NON-DESTRUCTIVE TESTING OF NANO-SILICA FOR ENHANCING THE DURABILITY OF LIMESTONE STRUCTURES IN THE VALLEY OF THE KINGS, LUXOR, EGYPT

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1. Introduction

The Valley of the Kings is a UNESCO world heritage site with more than thirty tombs that have been opened. Since the first tombs were constructed, at least 24 historical flash flood events have been identified, each of which has contributed to the destruction and deterioration of the tombs.

After the floods of 1994, most of these tombs were inundated and damaged. Theban Tomb 109 (or TT 109) is an example of one of these significant tombs. This study presents a novel technique – computer X-ray tomography (CT scan) – as a non-destructive method to capture the morphology of the limestone's internal structure at Tomb 109 (TT 109), as well as the stone's grain texture and the surface features, through 3D images and videos. Additionally, this research examines the ability of a nanomixture consisting of tetraethoxysilane (TEOS) and nanosilica to consolidate the limestone, which is also a novel approach that this study introduces. It is worth noting that the limestone of Tomb 109 has suffered harsh weather conditions, such as groundwater and has been in an unfavourable burial environment, causing geostatic stress which in turn has led to stone abrasion and weakness in its mechanical properties.

The study, moreover, presents a comprehensive morphological and spectroscopic study to confirm the efficiency of the nanomixture in the consolidation of the limestone structures. A cross-examination method using CT scanning, SEM, and XRF analysis before and after consolidation was employed. The final result shows that the nanomixture significantly enhanced the physical and mechanical properties of the limestone.

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1.1. Archaeological context

The Theban Tomb (TT 109) is located on Luxor's West Bank, in the Necropolis of Sheikh Abd-el-Qurna, and dates back to the XVIII Dynasty, specifically to the reign of Thutmosis III. In the Valley of the Kings (tomb number KV TT 109), Min, was the Mayor of Tjeny (Thinis), and the Tutor of Amenhotep II.

The tomb has some beautiful funerary scenes of everyday life and scenes where Min is teaching Amenhotep II as a child, but unfortunately, they are not well preserved. The hall and the chambers of the New Kingdom rock-cut tombs were carved into a limestone hill. The entrance facade, on the left side, has been reconstructed from fragments of limestone and cement (red). The entrance to the tomb has also been rebuilt with the same materials (blue).

This reconstruction work, done between 1889 and 1920 has helped protect the tomb from the weather and looting, and also blocks a window that could lead to further damage caused by water entering the tomb in the case of major storms and floods (Figure 1).

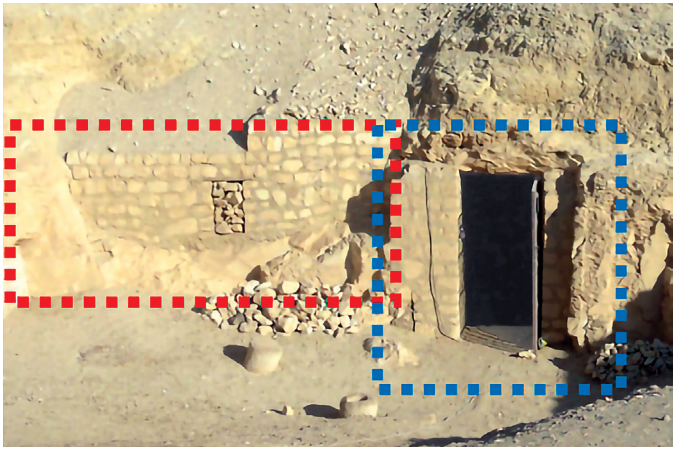

Figure 1. The entrance to the tomb rebuilt with the same materials (blue); enclosure with limestone and cement (red).

