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Research Article

Experimental Comparative Study on the Performance of Nanolime and Phosphate-Based Treatment as Consolidants for Monumental Limestone

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Abstract This paper deals with a comparative study between limestone consolidants based on $Ca(OH)_2$ nanoparticles (nanolime) and phosphate-based treatments severally. The idea of using phosphate-based treatments is forming calcium phosphates (ideally hydroxyapatite) as the reaction product between the substrate and an aqueous solution of a phosphate salt that the stone is treated with. The experimental study was conducted on limestone samples from Tihna El-Gabal archaeological area, Minia, Egypt. Some tests were performed for studying the behavior of the consolidants used. The main aim of these tests to estimate the consolidants efficiency and investigate the changes of physio-mechanical properties of the studied samples before and after consolidation. Some laboratories measurements such as weight change, chromatic variations, physio-mechanical and SEM were performed for realizing aim of the work. It was observed that there are noticeable differences among studied limestone physio-mechanical properties of samples after treatment according to the types of consolidant. The obtained results showed a significant improvement in physio-mechanical properties of the samples treated by both types of consolidants but DAP was the most efficient as innovative consolidant with studied limestone.

Keywords Diammonium hydrogen phosphate - CaLoSiL- North Chapel - Akoris (Tihna El-Gabal) – Compressive strength

1. Introduction

Conservation studies on historic building materials and particularly stone conservation returns back to the nineteenth century. However, successful conservation treatments of stone are rather recent. Advances in science and technology have contributed to advances in conservation science and the process of conducting stone conservation research [1]. As of their extended use in historical buildings and architecture, the consolidation of weathered carbonate stones, such as limestone and marbles, is a key goal in cultural heritage conservation and many experimental studies have been aimed at improving the existing consolidating treatments and developing materials (micro and nano) compatible with natural and artificial stone [2].

In the last decades, polymeric organic materials as consolidants and surface coatings have been used for the conservation of stone-made supports of artistic and historical interest such outdoor architectural monuments, sculptures, wall paintings, and so forth. In particular, acrylic copolymers have met with an increasingly high interest and relevance thanks to their adhesion and film forming ability. Among this class of products, one of the most largely applied copolymers, which is poly ethylmethacrylate/ methylacrylate (70:30) [Poly (EMA/MA), commercial named Paraloid B-72] [3] which has a disadvantage reflected from its macromolecules size in the acrylic copolymers does not allow a uniform and deep penetration into the porous matrix [4]. In order to avoid all these limitations, a new technology for the superficial consolidation of carbonate matrixes (i.e., aerial mortar, limestone, and marble), based on the application of alcohol dispersions of $Ca(OH)_2$ nanoparticles (nanolime) [4]. Some studies such as [1,5 and 6] deserve serious attention because they have a similar chemical nature to calcium carbonate building stones. As performing restoration work, specifically consolidation, consolidants should fulfill many requirements not only in terms of consolidating efficiency (ability to recover the cohesion of the decayed material), but also in terms of compatibility with the substrate (i.e. should not cause any damage to the substrate or adjacent material) and, at the same time, be durable. Based on this point of view, inorganic consolidants seem quite attractive, as they are generally stable and durable.

In the recent paper, two relatively innovative inorganic consolidants calcium hydroxide $Ca(OH)_2$ nanoparticles (nanolime) and an aqueous solution of diammonium hydrogen phosphate (DAP, $(NH_4)_2HPO_4$ were used and applied to limestone samples from Tihna El-Gabal archaeological area, Minia, Egypt to compare between them as two innovative consolidants for restoration of monumental limestone Tihna El-Gabal archaeological area, Minia, Egypt.

2. Materials and methods

2.1. Studied samples

Representative limestone samples were carefully selected from the archaeological studied area. Studied samples used were prepared on cubes forms of 5×5×5 cm. Untreated specimens were also tested for reference purposes.

