done by the author



[FIGURE 15]: XRD diffractogram for the support of hand-colored tintype © Done by the researchers

IV. THE CONSERVATION OF VINTAGE MONOCHROME AND HAND-COLORED TINTYPES

The conservation procedures were selected based on the tintypes' condition of preservation²⁷. The conservation of the monochrome tintype involved performing the following procedures: mechanical cleaning, minor chemical cleaning, consolidation, compensation for losses and housing. Since the hand-colored tintype was in relatively good condition, conservation treatments were limited to mechanical cleaning with a manual air pump to avoid touching the delicate image surface and housing. A magnifying glass was employed during cleaning to ensure the accuracy of performance.

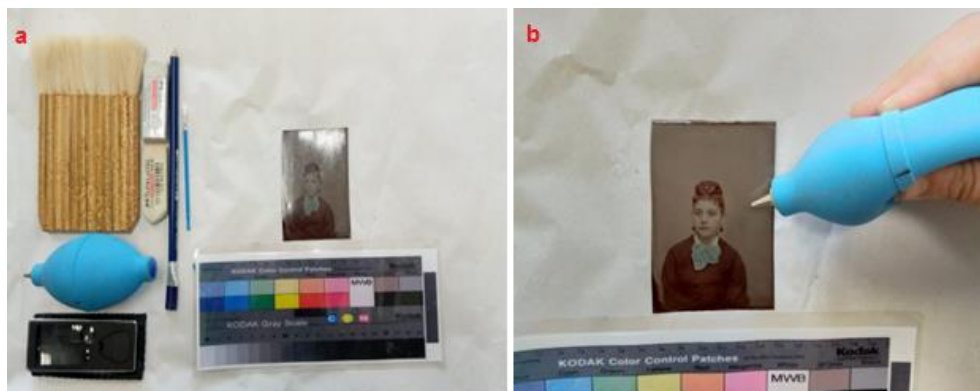
1. Mechanical Cleaning

Cleaning is considered one of most critical steps in the preservation of tintype images²⁸. Cleaning aims to remove dust, dirt and stains which disfigure the contaminated

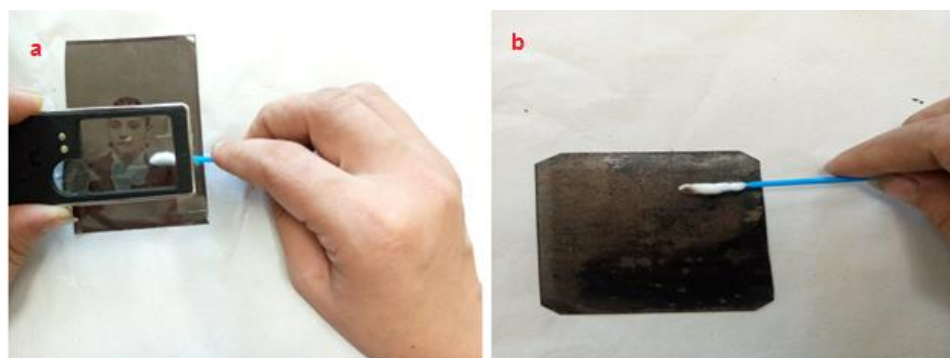
²⁷ LAVÉDRINE 2003: OP.CIT. 32-64

²⁸ KIM 2010: 21-44

artifact; however, it may cause further damage in the future²⁹. Rust represents a major form of degradation that must be carefully removed to prevent the complete loss of the image layer. The surface of the tintypes was cleaned using a gentle brush. [FIGURE 16/A] with the aid of a manual blower [FIGURE 16/B]. In delicate areas, cleaning was performed using a cotton swap under a manual magnifying glass [FIGURE 17/A]. Finally, citric acid at a concentration of 3% was used to remove rust compounds from the metal support [FIGURE 17/B].



[FIGURES 16/A-B]: Mechanical cleaning of the monochrome and hand-colored tintypes. A. The tools used for mechanical cleaning «e.g., fine brushes». B. The use of a manual blower for surface cleaning the hand-colored tintype © Done by the researchers



[FIGURES 17/A-B]: Cleaning of the hand-colored tintype; A. Mechanical cleaning using a cotton swab; B) Rust removal by chemical means using a cotton swab moistened with citric acid at a concentration of 3% © Photo taken by HADEER M. ELDEEB

2. Consolidation and Compensation

The monochrome image exhibited fine cracks and a fragile image layer [FIGURE 18/A]. Consolidation was carried out using Paraloid B-72 diluted in acetone at a concentration of 5% [FIGURE 18/B], applied using a 000 brush. This concentration was found optimal, as³⁰ stated that higher ratios were too viscous to penetrate the cracks effectively, while lower ones were too thin to achieve proper consolidation. The detached parts of the image were

²⁹ JOHANSSON & SOMASUNDARAN 2007: 1-53.

³⁰ BEEMAN 2009: 160-169.

fixed into place using Paraloid B-72 dissolved at a 50% concentration in acetone [FIGURE 18/C], due to its high strength of adhesion, resistance to light and oxidation, clarity and mechanical resistance³¹. Although acetone is the best and most appropriate solvent, paraloid can also be dissolved in alcohol and toluene. It has low toxicity and provides a quick spread that works well with acrylate adhesives³² has noted that exposure to photodegradation causes Paraloid to yellow.

Paraloid B-72 demonstrated exceptional performance in every test, including heat, yellowing, enough working time for this adhesive and great resistance to the effects of various chemical compounds, according to the numerous trials³³. Additionally, paraloid B-72 is a slightly reversible substance that can be broken down in the future with acetone solvent. This is especially crucial when the adhesive deteriorates or when a new substance with improved adhesion qualities is being introduced³⁴. The possibility of using Paraloid as a compensating material was proposed. It was utilized when dissolved in acetone at a 20% concentration. The Paraloid was given a brown glass hue and a microballon [FIGURE 18/D]³⁵.



[FIGURES 18/A-B]: Consolidation of the monochrome tintype and the restoration of losses. A. Detached parts. B. Consolidation of fragile parts. C. Fixing of the detached parts. D. Compensating for losses ©
Done by the researchers

³¹ MOLINA *et Al.* 2023: 99-113.

³² FERRARI 2019: 99-111; RĂDVAN & CORTEA 2016: 330-337.

³³ CENTENARO *et Al.* 2023: 132-143.

³⁴ DAVIDSON & ALDERSON 2009: 53-62.

³⁵ UNRUH & HARBECK 2021: 3-24.

3. Coating the Support with Atmospheric Pressure Plasma jet (APPJ)

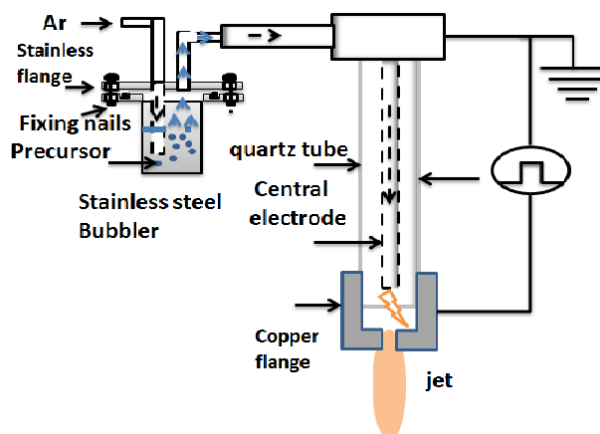
The application of protective coatings is a standard procedure for heritage metal conservation to prevent corrosion³⁶. Such coatings serve as barriers that inhibit interactions between the metal and external agents such as moisture, oxygen and atmospheric pollutants, the primary causes of corrosion. However, the effectiveness of these coatings is often limited in both performance and durability³⁷. In metal heritage preservation, the selection of appropriate coatings is further constrained by several critical factors, including the need to preserve the artifact's aesthetic and historical integrity, ensure reversibility, avoid toxicity, minimize health and environmental hazards and allow ease of application. Consequently, many conventional protective treatments are unsuitable for heritage objects. Atmospheric pressure plasma (APP) presents several advantages over low-pressure plasma systems. It enables surface modification and coating deposition at ambient conditions with greater simplicity and lower toxicity. Due to these advantages, APP was employed to deposit a thin layer of silicon dioxide (SiO₂) on the primary metal support of tintype photographs. This technique is particularly appropriate for tintypes due to their complex structure and sensitivity to heat, which limits the use of conventional heat-dependent coating techniques³⁸. A schematic representation of the specially designed Atmospheric Pressure Plasma Jet (APPJ) system is displayed in [FIGURE 19]. The jet system comprises a central hollow stainless-steel electrode housed within a quartz tube and connected to the power terminal of an adjustable audio-frequency high-voltage power supply «1–20 kHz, 0–5 kV». An external ring electrode, placed 2 cm away from the central electrode and surrounding the quartz tube, is connected to ground. Tetraethyl orthosilicate (TEOS) was used as the precursor and introduced via argon gas through a stainless-steel bubbling chamber. When an enough voltage «breakdown voltage» is applied, a spark discharge is initiated between the central and ring electrodes. The argon gas (99.99%) and TEOS vapor enter the discharge region through the quartz tube, stabilizing the plasma and forming a reactive plasma jet. The decomposition of TEOS in the discharge zone produces reactive radicals that contribute to the formation of the SiO₂ coating. The flow rate of argon was maintained at 2.5 L/min. Before coating, the surface of the metal support was cleaned by sputtering with an argon plasma jet for five minutes to remove surface contaminants. Based on an experimental study in which deposition was tested at various times, it was determined that a seven-minute deposition using an atmospheric pressure plasma jet (APPJ) with Ar/TEOS yielded optimal results. Following the deposition process on the metal support of the photograph «tintype image», infrared analysis (ATR-FTIR) was performed to assess the differences between the sample before and after treatment, as shown in [FIGURE 22]. The results confirmed that after deposition, the Si-O-Si antisymmetric stretching band appeared at 1064 cm⁻¹, At 883 cm⁻¹, the Si-O-Si symmetric

³⁶ ARTESANI *et Al.* 2020: 217.

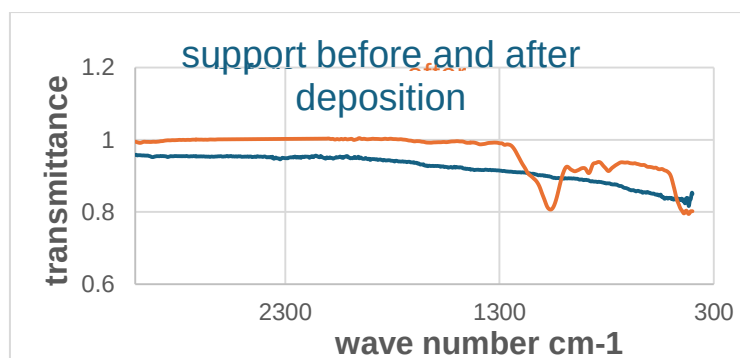
³⁷ ARGYROPOULOS *et Al.* 2007: 166-170.

³⁸ KIM *et Al.* 2003: 839-844.

stretching functional group band and the Si-O-Si rocking vibration were detected at 437 cm^{-1} [FIGURE 21]³⁹.



[FIGURE 19]: A schematic of the atmospheric pressure plasma jet experimentation equipment used for film deposition © Done by the researchers



[FIGURE 20]: FTIR to the samples after deposition by atmospheric pressure plasma jet | Ar | TEOS © Done by the researchers



[FIGURE 21]: Housing of the monochrome and the hand-colored tintypes © Photo taken by HADEER M. ELDEEB

³⁹ YUAN *et Al.* 2016: 870-877.

4. Housing

Dealing with photographs in general, particularly monochrome or hand-colored tintype images, requires exceptional care due to their complex multilayered structure, the inherent sensitivity of their materials and their rarity. Therefore, strict precautionary measures must be followed to ensure their protection and preservation⁴⁰. The hands must be clean and cotton gloves must be worn, as the oils and fats from skin contact can cause irreversible damage. Special attention must be given to the quality of handling and storage materials. All storage components should be acid-free, since acidic environments can promote yellowing and rusting of the metal support⁴¹, particularly in the presence of high relative humidity. Accordingly, it was necessary to prepare proper housing for the photographs to safeguard the tintypes from dust, airborne pollutants and physical damage. Two custom-made boxes were constructed using acid-free cardboard and acid-free compressed foam, which was precisely emptied from the inside to match the dimensions of the studied photographs. A layer of Japanese paper was placed as a separator between the image and the foam. The images were then covered with a sheet of polyester [FIGURE 21].

V.CONCLUSION

Tintype images are unique photographs of great significance. This paper sheds light on the history and technical development of tintypes. Two images were selected for this study, a monochrome tintype and a hand-colored tintype. Several techniques were employed to identify the materials constituting these images and to assess their preservation state, with the aim of establishing an appropriate conservation strategy. Investigation by portable digital microscope and stereomicroscope revealed that the monochrome tintype exhibits fine cracks, scratches, areas of image loss and detachment and rusting of the primary support. The hand-colored tintype also showed the presence of scratches, fine cracks and rust. Scanning electron microscopy confirmed the presence of fissures on the surfaces of both photographs. Elemental analysis using EDS detected carbon which is attributed to the photographic binder «i.e., collodion» and silver, representing the final image material. The red pigment used to color the cheeks was identified as vermilion red as indicated by the presence of sulfur and mercury. EDS analysis also revealed traces of chlorine, likely resulting from inadequate washing or image deterioration and sodium, which may be associated with the use of sodium thiosulfate (hypo) as a fixing agent.

The blue pigment was identified as Prussian blue, while the red pigment has been proven to be iron oxide. FTIR analysis results revealed distinct absorption bands at 1632 cm^{-1} , 1641 cm^{-1} , 1059 cm^{-1} , 1268 cm^{-1} , 1273 cm^{-1} , 824 cm^{-1} and 833 cm^{-1} , which are characteristic of nitrocellulose «i.e., collodion». The recto varnish of both the monochrome

⁴⁰ ROOSA & ROBB 2004: 1-29.

⁴¹ INCH 2013: 283-298.

and hand-colored photographs was identified as a mixture of shellac and mastic, as indicated by the presence of bands at 1710 cm^{-1} and 1463 cm^{-1} . In contrast, the varnish applied to the verso of both images was identified as carbon black.

The Raman analysis results supported the findings of the EDS analysis showing the use of Prussian blue and hematite in the hand-colored image. It also revealed the presence of silver chloride and silver (Ag^3) in the image side of the monochromatic tintype. The XRD analysis of the metal support showed the formation of iron oxide, as the percentage of oxide in the monochrome image reached 71%, while for the hand-colored image, the percentage reached 100%.

Based on the examinations and analysis carried out to evaluate the current condition of the photographs under study, a set of conservation and preservation procedures were implemented. These included mechanical cleaning and limited chemical cleaning, as well as the strengthening and fixing of the detached parts of the image. Following chemical cleaning, the metal support of the monochrome image was coated using an atmospheric pressure plasma jet (APPJ) with Ar/TEOS. The thin film deposited was characterized using ATR-FTIR spectroscopy, which confirmed the presence of the Si–O–Si antisymmetric stretching band at 1064 cm^{-1} , the symmetric stretching band at 883 cm^{-1} and the rocking vibration band at 437 cm^{-1} . Finally, the photographs were housed in enclosures made from materials that conform to standard specifications and are not harmful to the photograph.

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No Potential conflict of interest was reported by the authors

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MULTI-ANALYTICAL METHODOLOGIES FOR THE CHARACTERIZATION AND EVALUATION OF MATERIALS AND TECHNIQUES USED IN MURAL PAINTINGS WITHIN THE ANFUŠĪ TOMBS IN ALEXANDRIA, EGYPT

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ABSTRACT

[EN] al-Anfušī Necropolis, located in the western region of Alexandria adjacent to Ra's al-Tin Palace, is a significant burial site that dates from the late Ptolemaic to the early Roman periods, particularly the first half of the third century. Applying pigment layers onto a smooth white substrate facilitates effortless brush application and enhances the visual harmony and aesthetic appeal of the mural colors. Architectural elements from both Greek and Egyptian origins were employed to develop diverse color palettes for the walls and ceilings. Moreover, five tombs exhibiting identical designs were discovered at the site. The second tomb, adorned with vibrant artworks, was examined with multiple techniques, including optical microscopy (OM), scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX), X-ray diffraction (XRD), portable X-ray fluorescence (XRF) and Fourier transform infrared spectroscopy (FTIR). Analytical techniques revealed the presence of red hematite (red ochre) and yellow goethite in the painting layers, in addition to Egyptian blue, green earth and black charcoal. Additionally, the results indicated the use of an organic medium to bind the color pigments, demonstrating that both fresco and tempera techniques were employed. This study enriches the literature by providing new insights into pigment mixing practices, binder variability and the coexistence of fresco and tempera techniques in the Anfoushi tombs.

KEYWORDS: Egyptian blue, green earth, mural artworks, portable XRF, Ptolemaic period, tempera, FTIR.

[AR] تقنيات تحليلية متنوعة لتشخيص وتقييم المواد والتقنيات المستخدمة في اللوحات الجدارية بجبانة الأنفوشي بالإسكندرية، مصر
جبانة الأنفوشي، تقع في الجانب الغربي من الإسكندرية بالقرب من قصر رأس التين، وهي جبانة مهمة من العصور البطلمية المتأخرة والعصور الرومانية المبكرة، تعود إلى النصف الأول من القرن الثالث الميلادي. تطبيق الأصباغ الملونة على طبقات بيضاء ناعمة يجعل حركه الفرشة سهلة ويجعل الأصباغ مناسبة و مريحة للعين. تم استخدام العناصر المعمارية اليونانية والمصرية لإنشاء مجموعة متنوعة من اللوحات الجدارية لتزين الحوائط والأسقف. يمكن العثور على خمسة قبور بتصميم مشابه في الموقع. تم دراسة عينات القبر الثاني، بزخارفه الملونة باستخدام طرق تحليلية مختلفة، منها الميكروسكوب الضوئي (OM) والميكروسكوب الإلكتروني الماسح المزود بوحده تحليل العناصر EDX وجهاز حيود الأشعة السينية (XRD) والتحليل بجهاز تفلور الأشعة السينية المحمول (pXRF) والتحليل بطيف الأشعة تحت الحمراء (FTIR). أشارت التقنيات التحليلية إلى وجود الهيماتيت الأحمر (المغرة الحمراء) وأصفر الجوثيت داخل طبقات التلوين، إلى جانب الأزرق المصري، والأخضر الأرضي، وأسود الفحم. بالإضافة إلى ذلك، أظهرت النتائج استخدام وسط عضوي لربط الألوان بالجدران والعثور على تقنية التمبرا والفريسك معا.
الكلمات الدالة: الأخضر الأرضي، الأزرق المصري، اسلوب التمبرا، التحليل بطيف الأشعة تحت الحمراء، تفلور الأشعة السينية المحمول، العصر البطلمي، لوحات فنية.

I. INTRODUCTION

This site features five tombs within the western necropolis of Alexandria. They originate from the Ptolemaic period and were unearthed in 1901. The walls of the second tomb are adorned with numerous mural paintings and artworks inspired by ancient Egyptian art. For instance, a mural opposite the staircase depicts the deceased attired as a priest, positioned between Horus, the falcon-headed deity and two pharaohs, likely from the Ptolemaic period. The tomb was subsequently repurposed during the Roman period. The necropolis is hewn from oölite limestone and comprises biological, clayey and sandy deposits that exhibit inadequate cohesion. This renders them exceedingly prone to erosion and more susceptible to seismic effects [FIGURES 1/A- C]¹.

The wall decorations consist of a chessboard-like pattern made up of alternating black, white and red squares, the same pattern found in a Roman tomb in Jordan². This style mimics the use of marble slabs or the covering of walls with stone pieces or colored tiles, imparting a distinctive architectural character without the need for expensive materials. This technique was employed during the Roman period to deceive and create an illusion of depth and space³ [FIGURES 2/A, C & F].

The study focuses on the second tomb due to its ornamental features and various designs. The preservation condition of this tomb surpasses that of the other four, thereby facilitating easier study, unlike the others, where access and examination are more difficult.

The diversity of the mural components is one of their most significant features, suggesting various materials employed. The murals comprise a mixture of natural materials, occasionally combined with additives derived from inconsistent sources⁴. The walls were prepared with rough layers followed by fine layers to improve surface smoothness, providing an ideal substrate for the painting layer⁵. Thus, painting techniques varied according to the artistic and technological requirements of each period.

The conservation of murals in the Anfušī Necropolis is a significant challenge due to the inherently high porosity of the painting layers. This porous interface between the mural substrate and the surrounding environment facilitates the ingress and crystallization of saline solutions, which generate mechanical stress that accelerates material degradation under fluctuating⁶ environmental conditions⁷. Consequently, the structural stability of the mural strata is compromised by multiple deleterious factors, including fluctuating humidity and temperature, rising groundwater levels and the proximity of the site to the Mediterranean Sea coastline. These environmental stressors,

¹ FAHMY *et Al.* 2022:1-34.

² NASSAR & AL MUHEISEN *et Al.* 2024: 69-81.

³ LAURITSEN 2021: 123-140.

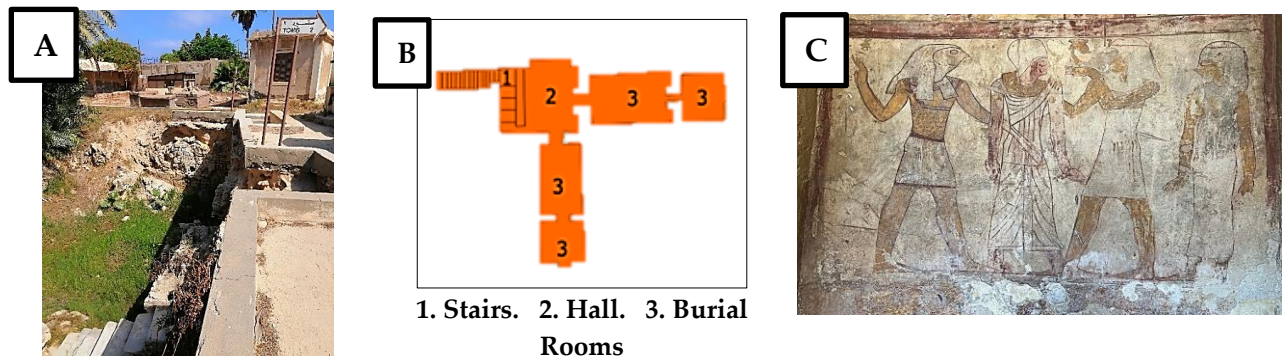
⁴ PACHTA *et Al.* 2020: 21-30.

⁵ PADOVNIK *et Al.* 2016: 993-1007.

⁶ ABD EL SALAM 1999: 449-461; SAVVOPOULOS 2013: 215-243.

⁷ STEFANIDOU & PAVLIDOU 2018: 1-8.

compounded by seasonal weather patterns characterized by wet and cold winters, as well as hot summers exceeding 30°C from June through September, intensify the risk of deterioration. Additionally, limited accessibility to the murals hinders systematic study and conservation efforts, despite the evident vulnerability of these cultural assets⁸. This environment has induced multiple problems, including accumulated salts between layers, resulting in microcracks and detachment of the inner layers [FIGURE 4/A], which in turn causes pigment loss, decreased aesthetic value and diminished ornamental features. Furthermore, the porous structure of the layer constituents allows saline water to easily penetrate the mural layers under various environmental conditions, exacerbating the depletion of the upper layers [FIGURES 2/D-E]⁹.



[FIGURES 1/A-C]: A. Overview of the Necropolis location; pertains to the elevation of the terrain surrounding the tombs, estimated to be approximately 3 meters; B. The design of the second tomb; C. Exemplifying the impact of ancient Egyptian artistry © A & C Photos taken by MOHAMED ABD ELRAHIM; B. FAHMY *et Al.* 2022.

Elevated humidity fosters the proliferation of microorganisms, especially fungi, which diminish the visual appeal of decorations by obscuring painted surfaces.

Furthermore, fungi exert physicochemical effects as they penetrate the pores and undergo continuous development, generating internal pressures and interacting with the layer components. This interaction makes the grain binding weaker, which causes the layers to breakdown¹⁰. Additionally, fungal colonization facilitates the accumulation and adherence of dust to the layers. Additionally, the region's high traffic and seismic activity due to its coastal location, approximately 300 m from the Mediterranean Sea coastline, pose additional risks to the preservation of these decorative surfaces¹¹. The Anfušī Necropolis is threatened by heavy rainfall and flooding¹², exposing it to significant water damage. When the Necropolis was established, artists employed various pigments to decorate the murals. The execution styles varied between sites; the fresco technique was predominant in the Temple of Deir El-Ḥagar and the Ptolemaic Osirian catacombs of Karnak temples and tempera was used in 'Ayn al-Lebeḥa. Despite these technical differences, artists were notably influenced by ancient Egyptian artistic traditions.

⁸ MAHFOUZ *et Al.* 2020: 323-339.

⁹ COMITÉ *et Al.* 2023: 1-15.

¹⁰ SAKR *et Al.* 2013: 1644–1656; BADER & AHMED 2017: 923-944.

¹¹ ELNAGGAR *et Al.* 2024: 1-17.

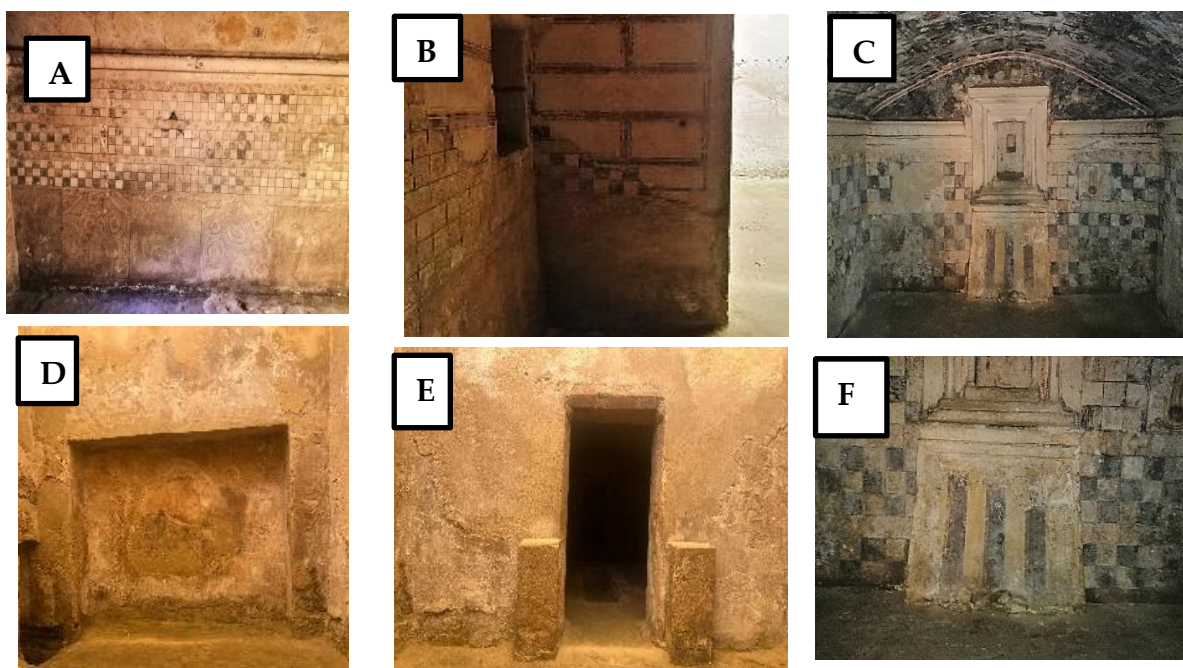
¹² BHATTACHARYA & ZEVENBERGEN 2021: 1-16.

Those artists employed the conventional ancient Egyptian color palette, with a few significant exceptions¹³. Since time immemorial, humans have utilized painting to convey their life, culture, beliefs, religion, tradition¹⁴ and the surrounding environment¹⁵.

The walls and ceilings of the second tomb were embellished with an art of pigments, including red, yellow, green and black. During the Roman period, painters diversified their techniques and materials¹⁶. Greek and Roman artists incorporated new pigments into their palette, including red lead «minium», white lead and cinnabar¹⁷.

A binding medium was essential to bind the pigments. The artist intended to utilize organic binders, particularly for the tempera technique. The predominant binders were animal glue, egg and gum Arabic, which appeared frequently during the Roman period. Gum Arabic was employed in Egypt because of the abundant acacia trees and its high solubility in water, allowing painters to move the brush with greater ease, making it a feature for binding colors¹⁸.

Its phenolic content, capable of inhibiting the growth of specific microbes, was frequently the most notable attribute for its application in pigment fixation¹⁹. It may have facilitated the preservation and resilience of the murals against microbial assaults.



[FIGURES 2/A-F]: Diverse models depicting the internal condition of the tomb; A. A wall adorned with a mural in a chequerboard pattern; B. Over paintings; C. An interior chamber featuring a barrel ceiling adorned with paintings; D & E. The effects of salt on the walls of the hall between the rooms, exhibiting mold formations; F. Degraded portions of the imaging layers © Photos taken by MOHAMED

ABD ELRAHIM

¹³ MAHMOUD & EL-BADRY 2020: 741; KHEDR *et Al.* 2024: 109-119.

¹⁴ HUSSEIN & EWAIS 2025: 104.

¹⁵ FABBRIZZI 2025: 9.

¹⁶ JORGE & EDWARDS 2021: 2190-2203.

¹⁷ SCOTT 2016: 185-202.

¹⁸ SAKR *et Al.* 2021: 1-13.

¹⁹ SAKR *et Al.* 2013: 1644-1656.

Concerning the pigments utilized during this period, the literature on various Egyptian sites, including the 'Ayn al-Lebeḥa Temple in Ḥargā Oasis, indicated the use of hematite red for red coloring and carbon black for black. Meanwhile, the Ptolemaic Osirian catacombs in the Karnak temples revealed yellow ochre, Egyptian blue and red ochre. The research on the Temple of Deir El-Ḥagar in the Daḥla Oasis reported the use of a red color obtained by heating goethite to produce synthetic hematite and Egyptian blue for a specific blue color by mixing it with orpiment.

This study aims to identify the components of Roman mural layers in Alexandria using various analytical methods to discover the causes and manifestations of damage to the painting layers and to identify the methods for applying mural layers.

These measures are essential for the safeguarding and conservation of cultural heritage assets. In comparison to ABD ELSALAM²⁰, this research applies a broader range of analytical techniques, enabling the detection of minor elemental traces, such as copper in non-blue pigments and providing a more nuanced interpretation of green pigments and binders.

II. MATERIALS AND METHODS

1. Sampling

The samples were collected from diverse damaged and fallen parts of the Anfušī Necropolis (AN) without any scratches or damage to the surface of the murals. The samples represented all the layers and contained a layer of plaster mixed with pigments. They were tiny fragments ranging from 4 to 6 mm, with a thickness of 1 to 3 mm. The Necropolis is characterized by the extensive application of illustrations on the ceiling and all walls.

Initial findings indicated the presence of multilayered paintings «overpainting» [FIGURE 2/B] & [FIGURE 3/B] featuring lustrous surface layers, accompanied by extensive salt formation and efflorescence [FIGURE 3/A].



[FIGURES 3/A-B]: Areas for sample collection; A. Fading pigments and salt efflorescence on the surface; B. Broken film layers with a growing fungus in the regions near the ground © Photos taken by MOHAMED ABD ELRAHIM

²⁰ ABD ELSALAM 1999.

2. Methods of Investigation and Analysis

A. Optical Light Microscope «OLM»

This technique was employed to analyze the surface characteristics of mural components²¹, particularly the color, utilizing various magnifications to facilitate the identification of surface issues, such as stains, dirt and cracks, which alter the visual appearance of the colors. The images were captured with a Super Eyes PZ01 500X USB digital microscope.

B. Scanning Electron Microscope «SEM»

Samples were analyzed uncoated, using a variable pressure SEM «FEL Quanta 3D 200i EDX» thermo fisher pathfinder in the Grand Egyptian Museum (GEM), operated under conditions of low vacuum for the acceleration voltage of 20.0 ~ 30.0 kV using a large field detector with working distance 15~17mm α .

C. X-ray Diffraction Analysis «XRD»

X-ray diffraction test utilized RUKER, D2 PHASER 2nd gen. using CuK α radiation at 30KV and 10 mA. Data were collected within the 2 θ range of 5-80° with a step size of 0.02° and 0.2 seconds per step. Then, the analysis was carried out at the Desert Research Center.

D. Portable X-ray Fluorescence «pXRF»

XRF analysis was conducted using a portable Oxford Instrument «X-MET7000». It covered a wide elemental range from chlorine (Cl) to uranium (U), with the SDD models enabling analysis starting from lighter elements, such as potassium (K). The analyzer operated with a 40 kV Rh-anode X-ray tube, exhibiting a count rate of 40 counts per second, approximately four to five times faster, at the Faculty of Science, Cairo University.

E. Fourier Transform Infrared Spectroscopy «FTIR»

The analysis was conducted using a Nicolet 380 FTIR Spectrometer, within the frequency range of 400 cm⁻¹, with a resolution in absorbance mode employing the KBr pellet technique, at the National Institute for Standards (NIS) in Cairo, Egypt. Special attention was given to potential interference from carbonates in FTIR spectra, which may obscure or mimic bands associated with organic binders.

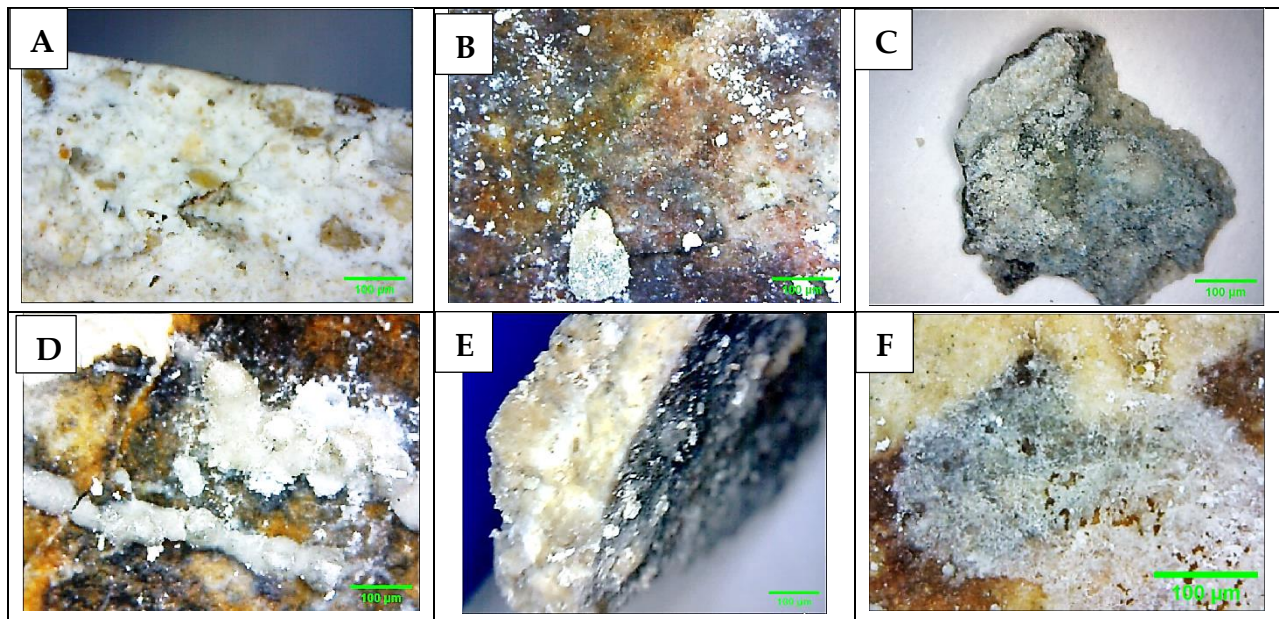
III. RESULTS AND DISCUSSION

A. Results of Optical Examination

A morphological examination was performed utilizing a digital optical microscope to evaluate the characteristics of the painting and mortar samples employed in the murals of the Anfušī Necropolis «tomb 2» [FIGURES 4/A-F]. The results showed surface irregularity and salts penetrating layers and spreading on the surface, as well as cracks caused by salt crystal pressure. Additionally, darkness was noted in various regions of the paint layer, particularly in blue areas [FIGURE 4/C], which was caused by

²¹ ALI & ABD ELRAHIM 2021: 55-65.

excessive humidity, causing the degradation of pigments, particularly blue. This extreme humidity impact was caused because of being close to the sea.



[FIGURES 4/A-F]: Morphological study A. Cracks in lime-based mortar showing calcite and quartz grains; B & C. Fine surface cracks and salt crystallization; D. Discoloration and accumulation of dirt and mold; E. Cross-section layer; F. Thin film of salt efflorescence © Photos taken by MOHAMED ABD ELRAHIM

B. Results of Morphological Investigation

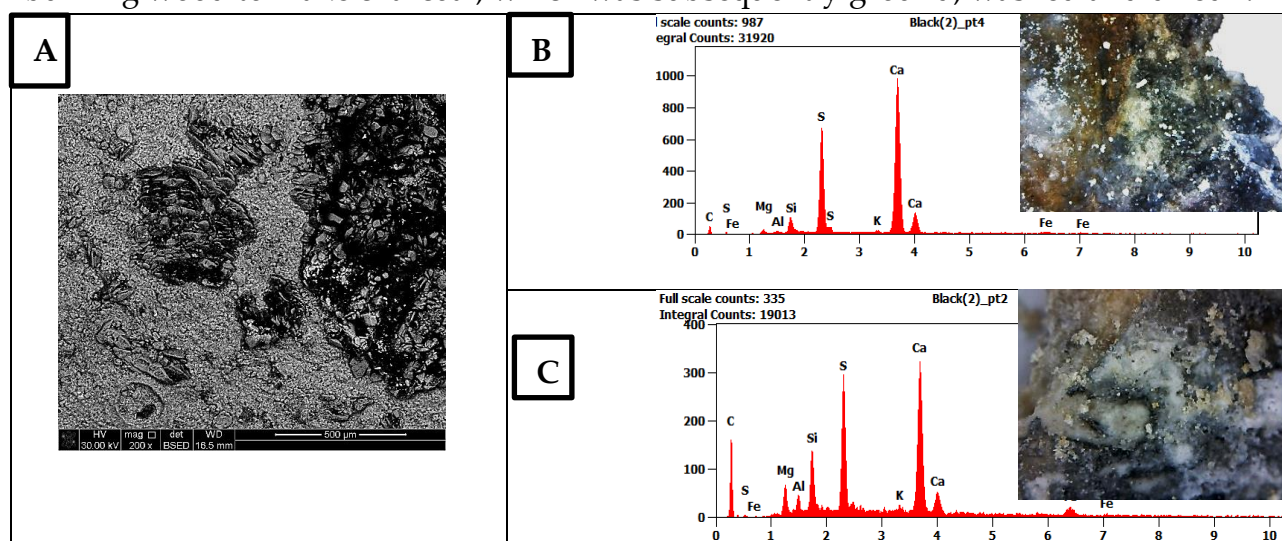
The extreme conditions of these murals have caused significant distortions in the physical shape of the visible grains. Microscopic investigation revealed that this effect extended beyond the external appearance, impacting the internal components of the layers and significantly altering the proportions of the materials of the painting layers.

Microscopic investigation and field studies revealed the presence of insulating layer remnants, which were probably applied in past restoration works between 2014 and 2019 but, were not documented in previous studies. This finding could also explain the low concentrations of the characteristic constituents of the color pigments, as well as the possibility of an unintentional minor overlap of the pigments during the application of the insulation layer.

samples	Elements %										
	C	Na	Mg	Al	Si	S	Cl	K	Ca	Fe	Sr
Black. p	15.04	–	1.53	0.74	3.65	23.48	–	0.55	54.97	–	–
	48.43	–	3.39	1.69	6.13	13.60	–	0.73	22.65	3.29	–
Green. p	27.46	2.61	0.23	0.95	1.79	20.38	5.22	1.53	38.65	1.14	–
	10.32	0.62	0.99	0.93	1.38	36.23	–	0.28	48.90	0.81	–
Red. P	2.60	–	0.40	0.26	–	33.89	–	–	55.96	3.31	3.54
	2.50	–	0.74	0.253	–	33.69	–	–	57.97	2.75	2.06
Yellow. p	18.88	–	0.36	0.62	1.20	26.86	0.88	–	49.82	1.34	–
	30.40	–	0.90	0.75	1.36	26.01	0.93	0.45	37.17	2.03	–

[TABLE 1]: Summary of EDX analysis of pigment and plaster samples © Done by the authors

The SEM examination of the black region used in the study revealed wear, loss of painting areas and a whitewash layer, along with salt deposits [FIGURE 5/A]. The EDX results of the black pigment analysis indicated a high carbon content of up to 48%, along with potassium, magnesium and calcium, which are elements commonly associated with wood and plants due to incomplete combustion. In contrast, soot always appeared with high and pure carbon content in the presence of traces of heavy metals, such as Pb and As, depending on the fuel used. Therefore, the presence of calcium, potassium and magnesium with these carbon levels supported the finding that the black pigment is charcoal and not soot²² [TABLE 1]. The presence of calcium sulfate, magnesium, potassium salts and sodium chloride signified deterioration rather than deliberate additions. These salts ascend to the surface via pores and are frequently observed in the Egyptian environment. The presence of iron suggests the use of yellow goethite alongside the black pigment [FIGURES 8/B-C], which may represent an intentional juxtaposition to enhance visual contrast within the composition. Previous research demonstrated that the deep black pigment was historically produced by burning wood to make charcoal, which was subsequently ground, washed and dried²³.



[FIGURES 5/A-C]: Micrographic examination of black pigment; A. Displaying the areas of the black pigment under examination; B & C. EDX illustrating the scanned surface of the sample © Done by the authors

The SEM study [FIGURE 6/A] illustrated broad cavities, fine cracks and visible degradation within the whitewash layer, resulting from severe damage caused by salts, humidity, sea spray, environmental conditions and vibrations induced by traffic movement and earthquakes, due to the site's proximity to the sea. Additionally, stresses from salt recrystallization between the layers²⁴ motivated deterioration. The EDX analysis of the green sample revealed concentrations of Mg, Al, Na, K and Si, suggesting the use of the green earth pigment in the absence of Cu, thereby excluding Egyptian green. This finding aligns with previous studies confirming the extensive use of green earth during the Ptolemaic period²⁵.

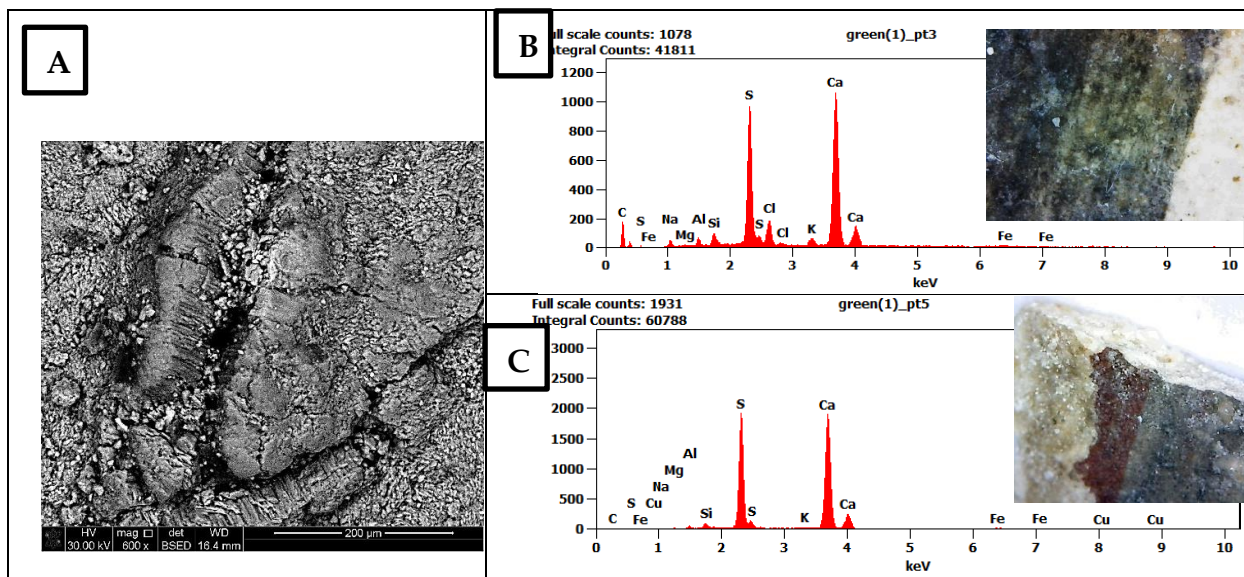
²² SIRACUSANO & MAIER 2012: 28-37; MOHIE & MOUSSA 2022: 799-810; RAMADAN *et Al.* 2022: 85-96.

²³ MAHMOUD & BRANIA 2019: 735-746.

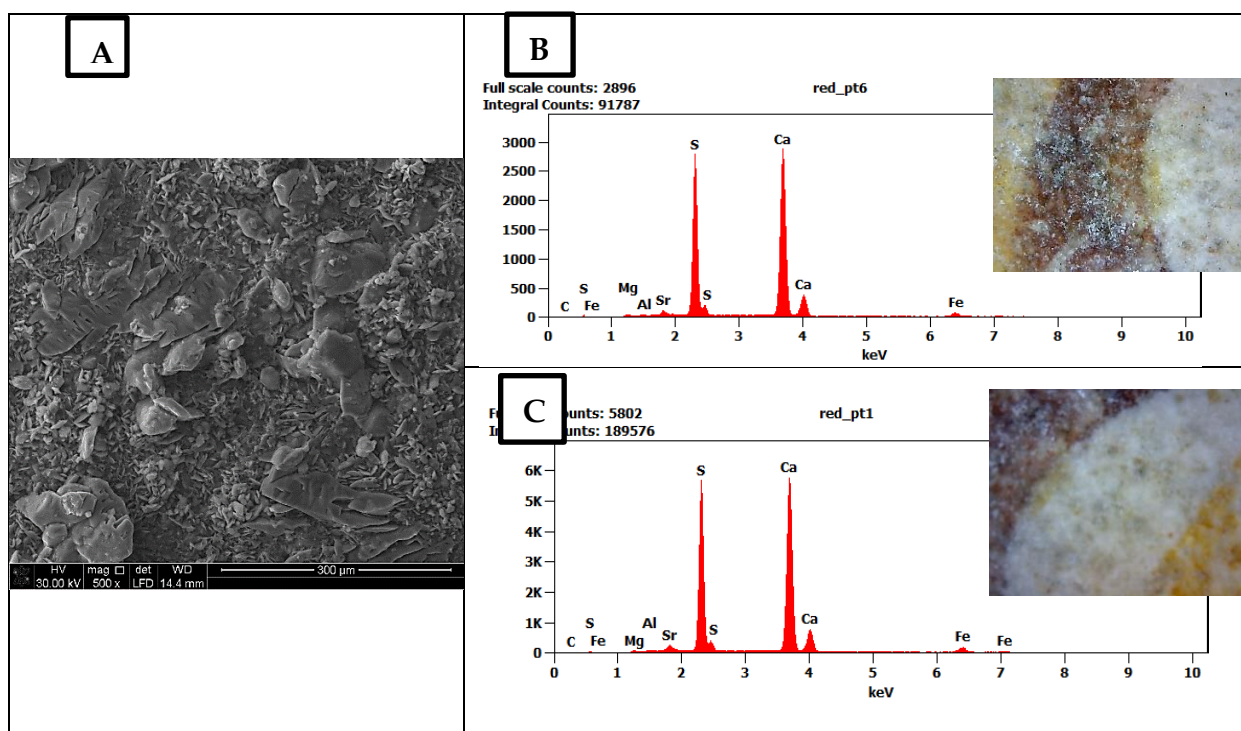
²⁴ EL-GOHARY & ABDEL MONEIM 2021: 261-274

²⁵ MAHMOUD & EL-BADRY 2020: 741.

Celadonite and glauconite are the green pigments; however, their low silicon and iron content, along with the absence of aluminum in the spectrum, confirmed their presence. The lack of copper in the analysis of the green sample precluded the use of Egyptian green and malachite²⁶. Both pigments were primarily composed of copper (Cu). Celadonite and glauconite are two minerals with similar chemical²⁷.



[FIGURES 6/A- C]: Micrographic analysis of the green pigment; A. Cracks and degradation of the green-painting patches; B & C. EDX analysis showing the elemental concentrations in green pigments
© Done by the authors



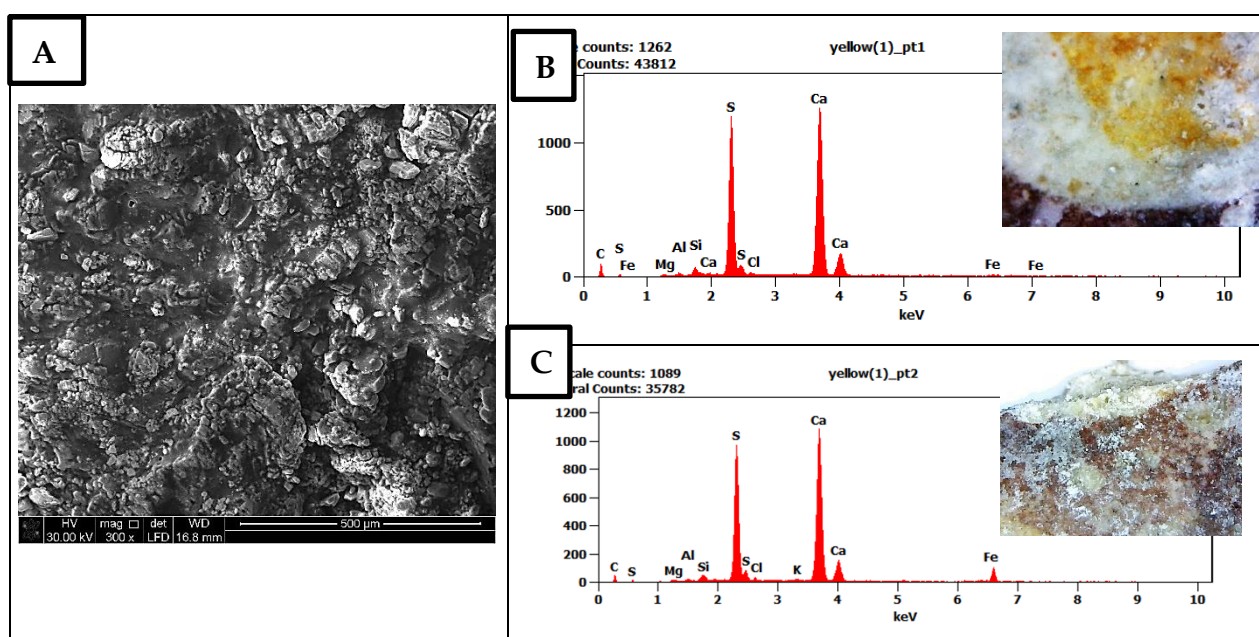
[FIGURES 7/A- C]: Micrographic examination of the red pigment; A. Demonstrating the variability in granule size; B & C. EDX indicating the elemental concentration within the sample © Done by the authors

²⁶ ABD ELSALAM 1999: 449-461.

²⁷ MOHIE, MOUSSA *et Al.* 2022: 799-810; AVLONITOU 2016: 668-678.

The SEM study [FIGURE 7/A] revealed that the accumulation of dirt and its adherence to the surface, together with the visible activity of salt spread, decreased the clarity of the painting layers.

The microanalysis EDX of the red pigment sample [FIGURES 7/B-C] revealed iron «Fe, 3.31%: 2.75%», major concentration expressing the substance of the red pigment hematite (Fe_2O_3)²⁸, as well as calcium «Ca, 55.96%: 57.97%» and sulfur «S, 33.89%: 33.69%». The high concentrations of (Ca) indicated a white layer (whitewash) beneath hematite and confirmed the severe erosion of the pigment due to calcium sulfate and magnesium salts. Additionally, (Al) and (Sr) migrated through the movement of saline solutions via the pores, with (Al) associated with the clay minerals in the bedrock formation, while (Sr) appeared due to its association with normal movement, particularly in carbonate sedimentary rocks and gypsum²⁹.



[FIGURES 8/A-C]: Micrographic analysis of the yellow pigment; A. Surface irregularity; B & C. EDX showing the concentration of elements in the yellow sample © Done by the authors

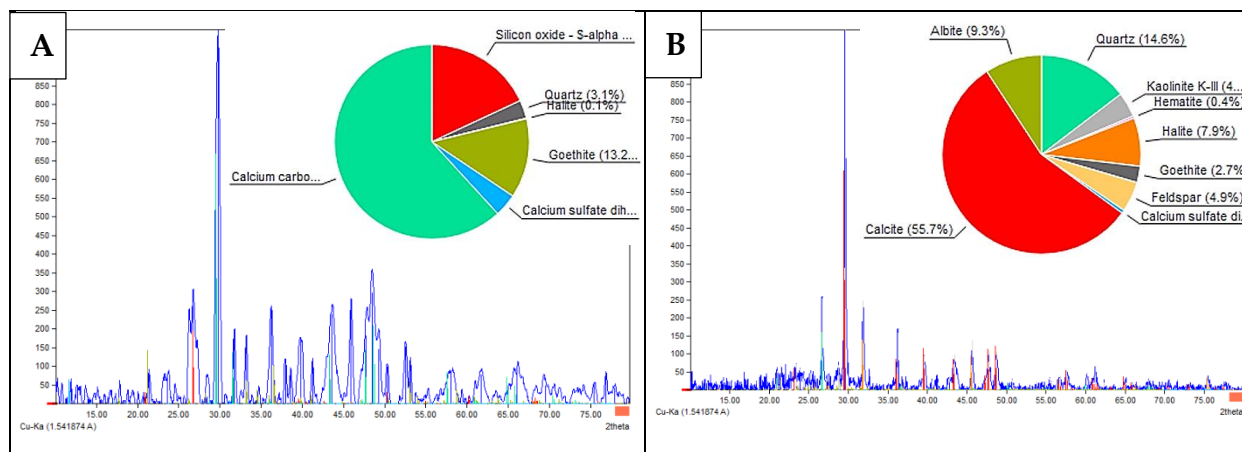
SEM revealed surface irregularities [FIGURE 8/A], exfoliation in several areas of the paint layer and contaminants that altered its appearance. EDX results indicated the presence of iron oxides in the yellow regions, suggesting the existence of iron pigments like goethite ($\text{FeO}(\text{OH})$). The analysis excluded the possibility of yellow ochre due to the low concentrations of silicon (Si) and aluminum (Al), which are characteristic of natural yellow ochre. These results were validated by XRF [TABLE 2]. Furthermore, the flow of saline solutions contributed to increased blending.

The artist probably completed the murals in haste, likely driven by the urgent need to prepare the tomb and perform the burial rituals. This is potentially supported by the presence of multi-layered painting, which may indicate that the death was unexpected and the tomb was later reused.

²⁸ AL-EMAM *et Al.* 2015: 113.

²⁹ FRANCESCHI & LOCARDI 2014: 522-527.

C. X-ray Diffraction Analysis «XRD»



[FIGURES 9/A-B]: X-ray diffraction; A & B. Displaying the components of a lime-based mortar sample
© Done by the authors

Mortar samples (A-B) were collected from different locations in the burial chamber to ensure that the results accurately show the composition of this layer. The mortar «plaster» samples had an average mineralogical composition of 8.85% quartz «SiO₂, ICSD #96-901-2605» and 58.75% calcite «CaCO₃, ICSD #96-101-0929», as shown by XRD. This finding explained the main components of the mortar.

The results of the mineral analysis revealed that calcite constitutes 58.75%, indicating the use of lime as a binder, while quartz accounted for 8.85%, suggesting the incorporation of sand mixed with lime in this layer. This composition aligns with the structure of the preparatory ground layers, which are executed in two phases: the initial phase involving the coarse layer, followed by the fine layer³⁰.

The preparation layers functioned to obscure imperfections in the supports. The study's findings revealed the existence of goethite and clay minerals, which might result from either natural impurity in the mortar during preparation or environmental influences, including the migration of saline solutions and the deterioration of the paint layers. This finding indicated that these samples were not directly coated with pigment layers³¹. The elevated concentration of goethite in the mortar could be attributed to the underlying painting layers applied before this mortar «overpainting», as the tomb was repurposed during the Roman period, with an earlier painting layer originating from the Greek period. The pigments located beneath it likely influenced these percentages due to surface contact, along with the previously mentioned factors. The blue pigment sample included a part of the prepared ground layer, the whitewash layer and a section of the blue color. The results of the blue pigment analysis [FIGURE 10] revealed the presence of the mineral cuprorivaite «CaCuSi₄O₁₀»³², the main component of Egyptian blue³³. It was associated with gypsum, which corresponded to the whitewash layer, as well as with calcite and quartz from the plaster layer and with halite. These elements

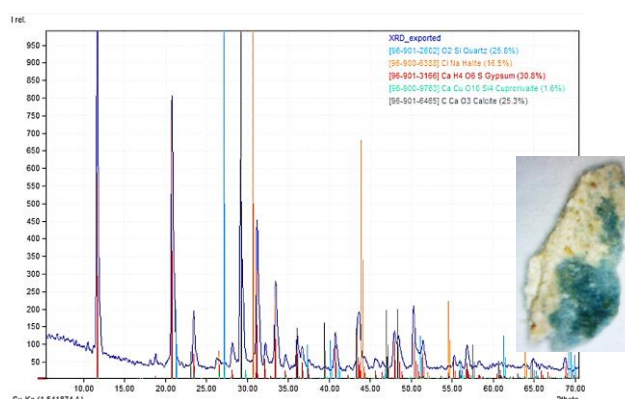
³⁰ RAVA 2012:1-14.

³¹ ORABI 2020: 238-249; MAHMOUD 2022: 249-258; ALI *et Al.* 2023: 47-59.

³² HUSSEIN & EWAIS 2025: 1-11.

³³ AVLONITOU 2016: 668-678.

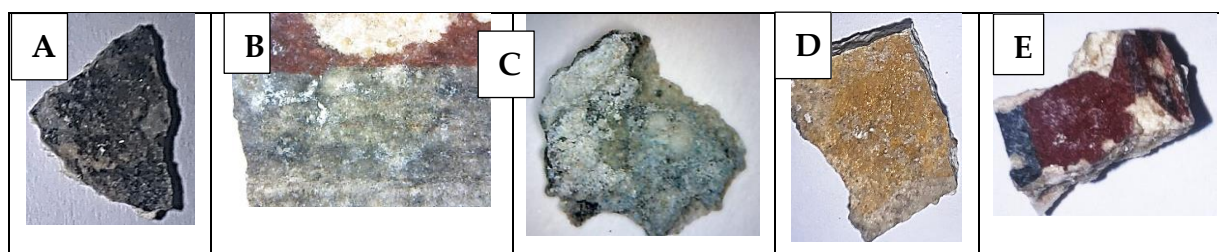
contributed to the damaging effects on the painting layers and were found in high amounts. The presence of halite and calcium sulfate indicated damage levels in the walls. Through the bedrock in which the tomb was excavated, saline solutions began their journey through fine pores, reaching the plaster and other components.



[FIGURES 10]: X-ray diffraction. Sample results: blue pigment
© Done by the authors

D. Portable X-ray Fluorescence Analysis «pXRF»

The investigation was conducted on five distinct painting samples [FIGURES 11/A-E] to ascertain the materials employed in the creation of wall and ceiling decorations and to validate the EDX findings. The outcomes are displayed in [TABLE 2].



[FIGURES 11/A-E]: Samples used in XFR analysis; A. Black pigment; B. Green pigment; C. Blue pigment; D. Yellow pigment; E. Red pigment. The samples range from 2 mm to 6 mm © Photos taken by MOHAMED ABD ELRAHIM

Pigments Samples	Elements that were found	Results
Black. pigment	(Ca 19.57), (Cl 31.94), (Fe 1.27), (S 4.90), (Si 12.19), (Ti 0.31), (Zn 1.76)	Black charcoal
Green. Pigment	(Ca 15.24), (Cl 31.46), (Cu 0.19), (Fe 1.99), (S 4.01), (Si 11.94), (Sr 0.21), (Zn 3.12)	Green earth
Blue. Pigment	(Ca 17.51), (Cl 25.48), (Cu 0.15), (Fe 1.74), (P 1.93), (S 4.87), (Si 13.14), (Sr 0.16), (Zn 2.35)	Egyptian blue
Yellow. Pigment	(Ca 18.59), (Cl 30.32), (Cu 0.10), (Fe 1.60), (P1.41), (S 3.16), (Si 11.78), (Sr 0.20), (Zn 2.28)	Yellow goethite
Red. Pigment	(Ca 16.74), (Cl 24.33), (Cu 0.09), (Fe 1.60), (S 6.74), (Si 15.58), (Zn 2.81)	Hematite

[TABLE 2]: Overview of the pXRF analysis results for the different pigments © Done by the authors

According to the component ratios associated with the pigment, the analytical findings of the black pigment revealed the presence of inorganic elements in the pigment materials. However, they did not indicate the presence of organic materials, as shown in the EDX results³⁴. High proportions of calcium oxide and sulfur were detected, suggesting the existence of calcium sulfate salts in the white layer, as well as high ratios of silica in plaster. Black, which was probably black charcoal, was a result of the elements calcium, iron, sulfur and silica.

The analysis of the black pigment revealed the unexpected presence of traces of titanium (Ti) and zinc (Zn). This could be due to past restoration procedures or environmental deposits.

Green earth was confirmed by the pXRF analysis of the green color [TABLE 2], which contained substantial quantities of calcium, chlorine, sulfur and silica. Iron, as well as other contaminants like Sr and Zn, was identified. Therefore, the material for the green color was suggested to be green earth.

The analysis results indicated Low copper levels. During the Roman period, a small amount of Egyptian blue was usually added to green earth to lighten its dull color³⁵. The presence of these pigments in Egypt during this period, especially in wall paintings, was documented in previous studies, where they were found in Al-Diabat, Sohag³⁶ as well as in some coffins³⁷. Furthermore, deposits of this pigment were widespread in the Western Desert; however, it was not used in the early Pharaonic periods, while its use increased during the Ptolemaic period.

Egyptian blue «CaCuSi₄O₁₀» was identified based on the analytical results, especially XRD. The identification was reinforced by the high concentrations of silica and calcium, as well as the presence of copper³⁸.

Iron, calcium, silica and chlorine were detected in the yellow region during the examination. In addition, the presence of Fe, Ca, Si, S and Cl was confirmed, which supported the identification of FeO(OH) **yellow goethite** based on EDX and XRF.

