An experimental study for evaluating the efficiency of consolidated materials for limestone treatment.

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Abstract:

Historical limestone surface and historical building may be exposed to many changes due to the exposure to many mechanical, Physiochemical deterioration factors Which represents a threat to our cultural heritage so the aim of this study was to preserve monuments by consolidating limestone by various consolidating materials to evaluate the efficiency of treatment process, in this study we used Nanoparticles of calcium hydroxide(NANO RESTORE), SILRES® BS OH 100 (solventless mixtures of ethyl silicates (TEOS) tetraethoxysilane) were used to improve the physicochemical and mechanical properties of the stone material, Remmers KSE 300 E (Solvent-free stone strengthener on a silicic acid ethyl ester (KSE) base), highly penetrating, safe and easy to use, has and is resistant to high weather and ultraviolet radiation, Paraloid B72 it is a joint polymerization consisting of ethyl acrylate and methyl acrylate by 70: 30%, Produced by Rhom & Haas and commercially produced by the Italian company CTS, transparent crystals, dissolved in organic solvents, this type of polymers are characterized by high molecular weight and resistance For friction, flexibility and resistance to yellowing, Paraloid B44 copolymer resin consisting of polyethyl acrylate (PEA), PMMA and ethyl acrylate (EA), a soluble in acetone and toluene, good resistance to UV radiation, corrosion, oxidation and its resistance to external factors to some extent and the degree of its glass transition is high and adding Nanoparticles of calcium hydroxide (NANO RESTORE) to copolymer of acrylic by concentration 1: 1, treatments were evaluated by scanning electron microscopy, general appearance water repellency, compressive strength, porosimetry water absorption and Density.

Key Words:

Limestone, Consolidation, Calcium hydroxide nanoparticles, Nanocomposites, Penetration, Mirovski, Immersion method.

(1) Introduction:

the Egyptian limestone one of the major types of building stone used from ancient Egyptian structure until today was quarried in geological formation dating from the Paleocene especially the Eocene epoch of the Paleocene period [1] [2]the Egyptian limestone is mainly composed by calcite(Calcium Carbonate)along with secondary minerals, of this the clay minerals, soluble salt are partially relevant to the deterioration mechanism of the stone[3] In addition to external damage factors chemical, physical and biological weathering phenomena, These deleterious processes include, but are not limited to, the action of atmospheric

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pollutants, salt crystallization, hydric and thermal expansion such as temperature, humidity and others, which ultimately lead to weakness of the impact, which may lead to the fall of parts From it in the body layers[4] [5] [6] and hence the aim of this research is evaluating consolidates materials for consolidating limestone.

(2) Materials

(2-1) Sample preparation

Limestone samples have been used from the quarries of Tura, one of the most important quarries of limestone in Egypt, Tura quarries are located about 15km north from Cairo, after bringing the limestone tiles, and they were cutting into small cubes 3 X 3 X 3 cm.

(2-2) Consolidates: -

- **NANO RESTORE®**

Is one of the catalysts produced by CTS and consists of the Nano Calcium Hydroxide is one of the most common Nanomaterials with inorganic effects, especially wall paintings and carbonate stones, as the calcium hydroxide “lime water” is one of the oldest products used in construction, which can be used to recover Loss of cohesion by filling the pores of limestone, especially limestone, The mechanism of the reaction depends on carbonation, in which calcium hydroxide is converted to calcium carbonate in the presence of carbon dioxide (CO_2) in the presence of a low percentage of moisture, a material that improves the mechanical properties of stones and murals, and is characterized by the formation of a glossy surface to allow evaporation, Any color changes on the archaeological surfaces, produced in the form of white liquid, the content of the active material (0.5), density 0.8), and the viscosity at 25 ° C is 2.75.[7] [8] [9]

- **Remmers® KSE 300 E**

It is the most widely used stone consolidant in Central Europe. This is a solvent-free tetraethyl-orthosilicate with a gel deposition rate of approximately 30%, which corresponds to 300 g of solid silica content per litre of consolidants, the temporary hydrophobicity of KSE 300 lasts for a longer time in the silicate substrate but it does not affect the carbonate substrate [10] [11].

- **SILRES® BS OH 100**

SILRES® BS OH 100 (solventless mixtures of ethyl silicates) was used as supplied by Wacker Silicons (Germany), many of study worked on **SILRES® BS OH 100** showed a homogeneous coating an aqueous colloidal solution of silica, it is commonly used as water-repellent consolidates material[12] [13] .

- **Paraloid® B72**

Paraloid B-72 is a well-known polymer used as an adhesive and consolidant for stone materials it many of study worked on paraloid b72 and reached that the consolidant filled most of the pores and obscured many of particle, good stability, this type of polymers is characterized by high molecular weight, resistance to friction, flexibility and resistance to yellowing [14] [15] [16] [17].

- **Paraloid® B44**

copolymer resin consisting of poly ethyl acrylate (PEA), PMMA and ethyl acrylate (EA), Many studies have dealt with its Paraloid® B44 and showed the crystals are transparent and not yellowish, good UV resistance, corrosion, Oxidation, resistance to external factors to some degree and its glass transition rate is high[18] [19] [20].

(2-3) SEM Examination:

SEM Scanning Electron Microscope Model Quanta 250 FEG) Field Emission Gun) (with EDX unit (Energy Dispersive X-Ray Analysis) with Accelerating voltage 30 K.V., Magnification 14x up to 1000000 resolutions for Gun 1n) was used to evaluate the effectiveness of the consolidation materials used. Fig (13to 20).