2.2. Consolidants

The first one is a solution of calcium hydroxide nanoparticles dispersed in ethanol (nanolime), figure (2a). Scientifically it is proven that 'if a saturated solution of calcium hydroxide is allowed to penetrate into limestone, subsequent evaporation of the solution will lead to the deposition of calcium hydroxide within the stone'. This, upon reaction with carbon dioxide in the air forms calcium carbonate (carbonation) which then acts as the cementing binder to restore the bonds between the grains and, consolidate the stone.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + HO_2 \quad \text{(Carbonation process) [4]}$$

The second consolidant is an aqueous solution of diammonium hydrogen phosphate (DAP, (NH4)2HPO4), figure (2b). DAP is a novel inorganic consolidant has recently been proposed for the treatment of carbonate stones used in architectural and cultural heritage. The mechanism is that stone can be consolidated by formation of hydroxyapatite [HAP $(Ca_5\ (PO_4)_3(OH)$, usually written as $Ca_{10}(PO_4)_6(OH)_2$] inside pores and micro-cracks between grains. According to the following equation, HAP can be formed from the reaction between Ca^{+2} ions deriving either from partial dissolution of the stone or externally added and PO43- ions coming from the aqueous solution of diammonium hydrogen phosphate (DAP) [7]:

$$5\ Ca^{2+} + 3\ PO_4^{3-} + OH^{-} \rightarrow Ca_5\ (PO_4)_3(OH)$$

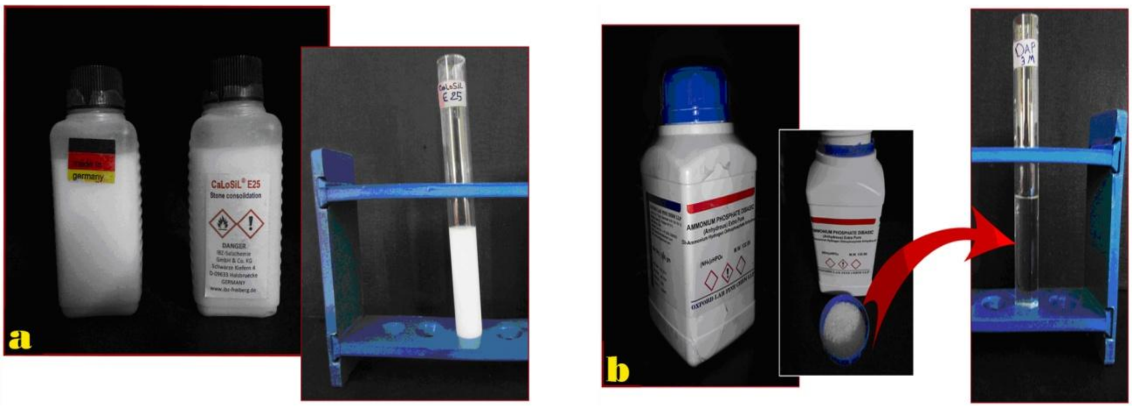


Figure 1: a) Nanolime CaLoSiL E25; b) Diammonium hydrogen phosphate package.

3. Methods and techniques

Different analytical and investigation methods were used to study the experimental samples:

3.1. Polarizing microscope

Petrographical investigation conducted for the studied samples according to [8] using the polarizing microscope (Olympus BX50, Japan) associated with computer software imaging system called (analysis) in the geology and petrographical investigation laboratory of National Housing and Building Research Centre (HBRC), Cairo. It aims to identify the texture, fabric and micro-structure of the samples under investigation. On the other hand, it is also used to identify the presence or absence of weathered or altered minerals and its effect on the properties of the stone.

3.2. XRD (Mineralogical analysis)

X-ray diffraction used for identification of the mineralogical composition of studies samples, using X-ray model X' Pert Pro Phillips MPD PW 3050/60 X-ray diffractometer in the XRD lab of the HBRC.

3.3. Scanning electron microscope (SEM)

Scanning electron microscope, (JEOL JSM-5400LV) at Assiut University, was used to determine the morphology of the particles, voids and to detect the consolidants penetration efficiency for the treated samples to determine the best of these substances in penetration.

Moreover, the physico-mechanical properties (bulk density “B”, water absorption “WA”, apparent porosity “AP”, and compressive strength “C”) were measured for the studied samples based on documented standard typical methods [9-11].

The water repellency of the standard and treated samples was evaluated by carrying out the test of static water contact angle using Drop master DM-701, fully automated contact angle meter.

According to Shihang and Kezhong, color photography, the technique most frequently used in conservation, is an effective tool for quickly documenting the color and condition of objects [12].