The results of the red sample indicated that the red-colored areas of the surface contained essential concentrations of iron, silica, calcium, chlorine and sulfur, as well as a minor proportion of impurities, such as copper. After comparing the EDX findings with these data, it was suggested that **hematite** (Fe₂O₃), commonly referred to as red ocher, was used to paint the red areas.

Although the yellow «goethite» and red «hematite» samples contained Cu in extremely low quantities «0.09-0.10wt%», numerous hypotheses could account for this finding. First, small copper traces might be the result of deliberate pigment mixing during production, since Greco-Roman artists sometimes mixed copper-based pigments, such as Egyptian blue or azurite/malachite, with iron oxides to achieve particular tonal variations³⁹.

³⁴ RAMADAN *et Al.* 2022: 85-96.

³⁵ CASTILLO *et Al.* 2024: 2709-2729.

³⁶ MAHMOUD & ABO EL-YAMIN 2021: 31-45.

³⁷ CARTWRIGHT & SVOBODA 2020: 134 :145.

³⁸ MOUSSA, BADAWEY & SABER 2021: 1-15.

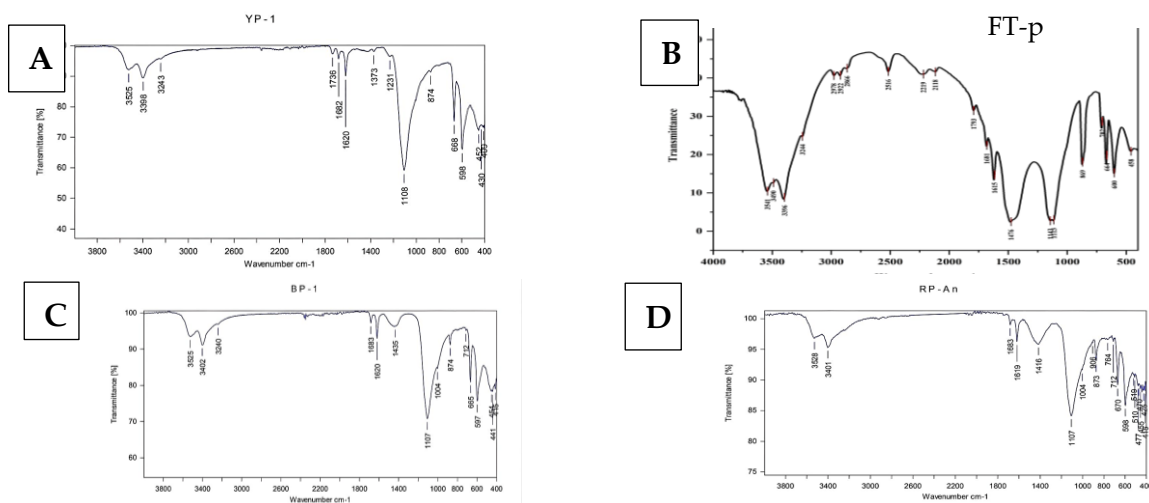
³⁹ ALIATIS *et Al.* 2010: 1537-1542; SIDDALL 2018: 201.

Second, natural iron oxide sources «hematite and goethite» may inherently contain copper-bearing accessory minerals as impurities⁴⁰. Furthermore, the migration of copper from the blue pigment areas to the adjacent red and yellow areas was caused by the application of insulating layers, previous restoration activities, or the influence of groundwater.

E. Fourier Transform Infrared Spectroscopy «FTIR»

An analysis was performed to determine the organic substance employed to bond the pigment grains to the whitewash layer. It also enabled the identification of inorganic compounds found in the samples⁴¹. The investigation included four samples: two from the walls and two from the ceilings. The results were compared to reference samples, revealing an organic binder likely of plant origin, such as gum Arabic or proteins representing animal glue [TABLE 3], which makes distinguishing the medium used a difficult task [FIGURES 12/A-D]. The medium allows the brush to move freely while forming the necessary shapes⁴². Coastal conditions and high humidity have significantly contributed to the deterioration and deformation of the binding material. The identification of the organic medium was challenging. Its presence was confirmed by a sharp, strong band in the region of 1000-650 cm⁻¹ stretching of polysaccharides/phenolic compounds⁴³.

A broad O-H stretching band between 3600–3200 cm⁻¹ was observed, which is characteristic of hydroxyl groups originating from either absorbed water or organic materials, such as polysaccharides and proteins; a C-H stretching band around region in 3000-2800 cm⁻¹; and C-H bending between 1480-1300 cm⁻¹. The band observed at 1476 cm⁻¹, while sometimes associated with gum Arabic, is also characteristic of carbonate groups (CO₃²⁻)⁴⁴.



[FIGURES 12/A-D]: FTIR-ATR spectra for organic binder. A & C ceiling samples; B & D walls samples
© Done by the Authors

⁴⁰ CAPRIOTTI *et Al.* 2022: 1-10.

⁴¹ BADER & RASHEDY 2014: 349-349.

⁴² ABDELAAL 2019: 171-181.

⁴³ SAKR *et Al.* 2021: 1-13.

⁴⁴ DOEHNE 2002: 51-64.

Functional Groups Bands	Samples				Substance
	Sample (A)	Sample (C)	Sample (B)	Sample (D)	
	YP – 1	BP- 1	FT- P	RP- An	
	cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	
OH +NH stretching	3398, 3525, 3243	3525, 3402	3396	3401, 3528	Organic media, Gypsum
CH stretching	—	—	2866	—	Organic media
S-O stretching C=O (Amide I)	1620, 1628	1620	1615	1619, 1683	Organic media, Gypsum
C-H bending	1372, 1231	1435	1476	1416	Organic media, carbonate
C-O Stretching	1108	1107, 1004	1143	1107	Organic media, Gypsum

[TABLE 3]: The main functional groups of the color layer and plaster samples © Done by the authors

The samples «FT-P, RP-An» represented a model of the coloring layers applied to the walls. Lime was also visible in 1473 cm⁻¹, with a weak presence of gypsum. Therefore, it could be said that the applied painting layer adopted the fresco technique. On the other hand, the results showed that an organic medium was present in the samples «BP-1, YP-1» taken from the ceilings. The whitewash layer was applied using the tempera method and gypsum was visible between 1107 and 1143 cm⁻¹, with a weak presence of lime⁴⁵.

The high humidity caused the medium to deteriorate, which affected the C–H stretching bands. This finding does not negate the existence of the organic medium, as a broad band of O–H could be observed at 3398 cm⁻¹, as well as weak carbonyl/unsaturated bands at approximately 1600–1720 cm⁻¹ (C=O), which indicated the presence of the organic material.

IV. DISCUSSION

Calcite, silica, certain clay minerals and traces of gypsum were all found in considerable amounts in the mortar samples, according to XRD analysis. This is explained by a lime chemical change, which can happen in situations of extreme damage⁴⁶.

Due to the widespread use of ovens, the Romans were better at using lime in their constructions than the ancient Egyptians. In addition, the presence of gypsum may suggest the presence of calcium sulfate salts that are frequently encountered in the Egyptian environment⁴⁷.

The results of EDX, XRF and XRD revealed the employment of the fresco technique, particularly on the walls. This method primarily entails the application of pigments to fresh lime, which cannot be recognized through microscopic examination due to severe damage and high humidity conditions.

⁴⁵ ALI, EL-SHAFFEY & MAHMOUD 2021: 33-47; ALI, MOUSSA & EL-SAYED 2022: 1-16; MAHMOUD *et Al.* 2023: 223-232.

⁴⁶ HARRELL 2017: 536-545.

⁴⁷ MAHMOUD 2014: 18.

The study also revealed the use of the tempera technique on ceilings, as evidenced by FTIR analyses that detected an organic medium used to bind pigments to surfaces.

Although identifying the exact material was challenging, it was narrowed down to either gum Arabic or animal glue. This technique was common in ancient Egypt but, became less widespread during the Roman period. Whereas fresco is applied to fresh lime and depends on the interaction with the lime layers to create the connection, tempera is based on applying colors to dried surfaces. This finding aligns with the findings of ABD ELSALAM⁴⁸.

Other analyses, such as micro-FTIR, Raman spectroscopy and GC-MS, confirmed the nature of the binders and distinguished between proteinaceous and polysaccharide-based materials.

Egyptian blue, red ochre, yellow goethite, green earth and charcoal black were all identified as color pigments. The use of the blue color was widespread during the ancient Egyptian period and persisted into later eras. It was the first synthetic pigment successfully manufactured by the Egyptians and its color purity was influenced by the proportions of the materials used in its formulation. It was observed at several sites from the same period, including Deir El- Ħagar in the Daħla Oasis.

The black pigment analysis showed the presence of charcoal black, which was used during the same period, especially in Deir El-Ħagar in the Daħla Oasis.

The results of the green pigment showed that al-Diabāt, Sohag, had green earth, one of the pigments frequently used during the Roman period⁴⁹. This pigment was particularly found in shrouds and coffins; however, there is no documented evidence of its use in murals from the ancient Pharaonic periods, despite its ready availability in the Western Desert⁵⁰. While ABD ELSALAM identified malachite as the primary green pigment, our results indicated green earth «celadonite/glaucosite». Furthermore, this study documented the coexistence of fresco and tempera techniques, which were not recognized in the earlier work. Micro-analytical mapping, such as SEM-EDX elemental mapping and Raman spectroscopy, would be valuable for determining whether copper is present as a pigment component, contamination, or due to elemental migration.

The results of the yellow pigment confirmed the presence of goethite, as evidenced by ABD ELSALAM of the Anfušī tombs. The use of pigment was further validated at various sites, including the Ptolemaic Osirian catacombs of the Karnak temples. The red pigment was confirmed as red ochre «hematite», as evidenced by EDX and XRF. Expanding the comparative framework to include a greater variety of Graeco-Roman sites in Egypt and the Mediterranean would enhance our understanding of pigment trade, workshop practices and technological adaptation.

⁴⁸ ABD ELSALAM 1999.

⁴⁹ For more information about the colors in this period, see: ELANTABLY 2026: 103.

⁵⁰ MAHMOUD & ABO EL-YAMIN 2021: 31-45.

V.CONCLUSION

The Roman murals in Alexandria's Anfušī tombs «the second tomb» were created using lime mortar containing impurities from clay minerals and burnt bricks. To decorate the ceilings, a thin and smooth coating of gypsum was applied first, while the walls were executed using the fresco technique, followed by a paint layer. Most of the patterns consisted of geometric forms resembling a checkerboard. The pigments identified included black charcoal, green earth, yellow goethite and hematite «red ochre», as confirmed by EDX, XRF and Egyptian blue was validated by XRD analyses.

According to the FTIR spectra, either gum Arabic or animal glue was used as a binding medium for the pigments, providing a flexible texture to the surface. These murals were affected by various degradation mechanisms, including high humidity in different forms and salt crystallization between the layers and within the fine pores, as evidenced by OLM and SEM results. Additionally, microbial degradation occurred due to the favorable environmental conditions. All these factors compromised the murals both aesthetically and physicochemically, resulting in microfractures across all layers, loss of binding capacity, exfoliation of the paint layer and hydrolysis of the organic medium.

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EVALUATION OF SOME NANO-COMPOSITES FOR THE PROTECTION OF WATER-IMMERSED MARBLE SCULPTURES IN THE FOUNTAIN OF MUHAMMAD ALI PALACE, SHUBRA

BY

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ABSTRACT

[EN] The marble sculptures of the fountain at Muhammad Ali palace in Shubra suffer from extensive deterioration due to continuous exposure to humid conditions, soluble salts and climatic factors. This study aims to investigate the composition of the original marble, identify its deterioration mechanisms and evaluate the effectiveness of selected nanocomposites in strengthening and protecting it. A series of analytical techniques was employed on detached archaeological fragments, including Scanning Electron Microscopy (SEM), Polarized Light Microscopy (PLM), X-ray Diffraction (XRD), X-ray Fluorescence (XRF) and Raman spectroscopy. In parallel, experimental marble cubes were prepared to simulate the original stone and subjected to artificial aging according to the European standard EN 14066:2003, involving sodium chloride crystallization and thermal cycling to reproduce realistic weathering conditions. Two nanocomposite treatments were tested: «Regalrez 1126 polymer combined with nano-calcium hydroxide» and «Primal™ CM 330 polymer combined with nano-calcium hydroxide». Their performance was assessed through a set of physical and mechanical tests, including bulk density, porosity, water absorption (ASTM C97) and compressive strength (ASTM C170), in addition to water contact angle and colorimetric measurements using the CIE Lab* system. The results demonstrated that the nanocomposite «Primal™ CM 330/nano-calcium hydroxide» provided relatively higher efficiency in enhancing the mechanical properties, reducing water absorption and improving resistance to environmental stress, while maintaining acceptable chromatic stability. Quantitative results showed that the Primal™ CM 330 composite reduced water absorption by over 11% compared to the untreated aged stone and maintained 95% of its post-treatment compressive strength after salt aging (184.7 kg/cm²), significantly outperforming the Regalrez-based treatment. Furthermore, it induced minimal color change ($\Delta E < 2.7$ under all conditions), ensuring visual compatibility. These findings highlight the potential of nanotechnology-based treatments in the conservation of historic marble, with a recommendation for further optimization of polymer–nanoparticle ratios to achieve improved hydrophobicity and long-term durability.

KEYWORDS: Consolidation, Muhammad Ali palace, nano-calcium hydroxide, protection, raman spectroscopy, SEM, water-immersed marble.

[AR]

تقييم بعض المتراكبات النانوية لحماية التماثيل الرخامية المغمورة بالمياه في نافورة قصر محمد علي بشبرا

تتعرض المنحوتات الرخامية في نافورة (فسقية) قصر محمد علي بشبرا من مظاهر تلف متراكمة نتيجة التعرض المستمر للبيئة الرطبة وما يصاحبها من أملاح وعوامل مناخية. يهدف هذا البحث إلى دراسة تركيب الرخام الأصلي، وتحديد آليات تدهوره، ثم تقييم فاعلية بعض المتراكبات النانوية في تحسين خصائصه وحمايته. وقد اعتمدت الدراسة على مجموعة من وسائل الفحص والتحليل شملت: الميكروسكوب الإلكتروني الماسح (SEM)، الميكروسكوب المستقطب (PLM)، حيود الأشعة السينية (XRD)، تفلور الأشعة السينية (XRF)، والتحليل الطيفي بالرامان، وذلك على عينات أثرية متساقطة من النافورة. كما أُعدت نماذج تجريبية من مكعبات رخامية ماثلة، خضعت لتقادم اصطناعي وفق المواصفة الأوروبية EN 14066:2003 باستخدام أملاح كلوريد الصوديوم والدورات الحرارية، بهدف محاكاة ظروف التلف الفعلية. جُربت معالجات باستخدام متراكبات نانوية: «Regalrez 1126 بوليمر + نانو هيدروكسيد الكالسيوم» و«Primal™ CM 330 بوليمر + نانو هيدروكسيد الكالسيوم». وقيمت النتائج

من خلال اختبارات فيزيائية وميكانيكية تضمنت الكثافة، المسامية، امتصاص الماء (ASTM C97)، ومقاومة الضغط (ASTM C170)، إضافة إلى قياسات زاوية اتصال الماء والتغير اللوني وفق نظام CIE Lab*. أظهرت النتائج أن المتراكب النانوي «Primal™ CM 330/نانو هيدروكسيد الكالسيوم» حقق كفاءة أعلى نسبياً في تحسين الخصائص الميكانيكية وخفض قابلية امتصاص الماء وزيادة مقاومة العوامل البيئية، مع المحافظة على استقرار لوني مقبول. وأظهرت النتائج الكمية أن المتراكب النانوي «Primal™ CM 330/نانو هيدروكسيد الكالسيوم» قلل من امتصاص الماء بنسبة تزيد عن 11% مقارنة بالحجر الأثري غير المعالج والمُقادِم، وحافظ على 95% من قوة ضغطه بعد المعالجة والتقادِم الملحي (184.7 kg/cm^2)، متفوقاً بشكل كبير على المعالجة القائمة على Regalrez 1126. علاوة على ذلك، فقد أحدث حداً أدنى من التغير اللوني ($\Delta E < 2.7$) في جميع الظروف، مما يضمن توافقاً بصرياً مقبولاً. وتؤكد هذه النتائج أهمية تطبيق تقنيات النانوتكنولوجيا في مجال صيانة التراث الرخامي، مع التوصية بمزيد من الدراسات المستقبلية لتحسين نسب المكونات للوصول إلى خواص طاردة للماء أكثر فاعلية.

الكلمات الدالة: التدعيم، الحماية، الرخام المغمور في الماء، قصر محمد علي، المجهر الإلكتروني الماسح، مطياف الرامان، نانو هيدروكسيد الكالسيوم.

I. INTRODUCTION

The construction of Muhammad Ali palace in Shubra began in 1808 AD and continued until 1821 AD. Its vast area allowed for the adoption of the Turkish architectural style¹. It became known as the «fountain palace»². In 1812 AD, Muhammad Ali established several waterwheels to provide water for the palace and for the fountain, which is the focus of this study. The humid environment has led to severe deterioration of the marble elements of the fountain, leading to the collapse of the bonds between their outer layers. This resulted in successive flaking of surface layers, causing distortion and the loss of delicate carvings and in some cases threatening the stability of the architectural units themselves³. The deterioration caused by soluble salts, such as halite (NaCl) is a primary threat to porous marble. The damage mechanism involves the crystallization pressure (P_c) exerted by growing salt crystals inside the stone's pores. This internal tensile stress leads to the formation of micro-cracks and subsequent granular disintegration and surface flaking, necessitating consolidation strategies that enhance the stone's resistance to these expansive forces⁴. Continuous exposure of these sculptures to water has also caused phase transformations in the main compounds of marble and the formation of secondary products such as iron oxides, calcium bicarbonate and others⁵. Moisture weathering has contributed to the delamination of marble layers, a significant reduction in density and the weakening of the stone's internal structure⁶. The impact of weathering cannot be underestimated, given the extensive damage and losses it inflicts on archaeological and historical structures⁷. Reused monuments are particularly vulnerable to collapse and severe deterioration, especially those located near coastal zones or in contact with water sources.

In Egypt, many sites face additional risks from heavy rainstorms linked to climate change, which recur over decades and exacerbate the impact of deterioration⁸.

Conservation efforts often resort to chemical cleaning methods, which rely on chemical reactions between surface deposits and cleaning agents. These reactions break

¹ GHANAM 2013: 979.

² HAMADAT 2006: 5-6.

³ HAWASS 2005: 14.

⁴ MOUSSA 2019: 7-20.

⁵ STEIGERET *et Al.* 2014: 274.

⁶ ABD EL HAFEZ *et Al.* 2023: 482.

⁷ ABDEL RASHEED 2023: 278 – 303.

⁸ FRANK-KAMENETSKAYA 2009: 17-22; ALBAZ 2023: 71-89.

the primary bonds of foreign materials adhering to marble surfaces. Cleaning agents may be applied with water, alcohol, cotton compresses, shredded paper, or clay poultices. In addition, carriers such as carboxymethyl cellulose are sometimes used to deliver chemicals for the removal of grease, soot and other deposits⁹. Recently, nano-composites have been applied for the consolidation and protection of marble elements immersed in fountain water¹⁰. Nano-composites can produce hydrophobic and self-cleaning surfaces¹¹. Certain nanomaterials, such as nano-TiO₂, also help stabilize thermal expansion coefficients¹².

Moreover, nano-materials have been proposed as effective consolidants and protective agents against harmful radiation, microbiological attack and air pollutants¹³. For example, nano calcium hydroxide increases the surface area of active compounds, thereby enhancing the mechanical and physical properties of treated marble¹⁴.

Nano-calcium hydroxide (nano-Ca OH)₂) is a key consolidant for calcareous stones, functioning through re-carbonation. Its high surface area and nano-scale size facilitate deep penetration into the pores, reacting with atmospheric CO₂ to form stable calcite (CaCO₃). This neo-formed calcite effectively reinforces the granular structure and restores cohesion, while avoiding the problematic surface crusting associated. Polymer selection balances stability and visual impact. Acrylic resins (Primal™) offer high flexibility and visual compatibility due to their refractive index matching that of calcite but, hydrocarbon resins (Regalrez) provide superior photochemical stability and resistance to yellowing upon UV exposure. The selection is a trade-off between the acrylic's flexibility and neutral appearance versus the hydrocarbon's long-term chemical inertness. Studies further indicate that when nanoparticles are dispersed on marble surfaces, they impart beneficial properties including improved surface energy, solubility, plasticity, hardness, melting point and reactivity compared to traditional materials¹⁵. Nanoparticles also exhibit high penetration, spreading and coating efficiency¹⁶. However, if their concentration in the solution exceeds 10%, the protective layer may become heterogeneous, fragile, porous, prone to flaking and accompanied by undesirable color changes¹⁷.

Due to their high surface reactivity, nano calcium hydroxide particles interact effectively with marble elements of the fountain and watercourse under study. Their extremely small size allows them to remain in suspension and deposit homogeneously on marble surfaces, which is the desired effect¹⁸. Previous studies, such as those conducted on the Acropolis in Athens, confirmed the suitability of spraying techniques for applying nano-protective materials. Evaluations included color change measurements and water contact angle tests, which indicated enhanced hydrophobicity of treated marble surfaces.

⁹ RUSU 2017: 5.

¹⁰ ABD EL-TAWAB 2012: 175- 177.

¹¹ SANJEEV *et Al.* 2020: 1-5.

¹² HARIFI & MONTAZER 2024: 1-2.

¹³ YAKYMECHKO *et Al.* 2020: 1; ILIES 2024: 1-5.

¹⁴ POUDYAL *et Al.* 2021: 1-3; GHERARDI & MARAVELAKI 2022: 20; KHALLAF 2023: 5.

¹⁵ GUO *et Al.* 2014: 1-6; MEGAHED & AGWA 2018: 398; SALAMA *et Al.* 2019: 35 -40.

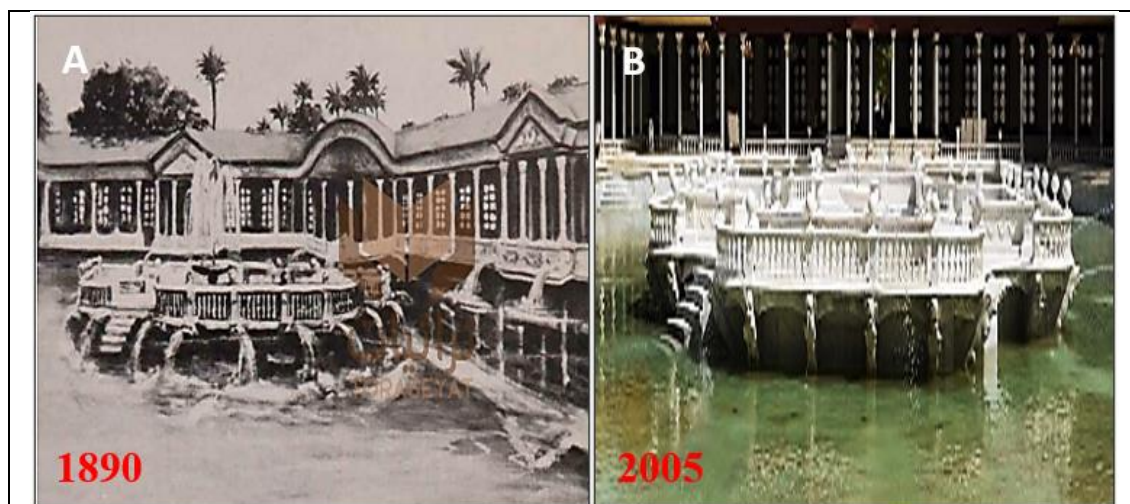
¹⁶ PAGLIOLICO *et Al.* 2016: 267 -276; GHERARDI *et Al.* 2018: 11-32.

¹⁷ MANOUDIS *et Al.* 2009: 1322 –1328; XIE *et Al.* 2017: 9037- 4409.

¹⁸ BJÖRNSTRÖM *et Al.* 2004: 1-3.

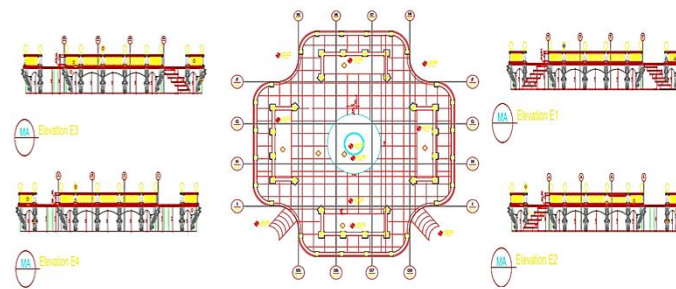
Similarly, experimental applications carried out on historic marble blocks from *al-fasqīyya* «fountain»—removed and replaced due to their poor condition—demonstrated that spraying provided superior performance compared to brush application¹⁹. This study hypothesizes that the Primal™ CM 330 composite will demonstrate superior penetration, stability under hygro-thermal stress and visual compatibility compared to the Regalrez 1126 composite when used to consolidate water-weakened marble. At present, the marble sculptures of the fountain in Muhammad Ali palace suffer from severe deterioration, particularly due to their continuous immersion in water and exposure to a humid environment. To provide visual context for the conservation challenge, the overall layout and scale of the Muhammad Ali palace fountain are illustrated in [FIGURES 1-3], along with the fountain projection. Building upon the identified knowledge gaps and the study hypothesis, this research aims to achieve the following specific objectives:

- **Characterization:** To determine the precise mineralogical and chemical composition of the archaeological marble from the Muhammad Ali palace fountain using advanced analytical techniques «XRD, XRF, Raman, PLM and SEM».
- **Deterioration Mechanism:** To identify and confirm the primary microstructural deterioration mechanisms «specifically salt crystallization and thermal stress» affecting the water-exposed marble through petrographic and SEM analysis.
- **Treatment Evaluation:** To comparatively evaluate the performance of two distinct nano-composites «Primal™ CM 330/ nano-Ca(OH)₂» and «Regalrez 1126/ nano-Ca(OH)₂» in terms of mechanical strength, reduction of water absorption, hydrophobicity and color stability.
- **Recommendation:** To determine the optimal nanocomposite formulation that provides long-term protection and meets aesthetic compatibility requirements for the conservation of the historic fountain marble.



[FIGURES 1/A-B]: The marble fountain in Muhammad Ali palace, Shubra, featuring 24 cantilevers in the form of crocodiles and four statues in the form of lions; (A). Photograph dated 1980; (B). Photograph dated 2005. <https://www.faroukmisr.net/report50.htm>, accessed on (07/01/2025)

¹⁹ MANOUDIS *et Al.* 2008: 1 -2; ALDOSARI *et Al.* 2017: 2.



[FIGURE 2]: The horizontal and vertical layout of the marble fountain in Muhammad Ali palace, Shubra
©Done by the authors



[FIGURE 3]: The impact of common external factors including wind, heat and pollution on the marble statues, resulting in color darkening, the appearance of stains, the formation of cracks and progressive disintegration ©Photo taken by MOHAMED ABDAL AZYZ

II. MATERIALS AND METHODS

1. Materials

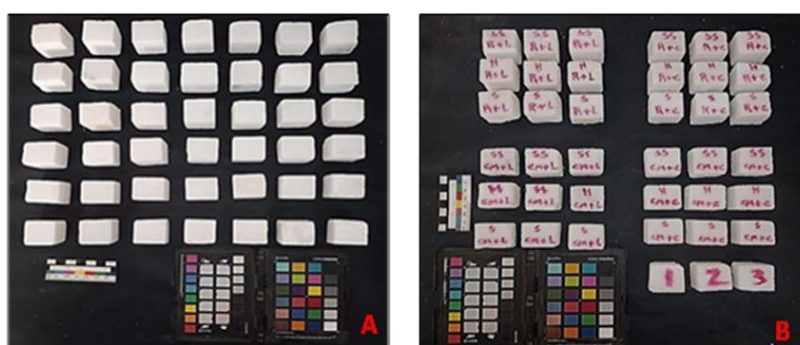
A. Preparation of Marble Samples and Artificial Aging

For the purposes of the experimental program, a total of thirty-six cubic marble specimens (3×3×3 cm) were prepared. These specimens were deliberately subjected to controlled artificial aging procedures designed to reproduce, as closely as possible, the physical and chemical alterations typically observed in archaeological marble. The pre-aged samples provided a realistic baseline for evaluating the efficiency of the proposed conservation treatments. Following this stage, the specimens were conditioned and prepared for the application of the selected nanocomposite formulations, ensuring uniform penetration and consistent testing conditions [FIGURES 4/A-B].

The artificial aging program for the experimental marble specimens, prior to the application of the nanocomposites, involved successive stages of salt weathering, acid weathering, and combined thermal–moisture weathering. Salt weathering was first carried out by immersing the specimens in a sodium chloride solution «50% concentration» for ten consecutive days. This was followed by immersion of the dried specimens in a sulfuric acid solution «30% concentration» for another ten consecutive days. Subsequently, the specimens were subjected to thermal–moisture cycles, consisting of heating at 105°C for eight hours followed by immersion in water for sixteen hours, repeated for ten complete cycles.

Despite these preliminary treatments, the specimens did not reach the desired level of deterioration comparable to the archaeological marble. Consequently, an amended

accelerated aging protocol was developed and applied. This protocol involved exposing the specimens to alternating cycles of immersion in the saline solution for eight hours, followed by oven drying at 150°C for sixteen hours, a process that continued for two full months. This protocol was rigorously established as a targeted empirical methodology. The protocol's specific parameters were optimized to achieve the sole objective of obtaining weakened experimental specimens that accurately match and realistically simulate the complex, observed degradation state of the original marble at the Muhammad Ali palace fountain²⁰.



[FIGURES 4/A-B]: Experimental marble specimens prepared for treatment; A. Before initial artificial aging; B. After initial artificial aging © Photo taken by MOHAMED ABDAL AZYZ

B. Preparation of Nanocomposites

In this study, two nanocomposites were applied in the treatment of the experimental marble specimens: Regalrez 1126 polymer²¹ combined with nano-calcium hydroxide and Primal™ CM 330 polymer combined with nano-calcium hydroxide. The statistical analysis of the TEM micrographs indicated that the synthesized nano-calcium hydroxide particles ranged in size from 42.51 nm to 100.5 nm, confirming their suitability for deep penetration into the marble structure. [TABLE 1] presents the different concentrations and the solvents used in the preparation of these nanocomposites.

Nº.	Nanocomposites	Solvent used	Concentration	
			Polymer	Nano enhancer
1	Regalrez 1126 polymer + Nano calcium hydroxide	White spirit	7%	3% by volume of Regalrez 1126 crystals
2	Primal™ CM 330 polymer + Nano calcium hydroxide	Ethanol	10%	3% of the solid volume of Primal

[TABLE 1]: Percentages of polymers and nano-composite enhancers used in the study ©Done by the authors

The nanocomposites were homogenized using both an ultrasonic device and a magnetic stirrer at 50°C, at 1200 revolutions per minute (rpm). Each mixing step was

²⁰ KATERINA 2016: 352.

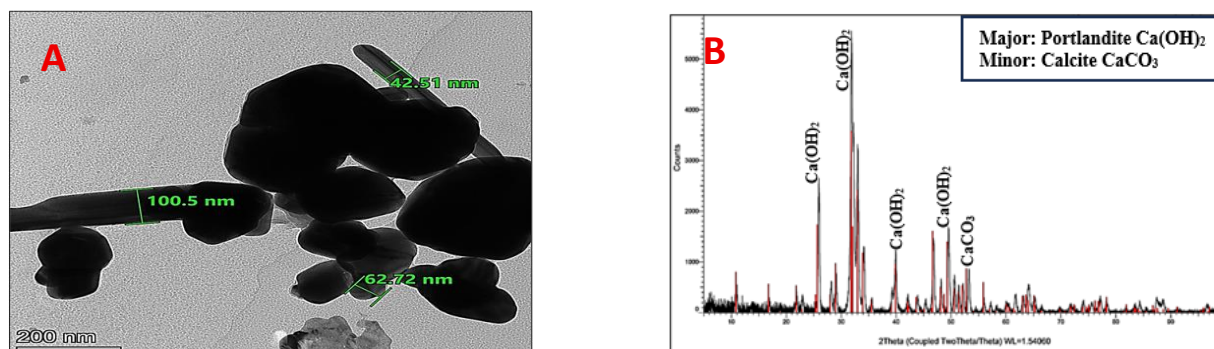
²¹ Regalrez 1126 is a fully hydrogenated C9 or C5/C9 copolymer, low molecular weight alkane hydrocarbon resin.

carried out for 30 minutes to ensure complete dispersion and uniform distribution of the nano-enhancer within the polymer matrix [FIGURES 5/A-C].



[FIGURES 5/A-C]: Different stages of preparation of the nanocomposites used in the study © Photo taken by the authors

To further characterize the nanomaterials employed, nano-calcium hydroxide was analyzed using two complementary techniques. Transmission Electron Microscopy (TEM) provided direct evidence of the particle size and morphology, while X-ray Diffraction (XRD) confirmed its crystalline structure and purity [FIGURES 6/A & B].

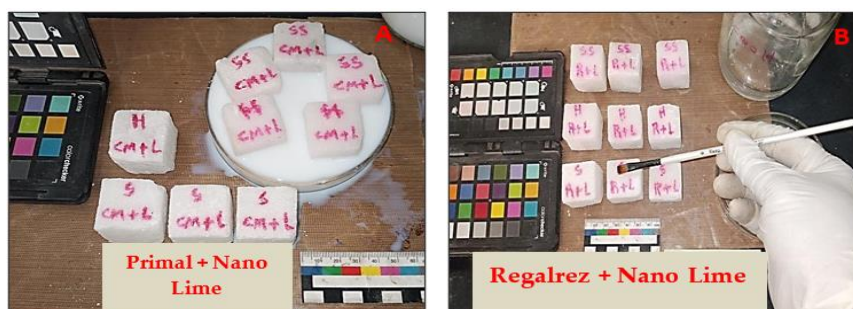


[FIGURES 6/A & B]: A. Transmission electron microscopy (TEM) image showing the particle size of the nano-calcium hydroxide; B. X-ray diffraction (XRD) analysis of the nano-calcium hydroxide used in the study © Done by the authors

C. Application of Nanocomposites

The nanocomposite formulations were applied to the experimental marble specimens using a soft brush to ensure gradual and uniform penetration into the stone pores. The application protocol involved a total of three successive coats, applied to the point of refusal (saturation). A 24-hour drying period was strictly maintained between each coat to allow for solvent evaporation and penetration. The total procedure was carried out under controlled laboratory conditions «23C, 50% RH». The average material uptake was measured by weighing the specimens before and after the application of each coat, resulting in an average material uptake of 0.045 g/cm² for the nano-Ca(OH)₂ composites.

Following the final coat, the treated specimens were left to fully stabilize under controlled laboratory conditions «23C, 50% RH» for a period of 21 days until complete curing was achieved. In order to evaluate the long-term performance of the treatments, three marble cubes of each formulation were subjected to a salt-aging program (S), while another three cubes of each formulation were preserved under the same laboratory conditions without aging (SS). This setup provided a clear basis for comparative assessment between aged and non-aged treated samples [FIGURES 7/A-B].



[FIGURES 7/A-B]: Application of the nanocomposites; A. Primal CM 330 + Nano calcium hydroxide; B. Regalrez 1126 + Nano calcium hydroxide © Done by the authors

D. Accelerated Aging of Treated Marble Specimens

To simulate long-term deterioration under controlled laboratory conditions, the experimental marble specimens were subjected to an artificial aging program based on the European Standards EN 14066:2003 and EN 12370:1999. The procedure included two main weathering regimes: thermal cycling and salt crystallization. A total of 21 complete cycles were performed. In the salt crystallization test, the specimens were immersed in a sodium chloride solution «10% concentration» for 2 hours, followed by drying in a ventilated oven at 60°C for 16 hours. For the thermal cycling test, specimens were exposed to repeated heating and cooling, with heating carried out in an oven at 105°C for 8 hours, followed by reconditioning in ambient laboratory conditions for the remaining 16 hours of the cycle.

Unlike routine durability tests, this artificial aging protocol was specifically applied to the treated specimens in order to evaluate the performance and long-term effectiveness of the selected nanocomposites. The aim was to assess their ability to withstand salt crystallization, thermal stress and moisture fluctuations while preserving the physical and mechanical integrity of the marble²².

2. Methods

As part of the methodology adopted to achieve reliable results in the conservation and treatment of ancient marble sculptures immersed in water, a series of advanced examinations and analytical techniques was undertaken. These procedures aimed to assess the condition of the marble, identify the underlying deterioration mechanisms and thereby support the selection of the most appropriate nanocomposite treatments for isolation and protection. The analyses were carried out directly on the archaeological material, using detached fragments collected from the water-damaged sculptures.

A. X-Ray Diffraction Analysis «XRD»

X-ray diffraction analysis was conducted using a Philips PW 3710/31 diffractometer at the Grand Egyptian Museum. The technique was employed to identify the mineralogical phases of the marble from the Muhammad Ali palace fountain and to detect structural modifications that may have resulted from long-term environmental exposure. Analyses were carried out at room temperature, operating at 45 kV and 40 mA, with scans performed across a defined 2θ range to ensure precise characterization of crystalline phases²³.

²² CEN, EN 12370: 1999: 1-10; ABD EL HAFEZ 2023: 1-2.

²³ JOSE *et Al.* 2023: 23.

B. X-Ray Florescence Analysis «XRF»

A handheld XRF analyzer «model: Niton XL3t, equipped with an x-ray tube and Ag anode, 50 kV» was utilized at the Grand Egyptian Museum to determine the elemental composition of the marble from the Muhammad Ali palace fountain. This technique served as a confirmatory tool, enabling the detection of trace elements commonly associated with calcium, including sulfur, silica, potassium, iron, titanium and chlorine—some of which may be linked to materials historically used in water circulation and filtration systems.

C. Laser- Raman Spectroscopy

Raman laser spectroscopy was performed at the Raman Laboratory of the Grand Egyptian Museum Authority using a Bruker Senterra II instrument. The analysis utilized a diode laser with a wavelength of 785 nm and an adjustable power setting, typically maintained below 50 mW at the sample surface to prevent thermal damage. This technique was employed to characterize the mineralogical composition of the marble from the Muhammad Ali palace fountain, with particular focus on distinguishing between the different crystalline phases of calcium carbonate present within the stone.

D. Polarizing Microscope «PLM»

A Zeiss-Image.A1m polarized light microscope, located at the Geology Workshop of the Faculty of Science, Cairo University, was employed to examine thin sections prepared from the marble of the Muhammad Ali palace fountain. This method was applied to determine the mineralogical composition of the stone, differentiate between primary and secondary crystalline phases and provide petrographic insights into its structural characteristics. These observations are fundamental for recognizing alteration features and for evaluating the potential effectiveness of conservation treatments²⁴.

E. Scanning Electron Microscope «SEM»

A QUANTA 3D 200i scanning electron microscope, housed at the Grand Egyptian Museum, was utilized under high vacuum mode. The analysis was conducted using an accelerating voltage of 15 kV (Kilovolts), which provided optimal resolution for the marble's surface morphology. The working distance (WD) was maintained between 10 mm and 12 mm and the samples were prepared with a thin layer of gold coating to ensure conductivity and minimize charging effects during imaging. The instrument was applied both to assess the original microstructural condition of the archaeological material and, in the experimental stage, to evaluate the effects of nanocomposite treatments. This analysis provided high-resolution observations of surface morphology and microstructural alterations, allowing for a detailed assessment of changes induced by treatment processes²⁵.

F. Colorimetric Measurement of Studied Specimens

Assessing color stability is an essential step in the evaluation of conservation treatments, as applied materials must enhance durability without inducing noticeable

²⁴ HEMEDA *et Al.* 2019: 157.

²⁵ MAKY *et Al.* 2023: 498-518.

visual alterations. To this end, the treated experimental marble specimens —both prior to and after artificial aging— were subjected to colorimetric measurements. The analysis was conducted using the CIE Lab* color system, a standardized method for quantifying chromatic variation. Within this system, L* denotes lightness on a scale from 0 (black) to 100 (white), a* measures chromaticity along the red–green axis «positive values for red, negative for green» and b* reflects the yellow–blue axis «positive values for yellow, negative for blue». Differences between two readings are expressed as ΔL^* , Δa^* and Δb^* , while the total color variation is determined by the overall color difference (ΔE), calculated according to the following equation: $\Delta E = \sqrt{(\Delta L^* + \Delta a^* + \Delta b^*)^2}$. This procedure provided an objective framework for monitoring the potential chromatic impact of the nanocomposite treatments on the experimental marble specimens²⁶. Colorimetric analysis was performed using a Minolta spectrophotometer «model CM-2600D, Konica Minolta, Japan», available at the Grand Egyptian Museum Authority. The instrument operates according to the CIE Lab* color system, ensuring accurate and standardized assessment of chromatic variations in stone surfaces.

G. Water Contact Angle Measurement of Studied Specimens

The water contact angle test was employed to assess the hydrophobic performance of the treated marble specimens, providing an indicator of the effectiveness of the applied nanocomposites in reducing water absorption and improving surface protection. The measurements were conducted using a PHOENIX-300 contact angle analyzer at the laboratories of the Faculty of Science/Sohag University. This technique evaluates the degree of interaction between water droplets and the treated surfaces, allowing the characterization of wetting behavior and the potential development of water-repellent or self-cleaning properties²⁷.

H. Physical and Mechanical Properties

The evaluation of the treated marble specimens involved four complementary tests —bulk density, porosity, water absorption and compressive strength— designed to assess the overall efficiency of the applied nanocomposites in enhancing durability and mechanical performance. Density and porosity, together with water absorption, were measured according to ASTM C97²⁸, as these parameters are critical indicators of stone vulnerability to moisture transport, salt crystallization and long-term decay. Compressive strength testing was conducted at the Institute of Measurements and Calibration using a Tinius Olsen H5KT universal testing machine «SDL ATLAS – Textile Testing Solutions», in accordance with ASTM C170²⁹ – Standard Test Method for Compressive Strength of Dimension Stone, providing insight into the improvement of the stone's load-bearing capacity after treatment. Together, these standardized tests established a reliable

²⁶ ABD EL HAFEZ 2023: 406.

²⁷ MARMUR *et Al.* 2017: 1; DARBAND *et Al.* 2020:1763-1802.

²⁸ ASTM International. ASTM C97/C97M-18 Standard Test Methods for Absorption and Bulk Specific Gravity of Dimension Stone. ASTM INTERNATIONAL 2018.

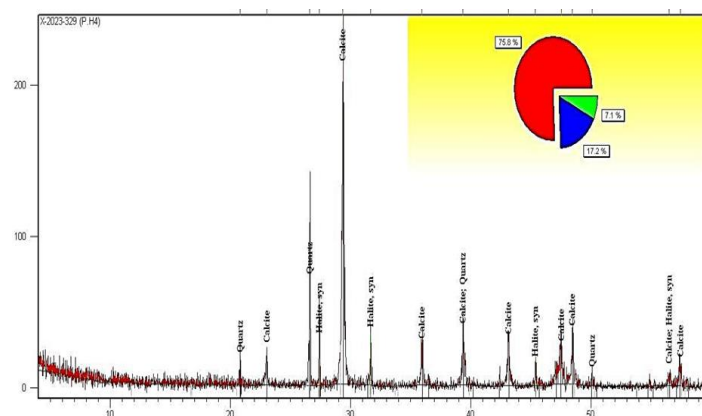
²⁹ ASTM International. ASTM C170/C170M-24a Standard Test Method for Compressive Strength of Dimension Stone. ASTM INTERNATIONAL 2024.

framework for evaluating both the physical stability and mechanical reinforcement achieved by the nanocomposite applications.

III. RESULTS AND DISCUSSION

A. X-Ray Diffraction Analysis «XRD»

The XRD pattern of a detached archaeological marble sample from the watercourse of the fountain [FIGURE 8] revealed that the stone is primarily composed of calcite « CaCO_3 , ~75%». In addition, the presence of halite (NaCl , ~7.5%) was detected, which reflects the effect of sodium chloride salts on the deterioration of the marble. The crystallization of halite within pores and along cleavage planes is a common cause of granular disintegration and layer detachment in carbonate stones exposed to saline water³⁰. The analysis also indicated a significant proportion of quartz (SiO_2 , ~17.5%). This quartz may partly represent a natural accessory phase within the original marble fabric but, it is likely that an additional fraction originates from secondary encrustations or soil-derived deposits adhering to the sample in situ. The coexistence of calcite, halite and quartz suggests a complex deterioration pathway, where salt crystallization and external contamination act in parallel with the intrinsic mineralogical features of the stone³¹.



[FIGURE 8]: XRD pattern of a detached archaeological marble sample from the fountain watercourse, showing calcite as the main component (~75%), with secondary phases of halite (~7.5%) and quartz (~17.5%) © Done by the authors

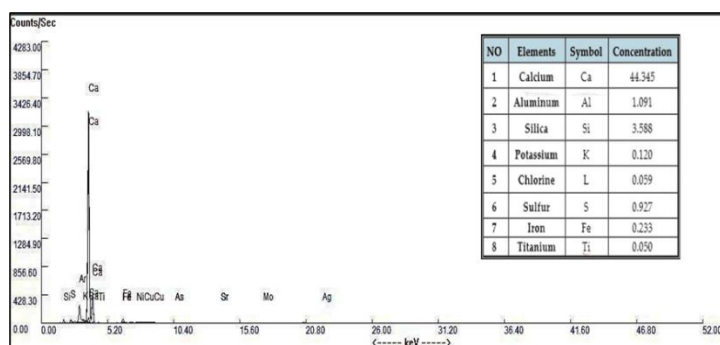
B. X-Ray Florescence Analysis «XRF»

The XRF analysis of a detached marble sample from the fountain revealed that calcium (Ca) is the dominant element (44.35%), confirming the carbonate nature of the stone and its classification as calcitic marble. Minor constituents were also detected, including silica (Si, 3.59%), aluminum (Al, 1.09%) and sulfur (S, 0.93%), which may reflect secondary inputs such as soil particles, atmospheric pollutants, or gypsum crusts formed through chemical weathering. Trace amounts of iron (Fe, 0.23%), potassium (K, 0.12%), chlorine (Cl, 0.06%) and titanium (Ti, 0.05%) were also recorded. The occurrence of chlorine and sulfur is particularly significant, as it suggests the influence of soluble salts «e.g., sodium chloride and calcium sulphates» that are known to promote salt crystallization and granular disintegration in marble. Similarly, the presence of silica and

³⁰ VILES 2002: 215-224.

³¹ ABD EL HADY *et Al.* 2019: 957.

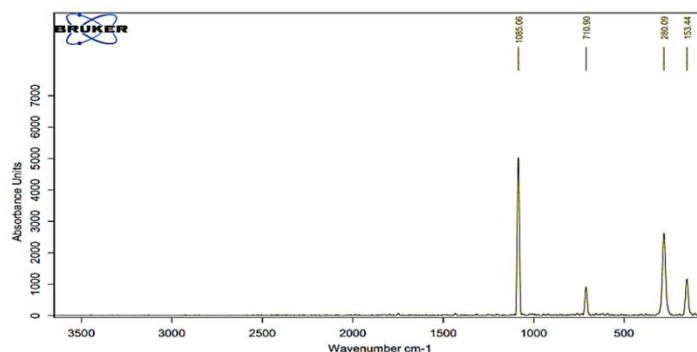
alumina points to either natural impurities within the stone matrix or the deposition of exogenous materials, possibly linked to environmental dust and encrustations in the archaeological setting. Overall, the elemental composition derived from XRF supports the mineralogical data obtained from XRD, highlighting calcite as the primary constituent with additional phases that play a role in the ongoing deterioration of the marble³² [FIGURE 9].



[FIGURE 9]: XRF spectrum of a detached marble sample from the fountain, showing calcium as the dominant element (44.35%), with minor and trace amounts of silica, aluminum, sulfur, iron, potassium, chlorine and titanium © Done by the authors

C. Laser- Raman Spectroscopy

The Raman spectrum of the archaeological marble sample from the Muhammad Ali palace fountain [FIGURE 10] revealed distinct vibrational bands characteristic of calcium carbonate polymorphs. The most prominent peaks were recorded at $\sim 1085 \text{ cm}^{-1}$, 710 cm^{-1} and $280\text{--}153 \text{ cm}^{-1}$, corresponding to the fundamental modes of calcite, which represents the primary mineral phase of the marble. These findings corroborate the XRD results, which confirmed calcite as the dominant constituent, while also providing complementary insights into the microstructural stability and phase purity of the carbonate minerals. The spectrum further suggests the presence of secondary alterations, consistent with the XRF results that detected soluble salts «e.g., halite, sulfates» and trace elements likely introduced through prolonged water interaction. Overall, Raman spectroscopy served as a highly sensitive and non-destructive technique, reinforcing the mineralogical characterization and highlighting the extent of physical and chemical changes affecting the historic marble³³.



[FIGURE 10]: Raman spectrum of an archaeological marble sample from the Muhammad Ali palace fountain, showing characteristic peaks of calcite at ~ 1085 and 710 cm^{-1} , confirming the dominance of calcium carbonate and supporting the XRD and XRF results © Done by the authors

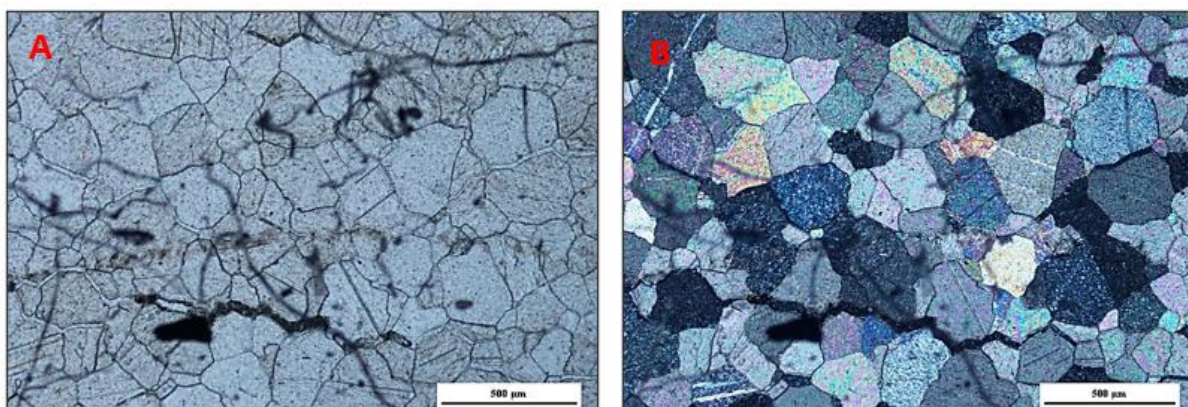
³² AL-DOSARI 2017: 1-15.

³³ ABD EL HAFEZ 2022: 463-480.

D. Polarizing Microscope «PLM»

Petrographic examination of thin sections from the marble of the Muhammad Ali palace fountain [FIGURES 11/A & B] provided valuable information on the mineralogical composition and microstructural deterioration of the stone. Under plane-polarized light [FIGURE 11/A], the calcite grains appeared as the dominant phase, showing clear grain boundaries with widespread micro-cracks traversing the crystal lattice. These features indicate progressive weakening of the intergranular matrix and loss of cohesion, which are consistent with advanced stages of physical and chemical weathering. Under cross-polarized light [FIGURE 11/B], the calcite crystals displayed characteristic interference colors, confirming their predominance within the marble. The sections also revealed secondary inclusions of biotite and iron oxides, in addition to heterogeneities suggestive of recrystallization and infiltration by exogenous materials.

Further examination of the thin sections, particularly under higher magnification, revealed the marble exhibits a typical interlocking mosaic texture «Sutured Fabric». However, this fabric is significantly compromised by the presence of numerous intergranular micro-fissures and solution voids. These features are critical as they represent the primary pathways for the deep ingress of aggressive soluble salts and water, suggesting that the deterioration is not confined to the surface layer but, extends significantly into the stone's microstructure, highlighting the need for consolidants with high penetrability³⁴. The presence of these secondary phases, together with microstructural disintegration, highlights the complex deterioration mechanisms affecting the stone, including salt attack, thermal stress and pollutant-induced chemical reactions. These petrographic observations are in full agreement with the results obtained from XRD and XRF analyses, which confirmed calcite as the primary mineral with associated secondary compounds. Collectively, these findings underline the vulnerability of the archaeological marble to multi-factorial deterioration processes and emphasize the need for targeted conservation interventions³⁵.



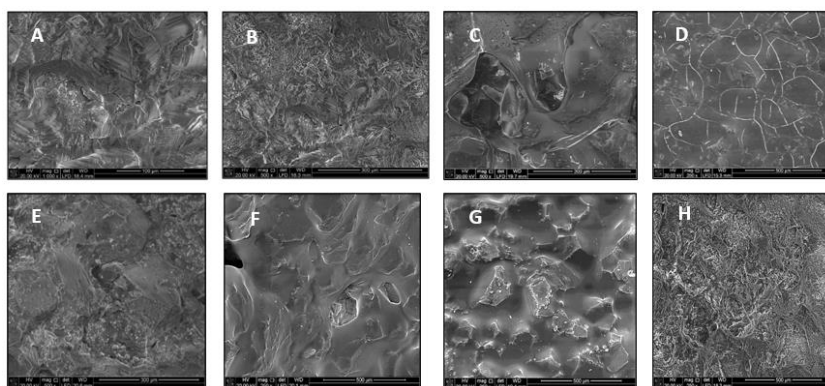
[FIGURES 11/A-B]: Polarized light micrographs of marble samples from the Muhammad Ali palace fountain at 25× magnification. A. Plane-polarized light showing calcite grains with extensive micro-cracks and matrix erosion; B. Cross-polarized light highlighting calcite crystals with interference colors, secondary inclusions «biotite and iron oxides» and evidence of microstructural disintegration © Done by the authors

³⁴ MOUSSA *et Al.* 2021 : 4057-4067.

³⁵ ABDEL HAFEZ *et Al.* 2023: 403-414.

E. Scanning Electron Microscope «SEM»

The scanning electron microscope (SEM) investigation provided clear evidence of the differences between untreated marble, specimens treated with the two nanocomposites and those subjected to accelerated aging. Untreated samples [FIGURES 12/A–B] displayed severe granular disintegration, interconnected micro-cracks and widespread porosity, reflecting the advanced state of deterioration caused by prolonged exposure to water and salt³⁶. Application of the nanocomposite Regalrez 1126 polymer + nano calcium hydroxide [FIGURE 12/C] resulted in partial pore filling and the formation of a thin protective coating on the marble surface, indicating its ability to penetrate under controlled indoor conditions. However, after thermal and salt aging [FIGURES 12/D–E], this treatment showed poor durability, as manifested by micro-cracking of the consolidant film, loss of cohesion and recrystallization of salt within voids—suggesting its limited efficiency in open-air environments exposed to fluctuating temperature and humidity. In contrast, the specimens treated with Primal™ CM 330 polymer + nano calcium hydroxide [FIGURE 12/F] exhibited a more homogeneous distribution of the consolidant and effective sealing of micro-pores. Even after thermal [FIGURE 12/G] and salt aging [FIGURE 12/H], this composite maintained its stability, with fewer cracks and reduced salt penetration compared to the Regalrez-based treatment. These results confirm that Primal CM 330 with nano calcium hydroxide provides superior consolidation and long-term protective performance under environmental stress conditions, making it more suitable for the conservation of the submerged marble sculptures in the Muhammad Ali palace fountain.



[FIGURES 12/A-H]: Scanning electron micrographs of marble samples; A & B. Untreated archaeological marble showing granular disintegration and micro-cracks; C. Sample treated with Regalrez 1126 polymer + nano calcium hydroxide; D & E. The same treatment after thermal and salt aging, respectively, showing loss of cohesion and salt crystallization; F. Sample treated with Primal™ CM 330 polymer + nano calcium hydroxide; G & H. The same treatment after thermal and salt aging, respectively, demonstrating improved stability and resistance to deterioration © Done by the authors

F. Colorimetric Measurement of Studied Specimens

The results of colorimetric measurements reveal clear differences in the degree of chromatic variation (ΔE) between the two applied nanocomposites and across the different aging conditions. The samples treated with Regalrez 1126 polymer + Nano calcium hydroxide exhibited relatively high ΔE values in all cases—whether directly after treatment, or following thermal and salt aging—indicating a noticeable color alteration

³⁶ EL-SAYED 2024: 338–351.

that may negatively affect their visual compatibility with the original marble. In contrast, the samples treated with Primal™ CM 330 polymer + Nano calcium hydroxide maintained markedly lower ΔE values, both in the untreated aged state and after exposure to thermal and salt aging cycles. This reflects a higher level of chromatic stability and visual compatibility, which is a critical factor in conservation practice where minimizing color change is essential. These findings suggest that Primal CM 330-based nanocomposite provides more effective long-term stability under aggressive environmental conditions, reinforcing its suitability for the consolidation and protection of marble elements exposed to water and fluctuating climatic stresses [TABLE 2].

Nanocomposites	ΔE (After Treatment)	ΔE (After Thermal Aging)	ΔE (After Salt Aging)
Regalrez 1126 polymer + Nano calcium hydroxide	6.88	7.79	6.78
Primal™ CM 330 polymer + Nano calcium hydroxide	2.69	1.37	2.15

[TABLE 2]: ΔE values for treated and aged marble specimens © Done by the authors

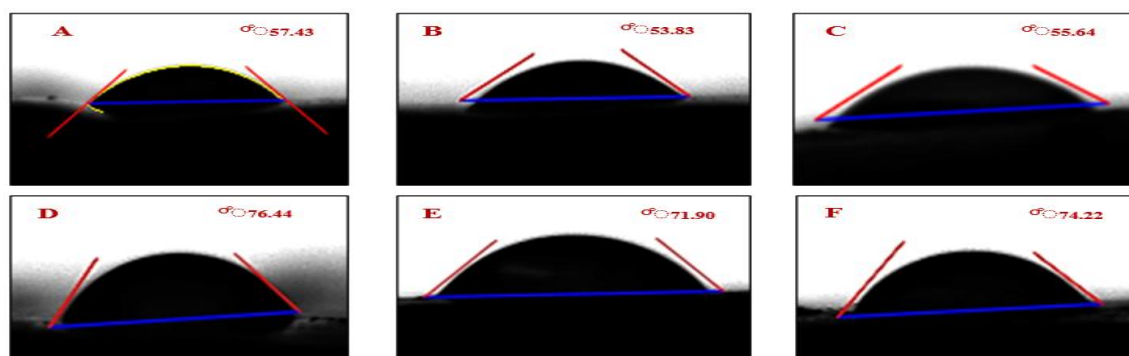
Aesthetic compatibility is a mandatory requirement in conservation. The colorimetric measurements revealed that the Primal CM 330 composite maintained markedly lower ΔE values across all conditions «untreated aged, thermal and salt aging». This reflects its superior chromatic stability and visual compatibility with the original marble.

Conversely, the Regalrez 1126 treatment resulted in relatively high ΔE values, suggesting a noticeable and potentially undesirable color alteration. This distinction is critical: the minimal color change induced by Primal CM 330 ($\Delta E < 2.7$) reinforces its suitability for treating archaeological marble where minimizing visual impact is paramount and aligns with the expected properties of high-quality acrylic resins [TABLE 2].

G. Water Contact Angle Measurement of Studied Specimens

The evaluation of water contact angle provided valuable insights into the hydrophobic efficiency of the applied nanocomposites. Samples treated with Regalrez 1126 polymer + Nano calcium hydroxide (codes A–C) exhibited relatively low contact angles, with values of 57.43° immediately after treatment, 53.83° following thermal aging and 55.64° after salt aging. These results indicate limited hydrophobicity, suggesting that although the treatment improved water repellence to some extent; its performance remained modest and further decreased under accelerated aging conditions. In contrast, the samples treated with Primal™ CM 330 polymer + Nano calcium hydroxide «codes D–F» showed consistently higher contact angle values of 76.44° after treatment, 71.90° after thermal aging and 74.22° after salt aging. This demonstrates the relative efficiency of Primal CM 330-based formulations in enhancing hydrophobicity and sustaining performance after exposure to both thermal and saline stresses. However, it is important to note that neither of the two composites reached the hydrophobic threshold, as a water

contact angle of 90° or above is generally required for a surface to be classified as water-repellent. This suggests that while Primal™ CM 330 polymer + Nano calcium hydroxide represents a more promising option, further optimization of the treatment—such as adjusting the concentration of either the polymer or the nano-calcium hydroxide—could yield improved results in future studies, enhancing the protective performance of treated marble³⁷ [FIGURES 13/A-F].



[FIGURES 13/A-F]: Water contact angle measurements of the treated marble specimens; A–C. Regalrez 1126 polymer + Nano calcium hydroxide (after treatment, after thermal aging and after salt aging, respectively); (D–F). Primal™ CM 330 polymer + Nano calcium hydroxide «after treatment, after thermal aging and after salt aging, respectively» © Done by the authors

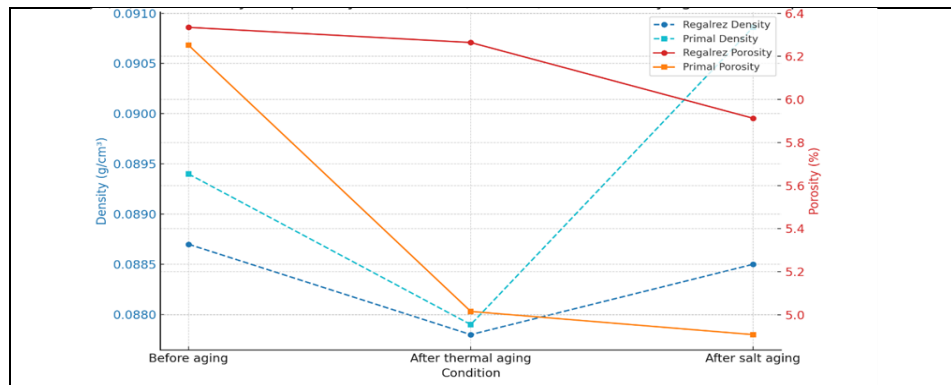
The assessment of water contact angle provided a direct measure of the surface modification achieved by the two composites, which is intrinsically linked to the stone's open porosity [FIGURE 14] and resistance to salt ingress. The consistently higher contact angles achieved by the Primal™ CM 330 composite «71.9° to 76.4°» compared to the Regalrez 1126 composite «53.8° to 57.4°» directly confirms the superior hydrophobic efficiency of the acrylic-based formulation. This improved repellency, combined with the declared reduction in porosity, effectively hinders the direct mechanism of salt damage by reducing water transport into the stone pores. Although neither composite reached the full hydrophobic threshold $\geq 90^\circ$, the superior performance of the Primal™ CM 330 under both thermal and saline stress is attributed to its relative flexibility and stability compared to Regalrez, which strongly supports the study's hypothesis regarding its superiority under high humidity and thermal conditions [FIGURES 13/A-F].