(2-4) Mechanical and Physical Properties:

(2-4-1) Physical properties measurement

- **Density** is one of the most important properties of geological materials such as limestone, Density is the relationship between the weight of the sample and its external size, estimated at g / cm^3.
- **Apparent Porosity and water Absorption:**

Porosity and pore distribution are essential factors for the absorption and transfer of water.

- Measurement of **water absorption** is one of the most important tests to determine the properties of limestone, the water absorption property describes the maximum stone ability to absorb water and this property is associated with the porous structure of the stone, the physical properties of lime stone was measured according to this refereces [21] [22].

(2-4-2) Mechanical properties measurement

The measurement of compressive strength was carried out before and after treatment, using an Amsler compression-testing machine, three weeks after treating samples [23] with Nanomaterial's, Siloxan material, acrylic polymer, and nanocomposite. The values of compression strength were recorded in a (6), Fig.23.

(3) Methods:

(3-1) Consolidation Process: -

Two methods of reinforcement were used, the first was the Mirovski method[24], This method is based on the spread of the consolidation material within the impact in the semi-circular form, and the repetition of the application of previous operations can be strengthened large areas of the impact surface by the convergence and overlap of semi-circles, This method is based on the spread of the consolidation material within the impact in the semi-circular, the stone cube of the reinforcement material was followed up every hour and the results were recorded Fig.1-10, Tab.1, for consolidating cube stone with NANORESTORE, the consolidating process continued for 252 hours, where the cube continued to absorbed for the consolidating material up to 248 hours, and then the cube stopped from absorbing till four hours after that and the cube absorbed 50 mm of NANORESTORE, While the consolidating of Remmers KSE 300 E process continued for 23 hours, where the cube continued to absorb up to 19 hours, and then stopped about absorbing for four hours and the cube absorb 9 mm of Remmers KSE 300 E however the consolidating of SILRES BS 100 OH process continued for

100 hours, where the cube continued to absorb up to 98 hours, and then the cube stopped from absorbing for two hours and the cube absorbed 11.5 mm of SILRES BS 100 OH, while the process of consolidating stone cube did not succeed in with Paraloid B72 and Paraloid B44 materials and Paraloid B72 concentration 3% concentration Paraloid B44 concentration 3%, and Ca (OH)2/polymer nanocomposites, as the acrylic polymers have blocked the sponge pores used in the tube nozzle, and when we measure the diameter of the dispersed treatment material Fig. 11, SILRES BS 100 OH achieved 27.5 mm, Remmers KSE 300 E achieved 24 mm and NANORESTORE achieved 18 but The process of consolidating stone, In the immersion method, the stone cube was left for 24 hours in the reinforcement material, Fig.2, Tab.1 and the result of reinforcement materials showed that the cube which treated with Nano restore absorbed 17.5 mm, and absorbed 10 mm from SILRES BS 100 OH and Remmers KSE 300 E, however, the stone cube absorbs 30 mm from Paraloid B72 concentration 3% but absorbed 20 mm from Paraloid B44 concentration 3%, and from Nanocomposite materials, the stone cube absorbed 20 mm from paraloid B72 concentration 3%), and Ca (OH)2/polymer nanocomposites while the cube absorb 15 from Paraloid B44 concentration 3%, paraloid B44 concentration 3%), and Ca (OH)2/polymer nanocomposites.

(3-2) Visual Inspection:

The consolidation process with Mirovski and Immersion methods were followed up and recorded the results Fig. (1-11), Table (1).

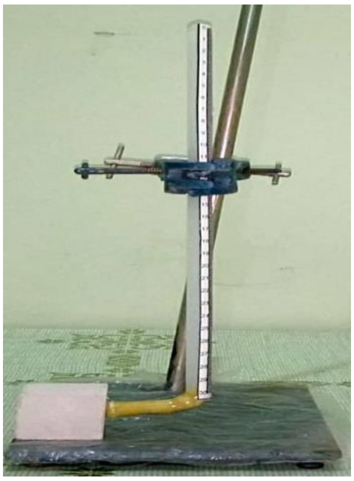

Fig.1 Showing the Meroviski consolidation process.