3.4. Treatment process

The experimental study was carried out on selected samples from the archaeological area. The samples were prepared as cubes (5×5×5cm) and they were used as a target for the consolidation process using an aqueous solution of diammonium hydrogen phosphate, DAP (3.0 M) and $Ca(OH)_2$ nanoparticles 2.5% in ethanol (CaLoSiL E25). According to [13], the samples were cleaned perfectly to remove the dust. Finally, they were dried in the oven at 60°C. Consolidants were applied by a capillary absorption with covering the path by glass cover to minimize solvent evaporation (Figures 2 and 3).

As for the phosphate treatment, treatment with DAP solution alone however has two drawbacks: (i) not only HAP, but also other metastable calcium phosphate phases are formed; (ii) small unreacted phosphate fractions remain in the stone. To overcome these drawbacks, different strategies have been proposed, such as providing additional calcium sources, controlling the DAP solution ph and applying a limewater poultice as a second step [14].

The second step of the treatment, which consisted of applying a limewater poultice onto the treated surface of the samples (a sheet of filter paper being inserted between the sample and the poultice to avoid sticking). The limewater poultice was prepared using dry cellulose pulp and limewater, i.e. a saturated solution of calcium hydroxide and de-ionized water. The weight ratio of limewater to dry cellulose pulp was 6:1. After poultice application, samples were wrapped in a plastic film for 24 hours (to avoid limewater evaporation), figure (2c). Afterwards, the samples were unwrapped and the poultice was left to dry in contact with the samples until constant weight (about 4-5 days). The poultice was then removed, the samples were rinsed with de-ionized water and finally left to dry until constant weight (about 2-3 days) [14-15]. On the other hand, treated samples by nanolime were left to dry for 60 day after treatment before evaluating the treated samples.

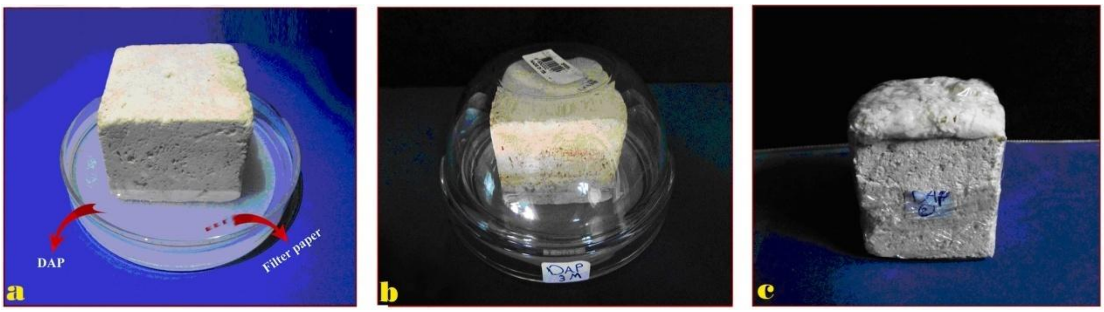


Figure 2: A and b) prepare the samples and place them in the consolidant with careful covering process; c) Applying a limewater poultice onto the treated samples, and wrap the samples in plastic film.

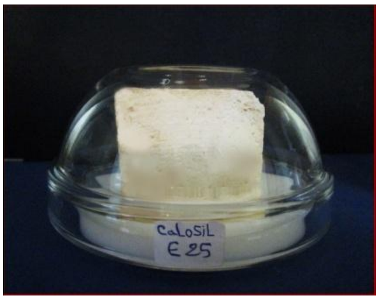
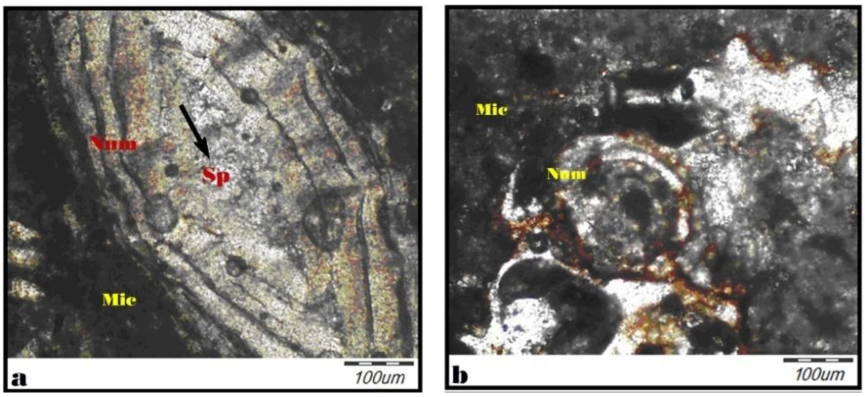