H. Physical and Mechanical Properties

The density and porosity data provide valuable insight into the performance of the applied nanocomposites. For density, only slight variations were recorded across treatments and aging conditions: samples treated with Regalrez 1126 polymer + Nano calcium hydroxide ranged between 0.0887 and 0.0885 g/cm³, while those treated with Primal™ CM 330 polymer + Nano calcium hydroxide ranged between 0.09266 and 0.09086 g/cm³. These results indicate that the nanocomposites did not substantially alter the bulk density of the marble. Porosity, however, revealed more significant differences. The Regalrez 1126–treated specimens showed an initial decrease from 6.3347% (untreated) to 5.0944% after treatment but, porosity increased again to 6.2642% and 5.9129% following thermal and salt aging, respectively, reflecting the partial loss of consolidating efficiency

³⁷ WIDATI *et Al.* 2024: 1303-1314.

under aggressive conditions. By contrast, samples treated with Primal™ CM 330 exhibited a consistent and more effective reduction in porosity, decreasing from 6.2518% (untreated) to 4.4112% after treatment and maintaining relatively lower values of 5.0160% (thermal aging) and 4.9083% (salt aging). These findings highlight that while both treatments improved the pore structure initially, the Primal™ CM 330 composite provided greater long-term stability and resistance to porosity increase under accelerated aging conditions, confirming its superior consolidating efficiency³⁸ [FIGURE 14].



[FIGURE 14]: Porosity and density values of treated marble specimens before and after artificial aging
©Done by the authors

The data in [TABLE 3] demonstrate that both nanocomposites were effective in slightly reducing the water absorption capacity of marble compared to the untreated specimens (2.56% for Regalrez 1126 and 2.65% for Primal™ CM 330). After treatment, both composites maintained lower absorption rates, with Primal™ CM 330 polymer + Nano calcium hydroxide showing relatively greater efficiency (2.35%) than Regalrez 1126 (2.42%). Following artificial aging, whether by thermal or salt cycles, the absorption values remained nearly stable, indicating that both treatments enhanced the hydrophobic properties of the marble. The results confirm that Primal™ CM 330 provided a more consistent performance under aging conditions, achieving values of 2.48% (thermal aging) and 2.44% (salt aging), compared to 2.51% and 2.48% for Regalrez 1126, respectively.

Nanocomposites	WA (%) (Untreated)	WA (%) (After Treatment)	WA (%) (After Thermal Aging)	WA (%) (After Salt Aging)
Regalrez 1126 polymer + Nano calcium hydroxide	2.56	2.42	2.51	2.48
Primal™ CM 330 polymer + Nano calcium hydroxide	2.65	2.35	2.48	2.44

[TABLE3]: Water absorption (WA) of marble specimens before and after treatment and artificial aging © Done by the authors

As shown in [TABLE 4], compressive strength improved significantly after treatment with both nanocomposites, highlighting their consolidating effect. Regalrez 1126 polymer + Nano calcium hydroxide exhibited the highest immediate increase, from 101.6 kg/cm² (untreated) to 197.4 kg/cm² «after treatment». However, this improvement was less stable

³⁸ BOBROWSKA 2024: 1311-1325.

under thermal aging, where the value dropped to 147.01 kg/cm². By contrast, Primal™ CM 330 polymer + Nano calcium hydroxide provided a more balanced improvement, rising from 109.3 kg/cm² (untreated) to 193.5 kg/cm² after treatment and maintaining higher stability after aging «175.1 and 184.7 kg/cm² under thermal and salt aging, respectively».

Nanocomposites	CS (kg/cm ²) (Untreated)	CS (kg/cm ²) (After Treatment)	CS (kg/cm ²) (After Thermal Aging)	CS (kg/cm ²) (After Salt Aging)
Regalrez 1126 polymer + Nano calcium hydroxide	101.6	197.4	147.01	177.5
Primal™ CM 330 polymer + Nano calcium hydroxide	109.3	193.5	175.1	184.7

[TABLE 4]: Compressive strength (CS) of marble specimens before and after treatment and artificial aging
© Done by the authors

The previous results suggest that while both composites are effective consolidants, Primal™ CM 330 ensures greater long-term physical and mechanical durability, especially under environmental stress.

Crucially, the superior mechanical and physical performance of the Primal™ CM 330 composite, evidenced by its higher stable compressive strength after salt aging [TABLE 4] and its effective reduction in open porosity [FIGURE 14], is directly correlated with microstructural observations. The SEM micrographs of the Primal™ CM 330 treated specimens [FIGURES 12/G-H] showed a more homogeneous, cohesive and crack-free polymer-nanoparticle matrix bridging the marble grains, indicating effective consolidation. Conversely, the Regalrez composite often exhibited signs of minor cracking or less uniform coverage under the same aging conditions, providing a structural explanation for its lower mechanical resistance post-aging. This explicit link confirms that the differences in the micro-morphology imparted by the polymer type directly translate into the macro-performance of the treated marble.

IV. CONCLUSION

This study demonstrates that the nanocomposite formulation based on Primal™ CM 330 and nano-calcium hydroxide is a highly promising consolidant for water-immersed marble, offering a favorable balance of mechanical reinforcement, durability under environmental stress and aesthetic preservation. Through an integrated program of analytical techniques and experimental simulations, the marble was shown to suffer from significant structural and chemical alterations, primarily induced by salt crystallization, moisture ingress and prolonged environmental exposure. The application of two nanocomposite consolidants—Regalrez 1126/nano-calcium hydroxide and Primal™ CM 330/nano-calcium hydroxide—was systematically tested under both laboratory and simulated aging conditions. The comparative results demonstrated that while both formulations improved the physical and mechanical properties of the treated marble, the Primal™ CM 330-based nanocomposite exhibited relatively higher efficiency in enhancing compressive strength, reducing porosity and water absorption and maintaining acceptable color stability. Although neither treatment achieved the ideal hydrophobic threshold, the outcomes highlight the promise of nanotechnology-based materials in addressing the

challenges of marble conservation. The findings not only provide a scientific basis for the treatment of the Muhammad Ali palace fountain but, also establish a framework for future research aimed at optimizing nanocomposite formulations to achieve long-term stability and improved hydrophobic performance in historic stone conservation. Based on the results, the Primal™ CM 330 nanocomposite is recommended for pilot-scale in situ application on the Muhammad Ali palace fountain. Furthermore, future work should specifically focus on optimizing the nanoparticle-to-polymer ratio to further enhance hydrophobic properties without compromising compatibility and the long-term «e.g., 1–2 year» monitoring of treated specimens in the actual fountain environment is considered the critical next step for full validation.

DISCLOSURE STATEMENT

No Potential conflict of interest was reported by the authors

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EVALUATION OF ALPHA AND BETA GYPSUM UNDER AGGRESSIVE CONDITIONS FOR APPLICATION IN THE RESTORATION OF LIGHTWEIGHT STUCCO DOMES «THE CASE STUDY OF ZAINAB KHATUN HOUSE»

By

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ABSTRACT

[EN] This study aims to evaluate the performance of α - and β -gypsum under aggressive environmental conditions in order to determine their suitability for the restoration of lightweight stucco domes. The case study is the dome above the bathroom of an historic residential building dating to the Mamluk period, namely the House of Zainab *Khatun* 873 AH/1486 AD. The bathroom ceiling represents a distinctive structural element executed using stucco materials. Mineralogical characterization by X-ray diffraction (XRD) analysis revealed that the stucco composition consists of approximately 60% calcite and 40% gypsum. Accordingly, the restoration strategy focused on the selection of appropriate treatment, completion and protective coating materials for the upper surface of the dome, with emphasis on materials exhibiting low density, resistance to acidic deterioration and durability under environmental exposure. The evaluation of the performance of both gypsum types « α - and β -gypsum» was therefore based on several criteria, including sample weight, resistance to acid erosion and mechanical load-bearing capacity assessed through flexural strength tests. In addition, differences in the crystalline structure of the two gypsum types and their influence on material properties were investigated. Transmission electron microscopy (TEM) was employed to determine the crystal size of both gypsum types, while resistance to acidic attack was evaluated by measuring weight loss after successive immersion cycles in an acidic solution with a pH value below 5.7. The surface condition of the tested samples was examined using a portable digital microscope (p-DM), whereas the internal microstructure was characterized by scanning electron microscopy (SEM). Mechanical testing was conducted to identify the material most suitable for fulfilling the structural requirements of the ceiling. The results indicated that α -gypsum outperformed β -gypsum, demonstrating superior crystalline structure, enhanced chemical resistance to acid erosion and improved mechanical properties, thereby making it the most suitable material for use in the restoration of the studied dome.

KEYWORDS: Acid erosion, Alpha gypsum, Beta gypsum, calcareous materials, mechanical load capacity, structural properties, the Stucco dome.

[AR]

تقييم الجبس الفا وبيتا تحت الظروف القاسية لامكانية تطبيقه في عمليات ترميم القباب الجصية «بمنزل زينب خاتون» تهدف هذه الدراسة إلى تقييم كفاءة جبس ألفا (α -Gypsum) و جبس بيتا (β -Gypsum) مع الظروف البيئية ، بغرض اختيار المادة الأنسب لترميم القباب الجصية خفيفة الوزن، حيث ان موضوع التطبيق هو قبة اعلا حمام احد المنازل الاثرية التي تعود للعصر المملوكي «منزل زينب خاتون 873هـ/ 1486م» وسقف الحمام يعتبر من العناصر الانشائية الفريدة التي نفذت بخامات مكونة من الجص والذي تبين من خلال تحليل حيود الاشعة السينية (XRD) انها تتكون من الكالسيت بنسبة 60% والجبس بنسبة 40% لذا فان اعتبارات الترميم ستكون اختيار مواد المعالجة او الاستكمال او التغطية للسطح العلوي للقباب شريطة ان تتوفر فيها الصفات التالية الوزن الاخف ، مقاومة التلف الحمضي والظروف البيئية ولذلك كانت مفردات تقييم مدي كفاءة كلا نوعي الجبس (الفا وبيتا) قائمة علي تحديد وزن العينات ومعرفة مدي المقاومة للتأثير الحمضي ومدي التحمل الميكانيكي سواء اختبارات الضغط او الانحناء ، واطهار الفوارق بين التكوين البلوري لكلا النوعين واثار ذلك في تغير خواصهما . لك تم الفحص

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باستخدام الميكروسكوب الإلكتروني النافذ (TEM) للوقوف على حجم بلورات كلا النوعين ، وتقدير المفقود من الوزن لكلا النوعين من خلال النقع لدورات متتالية في محلول حامض قيمة ال PH له اقل من 5.7 وتم تقييم حالة سطح العينات المختبرة بالميكروسكوب الرقعي المحمول (p- DM) وتم تقييم حالة البنية الداخلية للعينات باستخدام الميكروسكوب الإلكتروني الماسح (SEM) واجراء الاختبارات الميكانيكية مثل اختبارات الضغط والانحناء للوصول الى المادة الاكفأ التي تخدم الغرض الانشائي للسقف ، وتبين ان النوع الفا يتميز عن النوع بيتا بخواص بنائية علي المستوي البلوري وخواص كيميائية مقاومة للتلف الحامضي وخواص ميكانيكية ايضا فكان هو الافضل في الاستخدام اثناء عمليات الترميم التي جرت علي القبة .
الكلمات الدالة: الجبس ألفا، الجبس بيتا، الحت الحمضي، قابلية التحميل الميكانيكي، القبة الجصية، مواد كلسية، المواصفات الانشائية.

I. INTRODUCTION

The conservation and restoration of stucco architectural monuments constitute a particularly sensitive process due to the vulnerability of their primary constituents—especially gypsum—to external environmental conditions and deterioration agents. Stucco is predominantly composed of calcareous materials, such as lime and gypsum, both of which exhibit high susceptibility to acidic environments resulting from humidity, rainfall and atmospheric pollutants in outdoor settings¹. One of the major challenges in the conservation and maintenance of stucco elements exposed to external environments lies in the heterogeneity of stucco compositions, as they often consist of multiple materials with differing physical and chemical properties. This compositional diversity complicates the selection of appropriate conservation treatments, particularly with regard to achieving adequate resistance to environmental deterioration factors. The known forms of gypsum «α- and β-gypsum» can be employed in conservation and maintenance interventions to take advantage of their distinct physical and mechanical properties, thereby supporting the specific requirements of the restoration application.

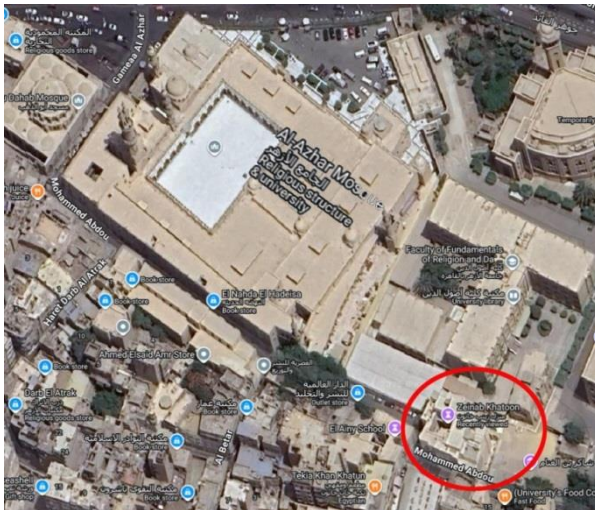
Zainab Khatun's House 873 AH/1468 AD

A. House Location

Zainab Khatun's House is situated at the intersection of al-Azhari Lane and al-^cAnaba Alley, behind al-Azhar Mosque, within a distinguished ensemble of Islamic monuments located to the north of al-Azhar Mosque [FIGURE 1].

Zainab Khatun's House represents one of the most significant examples of domestic architecture from the Mamluk period. The building reflects a high level of artistic and architectural achievement, particularly in its spatial planning, which conforms to the principles of the traditional Islamic house. Its architectural and decorative elements include stucco windows, *mashrabiya*s, ceilings, decorated and gilded corbels and marble flooring [FIGURE 2].

¹ For information on gypsum and the effects of environmental conditions on its deterioration, see: KHALIL 2023:415-416.



[FIGURE 1]: Shows the location of the *Khatun's* house next to al-Azhar Mosque © Google Maps: <https://maps.app.goo.gl/8qwwaexLpkKPeCww7>, accessed on (04/07/2024)



[FIGURE 2]: Shows main house facade and main entrance © Photo taken by MOHAMED ATYIA HAWASH

B. House Description

The house comprises a ground floor organized around a central open courtyard, in addition to two upper floors².

C. Ground Floor

The ground floor is organized around a principal southern façade containing a low main entrance that leads through a bent passageway. To the right of this passageway is the house mill, which opens onto an approximately square central courtyard. On the eastern side of the courtyard, a doorway provides access to the men's reception hall «*mandara*».

Adjacent to this, at the northern end of the same side, another doorway leads to the staircase ascending to the first upper floor, where the main reception hall is located³.

D. First Upper Floor

This floor comprises a rectangular summer sitting area overlooking the courtyard, featuring a two-arched arcade supported by a central marble column. The space contains several wall-mounted cupboards fitted with wooden shutters, used for storing household belongings. On the eastern side, a doorway leads to a bedroom closet. The main «great» hall on this level consists of a rectangular space covered by a wooden ceiling decorated with square and rectangular panels adorned with Ottoman-style vegetal motifs. Access to the smaller hall is provided through a doorway on the northern side of the great hall. This space is rectangular in plan and features a central arcade flanked by two small *iwans*. The hall overlooks the courtyard through latticework *mashrabiya*s⁴.

² YAGHI 2004: 485.

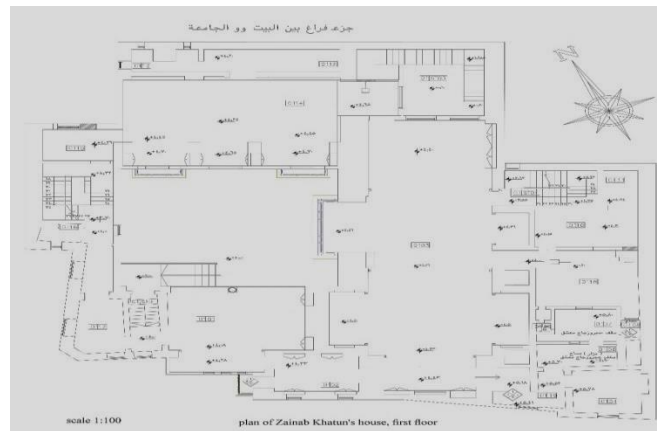
³ RIZQ 2003: 455.

⁴ YAGHI 2004: 486.

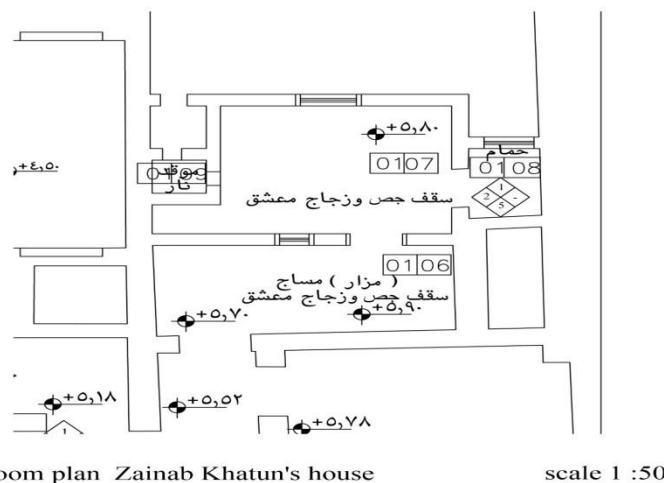
E. The Second Upper Floor

This floor includes a small hall and an adjoining two-level room with an attached bathroom. The ceiling is composed of stucco domes interspersed with colored glass panels. The floor also contains a small kitchen and a connecting corridor linking the spaces. Two windows overlook the central courtyard: the first, crafted from Maimon stone, is decorated with a carved vase motif, while the second, made of plaster, features inlaid colored glass⁵.

II. ARCHITECTURAL DOCUMENTATION AND DETERIORATION MAP FOR SECOND UPPER FLOOR BATHROOM STUCCO CEILING

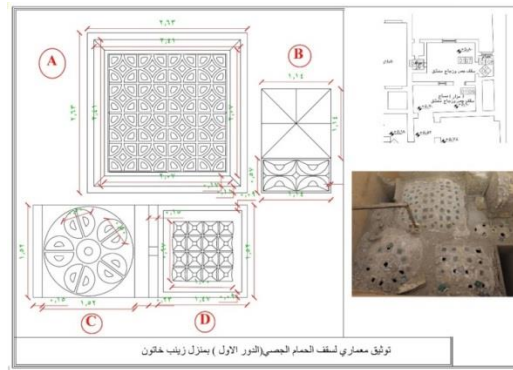


[FIGURE 3]: Shows the first floor plan, Zainab Khatun's house 873 AH /1468 AD © Done by the authors



[FIGURE 4]: Shows the second-floor bathroom plan, Zainab Khatun's house, 873 AH/1468 AD
© Done by the authors

⁵ YAGHI 2004: 488.

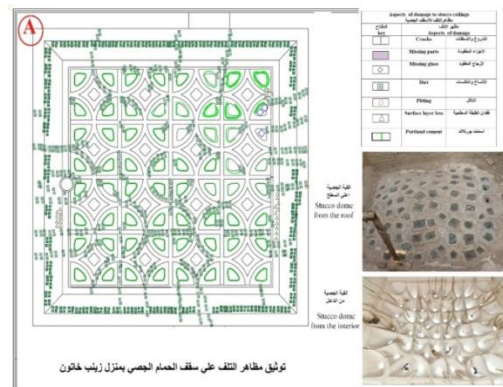


[FIGURE 5]: Shows the architectural elevation of the bathroom ceiling domes of Zainab Khatun's house, 873 AH-1468 AD © Done by the authors

III. STATE OF PRESERVATION

The deterioration of stucco domes exhibits diverse manifestations, reflecting the variety of factors affecting their condition. The primary types of damage documented include cracks and fissures in the stucco layer, surface erosion and pitting and peeling or detachment of stucco layers. Additionally, accumulation of dirt—predominantly dust—was observed on both external and internal surfaces. Some colored glass elements have been lost, while many others were reattached using gray Portland cement mortar, which differs significantly in physical and chemical properties from the original stucco, typically composed of lime and gypsum.

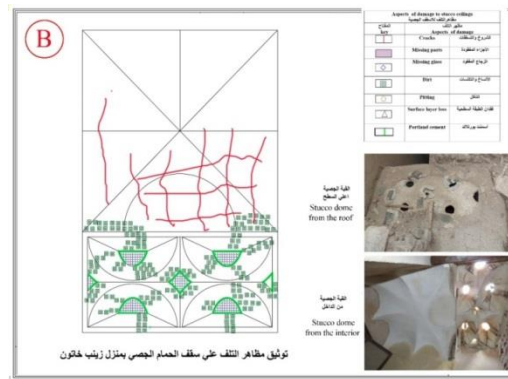
The principal cause of damage to the domes is environmental pollution, with the most significant pollutants being carbon dioxide (CO₂), sulfur dioxide (SO₂) and nitrogen oxides (NO_x). These gases react with rainwater to form acidic solutions, including sulfuric acid (H₂SO₄), nitric acid (HNO₃) and carbonic acid (H₂CO₃)⁶, which accelerate the deterioration process. The severity of damage depends on the type of pollutants, their atmospheric concentration and the duration of exposure. These factors must be carefully considered when assessing the conservation needs of stucco domes⁷.



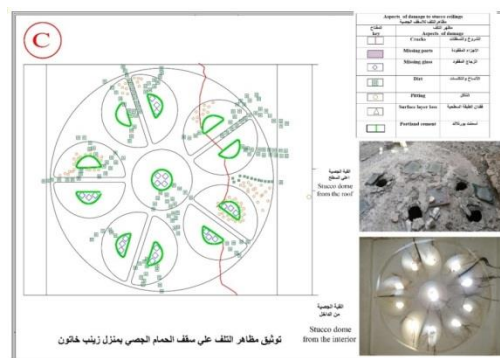
[FIGURE 6]: Shows the deterioration map (Dome A) bathroom ceiling of Zainab Khatun's house 873 AH/1468 AD © Done by the authors

⁶ BRIMBLECOMBE 2002: 126.

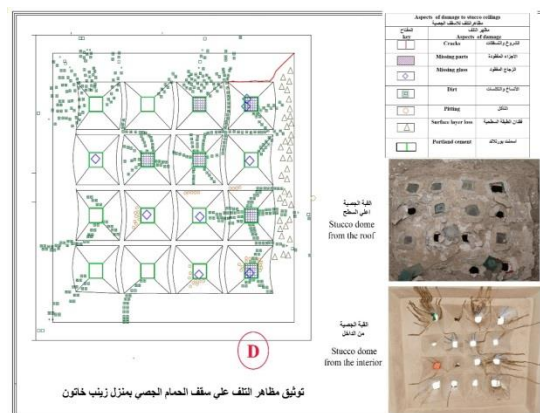
⁷ COLLS 1997: 245.



[FIGURE 7]: Shows the deterioration map «Dome B» bathroom ceiling Zainab *Khatun's* house 873 AH/1468 AD © Done by the authors



[FIGURE 8]: Shows the deterioration map «Dome C» bathroom ceiling Zainab *Khatun's* house 873 AH/1468 AD © Done by the authors



[FIGURE 9]: Shows the deterioration map «Dome D» bathroom ceiling Zainab *Khatun's* house 873 AH/1468 AD © Done by the author

IV. MATERIALS AND METHODS

A. Sampling

Representative samples of the glass-fixing mortar and the stucco dome mortar were collected for characterization using X-ray diffraction (XRD) to determine their mineralogical composition.

B. X-Ray Diffraction «XRD»

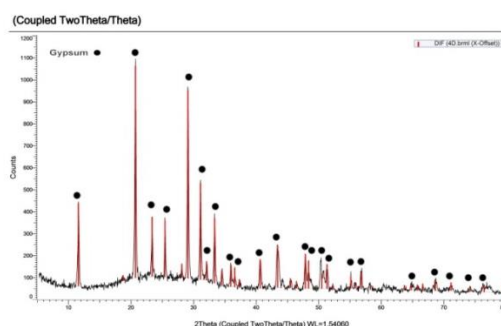
X-ray diffraction «XRD» analysis was conducted using a second-generation D2 PHASER powder diffractometer «Bruker Corporation, Germany» to determine the mineralogical composition of samples collected from the stucco domes of the bathroom ceiling. Two samples were analyzed: the first (4D) was taken from the upper surface of the dome and represents the old, damaged glass-setting mortar, while the second (1A) was collected from the interior of the dome and corresponds to the stucco mortar forming the domes.



[FIGURE 10]: Shows taking 1A, 4D samples from bathroom ceiling stucco dome © Photo taken by MOHAMED ATYIA HAWASH

Sample 4D Glass Fixing Mortar

A sample of the glass- fixing mortar from the dome «sample 4D» was analyzed using X-ray diffraction «XRD». The analysis revealed that the sample is composed of a single mineral phase, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), consistent with ASTM reference cards 33-0311 and 6-46.



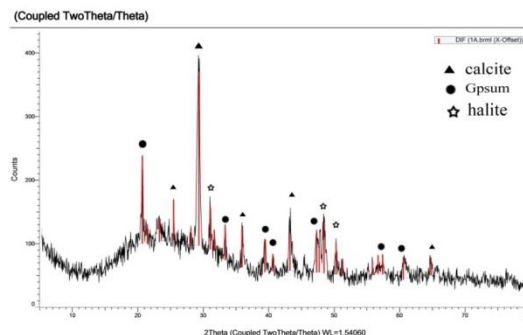
[FIGURE 11]: Shows the XRD pattern of the 4D sample of glass fixing mortar © Done by ABD ALLAH MAHMOUD KAMEL

A Mortar Sample 1A from the Stucco Dome

X-ray diffraction (XRD) analysis of sample 1A indicated that its mineralogical composition consists, semi-quantitatively, of approximately 61.5% calcite (CaCO_3), 31% gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and 7.4% halite (NaCl).

The analysis indicates that the mortar of the stucco domes in the bathroom ceiling is primarily composed of lime and gypsum. The presence of halite is interpreted as a

deterioration byproduct. Therefore, any restoration or completion mortars must replicate the original materials and should not include any salts⁸.



[FIGURE 12]: Shows the XRD pattern of the 1A sample stucco dome © Done by Abd Allah Mahmoud kamel

V. THE PRACTICAL PROTOCOL

Experimental samples were prepared following the composition confirmed by X-ray diffraction analysis [FIGURE 12] consisting of 60% lime and 40% gypsum. The proportion of halite was calculated and incorporated into the gypsum fraction. Samples were cast into 3 cm³ molds and allowed to cure for a minimum of three months to ensure complete carbonation of the lime. Two sets of samples were produced: one containing lime and α -gypsum and the other containing lime and β -gypsum⁹.

Alpha Gypsum Compared to Beta Gypsum

1. Hemi-hydrate $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$

Several methods exist for producing α -gypsum. One approach involves the by-product of hydrochloric acid production. In this method, calcium chloride (CaCl_2) is added at concentrations up to 5 mol/L to concentrated sulfuric acid (H_2SO_4) at concentrations up to 18 mol/L, under temperatures ranging from 13 to 60 °C. The crystal size of the α -hemihydrate can be controlled by adjusting the calcium chloride concentration between 0.1 and 0.4 mol/L, yielding α -hemihydrate crystals with sizes ranging from 30 to 60 μm ¹⁰.

α -Hemihydrate can also be prepared by the thermal conversion of calcium sulfate dihydrate at 110–140 °C in the presence of catalysts such as magnesium chloride (MgCl_2), sodium stearate, sodium citrate, or sodium dodecylbenzene sulfonate¹¹.

α -Hemihydrate can also be prepared by heating under high-pressure conditions in the presence of water vapor within an autoclave. It is synthesized under elevated water

⁸ A stucco sample was taken from inside the dome and it is representative of the dome's stucco composition, because taking a sample from the outside was difficult and dangerous.

⁹ Sample preparation and testing were carried out according to W. (Bill) Wei, Art Conservation: Mechanical Properties and Testing of Materials Copyright © 2021 Jenny Stanford Publishing Pte. Ltd.

¹⁰ THOMAS *et Al.* 2015: 24.

¹¹ CHEN *et Al.* 2013: 3260.

vapor pressure¹² at temperatures above 45 °C in an acidic or saline medium or at temperatures above 97.2 °C in the presence of water under pressure. If the calcination chamber retains moisture, the hemihydrate crystals form more slowly and grow larger in size, resulting in a lower specific surface area and a slower setting rate when mixed with water¹³.

The crystal size of α -hemihydrate gypsum ranges from 0 to 140 μm and variations in crystal size directly influence its mechanical properties through changes in specific surface area. Smaller crystals hydrate more readily, resulting in a denser and mechanically stronger material¹⁴.

2. B- Hemihydrate $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$

β -Hemihydrate gypsum, commonly known as «microporous Plaster of Paris»¹⁵, is produced by dry calcination. In this process, heating in a dry atmosphere yields small crystals with a large specific surface area¹⁶ and high affinity for water. The resulting plaster sets quickly but, exhibits relatively low mechanical strength. β -Hemihydrate is more widely used than α -hemihydrate due to its lower production cost¹⁷.

The primary differences between α - and β -hemihydrates lie in their thermal properties, density, water demand and crystal morphology. X-ray diffraction is not effective for distinguishing between them¹⁸. However, they can be differentiated by their reactivity with water: α -hemihydrates require less water for hydration, whereas β -hemihydrates consume a larger amount. When equal amounts of water are used, α -hemihydrate forms crystals with a more compact arrangement, resulting in mechanically stronger gypsum compared to β -hemihydrate¹⁹.

Samples were cast for mechanical bending tests with dimensions of $2 \times 1 \times 10$ cm, in accordance with the specifications of the mechanical testing apparatus available at the laboratories of the Grand Egyptian Museum.

Following sample preparation and the completion of the designated aging procedures, the specimens were conditioned and subsequently subjected to the following experimental procedures:

- Determination of the physical properties of both formulation groups.
- Immersion of the samples in an acidic solution «sulfuric acid» with a pH below 5.7 for four consecutive soaking cycles.
- Measurement of sample mass after completion of the soaking cycles to evaluate weight loss and identify the formulation exhibiting greater resistance to acid dissolution.

¹² SINGH & MIDDENDORF 2007: 63.

¹³ TORRACA 2009: 87.

¹⁴ BAOHONG *et Al.* 2010: 138.

¹⁵ TORRACA 2009: 50.

¹⁶ ATTIA 2002: 78.

¹⁷ COBURN *et Al.* 1987: 7.

¹⁸ MORRIS 1963: 1299.

¹⁹ FELIX *et Al.* 2001: 840.

- Performance of mechanical bending tests to determine the load-bearing capacity of each formulation group.
- Examination of alpha-gypsum and beta-gypsum specimens using transmission electron microscopy (TEM).
- Observation of sample surfaces after the acid attack cycles using a digital microscope.
- Investigation of the internal microstructure of the samples after acid exposure using scanning electron microscopy (SEM).

VI. CASTING SAMPLES GROUPS

The first group comprised three cubic specimens 3 cm^3 formulated with 60% lime and 40% alpha-gypsum. The second group consisted of three cubic specimens of identical dimensions 3 cm^3 , prepared using 60% lime and 40% beta-gypsum.

A third set of specimens was prepared for mechanical bending tests, with dimensions of $2 \times 1 \times 10\text{ cm}^{20}$. These specimens were formulated using the same compositional ratios as the previous groups «60% lime and 40% gypsum». Three samples incorporated alpha-type gypsum, while the remaining three were prepared with beta-type gypsum.

Both alpha- and beta-gypsum incorporated into the prepared samples were examined using transmission electron microscopy (TEM) in order to characterize and compare their crystalline morphology and particle size distribution.

A sulfuric acid solution with a pH value lower than 5.7 was prepared to simulate acidic environmental conditions. A one-liter beaker was filled with distilled water and concentrated sulfuric acid was added drop wise to increase the acidity of the solution. The pH was continuously monitored using pH indicator strips until the solution reached a value below 5.7. This pH level was selected to approximate the characteristics of acid rain in the environment where the stucco domes are located.

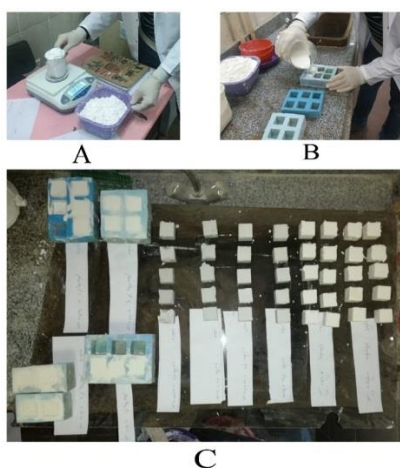
The cubic specimens were immersed in the prepared acidic solution for 60 minutes and subsequently allowed to dry at room temperature. This immersion–drying procedure was repeated for four consecutive cycles. The samples were weighed before and after the soaking cycles to determine mass loss resulting from acid exposure. In addition, physical properties, including bulk density and porosity, were evaluated to assess the extent of deterioration and structural changes induced by the acidic environment.

The condition of the specimens and their resistance to acid-induced deterioration were assessed by calculating the percentage of mass loss resulting from exposure to the acidic solution. Surface alterations were examined using a digital microscope to evaluate morphological changes and signs of erosion. Furthermore, the internal microstructure of the specimens was investigated using scanning electron microscopy (SEM) to identify structural modifications associated with acid attack.

A mechanical bending test was performed to evaluate the load-bearing capacity of the specimens and to determine which gypsum type—alpha or beta—exhibited superior

²⁰ ISO 3051:1974 gypsum plaster, tests, mechanical tests, hardness tests, bend tests, compression tests, test specimens, bending stress, bearing stress.

mechanical resistance, thereby identifying the most suitable material for use in restoration applications.



[FIGURES 13/A-C]: A. Shows Preparation of the proportions of the components of each group of samples; B. Casting in silicone molds with a cube size of 3 cm³; C. Preparation of sample groups for evaluation of physical properties, acid resistance and mechanical tests

© Photo taken by OSAMA SAMIR



[FIGURES 14/A- C]: A. Shows Preparing an acidic sulfuric acid solution; B. Soaking samples in the acidic solution; C. Weighing samples before and after soaking in the acidic solution © Photo taken by

MOHAMED ATYIA HAWASH

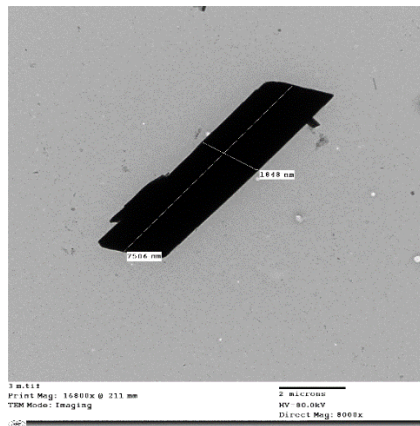


[FIGURES 15/A-B]: Shows Mechanical testing apparatus and three-point bending test method © Photo taken by OSAMA SAMIR

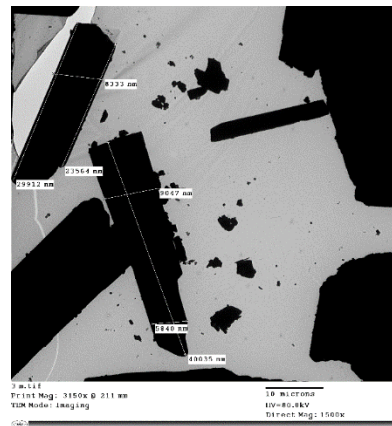
VII. EVALUATION OF PHYSICAL AND MECHANICAL PROPERTIES AFTER AGING WITH ACID SOLUTION

The alpha- and beta-gypsum present in the samples were examined using a JEM-1400 Plus LaB₆ «Lanthanum Hexaboride» transmission electron microscope (TEM) at 120 kV and a magnification of $\times 1,200,000$ to characterize the morphology and size of their crystals.

The analysis revealed that alpha-gypsum crystals were significantly larger than beta-gypsum crystals, with the size of alpha-gypsum crystals being approximately 12 times greater than that of beta-gypsum crystals .



[FIGURE 16]: Shows beta gypsum under the transmission electron microscope (TEM)8000x
The crystal size appears to be around 2- 3 microns of fallacy shaped crystal © Done by OSAMA SAMIR



[FIGURE 17]: Shows alpha gypsum under the transmission electron microscope (TEM) 1500x The crystal size appears to be around 30- 40 microns of prismatic shaped crystal © Done by OSAMA SAMIR

Code A Sample Components	Weight of Cubes Before and After Soaking in Water	
Group(1) consists of 60% lime + 40% beta gypsum.	Weight before soaking	18.89 g
	Weight after soaking	33.72 g
Density (g/cm ³)	0.69	
Porosity (%)	54	

[TABLE 1]: Shows the physical properties of samples «group A» © Done by OSAMA SAMIR

Code B Sample Components	Weight of Cubes Before and After Soaking in Water	
Group (2) consists of 60% lime + 40% Alpha Gypsum.	Weight before soaking	17.84 g
	Weight after soaking	33.25 g
Density (g/cm ³)	0.66	
Porosity (%)	57	

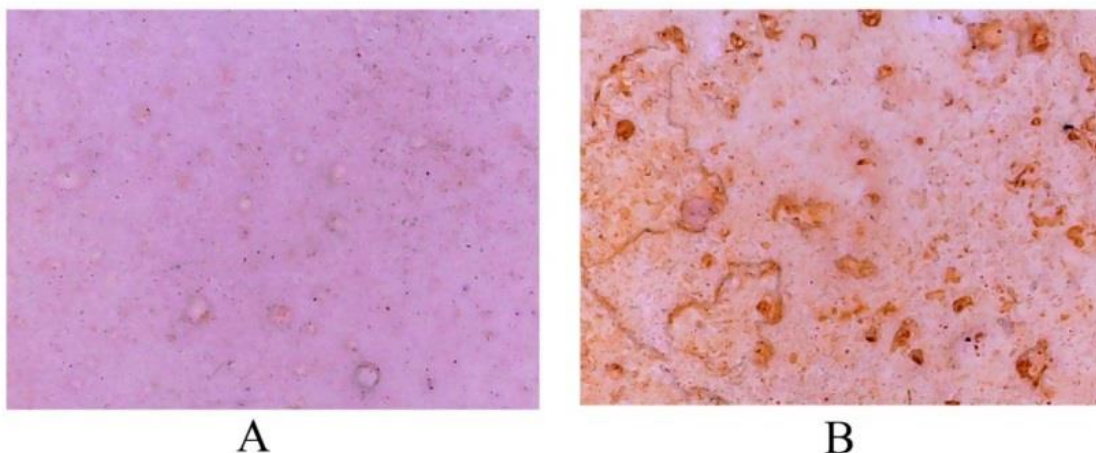
[TABLE 2]: Shows the physical properties of samples «group B»© Done by OSAMA SAMIR

	Weight of Cubes Before and After Soaking in the Acid Solution			
Code A Sample components	cycle 1	Cycle 2	Cycle 3	Cycle 4
Group (1) consists of 60% lime + 40% beta gypsum.	18.89	19.02	18.39	17.79
	33.72	33.94	34.29	35.64
Density (g/cm ³)	0.69	0.70	0.68	0.65
Porosity (%)	54	55	58	66

[TABLE 3]: Shows the physical properties changing with repeated soaking cycles in acid solution of samples «group A» © Done by the authors

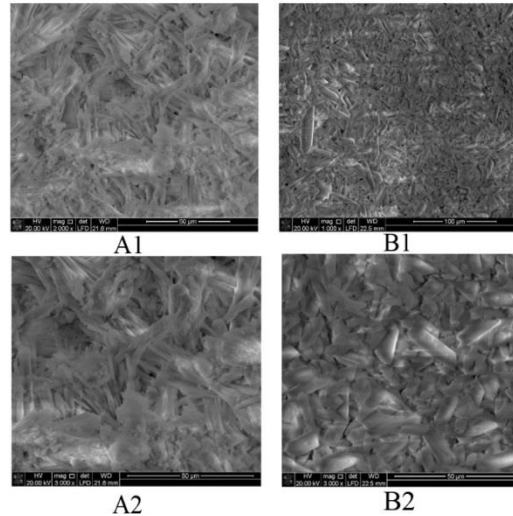
	Weight of Cubes Before and After Soaking in the Acid Solution			
Code B Sample components	cycle 1	Cycle 2	Cycle 3	Cycle 4
Group (2) consists of 60% lime + 40% Alpha Gypsum.	17.84	18	17.02	16.24
	33.25	33.44	35.69	37.53
Density (g/cm ³)	0.66	0.66	0.63	0.60
Porosity (%)	57	57	69	78

[TABLE 4]: Using a portable digital microscope «p-DM» © Done by the authors



[FIGURES 18/A-B]: Shows Surface morphology study using «p-DM»100X for samples code A and B© Photo taken by OSAMA SAMIR

Study of the Internal Structure Using a Scanning Electron Microscope SEM



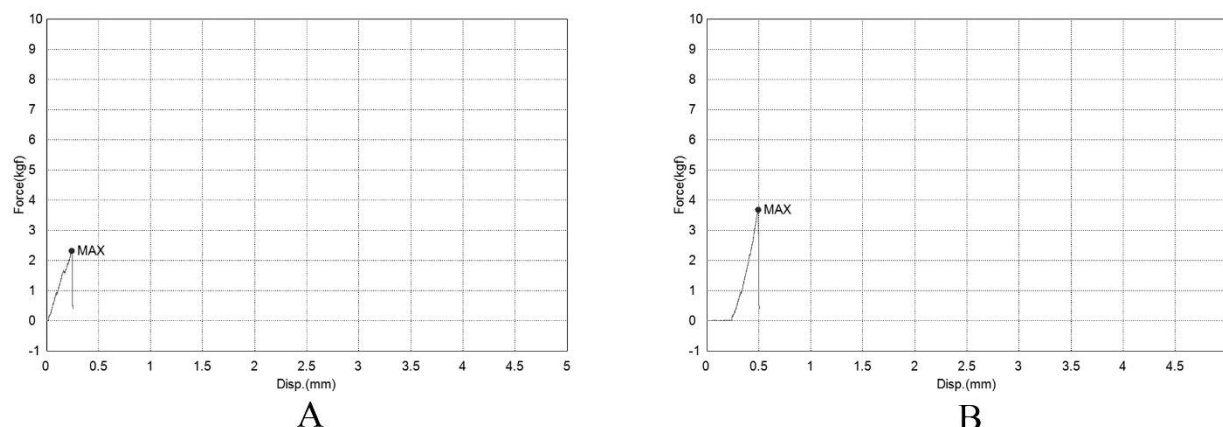
[FIGURES 19/A1-B2]: Shows internal structure using SEM; A1. 2000x beta- needle gypsum crystals and their interpenetration with the eroded calcite crystals; B1. 1000x the large alpha- needle gypsum crystals with the smaller calcite crystals, creating a cohesive and homogeneous structure; A2. 3000X the beta-needle gypsum crystals is shown with their interpenetration with the eroded calcite crystals, revealing a depression in the plane, creating voids in the internal structure; B2. 3000x the large alpha- needle gypsum crystals with the smaller calcite crystals, which take on semi-circular or rhomboidal shapes, creating a cohesive and homogeneous structure © Photo taken by OSAMA SAMIR

VIII. BENDING TEST FOR SAMPLES TO DETERMINE THEIR SUITABILITY FOR THE STRUCTURAL FUNCTION ON THE STUCCO DOMES STUCCO DOMES

The bending tests were conducted using an AGS-V Series Shimadzu testing machine equipped with 50 N load cells. The tests employed a precision ball-screw drive under strain-controlled conditions, utilizing a high-precision setup with a measurement accuracy of 1/500.

Test Mode	Single	Test Type	3 Point Bend
Speed	1mm/min	Shape	Plate
No of Batches:	1	Qty/Batch:	1
	Max_Force Calc. at Entire Areas kgf	Max_Stress Calc. at Entire Areas kgf/mm2	Max_Stroke Calc. at Entire Areas mm
group A	2.30931	0.09622	0.24263
group B	3.66559	0.15273	0.49444

[TABLE 5]: Shows Mechanical bending test values of samples «group A, B»



[FIGURES 20/A-B]: A. Shows diagram illustrates the results of the mechanical bending test for Group A sample; B. Diagram illustrate the results of the mechanical bending test for Group B sample © Photo taken by OSAMA SAMIR

IX. DISCUSSION

Sample groups A and B were prepared to evaluate their physical properties and resistance to acid attack under conditions simulating the environmental exposure of archaeological domes. The objective was to identify the gypsum type that provides superior mechanical performance, as domes function as structural elements requiring adequate mechanical strength. Achieving this is challenging because stucco is inherently weak in both physical and mechanical properties²¹. Most stucco components are traditionally used for architectural finishing, such as decorative elements or surface rendering, rather than for structural construction applications.

X-ray diffraction analysis [FIGURE 12] confirmed that the stucco used in the domes consists of 60% lime and 40% gypsum. Both constituents are calcareous minerals, rendering the stucco highly susceptible to attack by dilute acids²² naturally present in the environment. This acidity arises from atmospheric pollutants in Cairo, which react with rainwater or dew to form weak acids. Such acidic exposure can adversely affect the stucco domes, causing various forms of deterioration including cracking, layer delamination, surface erosion and pitting, as illustrated in [FIGURES 6-9].

Significant damage was observed due to the use of cement to fix the glass into the stucco cavities of the domes, as the cement easily detached from the underlying stucco. Consequently, the glass elements were lost again, along with remnants of the cement. X-ray diffraction analysis [FIGURE 11] indicates that the original fixing material was gypsum paste. Gypsum is generally sensitive to water, dissolving in concentrations ranging from 0.0147 to 0.0182 mol/L at 25 °C «equivalent to 2–2.5 g/L»²³ and is even more susceptible to acidic water, which accelerates dissolution and leads to glass detachment. The use of

²¹ KHALIL *et Al* 2013: 533.

²² BERNHARD 2002: 171.

²³ LEBEDEV & KOSORUKOV 2017: 207.

cement proved ineffective because of its incompatibility with the physical and mechanical properties of the dome's stucco. This issue motivated the present research, which aims to enhance the properties of the gypsum material used in the restoration and completion of the domes' exterior.

To enhance the durability of the domes, an external protective layer was applied following the reinstallation of the lost glass elements. Two groups of samples, Group A and Group B, were prepared using the same stucco composition found in the domes, consisting of 60% lime and 40% gypsum. The objective of this study was to improve the properties of the gypsum by incorporating two different types—alpha and beta gypsum—and comparing their performance. This comparison aimed to identify the most suitable type for restoration applications, providing both adequate mechanical properties for the dome as a structural element and enhanced resistance to environmental exposure. Gypsum was selected as the primary material because, although it is generally poorly soluble in water, it is more susceptible to water and acidic solutions than lime, the secondary component of the stucco. By varying the type of gypsum used, it is expected that the material properties can be improved, as alpha and beta gypsum differ in their production methods and resulting physical and mechanical characteristics.

In conclusion, alpha-gypsum crystals are larger than beta-gypsum crystals. In the prepared samples, the length of alpha crystals ranged from 30 to 40 μm and their width from 8 to 9 μm , making them approximately 12 times larger than beta-gypsum crystals, which measured about 2.5 μm in length and 2 μm in width [FIGURES 16-17]. The difference in crystal size significantly influenced the properties of the two cast sample groups A and B. Group A, containing beta-gypsum, exhibited a density of 0.69 g/cm^3 and a porosity of 54% [TABLE 1]. In contrast, Group B, containing alpha-gypsum, showed a slightly lower density of 0.66 g/cm^3 and higher porosity at 57% [TABLE 2], indicating that the samples in Group B are less dense and more porous than those in Group A.

The physical properties of both sample groups, Alpha and Beta gypsum, were evaluated after subjecting them to artificial weathering using an acidic solution. The results showed significant changes due to acid exposure:

- **Group A «Beta gypsum»:** After the first soaking cycle, the density was 0.69 g/cm^3 and porosity was 54%. Following the fourth acid-aging cycle, the density decreased to 0.65 g/cm^3 , representing a 6% reduction, while the porosity increased to 66%, a 22% increase compared to the initial value [TABLE 3].
- **Group B «Alpha gypsum»:** After the first soaking cycle, the density was 0.66 g/cm^3 and porosity was 57%. After the fourth cycle, the density decreased to 0.60 g/cm^3 , a 9% reduction and the porosity increased to 78%, corresponding to a 31% increase from the initial measurement [TABLE 4]. These results indicate that Alpha-gypsum samples experienced a greater decrease in density and a more pronounced increase in porosity under acidic conditions compared to Beta-gypsum samples.

The results indicate that the deterioration in physical properties—density and porosity—was less pronounced in Group A «Beta gypsum» than in Group B «Alpha

gypsum». Specifically, the reduction in density and the increase in porosity were both greater in Group B compared to Group A.

This decline in physical properties is further supported by observations of the sample surfaces under a digital microscope. The surface of Group A «Beta gypsum» samples maintained better cohesion, whereas Group B «Alpha gypsum» samples exhibited peeling of the surface layer and the formation of pits [FIGURES 18/A-B]. Examination of the internal structure revealed that Group A «Beta gypsum» samples contained needle-shaped gypsum crystals alongside calcite crystals with eroded edges, resulting in a relatively weak internal structure characterized by high porosity and large voids [FIGURES 19/A1-A2].

The internal structure of Group B «Alpha gypsum» samples was observed to be cohesive, with a well-distributed arrangement of large alpha-gypsum crystals interspersed with semi-circular calcite crystals [FIGURES 19/B1-B2]. Interestingly, although Group A «Beta gypsum» exhibited better physical properties in terms of density and porosity, the internal microstructure of Group B appeared more organized under scanning electron microscopy. This apparent contradiction can be explained by the large size of alpha-gypsum crystals, which are naturally less dense than beta-gypsum crystals.

These large alpha crystals acted as nucleation centers around which smaller calcite crystals cohered, resulting in a structurally cohesive internal framework for Group B. This cohesive microstructure contributed to the superior mechanical performance of Group B samples. In bending tests, Group B achieved a maximum bending stress of 3.68 kg on samples measuring 2 cm × 1 cm × 10 cm, compared to 2.3 kg for Group A. Moreover, the displacement before complete failure in Group B was approximately 0.49 mm, nearly double that of Group A, which reached only 0.24 mm. These results indicate that Group B «Alpha gypsum» outperformed Group A «Beta gypsum» in terms of both load-bearing capacity and deformation before collapse [TABLE 5 & FIGURES 20/A-B].

X. CONCLUSION

The tests indicate that Alpha gypsum exhibited superior internal structural cohesion and mechanical performance. Although its physical properties—density and porosity—were lower than those of Group A «Beta gypsum», the microstructural arrangement of Alpha gypsum provided a more effective and efficient framework for fulfilling the structural function of the domes, even under exposure to acidic conditions that promote migration of stucco components. Therefore, for restoration and conservation of the domes, Alpha gypsum is recommended over Beta gypsum, while maintaining the lime proportion as determined by X-ray diffraction analysis of the original stucco material in the domes under study.

DISCLOSURE STATEMENT

No Potential conflict of interest was reported by the authors

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BIOCLEANING OF BLACK CRUSTS-AFFECTED HISTORIC BUILDINGS USING SULFATE-REDUCING BACTERIA AS A SUSTAINABLE CONSERVATION STRATEGY

By

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ABSTRACT

[EN] This study aims to evaluate the effectiveness of the sulfate-reducing bacterium *Desulfovibrio desulfurican* strain 27774, combined with a non-ionic detergent as a pre-treatment, for the removal of black crusts from the limestone façades of the Sultan Qalawun Complex in Historic Cairo. The Sultan Qalawun Complex is a significant Mamluk-era monument whose intricately carved limestone façades have been heavily affected by the accumulation of black crusts, mainly composed of gypsum and atmospheric particles resulting from prolonged exposure to pollution. These deposits obscure the original appearance of the stone and accelerate its deterioration. Although sulfate-reducing bacteria have proven effective in removing black crusts from stone monuments, the lengthy treatment time required for thick crusts remains a major challenge. To address this issue, the performance of *Desulfovibrio desulfurican* strain 27774 in combination with a non-ionic detergent pre-treatment was investigated. The proposed treatment achieved complete crust removal and reduced the cleaning time by 50% compared to biological treatment alone. Various analytical techniques, including visual inspection, colorimetric measurements, stereomicroscopy, scanning electron microscopy coupled with energy-dispersive X-ray analysis (SEM-EDX), X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR), were employed before and after treatment. The results confirmed the successful removal of the black crust and the restoration of the limestone's original color and surface features without causing damage. Furthermore, the findings demonstrated that the proposed biocleaning approach is highly selective, sustainable and safe for the conservation of historic limestone buildings.

KEYWORDS: Biocleaning, black crusts, Gypsum, historical buildings, limestone, pre-treatment, sulfate-reducing bacteria.

[AR] التنظيف الحيوي للمباني التاريخية المتأثرة بالقشور السوداء باستخدام البكتيريا المختزلة للكبريتات *Desulfovibrio desulfurican* سلالة 27774، مع منظف غير أيوني كمعالجة مسبقة لإزالة القشور السوداء من الواجهات الحجرية لمجمع السلطان قلاوون في القاهرة التاريخية. يعد هذا المجمع أثراً هاماً من العصر المملوكي، ويشتهر بواجهاته المنحوتة بدقة من الحجر الجيري، والتي تأثرت بشدة بتراكم القشور السوداء المكونة أساساً من الجبس وجزيئات الغلاف الجوي نتيجة التعرض طويل الأمد للتلوث، مما يحجب المظهر الأصلي للحجر ويسرع من تدهوره. وعلى الرغم من أن البكتيريا المختزلة للكبريتات أثبتت فعاليتها في إزالة هذه القشور، إلا أن العملية الطويلة لإزالة القشرة السميكة لا تزال تشكل تحدياً ومخاوف كبيرة. وقد حققت المعالجة المقترحة في هذه الدراسة إزالة كاملة للقشرة وخفضت وقت التنظيف بنسبة 50% مقارنة بالمعالجة البيولوجية وحدها. وللتحقق من ذلك، تم إجراء تحليلات متعددة قبل وبعد المعالجة تشمل: الفحص البصري، القياسات اللونية، الميكروسكوب المجسم، الميكروسكوب الإلكتروني الماسح المقترن بوحدة تشتت طاقة الأشعة السينية، حيود الأشعة السينية، والتحليل الطيفي بالأشعة تحت الحمراء؛ والتي أكدت نجاح إزالة القشرة السوداء واستعادة اللون والخواص الأصلية للحجر الجيري دون التسبب في أي ضرر. وأظهرت النتائج أن طريقة التنظيف الحيوي انتقائية للغاية ومستدامة وأمنة لحفظ المباني التاريخية.

الكلمات الدالة: البكتيريا المختزلة للكبريتات، التنظيف الحيوي، الجبس، الحجر الجيري، القشور السوداء، المباني التاريخية، المعالجة المسبقة.

I. INTRODUCTION

The preservation of cultural heritage has become a global concern due to the rapid deterioration of stone materials caused by environmental conditions¹. Air pollution poses a significant threat to stone cultural heritage, especially in urban areas where limestone monuments are constantly exposed to atmospheric pollutants². Pollutants, such as sulfur dioxide SO₂, nitrogen oxides NO_x, and particulate matter, cause various forms of deterioration, including salt efflorescence, erosion, soiling and encrustation³.

One phenomenon affecting limestone monuments, especially in sheltered areas, is the formation of black crusts⁴. These crusts develop on stone surfaces protected from rainfall and washout⁵. Black crust forms when atmospheric SO₂ reacts with calcite CaCO₃ in limestone, producing gypsum CaSO₄·2H₂O⁶. As this layer grows, it traps atmospheric particles, mainly carbonaceous particles, fly ash, dust and metallic debris, forming dense, dark deposits that strongly adhere to the surface⁷. The accumulation of this crust causes significant material deterioration; its different properties from limestone lead to fissures, scaling, granular disintegration and the detachment of the original surface⁸.

Removing these crusts is essential for preserving cultural heritage, restoring its authentic appearance and preventing further decay. However, cleaning these altered layers remains one of the most delicate tasks in stone conservation⁹. Mechanical and chemical methods are commonly used; they can be non-selective and too aggressive¹⁰.

The laser cleaning method greatly contributes to the treatment of stone alterations. However, it provides precise control and high selectivity; in some cases, it may not completely remove deposits and can cause color changes. Additionally, cleaning large surface areas can be cost-prohibitive¹¹.

Recently, biotechnological methods have become sustainable, scientifically grounded alternatives for stone cleaning. They use specific microorganisms to target and modify undesired deposits under controlled conditions. Sulfate-reducing bacteria (SRB), *Desulfovibrio spp.*, have shown promising potential for selectively removing gypsum crusts from carbonate stones¹². Many studies confirmed the effectiveness of strains *Vulgaris* and *Desulfuricans*. Their consistent performance in laboratory settings and large-scale field applications demonstrates high selectivity and efficiency in

¹ ALSHEHHI & SIRAY 2025: 244.

² COMITE *et Al.* 2021: 111565-111573; ROVELLA *et Al.* 2021: 1-9; LI *et Al.* 2025: 247.

³ AURAS *et Al.* 2018: 323; YAN & WANG 2024: 1-21; ROPIQUET *et Al.* 2025: 1-10.

⁴ MOROPOULOU *et Al.* 1998: 967-982; HAMAD *et Al.* 2022: 441-450.

⁵ CALPARSORO *et Al.* 2017: 9468-9480; RUFFOLO *et Al.* 2023: 119.

⁶ AUSSET *et Al.* 1998: 2859-2863; ALLEN *et Al.* 2000: 35-38.

⁷ SAMARA *et Al.* 2020: 1-13.

⁸ FRONTEAU *et Al.* L 2010: 25-34; TÖRÖK *et Al.* 2011: 675-693.

⁹ ORMSBY *et Al.* 2024: 1-4.

¹⁰ BOSCH-ROIG *et Al.* 2015: 1227-1241; RANALLI & ZANARDINI 2021A: 583-603.

¹¹ SALIMBENI *et Al.* 2003: 72-76; RANALLI & ZANARDINI 2021B: 263-280.

¹² SOFFRITTI *et Al.* 2019: 3853; GUEIDÃO *et Al.* 2021: 22-44; PYZIK *et Al.* 2021:177; RANALLI & ZANARDINI 2021A: 583-603.

removing black crusts from various white and colored lithotypes, including limestone¹³, marble¹⁴, green serpentine, red marlstone¹⁵ and sandstone¹⁶.

During its metabolic processes, SRB disintegrates gypsum crusts by reducing sulfate ions (SO_4^{2-}) to sulfide (S^{2-}), while the released calcium ions react with carbon dioxide, resulting in calcite precipitation. This makes biological treatment a cleaning and a consolidation process¹⁷. SRB specifically targets sulfates, thereby softening and dissolving black crusts. This selectivity helps preserve the substrate and the noble patina¹⁸. However, when crusts are thick and compact, the biological method can be slow and may require multiple applications¹⁹. Combining chemical pre-treatment with biological cleaning has been shown to improve results, since chemical treatment removes less cohesive particulate matter within crusts, thus reducing overall cleaning time²⁰.

The primary aim of this study is to evaluate the potential of the sulfate-reducing bacterium *Desulfovibrio desulfuricans* strain 27774, combined with chemical pre-treatment, for removing black crusts from the limestone surface of the Sultan Qalawun Complex. The effectiveness of this approach was thoroughly assessed using various microscopic and analytical techniques, including visual inspection, colorimetric measurements, stereomicroscopy, scanning electron microscopy with an energy-dispersive X-ray spectrometer (SEM-EDX), X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR).

II. MATERIALS AND METHODS

1. Sampling

Blackened limestone samples from the Sultan Qalawun Complex were used. Two treatments were tested:

A. Biological treatment, labeled as [SAMPLE N°.1].

B. Combined chemical-biological treatment, labeled as [SAMPLE N°.2].

2. Cleaning Procedures

A. Biological Treatment

The biological cleaning treatment used the sulfate-reducing bacterium *Desulfovibrio desulfuricans* strain 27774. The cells were cultivated in DSMZ 63 medium, containing K_2HPO_4 (0.5 g/L), NH_4Cl (1.0 g/L), Na_2SO_4 (1.0 g/L), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1 g/L), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (2.0 g/L), DL-sodium lactate (2.0 g/L), yeast extract (1.0 g/L), resazurin (1.0 mg/L), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.5 g/L), sodium thioglycolate (0.1 g/L) and ascorbic acid (0.1 g/L). They were incubated at 30°C for four days under anaerobic conditions.

¹³POLO 2010: 1-14.

¹⁴GAURI 1992: 160-165; CAPPITELLI *et Al.* 2005: 77; CAPPITELLI *et Al.* 2007: 5671-5675; GIOVENTÙ *et Al.* 2011: 832-839; GIOVENTÙ & LORENZI 2013: 123-129; TROIANO *et Al.* 2013: 294-304.

¹⁵GIOVENTÙ *et Al.* 2011: 832-839.

¹⁶ALFANO *et Al.* 2011: 1004-1011.

¹⁷CAPPITELLI *et Al.* 2006: 3733-3737; BALLOI *et Al.* 2015: 109-119.

¹⁸BATABYAL 2020: 13-24; SINGH & GHOSH 2025: 1-10.

¹⁹GIOVENTÙ & LORENZI 2013: 123-129.

²⁰TROIANO *et Al.* 2013: 294-304.

The cultures were then filtered through a cellulose filter «Rapida A Perfecte, 8 µm» to remove iron sulfide precipitates while allowing bacteria to pass through. After centrifugation, the cell pellet was suspended in an anoxic phosphate buffer «containing KH_2PO_4 , $0.408 \text{ g}\cdot\text{l}^{-1}$ and K_2HPO_4 , $0.522 \text{ g}\cdot\text{l}^{-1}$ », supplemented with $0.599 \text{ g}\cdot\text{l}^{-1}$ sodium lactate at pH 7.0, reaching a final cell density of approximately 10^8 cells/mL. All procedures were conducted under anaerobic conditions within a glove box²¹.