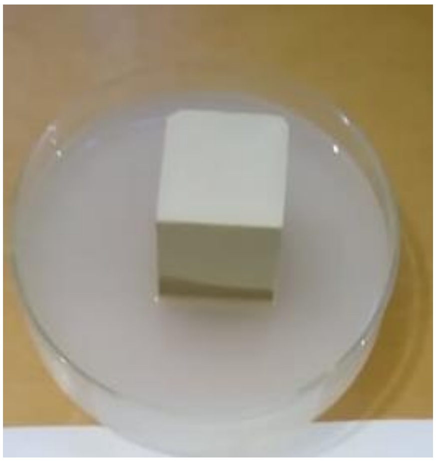

Fig. 2 Showing Immersion consolidation process

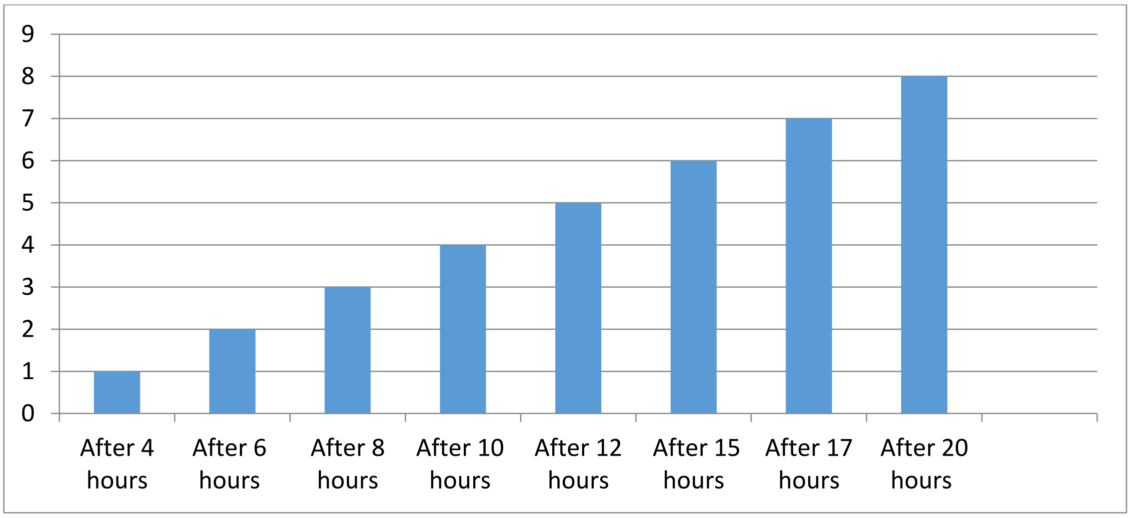

Fig. 3

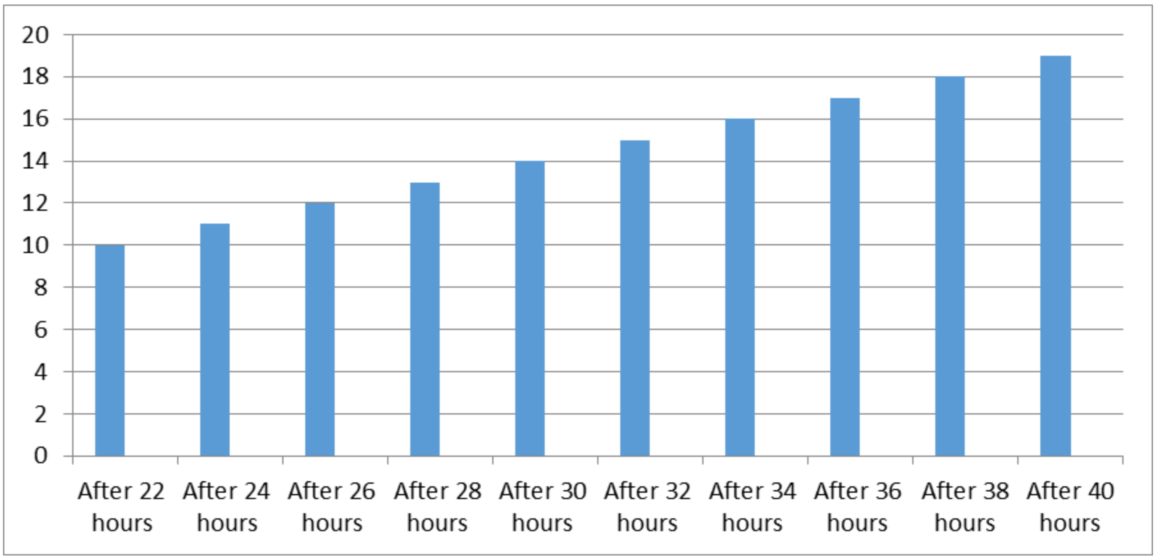

Fig. 4

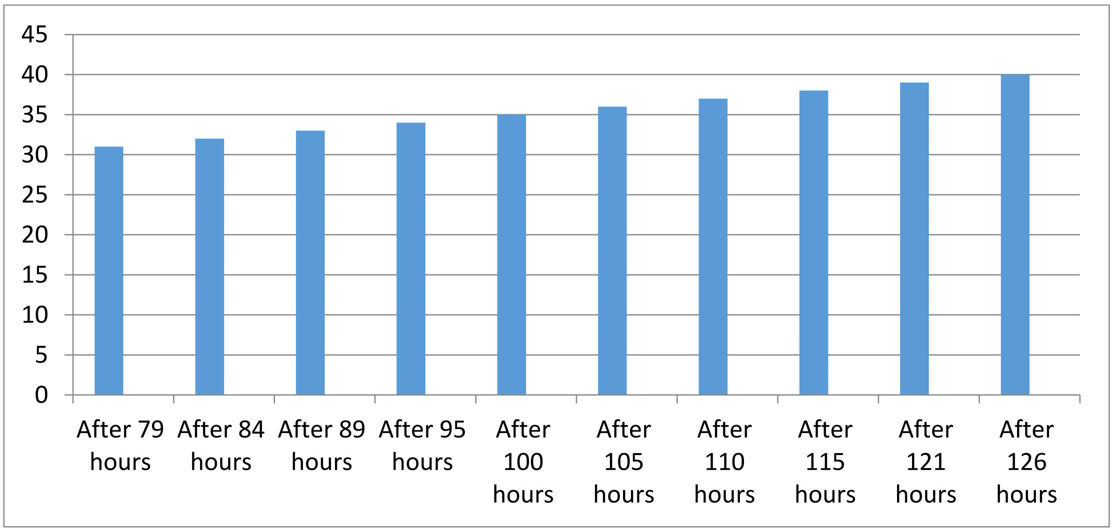

Fig.5

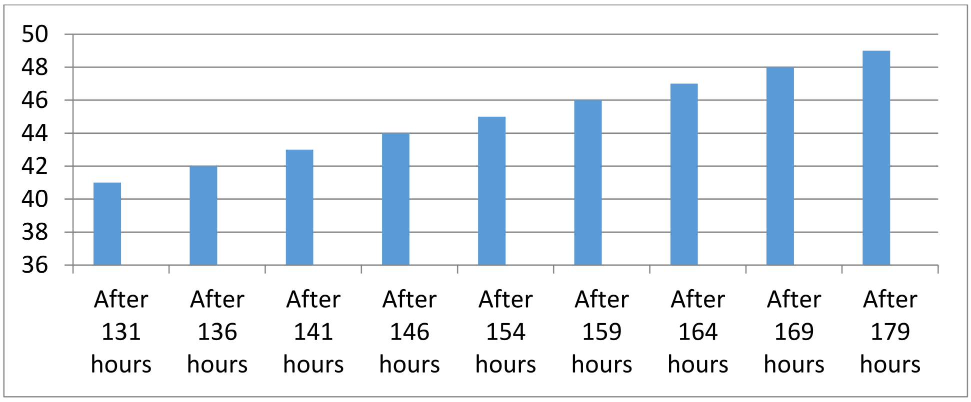