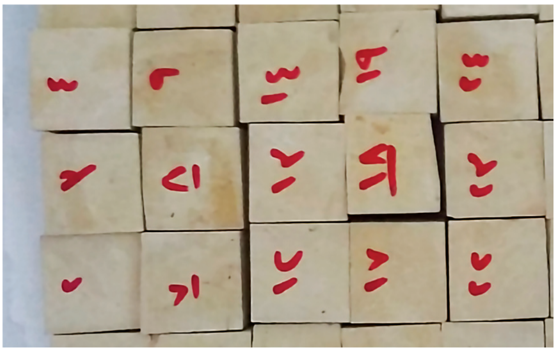

Figure 2. The building materials of limestone and samples cut into cubes (3x3x3 cm) from boulders detached from the tomb of TT 109; red marks refer to the number of each sample.

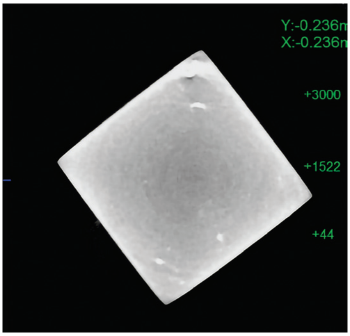

Figure 3. The CT image shows the morphological features of the limestone at the tomb (TT 109) on the West Bank, Luxor.

The limestone that was used to build the tomb which dates back to the XVIII Dynasty and specifically to the reign of Thutmosis III [1], shows that it has been exposed to high temperatures and groundwater. Both factors are common deterioration agents in this area; Figure 2 shows the physical impact of the deterioration on the limestone [2-6].

The study provides an evaluation of the limestone before and after applying the nanomixture consolidant, while the SEM-EDX analysis [5-6] reveals the change in the surface morphology and stone properties; the CT scan, as a non-destructive method, provides fine details of the surface morphology and the internal structure [7-9]. This cross-examination, using CT scanning and SEM confirm the result of this study (Figures 3 and 4).

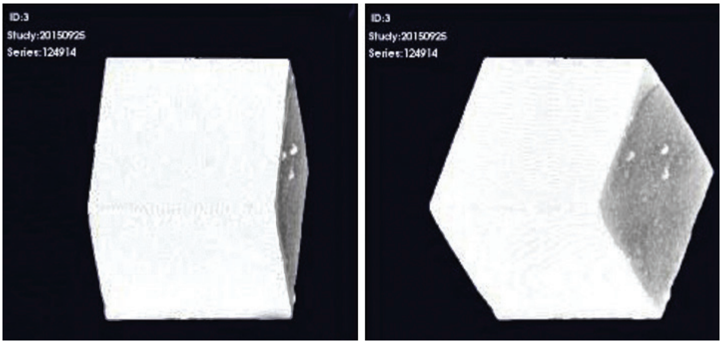

Figure 4. The 3D CT image shows the morphological features of the limestone after treatment.

2. Materials and Methods

2.1. Sample Collection

The limestone samples were collected from the archaeological site and were cut into cubes measuring 3 × 3 × 3 cm, as required for the analysis instruments. CT scanning, SEM and XRF analyses were used to examine the grain texture, material structure, and the morphological features of the sandstone before and after treatment. The samples were treated using the nanomaterial mixture, which includes tetraethoxysilane (TEOS), nanosilica, and TEOS polymer.

2.2. Preparation of the nanomaterials for consolidation

The nanosilica (average size 40-50 nm) was dispersed in an ethanol concentration of 1% mixed with TEOS in a 1:1 ratio. The nanomixture was then treated using the sonication technique by dispersing 10 gm wt% of nanosilica powder in 1000 mL of ethanol for 20 min using an ultrasonic mixture and magnetic stirrer.

2.3. Consolidation samples

The samples were dried at 108 °C for 24 hours [2,5], after which the nanomixture was applied on the limestone surface via multiple brushing once per day for five consecutive days. The stone surface was also covered with sheets of polyethylene to prevent evaporation of the consolidant.

2.4. CT scanning imaging

Generally, the nature of CT images allows the reconstruction of high-resolution 2D and 3D images. In this study, CT scanning, as a non-destructive technique, gave an accurate analysis of the surface morphology and assessed the substrate before and after consolidation. The analysis also helped to evaluate the penetration of the nanomixture inside the limestone. To our knowledge, this is the first study in heritage conservation that uses CT scanning for investigation of limestone treated with nanomaterials. The scans were made using a tube voltage of 90 Kv, a tube current of 160 μA, a field of view (FOV) at 20 mm, and a scan time 4.5 min. The CT scan investigation of the sandstone samples was prepared at the Institute of Karolinska, Sweden.