Figure 3: Sample in the Nanolime consolidant with a glass cover

4. Results

4.1. Polarizing microscope investigations of the standard samples

Petrographically, two investigated microfacies: one is a standard limestone sample non- affected by firing as shown in figure (4a), while the other is a fired limestone sample, figure. (4b). the results of the investigation indicated that the studied non-fired limestone is comprises over 50% allochems These grains embedded in a micritic matrix represent over 2/3 of these facies with less sparry calcite cement, so they can be classified as packed biomicrite microfacies based on [16]. Moreover, investigation of fired microfacies figure (4b) revealed the presence of textural deformation as results of firing but some relicts of the original can be observed such as nummlites outlines.



Mic: Micritic calite, Num: Nummlites, Sp: Sparite

Figure 4: Photomicrographs of the studied limestone: a) standard sample; b) Fired sample.

4.2. (XRD) of the standard and treated samples

The analysis indicated that all of studied samples fresh sample and treated samples are consist mainly of Calcite ($CaCO_3$). On the other hand, the analysis exhibited presence of appreciate hydroxyapatite $Ca_{10} (PO_4)_6 (OH)_2$ in samples treated by DAP, figure (5). Finally, the XRD obtained results in a complete agreement with investigation by polarizing microscope for studied limestone (Tihna El-Gabal archaeological area) as it composed substantially of calcite as a main component.