The biomass was embedded in an Arbocel polymeric matrix (CTS, Italy) used as a delivery system. Surfaces designated for treatment were pre-moistened with phosphate buffer and then covered with tissue paper before application. To minimize evaporation, the biological cleaning system was covered with a polyvinyl chloride film. After treatment, the bioformulation was removed by removing the tissue paper, then thoroughly rinsing the area with distilled water. Treatments lasting 22 hours were applied to the affected surfaces until the black crust was completely removed²².

B. The Combined Chemical-Biological Treatment

The combined chemical-biological treatment was conducted in two stages. First, chemical pre-treatment involved applying a wet poultice composed of Arbocel in a 1.5% solution of the non-ionic detergent «Tween 80» in distilled water. This poultice was placed on the black crust for 6 hours and the treated area was covered with a polyvinyl chloride film. Next, the area was rinsed and any remaining poultice was removed by washing with distilled water and gentle brushing. The second stage involved biological treatment, as previously described, consisting of 22-hour applications until the black crust was completely removed²³.

3. Methods of Treatment Evaluation

A. Visual Inspection

Visual inspection is essential for evaluating cleaning effectiveness, as systematic observation before, during and after treatment helps documents the progress of crust removal and surface changes.

B. Colorimetric Measurements

Color variations were measured using the Optimatch 3100 device, with color values quantified based on the L^* , a^* and b^* coordinates. Different areas of the treated, untreated and reference samples were selected for measurement. The color data were recorded in the CIE Lab* color space²⁴. The colorimeter detects chromatic shifts associated with cleaning and the removal of the black crusts. It is essential for verifying cleaning effectiveness and ensuring that interventions remain visually consistent with the substrate²⁵.

²¹ CAPPITELLI *et Al.* 2006: 3733-3737; CAPPITELLI *et Al.* 2007: 5671-5675.

²² POLO *et AL* 2010: 1-14; GIOVENTÙ & LORENZI 2013: 123-129.

²³ TROIANO *et Al.* 2013: 294-304.

²⁴ MONACO *et Al.* 2011: 189-202.

²⁵ DE ROSA *et Al.* 2025: 1-23.

C. Stereo Microscope

Surface morphology was examined using a Leica NZ6 stereomicroscope, which enabled a detailed assessment of surface texture, crust adhesion and the overall appearance of the limestone before and after treatment.

D. SEM-EDX Analysis

A Quanta 250 FEG microscope equipped with an energy dispersive X-ray spectrometer (EDX) was used to study microstructural changes after the treatment. Additionally, EDX analysis was performed to determine the elemental composition of the treated surfaces.

E. X-ray Diffraction Analysis «XRD»

Mineralogical characterization was carried out using a Philips PW1840 X-ray diffractometer, equipped with a copper (Cu) anode source and operated at 40 kV and 25 mA. It used characteristic wavelengths of $K\alpha_1 = 1.54056 \text{ \AA}$ and $K\alpha_2 = 1.54439 \text{ \AA}$, with an intensity ratio of 0.500 and a 0.2 receiving slit; no monochromator was used. XRD analyses were performed to assess mineralogical changes related to the bio-cleaning process.

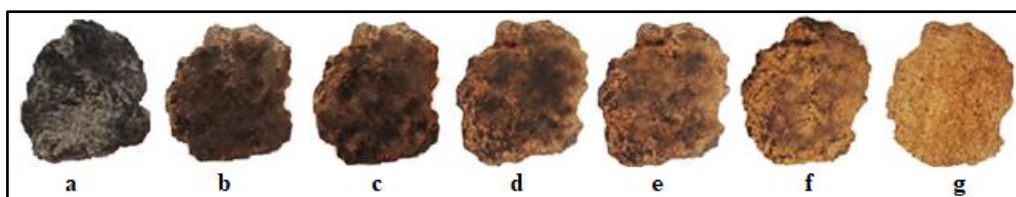
F. Fourier-Transform Infrared Spectroscopy «FTIR»

An ATR-FTIR spectroscopy was used with a Jasco 6100 spectrometer equipped with an attenuated total reflectance (ATR) accessory. Spectra were collected in the transmission mode using TGS detectors, with the following settings: a spectral range of $400\text{--}4000 \text{ cm}^{-1}$, a scan rate of 2 mm/s and a resolution of 4 cm^{-1} . FTIR analysis was performed before and after treatment to evaluate changes in the composition of the limestone surface.

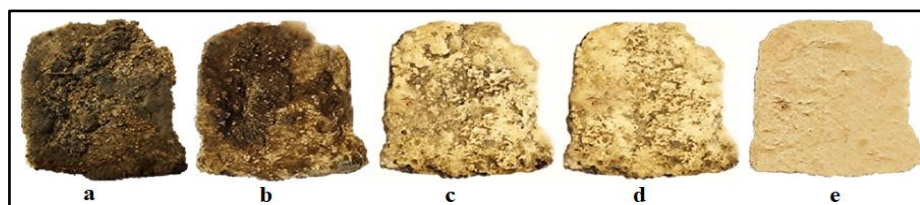
III. RESULTS

A. Visual Inspection

Visual inspection showed that the black crust was completely removed after six applications of the biological treatment alone [FIGURES 1/A-G] and four applications of the combined chemical-biological treatment [FIGURES 2/A-E]. The chemical pre-treatment involved a single application that softened and removed less compact particulate matter within the black crust. In some areas, the layers overlapping the limestone substrate were partially removed [FIGURE 2/B]. However, complete removal was only achieved after three biological applications. The final cleaning results of both biological methods were similar, with biological cleaning demonstrating high effectiveness in crust removal.



[FIGURE 1]: Evolution of the limestone surface showing the progress of the black crust removal during biological treatment [SAMPLE N°.1] © Photo taken by the researchers



[FIGURE 2]: Evolution of the limestone surface showing the progress of the black crust removal during chemical-biological treatment [SAMPLE N°.2] © Photo taken by the researchers

B. Colorimetric Evaluation

Colorimetric analysis showed a significant total color difference (ΔE) between the blackened and cleaned surfaces. The notable increase in lightness (ΔL) indicated the successful removal of the opaque black crust, revealing the lighter carbonate substrate.

Positive (Δa) and (Δb) values also suggest the restoration of the original limestone tones [TABLES 1-2]. The chemical pre-treatment resulted in a notable (ΔE), indicating the removal of less coherent opaque particulate matter within the crust [TABLE 2]. The comparison between the cleaned surface and the reference surface from the unweathered internal part of the stone showed a negligible chromatic difference (ΔE), confirming that the cleaning process preserved the original optical properties [TABLES 1-2]

Cleaned Surface vs. Altered Surface				
Sample	ΔL^*	Δa^*	Δb^*	ΔE^*
Nº. 1	35.62	4.18	5.11	44.98
Cleaned Surface vs. Reference Surface				
Nº. 1	0.27	0.05	0.30	0.62

[TABLE 1]: Shows changes in color parameters on the limestone surface [SAMPLE N°.1] after biological treatment © Done by the researchers

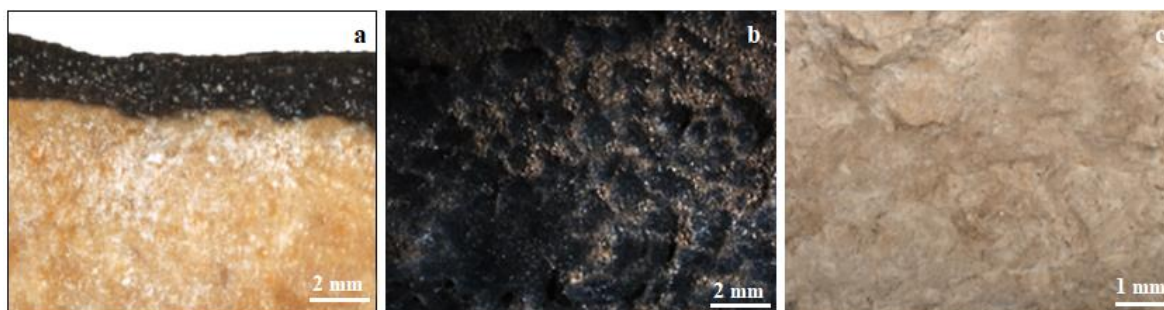
Pre-Treatment Surface vs. Altered Surface				
Sample	ΔL^*	Δa^*	Δb^*	ΔE^*
Nº. 2	25.9	0.44	0.30	26.64
Cleaned Surface vs. Altered Surface				
Nº. 2	34.2	5.44	3.30	42.94
Cleaned Surface vs. Reference Surface				
Nº. 2	0.6	0.04	0.13	0.77

[TABLE 2]: Shows changes in color parameters on the limestone surface [SAMPLE N°.2] after chemical-biological treatment © Done by the researchers

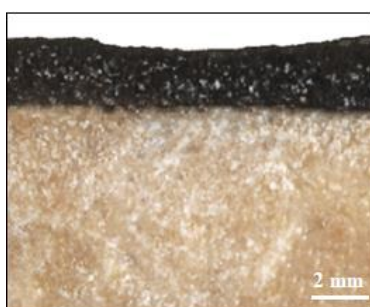
C. Stereo Microscope

Stereomicroscopic examination provided a detailed assessment of the limestone surface's morphology. The limestone was covered by a compact, dense, dark heterogeneous crust, giving it a granular appearance and obscuring its natural texture [FIGURES 3/B & 5/A]. The polished cross-sections revealed a stratigraphic structure; the samples appeared to consist of a single crust layer over the stone substrate. Alteration was observed to continue along the entire section, showing an irregular morphology and embedded with black- colored particles of various sizes, with a thickness ranging

from 1.21 cm to 1.42 cm in [SAMPLE N^o.1] and from 1.32 cm to 1.45 cm in [SAMPLE N^o.2] [FIGURES 3/A & 4]. The chemical pre-treatment effectively loosened superficial deposits that were less attached to the crust [FIGURE 5/B]. After biological treatments, a noticeable change in morphology was observed; the black crust was removed, exposing the underlying limestone and restoring the stone's original visual and morphological features [FIGURES 3/C & 5/C].



[FIGURES 3/A-C]: Stereo micrographs of a limestone [SAMPLE N^o.1]; A. A cross-section of the black crust and underlying limestone; B. Before treatment; C. After biological treatment © Done by the researchers



[FIGURE 4]: A cross-section of the black crust and underlying limestone [SAMPLE N^o.2] © Done by the researchers

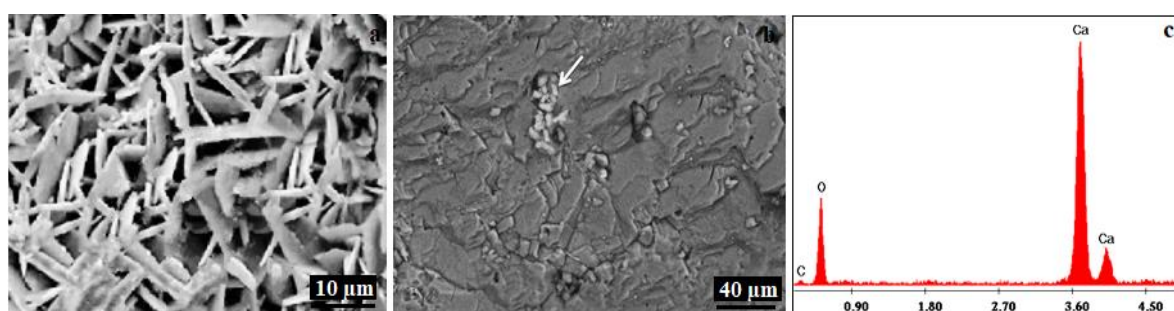


[FIGURES 5/A-C]: Stereo micrographs of a limestone [Sample N^o.2]; A. Before treatment; B. After chemical pre-treatment; C. After biological treatment © Done by the researchers

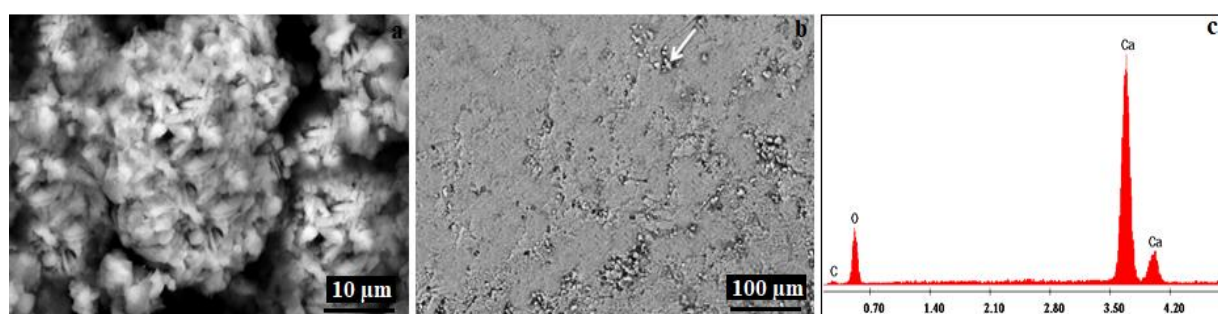
D. SEM-EDX Analysis

The scanning electron microscope was used to examine the limestone surface morphology, revealing a non-uniform layer of gypsum crystals, with well-formed, acicular and rosette-like shapes forming a continuous encrustation over the substrate [FIGURES 6/A & 7/A]. A cross-section analysis showed that the black crusts mainly consisted of Ca, S and Si, along with Fe, Al, Mg, K, Na and Cl [FIGURES 8/A-B & 9/A-B].

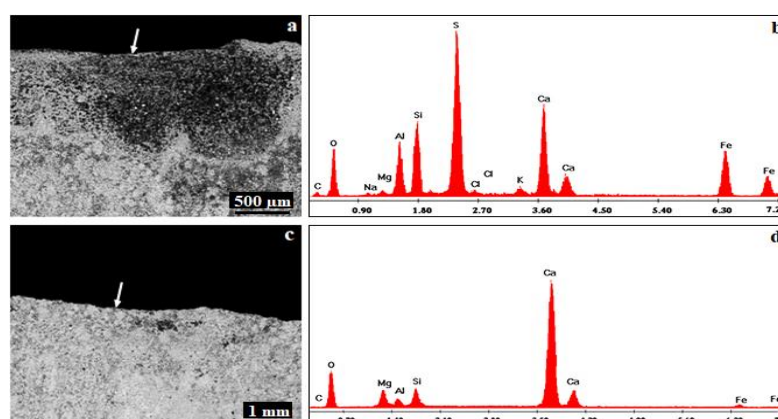
After chemical pre-treatment, gypsum crystals remained; however, there was a noticeable reduction in Si, Al, Fe and K [FIGURES 9/C-D]. Following biological treatments, SEM revealed a significant change: the gypsum crystals were removed, exposing the carbonate substrate without causing damage [FIGURES 6/B & 7/B]. SEM observations also detected calcite precipitation on the treated surfaces, resulting from the bio-cleaning process [FIGURES 6/B-C & 7/B-C]. EDX analysis further confirmed the removal of gypsum crystals, with no residual sulfates detected on the surfaces of treated samples [FIGURES 8/C-D & 9/E-F].



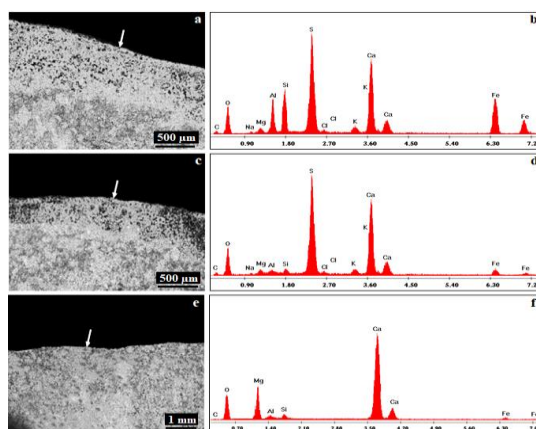
[FIGURES 6/A-C]: SEM micrographs of a limestone [SAMPLE N°.1]; A. Before treatment; B. After biological treatment, with the arrow pointing to calcite precipitation; C. EDX detection of calcite precipitation resulting from the biocleaning process © Done by the researchers



[FIGURES 7/A- C]: SEM micrographs of a limestone [SAMPLE N°.2]; A. Before treatment; B. After chemical-biological treatment, with the arrow pointing to calcite precipitation; C. EDX detection of calcite precipitation resulting from the biocleaning process © Done by the researchers



[FIGURES 8/A-D]: SEM-EDX analysis of a cross-section in [SAMPLE N°.1]; A & B. Before treatment; C & D. After biological treatment © Done by the researchers

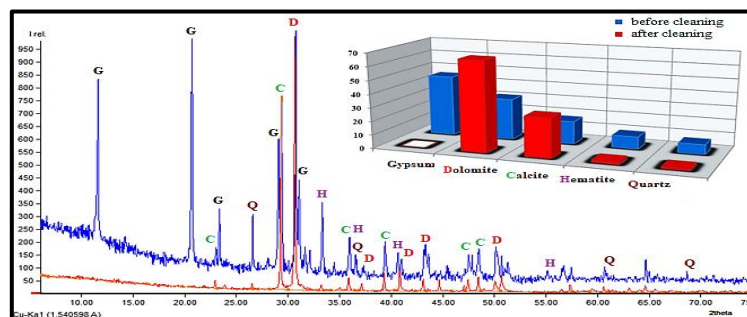


[FIGURES 9/A-F]: SEM-EDX analysis of a cross-section of [SAMPLE N°.2]; A & B. Before treatment; C-D. After chemical treatment; E-F. After biological treatment © Done by the researchers

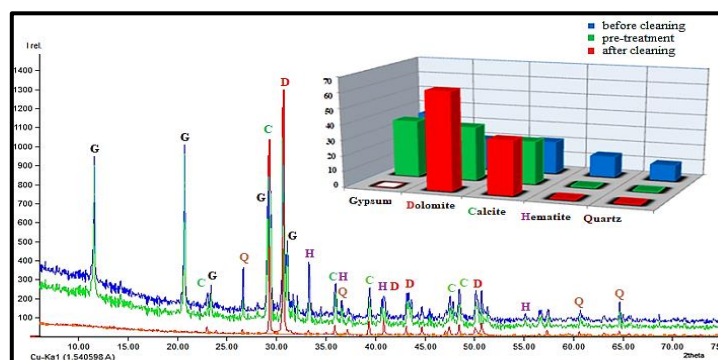
E. X-Ray Diffraction «XRD»

XRD analysis was conducted to determine the mineral composition of the limestone surfaces. Results indicated that the black crusts had varied and heterogeneous compositions. The pattern showed strong peaks for gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, along with calcite CaCO_3 and dolomite $\text{CaMg}(\text{CO}_3)_2$, as well as hematite Fe_2O_3 and quartz SiO_2 . The dominant gypsum peaks confirmed the presence of a thick, well-formed gypsum crust covering the carbonate substrate [FIGURES 10-11].

XRD results also showed a significant decrease in hematite and quartz after chemical treatment [FIGURE 11]. Following biological treatments, gypsum was no longer detected on the surface. Meanwhile, calcite and dolomite became dominant [FIGURES 10-11], suggesting the removal of the black crust and the exposure of the carbonate substrate.



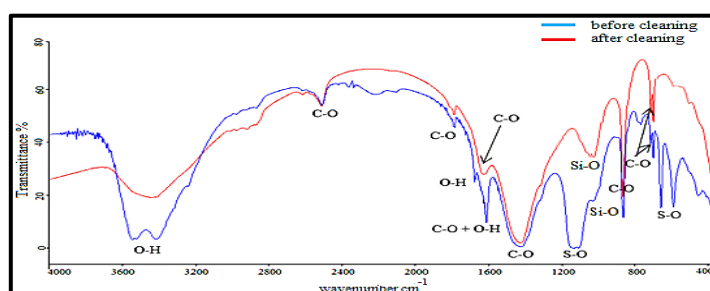
[FIGURE 10]: X-ray diffraction pattern of a limestone surface [SAMPLE N°.1]; before treatment and after biological treatment © Done by the researchers



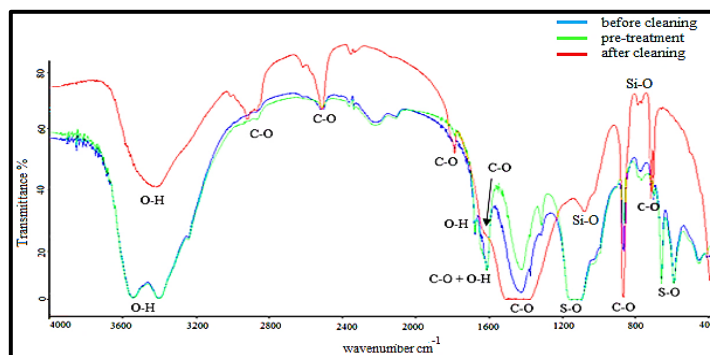
[FIGURE 11]: X-ray diffraction pattern of a limestone surface [SAMPLE N°.2]; before treatment and after chemical-biological treatment © Done by the researchers

F. Fourier-Transform Infrared Spectroscopy «FTIR»

FTIR analysis was conducted to assess changes in the composition of the limestone surface caused by the bio-cleaning process. The spectra showed a complex composition, mainly gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), with strong absorption bands at 3550, 3408, 1685, 1621, 1175, 1143, 1125, 1106, 667 and 605 cm^{-1} , associated with O–H stretching and S–O vibrations in hydrated sulfate minerals. In addition to calcite CaCO_3 , with bands at 1798, 1437, 877 and 715 cm^{-1} and dolomite $\text{CaMg}(\text{CO}_3)_2$, at 2927, 2860, 2520, 1798 and 877 cm^{-1} , absorptions for quartz SiO_2 at 779 and 468 cm^{-1} and calcium oxalate at 1621 and 779 cm^{-1} were detected. Following treatment, gypsum was no longer detectable on the surface, indicating that it had been completely removed. Following treatment, FTIR analysis showed only calcite at 1798, 1440, 877, 729 and 715 cm^{-1} and dolomite at 2927, 2862, 2520, 1798, 877 and 715 cm^{-1} . Peaks for quartz at 1089, 798, 779 and 464 cm^{-1} , along with calcium oxalate at 1621 and 779 cm^{-1} , were also observed [FIGURES 12 & 13].



[FIGURE 12]: FTIR spectra of a limestone surface [SAMPLE N°.1]; before and after biological treatment
© Done by the researchers



[FIGURE 13]: FTIR spectra of a limestone surface [SAMPLE N°.2]; before and after chemical-biological treatment © Done by the researchers

G. Application of the Combined Chemical–Biological Cleaning Method

The combined chemical–biological cleaning method was applied to a blackened wall surface at the Sultan Qalawun Complex [FIGURE 14]. A non-ionic detergent poultice (Tween 80) was first applied for 6 hours. It effectively softened and loosened superficial deposits that were less tightly attached to the surface. Then, biological treatment was carried out for 22 hours until the black crust was completely removed. Combining both treatments enabled the quick removal of the black crust, restoring the stone's original appearance after just three biological applications [FIGURES 15-16].



[FIGURE 14]: The Sultan Qalawun Complex with its façades affected by black crust, <https://www.cairo.gov.eg/ar/pages/CairoInLines.aspx?CiLID=6>, accessed on (01/11/2025)



[FIGURES 15/A-B]: A. Shows the blackened wall before treatment; (B). The cleaned area after chemical–biological treatment © Photo taken by the researchers



[FIGURES 16/A-B]: A. Shows the blackened limestone surface before treatment; B. The surface after chemical–biological treatment © Photo taken by the researchers

IV. DISCUSSION

The chemical, mineralogical and microscopic analyses of the limestone surface at the Sultan Qalawun Complex show that deterioration is closely linked to intergranular corrosion and mineral matrix disintegration caused by calcite dissolution from exposure to a polluted urban environment²⁶. The combined effects of atmospheric moisture and acidic pollutants are well known to cause significant damage to carbonate stones²⁷. Chemical and mineralogical analyses helped identify the crusts on the limestone surface as sulfatic black crusts containing Al, Fe, Si and K, which are related to soil dust particles and environmental pollutants typically embedded in the crust matrix²⁸.

²⁶ CORVO *et Al.* 2010: 359-375.

²⁷ SALEH *et Al.* 2021: 49-58.

²⁸ MARSZALEK *et Al.* 2024: 1-19.

The limestone surface was covered with a compact, continuous, dark, heterogeneous crust, giving it a granular appearance and concealing its natural texture.

Biological cleaning, whether used alone or combined with chemical treatment, selectively removes the sulfate layer even when the carbonate substrate is heavily damaged. The advantages and the effectiveness of the biocleaning process are well documented²⁹.

In biological treatment, the complete removal of the black crust required six applications, while the combined method, using a 1.5% solution of the non-ionic detergent «Tween 80» as a pre-treatment followed by biological cleaning, achieved similar results with only three biological applications. Bio-cleaning alone is a highly time-consuming process when thick, compact crusts are present³⁰. The gypsum layer, formed by the reaction of atmospheric SO₂ with calcite in the substrate, mostly exhibits high porosity, which facilitates the accumulation of atmospheric particles³¹. Many studies documented the thickness of black crusts, with measurements ranging from 5 µm to 4 cm³². Chemical treatments with neutral or alkaline detergents, alone or in aqueous solutions, are commonly used to remove deposits from building surfaces exposed to polluted atmospheric conditions³³. The results indicate that chemical treatment is effective in removing the less compact parts and deposits of the black crust.

It softens and loosens less coherent, embedded particulate matter within the crust «reducing layer thickness», thereby improving bacteria's access to the gypsum layer and accelerating sulfate removal³⁴. This process reduced cleaning time by 50% and decreased the number of biological applications needed. The surfaces appeared uniform, were satisfactorily cleaned and regained their original appearance, with no residual deposits remaining.

Colorimetric analysis provided a quantitative assessment of color changes resulting from cleaning procedures³⁵. The contrast between the blackened and cleaned surfaces showed a high total color difference (ΔE), mainly due to a substantial increase in lightness (ΔL), indicating the successful removal of the black crust and the exposure of the lighter carbonate substrate beneath. The positive shifts in chromatic parameters (Δa and Δb) suggest the restoration of the original limestone tones. Furthermore, the change in total color difference (ΔE) between the pre-treated and blackened surfaces indicated that the chemical pre-treatment caused a notable chromatic shift, denoting the removal of opaque, loosely embedded deposits. When comparing the cleaned area with the reference surface from the unweathered internal part of the stone, the chromatic difference (ΔE) was nearly negligible, suggesting that the cleaning process did not cause

²⁹ CAPPITELLI *et Al.* 2006: 3733-3737; CAPPITELLI *et Al.* 2007: 5671-5675; POLO *et Al.* 2010: 1-14; GIOVENTÙ *et Al.* 2011: 832-839.

³⁰ GIOVENTÙ & LORENZI 2013: 123-129.

³¹ MARSZALEK *et Al.* 2024: 1-19.

³² MARAVELAKI 2005:187-198; BARCA *et Al.* 2014: 122-131; LA RUSSA *et Al.* 2017: 297-309; WILHELM *et Al.* 2021: 143916; HAMAD *et Al.* 2022: 441-450; ROPIQUET *et Al.* 2025: 1-10.

³³ LOMBARDI 2014:103.

³⁴ TROIANO *et Al.* 2013: 294-304.

³⁵ DE ROSA *et Al.* 2025: 1-23.

a visible color change. As a result, the treated areas have optical properties identical to those of the original stone³⁶.

Stereomicroscopic observations showed that the chemical pre-treatment effectively reduced surface deposits. The current results align with previous findings, indicating that non-ionic detergents do not show specific activity toward sulfates in the black crust but, improve bacterial access to the gypsum layer³⁷. Biological cleaning, whether used alone or combined with chemical treatment, proved to selectively remove the sulfatic layer, even on severely degraded carbonate substrates, without causing further damage to the already deteriorated stone. Stereomicroscopy revealed the re-exposure of limestone substrate, with no traces of the previous crust observed, restoring the stone's natural appearance and features.

SEM-EDS analysis further confirmed previous findings at both the microstructural and elemental levels. Regarding the black crusts, SEM revealed morphologies typical of acicular and rosette-like shapes, as documented in the literature³⁸. EDX indicated that the black crusts mainly consisted of calcium, sulfur and silicon, along with iron, aluminum, magnesium, potassium, sodium and chlorine. The chemical composition of these crusts was confirmed to be characteristic of black crusts. Aluminum, iron, silicon and potassium were detected in the crust, associated with soil dust particles and environmental pollutants. Chemical analyses demonstrated a notable reduction of these elements after chemical treatment. Following biological treatments, SEM showed the complete removal of gypsum crystals. The cleaned surface appeared uniform and free of sulfates. SEM observations also indicated that the whitening on the treated surfaces was caused by calcite formation. A major advantage of using SRB is that calcium ions released during gypsum dissolution react with carbonate from bacteria-produced carbon dioxide (CO₂) to form calcite. This conversion makes biological treatment not just a cleaning process but, also enhances the surface through biocarbonatogenesis³⁹. Recent studies have highlighted carbonate mineralization as a methodology for conserving carbonate stone⁴⁰. Cross-sectional observation confirmed the effectiveness of the cleaning process. The substrate layer was the only remaining visible component; the crust layer previously observed on the stone was completely removed without damaging the underlying stone. Regarding substrate preservation, biological treatments did not seem to increase the existing granular disintegration of the stone. EDX analysis confirmed the complete removal of gypsum, with no residual sulfate traces detected on the treated surfaces. Furthermore, XRD and FTIR analyses confirmed that gypsum was no longer present on the surface, while calcite and dolomite became the dominant minerals. This mineral change clearly indicates the successful removal of the sulfatic black crust, exposing the carbonate substrate. The advantages of combining chemical and biological treatments are confirmed⁴¹, and this study supports this approach. Chemical pre-treatment did not interfere with biological

³⁶ GIOVENTÙ *et Al.* 2011: 832-839.

³⁷ DOEBLY 1991:54-85; LOMBARDI 2014:102.

³⁸ TÖRÖK 2008: 583-594; TÖRÖK *et Al.* 2011: 675-693.

³⁹ CAPPITELLI *et Al.* 2007: 5671-5675.

⁴⁰ JIMENEZ-LOPEZ *et AL* 2008: 352-363.

⁴¹ TROIANO *et Al.* 2013: 294-304.

treatment but, it accelerated the process, likely due to a reduction in surface deposits, which decreases cleaning time, an important factor for conservators when selecting a restoration method. Additionally, prolonged water exposure can worsen degradation when the surface is less cohesive. In these cases, combining chemical and biological methods helps reduce this risk.

V.CONCLUSIONS

This study highlights the high effectiveness of sulfate-reducing bacteria as a sustainable and advanced method for removing black crusts from historic building surfaces. At the Sultan Qalawun Complex, prolonged exposure to air pollution resulted in the formation of dense black crusts on its facades, causing further damage.

In this research, a combined chemical-biological approach was used to remove black crusts. The chemical pre-treatment effectively reduced surface deposits, enabling quick gypsum removal. Chemical, mineralogical and microscopic analyses of the treated surfaces confirmed the successful removal of black crusts without causing damage. For uniform, satisfactory cleaning results, chemical pre-treatment with the non-ionic detergent «Tween 80», followed by a safe biological treatment to remove black crusts quickly, is highly recommended.

DISCLOSURE STATEMENT

No Potential conflict of interest was reported by the authors

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EVALUATION OF ZINC OXIDE/PVA NANOCOMPOSITE LOADED WITH LIPASE FOR THE REMOVAL OF SOOT FROM THE PAINTED LAYER

BY

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ABSTRACT

[EN] This study aims to evaluate the effectiveness of a poly (vinyl alcohol) (PVA)/nano-zinc oxide hydrogel loaded with lipase enzyme for the removal of soot deposits from gum Arabic-painted surfaces. Mural paintings, which possess significant historical and cultural value, are highly susceptible to deterioration and require careful cleaning interventions. Conventional cleaning methods, such as gentle brushing, vacuuming, and swab rolling with aqueous solutions, may induce color alteration, mechanical stress on fragile surfaces, and uncontrolled liquid penetration that can lead to swelling or leaching of sensitive organic materials. In contrast, hydrogel nanocomposites provide a promising alternative owing to their three-dimensional cross-linked polymeric network, which enables controlled liquid retention and limited diffusion. Furthermore, the incorporation of nanoparticles and enzymes into hydrogel matrices enhances cleaning efficiency and enzyme stabilization because of the large surface area and unique properties of nanomaterials. The prepared PVA/nano-zinc oxide/lipase hydrogel was applied for 2–3 min, and its cleaning performance was evaluated using scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), colorimetric measurements, and stereomicroscopy. Colorimetric measurements demonstrated the effectiveness of the nanocomposite hydrogel in removing soot deposits while maintaining color saturation. FTIR analysis revealed only slight variations in the wavenumbers and intensities of the main absorption bands of gum Arabic, indicating minimal chemical alteration. Stereomicroscopic examination confirmed the absence of hydrogel residues on the treated surfaces. Overall, the results demonstrate that the incorporation of enzymes and nanoparticles into three-dimensional hydrogel matrices provides an effective and safe cleaning system for the removal of soot from painted surfaces while preserving the integrity of the original materials.

KEYWORDS: Colorimetric measurements, FTIR, Lipase, mural paintings, PVA, SEM, soot, ZnO NPs.

[AR] تقييم استخدام نانو أكسيد الزنك/بولي فينيل الكحول المحمل بالليباز لإزالة السناج من الطبقة الملونة تهدف هذه الدراسة إلى تقييم فعالية هيدروجيل بولي فينيل الكحول/أكسيد الزنك النانوي المحمل بإنزيم الليباز في إزالة السناج من سطح الطبقة الملونة ذات وسيط الصمغ العربي. وتعد اللوحات الجدارية من أهم عناصر التراث الثقافي والتاريخي، إلا أنها تتعرض لعوامل تلف متعددة تستدعي تطبيق أساليب تنظيف فعالة وآمنة. وتعتمد طرق التنظيف التقليدية، مثل التنظيف بالفرشاة، والشفط باستخدام المكينة الكهربائية، واستخدام المسحات القطنية المبللة بالمحاليل المائية، على إزالة الطبقات غير المرغوب فيها من سطح الأعمال الفنية، إلا أنها قد تؤدي إلى تغيرات لونية أو إحداث إجهاد ميكانيكي للأسطح الهشة، فضلاً عن التغلغل غير المتحكم فيه للسوائل داخل الطبقات العضوية الحساسة، مما قد يسبب الانتفاخ أو فقدان بعض مكوناتها. في المقابل، تمثل الهلاميات المائية النانوية المركبة (Nanocomposite Hydrogels) بديلاً واعدًا بفضل شبكتها البوليمرية ثلاثية الأبعاد المترابطة كيميائياً أو فيزيائياً، والتي تتيح التحكم في كمية السوائل ودرجة انتشارها. كما يساهم دمج المواد النانوية والإنزيمات داخل هذه المصفوفات في تحسين كفاءة التنظيف وتثبيت الإنزيمات، مستفيداً من صغر حجم الجسيمات النانوية

ومساحة سطحها الكبيرة. ولتحقيق أهداف الدراسة، استُخدمت تقنيات الميكروسكوب الإلكتروني الماسح (SEM)، والتحليل الطيفي بالأشعة تحت الحمراء (FTIR)، وقياسات التغير اللوني، والميكروسكوب المجسم لتقييم كفاءة عملية التنظيف. وتراوحت مدة تطبيق الهيدروجيل بين دقيقتين وثلاث دقائق. وأظهرت نتائج قياسات التغير اللوني فعالية الهيدروجيل النانوي المركب في إزالة السناج مع الحفاظ على درجة تشبع اللون. كما أوضحت نتائج التحليل الطيفي بالأشعة تحت الحمراء حدوث تغيرات طفيفة فقط في مواقع وشدات نطاقات الامتصاص الرئيسية للصبغ العربي، مما يشير إلى محدودية تأثير المعالجة على التركيب الكيميائي للمادة الرابطة. كذلك أكدت صور الميكروسكوب المجسم خلو الأسطح المعالجة من أي بقايا للهيدروجيل. وبوجه عام، أثبتت النتائج أن دمج إنزيم الليباز والجسيمات النانوية داخل مصفوفة هيدروجيل ثلاثية الأبعاد يوفر نظامًا فعالًا وآمنًا لإزالة السناج من الطبقات الملونة، مع الحفاظ على سلامة المادة الأصلية وخصائصها.

الكلمات الدالة: نانو أكسيد الزنك، الكحول، هيدروجيل بولي فينيل، نانو أكسيد الزنك، إنزيم الليباز، السناج

I. INTRODUCTION

Tempera wall paintings deteriorate due to the natural aging of their materials. Protecting our cultural heritage is essential for passing down our culture and traditions, as well as the means of thinking and behavior, to future generations¹. In conservation, surface cleaning is a complex process because of extremely restrictive guidelines. Enzymes may be regarded as beneficial substances and predictable approaches for operators in several disciplines of conservation². Like all proteins, enzymes are composed essentially of the twenty naturally occurring amino acids, which attach to compose a polypeptide backbone, thereby creating macromolecules that fold into three-dimensional conformations to expedite catalysis³. Hydrolytic enzymes «also known as hydrolases» have been most frequently utilized due to their remarkable ability to catalyze the hydrolysis of proteinaceous, polysaccharide and lipid sources, which ultimately alter the exterior manifestation and interior structure of works of art⁴. Combining organic hydrogels with nanomaterials yields nanocomposite hydrogels «NCHs», which exhibit exceptional characteristics.

Hydrogels represent a unique category of three-dimensional polymeric networks that exhibit excellent hydrophilic properties, allowing for the retention of significant amounts of aqueous solutions without dissolution⁵. The hydrophilic nature of the hydrogel arises from the functional groups like $-OH$, $-COOH$, $-NH_2$, $-CONH_2$ and $-SO_3H$ in the polymer structure or in the sidelong chains. Because of its resilience, constancy and resistance to solubility, which can be attributed to the three-dimensional networks formed through either physical or chemical cross-linking. These interconnected networks, which prohibit the dissolution of hydrogels, can contribute to regulating the swelling behavior in an aqueous solution⁶.

Consequently, the aquatic environment of hydrogels can decrease the denaturation of enzymes and assist their catalytic function⁷.

Nanocomposites have garnered attention for their applications in cleaning and consolidation, as well as serving as an adhesive and a protective coating. The integration of nanostructures within three-dimensional hydrogel matrices creates a

¹ MOHAMED *et Al.* 2025: 185.

² CREMONESI & CASOLI 2021: 73-87.

³ VAN DYKE 2004: 93-107.

⁴ ABDELAAL & SANDU 2019: 459-474.

⁵ TRINADHA RAO *et Al.* 2021: 12-17.

⁶ KANIEWSKA 2020: 1-17.

⁷ MAROUFI *et Al.* 2022: 309-318.

novel category of heterogeneous materials, nanocomposite hydrogels NCHs, which combine the advantageous features of both constituents. The interactions between the two components of the NCHs can work together synergistically, leading to new enhanced features that do not exist in either constituent individually⁸.

The utilization of nanoparticles has drawn significant attention as an effective strategy for creating superior supports that enhance conductivity, responsiveness, and enzyme stabilization, primarily due to their exceptionally small size and high surface-to-volume ratio. These characteristics provide abundant binding sites for enzyme attachment, minimize hindrance and facilitate favorable enzyme orientations. As a result, enzymes immobilized on nanoparticle-based carriers often exhibit enhanced structural stability, prolonged activity under inappropriate conditions and improved catalytic efficiency⁹.

The development of intermolecular hydrogen bonds between the O–H groups of PVA and the ZnO surface enhances the conductivity and internal structure of the backbone of ZnO/PVA composite¹⁰. PVA reinforces the preliminary solution; this helps facilitate ZnO nucleation. In addition, hydroxyl groups (–OH) present on the rims of PVA chains, once attached to the nanoparticle surfaces, can interact through intermolecular hydrogen bonding. These interactions facilitate the formation of bridges between adjacent nanoparticles, thereby enhancing interparticle connectivity and contributing to the overall structural integrity and stability of the nanocomposite. Such linkages also play a crucial role in strengthening mechanical strength, dispersing nanoparticles within the polymer matrix and improving the functional performance of the resulting material¹¹.

After the nucleation phase, the fibrous poly «vinyl alcohol» (PVA) network restricts the subsequent growth of ZnO nanoparticles, as the polymer chains and hydroxyl groups of PVA interact strongly with the nanoparticle surface, creating steric hindrance and preventing further particle enlargement. As a result, the nanoparticles are stabilized in their nanoscale dimensions, maintaining a uniform distribution within the hydrogel matrix and preventing agglomeration. PVA enhances stability and assists in the encapsulation of the formed particles and the confinement to the grain growth by improving dispersion in the polymer matrix¹². It functions as a template medium and a binder in fiber formation, which creates forces amongst particles¹³. The abundant, substantial quantity of free OH groups inside this polymer likely behaves as a physical hindrance against crystal formation by forming hydrogen bonds, which assist in maintaining nanoparticle dispersion¹⁴.

Natural enzymes present inherent limitations, including rapid inactivation and time-consuming extraction. The incorporation of nanoparticles typically enhances and improves the stability and sensitivity of enzyme-based biosensors. This improvement is

⁸ ARAÚJO *et Al.* 2022: 32863-32876.

⁹ MERYAM SARDAR 2015: 1-8

¹⁰ POLIUKHOVA *et Al.* 2022: 272-284.

¹¹ EROL *et Al.* 2023: 731-743.

¹² BARMAN *et Al.* 2020: 2248-2257.

¹³ ANERO *et Al.* 2021: 1-3.

¹⁴ ASADPOUR *et Al.* 2022: 1-24.

attributed to the ability of nanoparticles to impart their distinctive intrinsic characteristics to the biosensor system¹⁵.

ABDEL-NASSER *et Al.* used nanoparticles in conjunction with an α -amylase enzyme to enhance the quality of removing starch stains from the surface of accelerated heat-aged paper artifacts. The results showed that the α -amylase enzyme incorporated with Ag-NPs was better than its use alone. The addition of AgNPs to α -amylase enzyme for the removal of starch stain reduced the total color differences, improved the surface morphology and minimized the time required for enzymatic analysis, thereby reducing the harmful effect by using aqueous solutions, such as enzymes, which can affect historical paper manuscripts and writing materials during their application¹⁶.

GHERARDI *et Al.* demonstrated the use of α -amylase immobilized on gold nanoparticles to improve the efficacy of enzymatic treatments, thereby improving both the reactivity and the stability of the formulations. Gold nanoparticles coated with α -amylase exhibited significant advantages compared to free enzymes. The study reported up to 5 $\times$ greater resistance to environmental changes, up to 2 $\times$ higher efficacy toward the removal of starch-based glues from textiles and deeper penetration through the fibers, without causing damage or inducing salt precipitation¹⁷.

II. MATERIALS AND METHODS

1. Sample and PVA Hydrogel Blend Preparation

An experimental mock-up sample was prepared by mixing sieved sand, lime and gypsum in a ratio of 3:2:1, respectively. The blend was mixed well with water. Then, the mixture was poured into a mold to obtain a cube (3 $\times$ 3cm) with homogeneous porosity. After that, the cube was covered with a thin layer of whitewash made of gypsum. Two painting layers of goethite and gum Arabic mixture were applied on the tile using a soft brush and finally left to dry for two weeks¹⁸. The prepared sample was covered with a thin layer of soot from a candle.

Artificial accelerated ageing was executed in a PANACEA oven, where the sample was exposed to a temperature of 70 °C for 2 h and left for 3 days at room temperature¹⁹. Poly «vinyl alcohol» was obtained with these specifications «86.0–89.0% hydrolyzed, Mw 85,000-1,24,000, SDFCL - SD Fine Chemicals, Mumbai, India» and ZnO was a nano powder, <100nm particle size «SIGMA-ALDRICH®», Lipase, Mol.

Bio «ADVENT®, Mumbai, India». The preparation of nanocomposite PVA hydrogel initiated with dissolving 8wt.% of PVA in warm to hot water 60 °C under magnetic stirring until a homogeneous mixture was obtained²⁰. In a separate beaker, sodium tetra-borate decahydrate (borax) at 0.4% +0.1% ammonium carbonate + 2% enzyme +2% nanocomposite were separately dissolved in water. Following dissolution, the PVA solution and borax mixture were gradually mixed under continuous stirring

¹⁵ CHEN *et Al.* 2017: 914-930.

¹⁶ ABDEL-NASSER *et Al.* 2022: 14-23.

¹⁷ GHERARDI *et Al.* 2019: 5136-5143.

¹⁸ HAMDY *et Al.* 2023: 279–292.

¹⁹ EHAB AL-EMAM *et Al.* 2019: 7-22.

²⁰ ALTABELLI *et Al.* 2023: 1-8.

until the desired final concentration was reached²¹. A cleaning test was performed on a mock-up sample by applying the hydrogel slab to soot. The results were evaluated using a visual examination to assess the efficiency of the PVA hydrogel nanocomposite. It was observed that the time of removal ranged between 2-3 mins, then the slab was cautiously peeled off using a forceps in a cohesive state with no hydrogel residues observed on the surface [FIGURES 1/A-C].



[FIGURES 1/A-C]: Visual examination before, during and after the application process, which ranged between 2-3 mins. The hydrogel was removed by forceps as a cohesive unit. The cleaning efficacy of the soot stain with no residues observed on the surface © Done by the authors

After using visual examination as a preliminary method to evaluate soot removal efficacy, we accompanied the latter method with other instruments to provide more accurate results as follows:

A. FTIR Spectroscopy

FTIR is commonly employed to study organic binders²², FTIR measurements were performed using a KBr technique for sample preparation. Spectrum was measured in the absorption mode, all samples were scanned in the wavenumber region from 4000 to 400 cm⁻¹ at 4 cm⁻¹. IR Prestige-21 FTIR spectrometer and the IR solution software were used.

B. Stereo Microscope

The sample was examined after the soot removal process using a stereomicroscope «Zeiss-Stereo-Discovery V20».

C. SEM Scanning Electron Microscope

Scanning electron microscope unit (SEM) «Model FEI Quanta 3D 200i» attached with an EDX unit «Energy dispersive X-ray analyses/thermofisher pathfinder», the sample was subject to operating conditions of accelerating voltage 20~30 K.V, resolution for Gun.1nm, at different magnifications using SED «secondary electron detector» and BSED «Back scattered electron detector». Samples were properly set on aluminum stubs with a standard diameter via carbon double-stick tape.

D. Colorimetric Measurements

Color measurements were performed using the spectrophotometer **Optimatch 3100** «SDL company» in the National Institute of Standards (NIS).

²¹ SWAROOP KUMARASWAMY *et Al.* 2017: 2-7.

²² ABDELAAL 2019: 171-181.

III.RESULTS AND DISCUSSION

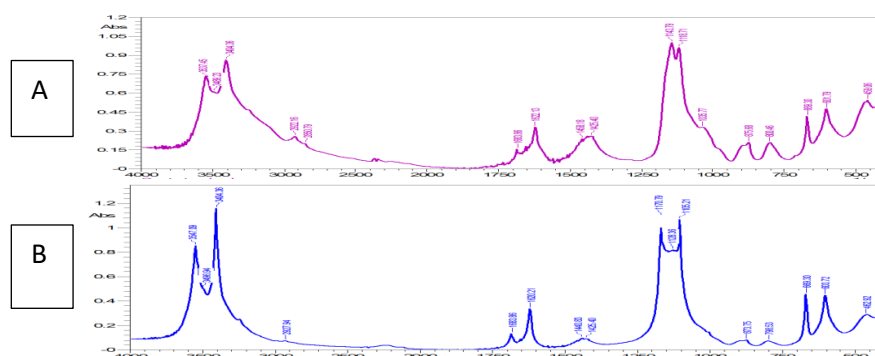
1. Results

A.FTIR Spectroscopy

The cleaning efficiency was evaluated by FTIR spectroscopy. Due to the glossy nature of the gum Arabic layer²³, the FTIR spectrum was dominated by strong and overlapping bands between gum Arabic and soot. The band at 3404 cm^{-1} was due to the O-H group. The band at 2922 cm^{-1} was attributed to C-H in gum Arabic, or it could correspond to the C-H aliphatic functional groups with wavenumbers 2850 cm^{-1} and 2922 cm^{-1} . In addition, polysaccharides contained moderately strong bands between $1600 - 1400\text{ cm}^{-1}$ of COOH, which was partially associated with intramolecular bound water and partially due to the existence of the carboxyl group.

The $1200\text{-}900\text{ cm}^{-1}$ fingerprint of carbohydrates, bands at 883 cm^{-1} and 798 cm^{-1} , were assigned to galactose and mannose and a band at 1033 cm^{-1} was due to the C-O of the glycosidic bond²⁴. The spectrum also presented absorption peaks between 1425 cm^{-1} - 1458 cm^{-1} , indicating the existence of a C-H aliphatic bond. The peaks originating at $1683\text{-}1622\text{ cm}^{-1}$ could be due to aromatic C=C functionalities in soot²⁵. The band at 459 cm^{-1} corresponds to Fe-O of Goethite 462 cm^{-1} .

The cleaning efficiency was evaluated by FTIR spectroscopy, which revealed a slight change in wavenumbers and a reduction in the intensities of the main absorption bands of soot. The fingerprint area of gum Arabic indicated a disappearance of the peak at 1035 cm^{-1} corresponding to the glycosidic bond, which suggests a partial solubility of the gum Arabic in water resulting from the hydrogel itself. Characteristic peaks of soot revealed a reduction in intensity and the disappearance of the band at 2850 cm^{-1} , corresponding to the C-H aliphatic functional groups, indicating the removal of the stain. The band at 459 cm^{-1} corresponding to Fe-O of goethite 462 cm^{-1} witnessed a reduction in intensity [FIGURES 2/A-B].



[FIGURES 2/A-B]: FTIR spectra; A. Gum Arabic+ goethite painted layer stained with soot (standard sample); B. The painted layer stained with soot after cleaning with PVA/borax loaded with lipase and +ZnO NPs © Done by the authors

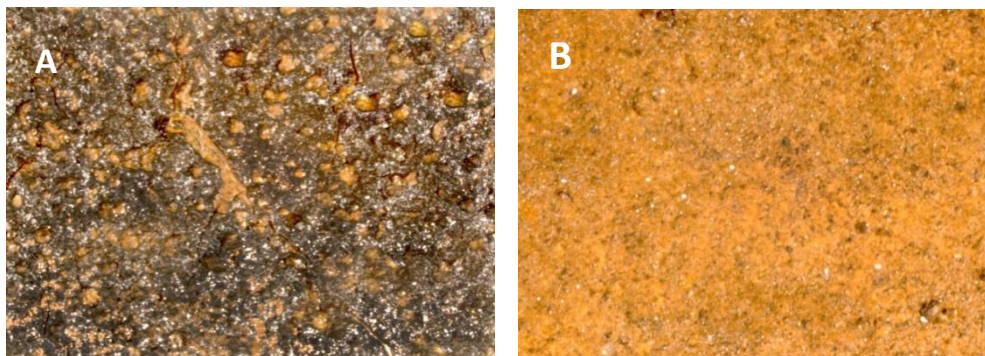
B. Stereo Microscope

²³ SIDDIG *et Al.* 2013: 174-178.

²⁴ APPOLONIA IBEKWE *et Al.* 2017: 28-36.

²⁵ SAMOUDI *et Al.* 2022: 1-11.

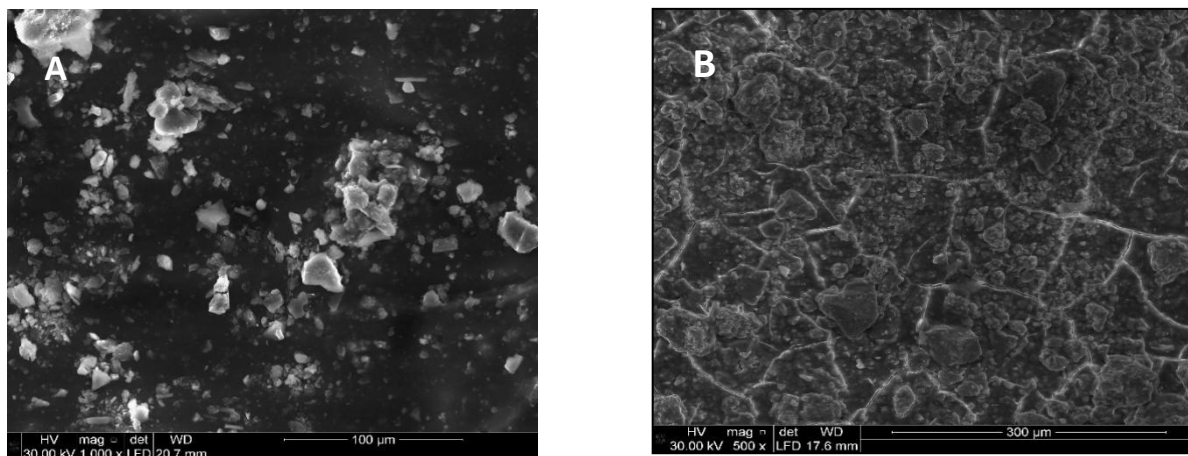
A stereo microscope was employed to assess the removal efficiency, which was acceptable; also, no hydrogel residues were detected on the cleaned surface [FIGURES 3/A-B].



[FIGURES 3/A-B]: A. Mag 14.5x surface of the sample covered with soot; B. 17.0 Mag, moderate stain removal efficiency after using PVA+ lipase+ ZnO with the existence of some soot particles ©Done by the authors

C. Scanning Electron Microscope «SEM»

SEM was utilized to accurately examine the morphological structures of the samples. Cracks were observed on the surface of the painted layer after the removal of the hydrogel slab, which could be a result of the dryness of the binder. The painted layer exhibited partial dissolution during the application of the hydrogel slab; probably, internal humidity, together with soot, was adsorbed in the hydrogel as it acts like a sponge [FIGURES 4/A-B].



[FIGURES 4/A-B]: SEM micrographs; A. Indicate a standard sample, which is a painted layer covered with soot; B. Show cracks after cleaning with PVA+ZnO NPs loaded with lipase ©Done by the authors

D. Colorimetric Measurements

The collected CIE Lab values, in this system, L axis «+L for light, - L for dark» represented the lightness, a «+ a for red - a for green» and b «+ b for yellow and - b for blue»²⁶. Then, the color difference (ΔE^*) was measured between the standard sample before applying soot and the sample after applying the hydrogel and removing the soot to assess the cleaning efficacy and the effect on the painted layer.

²⁶ HAMDY *et Al.* 2023: 279–292.

Concerning the **soot-stained** sample (**brightness L value**), the standard sample had an **L value** of 50.85, which increased to 52.29 after using PVA nanocomposite, with approximate stability in both hue b value «+b yellowness» and a value «+a redness» from 9.09 to 9.08 and 5.95 to 5.23, respectively.

Cleaning with a PVA nanocomposite was effective in removing soot stains and maintaining the saturation of color, with a total color difference ΔE of 1.61 [TABLE 1].

Sample	L	a	b	ΔE
Standard	50.85	5.95	9.09	-
PVA+ lip + ZnO	52.29	5.23	9.08	1.61

[TABLE 1]: Colorimetric measurement values between the standard sample and after using the hydrogel © Done by the authors

2. Discussion

In this study, we used a PVA-borax hydrogel loaded with lipase and a nanocomposite «ZnO NPs» to remove soot from the painted layer surface and evaluated cleaning efficacy while maintaining the safety of the painted layer as a priority. While applying and peeling off the hydrogel, the slab was peeled off as a single, cohesive unit without leaving any residues on the surface, as confirmed by stereo microscope images. Furthermore, it was observed that the hydrogel slab had a topical effect, preventing liquids from diffusing outside its limits. The contact time for the application was 2-3 minutes, which was a prominent advantage²⁷. *It was in situ* because the hydrogel slab lost flexibility and ability to be applied on inscriptions, and turned into an inflexible slab, which could only be applied to flat surfaces²⁸. In addition, enzyme effectiveness was reduced over time, which was observed after using a hydrogel nanocomposite on the sample, requiring significantly more time to remove the stain.

Zinc oxide «ZnO» nanoparticles have an exceptional capacity to accelerate electron transfer between enzymatically active sites and their substrates. Also, ZnO NPs are preferred due to their antimicrobial effect, high stability, self-cleaning and high biocompatibility. Owing to their intrinsic hydrophilicity, ZnO nanoparticles demonstrate excellent aqueous dispersibility, thereby enhancing the stability and functionality of the resulting complexes. Hydrogels can provide a matrix for an immobile enzyme because of their exceptional features, such as prominent water absorption capability, serving as a carrier for bioactive substances and enzymes, biocompatibility, safe handling and biodegradability²⁹.

A study by HAMAD and BADWY concluded that it was effective to use lipase enzyme in cleaning the glassy traces that contain waxy damage components combined with carbon granules «soot» from an archaeological glass candle stand, which gave better results³⁰. Hydrogels are an effective method of enzyme immobilization on both

²⁷ DINA YELSHERBINY 2022: 16.

²⁸ WERNECK *et Al.* 2023: 1-6.

²⁹ ABD-ELRAHMAN 2013: 194-203.

³⁰ HAMAD & BADWY 2021: 19-27.

soft and solid supports. Holding a substantial quantity of water within their three-dimensional structure creates optimal physiological conditions for enzyme activity. The aqueous environment of polymeric hydrogels can decrease the denaturation of enzymes, while also assisting in their functions. Consequently, the hydrogel polymer matrix is anticipated to preserve enzymatic activity by immobility of enzyme within its three-dimensional network³¹.

Enzymes can attach to the surface of nanoparticles, leading to the formation of a nanoparticle–protein corona that confers a biological identity to the nanoparticles. The orientations of enzymes towards nanoparticles are considered critical because improper orientations can result in blocking or hindering the enzymatic active sites by nanoparticles or other adjacent molecules. The physicochemical properties of nanoparticles, in conjunction with environmental factors, such as pH and temperature, govern their binding orientations and interactions with enzymes, thereby modulating enzymatic stability and substrate accessibility. In this respect, the interactions between nanoparticles and enzymes are internal, occurring among themselves. Nanomaterials have a high surface-to-volume ratio and when coated with a catalyst, they provide sufficient catalysis with a minimal quantity of material³². At higher enzyme concentrations, agglomeration tends to occur, which can obstruct substrate accessibility to the active sites and consequently decrease catalytic activity, even when the enzyme maintains its native structure³³.

IV.CONCLUSION

The incorporation of enzymes and nanoparticles into three-dimensional hydrogel matrices creates a new class of heterogeneous materials, nanocomposite hydrogels «NCHs». A PVA nanocomposite «ZnO NPs» loaded with lipase was observed to be an effective method for removing soot from a painted layer surface.

The hydrogel was peeled off after 2-3 min as a cohesive unit, which, by visual examination and stereo microscope, left no residues and was also safe to the painted layer. SEM micrographs revealed that the sample suffered from dryness, causing cracks because the hydrogel slab acts like a sponge, which probably adsorbed internal moisture inside the sample during application and humidified the stain. Colorimetric measurements were taken before applying soot and after removing the stain to assess the color change compared to the standard sample. It was implied that cleaning with PVA nanocomposite was effective in removing soot stain and maintained saturation of color with a total color difference of ΔE 1.61. FTIR results showed a slight change in the wavenumbers and intensities of the main absorption bands of soot, which correlates with the effective removal of stain observed by examination methods.

DISCLOSURE STATEMENT

No Potential conflict of interest was reported by the authors

³¹ MAROUFI *et Al.* 2022: 309-318.

³² CHEN *et Al.* 2017: 914-930.

³³ ARSALAN & YOUNUS 2018: 1833–1847.

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ENGINEERING FAILURE ANALYSIS IN SAFETY EVALUATION FOR PRESERVATION OF MODERN BUILT HERITAGE WITH APPLICATION ON AL BARON PALACE IN CAIRO

By

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ABSTRACT

[EN] Engineering failure analysis serves as a crucial interdisciplinary tool for diagnostics and prevention, adopting a comprehensive approach that accounts for design and maintenance, safety, reliability, integrity, environmental impact, sustainability, service loading conditions, and the processes for disposal and decommissioning once the useful life has ended. This paper discusses a pilot study focused on the micro and macro characterization of contemporary building materials used in Egypt's modern architectural heritage, specifically applied to EL BARON EMPAIN Palace in Cairo, which was built in 1906. The primary goals of this study are: 1. to ascertain the nature, chemical makeup, and engineering properties of the heritage reinforced concrete and cement materials utilized in Egypt during the 20th century; 2. to analyze the failure and deterioration mechanisms affecting these modern building materials; 3. to assess the palace's structural stability through numerical analysis codes; and 4. to select similar materials for the proposed restoration efforts. The research methodology employed a variety of modern destructive and non-destructive testing techniques to evaluate the uniaxial compressive strength, Young's modulus, tensile strength, and flexural strength, both in situ and in a laboratory setting, along with morphological and spectroscopic analyses utilizing advanced microscopes and chemical assessment methods. The findings revealed that the building materials consisted of reinforced concrete, steel, lime sandy brick, and cement mortar with specific engineering properties. This research contributed new insights into the variability of properties concerning the building materials of modern architectural heritage and highlighted the necessity for additional research and expansion of knowledge crucial for evaluating the engineering characteristics of contemporary architectural heritage. This applied study holds significance in the ongoing efforts toward the preservation and restoration of modern built heritage globally, particularly in terms of Egypt's modern architectural heritage.

KEYWORDS: Al-Baron Empain Palace, ancient reinforced concrete, conservation science, construction materials, mechanical testing, modern architectural heritage.

