The Nanolime as a Consolidating material for the Ornamental Hardened limestone of Sheikh Fadl, Egypt

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Abstract

Hardened limesstone is one of the most common building material generally, in the Eastern Mediterranean region particularly Egypt. Sheikh Fadl quarries are considered as a type locality for this limeston. It is widely used for restoration of the severely weathered archaeological sites but presents a sort of weathering. Consequently, the main aim of the current study are to test the positive impact of Nanolime as a consolidating material for such ornamental dense limestone. Five limestone samples had been collected representing this quarry at Sheikh Fadl, Red Sea to investigate the physico-mechanical and durability limits of this facies. Transmitting polarizing microscope, Scanning electron microscope and durability test using Sodium sulfate had been used before and after consolidation to achieve the aim of the current study.

Keywords: Nanolime, consolidation, ornametal hardened limestone

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1.INTRODUCTION

In the Mediterranean region, particularly Egypt, the hardened limestone is considered as one of the most common building material generaly used for wall cladding and landflooring purposes. Geologically, hardened limestone formed by advanced stages of diagensis e.g. recrystalization without metamorphism, thus, still representing its sedimentary origin. In the last decade and with increasing the number of hardened limestone quarries explored all-over Egypt many studies have been conucted for it [1-5].

As the hardened limestone have some specific and unique properties e.g. an attractive colors, physico-mechanical properties and its polishability which led to using it for their previous tradtional usages (i.e.wall cladding and landflooring). Recently, the hardened limestone should be utilized for reconstruction and replacement of decayed and weathered parts in archeological sites so, the current study bacames urgent and necessary to throw light on and investigate its durability against different ageing and weathering.

The major product of the hardened limestone in Egypt has been extracted from the Northern and Southern Galala quarries and it is considered as a type locality for this rock type. Selection of Sheikh Fadl facies as the subject of this work is not only depended on their formation as a part of the Southern Galala and represented source of wealth in Egypt but also on their wide range of mineralogical and physico-mechanical properties.

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The area under investigation is located in the central part of the Southern Galala, about 107 km to the East of El-Sheikh Fadl Village. It is located between latitudes 28° 24' and 28° 29' N and longitudes 31° 48' and 31° 55' E. It is accessible through the asphaltic road between El-Sheikh Fadl Village and Ras Gharib i.e. about 40 km north through the asphaltic road between El-Sheikh Fadl Village and Ras Gharib i.e. about 40 km north through unpaved road Fig. (1) [6].

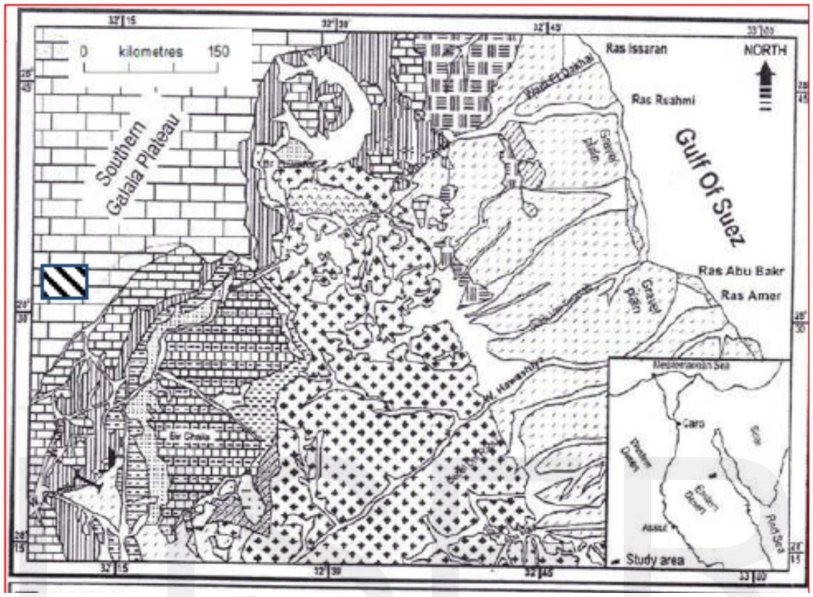

Fig. (1). Geological map of the Southern Galala plateau presenting the area of investigation .