Fig.6

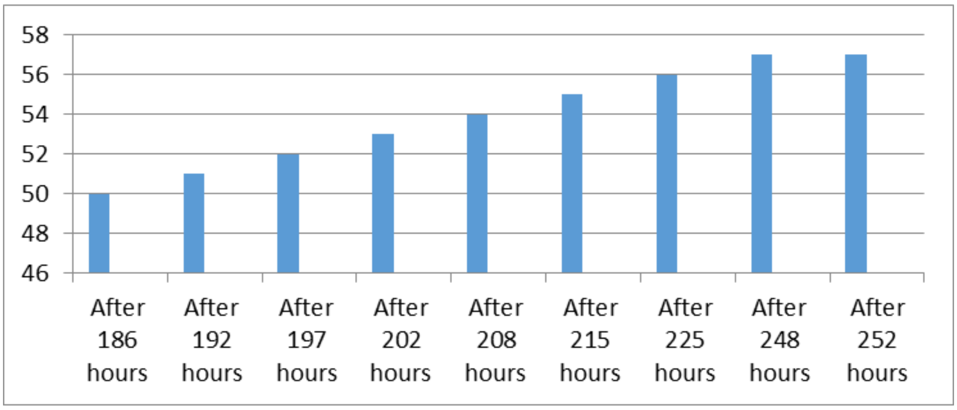

Fig. 7

Fig. (3 to 7) shows the degree of absorbing of the stone cube with NANORESTORE material.

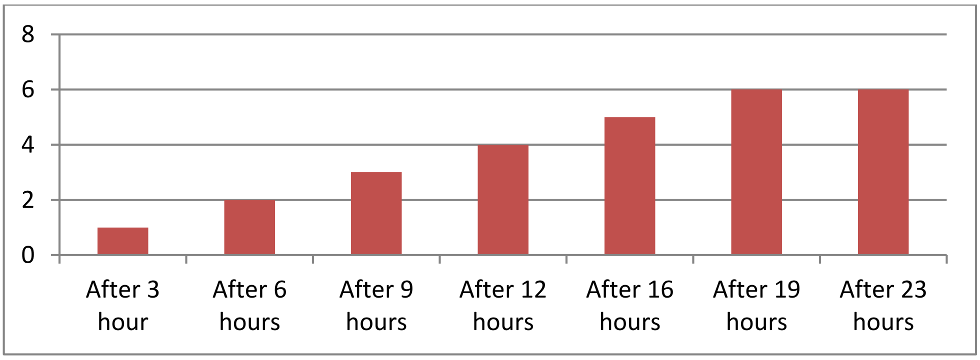

Fig. 8 shows the degree of absorbing the stone cube with the material of Remmers KSE 300 E