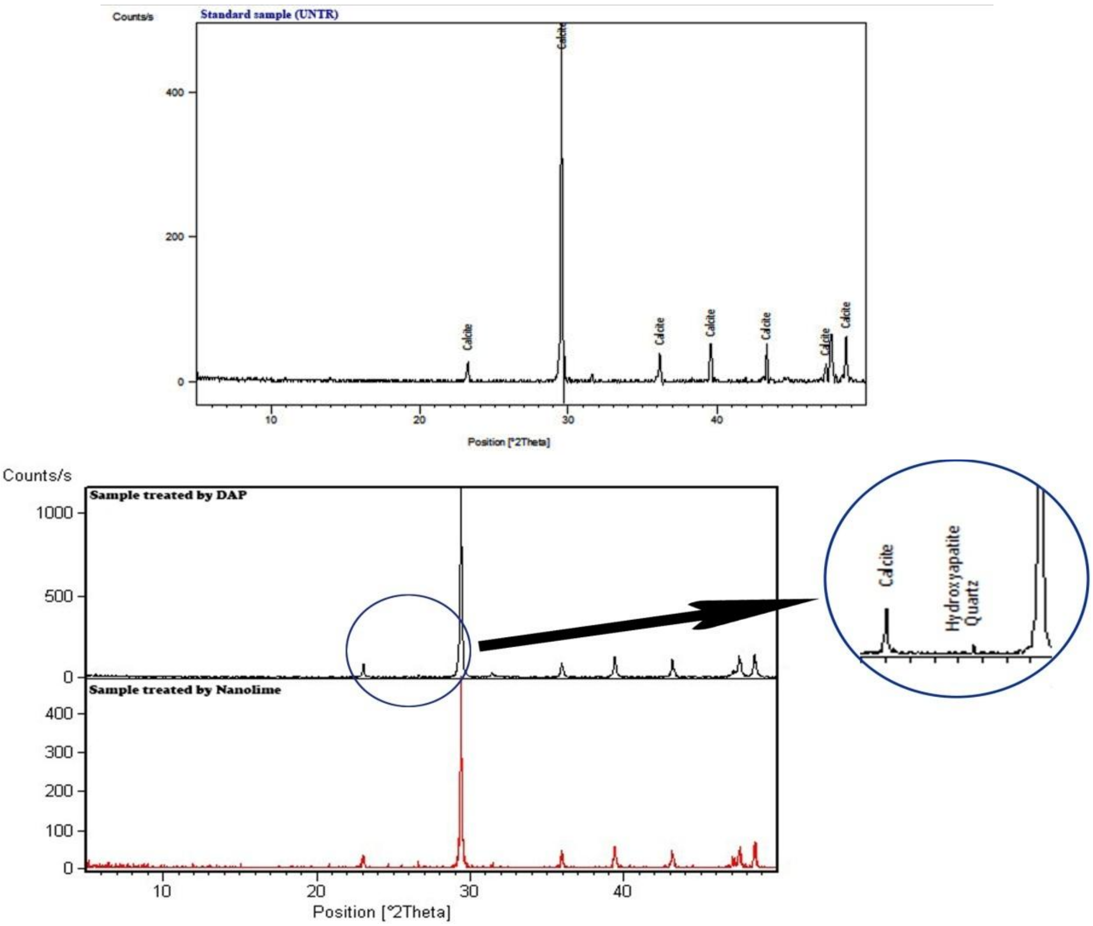


Figure 5: X-ray diffraction pattern of the reference sample and treated samples by Nanolime and DAP

4.3. Depth of penetration and visual observations of the standard and treated samples

According to [6], through laboratory observations, it could be showed that there is a clear difference in the time of penetration between the treated samples according to the consolidant types as shown in figure. (6). In addition, it could be noticed that there aren't any visual variations detected in the samples surfaces after treatment, as shown in figure. (7). It could be also observed that the time of penetration (average saturation time) is 1 h. in the samples treated by DAP and 1½ h. for nanolime treated samples. After the treated samples are completely dried, it could be noticed that there aren't any chromatic variations detected in the treated samples surfaces compared to the reference sample, as shown in figure (7).

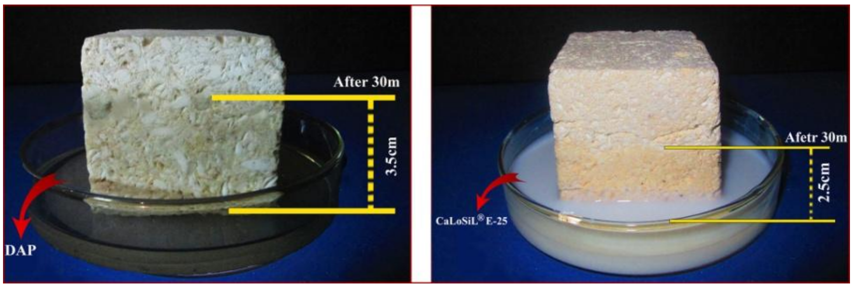


Figure 6: Illustrates the time of consolidants penetration in experimental samples.

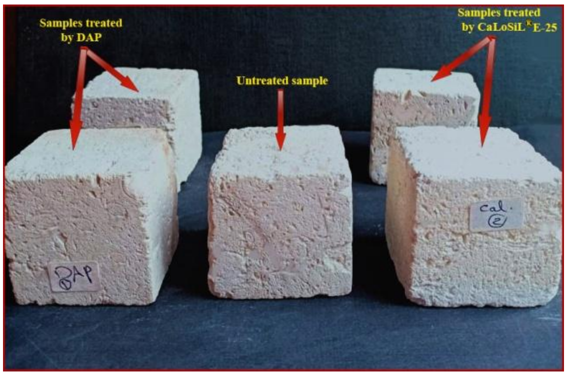


Figure 7: Effect of consolidants on the appearance of treated samples compared to the reference sample).

4.4. Measuring the contact angle of the standard and treated samples

Regarding the micro-drop test, it could be argued that there are some variations in static contact angle measurements, which give an indication of hydrophobation differences according to the applied consolidants. As shown in figure (8), the consolidants (DAP) caused an increase in the contact angle of treated samples (72.3°), but it remained below the 90° conventional threshold between hydrophilic and hydrophobic behavior. On the contrary, after consolidation by CaLoSiL E-25, treated stone acquires a hydrophobic behavior, as denoted by the contact angle [above the 90° (92.2°)] and time for water absorption (clearly increased with respect to the untreated reference), table (1).

Table 1: Results of measuring the contact angle (θ) of the studied samples.