Area under investigation

Geologically, an Eocene limestone rock covers the area at El-Sheikh Fadl village and extends eastward[7]. Hardened limestone at El-Sheikh Fadl area is stratigraphically related to Gabal Hof Formation [2] which had been introduced by [8].

Finally, the aim of this work is to improve the different physico-mechanical properties of Sheikh Fadl hardened limestone by using nanolime as a new consolidating material .It is also extend to involve consequent enhancement of their durability against salt weathering after treatment with nanolime.

2.MATERIALS and METHODS

2.1.Materials

2.1.1.Stone

Five rock samples coded Fd1 to Fd5 were collected from one of the currently used major quarry at El-Shiekh Fadl to investigate their physical and mechanical as well as durability limits before and after treatment by nanolime. This is to find out their utility for construction puroposes at the present day aggressive enviornments. The samples are visually described as creamy; stylolitic fossiliferous; hardened limestone Fig. (2).

Fig. (2). One of the hand specimen of Shiekh Fadl hardened limestone.

2.1.2. Consolidants

Nanolime products are an attractive choice mainly for the consolidation of substrates containing calcite considering the intended chemical compatibility between the treated substrate and the treatment product [9]. Nanolime commercially called (CaLo SiL) has been introduced in October (2006) as the first commercially available stone treatment product based on nano-calcium hydroxide solution according to [9,10].

The products contain $Ca(OH)_2$ nano particles dispersed in different alcohols (ethanol and isopropyl alcohol types were investigated). In the current study nano-lime was used this with concentration of 15 g/L ethanol for consolidation purposes of the studied samples.

2.2.Methods

Detailed investigation of the mineralogical composition for the collected stone samples has been conducted using a transmitting polarizing microscope (Olympus BX50, Japan), X-ray diffraction (X-ray model X´Pert ProPhillps MPD PW 3050/60 X-ray diffractometer). Scanning electron microscope model (Inspect SFEI Company, Holland) with accelerating voltage of 200 v to 30 kv and with magnification up to 300,000 X and used to detect of the penetration depth of the nanolime as consolidating materials. Transmission Electron Microscope (TEM) were used to analyze nanolime particles which dispersed in ethanol alcohol performed by a JEOL JEM-1230, model Oregon (Japan) at 80 kV.

Some physico-mechanical properties involving (Bulk density, Water absorption, apparent porosity and compressive strength) were measured before and after the treatment with nanolime according to the international methods of [11-13]. Moreover, artificial salt weathering is also conduct for studied samples before and after the treatment by nanolime and carried out according to [14].

Consolidation procedure by nanolime started after preparation and drying cubic sample (untreated) 5*5*5cm then immerse samples in a nanolime with concentration of 15 g/L ethanol. Repeating this process several times to ensure the penetration of nanolime deeply through the prepared cubic rock samples. After 10 cycles of immersion and drying of the rock samples, they were left to be cured in air.

3.RESULTS and DISCUSION

3.1. Results

3.1.1. Petrography and Mineralogy of the hardened limestone

It is essential to investigate different characterization of the studied stone before treatment process with nanolime. Firstly, thin sections of the studied samples of hardened limestone revealed that its major constituent are bioclasts (skeletal grains) with 80%. It is mainly nummlitic facies with sparite and micrite cement Fig. (3 a). The micrite is partly converted to microspars and spars size by aggrading neomorphism Fig. (3b). Partial dissolution of sparry calcite in the inner core of nummlites was clearly noticed leading to empty core of some of the shell fragments Fig. (3c). The petrographic investigations for the collected rock samples at El-Sheikh Fadl indicated that it can be classified based on its texture as Packstone [15] and Biosparite in composition [16].