2.5. Morphological study using the Scanning Electron Microscope (SEM)

The surface morphology of the limestone samples was observed using SEM (JEOL/JSM-5500LV). The Acel. Volt. was 30 kV. The samples were examined at the Central Laboratory, South Valley University, Qena, Egypt.

2.6. XRF analysis

X-ray fluorescence (XRF) was used to identify the limestone minerals. Samples were prepared at the Central Laboratory, South Valley University, Qena, Egypt.

2.7. Compression Test

A compression test was used to measure the compressive strength of the treated limestone and helped determine the maximum compression load that compels the specimen to fail. During the test, the sample was placed precisely in the center of the loading platen. The compression test was carried out using a Universal Testing Machine at the Central Laboratory, South Valley University, Qena, Egypt.

3. Results and discussion

3.1. CT scan imaging

CT scan imaging shows that the consolidant covered the stone surfaces and was effectively dispersed in the pores. The homogeneous distribution on the surfaces and between the stone grains led to increasing the stone's mechanical properties. Moreover, the CT scan images revealed the homogeneity between the nanocomposite nanosilica/TEOS polymer and the composition of the limestone (Figure 5).

The CT scanning rotated 360 degrees around a stationary sample, allowing a more in-depth investigation of the samples from different angles. This process is especially helpful in giving a better evaluation of the consolidants.

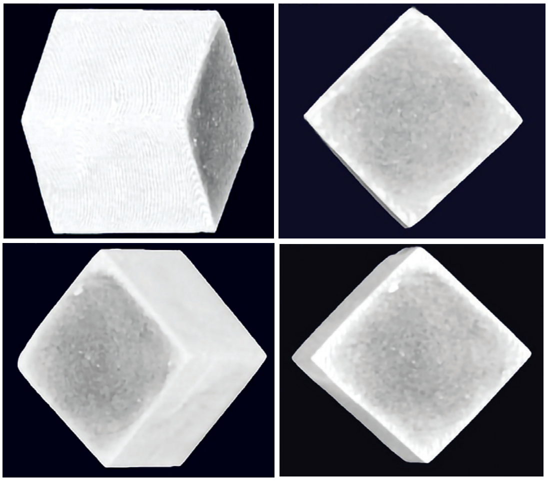

Figure 5. 3D CT images showing the limestone morphological features after treatment from different angles and CT sections showing nanocomposite cover dispersed homogeneously within the pores, which leads to improvement in the mechanical properties of the limestone.

3.2. Observation by SEM

SEM results confirmed that the morphological surface and grain texture changed after the consolidation (Figure 6).

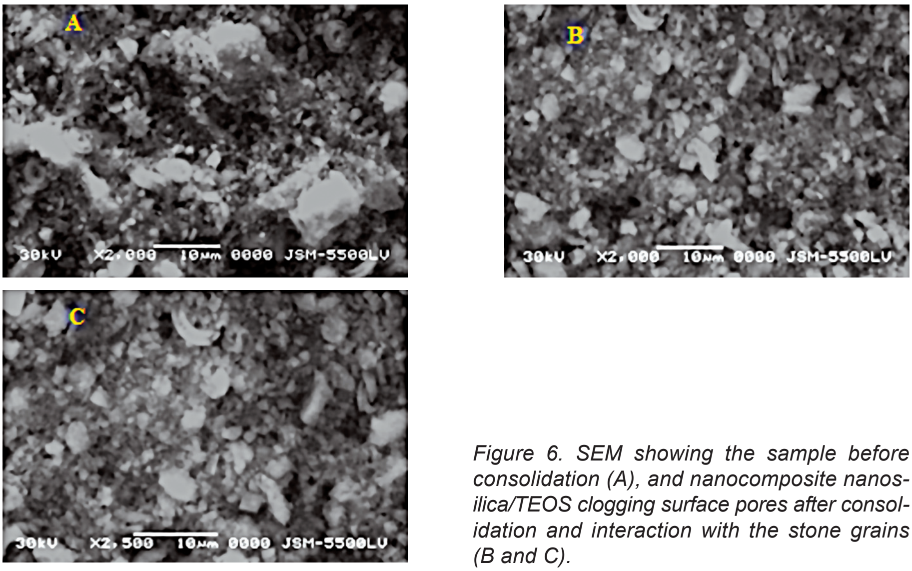

Figure 6. SEM showing the sample before consolidation (A), and nanocomposite nanosilica/TEOS clogging surface pores after consolidation and interaction with the stone grains (B and C).