[AR]

تحليل الإنهيار الهندسي في تقييم السلامة للحفاظ على التراث المعماري الحديث. تطبيقاً على قصر البارون في القاهرة يُعد تحليل الإنهيار الهندسي أداة متعددة التخصصات بالغة الأهمية للتشخيص والوقاية، إذ يتبنى منهجاً شاملاً يُراعي عوامل التصميم والصيانة، والسلامة، والموثوقية، والسلامة العامة، والأثر البيئي، والاستدامة، وظروف التحميل التشغيلي، وعمليات التخلص من المعدات وإخراجها من الخدمة بعد انتهاء عمرها الافتراضي. تتناول هذه الورقة البحثية دراسة تجريبية تركز على التشخيص الدقيق والشامل لمواد البناء المعاصرة المستخدمة في التراث المعماري المصري الحديث، وتحديدًا قصر البارون إيمان في القاهرة، الذي شُيّد عام ١٩٠٦. تتمثل الأهداف الرئيسية لهذه الدراسة فيما يلي: ١. تحديد طبيعة وتركيب وخصائص الخرسانة المسلحة والأسمنت المستخدمة في التراث المعماري المصري خلال القرن العشرين؛ ٢. تحليل آليات التلف والتدهور التي تؤثر على مواد البناء الحديثة هذه؛ ٣. تقييم الثبات الإنشائي للقصر من خلال برامج التحليل الرقمي؛ ٤. اختيار مواد مماثلة لجهود الترميم المقترحة. استخدمت منهجية البحث مجموعة متنوعة من التقنيات والاختبار الحديثة، المتلفة وغير المتلفة، لتقييم مقاومة الضغط

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أحادي المحور وتحديد اتجاهات الكسر وكذلك معامل المرونة لهذه المواد، ومقاومة إجهادات الشد، ومقاومة الانحناء، سواء في الموقع أو في المختبر، إلى جانب التحليلات المورفولوجية والطيفية باستخدام ميكروسكوبات متطورة وأساليب التقييم الكيميائي. وكشفت النتائج أن مواد البناء تتكون من الخرسانة المسلحة، والفولاذ، والطوب الرملي الجيري، وملاط الأسمنت ذات خصائص هندسية نوعية تميزها. وقد أسهم هذا البحث في تقديم رؤى جديدة حول تباين خصائص مواد بناء التراث المعماري الحديث، وسلط الضوء على ضرورة إجراء المزيد من البحوث وتوسيع المعرفة اللازمة لتقييم الخصائص الهندسية للتراث المعماري المعاصر. وتكتسب هذه الدراسة التطبيقية أهمية بالغة في الجهود المبذولة حاليًا للحفاظ على التراث المعماري الحديث وترميمه على مستوى العالم، ولا سيما فيما يتعلق بالتراث المعماري الحديث في مصر.

الكلمات الدالة: قصر البارون امبان، الخرسانات القديمة، علوم الصيانة، المواد الانشائية، الاختبارات الميكانيكية، التراث المعماري الحديث.

I. INTRODUCTION

The advantages of the current study can be summarized in the following points: 1. Emphasizing the significance of protecting and revitalizing «valuable historic palaces» and underscoring the importance of re-employment initiatives to maintain this crucial architectural heritage, particularly for short-term restoration efforts; 2. Highlighting the aesthetic qualities of modern built heritage, which serves to showcase and enhance its artistic and historical significance; 3. Fostering public appreciation for the effects on and the involvement of local stakeholders by selecting appropriate roles such as those performed by the surrounding community's buildings; 4. Emphasizing the necessity of preserving traditional patterns and the importance of integrating and harmonizing the older and newer urban environments¹.

Analyzing the original building and construction materials of heritage buildings contributes to achieving compatible and sustainable restoration of modern architectural heritage (MAH), as well as to understanding how these structures behave under various deterioration factors and action, particularly the geoenvironmental and seismic actions associated with geotechnical and structural influences; this understanding dictates the type, limits and extent of restorative actions taken. The methods employed for intervention retrofitting must not only be reliable and long-lasting but should also be easy to monitor and remove when necessary. This aligns with widely accepted policy and studies of protecting existing modern heritage buildings from unsuitable restoration practices, especially concerning historical and monumental structures², the technical evaluation and reinforcement of an aged monumental building are areas where decisions are made based on risk analysis to find a balance between historical significance and the cost of assessments. When selecting materials for restoring architectural and urban heritage, it is essential to consider their primary benefits and drawbacks³. Naturally, preference is given to materials that closely resemble the authenticity of the original materials in the structures being restored. However, neglecting or underestimating the aesthetic and technical properties of the chosen materials can result in detrimental outcomes for the restoration and adversely affect the structural capacity and functional viability of the object⁴.

¹ ABDEEN 2022: 12

² ASTM C880/ C880M-9 2009: 6; ASTM C170, 2020: 13; ASTM C1353/C1353M 2020: 5.

³ ASTM C97/ C 97M 2020: 13

⁴ ASTM C99/C99M 2020: 8.

The Baron Empain Palace, constructed between 1907 and 1911⁵, is a significant example of modern architectural heritage in Cairo, Egypt. It covers an area of 6 feddans with a built-up space of 1205 m² and consists of two floors. This remarkable structure was commissioned by Belgian Baron Eduard Empain in the district of Heliopolis, featuring a design that merges Hindu and European architectural styles. It was designed by French architect Alexander Marcel (1860-1928)⁶ with construction beginning in 1906 and ending in 1911.

The palace has welcomed many distinguished visitors; including the Belgian king Albert I. The Baron Palace stands out as one of Cairo's most notable landmarks, characterized by its striking silhouette located along the route connecting the city center to the airport. It is situated on a prominent point of the plateau along Avenue Al-Uruba, which was previously known as the 'town's Avenue des Palais⁷. The interior design was executed by Georges-Louis Claude. Baron Empain opted for a unique architectural style, resembling a fantastical Hindu temple constructed from reinforced concrete⁸. The villa's design incorporates concrete slabs that evoke the image of Lego pieces stacked atop one another. The concrete was sourced from France, and was pieced together on-site using the Hennebique system. The style draws inspiration from the 12th-century Angkor Wat temple in Cambodia. The proposal to infuse Indian architectural elements into Heliopolis came from Alexandre Marcel, who had previously designed a Cambodian pavilion for the 1900 Expo in Paris⁹.

The palace is surrounded by an expansive garden on all sides. Its layout includes a basement, ground floor, and rooftop, and features two stories above ground and two below, crowned by a central tower. Adorning the palace walls are exquisite marble statues of dancers from India and ornate elephants, embellished with small pieces of Belgian glass. Notably, the palace was designed to ensure that sunlight would flood its interiors throughout the day.

This study aims to contribute to the preservation of historically significant masonry structures and urban environments by merging microanalytical and mechanical testing techniques with principles of structural engineering. It provides a comprehensive assessment of the structural soundness necessary for the restoration and reinforcement of Al-Baron Palace in Cairo, which is acknowledged as a vital part of Egypt's modern architectural heritage. Presently, the Palace is under threat from a rising groundwater table caused by water infiltration from nearby regions and significant urban development in the vicinity. It is facing a range of geo-environmental and structural challenges, including soil consolidation settlement and various mechanical stresses, notably those resulting from the Dahshuor earthquake in 1992.

⁵ ASTM D4543-19 2019: 3.

⁶ BRUWIER & LOO 2010: 17.

⁷ DOBROWOLSKI & JAROSTAW 2020: 8.

⁸ ELYAMANI 2018: 10.

⁹ HEMEDA *et Al.* 2018: 2463.

The evaluation methodology employed a variety of modern destructive and non-destructive analytical and mechanical testing techniques to evaluate the uniaxial compressive strength, tensile strength, and flexural strength of the historic reinforced concrete, bricks and steel rebar. This was carried out both in situ and in a laboratory setting, along with morphological «microscopic» and spectroscopic analyses utilizing advanced microscopes and chemical assessment methods.

II. MATERIALS AND METHODOLOGY

In order to evaluate the structural weaknesses of the historical Baron Palace in Cairo, various building material samples and specimens were utilized in this study, including reinforced concrete, cement brick, mortar and steel, as depicted in [FIGURES 1/A-D].

Samples of construction materials were collected from remnants of the ongoing restoration efforts at Baron Empain Palace while ensuring that existing, undamaged elements remained intact. The samples were shaped into cylinders and were tested at the Rock Mechanics Laboratory, Faculty of Engineering/Cairo University, to assess the compressive and frictional responses of the materials. The following sections provide detailed information on the characterization of materials, specimen preparation, sampling procedures, and test setups.

This research employed a multidisciplinary strategy that combined traditional investigative methods with innovative experimental techniques. Consequently, a total of 27 samples were gathered, particularly from reinforced concrete, steel and cement bricks sourced from various locations within the palace, including slabs, beams, and load-bearing walls, alongside structural mortars. Standard thin sections were prepared to analyze the material composition using optical polarizing microscopy with transmitted light and scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX).

Circular cylinders measuring 50 mm in diameter were prepared in accordance with ASTM Standard D4543-19. The length-to-diameter ratios of the specimens ranged from 2.0:1 to 2.5:1. The apparent density under both dry and water-saturated conditions was calculated using the mass-to-volume ratio method outlined in Method B of ASTM Standard D7263-09. The effective porosity of the samples was determined through the water immersion method, following the approach suggested by ANDRIANI & WALSH¹⁰. The uniaxial compressive strength (UCS) measurement was conducted on both dry and saturated samples, based on the recommended method by ISRM for intact rocks¹¹, applying a constant stress rate load of 0.2 MPa/s. A low load rate was chosen to analyze the failure progression and stress-strain behavior of the concrete and bricks more effectively.

The modulus of elasticity for dry samples was computed from the UCS test using the slope of the stress-strain curves by means of tangent modulus (E_t). Disc specimens «54 mm in diameter with a height-to-diameter ratio of 0.5:1» were prepared from the cylindrical

¹⁰ ANDRIANI & WALSH 2007: 224- 238

¹¹ JAKUB 2010:12.

specimens to perform the indirect tensile strength test «Brazilian test». Additionally, tension and bending tests were conducted on the steel rebar.

III.RESULTS OF THE EXPERIMENTAL STUDY

A.Mechanical Test

The methodologies employed for assessing the physical and mechanical properties of construction materials include water absorption testing by ASTM C97¹², stain resistance evaluation as outlined in AS 4459:14¹³, strength determination following ASTM C170¹⁴, ASTM C880¹⁵ and ASTM C99¹⁶ standards, abrasion resistance testing based on ASTM C1353¹⁷ and durability assessment as per AS/NZS 4456.10 Method A¹⁸. The following sections will provide a comprehensive overview of the various tests conducted and analyses their respective results.

The compressive strength (σ_c), tensile strength (σ_t), and flexural strength (σ_f) were evaluated in accordance with (CEN, 2006), EN 1015-11:1999, on a total of six concrete cylinders, five lime cement bricks, and four steel specimens of various sizes. The specimens were subjected to loading using steel plates measuring 40 × 40 mm². The results are compiled in the following [TABLES 1-7]. The strength measured from each specimen, along with average values and corresponding coefficients of variation (CV), are represented in the following tables and figures. [FIGURES 1/A-D] represent the preparation and coding of the building materials specimens under investigations. [FIGURES 2/A-D] represent the uniaxial compression test setup for the reinforced concrete.



[FIGURES 1/A-D]: Preparation and coding of the building materials specimens and samples under investigation © Done by the authors.

¹² MAZZOLANI *et Al.* 2009: 14

¹³ ROYAL INSTITUTE OF CULTURAL HERITAGE CASE REPORT 2009: 1-23.

¹⁴ SELIM 2017: 13

¹⁵ SOBAIH & NAGUIB 2022: 5

¹⁶ STANDARDS AUSTRALIA AS 4459.14 1999: 4

¹⁷ STANDARDS AUSTRALIA /NZ54456.10 2003: 5

¹⁸ SUBBOTIN 2018: 6-13: 11

1. Reinforced Concrete

A. Compressive Strength



[FIGURES 2/A-D]: Uniaxial compression test setup for reinforced concrete, bricks and steel rebar
© Done by the authors

■ Concrete Slab (CS)

Sample	Load, KN	Area, mm ²	Length, mm	Compressive Strength, MPa
CS1	23.6	1527.36	89.75	15.45
CS2	34.1	1527.36	90.13	22.32
CS3	25	1527.36	92.66	16.36

[TABLE 1]: Results of compressive strength test for three samples from concrete slab of the palace © Done by the authors

■ Concrete Beams «CB»

Sample	Load, KN	Area, mm ²	Length, mm	Compressive Strength, MPa
CB1	15.1	1527.36	88.8	9.88
CB2	10.2	1527.36	88.55	6.67
CB3	3.8	1527.36	90.36	2.48

[TABLE 2]: Results of compressive strength test for three samples from concrete beams of the palace © Done by the authors

B.Splitting Tensile Strength

■ Concrete Slab «CS»

Sample	Load, KN	Dia, mm	Length, mm	Tensile Strength, MPa
CS4	1.7	44	36.75	0.669
CS5	5.7	44	38.12	2.164
CS6	4.1	44	36.88	1.609

[TABLE 3]: Results of tensile strength test for three samples from concrete slab of the palace
© Done by the authors

■ Concrete Beams «CB»

Sample	Load, KN	Dia, mm	Length, mm	Tensile Strength, MPa
CB4	1.7	44	30	0.820
CB5	3.5	44	36.2	1.399
CB6	0.7	44	36.44	0.278

[TABLE 4]: Results of tensile strength test for 3 samples from concrete beams of the palace
© Done by the authors

2. Lime Cement Bricks

A. Compressive Strength

Sample	Load, KN	Area, mm ²	Length, mm	Compressive Strength, Mpa
BK1	4.6	854.865	63.67	5.380
BK2	3	854.865	63.8	3.509
BK3	1.1	854.865	65.03	1.286

[TABLE 5]: Results of Compressive strength test for 3 Samples from lime cement bricks of the Palace
© Done by the authors

B. Splitting Tensile Strength

sample	Load, kN	Dia, mm	Length, mm	Tensile Strength, MPa
BK4	1	34	26.98	0.694
BK5	1	34		0.694
BK6	1	34		0.694

[TABLE 6]: Results of tensile strength test for 3 samples from lime cement bricks of the Palace
© Done by the authors

3. Reinforcing Steel

Mechanical testing of steel involves subjecting steel samples to various loads and conditions to evaluate their mechanical properties like strength, ductility and toughness. These tests help ensure the steel meets required standards and is suitable for its intended application. Common mechanical tests include tensile, compression, bend, hardness, and impact tests. The test involves applying a gradually increasing tensile «pulling» force to a steel specimen until it fractures. The tension test and bending test were performed on six different steel samples of palace «slabs and beams» and their results were as follows:

A. Tension Test

This test measures the steel's resistance to a stretching force. It determines properties like yield strength or «the point where the steel starts to deform permanently», tensile

strength or «the maximum stress the steel can withstand before breaking» and elongation or «how much the steel stretches before breaking».

Tension test was performed on three different steel samples of palace «slabs and beams» after processing these samples as in [FIGURES 3-4] to comply with the test device.



[FIGURES 3/A-C]: Preparing steel rebar samples in preparation for the tension test
© Done by the authors

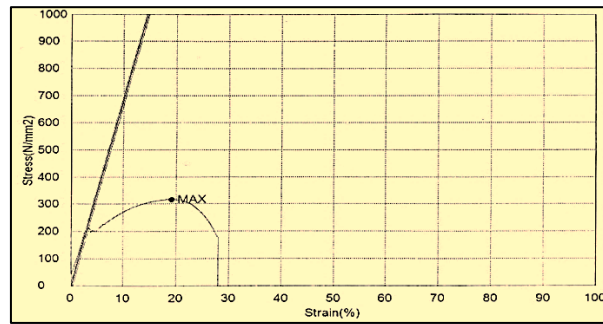


[FIGURES 4/A-F]: Setting steel rebar samples in the test device and conducting the tension test
© Done by the authors

• Sample 1: Slab Steel of the 1st Floor

Name	YP(%fs) _Stress	Yd 02	UTS	Yd 05	Elong	Elastic
parameters	0.1 %	0.2 %	Calc at Entire Areas	0.5 %		Stress 200 – 150 N/mm ²
unit	N/mm ²	N/mm ²	N/mm ²	N/mm ²	%	N/mm ²
Bst. 1	- -	210.193	316.310	213.608	24.2857	6933.29

[TABLE 7]: Results of tensile strength test for steel sample «Bst. 1» from the palace
© Done by the authors

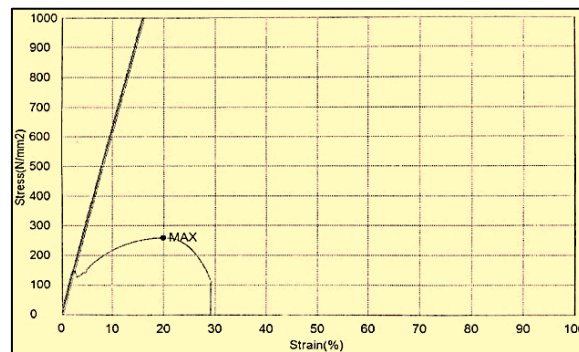


[FIGURE 5]: The maximum tensile strength value in the stress- strain curve of the steel sample of the palace «Bst. 1» © Done by the authors.

• **Sample 2: Slab Steel of the 2nd Floor**

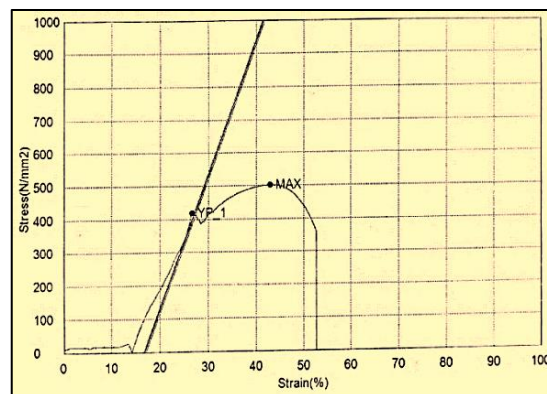
Name	YP(%fs) Stress	Yd 02	UTS	Yd 05	Elongation	Elastic
parameters	0.1 %	0.2 %	Calc at Entire Areas	0.5 %	-	Stress 100 –50 N/mm ²
Unit	N/mm ²	N/mm ²	N/mm ²	N/mm ²	%	N/mm ²
Bst. 2	--	146.246	259.338	148.307	24.5714	6280.05

[TABLE 8]: Results of tensile strength test for steel sample «Bst. 2» from the palace © Done by the authors.



[FIGURE 6]: The maximum tensile strength value in the stress- strain curve of the steel sample of the Palace «Bst. 2» © Done by the authors

• **Sample 3: Beams Steel of the 1st Floor**



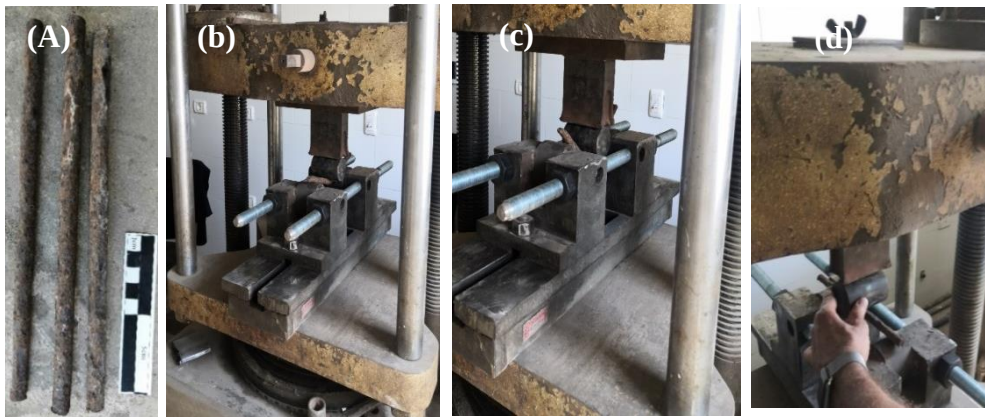
[FIGURE 7]: The maximum tensile strength value in the stress- strain curve of the steel sample of the palace «Bst. 3» © Done by the authors

Name	YP(%fs) _Stress	Yd 02	UTS	Yd 05	Elong	Elastic
parameters	0.1 %	0.2 %	Calc at Entire Areas	0.5 %		Stress 400 – 300 N/mm ²
Unit	N/mm ²	N/mm ²	N/mm ²	N/mm ²	%	N/mm ²
BSt. 3	418.030	413.574	501.380	413.739	24.0000	4040.26

[TABLE 9]: Results of tensile strength test for steel sample «Bst. 3» from the palace.

A. Bending Test and Determination of the Flexural Strength (σ_f) of Steel

This test assesses the steel's ductility and ability to deform without fracturing. A specimen is bent to a specified angle, and the surface is examined for cracks or defects, as shown in [FIGURES 8 -9]. Bend tests are also used to evaluate the quality of welds.



[FIGURES 8/A-D]: Sitting steel samples in the test device and conducting the Bending test
© Done by the authors

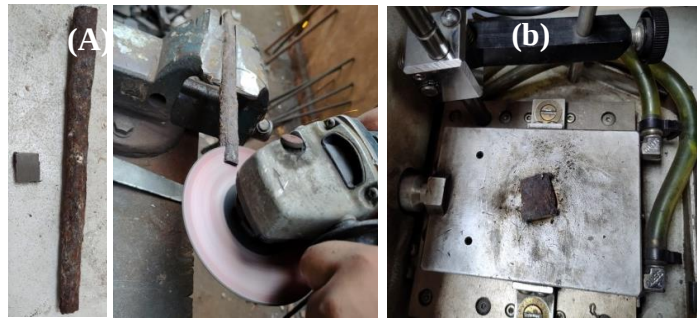


[FIGURES 9/A-C]: The results of the bending test, which showed good resistance to the bending strength and the absence of cracks. © Done by the authors

Examination and Analysis

1. Chemical Analysis of Reinforcing Steel

Chemical analysis was carried out for three samples of rebar used in the Baron Palace as shown in [FIGURES 10/A-B]. The results are summarized in [TABLE 10].



[FIGURES 10/A-B]: Preparing steel samples and sitting in the test device and conducting the chemical analysis © Done by the authors

Element	Fe	C	Mn	Si	P	S	Ni	Cr
Sample 1(%)	99.377	0.028	0.129	0.083	0.1999	0.0349	0.064	0.0097
Sample 2(%)	99.402	0.027	0.127	0.089	0.1986	0.0338	0.061	0.0049
Sample 3(%)	99.292	0.047	0.141	0.091	0.2012	0.0356	0.097	0.0125
Element	Cu	Mo	V	Ti	Al	B	Nb	----
Sample 1(%)	0.0283	0.014	0.0053	0.0031	0.007	0.0009	0.0015	----
Sample 2(%)	0.0277	0.0121	0.0049	0.0029	0.009	0.0011	0.0012	----
Sample 3(%)	0.0294	0.023	0.0096	0.0064	0.009	0.0019	0.0031	----

[TABLE 10]. Results of the chemical analysis for three steel samples from Al Baron Palace © Done by the authors

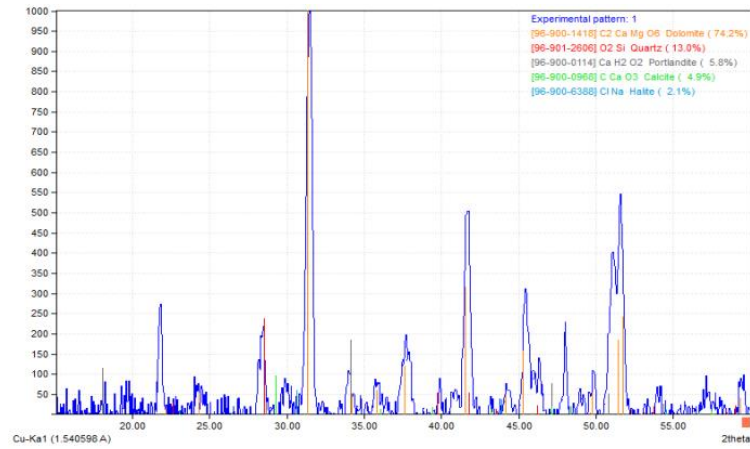
2. X-Ray Diffraction Analysis «XRD»

A.Reinforced Concrete

Through X-ray diffraction analysis, it was determined that the concrete is made up of sand «quartz grains SiO_2 ». The content of silicon oxide or free silica in the binder is assessed to be 27.9%. A comprehensive analysis of the binder indicated that it is of the aqueous variety, noted for the dominance of calcium, silicon and aluminum. Upon investigation, multiple non-humid water phases were observed, and an analysis of these phases revealed the presence of two compounds: Alite (C_3S) and Belite (C_2S). Refer to [TABLES 11-14]. Based on this information, the binder type can be classified as cement [FIGURES 11-14].

Index	Amount (%)	Minerals
A	74.2	Dolomite
B	13.0	Quartz
C	5.8	Portlandite
D	4.9	Calcite
E	2.1	Halite
	48.0	Unidentified peak area

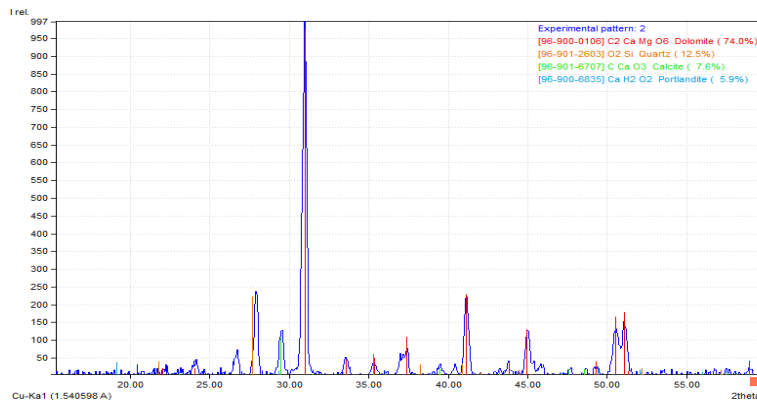
[TABLE 11]: XRD analysis results of ground floor slab concrete sample © Done by the authors



[FIGURE 11]: XRD pattern for a concrete sample of ground floor slab at the Baron Palace © Done by the authors

Index	Amount (%)	Minerals
A	74.0	Dolomite
B	12.5	Quartz
C	7.6	Calcite
D	5.9	Portlandite
	28.9	Unidentified peak area

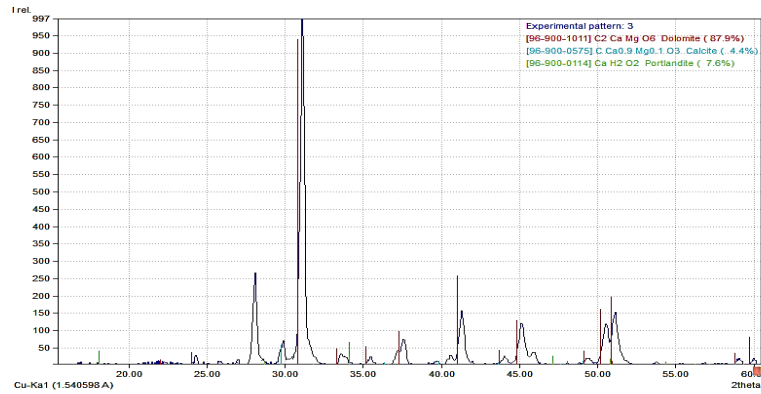
[TABLE 12]: Results of XRD analysis of a sample of concrete slab on the first floor in the palace © Done by the authors



[FIGURE 12]: XRD pattern for a sample of first-floor slab concrete at the palace © Done by the authors

Index	Amount (%)	Mineral
A	87.9	Dolomite
B	4.4	Calcite
C	7.6	Portlandite
	48.7	Unidentified peak area

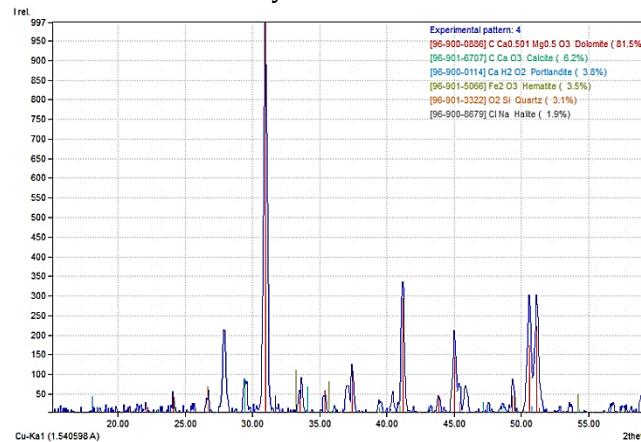
[TABLE 13]: Results of XRD analysis of a concrete sample from the ground floor beams in the palace © Done by the authors



[FIGURE 13]: XRD pattern for a concrete sample from the ground floor beams at the palace
© Done by the authors

Index	Amount (%)	Minerals
A	81.5	Dolomite
B	6.2	Calcite
C	3.8	Portlandite
D	3.5	Hematite
E	3.1	Quartz
F	1.9	Halite
	23.9	Unidentified peak area

[TABLE 14]: Results of XRD analysis of a beams concrete sample of the 1st floor in the Palace
© Done by the authors



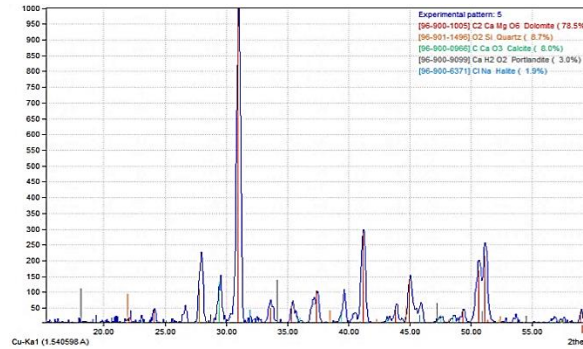
[FIGURE 14]: XRD pattern for a concrete sample from the beams of the first floor of the Palace
© Done by the authors

B. Cement Bricks

The cement bricks in the palace consist mainly of quartz (sand) at 70%, calcium carbonate (lime) at 20% and Anorthite, a component of Portland cement, at 10%. The results are summarized in [TABLE 15] & [FIGURE 14].

Index	Amount (%)	Minerals
A	78.5	Dolomite
B	8.7	Quartz
C	8.0	Calcite
D	3.0	Portlandite
E	1.9	Halite
	23.0	Unidentified peak area

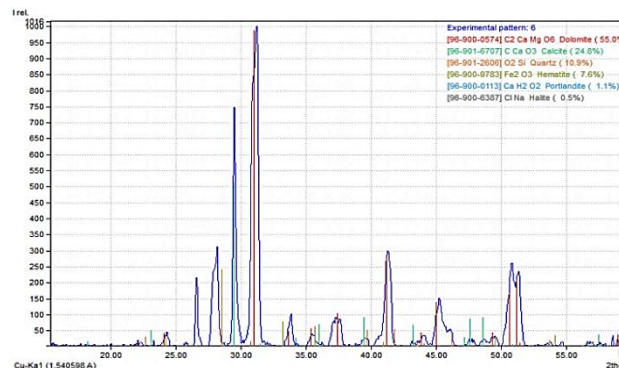
[TABLE 15]: Results of XRD analysis of a cement bricks sample on the ground floor of the Baron Palace
© Done by the authors



[FIGURE 15]: XRD pattern of a cement bricks sample on the ground floor of the palace
© Done by the authors

Index	Amount (%)	Minerals
A	55.0	Dolomite
B	24.8	Calcite
C	10.9	Quartz
D	7.6	Hematite
E	1.1	Portlandite
F	0.5	Halite
	31.0	Unidentified peak area

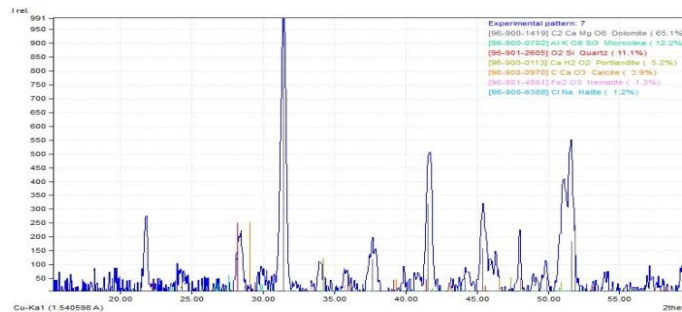
[TABLE 16]: Results of XRD analysis of a cement bricks sample on the ground floor of the Baron Palace
© Done by the authors



[FIGURE 16]: XRD pattern of a cement bricks sample on the ground floor of the palace
© Done by the authors

Index	Amount (%)	Minerals
A	65.1	Dolomite
B	12.2	Microcline
C	11.1	Quartz
D	5.2	Portlandite
E	3.9	Calcite
F	1.3	Hematite
G	1.2	Halite
	41.8	Unidentified peak area

[TABLE 17]: Results of XRD analysis of a cement bricks sample on the first floor of the Palace © Done by the authors



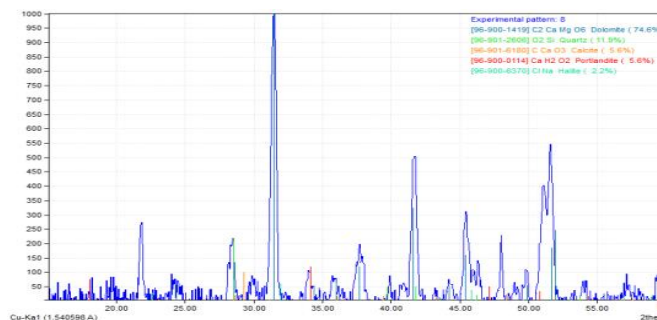
[FIGURE 17]: XRD pattern for a cement bricks sample on the first floor of the Palace © Done by the authors

C. Cement Mortar

The cement mortar in the palace consists mainly of Calcium Carbonate (lime) at 71%, Quartz (sand) Calcium Carbonate (lime) at 12%, and Anorthite, a component of Portland cement, at 6%. Results are summarized in [TABLES 18-20] & [FIGURES 18-20].

Index	Amount (%)	Minerals
A	74.6	Dolomite
B	11.9	Quartz
C	5.6	Calcite
D	5.6	Portlandite
E	2.2	Halite
	45.1	Unidentified peak area

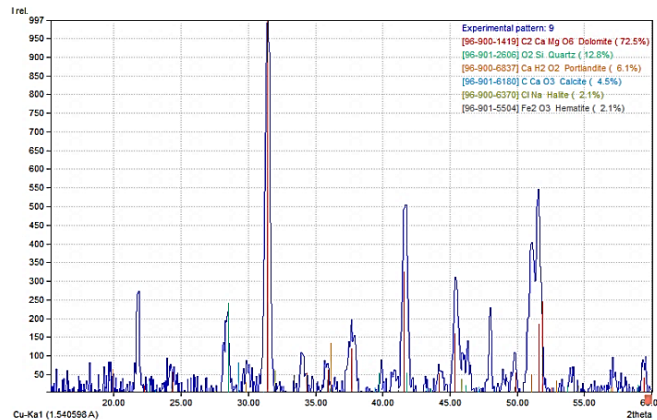
[TABLE 18]: Results of XRD analysis of a cement mortar sample on the ground floor of the Baron Palace



[FIGURE 18]: XRD pattern for a cement mortar sample on the ground floor of the palace © Done by the authors

Index	Amount (%)	Minerals
A	72.5	Dolomite
B	12.8	Quartz
C	6.1	Portlandite
D	4.5	Calcite
E	2.1	Halite
F	2.1	Hematite
	43.4	Unidentified peak area

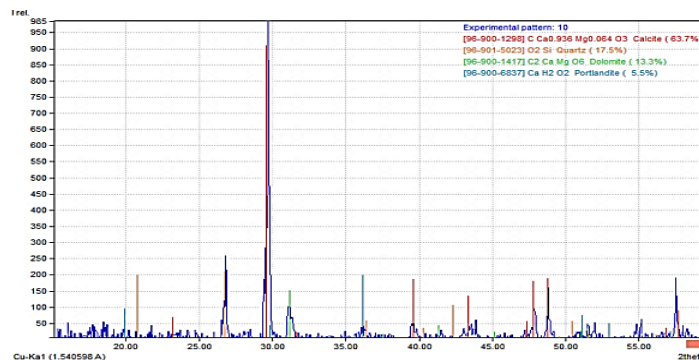
[TABLE 19]: Results of XRD analysis of a cement mortar sample on the ground floor of the Baron Palace©
Done by the authors



[FIGURE 19]: XRD pattern for a cement mortar sample on the ground floor of the palace © Done by the authors

Index	Amount (%)	Minerals
A	63.7	Calcite
B	17.5	Quartz
C	13.3	Dolomite
D	5.5	Portlandite
	81.3	Unidentified peak area

[TABLE 20]: Results of XRD analysis of a cement mortar sample on the first floor of the Baron Palace ©
Done by the authors

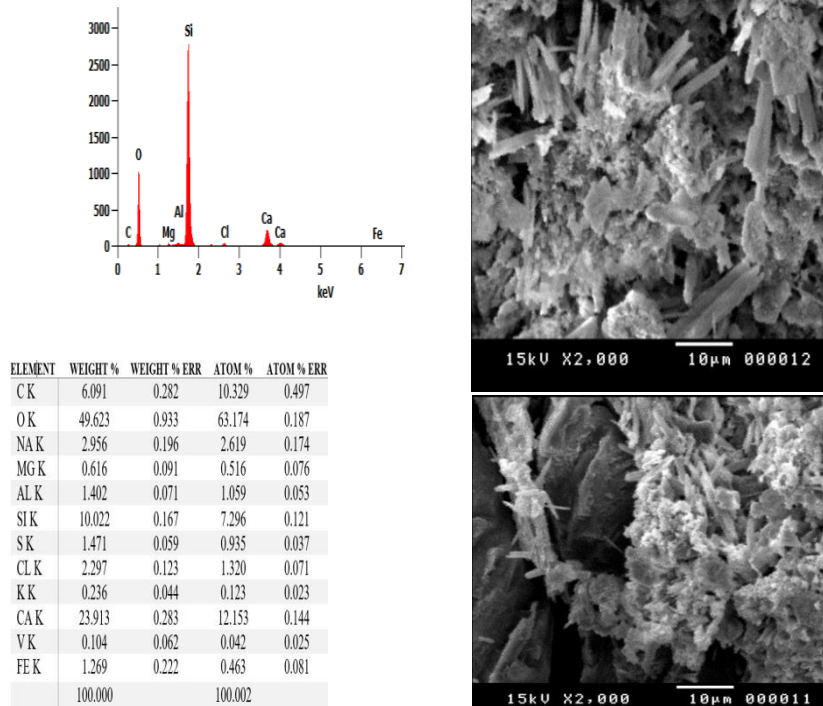


[FIGURE 20]: XRD pattern for a cement mortar sample on the first floor of the palace © Done by the author

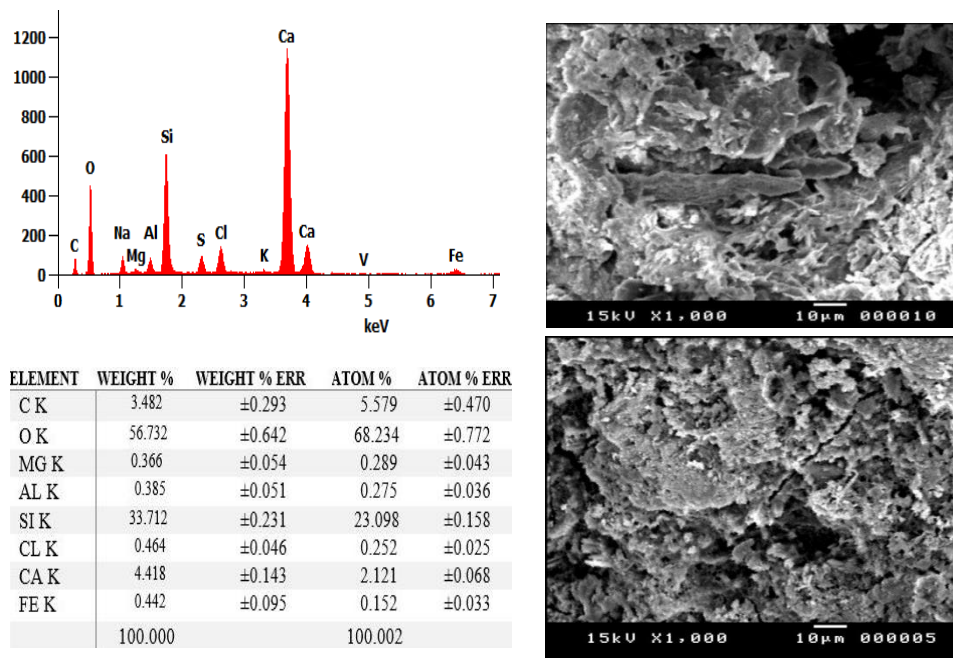
D.SEM attached with EDEX

▪ Reinforced Concrete

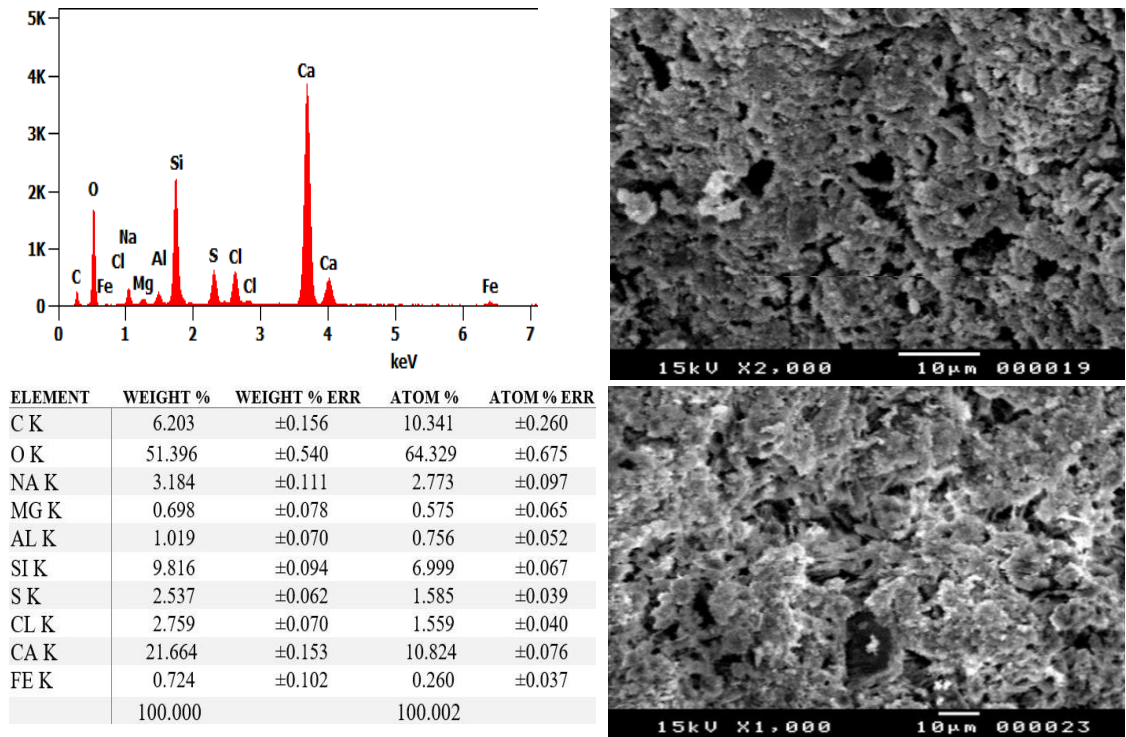
Concrete consists of silica, calcium and oxygen (cement) largely with different proportions of other elements, such as chlorine or sodium «Halite», which represent impurities and salts present during manufacturing, or formed after as a result of destructive factors [FIGURES 21-24].



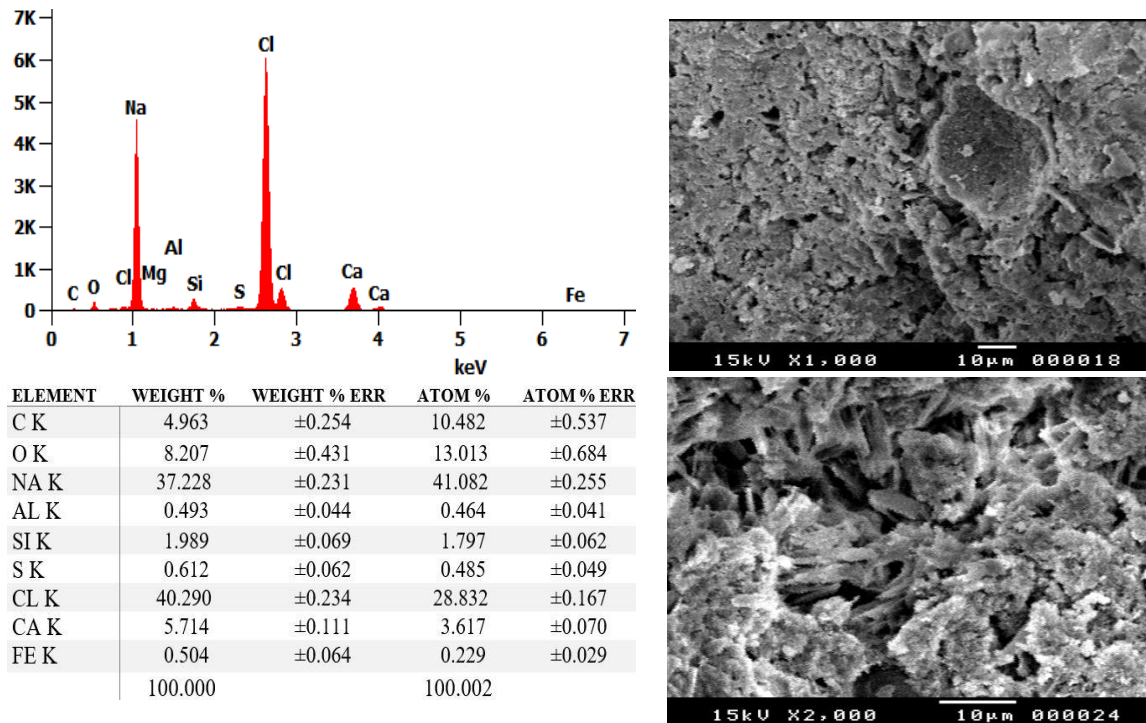
[FIGURE 21]: SEM analysis results of a palace concrete sample «Slabs Concrete» © Done by the authors



[FIGURE 22]: S.E.M analysis results of a palace concrete sample «Slabs Concrete» © Done by the authors



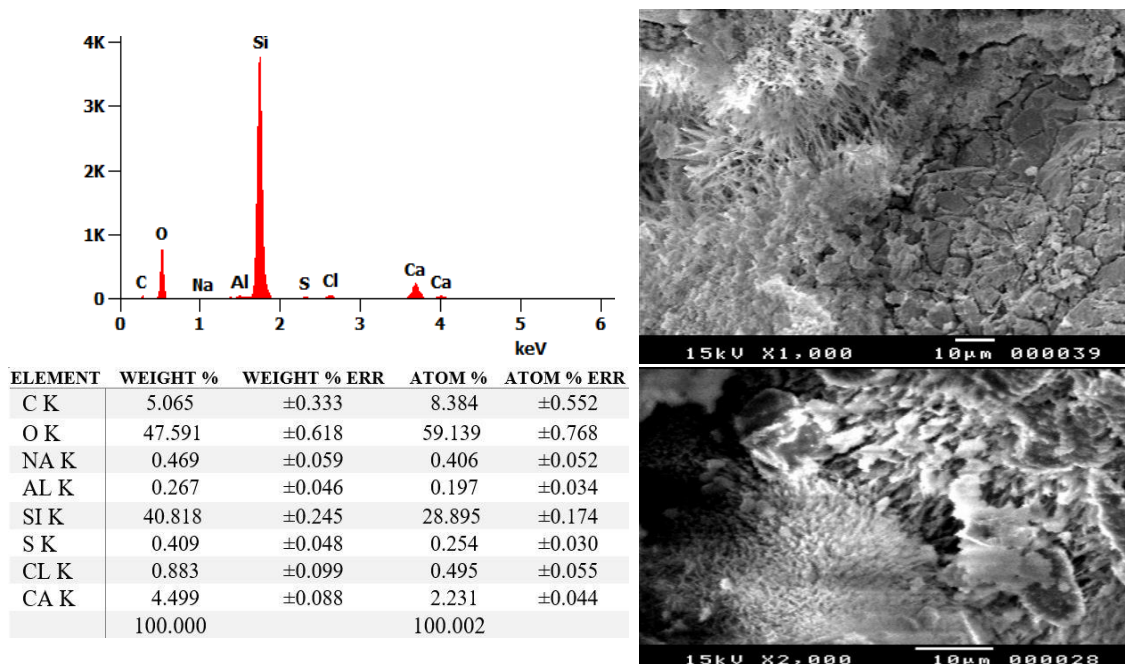
[FIGURE 23]: S.E.M analysis results of a palace concrete sample «Beams Concrete» © Done by the authors



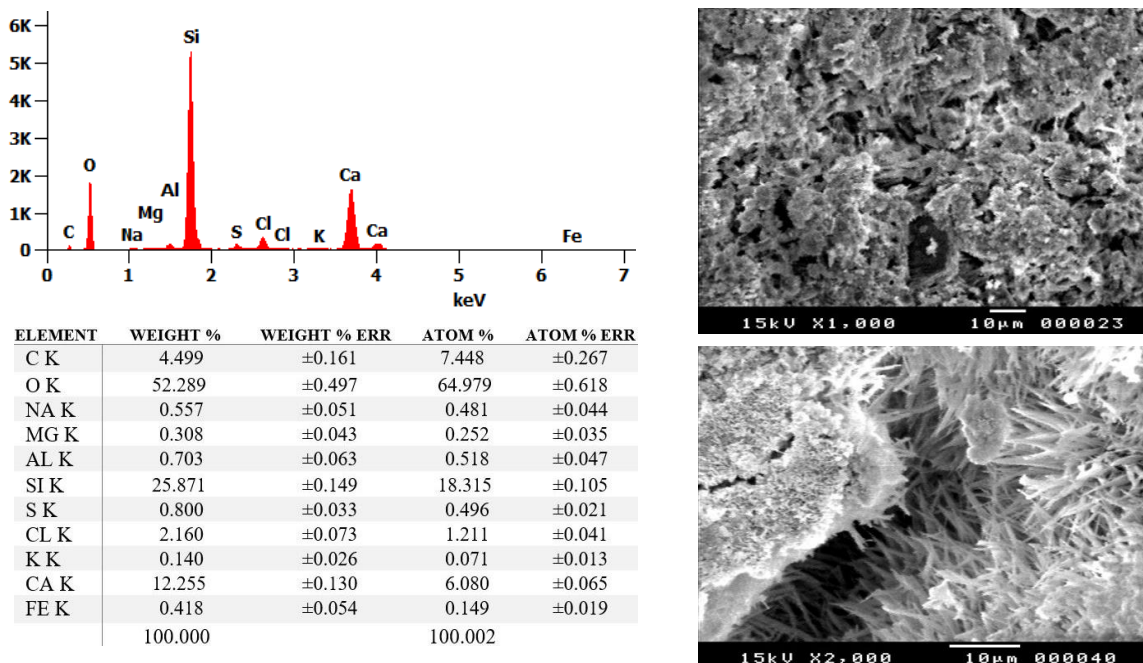
[FIGURE 24]: S.E.M analysis results of a palace concrete sample «Beams Concrete» © Done by the authors

■ Cement-Lime Brick

Cement-lime brick consists mainly of silica, calcium and a small percentage of other elements [FIGURE 25].



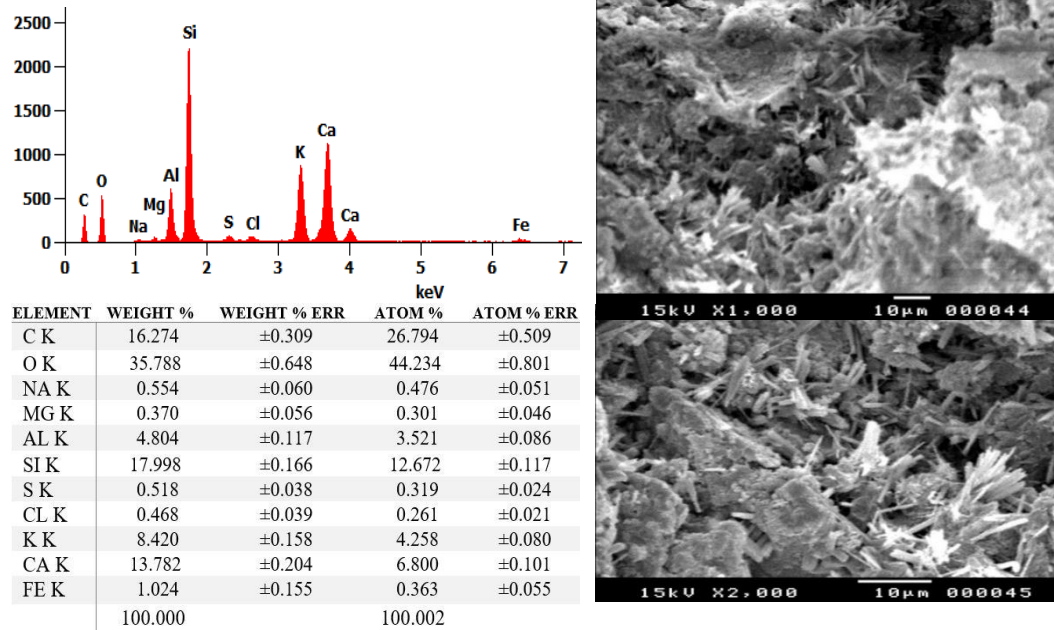
[FIGURE 25]: S.E.M analysis results of a palace cement-lime brick sample © Done by the authors



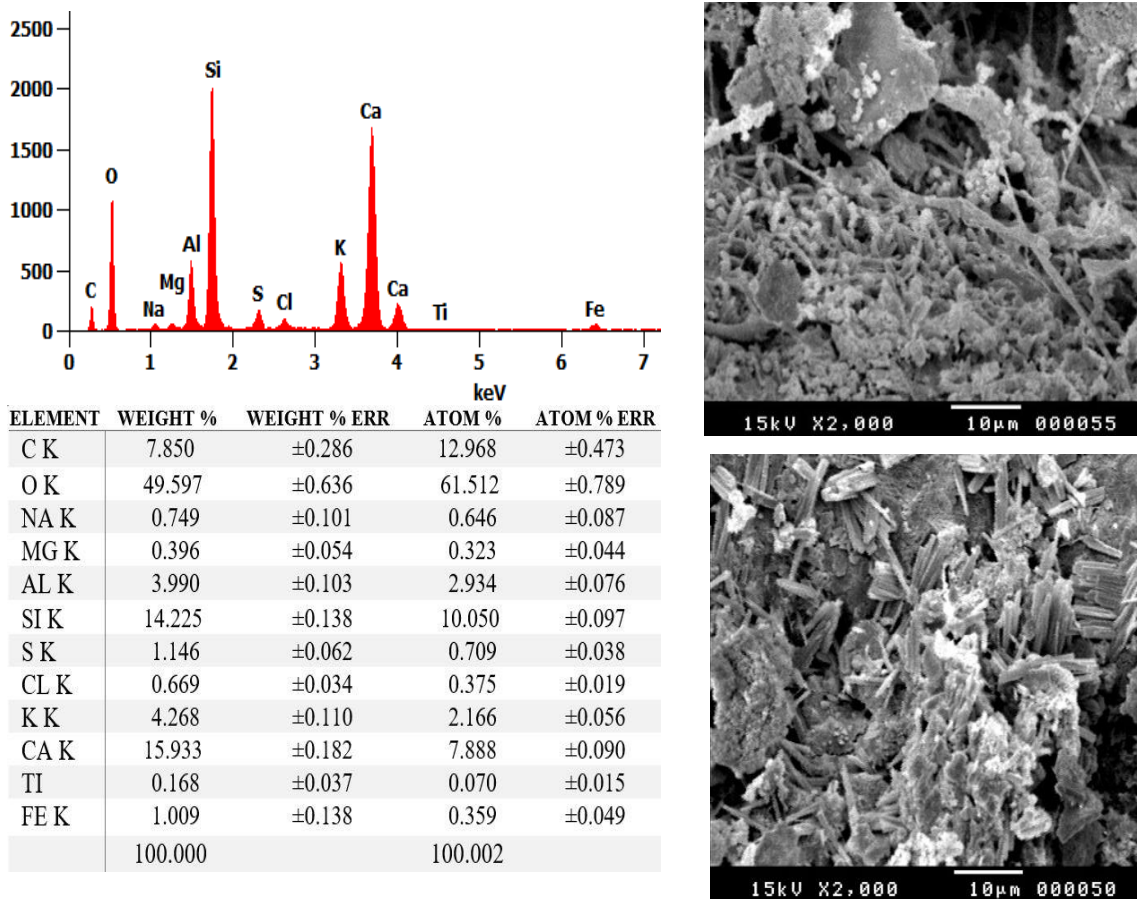
[FIGURE 26]: S.E.M analysis results of a palace cement-lime brick sample © Done by the authors

■ Cement-Lime Mortar

Cement-lime mortar consists mainly of silica, calcium and a small percentage of other elements very similar in composition to lime-cement bricks [FIGURE 27].



[FIGURE 27]: S.E.M analysis results of a palace cement-lime mortar sample © Done by the authors



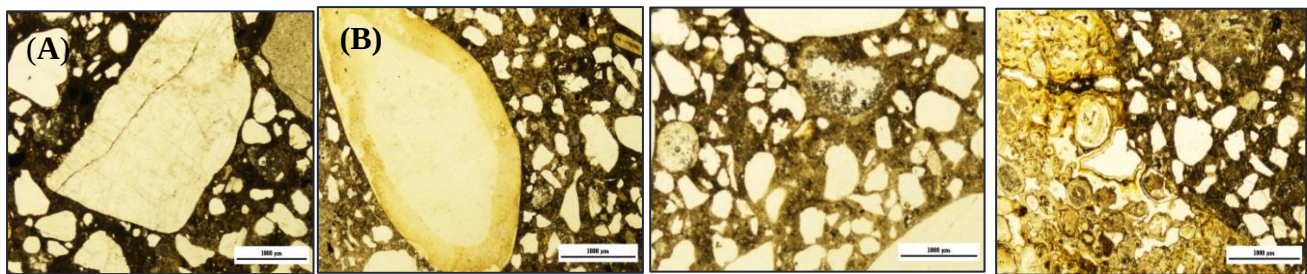
[FIGURE 28]: S.E.M analysis results of a palace cement-lime mortar sample © Done by the authors

D. Petrographic Study by the Polarizing Microscope «P. M.»

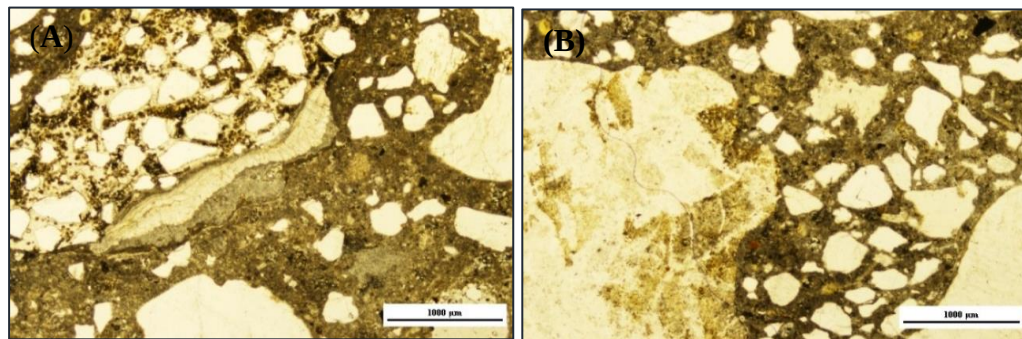
A petrographic study was conducted on building material samples, «concrete, cement bricks and mortar», from Al-Baron Palace show their mineralogical composition and alterations. The investigations were carried out in the Faculty of Science's laboratories at Cairo University.

▪ Reinforced Concrete

The thin section of the reinforced concrete samples from slabs and beams revealed that reinforced concrete is a mixture of a group of components with a cement-hydraulic binder. There is a relatively average relationship between aggregate and binder «about 2.5 percent of the aggregate amount per binder amount». The slide image showed high porosity with concrete, some relatively small pieces of limestone, and charcoal with a diameter between 10-30. The aggregate is round quartz sand, interspersed with coarse sand with a diameter of 70% exceeding 2 mm, such as large, multi-colored gravel. The ratio of the binder to the granules is rather weak. There are cracks around the granules, as shown in [FIGURES 29 - 30].



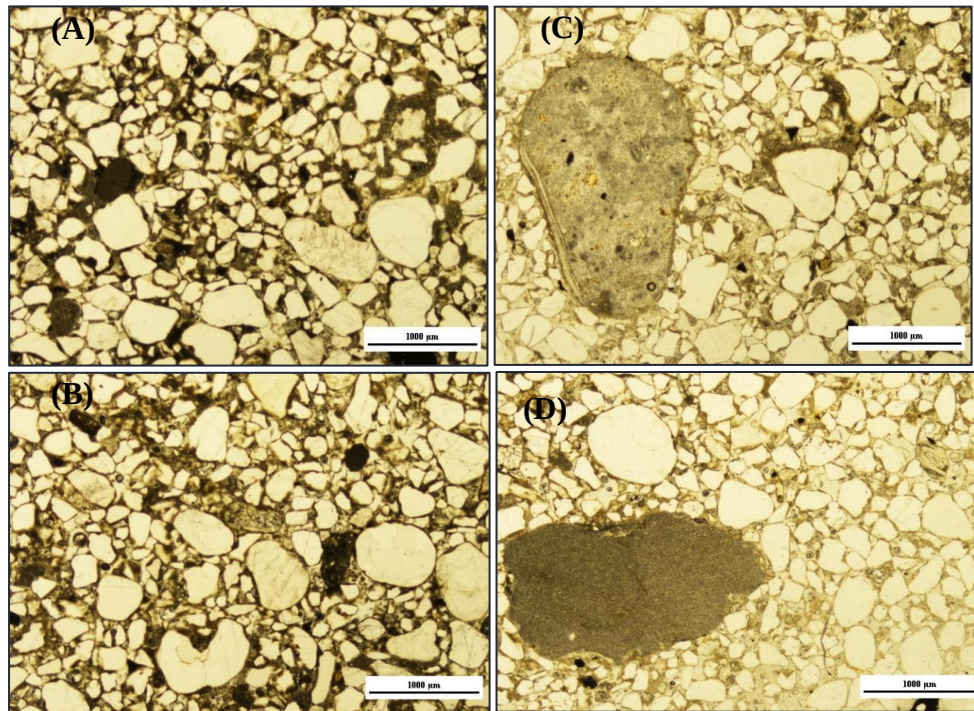
[FIGURES 29/A-D]: Petrographic investigation of the palace concrete samples «Concrete slabs» © Done by the authors



[FIGURES 30/A-B]: Petrographic investigation of the palace concrete samples «Beam Concrete» © Done by the authors

▪ Cement Lime Bricks

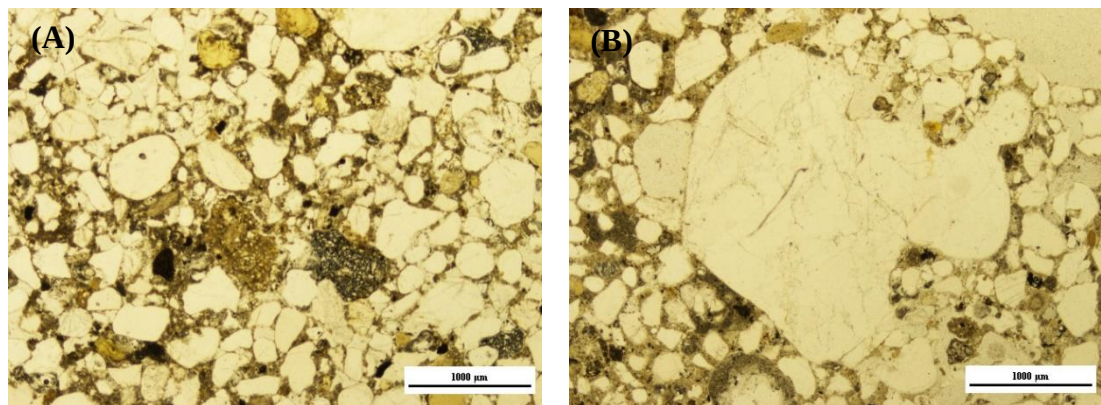
The thin section analysis revealed that the bricks samples are composed of crystalline sand (quartz) in a cement-type hydraulic (mixable) binder based on calcium silicate. Aggregates are round crystalline (quartz) sands. The «medium sand» looks light beige in color. The size of the granules is continuous gradients. There are some agglomerates as impurities in the mixing process that may represent weaknesses in these bricks, as shown in [FIGURES 31/A-D].