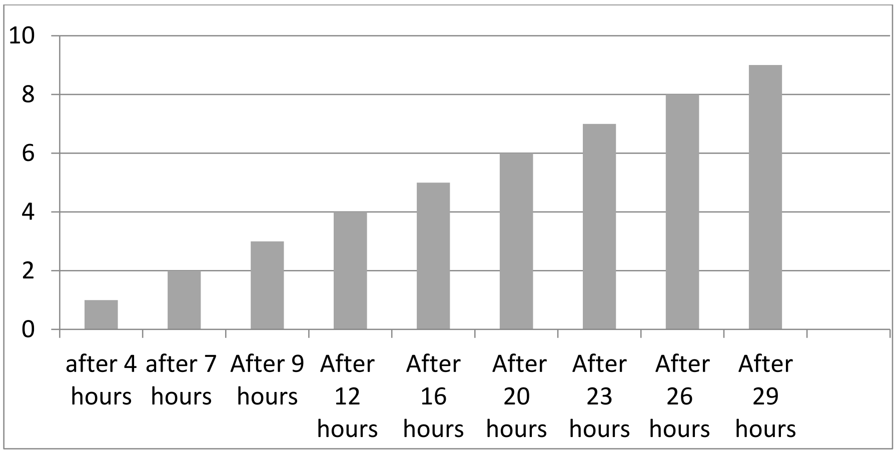

Fig.9

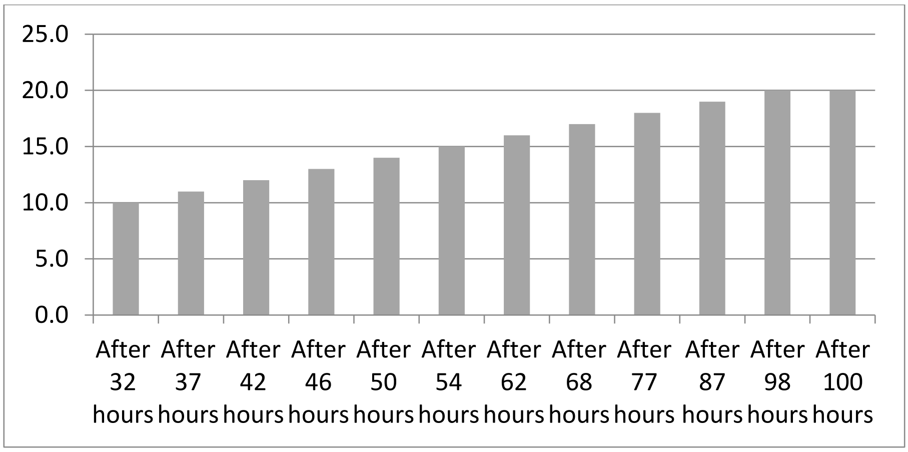

Fig.10

Fig. (9-10) shows the degree of absorbing of the stone cube with the material of SILRES BS OH 100.

Fig. 11 Measurement of the diameter of the dispersed consolidation materials.

Table. 1 shows the degree of absorbing stone cube from consolidation material with Meroviski and Immersion methods.

Consolidation materials	The degree of absorbing stone cube from consolidation material (Mirovski method)	The degree of absorbing stone cube from consolidation material (immersion method)
NANORESTORE	The cube absorbed 50 mm from consolidation material	The cube absorbed 17.5 mm from consolidation material
SILERS BS 100 OH	The cube absorbed 11.5 mm from consolidation material	The cube absorbed 10 mm from consolidation material
Remmers KSE 300 E	The cube absorbed 9 mm from consolidation material	The cube absorbed 10 mm from consolidation material
Paraloid B72 concentration 3%	The process of consolidating the stone didn't succeed with this material	The cube absorbed 30 mm from consolidation material
Paraloid B44 concentration 3%	The process of consolidating the stone cube didn't succeed with this material	The cube absorbs 20 mm from consolidation material
Paraloid B72, 3% + Nano Restore	The process of consolidating the stone cube didn't succeed with this material	The cube absorbed 20 mm from consolidation material
Paraloid B44, 3% + Nano Restore	The process of consolidating the stone cube didn't succeed with this material	The cube absorbed 15 mm from consolidation material

(3-3) General Appearance and Water repellency

We evaluated General Appearance of treated samples by visual evaluation and measured the water repellency properties by dripping water on the treated surface using a dropper and the results were assessed through visual evaluation also. **Table** 3.

(3.5) Physical properties measurement The measurement physical properties was carried out before and after treatment, The values of Denisity, porosity and water absorbation were recorded in **Table** (4.5), Fig. 21,22.

(3.4) Mechanical properties measurement The measurement of compression strength was carried out before and after treatment, using an Amsler compression-testing machine, three weeks after treating samples with Nanomaterials, Siloxan material, acrylic polymer and nanocomposite. The values of compression strength were recorded in **Table** (6), Fig.23.

(4) Results and Discussion.

(4-1) SEM Result.

The examination by SEM were used in order to study the ability of consolidation materials to consolidate and protect the limestone samples, the SEM images of the samples were shown in Figs.14- 20, The SEM micrographs of the untreated sample in Fig.13 showed the suffered from granular disintegration, and presence of some voids, The SEM examination of the sample treated with pure Nanorestore Fig.14 showed the ability in spread, and packaging of metal granules with a dense layer of polymer, deep penetration due to the small size of nanoparticles and using the substance at a concentration of 5% without dilution, the sample treated with SILERS BS 100 OH Fig.15 shows a homogeneous diffusion, good penetration, metal granulation, and high polymer density were in many places of the stone cube, the sample treated with Remmers KSE 300 E Fig.16 showed the penetration and Extensive spread of the material in addition to the presence of cracks in the polymer was clearly, the sample treated with pure Paraloid B-44 concentration 3% (see Fig.17) showed that Coating using (B44) succeeded in packing metal granules, filled the pores and spreading in some places, however, the film of Paraloid B-72 concentration 3% is more homogeneous, partially distributed between the grains of limestone and it covers partially the grains of limestone, Paraloid 72 can penetrate through cracks(see Fig.18), the sample treated with (paraloid B72 concentration 3%), and Ca $(OH)_2$/polymer nanocomposites Fig.19 showed a spreading homogeneous, thick and close the pores and forming a film around the metal granules while (paraloid B44 concentration 3%), and Ca $(OH)_2$/polymer nanocomposites Fig.20 had succeeded in packing metal granules, filled the pores and spreading in some places.

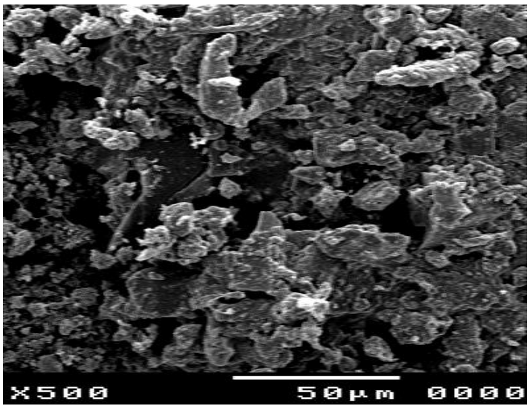

Figure (13) untreated sample under SEM 500x.