Sample	Left	Right	Mean [contact angle (θ)]	Height	Width
Untreated sample (reference)	41.8	22.8	32.3	0.431	7.776
Treated sample by DAP	71.1	73.5	72.3	1.279	3.703
Treated sample by CaLoSiL E25	30.4	154	92.2	1.325	4.415

Figure 8: The micro drop test: water droplet on the studied samples surfaces

4.5. Physico-mechanical properties of the studied samples

The average values of the studied physico-mechanical properties of references and treated samples are listed in table (2).The obtained results proved that there are clear differences in the samples physico-mechanical properties due to the consolidation efficacy of the materials used. It can be also noticed that obtained results average values plotted and represented graphically in figure (9). The obtained measured physico-mechanical average values revealed that: Both DAP and Nanolime have a positive effect as a consolidation material for treatment of reference sample. It can be also noticed that treated samples by DAP achieved relatively more efficiency than Nanolime treated samples. As treated sample by DAP have average values of bulk density and uniaxial compressive strength exhibited relative increase than others treated by Nanolime. On the hand, treated sample by DAP have average values of water absorption % and apparent porosity relatively less than others treated by Nanolime.

Table 2: The change in physico-mechanical properties of the treated samples compared to the Ref. sample (standard)

Properties Samples		Bulk density (g/cm^3)	Water absorption (%)	Apparent porosity (%)	Uniaxial compressive strength (Kg/cm^2)
Standard sample		2.01	10.9	21.9	85
Consolidated samples	By DAP	2.2	8.25	18.15	122
	By Nanolime	2.2	9.3	20.46	101

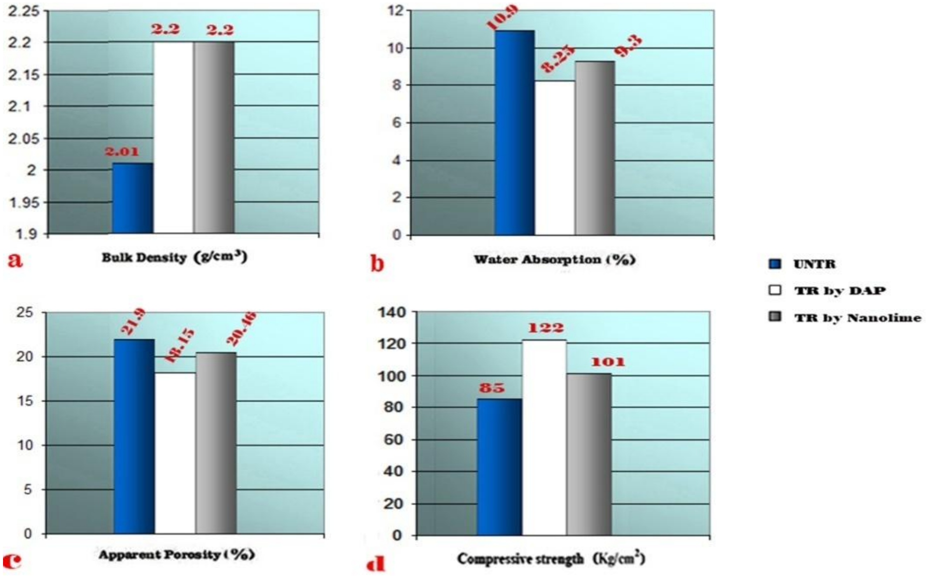


Figure 9: Physico-mechanical measurements of the Ref. and treated samples: (a) bulk density, (b) water absorption, (c) apparent porosity, and (d) compressive strength

4.6. SEM investigations of the standard and treated samples

The investigation for the studied samples both of standard and treated samples by (SEM) exhibited as shown in figure (10) the following: the morphological features of these samples were highly affected and changed after treatment as treated samples showed different forms of consolidants penetration in the samples. It is also noticed that there is a satisfied diffusion of the two consolidants inside the stone pores, but the superiority of DAP over nanolime is also evident.