[FIGURES 31/A-D]: Petrographic investigation of the palace cement lime bricks samples © Done by the authors

▪ Cement Lime Mortar

The thin-section analysis of the mortars indicated a semi-homogeneous structure with poor consistency. The binder is hydraulic lime cement. It contains round crystalline sand grains (quartz) in small quantity, light gray in color and similar to medium sand, with continuous grains that allow the mortar to be worked into a compact form. The bond ratio to the grains shows small pores (2–3%) and no cracks [FIGURES 32/A-B].



[FIGURES 32/A-B]: Petrographic investigation of the palace cement lime mortar samples © Done by the authors.

IV. DISCUSSIONS

1. Reinforced Concrete

Upon examining the concrete samples from the beams and slabs, it was discovered that the bond used in the palace's concrete is hydraulic Portland cement, which is characterized by high porosity; the bond's silicon content measures 27.9% and exhibits low fluidity. The fine aggregates consist of rounded quartz (crystalline) sand with a diameter of 2 mm (70%), complemented by larger gravel of various sizes. The aggregate-to-calcium binder ratio is 1 to 2.5 of the volume, indicating weakness, as the bond did not adequately occupy the spaces between the granules. The engineering characteristics of the concrete samples retrieved from the palace revealed an average compressive strength of 16.1 N/mm², which is considered weak when compared to the standards outlined in ASTM C 170. The average volumetric mass stands at 2.409 k/m³. These low strength values may arise from numerous cracks observed between the larger granules and the mortar (cement/sand), as indicated by the results from the SEM analysis, or could be attributed to the high binder ratio in the mix and elevated water/cement ratio, coupled with the rapid drying of the concrete immediately after pouring. Another factor contributing to the poor strength is that larger particles detached from the cylindrical sample during preparation, leading to a reduction in the concrete's effective components under testing. Assuming the mortar contains a high level of binder using 250 kg of cement per ton of concrete, the chloride concentration measured at 0.124% translates to $0.124/0.25 = 0.496\%$ of the binder mass in the concrete.

This value surpasses the theoretical maximum of 0.4% but may not negatively affect the material if the carbon saturation levels and/or relative humidity are appropriately regulated. Given these findings, the roofs consist of reinforced concrete with high porosity.

This concrete is weak and lacks density, failing to create a protective environment for the reinforcing steel due to its high pH level. The carbonization of this concrete is crucial for the building's upkeep. Iron is prone to corrosion when exposed to moisture, while dry layers suggest that the concrete may rapidly lose moisture right after application. By converting the chloride percentage of the binder's weight, the estimated NaCl ratio is $0.16/0.4 = 0.04$, indicating the maximum percentage. Elevated chloride levels are hazardous for the steel when moisture is present. When calculated relative to the binder's weight, the sulfate ratio stands at $1.40/0.4 = 3.5\%$ and in conditions of high humidity, this increased sulfate concentration poses a risk to the concrete itself by generating an expansive gel in the form of a secondary compound «where the calcium tri-aluminate reacts with sulfates to form the compound». Such expansion can lead to a notable increase in the cement volume. Given the hollow mortar's composition, this expansion is unlikely to cause damage, and no formation of the secondary compound has been detected.

2. Reinforcing Steel

The steel samples utilized for the construction of beams and slabs consist of smooth steel. For mechanical testing, samples measuring 8 mm in diameter and 30 cm in length

were employed, as previously mentioned. It was noted that these samples exhibited varying degrees of rust. Results from the mechanical testing showed an elastic limit of 346 N/mm² and a tensile strength of 380 N/mm². This type of steel is classified as ordinary non-alloyed construction steel, referenced between S235 and S355. With a low carbon content of 0.035%, this steel is characterized as relatively soft and has a low resistance to corrosion in natural environments.

3. Lime- Cement Bricks

A significant portion of the bricks used to construct Al-Baron Palace may have originated from a local factory situated in the Heliopolis district, where the palace is located, which was established to provide bricks for nearby construction projects. The dimensions of these bricks are 23 cm in length, 11 cm in width, and 6.5 cm in height. The binding agent used is cement «specifically hydraulic Portland cement», which can be mixed with water. The silicon ratio in the binder is 0.38% «indicating medium hydraulic properties», with the aggregate being medium-sized round crystal sand (quartz) that is light in color. The binder-to-aggregate ratio is relatively weak «approximately 1:4 by size» and exhibits high porosity. There are considerable amounts of soluble salts present, including gypsum, sodium chloride, calcium chloride, and nitrates. The total chloride percentage (NaCl + CaCl) amounts to 0.40% (0.29 + 0.10 + 0.01). Inside the composition of the brick, there are small lumps of lime measuring 10 mm and fragments of wood charcoal .

The Royal Institute for Cultural Heritage of Belgium conducted a comparative analysis between a sample of lime sand bricks taken from the Baron Empain Palace and another sample of contemporary bricks. The analyses revealed that these are lime sand bricks made up of crystalline sand (quartz) with a bond based on calcium silicate. This technique was relatively new during that period. The Royal Institute for Cultural Heritage operates under the Belgian Federal Office for Science Policy and is committed to studying and preserving Belgium's artistic and cultural heritage. Its responsibilities encompass research, assessment, preservation and restoration within heritage sciences, as well as documenting inventories and heritage. This study was commissioned by the Belgian Ministry of Foreign Affairs as part of the Belgian mission to investigate the Baron Empain Palace case in 2009.

4. Lime- Cement Mortar

The structural mortars exhibit a uniform structure and low cohesion, with a porosity observed at 2-3%. No cracking is noted. The fine aggregates consist of rounded crystalline sand grains. The mortar appears to be poorly mixed and lacks a sufficient binder «cement and lime». The composition of the adjacent lime-sand brick mortar proved to be suitable.

Carbonization does not have a significant impact on it. The chloride to binder weight ratio is $0.40/0.25 = 1.6\%$, which exceeds the 0.4 limit established for reinforced concrete; however, this is not critical since it's intended as a building mortar. Nonetheless, water intrusion into reinforced elements may lead to salt deposits and potential damage. Dry

phases that are not moist can indicate the speed at which the mortar dries during application.

V.CONCLUSIONS

A program for testing was designed and carried out to evaluate the characterization and engineering properties of the construction materials used in Al Baron Empain Palace in Cairo. The analysis included microstructure examination, compressive strength testing, modulus of elasticity assessment, and splitting tensile strength determinations as detailed in earlier sections of this report. Based on the studies conducted and the researcher's involvement in the diagnostic and restoration efforts undertaken by the restoration project's executing authority at the palace, the following conclusions can be drawn:

- Cement and reinforced concrete constitute a widely employed approach in the Baron Palace. This includes not only structural elements like «reinforced concrete» but, also prefabricated decorative parts, or «reinforced mortar», that were formed using metal compositions. The types of steel present in the palace include round steel, which was used for primary reinforcement in the reinforced concrete constructions. Results from chemical analysis and tensile strength tests of the steel samples in the palace indicated that the tensile strength reached normal levels compared to contemporary steel used in buildings. In contrast, the carbon content was notably low (0.03%), which lessens the steel's susceptibility to corrosion and diminishes its efficiency. Additionally, flat skewers were employed as supports (pendants) in both reinforced concrete and prefabricated elements; these appear to be made of stiffer steel than the round skewers and are also galvanized. Iron connecting threads (spacers) were observed.
- When comparing with modern reinforcement structures, significant spacing between the iron reinforcements and inadequate iron quality were noted. Intense reactions within the concrete sections are considerable, both in horizontal (beams) and vertical (columns) components.
- Several variations in concrete and contamination do not jeopardize the building's integrity, except where reinforcing steel is present.
- On the ground and first-floor ceilings, steel was detected every 25-30 cm.
- The concrete utilized in the palace does not necessarily serve as reinforcement.
- Horizontal load-bearing components are reinforced, but not all vertical elements are. The central four columns of the roofed sections are reinforced, whereas the side columns consist of unreinforced cast concrete.
- The roofed heater units are reinforced.
- The mortar used in stone masonry or bonding is frequently not reinforcing.
- Some prefabricated components, such as stone balustrades and the upper sections of terrace fences encircling the palace, are also reinforced.
- Steel has been found in carbonized areas of various sections.
- The palace's walls and foundations have the capacity to bear new additional loads.

- Testing on the concrete slabs indicated they are relatively weak, and visual inspections revealed that they are experiencing deflection, falling concrete cover, and steel corrosion. Consequently, restoration measures are essential to prevent further structural issues.

DISCLOSURE STATEMENT

No Potential conflict of interest was reported by the authors

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STRUCTURAL EVOLUTION AND ANALYSIS OF COMPLEX HISTORIC BRICK MASONRY STRUCTURES: THE FORT OF ṬĀBIYAT 'URĀBĪ IN DAMIETTA, EGYPT

By

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ABSTRACT

[EN] This study presents a comprehensive structural assessment of the soldiers' barracks — «al-qašlāq» — a crucial element of the defensive system at Ṭābiyat 'Urābī Fort in Damietta Governorate, which has suffered continuous exposure to the marine environment and associated long-term deterioration. ^cUrābī Fort was built by the French expedition (1799-1801 AD) and used by Egyptian patriots during al-^cUrābīya revolution (1879-1882 AD). This study employed a multidisciplinary methodology, including detailed field surveys, crack mapping, material characterization and linear static finite element modeling using ETABs software. The stress distributions, deformation patterns and current dead load values were evaluated. The mechanical properties were calibrated using uniaxial compression tests on the obtained bricks samples and benchmarked against the Egyptian Code for Masonry Structures (ECP 201). The results of the numerical modeling and structural analysis revealed that al-qašlāq was constructed with load-bearing walls of fired brick and a roof of bricks supported by a wooden system, lacking any modern reinforcement elements. High humidity and fluctuating groundwater levels weaken load-bearing soil layers, leading to irregular settlement of shallow building foundations and causing significant structural deterioration, manifested as internal and external wall deformations, localized cracks and collapses affecting several load-bearing elements. The quantitative results revealed significant structural vulnerability under dead-load conditions alone. The maximum horizontal displacements reached 22.9 mm at the upper story, whereas vertical settlements of up to 43.7 mm were recorded at critical foundation nodes, indicating pronounced differential settlement. The computed tensile stresses in the masonry panels reached 1.9 kN/m², exceeding the negligible tensile capacity of unreinforced brickwork and correlating with the observed vertical and diagonal cracking. The compressive stresses remained below -2.9 kN/m², within the conservative masonry strength bounds. These findings emphasize the necessity of integrating numerical modeling with heritage-sensitive conservation strategies for historic masonry structures exposed to aggressive coastal environments.

KEYWORDS: Ṭābiyat 'Urābī, masonry structures, stress analysis, structural analysis, structural deficiency.

[AR]

التطور والتحليل الإنشائي للمنشآت التاريخية المعقدة المبنية من الطوب: حصن عرابي في دمياط، مصر
يقدم هذا البحث تقييماً إنشائياً شاملاً لحصن أو طابية عرابي بمحافظة دمياط، مع التركيز على ثكنات الجنود «القشلاق»، وهي عنصر أساسي في النظام الدفاعي للحصن، ولا سيما في ظل تعرضه المستمر للبيئة البحرية وما يصاحبها من تدهور طويل الأمد. شُيّد حصن عرابي خلال الحملة الفرنسية على مصر (1799-1801) ولاحقاً، استخدم الحصن من قبل الوطنيين المصريين أثناء الثورة العربية (1879-1882). كما استخدمت الدراسة منهجية متعددة الأدوات، شملت مسوحات حقلية تفصيلية، ورسم خرائط الشقوق، وتشخيص المواد، بالإضافة إلى التحليل الإنشائي الرقمي باستخدام طريقة العناصر المحددة عبر برنامج إيتابس. وتم تقييم توزيع الإجهادات، وأنماط التشوه، والقيم الحالية للأحمال الميتة. كذلك تمت معايرة الخصائص الميكانيكية باستخدام اختبارات الضغط أحادي المحور على عينات من الطوب المتحصل عليها، ومقارنتها بالمعيار المصري للإنشاءات الحجرية (ECP 201). وأظهرت نتائج المعاينة والفحص أن القشلاق مشيّد باستخدام جدران حاملة من الطوب المحروق غير المسلح، مع نظام سقف من الطوب مدعوم بعناصر خشبية، دون وجود أي عناصر تدعيم حديثة. وقد أدى التعرض المستمر لارتفاع الرطوبة وتذبذب منسوب المياه الجوفية

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إلى إضعاف طبقات التربة الحاملة، مما أدى إلى حدوث هبوط غير منتظم في الأساسات السطحية. وأسفر ذلك عن تدهور إنشائي ملحوظ تجلّى في تشوهات داخل وخارج مستوى الجدران، وظهور تشققات موضعية، وحدوث انهيارات جزئية طالت عدداً من العناصر الحاملة. وأوضحت النتائج الكمية عن ضعف هيكلي كبير في ظل ظروف الأحمال الميتة وحدها. إذ بلغ أقصى إزاحة أفقية نحو 22.9 مم عند مستوى الطابق العلوي، في حين سُجِّل هبوط رأسي وصل إلى 43.7 مم عند نقاط الأساس الحرجة، مما يشير إلى وجود هبوط تفاضلي واضح. كما بلغت إجهادات الشد المحسوبة في ألواح البناء نحو 1.9 kN/m^2 ، متجاوزةً قدرة الشد الضئيلة للطوب غير المسلح، وهو ما يتوافق مع أنماط الشروخ الرأسية والمائلة المرصودة ميدانياً. كما ظلت إجهادات الضغط أقل من -2.9 kN/m^2 ، ضمن حدود قوة البناء المحافظة. وتؤكد هذه النتائج على ضرورة الدمج بين تقنيات النمذجة العددية المتقدمة مع استراتيجيات الحفاظ على التراث التي تراعي البيئة، بما يضمن السلامة الإنشائية والحفاظ طويل الأمد على المنشآت التاريخية المبنية بالطوب والمعرضة لظروف بيئية ساحلية قاسية.

الكلمات الدالة: تحليل الاجهادات، التحليل الانشائي، التداعيات الانشائية، طابية عراقى، مبنى الطوب الاعتيادية.

I. INTRODUCTION

This study analyzes the barracks of the soldiers at the ^cUrābī Fort, revealing structural weaknesses due to environmental factors and recommending rehabilitation strategies for heritage preservation. This study presents a detailed structural diagnostic assessment and linear static stress analysis of the historical Ṭābiyat 'Urābī and focuses on the soldiers' barracks known as al-qašlāq, a critical component of the fort's defensive architecture. Utilizing a combination of field observations, photographic records and numerical modeling via ETABS, this study aims to uncover structural vulnerabilities, assess stress and displacement distributions under actual dead loads and formulate prioritized recommendations for enhancement and preservation.

^cUrābī Fort or «Ṭābiyat 'Urābī» is a masonry ensemble positioned near the Nile. It is distinguished by its rectangular configuration «approximately 300 m by 200 m» and its series of load-bearing brick walls, vaulted areas and timber roofing systems. Structurally, the fort consists of three primary segments: an outer defensive perimeter with an enclosing ditch, a western block facing the Nile with substantial masonry storage and utility edifices and an eastern cluster of residential and utility buildings featuring vaulted brick halls and stables. [FIGURES 1/A-D] shows the state of preservation of Ṭābiyat 'Urābī in the Damietta Governorate. Intensive structural deficiencies and building material decay are evident. [FIGURES 2/A-C] shows the 2D plans views for the first story, second story, and the third story of Ṭābiyat 'Urābī.

The static system of the analyzed structure primarily comprises robust load-bearing brick walls complemented by timber roof elements and compacted clay roofing infill. Notably, the absence of modern reinforced concrete frameworks within the examined sections was significant. Over the years, the fort has experienced detrimental effects due to moisture, fluctuating groundwater levels and differential settlement, leading to observable cracks, localized structural failures and material degradation. The findings of this study underscore the necessity of extensive refurbishment strategies aimed at ensuring the structural integrity and long-term preservation of this historical edifice.

The Fort of ^cUrābī was originally built by the French expedition (1799-1801 AD) to defend the country against sea attacks. Later it was used by Egyptian patriots during the al-^cUrābīya revolution (1879-1882 AD) and was thus named after that event. Originally built

by the French in the 18th century and developed during the reign of Mohammed ‘Ali, *Ṭābiyat ‘Urābī* later became associated with the ‘*Urābī* Revolt (1879–1882 AD), when it served as a symbol of national resistance against foreign intervention¹. Officially registered as an Islamic monument in 1985 AD, the site is one of the key archaeological landmarks in Damietta, although it has suffered severe deterioration due to neglect and limited restoration efforts².

Ṭābiyat ‘Urābī is situated in ‘*Izbat al-Burğ*, Damietta Governorate, on the eastern bank of the Damietta branch of the Nile at its confluence with the Mediterranean Sea, opposite Rās El Bar. Owing to this strategic location, the site controlled the northern entrance of the waterway and functioned as a significant coastal defensive and navigational landmark.

The site’s main significance lies in its military and defensive role, as it formed part of the coastal fortification system protecting the Nile mouth from naval invasions and securing one of Egypt’s most vital economic and strategic routes. The primary significance of the site lies in its military and defensive function, as it constituted an integral component of the coastal fortification system designed to protect the Nile mouth from naval incursions and secure one of Egypt’s most critical economic and strategic waterways.

The prediction of behaviors associated with complex historic masonry structures is pivotal in various engineering fields, driving the development of models that can accurately simulate these behaviors⁴. Three categories of models are predominantly used for this purpose: statistical, deterministic and hybrid mathematical models. Statistical models, which rely exclusively on historical data obtained through monitoring, offer insights into the correlation between external loads and resultant underground responses.

However, a significant limitation of these models is their parameters, which lack physical interpretation and can obscure the understanding of the underlying mechanisms⁵.

Multiple Linear Regression (MLR) models, as a subclass of statistical modeling, have become increasingly favored due to their simplicity and efficiency in computational requirements⁶. These models facilitate rapid predictions but may struggle to encapsulate the inherent complexities of subsurface behavior. In contrast, deterministic models are grounded in the principles of physics and require the resolution of differential equations to yield predictions. The intricate nature of these equations often results in challenges when seeking closed-form solutions, leading to a reliance on numerical techniques, such as the Finite Element Method (FEM), to derive approximate solutions⁷.

Hybrid models have emerged as an effective compromise, integrating elements from both statistical and deterministic approaches to enhance predictive accuracy, while maintaining interpretability. By leveraging the strengths of diverse modeling frameworks,

¹ ASTM C67-14 2014.

² CULTRONE *et Al.* 2005: 39-48.

⁴ HUANG *et Al.* 2022: 1020.

⁵ HEMEDA 2022: 3.

⁶ HOEK *et Al.* 2002: 267–273.

⁷ WOLDESENBET *et Al.* 2023: 1-14.

these hybrids capitalize on empirical data and physical principles, thereby providing robust predictions that can accommodate the intricacies of underground behavior⁸.

Continued advancements in computational power and data acquisition technologies offer promising avenues for refining these models, enabling more accurate forecasting of underground structure behavior⁹. This ongoing evolution emphasizes the importance of interdisciplinary collaboration among geotechnical engineers, data scientists and applied mathematicians to enhance the fidelity of predictive models. Moreover, addressing the limitations inherent in each modeling approach is crucial for developing a comprehensive understanding of subterranean systems, ultimately fostering improved decision-making and risk management in related engineering projects¹⁰.

Similar studies have investigated the deterioration of heritage buildings using different assessment methods. For example, ROMERO-SÁNCHEZ *et Al.*¹¹ developed an advanced 3D finite element model of the Giralda Tower (Spain) that integrated calibrated mechanical properties, modal analysis and nonlinear static analysis (NLSA) to evaluate the seismic behavior and damage patterns of complex masonry heritage buildings. Additionally, INVERNIZZI *et Al.*¹² emphasized that numerical models calibrated with non-destructive experimental data provide more reliable assessments of mechanical behavior than standalone analytical models.

Numerical modelling studies of masonry heritage structures often apply sensitivity analyses to quantify the effects of variations in material stiffness, mesh configuration and constitutive laws on the predicted damage and dynamic responses. In this respect, integrated experimental-numerical approaches, such as combining mechanical property testing «e.g., compressive strength and elastic modulus» with macro-scale FEM, have been used to assess the seismic performance and restoration strategies of historic masonry buildings. Large-scale numerical models calibrated with field data have been successfully used to evaluate failure patterns, displacements and drift limits, providing performance-based assessment criteria for heritage structures¹³.

Heritage masonry buildings classified as being at immediate risk are typically exposed to multiple interacting risk types. Structural risk arises from material degradation, cracking and loss of load-bearing capacity, potentially leading to partial or total structural collapse. Seismic risk is associated with the inherent vulnerability of unreinforced masonry to moderate earthquakes. Environmental risks, such as moisture ingress and salt crystallization, accelerate material decay and reduce structural performance, while human-induced risks result from a lack of maintenance, inappropriate use or nearby interventions that can trigger sudden failure¹⁴.

⁸ ONYELOWE *et Al.* 2024: 33.

⁹ VULOVIC *et Al.* 2024: 1-18.

¹⁰ AQUINO *et Al.* 2024: 74-85.

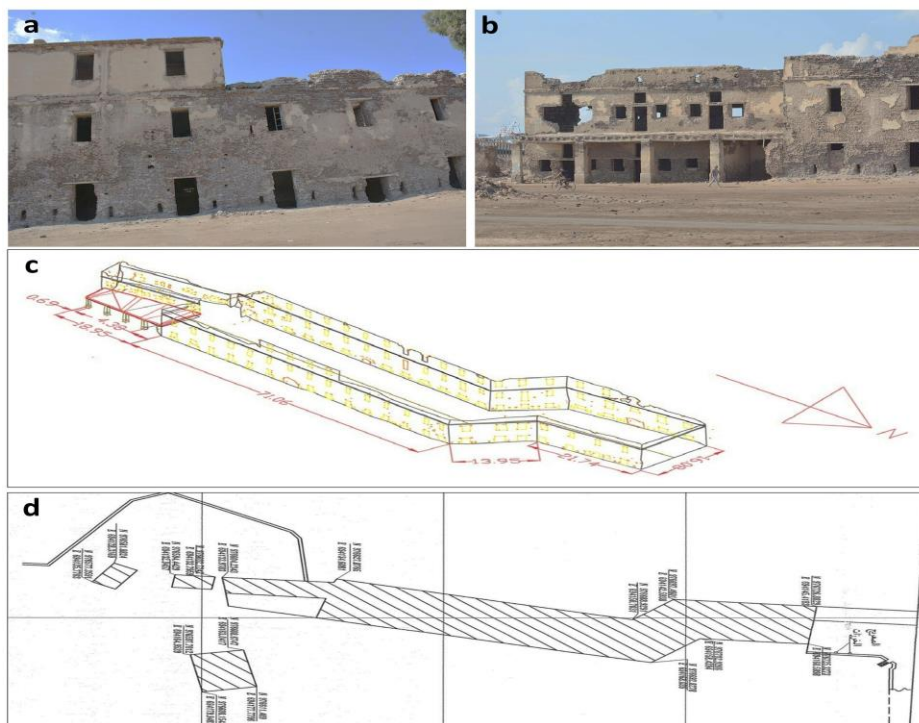
¹¹ ROMERO- SANCHEZ *et Al.* 2023: 4669–4701.

¹² INVERNIZZI *et Al.* 2016: 7.

¹³ MISIR *et Al.* 2023: 8.

¹⁴ ASTERIS *et Al.* 2025:1-18.

This research underscores the critical need for an integrated modeling paradigm, paving the way for innovative solutions that can adapt to the ever-evolving challenges posed by underground environments¹⁵.



[FIGURES 1/A-D]: A-B. The state of preservation of 'Urābī Fort in Damietta Governorate; C- D. 3D view of the degradation map for the 'Urābī Fort military barracks «as built» © Done by the authors



[FIGURES 2/A-C]: 2D plans views for A. First story, B. Second story and C. Third story of Ṭābiyat 'Urābī © Done by the authors

¹⁵ SAEED & MORADLOO 2024: 12.

II. METHODS: MODEL DEVELOPMENT AND NUMERICAL SIMULATION

A global finite element model of the selected building block was developed using the ETABS software; [FIGURE 3] shows the ETABS global model of the analyzed building block. The model captures the primary load-resisting components: brick walls «modeled as shell elements», timber beams and planks represented through equivalent floor loads, and mass distribution corresponding to the clay infill and roof finishes. The field dimensions and CAD layouts were used to reproduce the wall thicknesses, openings and pier locations¹⁶.

Two-dimensional plans, elevations and sections were developed using AutoCAD 2024 «Autodesk Inc., 2023» based on field measurements from total stations and laser scanning data. For the three-dimensional structural modeling and analysis, the model was developed using ETABS v22.5.1 «Computers and Structures, Inc. (CSI), 2023», a specialized software for building system analysis and design.

In the numerical model developed using ETABS, the slabs were modeled as shell elements with an average thickness of 200 mm, while the load-bearing walls were modeled as shell elements with thicknesses of 0.20, 0.70 and 1.20 m. The adopted geometrical properties represent the average wall and slab dimensions and were implemented based on the current conditions of the structure. [FIGURE 3] shows the ETABS global model of the analyzed building block. [FIGURE 4] illustrates the structural system of Ṭābiyat 'Urābī with the in-plane and out-of-plane deformation patterns.

1. Sample Collection

Samples of the constituent building materials were gathered from Ṭābiyat 'Urābī (OT) historic site in 'Izbat al-Burġ, Damietta. The samples included bricks, binding mortars and structural wooden components. The samples were selected based on the assumption that they would represent the original OT's early construction. In addition, entry to the investigated building was carried out in coordination with the competent antiquities authority, after obtaining the official approval to initiate the research activities. [FIGURE 5] shows the setup of the uniaxial compressive strength analysis of brick cubes from Ṭābiyat 'Urābī.

2. Mechanical Properties

The mechanical properties of the bricks were determined for samples collected from different sites, to illustrate the difference in mechanical properties resulting from the variation in site and, therefore, in the weather conditions, which affects the durability of the tested bricks.

A. Measurement of Bulk Density in Bricks

The bulk density of the brick specimens was determined to provide a key measure of the material compaction and weight per unit volume. The methodology employed is based on the principles of Archimedes and is consistent with the procedures outlined in

¹⁶ HBRC 2025: 116

established standards such as ASTM C20-00¹⁷. This method involves measuring the dry mass of the brick and its exterior volume, which is determined by the volume of water displaced.

Initially, a representative sample of at least three whole-brick specimens was selected for analysis. To ensure that the measured mass was solely that of the solid material and not influenced by the moisture content, the specimens were first dried to a constant mass. This was achieved by placing them in a ventilated oven maintained at a uniform temperature of 110-115°C. The specimens were weighed at 2 h intervals and the drying process was considered complete when the mass variation between consecutive weightings was less than 0.1% of the specimen's total mass. After reaching a constant state, the bricks were allowed to cool to room temperature in a desiccator to prevent reabsorption of atmospheric moisture. The mass of each cooled and dried specimen was accurately measured and recorded as the dry weight (Wd).

After determining the dry weight, the external volume of each specimen was measured using the water displacement method. This required complete saturation of the open pores of the specimen to prevent water infiltration during the volume measurement.

Saturation was achieved by submerging the specimens in a tank of distilled water and boiling them for a minimum of 5 h. After boiling, the specimens were left to cool to room temperature while remaining fully submerged in water.

Once cooled, the mass of each saturated specimen was determined under two conditions. First, the specimen was weighed while fully suspended in water using a harness or a basket. This measurement, recorded as the suspended weight (Wsusp), is crucial for determining the specimen volume based on Archimedes' principle.

Subsequently, each specimen was removed from the water and its surface was quickly patted dry with a damp cloth to remove excess water. It was then immediately weighed in air. The mass was recorded as the saturated weight (Wsat). The exterior volume (V) of the specimen was calculated from the difference between its saturated and suspended weights, which is equal to the mass of the displaced water.

The bulk density (qb) was calculated for each specimen using the following formula:

$$\text{Bulk Density (qb)} = Wd / (Wsat - Wsusp)$$

Where,

Wd = the dry weight of the specimen

The denominator (Wsat - Wsusp) is the exterior volume of the specimen in cubic centimeters (assuming the density of water is 1 g/cm³).

B. Measurement of Breaking Load and Compressive Strength

▪ Breaking Load

The measurement of the breaking load in bricks is a key indicator of their mechanical strength and durability. The term «breaking load» typically refers to two distinct types of tests: compressive strength and flexural strength «or Modulus of Rupture». Both

¹⁷ ASTM C20-00 2015.

methodologies are standardized and are commonly detailed in technical specifications, such as **ASTM C67**.

This test measures a brick's ability to resist forces that try to crush it. It is the most common and important test for determining the overall load-bearing capacity of a brick. A minimum of five whole bricks were dried in a ventilated oven to a constant weight at a temperature between 105°C and 115°C. For an accurate test, the two bearing surfaces «the faces that will be in contact with the testing machine» must be smooth and parallel to each other. If the surfaces are not naturally flat, they are «capped» with a thin, smooth layer of a high-strength material, such as sulfur-gypsum mortar or Portland cement paste.

The prepared brick specimens were placed in a universal testing machine. The specimen was carefully centered to ensure that the load was applied evenly. A continuous, uniform load was applied to the brick at a specified rate «e.g., between 1,000 and 2,000 lbf/min or 4.4 and 8.9 kN/min» until the brick failed. The maximum load at which the brick broke was recorded.

The compressive strength was calculated by dividing the maximum load by the gross cross-sectional area of the brick.

Compressive Strength=Gross Cross-Sectional AreaMaximum Load at Failure.The results are typically expressed in megapascals (MPa) or pounds per square inch (psi).

▪ **Flexural Strength Methodology «Modulus of Rupture»**

This test measures the brick's ability to resist bending forces, which is important for applications such as paving or lintels, where the brick may experience stress from its center. As with the compressive strength test, five whole bricks were dried. The length, width and depth of each brick were measured to the nearest 0.1 in. or 2.5 mm.

The brick is placed on two rounded supports spaced a specific distance apart «typically 7 in. or 178 mm» on the bed of the testing machine. The load was then applied to the top center of the brick at a uniform rate until the brick broke. The maximum load was recorded. The flexural strength or Modulus of Rupture (MR), was calculated using the following formula:

$$MR=2bd23PL$$

Where: P = Maximum load recorded at failure, L = Span between the supports, b = Average width of the brick and d = Average depth of the brick.

The results are also expressed in MPa or psi. This test is often performed first and the resulting broken halves of the brick can be used as specimens for the compressive strength test.

▪ **Masonry Compressive Strength Evaluation**

The compressive strength of the masonry was evaluated using the following empirical relationship¹⁸:

$$f_m=0.5(f_b)^{0.7}(f_{mo})^{0.2}$$

Where f_b is the compressive strength of the masonry unit and f_{mo} is the compressive strength of the mortar.

¹⁸ ZHANG *et Al.* 2024: 14.

The value of f_b was taken as 7.51 N/mm², representing the average of the best five results obtained from compressive strength tests performed on brick specimens with dimensions 6 × 6 × 6 cm. The tested specimens were collected from different locations within the building to ensure representative results were obtained. [FIGURE 6] shows the stress Vs. strain curves for the brick cubes from *Ṭābiyat 'Urābī*.

The mortar compressive strength f_{mo} was assumed according to the Egyptian Code of Practice as a reference value of 5.0 N/mm², owing to the unavailability of direct test results for the mortar. The calculated f_m was approximately 2.83 N/mm². The calculated masonry compressive strength was based on an assumed mortar strength adopted from the Egyptian Code; therefore, the obtained value should be considered an indicative assessment pending confirmation by actual mortar testing.

3. Modelling Assumptions

- A. The masonry walls were represented by linear elastic shell elements with an assumed uniform thickness of 1.2, 0.7 and 0.20m. [FIGURE 4] shows the structural system of the *Ṭābiyat 'Urābī* with in-plane and out-of-plane deformation patterns.
- B. The materials were characterized by average mechanical properties derived from the ECP 201 guidelines and field mechanical and physical studies.
- C. For the support condition at the base of the walls, hinge supports were assigned to each base node instead of fixed at the foundation levels to better represent the realistic boundary conditions.
- D. Dead Load and Live load cases, «self-weight plus permanent finishes», were considered in this chapter; wind and seismic actions are recommended for subsequent studies.
- E. In addition, the numerical modeling adopted in this study follows the Egyptian Code of Practice for Masonry Structures (ECP 204), which treats masonry as a composite material rather than modeling bricks and mortar as separate constituents. According to the code provisions, the compressive strength of masonry is defined as a reduced characteristic value that inherently reflects the combined behaviors of clay brick units, mortar joints, and unit–mortar interaction. Therefore, the effect of mortar is implicitly accounted for by using conservative masonry compressive strength values lower than the nominal compressive strength of individual brick units. Consequently, mortar was not explicitly modeled as an independent material in the numerical analysis. This macro-modeling approach is consistent with the Egyptian Code recommendations and is widely adopted in masonry analysis when the focus is on the global structural response under compressive loading rather than local failure mechanisms at the brick–mortar interface. The use of reduced material properties ensures a higher level of safety and a code-compliant structural assessment.

F. The Material Properties and Load Values «ETABS Inputs»

In the numerical model developed using ETABS, the slabs were modeled as shell elements with an average thickness of 200 mm, while the load-bearing walls were modeled as shell elements with thicknesses of 0.20, 0.70 and 1.20 m. The adopted

geometrical properties represent the average wall and slab dimensions and were implemented based on the current condition of the structure. [TABLES 1-2] summarize the mechanical properties of the masonry brick and timber samples and specimens from Ṭābiyat 'Urābī.

Property	Value	Unit
Material Name	masonry	-
Material Type	Masonry	-
Directional Symmetry	Isotropic	-
Weight per Unit Volume	1.0787	KN/m ³
Mass per Unit Volume	0.11	kN·s ² /m ⁴
Modulus of Elasticity (E)	27,066,354.55	KN/m ²
Poisson's Ratio (ν)	0.20	-
Coefficient of Thermal Expansion (α)	0.000005	1/°C
Shear Modulus (G)	11,277,647.73	KN/m ²

[TABLE 1]: Properties of masonry samples © Done by the Authors

Property	Value	Unit
Material Name	wood	-
Material Type	Other	-
Directional Symmetry	Isotropic	-
Weight per Unit Volume	4.9033	KN/m ³
Mass per Unit Volume	0.50	kN·s ² /m ⁴
Modulus of Elasticity (E)	68,646,551.40	KN/m ²
Poisson's Ratio (ν)	0.25	-
Coefficient of Thermal Expansion (α)	0.0000003	1/°C
Shear Modulus (G)	27,458,620.56	KN/m ²

[TABLE 2]: Properties of wood samples © Done by the Authors

4. Analysis Methodology

1. A Step-by-Step Review of the Analytical Procedure

- A. Creation of geometry and mesh in ETABS using shell elements for walls. [FIGURE 7] shows the 3D view for the ETABS model of Ṭābiyat 'Urābī.
- B. Assignment of material properties and thicknesses.
- C. Application of dead load and live load cases, «self-weight + permanent finishes».
- D. Linear static solver was used to obtain the displacements, element stress components, and base reactions.
- E. Post-processing: conversion of line forces to stress units (kPa), assuming a wall thickness of 1.20 m and interpretation according to the ECP 201 criteria.
- F. Localization of critical elements, «elements and joints with peak stresses and displacements» and mapping of field observations.

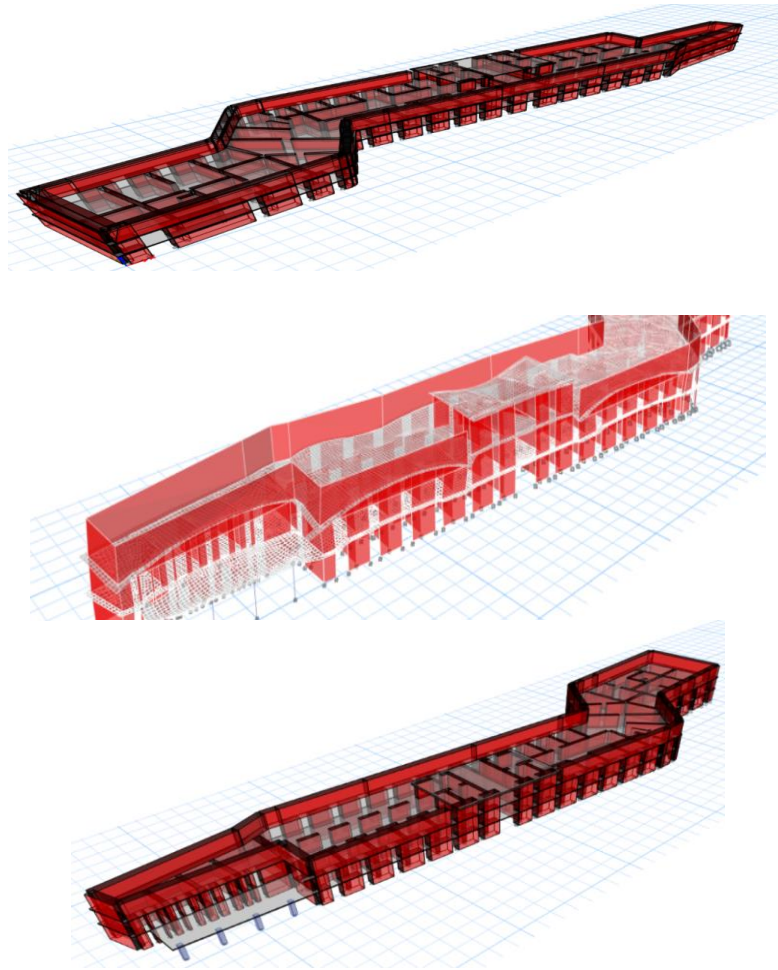
2. The Limitations of the Current Study

- A. Linear elastic behavior was assumed and no explicit crack propagation or material nonlinearity was modelled.
- B. Instead of using fixed supports, hinge supports were assigned to each base node to better represent the realistic boundary conditions. Therefore, differential settlements are reflected through the resulting stress and displacement patterns in the superstructure models.
- C. Dead and live loads were considered; wind, live load and seismic actions that may govern the retrofit design were considered.
- D. In the current model, the tensile strength of the bearing walls was neglected to simplify the analysis and to adopt a conservative assumption, considering that masonry materials typically exhibit very low tensile capacity compared with their compressive strength. Therefore, the walls were assumed to resist only compressive stresses, while any tensile stresses were not considered to contribute to the structural resistance.

If the tensile strength of the bearing walls is to be included in the model, it can be incorporated by assigning a finite tensile strength parameter to the masonry material in the constitutive model. This is typically implemented by defining a tension cutoff or a tension softening behavior within the material model. In such an approach, the masonry is allowed to carry tensile stresses up to a specified tensile strength limit. Once this limit is exceeded, cracking is assumed to occur and the tensile stress is reduced according to a predefined softening law.

Practically, this can be achieved by introducing the masonry tensile strength (f_t) obtained from experimental data or empirical relations «often expressed as a fraction of the compressive strength». The constitutive model then permits tensile stresses up to f_t , after which cracking starts and the stiffness in tension progressively degrades. This approach allows the model to capture crack initiation and propagation in the bearing walls, providing a more realistic representation of the structural behavior while maintaining numerical stability.

A clarification has been added to the manuscript to explain this modeling assumption and the procedure that would be followed if tensile strength were considered.



[FIGURE 3]: ETABS global model of the analyzed building block © Done by the authors

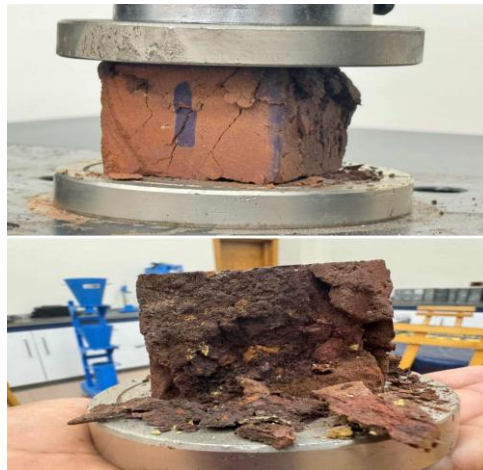


[FIGURE 4]: The structural system of Ṭābiyat 'Urābī with the in-plane and out-of-plane deformation patterns © Done by the authors

III. RESULTS AND DISCUSSIONS

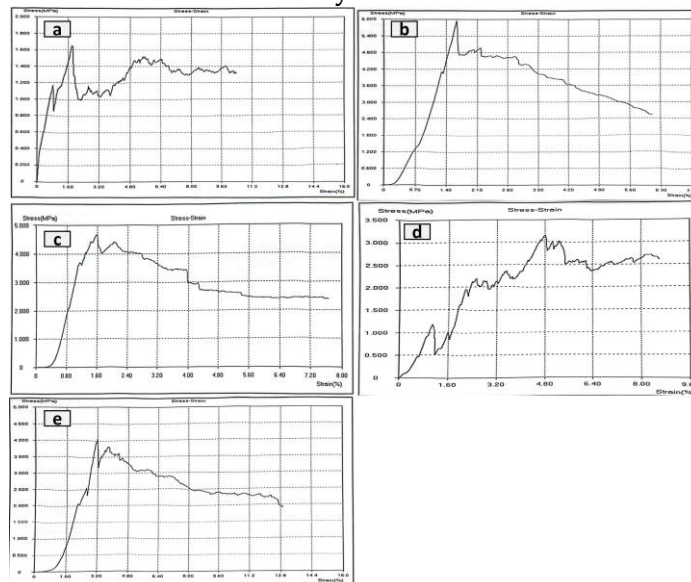
1. Material Properties and Assumptions

The results of the uniaxial compression test, as shown in [FIGURE 5], indicate that the uniaxial compressive strength σ_c of the brick specimens, the main building material of *Ṭābiyat 'Urābī*, ranges from 3 to 6 MPa. The corresponding stress-strain curves are shown in [FIGURE 6]¹⁹. The modulus of elasticity E was 4-6 GPa. Owing to the historic nature of the structure, comprehensive material testing data are not available for all zones²⁰. Therefore, conservative representative properties were adopted based on local field tests, the literature on traditional Egyptian masonry and the Egyptian Code for Masonry Structures (ECP 201)²¹.



[FIGURE 5]: Set up of the uniaxial compressive strength analysis of brick cubes from *Ṭābiyat 'Urābī*

© Done by the authors



[FIGURE 6]: Stress Vs. strain curves for the brick cubes from *Ṭābiyat 'Urābī* © Done by the authors

¹⁹ HAMID ET AL, 2026: 1-37

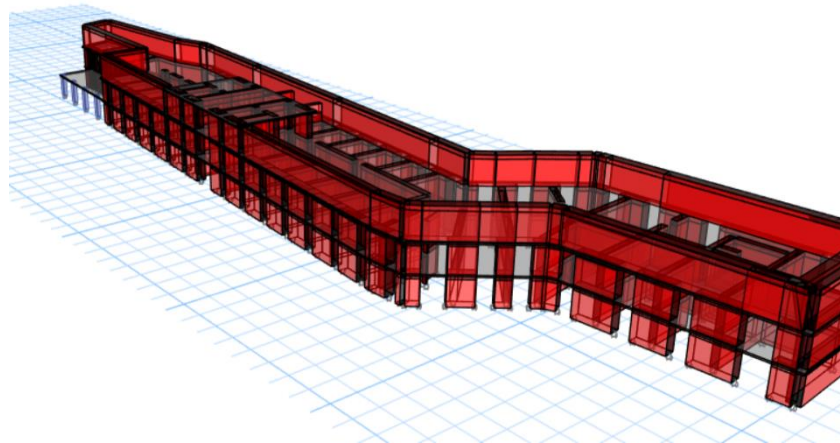
²⁰ HEMEDA 2024: 3.

²¹ HEMEDA 2012: 24.

Detailed note: These properties were used for first-order assessment and comparison with ECP 201 allowable stresses. Actual restoration design requires laboratory testing for accurate values. [TABLE 3] summarizes the mechanical properties adopted in the ETABS modelling and post-processing.

Property	Adopted Value	Unit	Remarks
Compressive strength of brick (f_b)	2000 - 3000	kPa	Approximate range for aged solid brick masonry (ECP reference)
Shear strength (f_v)	100 - 300	kPa	Depends strongly on mortar quality
Tensile strength (assumed)	Negligible	-	Masonry tensile strength is usually ignored in design
Unit weight	18 - 20	kN/m ³	Typical for compacted clay/clay bricks with mud infill

[TABLE 3]: Summarizes the mechanical properties adopted in the ETABS modelling and post-processing
© Done by the authors



[FIGURE 7]: 3D view for the ETABS model of Oraby Tabia © Done by the authors

2. Stress Analysis and Ddeformation Patterns

[TABLE 4] summarizes the maximum computed displacements extracted from the ETABS model for the dead load case. Following the table, a detailed discussion and interpretation are provided for each significant value.

Displacement Type	Maximum Value (m)	Maximum Value (mm)	Location
Ux (Horizontal X)	0.006675	6.675	Story 1, Joint 414
Uy (Horizontal Y)	0.022901	22.901	Story 2, Joint 452
Uz (Vertical)	-0.043748	-43.748	Story 1, Joint 506

[TABLE 4]: The maximum computed displacements extracted from the ETABS model
© Done by the authors

3. Discussion of Displacements

A. U_x «Horizontal X» = 6.675 mm «Story 1, Joint 414»

A horizontal drift in the X-direction of approximately 6.7 mm at the ground/story 1 level, indicates limited lateral stiffness. For unreinforced masonry, lateral drifts should be minimized; this value, although modest, may be symptomatic of reduced diaphragm action or local damage in wall continuity. Correlation with field observations: Minor separation and vertical cracking observed near the same joint on-site correspond to weakened mortar joints and possible loss of wall-panel connectivity.

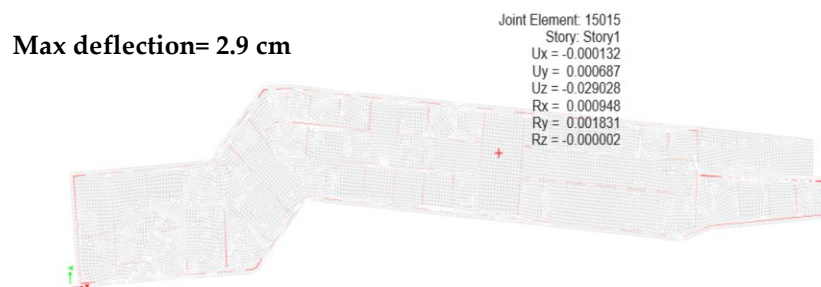
B. U_y «Horizontal Y» = 22.901 mm «Story 2, Joint 452»

A lateral displacement of ~23 mm at story 2 is significant for an unreinforced masonry structure and likely indicates a combination of reduced wall stiffness, possible out-of-plane vulnerability or foundation differential movement affecting the upper portion. Engineering significance: Such lateral movements can cause the progressive opening of vertical cracks, reduce the effective compressive stress across wall piers, and render arches or half-vaults unstable if present.

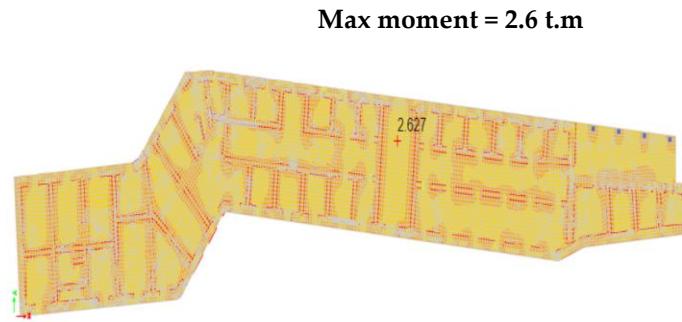
C. U_z «Vertical» = -43.748 mm «Story 1, Joint 506»

A downward settlement of ~44 mm is substantial and signals probable foundation distress or local bearing failure beneath the loaded wall. Differential settlement of this magnitude can easily induce diagonal shear cracks and overturning tendencies in the wall segments.

Recommended immediate action: A detailed geotechnical evaluation at the location corresponding to Joint 506 and temporary shoring or propping of heavily loaded spans until foundation remediation or underpinning decisions are made. [FIGURE 8] shows the displacement contours and position of the maximum displacement extracted from ETABS «Dead Load case». [FIGURE 9] shows the displacement contours and position of the maximum moment extracted from ETABS «Dead Load case».



[FIGURE 8]: Displacement contours and position of the maximum displacement extracted from ETABS «Dead Load case» © Done by the authors



[FIGURE 9]: Displacement contours and position of the maximum moment extracted from the ETABS
«Dead Load case» © Done by the authors

4. Base Reactions

The following paragraphs discuss the engineering implications of these concentrated reaction systems. [TABLE 5] lists the maximum base reactions obtained from ETABS analysis.

Reaction Type	Maximum Value	Unit	Location	Remarks
FX	-111.12	kN	Joint 405	Horizontal component
FY	-80.15	kN	Joint 798	Horizontal component
FZ	1950.20	kN	Joint 405	Major vertical reaction
MX	-55.32	kN/m ²	Joint 368	Base moment
MY	-35.04	kN/m ²	Joint 405	Base moment

[TABLE 5]: Lists the maximum base reactions obtained from ETABS analysis © Done by the authors

A.High Vertical Reaction «FZ = 1950.2 kN» at Joint 405

This indicates a strong concentration of vertical loads at joint 405, probably due to geometric or stiffness discontinuity «e.g., intersection of multiple load-bearing walls» and possibly an increased self-weight or surcharge in the area.

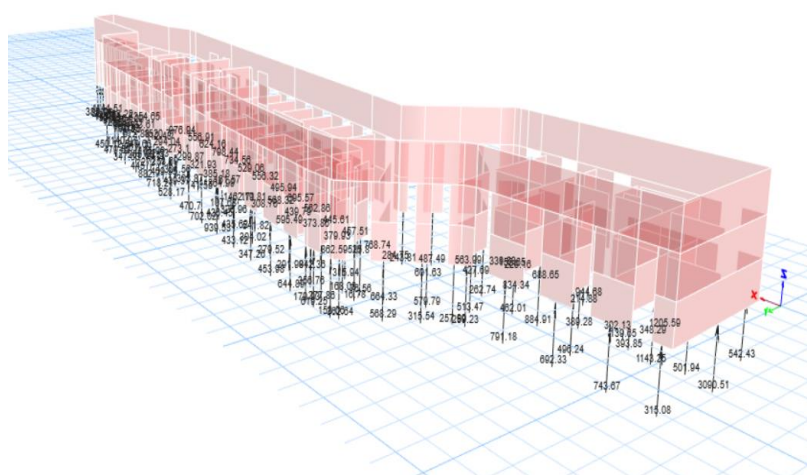
▪ **Field Correlation:** Visual evidence of heavy masonry piers and thicker wall sections in the western block corroborated this finding. However, such a large point load requires verification of the foundation bearing capacity and localized settlement monitoring.

B. Horizontal Base Reactions «FX, FY»

Nonzero horizontal reactions reflect the internal force transfer to the supports under the dead load model owing to geometric eccentricities or pre-existing deformations.

Although not caused by lateral loads in this analysis, they indicate asymmetry and the potential for lateral instability under additional actions «e.g., wind or seismic».

- **Recommendation:** Check the foundation shear capacity and frictional resistance and consider installing shear keys or grout injection to improve the load distribution if underpinning is undertaken. [FIGURE 10] shows the base reactions and support forces.



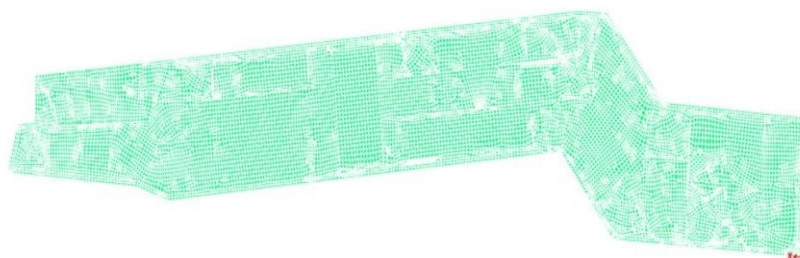
[FIGURE 10]: Base reactions and supporting forces © Done by the authors

5. Discussion of Stress Results

A.Compressive Stress «e.g., F22 = -2.9 kN.m»

The maximum compressive stress observed remained below the conservative lower bound of the adopted compressive strength of masonry (2000 kPa). This suggests that under dead loads alone, pure compressive failure is not imminent in most wall panels. Nevertheless, local material degradation and a reduced effective cross-section owing to cracking can significantly reduce the actual carrying capacity. [FIGURE 11] shows the maximum tensile strength of story 2.

Tensile stress (F11 = 1.9 KN.m, F22 = 2 KN.m):



[FIGURE 11]: Maximum tensile strength story 2 © Done by the authors

- B. Unreinforced masonry has negligible tensile strength; therefore, tensile stresses of the reported magnitudes are sufficient to induce cracks. The presence of through-thickness tensile stresses typically leads to vertical and diagonal cracks originating at openings and results to changes in the masonry's stiffness.
- **Observed Evidence:** Field cracks measured between 5 and 10 mm in width corroborated the model-predicted tensile stress zones, confirming ongoing propagation. Table [6] presents the maximum stress components extracted from the shell elements «top face» and converted to stress units by assuming a wall thickness of 1.20 m.

6. Stress Distribution in Structural Elements

Stress type	Maximum value (kN/m ²)	Location	Interpretation
F11 (Tension)	1.9	Story2, slab element	Indicates tensile cracking potential
F11 (Compression)	-2.8	Story2, slab element	Compressive stress within the lower bound
F22 (Tension)	2.0	Story2, slab element	Tensile stress across the orthogonal direction
F22 (Compression)	-2.9	Story2, slab element	Compression; acceptable with assumed masonry strength
F12 (Shear)	1.5	Story2, slab element	Shear near allowable limits
V13 (Shear)	4.5	Story2, slab element	Excessively high — indicates data/reporting or unit interpretation issue
V23 (Shear)	4.3	Story2, slab element F1	Exceeds allowable shear for masonry

[TABLE 6]: Presents the maximum stress components extracted from the shell elements «top face» and converted to stress units by assuming a wall thickness of 1.20 m © Done by the authors

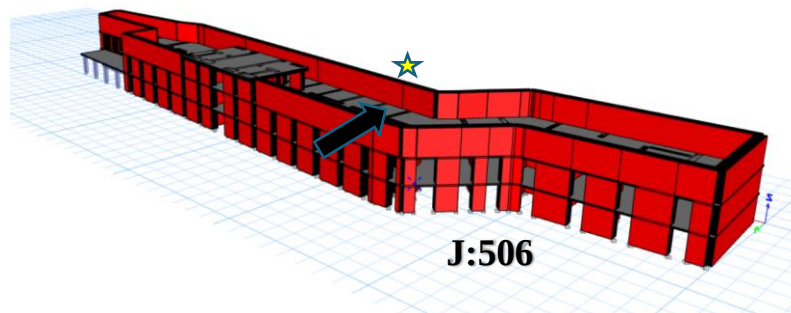
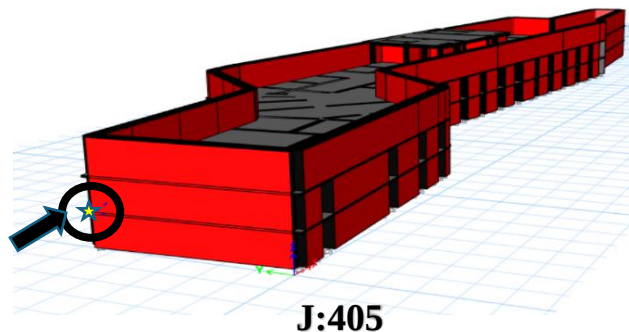
C. Shear Stress «F12, V13 and V23»

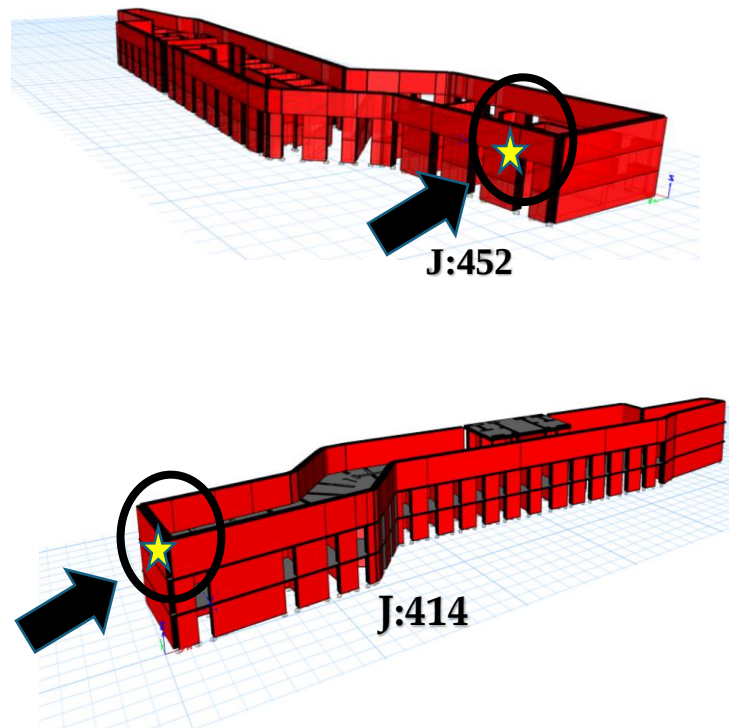
The reported shear components, especially V13 and V23, with exceptionally high numeric values, exceed any reasonable shear capacity for masonry (100–300 kPa). These anomalous magnitudes may indicate a unit conversion or extraction artifact from ETABS «e.g., internal force per unit length versus stress per unit area». It is essential to verify the post-processing conversion methodology «kN/m to kPa using the wall thickness» and check for data extraction errors.

- **Engineering Implications:** Even if the actual shear values are an order of magnitude lower, the trend of high shear concentration adjacent to openings and wall intersections is clear and consistent with the observed diagonal cracking and potential shear sliding failure.

7. Recommendations «Stress Verification»

- The ETABS shell force output was reprocessed to ensure correct conversion from force per unit length (kN/m) to stress (kPa) using the relation $\text{stress} = (\text{force_per_length}) / \text{thickness}$. The units should be verified carefully and the values should be cross-checked with the direct element reaction outputs.
- Perform localized material shear tests and diagonal compression/shear tests in the laboratory to determine the true shear capacity of the masonry. [FIGURE 12] shows the critical points and stress contours indicating the compression/tension distribution.





[FIGURE 12]: Critical points and stress contours indicating compression/tension distribution © Done by the authors

IV. CRACKING AND DAMAGE ASSESSMENT

Analytical outputs combined with site inspections indicated several critical cracking zones. The most vulnerable locations are wall intersections, regions adjacent to large openings and zones near foundation corners, where settlement is concentrated.

The observed Crack Patterns were as Follows

- Vertical cracks at wall corners and pier junctions «likely due to differential settlement and loss of axial continuity».
- Diagonal shear cracks at the mid-height of wall panels adjacent to openings «indicative of shear sliding or combined bending-shear».
- Progressive widening of some cracks (5–10 mm) suggesting active movement.

For each major crack zone, an explanatory paragraph follows to interpret the cause-effect relationship and recommend immediate remedial actions.

1. Crack Zone A: Intersection of Western Block Walls «Near Joint 405»

Description: This zone corresponds to the thick masonry piers where multiple walls intersect and the largest base reaction (FZ) was recorded. The cracks were primarily vertical, with branching diagonal cracks at lower levels.

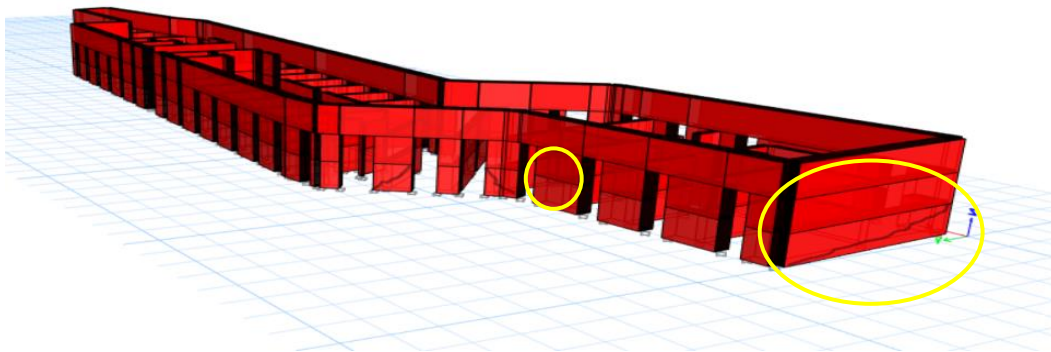
- **Mechanism:** The concentration of vertical load, combined with reduced mortar bond and localized foundation settlement, creates stress redistribution, leading to tensile splitting and shear initiation at the pier bases. The observed settlements corroborated the vertical displacement hotspot of the model at Joint 506.

Immediate measures included the shoring of the affected spans with timber or steel props, daily monitoring of crack widths and targeted underpinning after geotechnical investigation. Grout injection is considered to re-establish mortar continuity in the presence of voids.