3.3. XRF analysis

The X-ray fluorescence analysis aimed to identify the elemental composition of the limestone. Results showed the presence (as a percentage) of aluminum (Al), chloride (Cl), quartz (Si), iron oxide (Fe), calcium (Ca), and sulfur (S), and are presented in Figure 7; a summary is also given in Table 1.

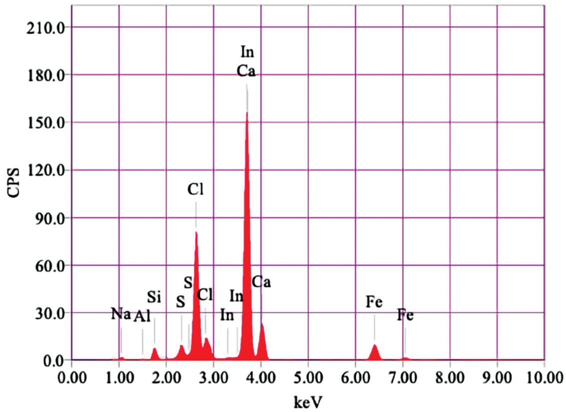

Figure 7. XRF spectrum of a sample taken from tomb 109 of the West Bank, Luxor

Table 1. XRF composition in wt. of a sample taken from tomb 109 of the West Bank, Luxor.

Element	Al	Si	S	Cl	Ca	Fe	Na	In	Total
Weight%	0.73	3.25	1.04	15.79	52.32	1.70	24.81	0.33	100

3.4. Mechanical properties and mechanical testing – uniaxial compressive strength (UCS)

Of all the tests carried out, that of establishing the compressive strength of the stones is very important, as the resulting value is used by structural design engineers to assess stability and structural conditions. Future research could consider combining the scratch test coupled with the on-site recoil hammer test which would give greater reliability in evaluating the stones on site without disturbing/destroying existing structures.

The compressive strength of stone is the maximum load per unit area that it can bear without crushing. A higher compressive strength indicates that the stone can withstand a higher crushing load. The required values range from 7569 psi (52 MPa) for marble (ASTM C 503) to 19,000 psi (131 MPa) for granite (ASTM C 615). To determine the compressive strength, according to the ASTM 170 at least 5 specimens must be tested for cubes of at least 2″ to 3″ on each side. Each face must be perfectly flat, and they must be parallel or perpendicular with each other; in addition, the faces must be smooth with no tool marks and there should be no nicks at the corners [10-13].

Five samples were equipped with electric strain gauges measuring 100 mm in length. Vertical pressure was gradually increased until failure. Table 2 shows the compressive strength results of the five backing limestone samples collected from the tomb. The compressive strength (σc) of the weathered / untreated specimens was between 21 to 22 MPa, indicating medium to poor geochemical characteristics. The average elastic modulus obtained for the five tested cubes was 21 GPa. By comparing the mechanical properties before and after treatment, as shown in Table 2, we can conclude that the nanocomposite nanosilica/TEOS polymer, which was effectively dispersed within the pores, enhanced the mechanical properties of the limestone and added a protective layer on the surface, where the uniaxial compressive strength (σc) of the treated/consolidated specimens was 27.4 MPa.