X-ray diffractograph had been used in the current study to investigate the mineralogical composition of the rock under investigation, it indicated that all of the samples have the same mineralogical composition, i.e. calcite. Moreover, two non-carbonate minerals (montmorillonite and gypsum) have been detected in Table 1. Mineralogically, all of the studied samples can be classified as high-calcium limestone [17] and had been graphically represented on [18] Fig. (4).

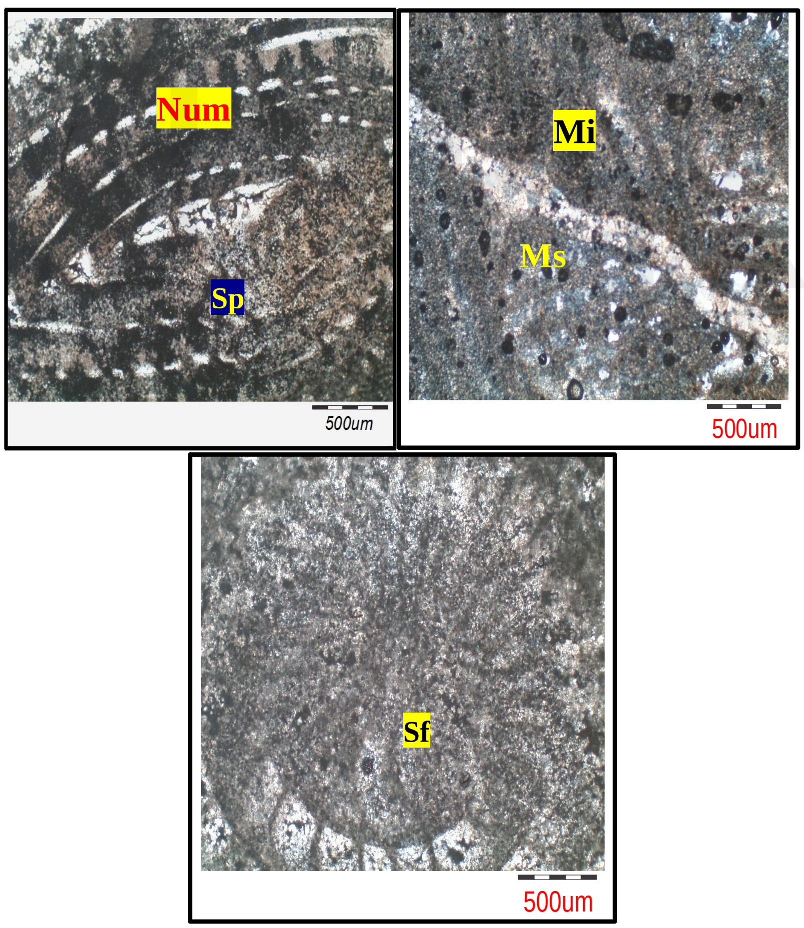

Fig. (3). Photomicrographs of hardened Sheikh Fadl limestone.

Num: Nummlites, Sp:Sparite Mi: Micrite, Msp:Microsparite Sf:Shell fragments

Table (1): The mineralogical composition of the studied samples.

Area	Samples	Carbonate minerals	Non carbonate minerals	Mineralogical Nomenclature
Shiekh Fadl	Fd1 Fd2 Fd3	Calcite	Montmorillonite and Gypsum	High-calcium limestone