2. Crack Zone B: Openings and Window/Door Jambs «Several Positions Including Element F1»

Description: Cracks are concentrated at the corners and jambs of openings that are oriented diagonally and vertically. The ETABS shell stress results showed high tensile and shear components around Element F1 in Story 2.

- **Mechanism:** The stiffness discontinuity produced by openings results in stress concentration under vertical loads and bending moments, producing tensile stresses perpendicular to the mortar beds and shear across bed joints. In the presence of moisture and poor mortar, these stresses cause crack initiation and propagation.
- **Mitigation:** Protect exposed masonry from further moisture ingress, install temporary lintel supports where necessary and design reinforcement «e.g., embedded stainless steel anchors or localized jacketing» to bridge tensile stresses. Repair work should use compatible lime-based mortars, as recommended for historic masonry. [FIGURE 13] shows the locations of the vertical and diagonal cracks and structural damage lines detected in the structure of Oraby Tabia. The numerical analysis results are consistent with reality.



[FIGURE 13]: Crack and Damage lines detected in the building © Done by the authors

V. STRUCTURAL REHABILITATION OF THE FORT

This section provides prioritized technical recommendations for the immediate, short-term and long-term actions required to secure and rehabilitate 'Urābī Fort building. Each recommendation includes a brief technical rationale.

1. Immediate «Emergency» Measures

- Evacuate occupants from the most severely affected rooms identified by large displacements and crack widths. Ensure public safety barriers around collapse-prone facades.

- Temporary shoring and props are installed beneath high-risk arches and long-span timber members. Adjustable steel props should be used where available.
- Temporary roof coverings and damp-proofing to reduce further moisture ingress.

2. Short-Term Measures «within 3–12 Months»

- Perform targeted laboratory testing of brick and mortar samples: «compressive, shear and tensile splitting tests».
- Reassess the ETABS model with verified material properties and cross-check the extreme stress results for conversion accuracy.
- Undertake localized underpinning where the bearing capacity is exceeded and implement grout injection to fill voids under the foundations.

3. Long-term Rehabilitation and Strengthening

- Evaluate retrofit options such as internal/external wall jacketing with compatible materials, localized reinforced concrete tie beams at floor levels, and stainless steel anchors across wall panels.
- Where walls are inextinguishably damaged, careful dismantling and reconstruction using salvaged bricks and matching mortars should be considered to preserve architectural authenticity.
- Implement a continuous structural health monitoring (SHM) program, which includes «crack meters, tilt sensors and periodic surveying».

VI. CONCLUSION

The ETABS linear static analysis under dead load indicates that the structure is in a compromised state with significant tensile and shear stresses in several masonry panels. Vertical settlements and lateral displacements exceeded the typical serviceability expectations for unreinforced masonry, indicating foundation distress and reduced structural integrity. Although compressive stresses remain within conservative bounds, the combined effect of tensile cracking and shear concentrations undermines the effective load-bearing capacity of walls. Immediate geo-environmental risks to occupants like seismic events and climate change are present; therefore, temporary evacuation of the most affected zones and emergency shoring are recommended until stabilization work is executed. Further detailed assessments, including nonlinear analysis and experimental material characterizations, are essential to develop a reliable rehabilitation scheme.

DISCLOSURE STATEMENT

No Potential conflict of interest was reported by the authors

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BUILDING MATERIALS AND STRUCTURAL ASSESSMENT FOR THE RESTORATION OF *Kiswa* Hall, Cairo

By

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ABSTRACT

[EN] Heritage buildings situated in seismically active and geotechnically unstable areas require advanced diagnostic strategies to ensure their preservation. Despite the architectural significance of al-Ğawhara Palace in Cairo, a few studies have addressed the structural vulnerability of its *Kiswa* Hall. This research paper bridges the gap by integrating material science, structural assessment and geotechnical analysis into a unified framework for heritage conservation. Comprehensive field inspections were combined with laboratory testing, including X-ray diffraction «XRD», petrography and mechanical strength evaluations, alongside geotechnical investigations. Results demonstrate that the principal construction materials—limestone «compressive strength 5.2 N/mm²» and red clay brick «7.3 N/mm²»—exhibited low load-bearing capacity. XRD and petrographic analyses identified salt crystallization and mortar incompatibility as dominant deterioration mechanisms, while soil investigations revealed expansive clay layers with high swelling potential. Structural cracking patterns were linked both to heterogeneous soil conditions and seismic stresses, most notably the 1992 Earthquake. Therefore, the study proposes a conservation protocol that prioritizes lime-based mortar repointing, desalination of masonry surfaces and mineral-compatible consolidation of limestone. Drainage upgrades are also recommended to reduce groundwater infiltration and salt migration. A preventive maintenance program is outlined, integrating routine monitoring with international conservation charters to ensure sustainability. By applying a multi-disciplinary methodology, this research advances the conservation field in three ways: 1- Developing a diagnostic model that links geotechnical instability with seismic vulnerability in heritage masonry; 2- Demonstrating material incompatibility as a driver of accelerated decay; 3- Presenting a replicable preventive maintenance strategy. The results offer transferable insights for conserving heritage sites across earthquake-prone regions with complex soil conditions.

KEYWORDS: al-Ğawhara Palace, architectural heritage conservation, geotechnical investigation, *kiswa* hall, petrographic analysis, structural deterioration, X-ray diffraction (XRD).

[AR]

مواد البناء والتقييم الإنشائي لترميم قاعة الكسوة، القاهرة

تتطلب المباني التراثية الواقعة في بيئات نشطة زلزاليا وغير مستقرة جيوتقنيا استراتيجيات تشخيصية متقدمة لتأمين الحفاظ عليها. على الرغم من الأهمية المعمارية لقصر الجوهرة في القاهرة، إلا أن الدراسات الفنية المحدودة تناولت الضعف الهيكلي لقاعة الكسوة. يسد هذا البحث هذه الفجوة من خلال دمج علوم المواد والتقييم الهيكلي والتحليل الجيوتقني في إطار موحد للحفاظ على التراث. تم الجمع بين عمليات المعاينات الميدانية الشاملة والاختبارات المعملية، بما في ذلك حيود الأشعة السينية (XRD)، والفحص البتروجرافي، وتقييمات القوة الميكانيكية، إلى جانب الفحوصات الجيوتقنية. وتظهر النتائج أن مواد البناء الرئيسية -الحجر الجيري- مقاومة الضغط 5.2 نيوتن/مم²، والطوب الطيني الأحمر 7.3 نيوتن/مم² وهي تظهر قدرة تحمل منخفضة. وأظهرت نتائج تحاليل حيود الأشعة السينية والفحص البتروجرافي تبلور الملح وعدم توافق الملاط كآليات تدهور سائدة، بينما كشفت فحوصات التربة عن وجود طبقات طينية لها قدرة عالية على الانتفاش. ارتبطت أنماط التشقق الهيكلي بظروف التربة غير المتجانسة والضغط الزلزالية، وأبرزها زلزال عام 1992 وبناءً على هذه النتائج، تقترح الدراسة بروتوكول حفظ يعطي الأولوية لإعادة استخدام الملاط القائم على

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الجير، وإزالة الأملاح من على أسطح مواد البناء، وتقوية الحجر الجيري. يوصى أيضا بتحديث الصرف للحد من تسرب المياه الجوفية وهجرة الملح. تم تحديد برنامج الصيانة الوقائية، الذي يدمج المراقبة الروتينية مع موثيق الحفظ الدولية لضمان الاستدامة. من خلال تطبيق منهجية متعددة التخصصات، يعمل هذا البحث على تطوير علم الحفظ بثلاث طرق: (1) إنشاء نموذج تشخيصي يربط عدم الاستقرار الجيوتقني بالضعف الزلزالي في البناء التراثي؛ (2) إظهار عدم التوافق المادي كمحرك لتداعيات وتدهور مواد البناء؛ (3) تقديم استراتيجية صيانة وقائية قابلة للتكرار. تقدم النتائج رؤى قابلة للتحويل للحفاظ على المواقع التراثية عبر المناطق المعرضة للزلازل ذات ظروف التربة المعقدة. الكلمات الدالة: التحقيق الجيوتقني، التحليل البتروغرافي، التدهور الهيكلي، الحفاظ على التراث المعماري، الحيوود بالأشعة السينية (XRD)، قاعة الكسوة، قصر الجوهرة.

I. INTRODUCTION

Kiswa Hall, located within al-Gawhara Palace at the Citadel of Cairo¹ is a unique historic space² named after the Ka'ba's ceremonial textile covering³, parts of which were traditionally preserved in this hall⁴. Despite its cultural value⁵, *Kiswa* Hall has suffered frequent fires⁶, seismic activity⁷ and environmental decay, threatening its structural stability. While several studies investigated the palace more broadly, little attention has been given to the material and structural condition of *Kiswa* Hall⁸. This study addresses this gap by conducting a multidisciplinary assessment of the hall's building materials and subsurface conditions to inform targeted conservation and rehabilitation strategies.

II. THE GEOLOGICAL NATURE OF THE CITADEL AREA

The Citadel area, which rests on the Mokattam Formation, is composed of alternating layers of limestone and clay of Lutetian to Bartonian age. These heterogeneous deposits influence the stability of structures, as clay intercalations are prone to swelling and settlement, while limestone layers exhibit variable strength⁹. Understanding this geological context is essential to interpreting the structural deterioration observed in *Kiswa* Hall.

III. FACTORS AFFECTING THE DETERIORATION OF KISWA HALL

A. Natural Factors

Earthquake, winds, soil subsidence, as well as biological factors, are the main natural deterioration factors that negatively affect the *Kiswa* Hall materials¹⁰. Furthermore, the earthquake waves that arrived at the Citadel's location caused different threats to the building materials used based on the wave strength [FIGURE 1].

¹ METWALY & ZAHARAN 2014 : 768; VAZ 2019: 416; ABDEL-AL EL-SAYED 2021: 2161.

² VAZ 2019: 416.

³ ABDEL-AL EL-SAYED 2021: 2161.

⁴ HIJAB 2020: 33; ORDÓNEZ 2022: 85-90.

⁵ VAZ 2019: 416.

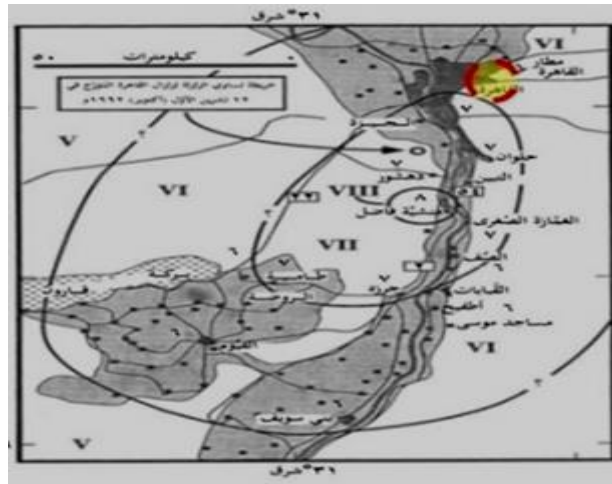
⁶ STONE 2023: 477.

⁷ DELLA TORRE 2019: 25.

⁸ ABD ELMOATY 2019: 109-141.

⁹ HAMMAD 2022: 34-44; ORDÓNEZ 2022: 85-90.

¹⁰ NAPOLEONE 2020: 110.



[FIGURE 1]: Distribution and propagation of seismic waves associated with the 1992 Cairo Earthquake, illustrating their impact on the Citadel of Cairo site. THENHAUS *et Al.* 1993: 63.

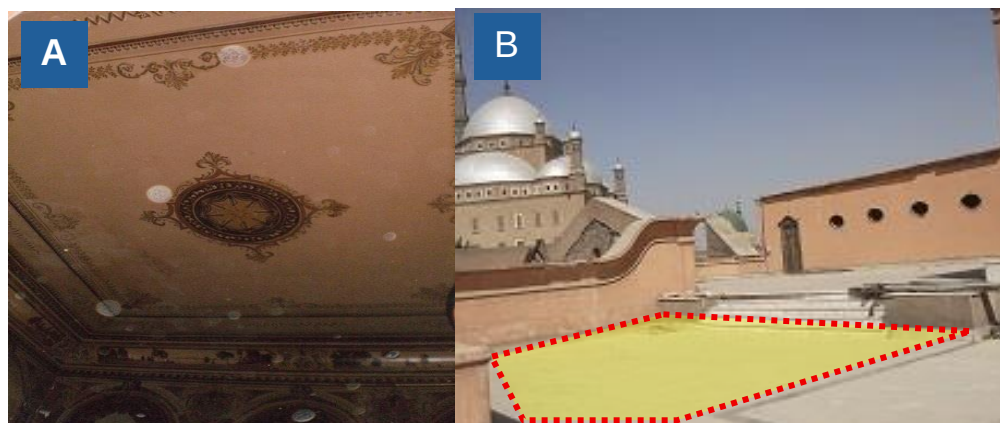
B. Human factors

The deterioration of *Kiswa* Hall is motivated by the following reasons:

- Deterioration of the means of drainage and nutrition, which leads to water leakage¹¹.
- Pollution from the nearby workshops, factories and car exhaust.
- Inconsistency between the agencies supervising the historical buildings¹².

IV. STRUCTURAL STYLE OF THE *KISWA* HALL

The style of construction of the studied hall is the load-bearing walls¹³. It depends on the structural balance of the stone walls that bear the ceilings and the loads transmitted through the walls to the foundations. Mamluk buildings¹⁴, in some parts, have wooden frames and walls to increase their rigidity and flexibility. The mortar was used for insulation. The hall ceilings are flat wood in the interior and the exterior is of stone tiles¹⁵ [FIGURE 2].



[FIGURE 2]: Interior and exterior views of the *Kiswa* Hall ceiling. A. Interior condition; B. Exterior condition © Photo taken by TAHA ATALLAH

¹¹ FERREIRA 2023: 73.

¹² VAZ 2019 : 416.

¹³ FERREIRA 2023: 11.

¹⁴ DELLA TORRE 2019: 25; ABDEL-AL EL-SAYED 2021: 21-61

¹⁵ MAHMOUD 2021: 22; FERREIRA 2023: 73.

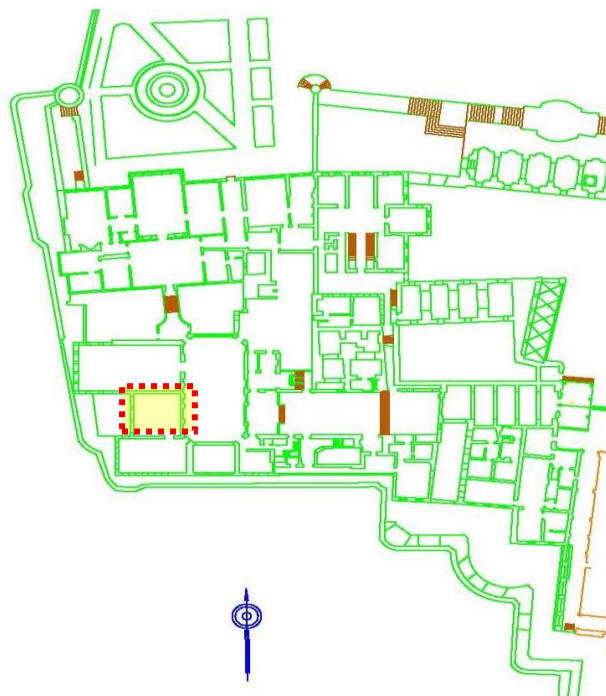
V. TESTS AND METHODS

A total of 18 material samples were collected from representative locations across *Kiswa* Hall, including limestone blocks (n=6), red clay bricks (n=6) and mortar joints (n=6). Sampling targeted areas with visible deterioration (cracks and efflorescence), as well as intact zones, to allow comparison. Care was taken to minimize the destructive impact¹⁶, with each sample limited to <5 cm³ volume. The building materials used in the Hall featured different techniques and methods and their main engineering parameters were determined. Also, geotechnical parameters for the soil were measured.

VI. RESTORATION AND REHABILITATION APPROACH OF *KISWA* HALL

A. The Cracks in the Structure of *Kiswa* Hall

A general plan of al-Ğawhara Palace and the location of *Kiswa* Hall are shown in [FIGURE 3]. Limestone was used in the construction of the walls and foundations in courses stacked as a load-bearing wall system. The red clay bricks were used in the construction of the upper parts¹⁷. Furthermore, cracks were observed in the adhesive mortar. This can be attributed to different types of mortars used in the building unit «mud mortar, gypsum mortar and lime mortar». The tile shows damage that may be due to natural atmospheric factors, such as the effect of humidity and rain¹⁸, as well as the effect of salt and dust [FIGURE 4]. These factors may lead to vertical, horizontal and inclined cracks in the walls and mortar of *Kiswa* Hall¹⁹ [FIGURE 5]. Additionally, [FIGURE 3] illustrates the components of *Kiswa* Hall that are referenced in [FIGURE 2].



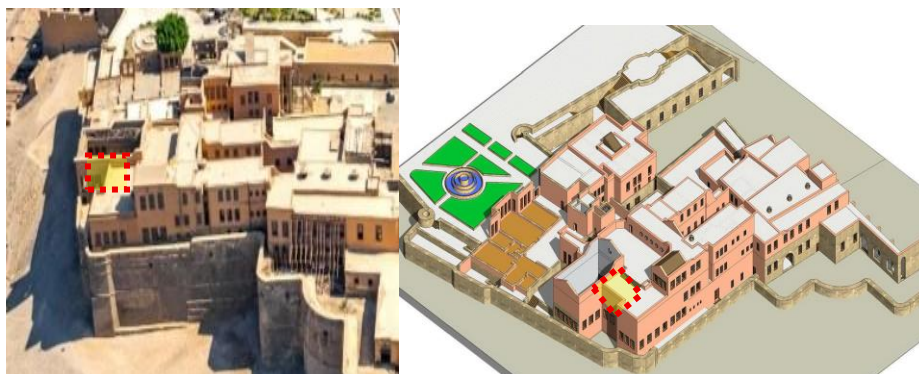
[FIGURE 3]: Architectural plan of al-Ğawhara Palace illustrating the location of the *Kiswa* Hall, highlighted by the dashed rectangular boundary, Cairo, Egypt © Done by the authors

¹⁶ ASTM INTERNATIONAL 2010: 9.

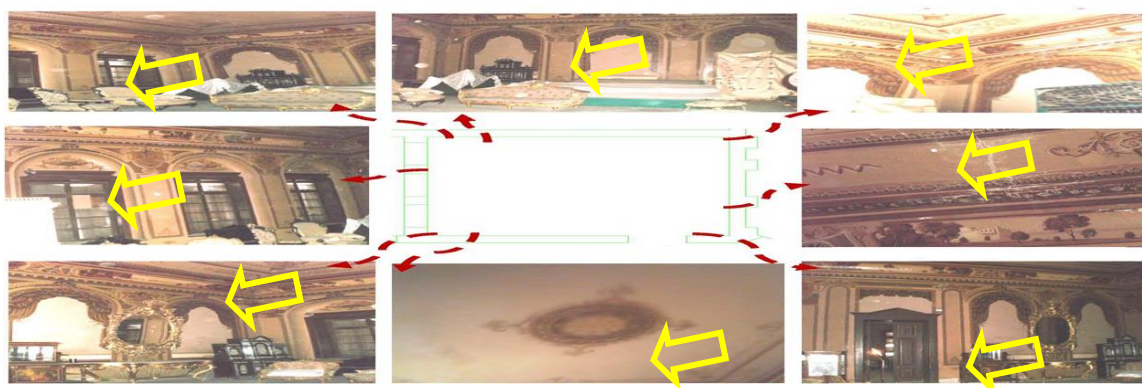
¹⁷ NAPOLEONE 2020: 110.

¹⁸ HAMMAD 2022: 34-44.

¹⁹ ABDEL-AL EL-SAYED 2021: 21-61.



[FIGURE 4]: General exterior view and roof surface of the *Kiswa Hall*, documenting the architectural features and conservation condition of the building prior to intervention © Done by the authors



[FIGURE 5]: Architectural and structural condition of the *Kiswa Hall*, illustrating the walls, ceilings, decorative elements and cracks affecting the structure, as indicated by the arrows © Photos taken by TAHA ATALLAH

Potential Causes of Cracks in the *Kiswa Hall*'s Structure

The fire that occurred in the palace in 1972 AD caused complete destruction in some parts²⁰. On the other hand, the earthquake in 1992 AD caused cracks and inclination of some marble columns in the façade of the Palace. It also separated large parts of the walls and deep cracks were generated²¹. The earthquake caused soil movement between the eastern and western parts of the building. In addition, the different conditions of foundation over old foundations or over heterogeneous stone layers «eastern and western» and reinforcing rebar rust may also be reasons for different patterns of cracks²² [FIGURE 6].



[FIGURE 6]: Structural deterioration in the walls and ceiling of the *Kiswa Hall*, showing the location and extent of cracks marked by the arrows © Photos taken by TAHA ATALLAH

²⁰ VAZ 2019: 416.

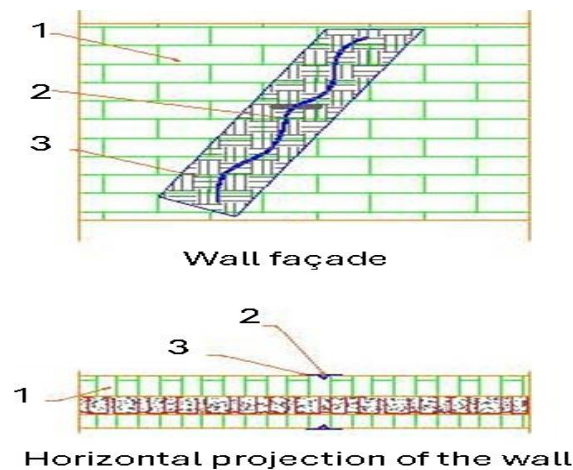
²¹ MUHAMMAD 2022: 13.

²² ABDEL-AL EL-SAYED 2021: 21-61.

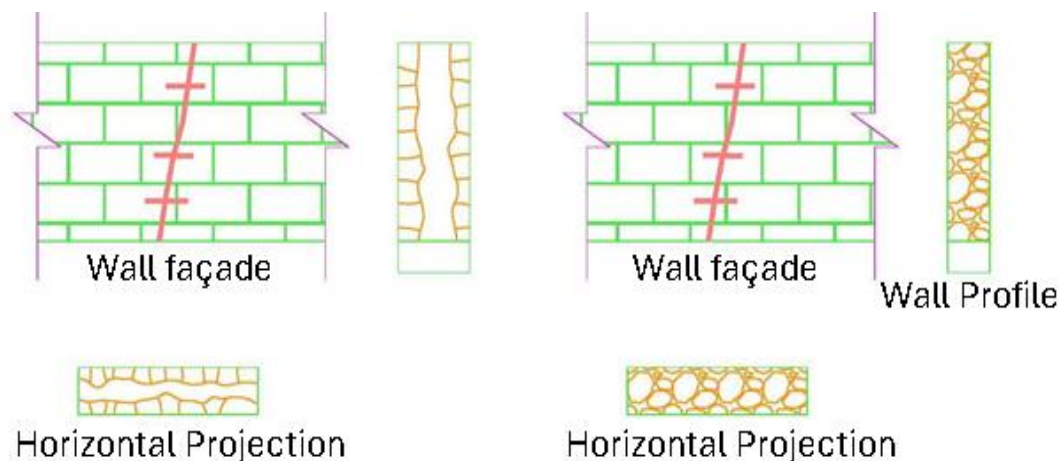
B. Restoration Steps of the Walls

Restoration of the internal and external walls was carried out after the completion of the treatment of the foundations and soil according to their conditions. Excavations were carried out on both sides of the wall in the form of a trench until reaching the foundation level of the wall. The excavations were carried out along the length of the wall in stages. The length of each stage did not exceed 3.00 m. The found cracks were renovated as follows:

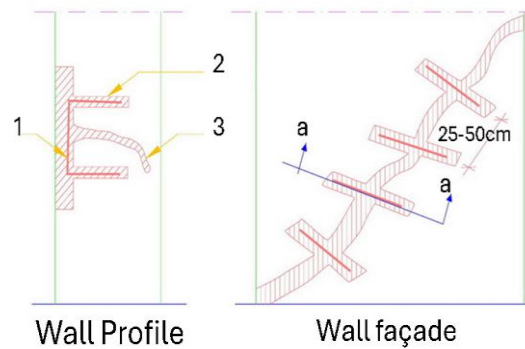
- Small-thick window cracks in the walls «less than 50 mm» were repaired by stitching on one side using wooden segments and fillers, while installing the stone itself or an alternative stone if necessary. It also included the injection of non-shrinkable mortar between the sectors of walls at the full depth of the wall [FIGURE 7].
- Large thick window cracks in the walls were buttoned from both sides [FIGURES 8-9]. Restoration Steps: 1. Steel Roof; 2. Unscrew the façade stones around the crack; 3. Wood button behind broken stone; 4. Preparing a healthy stone as a substitute for the original broken stone; 5. Reconstruction of healthy stones; 6. Removal of solids.
- If the wooden beam was cracked inside the walls, especially in the places of the threshold, the beam should be replaced.



[FIGURE 7]: Restoration and repair interventions for narrow cracks. 1. A narrow crack prior to treatment; 2. A narrow crack following the repair process; 3. The application of palm leaf fibers as a traditional reinforcement material © Done by the authors



[FIGURE 8]: Comparison between one-sided and two-sided crack formations observed in the examined masonry element © Done by the authors



[FIGURE 9]: Treatment of wall cracks through a stitching-button repair technique, incorporating. 1. Iron anchors spaced at 25–50 cm intervals; 2. Mona Adibond bonding agent; 3. Confis Mortar 2F as a compatible repair mortar © Done by the authors

▪ Treatment of the Corner Cracks

The corner cracks were repaired to achieve interconnection between the perpendicular walls by placing the wood and refilling the voids with non-shrinkable mortar, accompanied by the injection of mortar around the wood. The injection work was accomplished for the distance between the fixing panels and the entire wall sector.

▪ Wall Strengthening

Wall strengthening was conducted by replacing or removing defective stones or bricks. The intact stones were temporarily removed and stored in a safe place for reuse. To complete wall strengthening, the following steps were performed:

- Suitable mortar was used based on test results, material specification and recommendations.
- Suitable stones were reconstructed in their original places by maintaining the original dimensions and levels.
- Cracked or damaged stones shall be replaced with new compatible stones.
- The used stones must be tightly connected by a suitable mortar type.
- The brick walls should be re-constructed according to the relevant specifications using skilled laborers.

▪ Foundation Restoration

A. Description of the Foundation

The foundation was found at a depth of 1.75m from the ground level. It consisted of different foundation levels of varying thickness that increased in width at 30, 60 and 130 cm. These foundations were constructed from limestone. The foundation restoration was accomplished to treat the cracked walls and any detected weakness zones.

B. Repairing Foundation Components

The corroded foundation was injected with an appropriate mortar and the injection extended to the lower part of the anchored wall. The used mortar included shortbread, coal and lime. These components were mixed to show homogeneity and compatibility with the original stones and mortars, then injected through the holes in the grooved wall body using a pump under compressor pressure «more than 12 bars». The injection process started from the bottom to the top at an interval of 1.0m.

VII. RESULTS AND DISCUSSION

1. Environmental Effects «Salts and Pollution»

The low compressive strength of limestone (5.2 N/mm^2) compared with typical historic building limestones ($10\text{-}20 \text{ N/mm}^2$) indicates significant material weakening, likely due to recrystallization and salt weathering. The presence of sylvite (KCl) and gypsum in mortars confirms salt infiltration processes, exacerbated by rising damp and air pollution. Meanwhile, soil tests revealed high plasticity indices and swelling potential «free swell index 60-90%», consistent with differential settlement cracks observed in foundations. Together, these factors suggest a combined deterioration mechanism: earthquake-induced structural displacement aggravated by soil expansion and salt weathering.

2. Rock Compressive Strength

A compressive strength test was carried out on cylindrical limestone core samples of the soil citadel site taken from a depth of 12.00 m. It was found that the continuous samples greater than 15 cm height resulted in a range of between $50\text{-}75 \text{ kg/cm}^2$. This result suggests that the tested rock samples have weak strength and the treatment is urgently needed.

3. Rock Core Recovery «CR» Measurements

The results showed that the CR of the cored stone samples was between 30 and 55, while the percentage of the stone samples (ROD) ranged between 22 and 40%. The results of the tested core rock samples showed bad rock conditions and poor rock mass quality.

4. Soil Atterberg Limits and Free Swell Index Tests

The results of Atterberg limits tests on the soil samples that were taken from the clay layers between depths 4.0-6.0m showed the following results: Average liquid limits were between 52 and 63, average plastic limits were between 24 and 31 and average plasticity index was between 28 and 32. The results suggest that the tested samples belong to the alluvial clay soil of high plasticity with relatively high expansion potential.

The result of the tested soil samples located at a depth of 4.0m showed that the free swell index test results were between 60% and 90%. This means that the tested samples can be classified as a soil of a very high swelling potential according to HOLTZ and GIBBS classifications²³.

5. Underground Geoelectrical Testing

The electrical probing results are recorded in [TABLE 1] P. The interpreted electric resistivity values of corresponding underground soil types; H. The thicknesses of soil tested (cm). The result values mean that the thickness of the layer increased, the electrical resistivity increased, the electrical conductivity decreased and the salty water content in the layers decreased. This may be due to the seepage of surface water forming salts.

²³ HOLTZ & GIBBS 1956: 1.

The results showed no caves or voids from the ground surface up to a depth of 10.00 m in the measured areas. The heterogeneity of soil layers at the horizontal level was detected. The soil layers that were monitored to a depth of 10.00 m revealed that their compositions were mainly soft sedimentary soil «clay and limestone» and may contain fresh water, as obtained from the values of resistance to date, ranging between 30-60 Ohm meters²⁴.

Underground Layers	VES 1		VES 2		VES 3	
	Piec	H	P	H	P	H
1	14	0.93	32	0.45	42	0.65
2	60	116	125	270	301	130

[TABLE 1]: Results of the underground geoelectrical probing test © Done by the authors

6. Probes and the Nature of Soil Layers

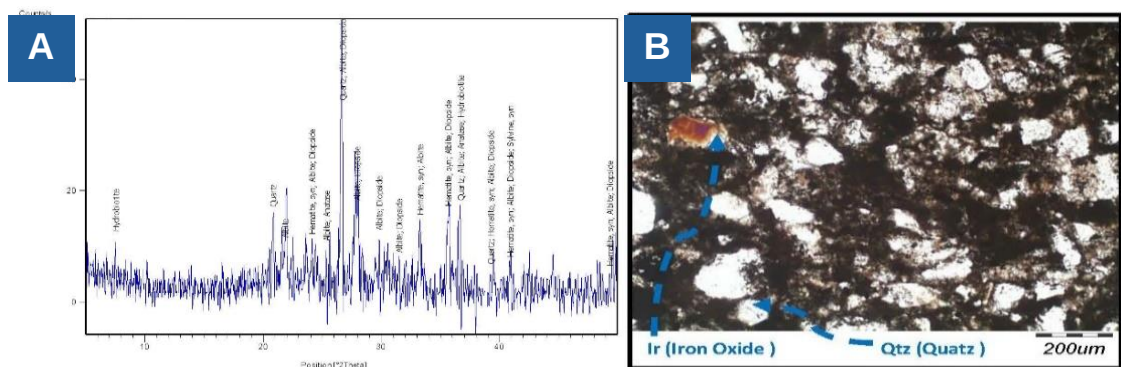
Three boreholes were drilled by a drilling machine to a maximum depth of 15m. The toe sample of bore holes (1) was taken and found to be composed of a backfill layer with a thickness of 11.20m of silty clay mixed with rock fragments. After this layer, the natural layer of intercalation of limestone and calcareous soil appeared till the end of boring at 15m. The samples of bore holes (2 and 3) showed that the underground layer was composed of a mix of clayey sand and rock fragments till the depth of 8.0m in borehole (2) and till 4.0m in borehole (3). The drilling process faced difficulties in continuity for more than 15.0m due to the hard rocks.

7. Red Clay Bricks

The results of analyses that were carried out on the red brick samples in terms of mineralogical (XRD), micro-structure «polarizing microscope», as well as mechanical tests on the cylindrical rock core sample «tensile strength, shear strength and compressive strength» are summarized as follows:

- The XRD pattern [FIGURE 10/A] showed that the tested brick sample consisted of quartz, hematite, albite, diopside, anatase, sylvite and hydrobiotite. The presence of sylvite (KCl) was used as an indicative mineral for the occurrence of soluble salt.
- The petrographic micrograph [FIGURE 10/B] showed a degree of fortification with no evidence of visible damage or cracked particles in the texture.
- [TABLES 2-4] show the test results of splitting tensile strength (0.4 N/mm²), shear strength (4.6 N/mm²) and compressive strength (7.3 N/mm²). Results of the test bricks suggested that they have reasonable mechanical properties for use as double-wall bricks.

²⁴ SAAD & TONNIZAM 2012: 369-376.



[FIGURES 10/A-B]: The XRD pattern; A. Polarizing microscope micrograph; B. The tested red brick sample © Done by the authors

Weight (g)	Average Measured Dimensions D*H (mm)	Ultimate Load (N)	Splitting Tensile Strength (N/mm ²)	Sample Type
46.2	30.2*54.6	1035	0.40	Cylindrical bricks

[TABLE 2]: The average results of the tensile strength test for the tested red brick samples © Done by the authors

Weight (g)	Average Measured Dimensions D*H (mm)	Ultimate Load (N)	Single Shear Strength (N/mm ²)	Sample Type
40.1	29.2*56.9	3110	4.6	Cylindrical bricks

[TABLE 3]: The average results of the shear strength test for the tested red brick samples © Done by the authors

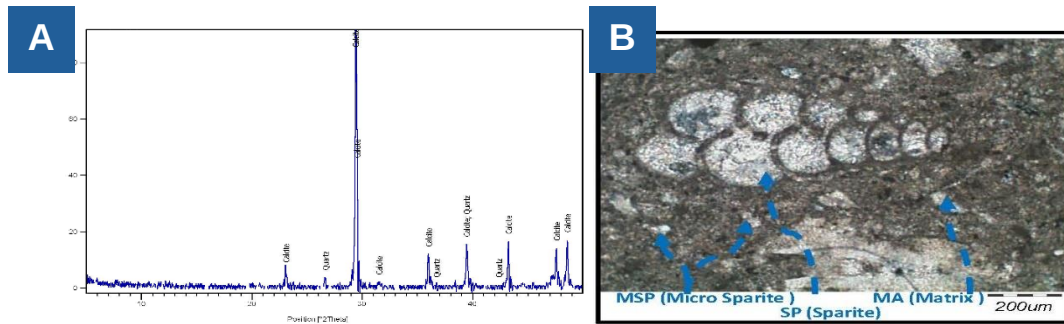
Weight (g)	Average Measured Dimensions D*H (mm)	Ultimate Load (N)	Compressive Strength (N/mm ²)	Sample Type
45.7	30.5*57.0	5335	7.3	Cylindrical bricks

[TABLE 4]: The average results of the compressive strength test for the tested red brick samples © Done by the authors

8. Limestone Blocks and Cylinders

The laboratory tests of the representative limestone samples are summarized as follows:

- The XRD pattern showed that the detected crystallized minerals were calcite and quartz [FIGURE 11/A].
- The petrographic analysis micrograph [FIGURE 11/B] showed calcite grains, mostly of the medium-grained type (2-4um), called microsparite. The sample also showed fossils (>4um) in coarse-grained calcite. The examined thin section reflected that the studied limestone sample could be classified as a fossiliferous limestone rich with foraminiferal fossils. Also, no clear evidence of damaged particles is detected in the texture.
- [TABLES 5-7] shows the results of splitting tensile strength (0.78 N/mm²), shear strength (12.4 N/mm²) and compressive strength (5.2 N/mm²). The results mean that the tested stones are of a weak type.



[FIGURES 11/a-b]: The XRD pattern; A. Polarizing microscope micrograph; B. The tested limestone sample © Done by the authors

Weight (g)	Average Measured Dimensions D*H (mm)	Ultimate Load (N)	Splitting Tensile Strength (N/mm ²)	Sample Type
167.6	40.9*59.4	16300	12.4	Cylindrical limestone

[TABLE 5]: The average results of the tensile strength test for the tested limestone sample © Done by the authors

Weight (g)	Average Measured Dimensions D*H (mm)	Ultimate Load (N)	Single Shear Strength (N/mm ²)	Sample Type
164.7	40.2*61.4	3790	0.98	Cylindrical limestone

[TABLE 6]: The average results of the shear strength test for the tested limestone sample © Done by the authors

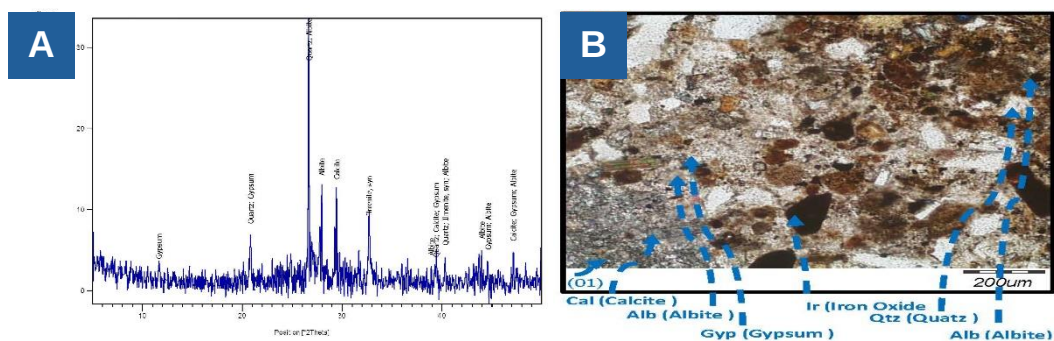
Weight (g)	Average Measured Dimensions D*H (mm)	Ultimate Load (N)	Compressive Strength (N/mm ²)	SampleT
76.8	27.3*62.3	3020	5.2	Cylindrical limestone

[TABLE 7]: The average results of the compressive strength test for the tested limestone sample © Done by the authors

9. Filling between the Double Walls

The XRD pattern showed that the mortar tested sample was composed of quartz, calcite and gypsum as primary minerals and albite as a secondary mineral [FIGURE 12/A]. It means that the used mortar of the lime type may be carbonated due to the longer brume action.

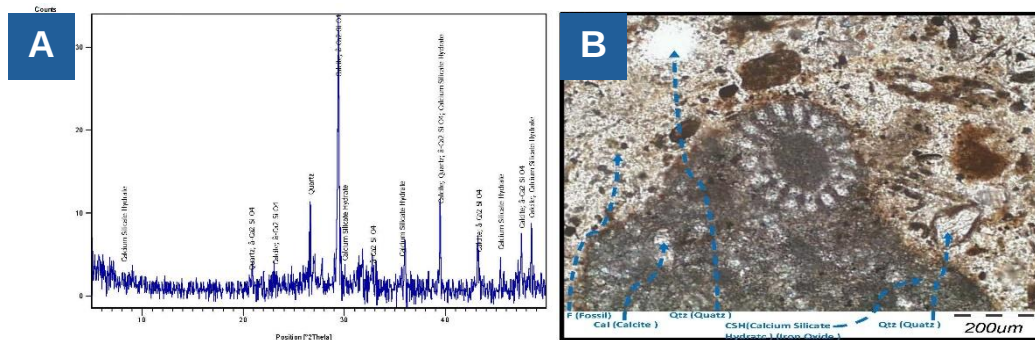
The petrographic analysis for the micrograph [FIGURE 12/B] illustrated medium quartz grains, in addition to some iron oxides. There were crystals of feldspar dispersed in the matrix. Also, fine-grained calcite mineral in the lower left part of the photo, indicated by arrow «Inv N^o.1», was detected and some salts and minerals appeared in the thin section as ferrous materials. It showed no visible signs of damage or particles.



[FIGURES 12/A-B]: The XRD pattern; A. Polarizing microscope micrograph; B. The tested mortar sample © Done by the authors

10. Mortar between the Stones

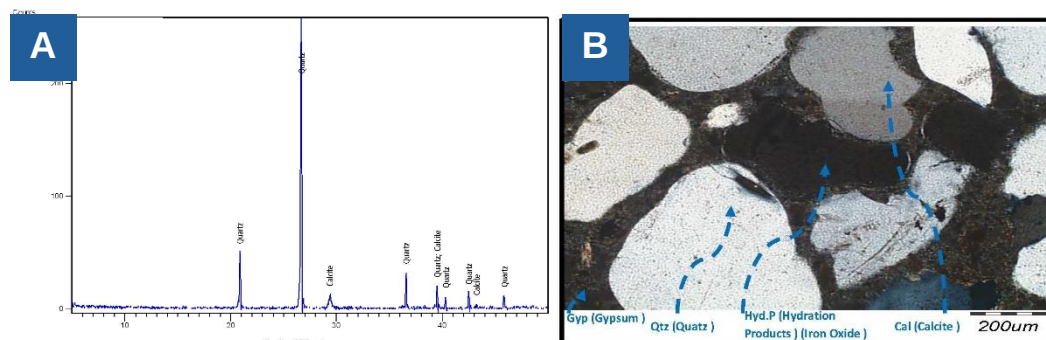
- The XRD pattern showed that the tested mortar used for the construction of stones was composed mainly of calcite and quartz, as well as C-S-H «calcium silicate hydrate, cementitious phase» as a secondary mineral. This finding means that the tested mortar may be contaminated. They detected C-S-H in the concrete slab mortar [FIGURE 13/A].
- The petrographic photo [FIGURE 13/B] showed honeydew mortar consisting mainly of quartz crystals (medium size). Also, coarse-grained calcite (sprite) was presented in the fossil and some fine-grained calcite (micrite) forming matrix is observed. Some traces of evaporated minerals appeared at the top of the micrograph. It was shown that the formation of a bonded material bound the mortar particles.



[FIGURES 13/A-B]: The XRD pattern; A. Polarizing microscope micrograph; B. The tested mortar sample
© Done by the authors

11. The Mortar Covered the Wall Bricks

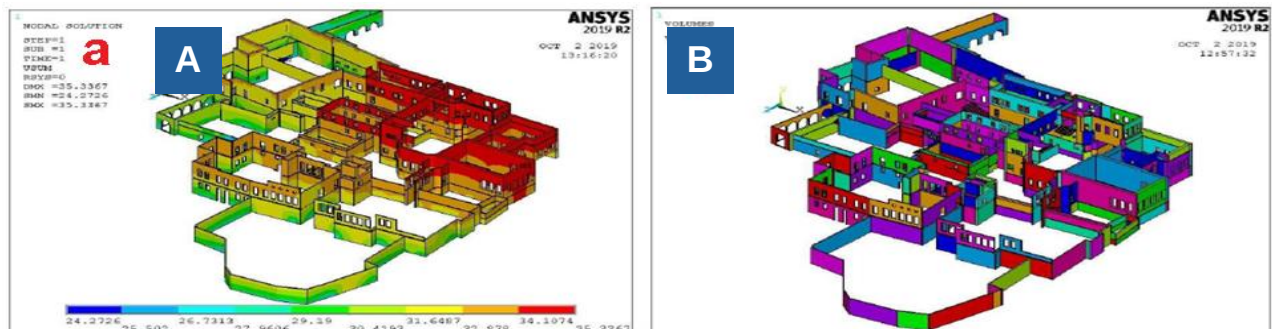
- The XRD result revealed that it was primarily composed of quartz and calcite as a secondary mineral [FIGURE 14/A]. This finding means that the mortar was of lime type.
- The polarized microscopy results illustrated the component of the studied mortar as quartz grains (filler) of large size with semi-circular shapes, representing more than 75% of the studied particles. There were traces of some evaporated minerals (gypsum). There was also a fine-grained calcite as a matrix between the quartz grains. There were traces of formation of hydrated metabolites on the edges of quartz crystals [FIGURE 14/B].



[FIGURES 14/A-B]: The XRD pattern; A. Polarizing microscope micrograph; B. The tested brick wall mortar sample © Done by the authors

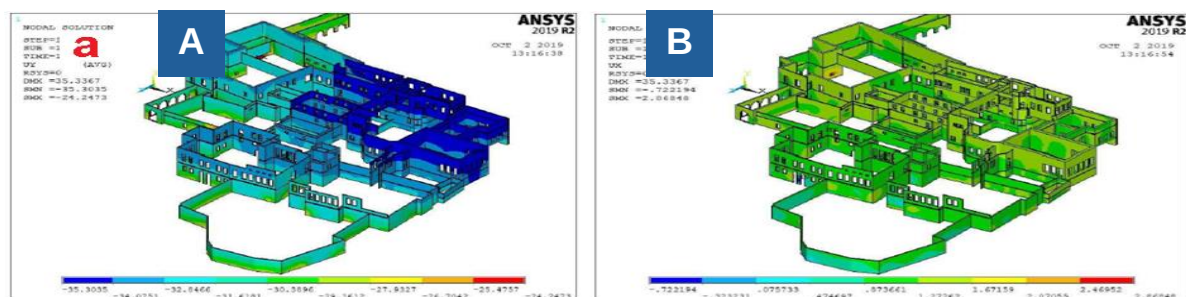
12. The Effect of Loads on Walls

To evaluate the structural behavior of the building and assess its response to external actions, a network of monitoring sensors was installed along the walls to detect and record any potential movements, deformations or structural instabilities. The results of the monitoring program and the corresponding structural analyses are presented in [FIGURES 10–13]. Furthermore, [FIGURE 15/A] illustrates the finite element model developed to simulate the structural performance of the building components under different loading scenarios. The numerical analyses revealed that the walls experienced measurable horizontal displacements, resulting in localized distortion under static loading conditions, as presented in [FIGURE 15/B]. In addition, seismic analysis conducted using the finite element software ANSYS demonstrated the development of horizontal deformation patterns in the Z-direction within several structural elements when subjected to seismic excitation. The corresponding displacement contours are illustrated in [FIGURES 16/A–B], which show the distribution of seismic-induced deformations, including vertical displacements in the Y-direction and horizontal displacements in the Z-direction (mm). These results provide valuable insight into the structural response of the historic building, enabling the identification of vulnerable areas and supporting the development of targeted conservation and structural strengthening interventions aimed at enhancing the seismic resilience of the monument while preserving its architectural authenticity.



[FIGURES 15/A-B]: Displacement response of the walls under static loading. A. Vertical deformation in the Y-direction induced by seismic actions; B. Displacement distribution in the Z-direction (mm)

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[FIGURES 16/A-B]: Seismic-induced deformation of the structure, showing (A) horizontal displacement in the Z-direction (mm) and (B) vertical displacement in the Y-direction (mm) © SUPREME COUNCIL OF ANTIQUITIES 2019: 37- 49

VIII. CONCLUSION AND RECOMMENDATIONS

Based on the results of the material characterization, structural assessment and deterioration analysis, a comprehensive conservation strategy is recommended to ensure the long-term stability and authenticity of the historic fabric. Repointing and masonry repairs should be carried out using compatible lime-based mortars with a lime-to-sand ratio of 1:2.5, consistent with the mineralogical composition of the original binding materials as identified by X-ray diffraction (XRD) analysis. Areas of weakened limestone should be consolidated using compatible and reversible conservation treatments, such as nanolime dispersions or ethyl silicate-based consolidants, following preliminary testing to evaluate their effectiveness and compatibility with the substrate. Salt-affected zones exhibiting sylvite and gypsum crystallization should undergo controlled desalination through the application of clay- or cellulose-based poultices to reduce soluble salt concentrations and mitigate further deterioration. Deteriorated timber elements should be replaced with well-seasoned cedar wood possessing similar mechanical and physical properties to the original material and treated with appropriate biological protection agents to enhance durability. To address moisture-related deterioration and geotechnical instability, an effective drainage system should be installed to reduce water infiltration and minimize the risk of soil swelling and differential settlement. Furthermore, a long-term structural health monitoring program should be implemented, incorporating crack gauges, displacement indicators, and humidity sensors to continuously assess structural behavior, environmental conditions, and potential future deterioration, thereby supporting preventive conservation and informed maintenance planning.

DISCLOSURE STATEMENT

No Potential conflict of interest was reported by the authors

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EVALUATION OF THE IMPACT OF CLIMATE CHANGE USING REMOTE SENSING AND GIS APPROACHES APPLIED TO THE ṬĀBIYAT 'URĀBĪ ARCHEOLOGICAL SITE

BY

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ABSTRACT

[EN] This study uses remote sensing and geographic information systems to evaluate the impact of climate change on the archeological site of Ṭābiyat 'Urābī in Damietta Governorate, Egypt. It used the remote sensing program «ENVI» on a set of equations on the thermal band in the image to determine temperatures. The geographic information systems program «ARC-GIS» was used to create thermal maps of Ṭābiyat 'Urābī over four decades from July 1993 to July 2024. The minimum and maximum temperatures were evaluated. It was found that there is a variation in the minimum and maximum temperatures, which increases damage rates to the structure and components of the monument. The experimental aspect was conducted on samples of burnt red bricks and limestone, the main element of Ṭābiyat 'Urābī. A digital microscope X1000 was used to determine the characteristics of the surface. Moreover, a polarization microscope was used to examine crystals and amorphous materials. A scanning electron microscope was used to examine the surface morphology components. X-ray diffraction was used to study the crystal structure, crystal size and strain of the materials composing the monument. The results showed the extent of the effect of temperatures resulting from climate change on the building components at the site in terms of density, porosity, absorption and mechanical properties.

KEYWORDS: Archeological sites, climate changes, geographic information systems, maps, remote sensing, satellite images, temperature.

[AR] تقييم تأثير تغير المناخ باستخدام تقنيات الاستشعار عن بعد ونظم المعلومات الجغرافية تطبيقاً على موقع طابية عرابي الأثري تهدف هذه الدراسة إلى تقييم تأثير التغيرات المناخية على الموقع الأثري لطابية عرابي بمحافظة دمياط بمصر، باستخدام الاستشعار عن بعد ونظم المعلومات الجغرافية. تم التطبيق باستخدام برنامج الاستشعار عن بعد «ENVI» على مجموعة من المعادلات الخاصة بالنطاق الحراري في الصورة لتحديد درجات الحرارة. تم استخدام برنامج نظم المعلومات الجغرافية «ARC-GIS» لإنشاء خرائط حرارية لطابية عرابي خلال الفترة من يوليو 1993 إلى يوليو 2024 على مدى أربعة عقود. تم تقييم الحد الأدنى والأقصى لدرجات الحرارة. وتوصلت الدراسة إلى وجود تباين في الحد الأدنى والأقصى لدرجات الحرارة مما يؤدي إلى زيادة معدلات الضرر على هيكل النصب ومكوناته. تم إجراء الجانب التجريبي على عينات من الطوب الأحمر المحروق والحجر الجيري الذي يعد المكون الرئيسي لطابية عرابي. وتم استخدام المجهر الرقعي بقوة تكبير ١٠٠٠ لتحديد الخصائص على السطح. تم استخدام المجهر المستقطب لفحص البلورات والمواد غير المتبلورة، كما تم استخدام المجهر الإلكتروني الماسح لفحص مكونات مورفولوجيا السطح، وتم استخدام حيود الأشعة السينية لدراسة البنية البلورية وحجم البلورة وإجهاد المواد المكونة للنصب التذكاري، وقد أعطت نتائج الدراسة مدى تأثير درجات الحرارة الناتجة عن تغير المناخ على مكونات البناء في الموقع من حيث الكثافة والمسامية والامتصاص والخصائص الميكانيكية. الكلمات الدالة: الاستشعار عن بعد، التغيرات المناخية، الخرائط، درجة الحرارة، صور الأقمار الصناعية، المواقع الأثرية، نظم المعلومات الجغرافية.

I. INTRODUCTION

The sustainability and preservation of archeological sites are seriously threatened by their growing susceptibility to degradation due to climate change¹. An important case study for assessing these effects is the *Ṭābiyat 'Urābī* archeological site in the Damietta Governorate, Egypt, especially when using geographic information systems and remote sensing². Recent research highlighted the negative impacts of climate change on cultural assets. For example, BAKER found that temperature fluctuations might worsen the degradation of archeological artifacts, causing irreparable harm³. Furthermore, CARTER & LEWIS showed how harsh weather conditions, including higher rainfall and temperature rises, exacerbate the deterioration of site constructions, especially those composed of delicate materials like red brick and limestone⁴.

Recently, there has been an increase in the use of remote sensing technology in archaeology. According to MARTIN, researchers can extract temperature data over long periods by analyzing thermal bands in satellite photos using tools like ENVI⁵, which helps gain a thorough knowledge of the effects of climate change on archeological sites.

Additionally, climate fluctuations and their effects on heritage sites have been shown using geographic information systems (GIS), which have produced essential data for conservation efforts⁶.

This study examines temperature data gathered over three decades (1993–2024) to assess the effects of climate change on the *Ṭābiyat 'Urābī* archeological site. The experimental evaluation focuses on the site's essential building elements, such as limestone and burned red bricks. According to ROBERTS, these materials are vulnerable to heat stress and can sustain major structural damage because of climatic fluctuations⁷. As shown in the work of WILLIAMS *et Al.*, methods like X-ray diffraction (XRD) and scanning electron microscopy (SEM) are used to examine the physical and chemical characteristics of these materials under various climatic circumstances⁸.

To create efficient conservation plans and guarantee the survival of these priceless cultural heritage sites, it is crucial to comprehend how climate change and archeological preservation interact⁹. This study aims to contribute to the larger field of heritage protection in the face of climate change by thoroughly assessing *al-Ṭābiyat 'Urābī* archeological site using cutting-edge technologies, e.g., remote sensing and GIS. *Ṭābiyat 'Urābī* Fortress is one of the military fortresses established by the French occupation on the ruins of the city of *'Izbat al-Burğ* in northern Damietta after fierce battles between the

¹ SMITH & JOHNSON 2020: 103-115.

² ADAMS & CARTER 2021: 129.

³ BAKER 2019: 945-960.

⁴ CARTER & LEWIS 2022: 920-930.

⁵ MARTIN 2020: 1501-1510.

⁶ NGUYEN & PATEL 2023: 72-85

⁷ ROBERTS 2021: 20.

⁸ WILLIAMS *et Al.* 2019; ADAM 2026: 285.

⁹ YOUNG & ZHANG 2022: 345-358.

occupation forces and the Egyptian popular resistance, which ended with the removal of the city and the establishment of the fortress on its ruins in revenge against its people¹⁰.

In 854 AD, the Abbasid Caliph Al-Mutawakkil ordered the construction of two towers at the entrance to the Nile River, one on the eastern side and the other on the western side. The towers were of interest to the governors and rulers of Egypt, given that Damietta was one of the important borders and a target for invaders, beginning with the Crusades against Egypt. Thus, the city was called *‘Izbat al-Burğ*¹¹. The area of the fort is 60 thousand square meters, equivalent to approximately 14.3 acres. It is divided by a longitudinal road extending to the south. The fort forms a rectangle with a length from north to south of about 300 meters and a width from east to west of 200 meters. *‘Urābī* Fortress is located on the eastern bank of the Nile in the city of *‘Izbat al-Burğ*, facing the *Al-Ġarbī* area and near Rās El Bar Beach¹². It was built by the French army during the French campaign in Egypt on the ruins of the city of *‘Izbat al-Burğ* in northern Damietta. The castle consists of two walls separated by a 15-meter-wide moat. It contains many military monuments, such as watchtowers and defense towers, several rooms used as residences for soldiers and weapons and a small mosque. Damietta *Ṭābiyat* contains a series of military fortifications built during the French campaign in Egypt to protect its shores from naval invasion. The mosque is in the middle and horse stables, gunpowder stores and military equipment are on the eastern side. There are also the gallows building and the kitchen, while the soldiers' barracks or the large *qīšlāq* that Abbas Pasha built are on the western side overlooking the Nile. Moreover, there are courses of fire lines represented by the inner wall of the *Ṭābiyat* outside the moat, which is about half a meter high. The remains of the towers on both sides of the eastern entrance to *al-Ṭābiyat* have some loopholes. All the buildings are now demolished [FIGURE 1].

The physical and mechanical properties of some samples of building materials for the archeological site were determined¹³. This study was conducted on experimental samples that were as similar as possible to the components of *Ṭābiyat ‘Urābī* archeological site in Damietta to validate and ensure the accuracy and integrity of the results.



[FIGURE 1]: Shows the archeological site of *Ṭābiyat ‘Urābī* in Damietta © Photo taken by Wael Gamal Hosam El-din

¹⁰ BROWN & CARTER 2018: 123-145.

¹¹ SMITH & JONES 2020: 45-67.

¹² ADAMS & PATEL 2021: 502-516.

¹³ WILLIAMS & LEWIS 2019: 344-358.

II. MATERIALS AND METHODS

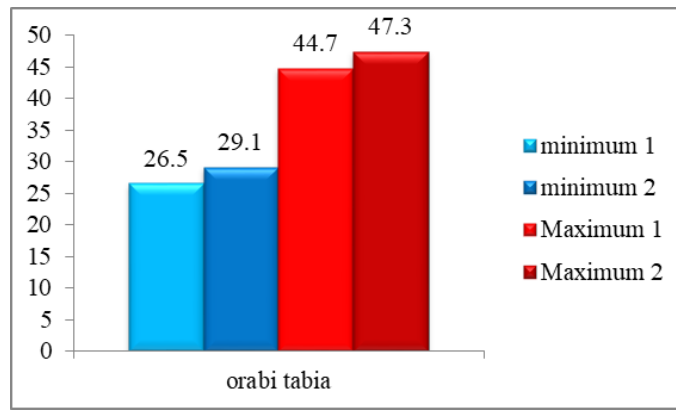
The analytical part of the study was conducted at the National Authority for Remote Sensing and Space Sciences in Cairo, Egypt. Thermal satellite images were analyzed to extract temperatures using remote sensing software for *al-Ṭābiyat 'Urābī* site in Damietta. Satellite images of the site were obtained from the Landsat Thematic Mapper (TM) with thermal band 6 in 1993, 2003 and 2011. Also, it used enhanced thematic mapper plus (ETM+) with thermal band 61 in 2013. It used land sat 8 thermal band 10 in 2023 and 2024.

Satellite images were downloaded from the USGS website. Accordingly, thermal satellite images were analyzed to extract temperatures using the ENVI remote sensing software by applying a set of equations to the thermal range of the image to extract temperatures of *Ṭābiyat 'Urābī* in the northern part of Damietta Governorate on the edge of the Mediterranean [FIGURE 2].

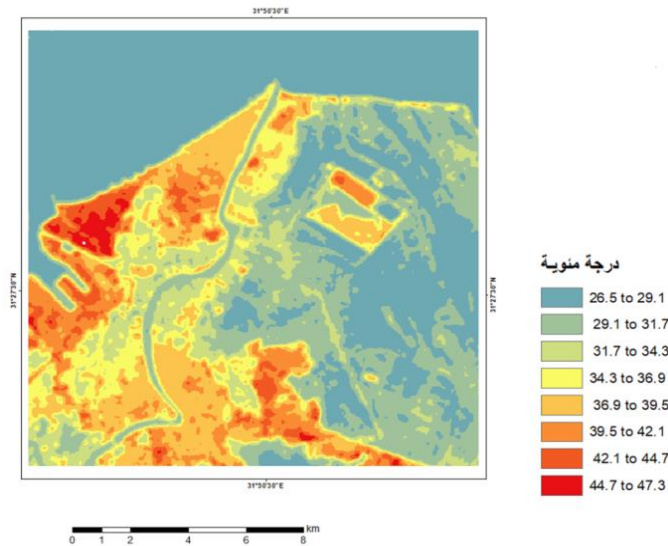


[FIGURE 2]: Shows the location of *Ṭābiyat 'Urābī* after downloading and analyzing satellite images using the remote sensing program; it demonstrates downloading satellite images from the USGS website to use the ENVI remote sensing program to analyze thermal satellite © Done by the authors

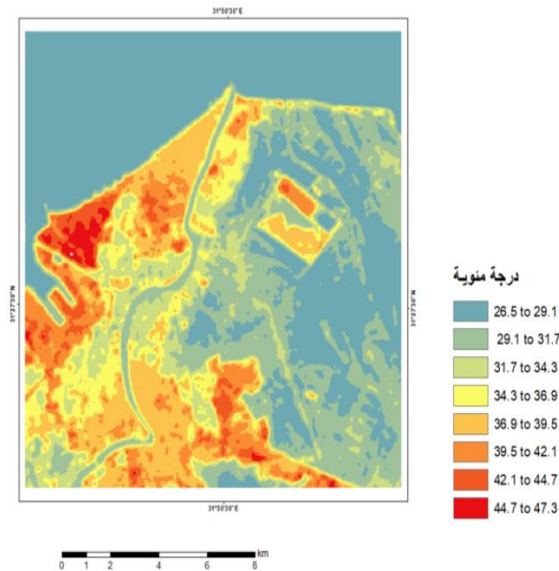
Arc GIS was used to extract the final temperature maps for *al-Ṭābiyat 'Urābī* site in Damietta. Arc Map (ARC GIS) was used to create the final maps expressing the temperature study of the site from 1993 to 2024 during July over four decades, [FIGURE 4]: (27/7/1993) – (14/7/2003) – (29/7/2011) – (26/7/2013) – (14/7/2023) – (24/7/2024). The results were as follows: Light blue represents the lowest temperature (minimum), from 26.5 to 29.1 and dark red represents the highest temperature (maximum), from 44.7 to 47.3. It was found that there is a noticeable difference in temperatures [FIGURES 3- 4].