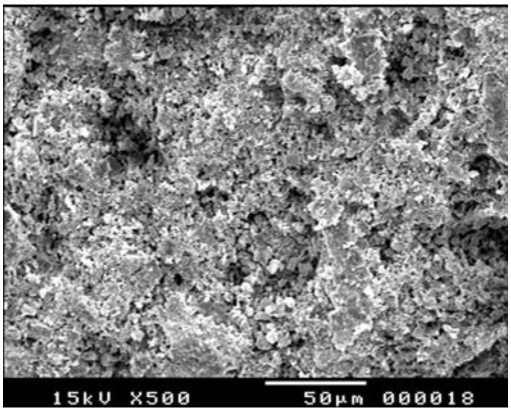

Figure (14) limestone cube treating with NANORESTORE under SEM 500x.

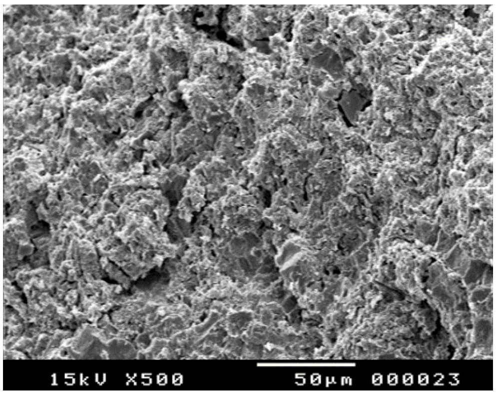

Figure (15) limestone cube treating with SILRES BS OH 100 under SEM 500x.

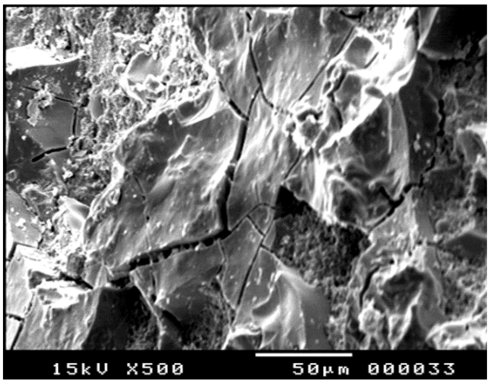

Figure (16) limestone cube treating with Remmers KSE 300 Ebunder SEM 500x.

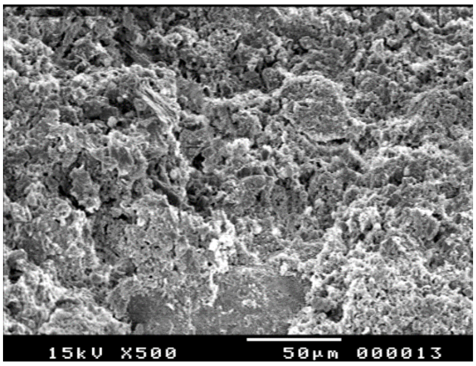

Figure (17) limestone cube treating with paraloid B 44 concentration 3% under SEM 500x.

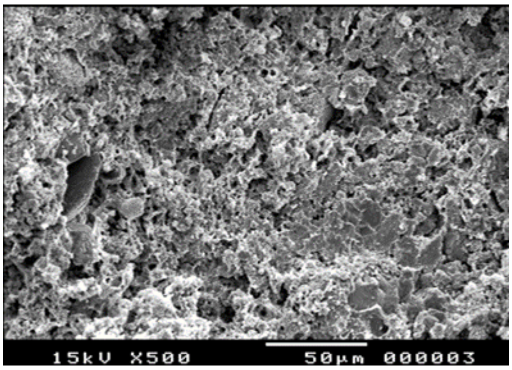

Figure (18) limestone cube treating with paraloid B 72 concentration 3% under SEM 500x.

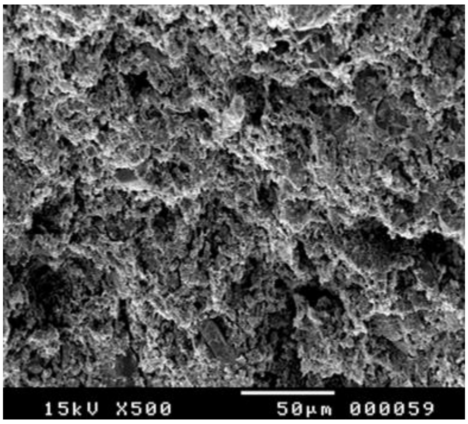

Figure (19) limestone cube treating with (paraloid B72 concentration 3%), and $Ca(OH)_2$ /polymer nanocomposites under SEM 500x.

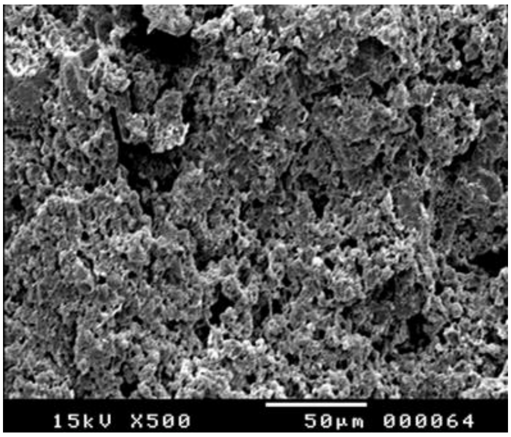

Figure (20) limestone cube treating with (paraloid B44 concentration 3%), and $Ca(OH)_2$ /polymer nanocomposites under SEM 500x.

(4-2) General Appearance and Water Repellents property of treated samples.