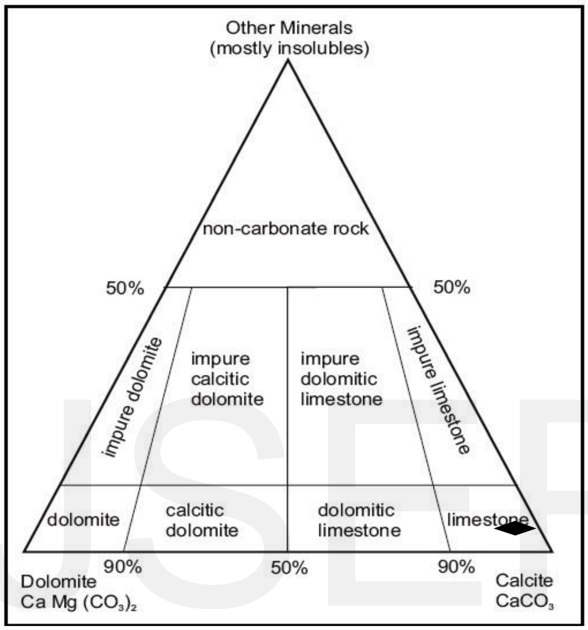

Fig. (4). Mineralogical classification of the studied samples

According to Trasimission Electron Microscope (TEM) Fig. (5) nanolime particles agglomerated in size rangs from 150nm to 550nm with mean size of 250nm. Most of nanoparticle agglmerates take hexagonal crystal form with regular edges.

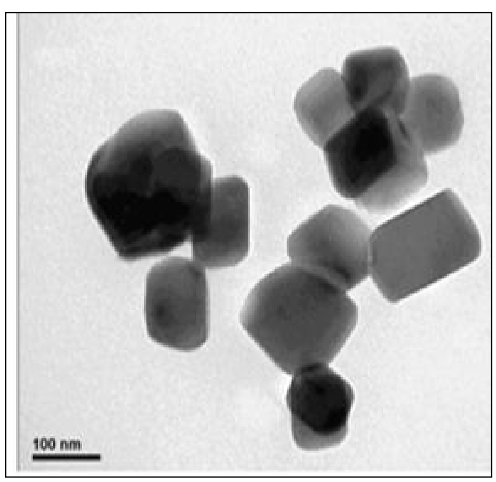

Fig. (5) TEM micrograph of used nanolime particles agglomerates.

3.1.2. Physico-mechanical properties

To investigate the effect of nanolime on the samples under investigation, some physico-mechanical properties were measured and their mean values had been calculated before and after this treatment. The obtained results are listed in Table 2 revealing that:

- The mean value of the bulk density had been increased from 2.5 gm/cm3"before treatment" to 2.77 gm/ cm^3 after treatment with nanolime with an increasing percentage of 10.8%. From the boarder of high –density limestone 2.5 gm/ cm^3 to exact value of high –density limestone according to [19].
- The mean value of water absorption had been decreased from 2.6% "before treatment" to 0.9% after treatment with nanolime with a decreasing percentage of 34%, consequently, the apparent porosity mean value had been dercreased from 5.4% to 2.48 with a percentage of 45%.
- Dry compressive strength mean value had been increased from 488 to 560 kg/cm^2 with rate of increasing 14.7% after treatment by nanolime. It also means that the mean value of the dry compressive strength moves from medium-dense limestone to high-density limestone according to [19].

After nanolime treatment, the enhancement in mean values of bulk density , water absorption and apparent porosity of the studied samples can be represented graphically as shown in Fig. (6) . The enhancement in mean value of compressive strength had been illustrated in Fig (7). Finally, the postive effect of nanolime on the studied samples can be revealed by increasing the mean values of both bulk density and compressive strength associated with decreasing the mean values of water absorption and consequently apparent porosity.

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Table 2. The mean values of the selected physico-mechanical properties for untreated and treated samples by nanolime.

Property	Mean Bulk density (gm/ cm^3)	Water absorption %	Apparent porpsity %	Dry compressive strength (Kg / cm^2)
Untreated samples	2.5	2.6	5.4	478
Treated samples	2.77	0.92	2.48	560