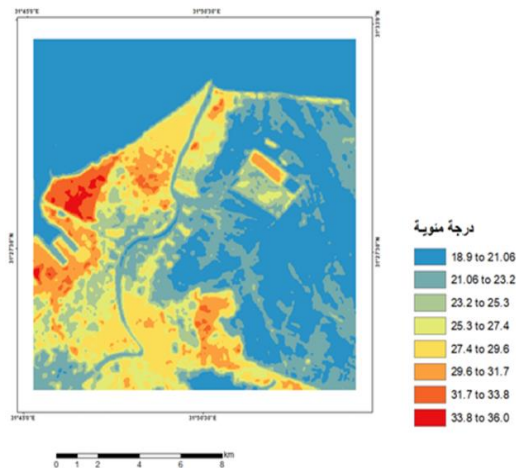
[FIGURE 3]: Shows the temperatures for *Tābiyat 'Urābī* site from 1993 to 2024 © Done by the authors



[FIGURE 4]: Shows temperature maps using ArcGIS for *Tābiyat 'Urābī* site in 2003 © Done by the authors



[FIGURE 5]: Shows temperature maps using ArcGIS for *Tābiyat 'Urābī* site in 2011 © Done by the author



[FIGURE 6]: Shows temperature maps using ArcGIS for *Tābiyat 'Urābī* site in 2024 © Done by the authors

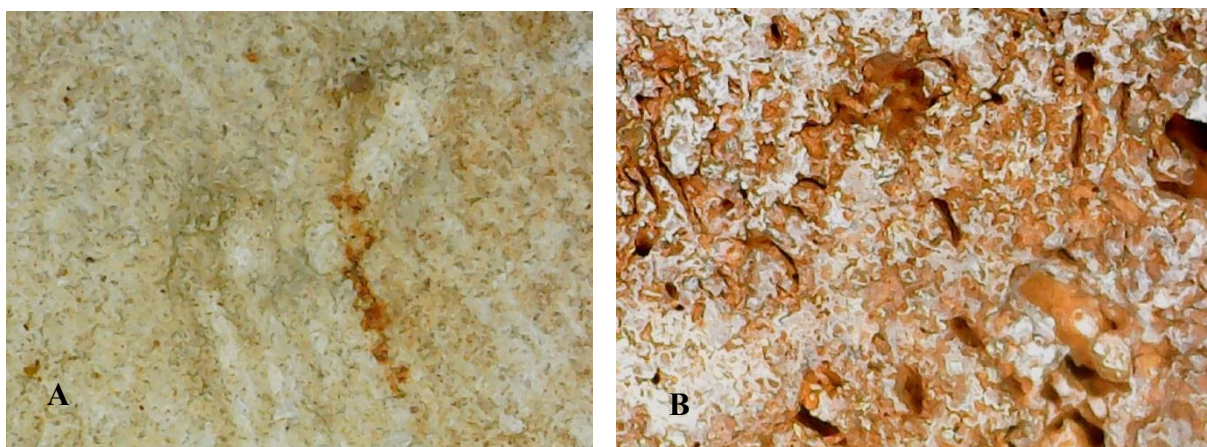
Similar experimental samples were prepared for the study site, which consisted of limestone cubes measuring 4 X 4 X 4 cm and red brick cubes measuring 6 X 6. Materials and tools for preparing experimental samples were limestone, red brick, scalpel, polyethylene bags and an aging oven. Stone samples were taken from the southeastern wall, from the upper left corners and far from the source of moisture, i.e., the sea.

III.INVESTIGATIONS AND ANALYSIS

Investigation and analysis of the building components at the archeological site were used to identify their chemical composition, internal structure and manifestations of damage, as well as the extent to which these manifestations affect the internal structure of these components, which may lead to the deterioration of the site as following:

1. Optical Microscope «OM»

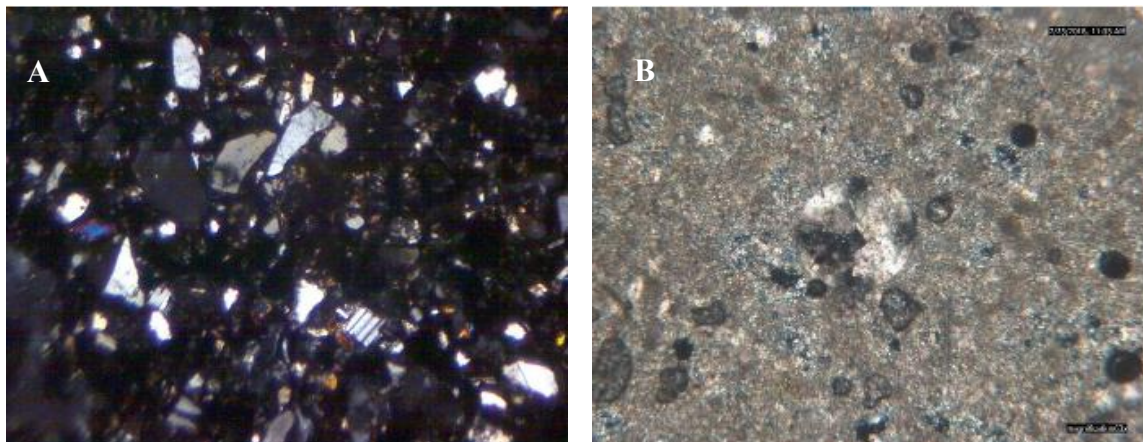
A portable optical microscope with a magnification of 1000x was used to identify the building components of the *Tābiyat 'Urābī* site in Damietta with an enlarged image and clear details [FIGURES 7/A-B].



[FIGURES 7/A-B]: Shows the examination with a portable optical microscope «30X magnification». A. Shows the examination of the red brick sample and highlights the appearance of salts; B. Shows the examination of the limestone sample and shows the appearance of salts © Done by the authors

2. Polarizing Microscope

The Compact Polarizing Microscope CX31-P- Olympus-IMS device was used at the research center to identify the mineral components, the texture, the shape and size of the mineral grains and their relationship with each other and to determine internal damage based on the optical properties of the metals [FIGURES 8/A-B].



[FIGURES 8/A -B]: Shows the examination with a polarized microscope «100× magnification». A. Shows the appearance of feldspar minerals in a background of iron oxides and the lack of cohesion of these grains in a red brick sample; B. Shows the presence of calcite grains, quartz, iron oxides and many fossils in limestone © Done by the authors

3. X-ray Diffraction Analysis

X-ray diffraction analysis was performed in the institution's laboratory to identify the samples' chemical and mineral composition, as this method is used to study crystalline materials with a regular crystal structure. The study was conducted to identify the mineral components and their impact on the damage processes that archeological sites are exposed to due to temperature fluctuations resulting from climate change. The analysis showed that the red brick sample consists of quartz (SiO_2), feldspar (albite) and hematite, in addition to mullite, which is a secondary component resulting from the burning of kaolinite. In contrast, the limestone sample consists mainly of calcite and a small percentage of quartz [TABLE 1].

Chemical Compounds	Chemical Formula	Limestone	Red Brick
Quartz	Si O_2	4	40
Albite	$(\text{Na}_{0.98} \text{Ca}_{0.02})(\text{Al}_{1.02} \text{Si}_{2.98} \text{O}_8)$	-	35
Hematite	Fe_2O_3	-	15
Mullite	$3\text{Al}_2\text{O}_3.2\text{SiO}_2$	-	10
Calcite	Ca CO_3	96	-

[TABLE 1]: Shows the results of the X-ray diffraction analysis © Done by the Authors

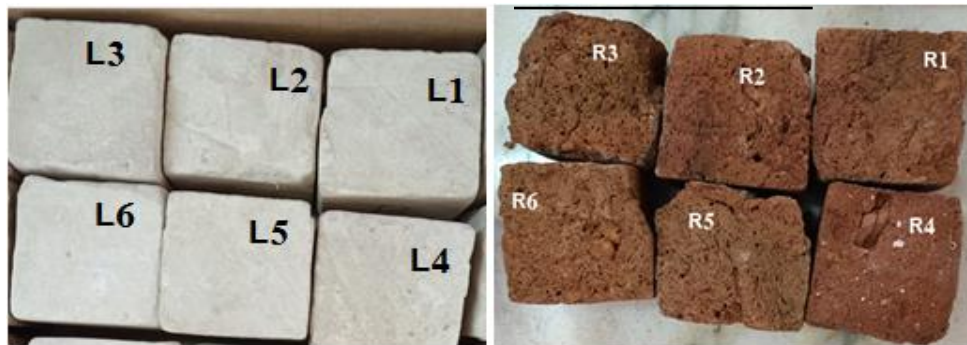
IV. EXPERIMENTAL STUDY

The physical and mechanical properties of the samples were studied before and after thermal aging to identify the effect of thermal aging resulting from climate change on the properties of building materials of *Tābiyat 'Urābī* site. Three samples were collected and their physical properties were measured. The thermal aging was carried out in a drying oven at 105 °C for 24 hours. Then, the samples were weighed after drying to determine their dry weight. After that, the three dimensions of the samples were measured to calculate their external volume and absorption by immersing them in water for 24 hours.

Then, they were weighed after immersion to determine the wet weight and porosity by drying the samples in a drying oven at 105 °C for 24 hours. Next, the samples were weighed after drying to determine their dry weight. After that, the samples were immersed in water for 24 hours and weighed after immersion to determine their wet weight. Then, the three dimensions of the samples were measured and their volume was calculated.

Their mechanical properties were measured by the compressive strength measurement method. The compressive strength of red brick and limestone samples was determined by substitution in equation 1:

$$\text{Compressive strength (kg/cm}^2\text{)} = \frac{\text{load (kg)}}{\text{area (cm}^2\text{)}} \quad 1$$



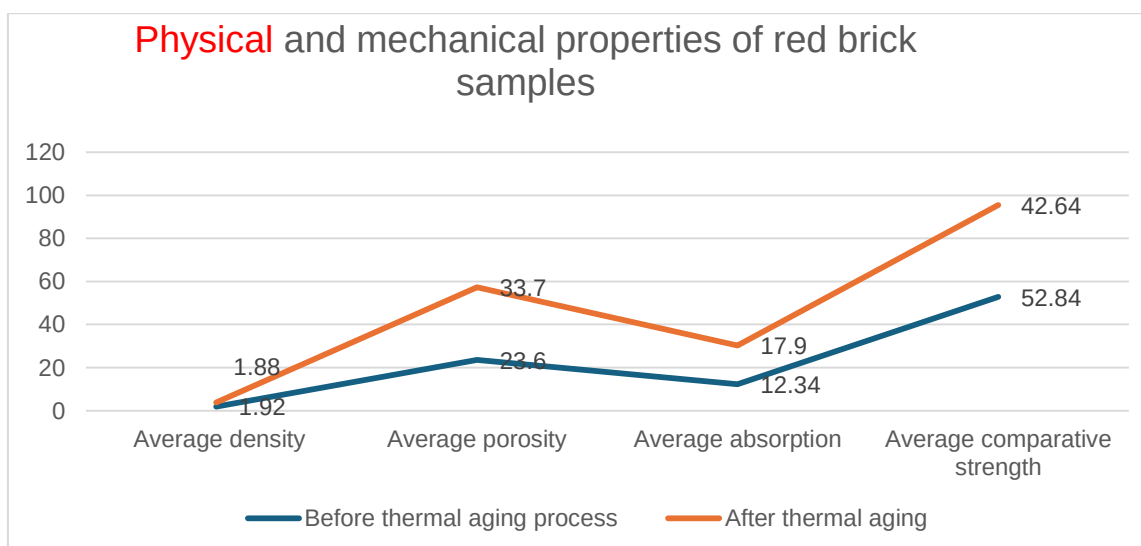
[FIGURE 9]: Shows the limestone and red brick samples used in the experimental study © Done by the authors

Property	Average Density	Average Porosity	Average Absorption	Average Compressive Strength
Result	1.92g/cm ³	23.6%	12.34%	52.84kg/cm ²

[TABLE 2]: Shows the physical and mechanical properties of red brick samples before thermal aging © Done by the authors

Property	Average Density	Average Porosity	Average Absorption	Average Compressive Strength
Result	1.88g/cm ³	33.7%	17.9%	42.64kg/cm ²

[TABLE 3]: Shows the physical and mechanical properties of red brick samples after thermal aging. © Done by the authors



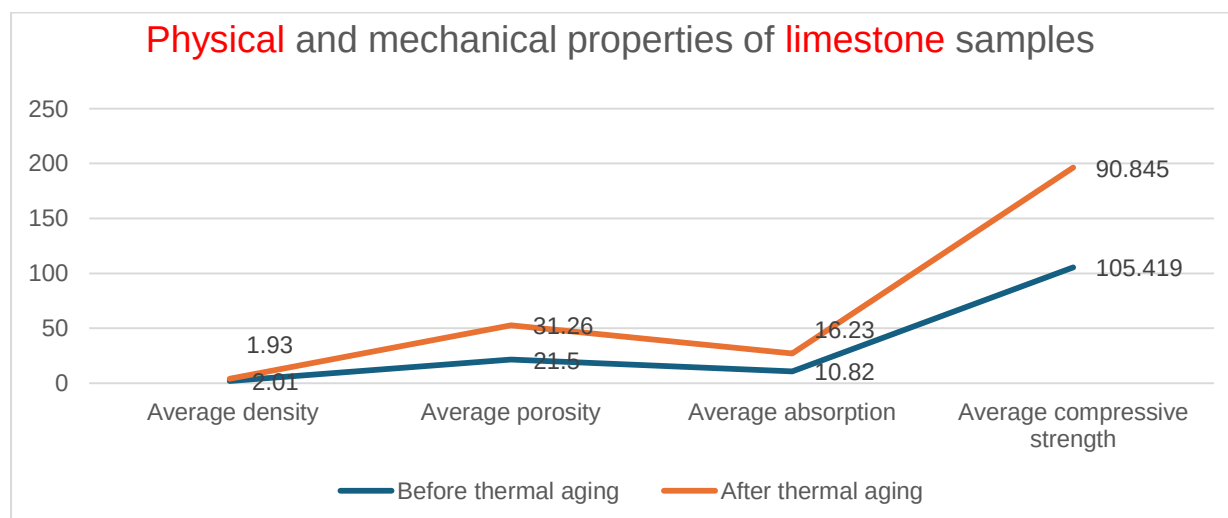
[FIGURE 10]: Shows the average of the physical and mechanical properties of red brick samples before and after thermal aging © Done by the authors

Property	Average Density	Average Porosity	Average Absorption	Average Compressive Strength
Result	10.82 %	21.5 %	2.01 g/cm ³	105.419 kg/cm ²

[TABLE 4]: Shows the physical and mechanical properties of limestone samples before thermal aging © Done by the authors

Property	Average Density	Average Porosity	Average Absorption	Average Compressive Strength
Result	1.93 g/cm ³	31.26 %	16.23 %	90.845 kg/cm ²

[TABLE 5]: Shows the physical and mechanical properties of limestone samples after thermal aging



[FIGURE 11]: Shows the average of the physical and mechanical properties of limestone samples before and after the thermal aging process © Done by the authors

By studying the physical properties «density- porosity- absorption» of red brick [TABLES 2-3 & FIGURES 9-10] and limestone samples [TABLES 4-5 & FIGURE 11] in *Tābiyat 'Urābī* site in Damietta, it was revealed that there was a decrease in density, which, in turn, led to a percentage increase. The porosity and high absorption rate result from the thermal aging process that took place on the samples. Studying the mechanical properties revealed a decrease in the compressive strength of all samples. Also, a result of the thermal aging process was the deterioration of the internal structure of the red brick and limestone samples that were studied, suggesting the effect on the site, the impact of rising temperatures resulting from climate change.

V.DISCUSSION

The results of applying remote sensing and geographic information systems to the archeological site of *Tābiyat 'Urābī* showed temperature fluctuations during the period to which it was applied from 1993 to 2024. The results showed a noticeable difference: the lowest temperature (minimum), 26.5 to 29.1 and the highest temperature, 44.7 to 47.3, as the fluctuation and continuous temperature change, whether daily or seasonal, represents a great danger to stone buildings.

The repetition of temperature cycles causes a complex damage mechanism that varies according to the type of stones and their ability to resist damage, as the mineral particles expand due to the high surface temperature during the day or in the summer and contract again when the surface cools at night or during the winter. Due to the processes of expansion and contraction, stresses and pressures arise in different directions, causing fragments of the minerals that make up the structure of these stones or bricks, the separation of these grains, known as granular disintegration, the pressure of the mineral components of the stones, causing a fracture parallel to their surfaces and the stones disintegrate, known as exfoliation. Whenever a layer falls, another layer peels off with the help of various factors of damage, which leads to distorting the surface of the monument and damaging the engravings and colored drawings on it, known as insolation.

The degree of granulation, texture, porosity, direction of the wind carrying heat and amount of moisture in the monument affect the stone's ability to absorb and attract heat in different ways according to its nature, as the stone absorbs amounts of heat depending on the size of the crystals and the capacity of the voids (pores). Coarse-grained sandstone allows the heat leaking between its components to penetrate, while fine-grained sandstone makes it difficult to penetrate heat between its components due to the lack of voids. In the case of low or no moisture, weathering depends primarily on the thermal conductivity of the stone, the expansion coefficients of the minerals, the degree of their absorption of heat, the daily change in temperature and its distribution in the rock.

The chemical effect of heat, as a factor of damage, lies in its direct relationship with moisture within the pores of the stone, as it increases the movement of salt solutions and their spread within the pores. It also attracts the salt solutions present in the internal structure of the monument, and then evaporates water from these solutions, leaving behind crystals of different types of salt on the surface below within the pores of the stone

or in fine surface cracks. Each case depends on the speed and rate of drying and evaporation.

The salt layer is dangerous in damaging archeological buildings if it forms on the external surfaces. It may lead to sunken blisters and protrusions on the surface, causing it to lose its smooth texture with repeated drying and moisture processes. Also, the change and difference in temperature lead to the expansion and contraction of the components of the archeological building.

It ultimately leads to the cracking and separation of some components of ancient buildings, causing internal cracking in most building components and sometimes leading to their collapse. Also, the high temperature causes rapid evaporation of salt-bearing liquids, causing crystallization. These salts are either on the surfaces of the stones or directly under the surfaces, which leads to their disintegration through thermal expansion.

The results of all examination and analysis methods were given on the samples studied at the site under study.

1. Stone Sample

The examination and analysis methods illustrated that the stone used in building the tabernacle is limestone and consists mainly of the mineral calcite, in addition to a small percentage of the mineral quartz, in addition to some other carbonate grains, including the micro-fossils that spread throughout the floor. There are also small grains of iron oxides, as shown by XRD and polarizing microscope.

2. Brick Sample

Analysis showed that it contains quartz grains and feldspar minerals, iron oxides and muscovite. Examining the results of the experimental study of each of the physical properties (density - porosity - absorption) of red brick and limestone samples in *Tābiyat 'Urābī* site in Damietta revealed that there was a decrease in density, which in turn led to a higher percentage of porosity and a higher rate of absorption, as a result of the thermal aging process that took place on the samples as well. Studying the mechanical properties revealed a decrease in the compressive strength of all samples due to thermal aging, which led to the deterioration of the internal structure of the studied red brick and limestone samples. This finding explains how much the archeological site is affected by high temperatures resulting from climate change.

VI. CONCLUSION

The archeological buildings in *Ṭābiyat 'Urābī* in Damietta are exposed to many factors of damage that lead to various clear forms of damage, such as temperature fluctuations resulting from climate change, humidity and salts.

Through the application of remote sensing and geographic information systems on the archeological site, temperature fluctuations are noted. As the temperature rises, internal interactions and stresses in the antiquity structure occur, ultimately leading to the collapse of the internal structure. Additionally, the combination of this factor with other factors, such as salt and humidity, has a severe destructive effect on the archeological site.

Bricks are the main component of the archeological site. You notice a decrease in density, which leads to a higher percentage of porosity and a higher rate of absorption. Studying the mechanical properties showed that there was a decrease in compressive resistance. So, we recommend rapid intervention by archeological restoration scientists and professionals to save such sites that are exposed to damage and enforce preventive maintenance or even rapid remedial maintenance to protect these sites from the risks of climate change.

DISCLOSURE STATEMENT

No Potential conflict of interest was reported by the authors

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USING NANO-MAGNETITE IN A PROTECTIVE COATING TO PREVENT THE CORROSION OF IRON INK APPLIED ON AN ISLAMIC MANUSCRIPT

BY

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ABSTRACT

[EN] This research paper aims to measure the distribution of magnetite nanoparticles on corroded iron ink and to understand the mechanism of protection for iron ink using iron oxide nanoparticles (Fe₃O₄NPs). When iron inks are affected by rust and corrosion, they cause weakness, brittleness and discoloration of the paper (yellowing or browning). This problem is addressed by reducing iron oxide (magnetite) to the nanoscale to utilize its novel physical and chemical properties. While previous studies have confirmed the successful use of nanomaterials in protecting paper itself, this is the first time magnetite nanoparticles have been used to protect iron ink. The study highlights the presence of numerous manuscripts suffering from corrosion, weakness, and brittleness, which constitute the core of the research problem, and demonstrates the properties of nanomaterials in protecting manuscript inks. The practical procedures involved using nano-magnetite on a test paper similar to the damaged manuscript and conducting various tests and analyses (color change, portable microscopy, atomic force measurement, contact point measurement) to confirm the safety of the work without damage and direct work on the damaged manuscript. The results prove the feasibility of using nano-magnetite due to its ease of access, lack of damage, and reversibility, which contributes to adding a new, safe step in the treatment of manuscripts using nanotechnology.

KEYWORDS: Coating, corrosion, iron ink, Islamic manuscript, nano-magnetite, restoration.

[AR] استخدام نانو الماغنيتيت في حماية الحبر الحديدي ضد التآكل – تطبيقاً على مخطوط إسلامي
تهدف هذه الورقة البحثية إلى قياس توزيع المغنيتيت النانوي على حبر الحديد المتآكل وفهم آلية حماية حبر الحديد باستخدام جسيمات أكسيد الحديد النانوية (Fe₃O₄NPs)، فعندما تتأثر أحبار الحديد بالصدأ والتآكل، فإنها تُسبب ضعفاً وهشاشة وتغيراً في لون الورق (اصفراراً أو تحولاً إلى اللون البني). وعلاج هذه المشكلة يتم عن طريق اختزال أكسيد الحديد (المغنيتيت) إلى مقياس النانو للاستفادة من خصائصه الفيزيائية والكيميائية الجديدة. وأكسيد الحديد (المغنيتيت) النانوي يستخدم لأول مرة في حماية الحبر الحديدي رغم وجود دراسات أكدت نجاح استخدام المواد النانوية في حماية الورق نفسه. توضح الدراسة ظهور العديد من المخطوطات المصابة بالتآكل والضعف والهشاشة، والتي تُشكل جوهر مشكلة البحث، كما يوضح خواص مواد النانو في حماية أحبار المخطوطات. والإجراءات العملية باستخدام مادة النانو الماغنيتيت على ورق تجريبي مشابه للمخطوط المصاب وأجراء الفحوصات والتحليلات المختلفة من (التغير اللوني، الميكروسكوب المحمول، قياس القوة الذرية، قياس نقطة الاتصال، وغيرهم) للتأكيد على سلامة العمل دون ضرر والعمل المباشر على المخطوط المصاب. والنتائج تثبت إمكانية استعمال مادة الماغنيتيت لسهولة الحصول عليه وعدم الضرر الناتج وإمكانية الاسترجاع مما يسهم في إضافة خطوة جديدة آمنة في علاج المخطوطات باستخدام النانو.

كلمات دالة: التآكل، ترميم، تغطية، الحبر الحديدي، مخطوطات إسلامية، نانو ماجنيتيت

I. INTRODUCTION

Design, methodology, approach– Traditional treatment methods can pose risks to manuscripts. We conducted this study by synthesizing and preparing nanomaterials, applying magnetite nanoparticles ($\text{Fe}_3\text{O}_4\text{NPs}$) for the stabilization of iron gall ink on an Islamic manuscript and using appropriate examination and analysis devices, such as visual examination, acidity measurement, atomic force microscopy (AFM), contact angle measurements and a polarizing device, to evaluate the effectiveness of the treatment of iron oxide nanoparticles using magnetite nanoparticles ($\text{Fe}_3\text{O}_4\text{ NPs}$).

The nano-magnetite was applied using a brush application technique on laboratory-prepared samples simulating an 18th century manuscript, after artificial aging «thermal aging and ultraviolet irradiation». Findings – We concluded the significant protective effect of nano-magnetite in stabilizing iron gall ink and reducing further degradation. This can help preserve human heritage.

Originality/value – This study highlights the application of nanotechnology in the stabilization of iron gall ink. It contributes to the growing body of research on nanomaterials in paper conservation that correlates modern technology with paper degradation.

The word manuscript means everything that is written in human handwriting, produced on writing supports, such as papyrus, parchment or paper, whether it is a letter, a document, a book, using ink, including carbon ink, iron ink and colored inks.

Iron gall inks are prepared from plant extracts rich in tannins, particularly gall nuts, which are extracted using warm water to form solutions rich in polyphenolic acids. The extract contains polyphenolic acids, such as gallic acid; when mixed with iron II sulfate, it forms a dark iron–tannate complex. Gum Arabic is added as a binder to improve viscosity and adhesion. Iron gall ink appeared in Egypt during the late Pharaonic and Greco-Roman periods and became widespread in the Roman era.

In the Coptic era, its performance was improved by adding gallic acid, tannins and iron sulfate and left to oxidation to form iron ink, which helped the ink to easily permeate the writing surface and act as a stabilizer¹. Iron ink features some resistance to microbial growth. It is not optically stable and bright and does not dissolve in water.

However, its defects are its poor resistance to light and color changing over time². Iron ink initially appears dark black, then light brown and may reach a pale yellow when a gradient appears. In a single letter, we find more than one chromatic degree, indicating the natural aging of the ink over time³. Acid formation results from the oxidation of iron II sulfate and subsequent acid hydrolysis of cellulose and iron II-catalyzed oxidation of cellulose⁴ in many cases, leading to ink corrosion and perforation of the paper support below the writing surface. It also increases the acidity of the manuscript, as iron gall ink adds acidity to the paper substrate. Acidity introduced by

¹ PALMISANO 2011: 3483.

² MALES'IC' 2014: 10.

³ MAHGOUB H 2016: 4.

⁴ PANDA 2021: 3.

iron gall ink is likely the main factor driving the faster degradation of paper, as iron-gall inks induce the scission of cellulose through acid catalysis and/or redox reactions⁵.

However, ink continued to be used in Islamic times, with the addition of some materials «such as linseed oil» to improve its performance⁶ and to protect the coatings of manuscripts written in iron ink. The large specific surface areas of nanoparticles allow for enhanced reactivity, superior adsorption, higher solubility, lower melting point and improved electronic properties. Due to the outstanding properties of nanoparticles, nano coatings are made by incorporating nanocomposites into polymer matrices.⁷ Nano-coating materials were used as corrosion inhibitors to enhance protection against active corrosion because they have many advantages, such as high inhibition efficiency, low cost and safety for human health. Iron ink is easy to produce and has antifungal and antibacterial properties due to its large surface area⁸. It is also self-cleaning, i.e., it is a dirt-repelling substance; dust does not stick to it and metallic nanomaterials have superior hardness and high resistance to corrosion.

Nano-coatings are produced using some compounds at the nanoscale. They are added to improve the properties of traditional coatings and produce new multifunctional coating materials. These nanostructured materials possess unique mechanical, electronic, physical and chemical properties due to their high surface area⁹. The ability of polymers to stick to a metal surface is weak and the porosity of these nanomaterials when applied allows water and metal ions to penetrate the coating and corrode the ink's surface. To overcome these defects, a protective coating, which is a mixture of polymers and nanomaterials, has been used to develop the nanocomposite and raise its efficiency¹⁰. Thus, the combination of nanomaterials and polymers used as inhibitors and protectors from ink corrosion causes good results. Nanomaterials are characterized by many mechanical and physical properties due to their precise grain size. So, they combine the properties of organic polymers of flexibility and water resistance and the properties of modern inorganic materials, such as hardness and permeability, together with resistance to bacteria and fungi¹¹. The Application of nanomaterials may avoid the disadvantages of oxidation inhibitors in the treatment of archaeological inks, namely that no inhibitors provide complete corrosion prevention and the shelf life of the coating is very short, which makes us prefer to use nanomaterials.

⁵ MELO 2022:11.

⁶ KNIPE 2018: 55.

⁷ MIRANDA 2023: 35.

⁸ EHSAN 2013: 2.

⁹ RIAZA 2014: 743.

¹⁰ KANNAIYAN 2016: 167.

¹¹ EL-MELIGI 2014: 3.

II. MATERIALS AND METHODS

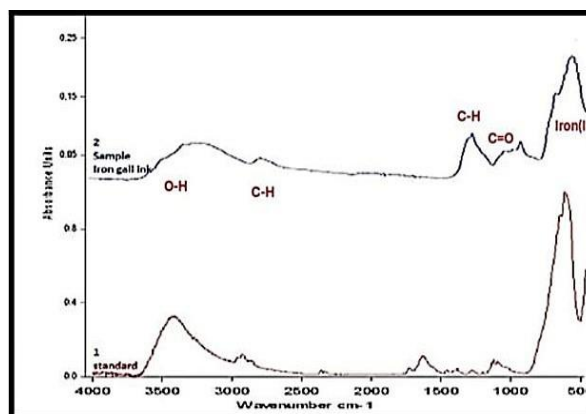
The Applied Historical Sample and the Experimental Sample Islamic manuscript [FIGURE 1]

A copy of al-Jāmi^c al-Ṣaḥīḥ «Ṣaḥīḥ al-Buḥārī» » by Muḥammad bin Ismāʿīl bin Ibrāhīm al-Buḥārī (D. 870 AD), the transcriber of the manuscript is Aḥmad bin ʿAlī Ḥallaf (D.1727 AD). The manuscript is written in *naskh* script in black and red. The text of the manuscript is surrounded by two red borders.

The manuscript is in the Manuscript Center at Minia University¹². It suffers from the corrosion of the iron ink, acidity, yellowing of the paper, dirt, stains, wrinkles and some tears¹³. Fourier Transform Infrared Spectroscopy (FTIR) was used to determine the type and ink of the manuscript¹⁴. First, a small sample of iron ink was taken from an inconspicuous place. It was done in the Infrared Laboratory, Research and Conservation Center, Projects Sector, Antiquities Research and Conservation Center using the Nicolet Nexus 750 device, which monitors spectra between 4000–550 cm⁻¹ with a spectral resolution of 4 cm⁻¹ and recording the spectra using the program OMNIC software (version 6.0)¹⁵ [FIGURE 2]. The experimental sample was made with the same type of ink [FIGURE 3].



[FIGURE 1]: The historical sample © Photo taken by AHMED HOSNI



[FIGURE 2]: Analysis of the applied manuscript using FTIR © Done by AHMED HOSNI

¹² HOSNI 2021: 75.

¹³ ABDELMAKSOUD 2011: 1606 .

¹⁴ DOUMENQ 2015: 3.

¹⁵ VAHUR 2010: 1066.



[FIGURE 3]: Experimental sample with the same type of ink © photo taken by AHMED HOSNI

The iron sulfate group peak was observed at (550 Cm^{-1} bending), indicating that the ink used was originally iron sulfate ink (IGI). Group (C-H) appeared on (2924 Cm^{-1}), group (C-O) appeared on (1074 Cm^{-1}) and group (O-H) appeared on (3298 Cm^{-1}). Gum Arabic was used with iron ink.

The experimental iron ink was prepared by adding water to the gallnut plant and adding gallic acid, tannins and iron sulfate. The mixture was left to react with oxidation, forming iron ink. The Gum Arabic solution was prepared by bringing the gum, adding water to it, dissolving it in a hot water bath and then filtering it from impurities. After that, the gum solution was added to the ink. Finally, it was used for writing. The tracing method was used to write the experimental samples, and then they were passed over with a fine brush in ink.

III.MATERIALS

Nano-Magnetite

Iron oxide nanoparticles (Fe_3O_4 NPs) were mechanically milled to obtain nanoscale particles at the Misr Center for Nanotechnology/Cairo University, Sheikh Zayed by grinding to a nano size. They were chosen to protect the black iron ink, which shows resistance to corrosion and the formation of a protective passive film on the metal surface¹⁶. They also have electrical and magnetic properties, chemical stability and protective performance material against iron corrosion¹⁷.

Paraloid B 72

It is an ethyl methacrylate–methyl acrylate copolymer, which was used to protect metals from corrosion, especially iron. It has good mechanical properties, such as hardness and good adhesion and shows good resistance to water, dilute acids, alkalis and environmental pollutants¹⁸. A 5% (w/v) solution of Paraloid B-72 in ethanol was applied as a rust preventive coating. Because it has flexibility, B72 5% was used in

¹⁶ HERRASTI 2012: 394.

¹⁷ ZHANG 2019: 9.

¹⁸ ULAETO 2023: 316.

ethanol as a rust preventive coating. But, it is not a chemical corrosion inhibitor in itself; rather, it acts as a physical barrier that isolates the surface from moisture and oxygen¹⁹.

Transmission Electron Microscopy «TEM» Examination of Nanomaterials

The nanocomposite «nano-magnetite» was prepared and examined under a transmission electron microscope (TEM) to confirm particle size in the nanoscale range.

JEOL JEM-1230 transmission electron microscope operated at 60 kV «JEOL Ltd., Japan». Water was used in preparation to dilute the samples at least 10 times; then, a drop of the well dispersed diluted sample was placed in a 200-mesh copper grid, carbon-coated and dried at room temperature²⁰.

Deacidification of Paper

Iron-gall inks promote the oxidation and decomposition of cellulose and thus increase the acidity of the paper as the hydroxyl group (OH) and carbonyl groups (C=O) are converted into acid (–COOH), breaking the cellulose chains, which reduces the strength of the paper and increases its fragility. Therefore, deacidification treatment is required for the paper. Calcium hydroxide Ca(OH)₂ is used at a concentration of 0.5% and a viscosity of (0.8 gm/L) dissolved in ethyl alcohol²¹.

Aging

The samples treated with nano-magnetite were subjected to thermal aging at 80°C and 65% relative humidity for 144 hours, in accordance with ISO 5630-3. For optical aging, the samples were exposed to a UV lamp for 150 hours «sterilizer ultraviolet – model SBS – G 8W – Vis 254» without affecting the manuscript²².

Methods

The following methods were used to assess the condition of the experimental samples before and after the application of the nano-magnetite material.

Visual Assessment

Photochemical changes were detected using a 60× smartphone clip-on microscope (OPPO 16) universal clip type 60× LED microscope.

Color Change

The Color Math Android application is a free utility for comparing and converting colors. It provides delta-E calculations, conversion between color spaces and on-screen display of colors using real ICC profiles.

The Color Math Application device was used to detect the ΔE values of experimental samples before and after consolidation and treatment, where:

$$\Delta E \sqrt{(\Delta l)^2 + (\Delta a)^2 + (\Delta b)^2}$$

ΔE represents the change in color, l,a,b the color space subject to change.

¹⁹ NTELIA 2019: 1.

²⁰ HUANG 2010: 2130.

²¹ KRORRA 2020: 6 .

²² ELNAGAR 2014: 4.

The calibration was calculated based on Delta-E calculator (CIE76, CIE94 and CIEDE2000)²³.

Measurement of Acidity

The pH of inked areas was determined using the cold extraction method, which was modified to minimize the sample consumption. Areas with ink were cut out with a scalpel and immersed 1.0 ± 0.01 gm in 100 ml water at room temperature $25 \pm 5^\circ\text{C}$ using an Adwa AD1040 pH meter according to ISO 6588-1. Four measurements were taken and the mean value was calculated²⁴.

Examination Using an Atomic Force Microscope «AFM»

AFM is a high-resolution surface characterization technique. It enables detailed analysis of the ink surface with two- and three-dimensional images of the surface by analyzing the topography on the surface and measuring surface roughness parameters «Ra, RMS», according to the topographical data²⁵. It was carried out using an AFM «model 5600LS, manufactured by Agilent Technologies in the United States of America» at the Nano Center/Cairo University, Sheikh Zayed, in order to examine iron ink samples after applying nanocomposites on them through 2D and 3D images, analyzing surface morphology. The morphology of the applied nano-layer was examined and they were evaluated to determine whether they contained pits, cracks and pores and the treatment quality of the different nanocomposites with scan areas of $100 \times 100 \mu\text{m}$ and $5 \times 5 \mu\text{m}$. A sample of the experimental paper was examined with AFM, while the sample of the applied paper was very small, from a previously cut place, to avoid damage to the manuscript.

Contact Angle Measurement

The contact angle of the samples with distilled water was measured using the contact angle analyzer model T200, manufactured by Biolin Scientific at the Nano Center/Cairo University, Sheikh Zayed. The amount of distilled water was $4.5 \mu\text{L}$ «microliters» «The micrometer is a unit of length, not volume». The contact angle was recorded after 9 s, where the interaction between iron ink and water or moisture is the primary cause of damage and corrosion of metal components. This necessitated the application of nanocomposite coating as a protective barrier to render surfaces repellent to water. Nanocomposite particles cover the pores and cracks in the surface resulting from corrosion to which this metal alloy was exposed by increasing the water contact angle between the liquid droplet and the ink surface.

Electrochemical Impedance Spectroscopy «EIS»

Electrochemical spectroscopy measurement is used to determine the electrochemical properties of ink during its exposure to water or humidity to evaluate the properties of thin films of oxides formed on the surface of metals, monitor the surface decomposition of nano-coating layers due to damage resulting from contact

²³ «Color Math», <https://apkpure.com/color-math/com.schnitzelware.colormath>, accessed on (22/8/2025).

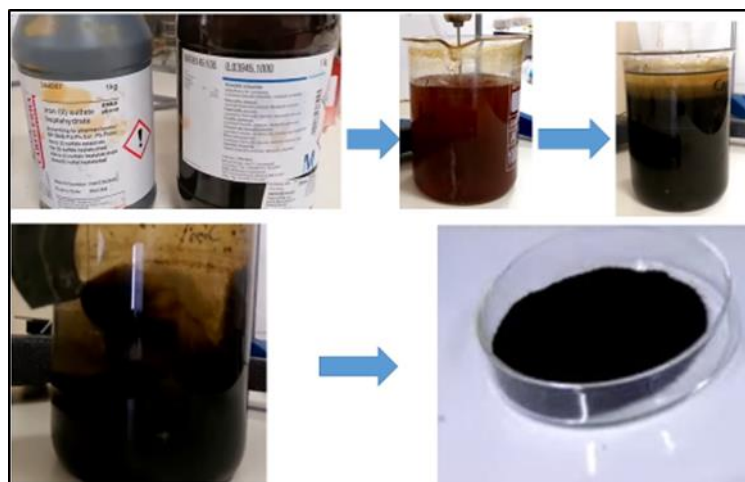
²⁴ MALES[~]IC 2014:10.

²⁵ANSARI 2022: 1.

with water and reveal surface changes to the corrosion process on the surface of iron-based inks; thus, it gives results on the effectiveness of nano-coatings to resist corrosion²⁶. It was carried out with an AUTOLAB potentiostat/galvanostat at the Nano Center/Cairo University, Sheikh Zayed. This included potentiodynamic polarization and corrosion resistance measurement of the iron ink samples covered with nanocomposites using dynamic polarization curves obtained from EIS. The sample was placed in sodium chloride solution, 3.5% by weight, using an open circuit OCP «open circuit potential» polarization time of 30 minutes, which was equipped with a three-electrode measurement system with a reference electrode (Ag/AgCL) and platinum mesh «counter electrode» that represented the counter electrode. Thus, we obtained Tafel curves to determine the corrosion resistance of the ink sample without treatment and with nano-magnetite.

IV.RESULTS AND DISCUSSION

The nanoparticles were prepared and applied to the iron ink samples in the Misr Center for Nanotechnology/Cairo University, Sheikh Zayed. Nanomaterials were prepared from 0.5 g or 0.5 wt% of nano-magnetite by the co-precipitation method of iron salt solutions «e.g., iron chloride and iron sulfide» in a basic medium «sodium hydroxide or ammonium hydroxide» at temperatures of 60–90 °C. This method allows for particle sizes of 10–100 nm. The co-precipitation method for preparing iron oxide nanoparticles: Materials required: iron salt «iron chloride and iron sulfide», iron salt «iron(II) salt» at a molar ratio, a base «such as ammonium hydroxide or NaOH», distilled water and a magnetic stirrer; solution preparation: Dissolve the iron salts in distilled water «0.09 M ferrous chloride»; precipitation: Slowly add the base to the iron solution while stirring continuously and rapidly at 70–75 °C, causing the solution to turn dark brown/black; washing and drying: Wash the precipitate several times with distilled water and ethanol to remove impurities, then dry at 40–60 °C. The particles are then heated at 300–600 °C for 2 hours²⁷ and mixed with Paraloid B-72 dissolved in 3% acetone solution [FIGURE 4].

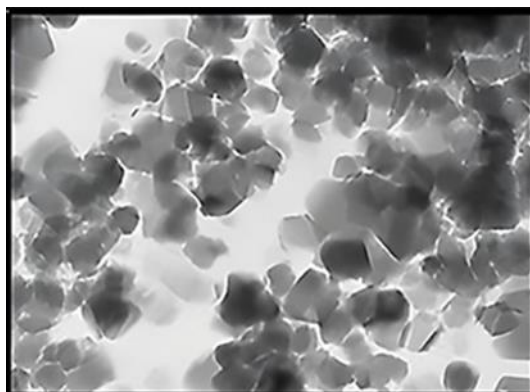


[FIGURE 4]: The co-precipitation method of nano-magnetite © Photo taken by ELQUDS MOKHTAR

²⁶ HERNÁNDEZ 2020: 6.

²⁷ CAMPOS 2015: 267-276.

This was done along with TEM examination when the materials reached a nano shape. The magnetite nanoparticles appeared clearly, until nanoparticles of the desired size, 28 nanometers, were obtained [FIGURE 5].



[FIGURE 5]: Verification of nanoscale particle size using TEM; The magnetite nanoparticles appeared in clear, sharp shapes and measured 28 nanometers © Done by the author ELQUDS MOKHTAR .

Nanomagnetite was applied to the experimental sample with a brush under magnification to coat the letters suffering from corrosion and to preserve the non-corroded letters [FIGURE 6].

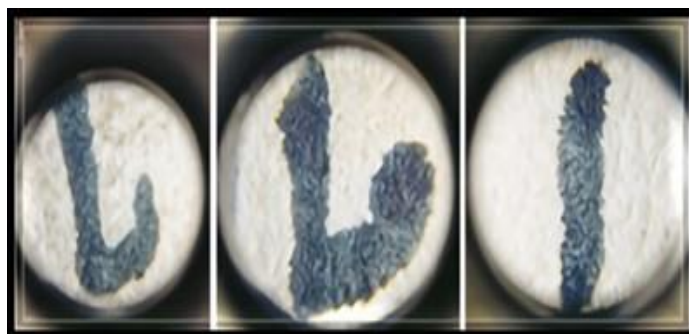


[FIGURE 6]: Applying the nanomaterial to the experimental sample © Photo taken by AHMED HOSNI

The visual evaluation shows the iron ink before and after the nano application and the detection of photochemical changes using the 60x 60x smartphone microscope, as well as the two [FIGURES 7-8].



[FIGURE 7]: Iron ink corrosion observed using a smartphone microscope (OPPO 16), showing brown spots, paper staining and ink fading © Photo taken by AHMED HOSNI



[FIGURE 8]: Examination of the treated sample using a smartphone microscope © Photo taken by AHMED HOSNI

Examination using a light microscope showed good coverage of the eroded ink areas, exhibiting good conformity with the archaeological ink and contributing to enhancing the contrast of the faded texts. This shows the ability of nano-magnetite to remove corrosion and achieve a good result in corrosion resistance of iron ink and paper. Super-magnetic iron oxide nanoparticles (SPIO) can adhere to it, enabling precise imaging techniques. The nanoparticles are characterized by their ability to penetrate fibers more easily to enhance stability without causing mechanical damage²⁸.

Color Change

The conservator is interested in studying the effect of restoration materials on the color of samples, especially in the case of manuscripts and documents. Therefore, the materials must be transparent and do not affect the aesthetic properties. Color change tests must be carried out. [TABLE 1] shows that nano-magnetite Fe_3O_4 NPs caused a slight optical change ΔE of about 2.03, which is barely perceptible, while A high ΔE value of 24.70 was observed in the aged paper, resulting in yellowing of the paper. Iron gall ink causes a significant degradation of the paper, causing browning and loss of mechanical properties. This led to the degradation of cellulose chains²⁹. The ΔE value between the untreated and treated samples was 24.73³⁰. By comparing the three samples «before, after treatment, compared with the control sample», we noted that the color change is slight in favor of the treatment paper with the original control sample, indicating the success of the magnetite nanoparticles Fe_3O_4 NPs in preserving the original color of the sample, which can maintain color stability. The nano coat had a good role in increasing the values of ΔE , which referred to the efficiency of the nano coat in covering the ink³¹.

Nanoparticles are invisible to the naked eye when embedded in a polymer matrix. They therefore do not affect vision and can transmit visible light, making them ideal coating materials for transparent layers. When nanoparticles are dispersed in the polymer to form transparent nanocomposites, they improve coating strength, thermal and scratch resistance and light absorption. With high levels of transparency, iron nanoparticles protect and reinforce manuscripts against damage without altering their

²⁸ NGUYEN 2021: 37.

²⁹ THOMPSON 2012: 249.

³⁰ OSMAN 2011: 82.

³¹ IBRAHIM 2019: 39.

appearance. They improve physical and chemical properties, such as strengthening aging fibers, increasing their resistance to environmental conditions and reducing acid damage³².

Sample	$L\Delta$	$a\Delta$	$b\Delta$	
Before Treatment	24.95	8.01	54.03	
Control	0.26	9.27	54.03	
After Treatment	0.26	5.49	52.77	

[TABLE 1]: shows the color change of the standard experimental sample and the experimental sample before and after the application of nano-magnetite © Done by the authors

Acidity

The acidity was measured on four samples. The aging process of the samples using ultraviolet rays before treatment resulted in the liberation of acidic materials used in the paper industry «alum, rosin and the interference of some acid gas impurities in the atmosphere, especially SO₂, which is the iron ink used in writing». The acidity of ink depends on the content of gallic acid, ferrous sulfate and acidic additives. This led to a rise in pH, in addition to oxidation of the cellulose and a cracking of the hydrogen bonds, resulting in a loss of the paper's durability and the appearance of yellowing³³. These complex reactions involve oxygen, such as peroxides and form hydroxyl. That iron gall ink-impregnated paper has a measurable negative effect on paper degradation in its vicinity. It was shown that iron in iron gall ink enhances the oxidative degradation of cellulose, thereby affecting the paper. The degradation of cellulose oxidation may be pH-dependent. As a result, environmental factors, the joint presence of oxygen and humidity and the presence of gallic acid, led to the iron oxidation, which could be related to the formation of rust but, also to the formation of precipitates of iron (III) with tannin or with cellulose molecules³⁴. The coating succeeded in stabilizing the pH, which decreased after the aging of the treated paper to a near-ideal ratio of 3.1. This confirms the ability of nano- magnetite to inhibit the acidity resulting from iron ink³⁵. The oxidation of the nano magnetite layer occurs in air, enhancing its stability and forming a hydrophobic layer that reduces the conversion of the iron ink into acids, thereby decreasing acidity. Iron oxide nanoparticles are used in the restoration of ancient manuscripts to increase their alkalinity «neutralize acidity». Due to their small size and penetrating ability, they act as highly effective cleaning and deacidifying agents, thereby protecting the manuscripts and extending their lifespan. Alkaline nanoparticles neutralize acids that cause paper to become brittle and deteriorate, restoring acidity

³² LESIAK 2019: 16.

³³ STIJNMAN 2006: 25.

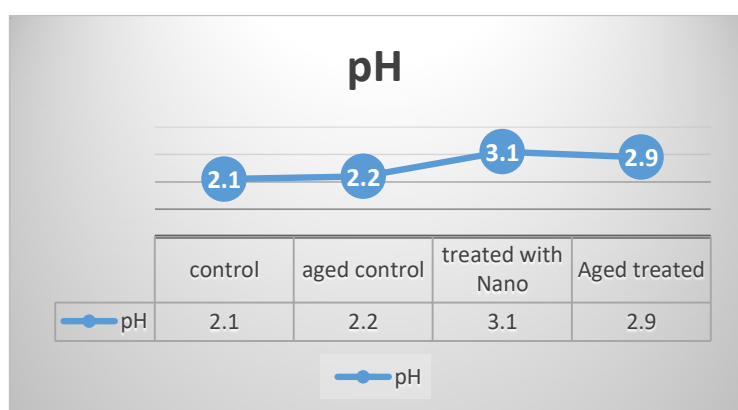
³⁴ HU 2018: 900.

³⁵ KRORRA 2020:18.

balance and preventing further deterioration. This also enhances the strength of weak and fragile manuscripts³⁶ [FIGURES 9-10]



[FIGURE 9]: Acidity measurement © Done by the authors



[FIGURE 10]: A chart showing the pH values of the sample before and after treatment 3-5 Analysis by polarizing device after applying nano-magnetite © Done by the authors

Stages of Acidification Treatment

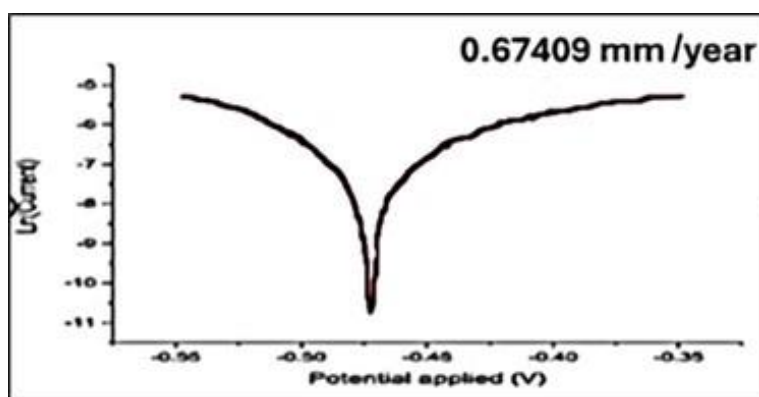
Acidity was reduced/ neutralized before applying the nanomaterial, as follows:

- A. The manuscript area was inaccurate, measuring 80 x 70, with a height of 10 cm and covered from the inside with polyethylene.
- B. A wooden frame was made with an area of 60 x 40 cm and covered or stretched with gauze fabric at a rate of 1.5 g per liter, which was dissolved well.
- C. The first basin contained a solution of sodium hydroxide at a concentration of 1.5 g/L, dissolved thoroughly.
- D. The paper sheet was placed on the first basin and immersed for 20 minutes with gentle agitation of the solution to avoid direct mechanical stress on the paper.
- E. The paper is transferred to the second basin for the same period and the same concentration of solution.
- F. It was transferred to the third basin containing distilled water for 5 minutes.
- G. The treated paper was placed on a smooth glass surface to dry completely.

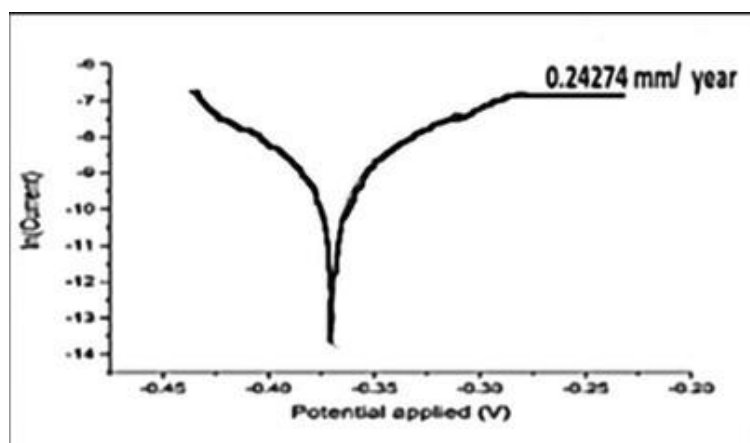
After ensuring that the acidity was removed, the next step was carried out using the nanomaterial to protect the ink from further corrosion³⁷ [FIGURE 11-12].

³⁶ NEEVLE 1995: 60.

³⁷ FORD 2014: 604.



[FIGURE 11]: Polarization analysis of the corrosion rate of a standard ink sample in a 3.5 wt% sodium chloride solution. The open-circuit potential (OCP) was monitored for 30 minutes; The measured corrosion rate was 0.67409 mm/year © Done by ELQUDS MOKHTAR



[FIGURE 12] Analysis of the rust rate of the ink sample covered with nano-magnetite coating in 3.5 wt% sodium chloride solution and using an open circuit (O, P) for 30 min was where it was 0.24274 mm/year © Done by ELQUDS MOKHTAR

It was found from the analysis by the polarizing device that the rust rate for the standard iron ink sample was 0.67409 mm / year and the rust rate for the iron ink sample on which the nano-coating was applied was 0.24274 mm/ year, as shown in [TABLE 2].

	ba (V/dec)	bc (V/dec)	Ecorr, Calc (V)	Ecorr, Obs (V)	jcorr (A/cm ²)	icorr (A)	Corrosion rate (mm/year)	Polarization resistance (Ω)
Fe ink without Nano- material	0.059447	0.071916	-0.47276	-0.47268	5.81E-05	0.000552	0.67409	25.598
Fe ink with Nano- material	0.11147	0.12294	-0.368	-0.36791	2.09E-05	0.000199	0.24274	127.68

[TABLE 2]: show the analysis by the polarizing device that the rust rate for the standard iron ink sample was 0.67409 mm/year and the rust rate for the iron ink sample on which the nano-coating was applied was 0.24274 mm/year © Done by the authors

The results of the polarization device illustrated that the nano-coating «nano-magnetite with Paraloid» gave greater resistance to iron ink from corrosion and damage. The corrosion of archaeological iron inks occurs because of contact with damaging environmental factors, such as water and oxygen, which cannot be controlled but, it is possible to prevent corrosion. Fe_3O_4 NPs are used as effective corrosion inhibitors and the spread of nano-magnetite on the surface of the ink by applying them to the surface of the corroded inks, as nanoparticle materials have a very high surface area when applied to the surface of the ink³⁸. Well-adhered protective nano-oxides are formed on the ink surface, which reduces corrosion compounds and increases the strength and corrosion resistance of the ink.

Iron oxide nanoparticles «or iron-gal ink stabilizers» are used to stabilize iron-gal ink. They convert acidic corrosion products (such as iron (II)) into stable compounds, reducing ink blemishes and paper or manuscript erosion. They also improve the physical and mechanical properties of the treated materials. In iron-gal ink stabilization, iron oxide nanoparticles act as gentle oxidizing agents, neutralizing corrosion-causing free ions and converting them into stable iron oxide. This halts the self-degradation of paper known as «iron-gal ink erosion». Furthermore, they strengthen weakened and deteriorated fibers caused by the ink, increasing the mechanical strength of historical documents. Due to their small size (1-100 nm), these particles penetrate the pores of paper and fibers, providing long-lasting protection and resistance to deterioration³⁹.

AFM Analysis Results

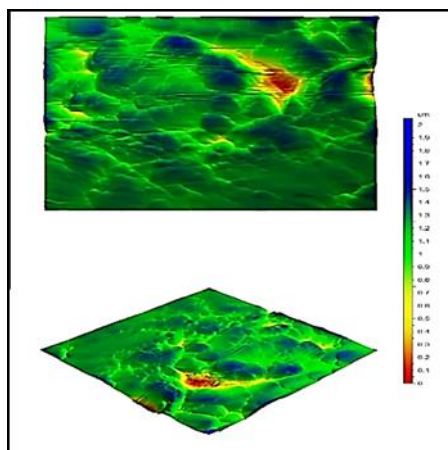
The Rz roughness value for the standard ink sample without the application of nanomaterials was (2 μm), with traces of corrosion products on its surface, which appeared in the form of grooves, valleys and pores, clearly defined and sharp. The roughness rate Rz for the ink sample on which the nano-coating was applied (was 0.85 μm) with the formation of a layer of the magnetite nanocomposite. In the absence of Fe_3O_4 NPs and the presence of only very small streams of the magnetite nanocomposite with Paraloid B72, Fe_3O_4 nanoparticles exhibited sharp-edged morphology with an average particle size of approximately 35 nm, with good adhesion to the ink surface, forming a uniform coating that reduced corrosion products.

Nano magnetite particles Fe_3O_4 NPs enhance corrosion resistance and durability and provide comprehensive corrosion inhibition. Iron nanoparticles «especially iron oxide nanoparticles» are used in the treatment of ancient ink using an advanced technique to strengthen and stabilize written texts. They penetrate the pores of the ink and the supporting surface «paper/papyrus», increasing its durability, resisting wear and improving its physical and mechanical properties without altering the overall appearance of the manuscript. They form a strong bonding network between the ancient ink molecules and the surface, increasing the ink's resistance to disintegration and deterioration. Due to their small size, these particles penetrate deep into the surface of the artifact, allowing for precise treatment without affecting the original color of the

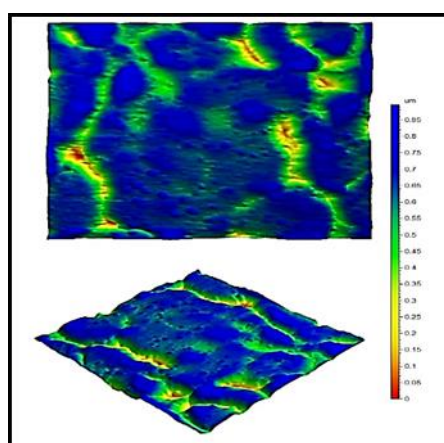
³⁸ LIU 2022: 13.

³⁹ HASSAN 2023: 8.

text or obscuring details⁴⁰. They provide a uniform and continuous coating over the ink, preventing future deterioration of the texts. This is attributed to the size of the ultra-fine particles because they do not affect the transparency of the coating. The nanostructure also improves the mechanical properties, particularly scratch resistance due to the combination with polymers, a small amount of which maintains the shape of the ink without causing any undesirable changes⁴¹ [FIGURES 13-14].



[FIGURE 13]: AFM examination of the surface of a standard iron ink sample showing rough topographical features, including ridges, gaps and sharp edges resulting from corrosion products on the ink surface; The average surface roughness is 2 μm © Done by ELQUDS MOKHTAR.



[FIGURE 14]: AFM examination of the surface of the iron ink sample coated with a nano-magnetite layer. The surface shows fewer grooves and gaps, reduced surface irregularities and a homogeneous distribution of nano-magnetite across the ink surface; the average surface roughness is 0.85 μm © Done by ELQUDS MOKHTAR.

Contact Angle Measurement

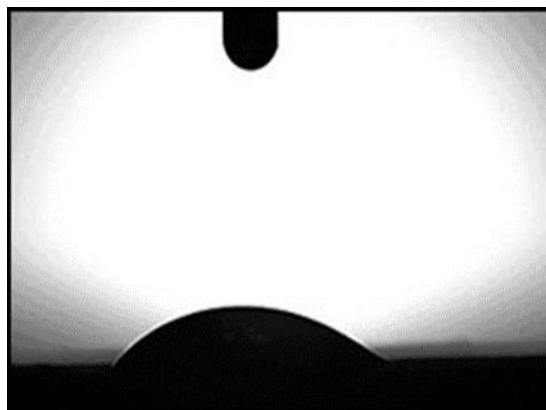
The contact angle of the standard was 43.16°, indicating hydrophilic properties and the contact angle of the ink sample on which the nano-coating was applied was 92.50°. Therefore, the protection layer had good water repellent properties. Magnetite nanoparticles are characterized by electrical and magnetic properties and a good degree of conductivity when the layer is exposed to moisture, contribute to reducing oxidation processes. They enhance stability by increasing surface area, which can help bind excess

⁴⁰ BAGLIONI 2012: 313.

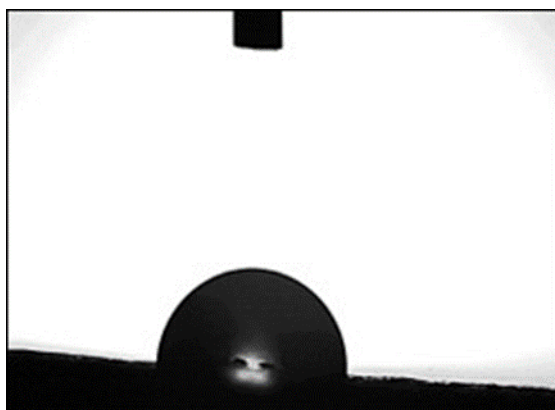
⁴¹ MELO 2022: 11.

moisture and reduce its damaging effects⁴². They also absorb moisture, helping to lower humidity levels that cause ink diffusion «dew or blotting» by promoting a stable environment.

They reduce ink damage caused by high humidity, which typically leads to fungal growth. They contribute to the erosion of iron ink. Furthermore, they improve mechanical properties, protecting the ink from physical degradation associated with humidity fluctuations⁴³. Nano magnetite particles $\text{Fe}_3\text{O}_4\text{NPs}$ with Paraloid B-72, a layer with good stability after coating, form a water-repellent coating layer with high adhesion, thus providing good protection from corrosion, as moisture is a primary factor in the degradation of iron inks. In addition, the chemical composition of the Paraloid B-72 polymer plays a role in its magnetite nanoparticles trapping air between the water droplets and the rough surface resulting from nano-coating. Magnetite nanoparticles trap air between the water droplets and the rough surface, resulting in a water-repellent surface⁴⁴ [FIGURES 15-16].



[FIGURE 15]: Contact angle measurement of a standard iron ink sample showing a hydrophilic surface with a contact angle of 43.16° © Done by ELQUDS MOKHTAR



[FIGURE 16]: Contact angle measurement of the iron ink sample covered with a layer of a water repellent nano-magnetite coating is 92.50° © Done by ELQUDS MOKHTAR

⁴² LIU 2022: 11

⁴³ SINGH 2025: 1-20.

⁴⁴ HELMI 2016: 87.

Paper Deacidification

After applying calcium hydroxide at a concentration of (CaCO_3) 0.5 % dissolved in ethyl alcohol, calcium ions strongly interact within the cellulose polymer network and are highly permeable, precipitate and can neutralize acidic functional groups, such as carboxyl groups, thereby reducing the acidity of the paper. In paper processing, $\text{Ca}(\text{OH})_2$ is converted to CaCO_3 and provides an alkaline reserve.

V.CONCLUSION

The nanoparticles used help to protect ancient inks by strengthening documents and stabilizing acidic inks «such as iron and oak ink» thanks to its magnetic properties and ability to withstand oxidation and catalytic effects, thus preventing the spread of stains and protecting manuscripts from environmental damage. The nano-magnetite Fe_3O_4 NPs compound with Paraloid B-72 is a successful nanocomposite that can be applied to protect the surface of the iron ink from corrosion. Magnetite nanoparticles Fe_3O_4 NPs form a thin layer resistant to corrosion and create an electrochemical film across the interface due to their unique mechanical, electronic, physical and chemical properties, because of their high surface area. This, in turn, increases the active centers, which help prepare a coating with greater resistance to corrosion, which covers the surface well and forms a water-repellent layer. A multifunctional and truly sustainable coating layer was developed for the applied manuscript, where the paint was prepared from magnetite nanocrystals Fe_3O_4 NPs. This significantly enhanced the historical paper before and after the aging process. Moreover, the nano-coating layer was hardened, providing outstanding transparency and good quality properties for optical paper. The nano material gave an improved, sustainable layer to protect against UV damage, achieving 49% enhancement in UV protection compared to the untreated script. We recommend conducting further research and applying nanomaterials in the protection of various inks.

DISCLOSURE STATEMENT

No Potential conflict of interest was reported by the authors

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