- **General Appearance** One of the conditions that must be met when choosing to consolidate materials is that do not affect the overall appearance of treated surfaces, the effect of consolidating materials on the overall appearance of the treated samples was evaluated by observing the differences in the color tones between the treated and untreated samples as well as comparing the color changes resulting from the consolidating materials with each other in order to choose the most suitable in of protection and not affect the overall appearance.
- **Water Repellents** The property that has been most sought in surface coatings is water repellency, the materials that prevent the penetration of water within the stones help to avoid this damage because the water of the main causes of the stone deterioration, this study showed that siloxan materials had achieved good result in Water repellent property [28], and how Nanorestore improved water repellency properties of acrylic polymer.

Table 3. Showing general appearance and water repellents property of treated samples.

Consolidation Materials	Effect of consolidating materials on the overall appearance of treated samples	Water Repellency	Photo of Water Repellency
Rammers KSE 300 E	Gloss and darkness	✓✓	
SILERS BS OH 100	Doesn't affect the surface	✓	
NANORESTORE	Doesn't affect the surface	_	
Paraloid B 44 concentration3%	Gloss and darkness	_	
Paraloid B 72 concentration 3 %	Gloss and darkness	_	
Paraloid B 72 concentration 3% + Nano Restore	Slight surface change	✓✓	
Paraloid B 44 concentration 3% + Nano Restore	Simple darkness	_	

- **Non-repellent water _, Medium waterproof ✓, repellent water✓✓.**

(4-3) Physical Properties: -

• **Density values** were determined for the samples treated with different consolidating materials. The results showed that the density values of treated samples were increased compared to the non-treated samples table 3, Fig 12. SILERS BS 100 OH achieved the highest value of density 2.16 KG/CM^3, followed by Rammers KSE 300 E and Paraloide B44 concentration 3% 2.06 KG/CM^3, then NANORESTORE material achieved 1.98 KG/CM^3, followed by (paraloid B72 concentration 3%), and $Ca(OH)_2$/polymer nanocomposites 1.95 KG/CM^3, then Paraloide B72 concentration 3% achieved 1.91 KG/CM^3 followed by (paraloid B44 concentration 3%), and $Ca(OH)_2$/polymer nanocomposites which achieved 1.90 KG/CM^3.

• **Apparent Porosity and Water Absorption**

The samples treated with the consolidation materials reduced the porosity ratio and the water absorption compared to the untreated samples, achieved the highest percentage 3.22%, 1.56%, followed by SILERS BS 100 OH which achieved 13.88%, 6.42%, then NANORESTORE achieved 18.9%, 9.50%, followed by (paraloid B72 concentration 3%), and Ca $(OH)_2$/polymer nanocomposites 17.77%, 9.09% then Paraloide B44 concentration 3%, 19.13%, 9.95% followed by Paraloide B72 concentration 3% which achieved 20.48%, 10.69 followed by (paraloid B44 concentration 3%), and Ca $(OH)_2$/polymer nanocomposites which achieved 21.95% , 11.51%.

Table 4. Values of Density for untreated, treated limestone samples.

Consolidation Materials	Size cm^3	Before Consolidation		After Consolidation		Rate change of Density %
		Weight G/ cm^3	Density	Weight G/ cm^3	Density	
Untreated sample	27	53.21	1.97	-	-	-
NANORESTORE	27	52.92	1.96	53.7	1.98	1.02
SILERS BS 100 OH	27	55.1	2	58.36	2.16	8
Rammers KSE 300 E	27	53.8	1.99	55.72	2.06	3.51
Paraloide B72 concentration 3%	27	50.91	1.88	51.7	1.91	1.59
Paraloide B44 concentration 3%	27.9	53.3	1.91	53.66	2.06	7.85
Paraloide, B72 concentration 3% + Nano Restore	27	51.90	1.92	52.8	1.95	1.56
Paraloide B44 concentration 3% + Nano Restore	26.1	49	1.87	49.78	1.90	1.60

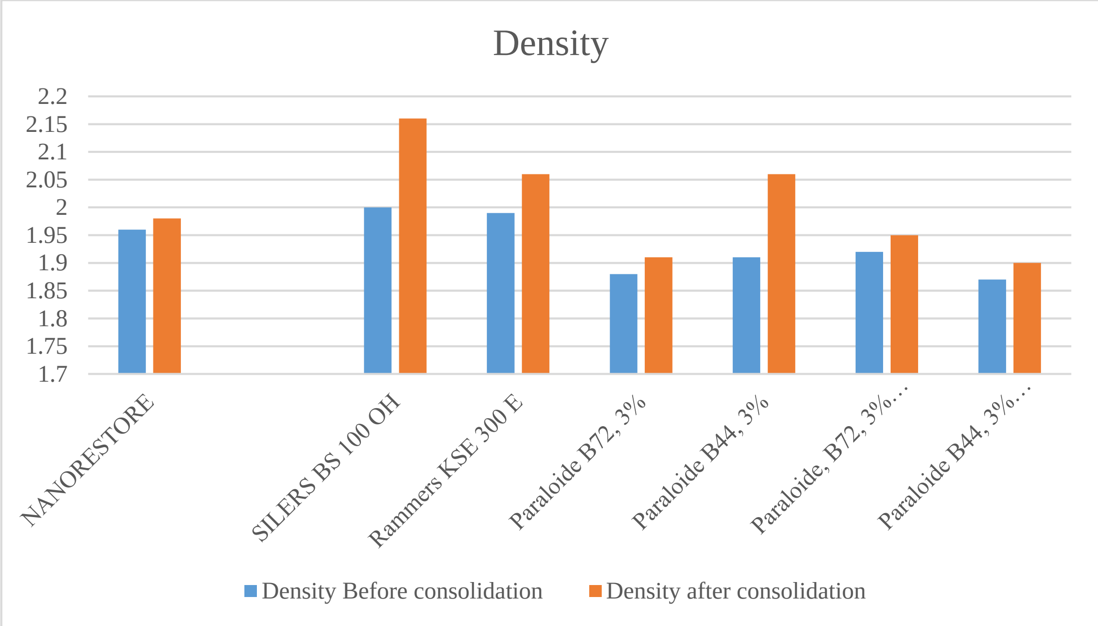

Fig.21 shows values of Density for untreated, treated limestone samples.