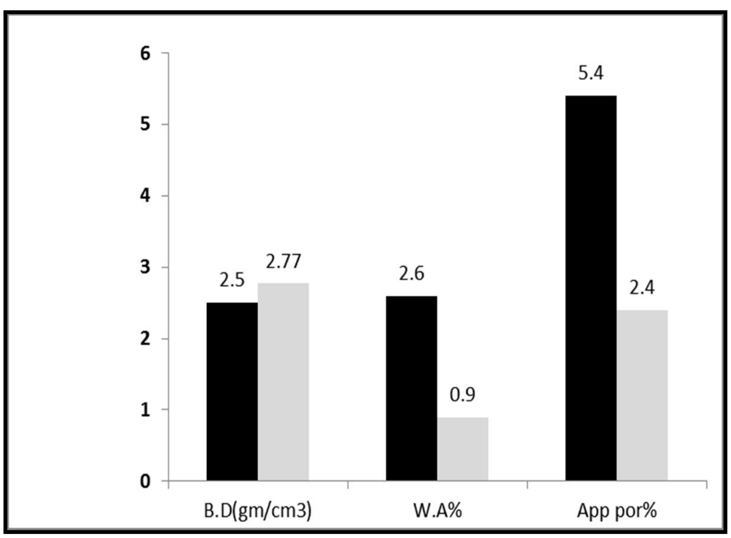

Fig.(6) The enhancement of mean values of bulk density, water absorption and apparent porosity after nanolime treatement.

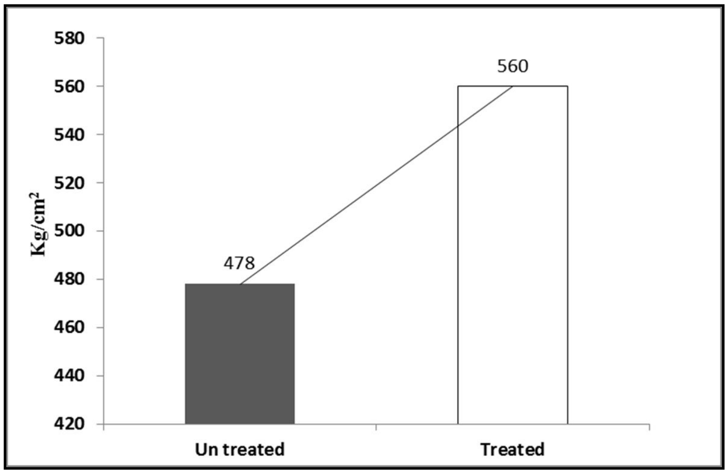

Fig.(7). The enhancement of mean values dry compressive strength after nanolime treatement.

3.1.3.Salt Crystalization Test

In this study, the (artificial weathering) acceleration salt crystalization test using sodium sulphate salt solution of concentration 14% was used as a guide for measuring the durability of the studied samples before and after the consolidation by nanolime. Three untreated samples symbolized (Fd1,Fd2,Fd3) and three treated samples(Fd4,Fd4,Fd6) had been exposed to acceleration salt crystalization test.

Wight loss ΔM% after 15 cycles and Alteration index (A.I) were noticed and measured carefully to followup the effect of nanolime on the studied samples after consolidation. The obtained results listed in Table 3 and represented graphically on Fig. (8). The results revealed that the average ΔM% of untreated samples (2.3%) after 15 salt crystalization cycles which means that it belongs to durability class (B) i.e. weight loss ranges between 1:5%. On the other hand, the average ΔM% of treated samples (-0.32 %) after 15 salt crystalization cycles which means that it belongs to durability class (A) i.e. weight loss less than 1% [20] it can be also shown that, Alteration index (A.I) i.e.cycle of first weight loss changes from **5th** in the case of untreated samples to **13th** Fig.(9) in the case of treated samples which means that the effect of sodium sulphate 14% solution requires longer duration to appear its effect on the treated samples by nanolime.

Finally, the postive effect of nanolime on Sheikh Fadl samples against salt crystalization can be clearly evidenced by the decrease in weight loss average value from (-2.3%) to (-0.32 %) consequently, change from class durability value B for untreated samples to A for treated. It can be also reflected from change A.I. from **5 th** in the case of untreated samples to 13 th in case of nanolime treated samples.

The plotting of the weight loss average value for treated and untreated samples on Barry diagram[21] showing their crossponding durability class value Fig. (10).

Table 3. The weight loss (ΔM %) and Alteration index (A.I) for untreated and treated samples.