Table 2. Compressive strength value before/after consolidation of the limestone

Limestone specimens	Ultimate load (kN)	Cross-sectional area (mm^2)	Compressive strength (Mpa)	Enhancement value (%)
Untreated specimens	19.4	900	21.1	-
Treated specimens (with Nanosilica/TEOS polymer)	24.7	900	27.4	30

4. Conclusions

This study presented a novel approach to consolidate limestone using a nanocomposite mixture. It also introduces CT scanning as a non-destructive method to analyze the limestone structure and the effectiveness of the nanocomposite consolidant. Therefore, this research shows that CT scanning can be a helpful instrument for restorers to investigate internal structures and evaluate treatments. The nanocomposite based on a mixture of TEOS polymer with nanosilica (dispersed in ethanol) was suitable for consolidation to increase the mechanical properties of the limestone used in tomb 109 of the West Bank, Luxor, Egypt.

The SEM post-treatment images show that the nanocomposite (nanosilica/TEOS) has successfully interacted with the stone grains and clogged the surface pores. XRF was able to identify the major and minor compositions of the limestone. More specifically, Calcite (Ca) was identified as the main element and Chloride (Cl) as a minor element. This study recommends applying nanocomposites in the treatment of the limestone at tomb 109 of the West Bank, Luxor, Egypt.

Our future research will build upon these findings, using MATLAB, to strengthen and retrofit intervention plans.

Acknowledgments

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Summary

The Valley of the Kings (KV) is a UNESCO world heritage site with more than thirty tombs that have been opened. Since the first tombs were constructed, at least 24 historical flash flood events have been identified, each of which has contributed to the destruction and deterioration of the tombs. After the floods of 1994, most of these tombs were inundated and damaged. Theban Tomb 109, or TT 109, is an example of one of these significant tombs. This study presents a novel technique which uses computer X-ray tomography (CT scan) as a non-destructive method to capture the morphology of the limestone's internal structure at Tomb 109 (TT 109), as well as the stone's grain texture and the surface features through 3D images and videos. Additionally, this research examines the ability of a nanomixture, consisting of tetraethoxysilane (TEOS) and nanosilica, to consolidate the limestone, which is also a novel approach that this study introduces. It is worth noting that the limestone of Tomb 109 has suffered harsh weather conditions such as groundwater and has been in an unfavourable burial environment, causing geostatic stress which in turn has led to stone abrasion and weakness in its mechanical properties. This study also presents a comprehensive morphological and spectroscopic study to confirm the efficiency of the nanomixture in the consolidation of the limestone structures. A cross-examination method using CT scanning, SEM, and XRF analysis before and after consolidation was employed. The final result shows that the nanomixture significantly enhanced the physical and mechanical properties of the limestone.

Riassunto

La Valle dei Re (KV) è un sito patrimonio mondiale dell'UNESCO con più di trenta tombe scoperte. Da quando sono state costruite le prime tombe, sono stati identificati

almeno 24 eventi storici di inondazioni improvvise, ciascuno dei quali ha contribuito alla distruzione e al deterioramento delle tombe. Con l'alluvione del 1994, la maggior parte di queste tombe è stata inondata e danneggiata. La tomba tebana 109, o TT 109, ne è un significativo esempio. Questo studio presenta una nuova tecnica che utilizza la tomografia computerizzata a raggi X (CT scan) come metodo non distruttivo per comprendere la morfologia della struttura interna del calcare nella Tomba 109 (TT 109), la grana della pietra e la caratteristica superficie attraverso immagini e video 3D. Inoltre, questa ricerca studia la capacità di una nanomiscela, costituita da tetraetossisilano (TEOS) e nanosilice, di consolidare il calcare: questo è un nuovo approccio introdotto dallo studio. Vale la pena notare che il calcare della tomba 109 ha subito condizioni meteorologiche avverse come le acque sotterranee e si è trovato in un ambiente di sepoltura sfavorevole, causando stress geostatico che, a sua volta, ha portato all'abrasione della pietra e all'indebolimento delle proprietà meccaniche. Questa ricerca presenta anche uno studio morfologico e spettroscopico completo per confermare l'efficienza della nanomiscela nel consolidamento delle strutture calcaree. È stato impiegato un metodo di esame incrociato che utilizza la scansione TC, SEM e l'analisi XRF prima e dopo il consolidamento. Il risultato finale mostra che la nanomiscela ha notevolmente migliorato le proprietà fisiche e meccaniche del calcare.