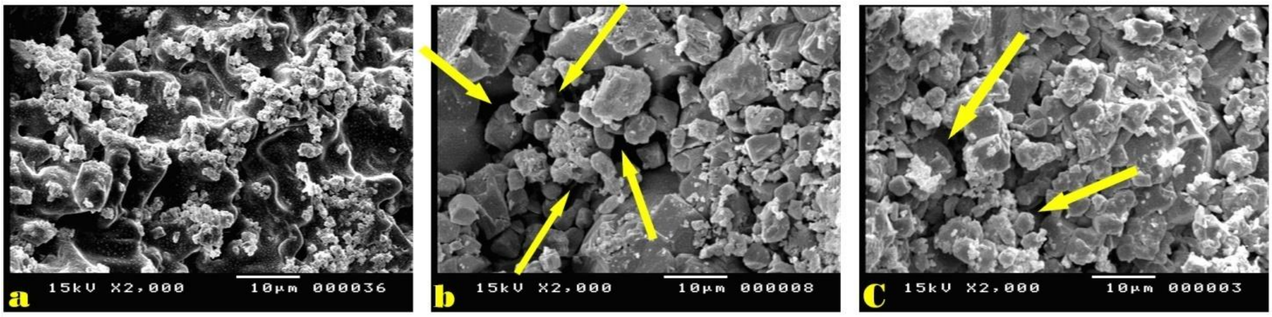


Figure 10: SEM photomicrograph shows: (a) a wide field of the grains consisting standard sample; (b) treated sample by nanolime (CaLoSiL), and shows a partially filling by $CaCO_3$; (c) treated sample by DAP, and shows a mostly filling by a considerable amount of hydroxyapatite

5. Discussion

Based on the previous promising results of application both of nanolime and DAP as two innovative consolidants for studied monumental limestone some points should be considered:

- Inorganic-mineral consolidating products are based on the penetration of water-soluble chemical precursors that _following mechanisms of hydrolysis, carbonation, or chemical interaction with the stone substrate develop a crystal-texture of new formed insoluble products that causes the consolidating effect [17]. Different physico-mechanical properties and chemical characteristics of building materials may be changed due to the effects of consolidation processes [18].
- The basic principle of stone consolidation is to introduce a compound that penetrates into the stone and reestablish grain to grain cohesion either by forming a bridge between grains or by forming a continuous film., it must be compatible with the unconsolidated stone in terms of color, water absorption, water vapor transmission, and thermal expansion [18].
- The obtained promising previous results for the application of the used innovative consolidants show that the studied samples' behavior before and after treatment are relatively changed. It is certain that there were important changes in the used monumental limestone properties due to the use of different consolidant types.
- The Explanation of relative enhancement in the average values of physico-mechanial properties including (Bulk density, compressive strength, water absorption and apparent porosity) with superiority of DAP treated samples than nanolime mostly depended upon this may be due to materials' viscosity, surface tension and rate of deposition [19], as well as the effects of solvent types, their evaporation rate and liquid transport within the pores. Also, some structural variations of the stone itself such as the pore structure (microstructure porosity, pore shape and pore connectivity), in addition to properties of consolidation products [20]. These increases were connected to the consolidation effects and they were mostly owed to the satisfied penetration of the consolidants within the stone pores which was confirmed by other researchers in similar cases [21-22].
- On the other hand superiority of sample treated by DAP as SEM photomicrographs showed partially filling by $CaCO_3$ in applying Nanolime, while the sample treated by DAP showed a mostly filling by a considerable amount of hydroxyapatite, agreed with XRD analysis, and this was reflected in the mechanical properties of the sample treated by DAP, Where it showed a clear improvement in its mechanical properties.
- Regardless the more relative improvement in different physico-mechanical properties by using DAP consolidant than nanolime it can be also exhibited the increase of hydrophobation and consequently contact angle by nanolime treated due to surface roughness resulting from nanoparticles, that lead to trapping of air between water droplets and the rough surface [23].

6. Conclusion

- In this paper, a systematic comparison was carried out between $Ca(OH)_2$ nanoparticles (Nanolime, German product under the trade name CaLoSiL E25) and phosphate-based treatments (DAP) for consolidation of studied monumental limestone Tihna El-Gabal archaeological area, Minia, Egypt..
- Both consolidants showed promising results, effectiveness, and good compatibility with the stone substrate.
- The different physico-mechanial and surface hydrophobation can be used as a parameters for evaluation the different impact of both used innovative consolidants on studied monumental limestone.
- Transport properties of the treated stones slightly altered by the treatment by both consolidants, so that water and water vapor exchanges between the treated stone and environment are not significantly blocked.
- The application of a 3 M DAP solution by capillary absorption, followed by application of a limewater poultice, proved to be a very effective method to enhance the studied limestone mechanical properties.

- Finally, and based on all of the results reported in this paper, DAP would be the most efficient for studied limestone consolidation in the present case, Whereas it was found that it totally improved the stone properties, in addition to its high compatibility with the stone substrate.

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