	Sample	Intial weight (gm) W0	Final weight, gm (W15)	ΔM %	Avg ΔM%.	A.I
Un treated	Fd1	147.294	143.279	-2.7	-2.3	5 th
	Fd2	147.837	142.902	-3.3		
	Fd3	146.04	142.68	-2.3		
Treated	Fd4	145.65	144.97	-0.46	-0.32	13 th
	Fd5	142.09	141.85	-0.16		
	Fd6	140.60	140.08	-0.36		

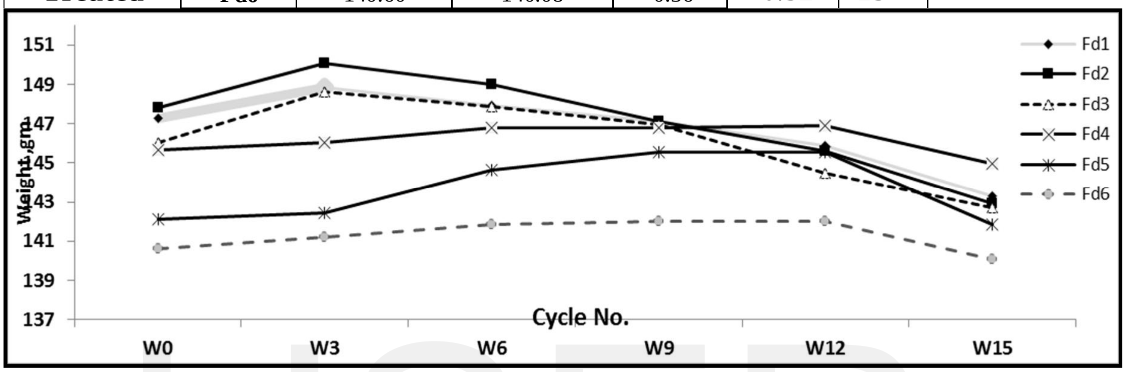

Fig.8. The weight loss (ΔM %) and Alteration index (A.I) for untreated and treated samples over 15cycles of salt weathering.

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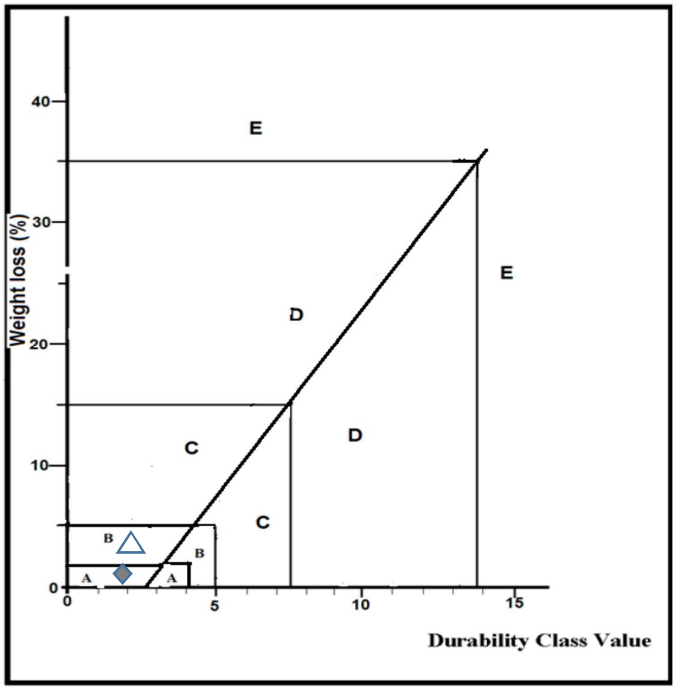

Fig.9. Barry diagram presenting durability class and value based on weight loss percentage.

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The noticeable enhancement that occurred by nanolime treatment on Shiekh Fadl samples can be followed by SEM as shown in Fig. (11). The SEM results ensure this enhancment and discussed their mechanism. SEM shows presence of partial pores filling due to the partial growth of $CaCO_3$ crystals on lime particles surface as aresult of incomplete carbonation process agreed with [22].

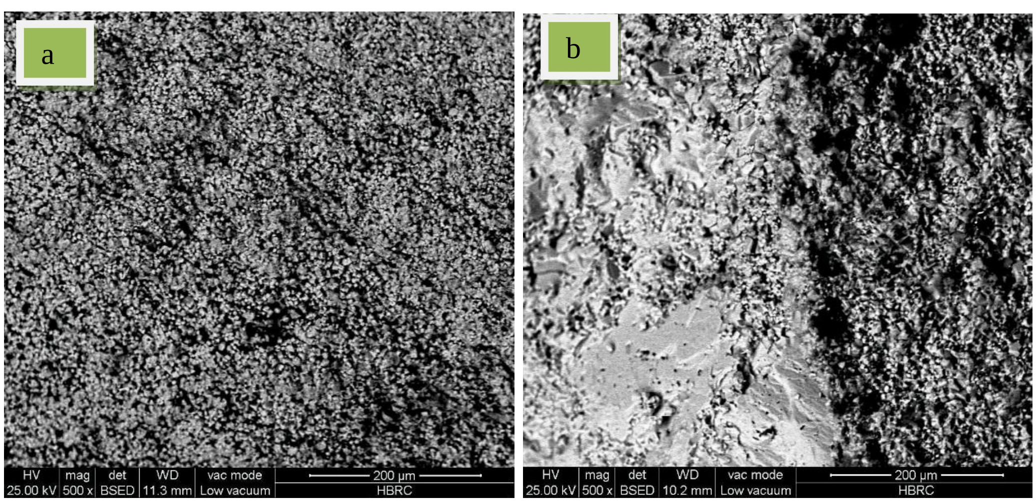

Fig.10.SEM micrographs of Sheikh Fadl.

a) Material surface berfore nanolime treatment
b) Penetration depth of treatment in a typical cross section.

3.2.Discusssion

On samples' drying in air, the alcohol (ethanol) is gradually evaporated leaving solid calcium hydroxide behind within rocks' pore system. Calcium hydroxide in the form of nanolime reacts with atmospheric carbon-dioxide forming calcium carbonate which deeply penetrates through the studied samples, filling their pores and finally consolidation process were occurred and by conversion untreated cubic samples to treated cubic samples with nanolime.

This process was associated with penetration depth about 400µm. Partial pores by $CaCO_3$ leds to decrease the water absorption , apparent porosity associated with increasing bulk densities and compressive strength mean value. This partial filling also leds to decrease the average weight loss by sodium sulphate 14% from -2.3% in untreated samples to -0.32% for treated samples and finally, elongate the A.I. duration from 5th in untreated samples to 13 th in treated samples.

4.CONCLUSION AND RECOMENDATIONS

1. Marbleized limestone in El-Sheikh Fadl area is stratigraphically related to Gabal Hof Formation.
2. Consolidating material are nanolime particles agglomerated in size rangs from 150nm to 550nm. Most of nanoparticle agglmerates take hexagonal with regular edge.
3. Petrographically, the studied samples as a microfacies can be classified pertographically as *Packstone* [18] or *Poorlywashed Biosparite* [19].
4. Mineralogically, all of the studied samples can be classified as high-calcium limestone.
5. The postive effect of nanolime on the studied samples can be revealed by increasing the mean values of both bulk density and compressive strength associated with decreasing the mean values of water absorption and consequently apparent porosity.
6. The postive effect of nanolime on Sheikh Fadl samples against salt crystalization can be clearly evidenced by the decrease in weight loss average value from (-2.3%) to (-0.32 %) consequently, change from class durability value B for untreated samples to A for treated. It can be also reflected from change A.I. from **5 th** in the case of untreated samples to 13 th in case of nanolime treated samples.
7. Explaination of this enhancement in different physico-mechanical properties and durability of Shiekh Fadl hardened limestone depended on partial filling of pores by $CaCO_3$ on particle surface then pentrated with 400 µm as illustrated by SEM.
8. Regardless the success of nanolime particles in the relative enhancement it needs an economic visibility study according to the final aim of its use.
9. It is recommended to use nanolime as consolidating material for hardened limestone particularly in archeological sites durring maintainance and replacement of weatherd parts.

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