Table 5. Values of apparent porosity and water absorption for untreated, treated limestone samples.

Consolidation Materials	Size cm3	Before Consolidation				After Consolidation				Rate of change of Porosity %	Rate of change Water Absorption%
		Dry weight	Wet weight	Porosity	Water Absorption	Dry weight	Wet weight	Porosity	Water Absorption		
Untreated sample	27	53.21	58.84	20.85	10.58	-	-	-	-	-	-
NANORESTORE	27	56.83	63.06	23.07	10.96	53.7	58.80	18.9	9.50	18.07	13.3
SILERS BS 100 OH	27	55.1	61.41	23.3	11.45	58.36	62.11	13.88	6.42	40.42	43.9
Rammers KSE 300 E	27	53.8	59.93	22.7	11.39	55.72	56.59	3.22	1.56	85.8	86.3
Paraloide B72 concentration 3%	27	50.91	56.66	21.30	11.29	51.7	57.23	20.48	10.69	3.84	5.31
Paraloide B44 concentration 3%	279.	53.3	59.37	21.7	11.38	53.66	59	19.13	9.95	11.84	12.56

Paraloide, B72 concentrati on 3% + Nano Restore	27	51. 90	57. 23	19.7 4	10.26	52. 8	57. 6	17.7 7	9.09	9.97	11.40
Paraloide B44 concentrati on 3% + Nano Restore	26 1.	49	55. 07	23.2 5	12.38	49. 78	55. 51	21.9 5	11.51	5.59	7.02

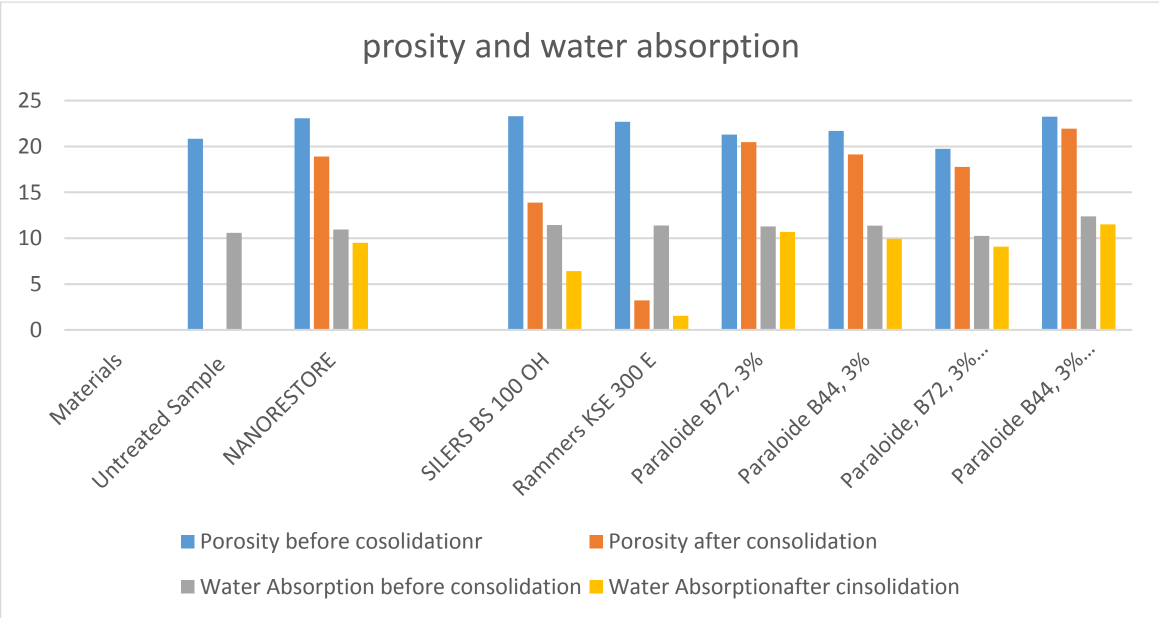

Fig.22 shows the values of apparent porosity and water absorption for untreated, treated limestone samples.

(4-4) Mechanical Properties: -

By evaluating the mechanical properties of the samples treated with different consolidating materials, the resistance of mechanical pressure of treated samples was increased by Rammers KSE 300 E Achieved the highest value of pressure resistance 98.14 KG/CM ^{2} followed by Paraloid B 44 concentration 3% .9804 KG/CM^2 then the sample which treated with (paraloid B72 concentration 3%), and Ca(OH)$_2$/polymer nanocomposites achieved 93.61 KG/CM^2, followed by NANORESTORE 88.83 KG/CM^2, followed by Paraloid B 72 concentration 3%, 84.09 KG/CM^2 then the sample which treated with (paraloid B44 concentration 3%), and Ca (OH)$_2$/polymer nanocomposites achieved 82.62 KG/CM^2 followed by SILERS BS 100 OH 82.62 KG/CM^2.

Table 6. Values of compressive strength for untreated, treated limestone samples.

Consolidation Material	Symbol	Kg /cm^2
Untreated Sample	A	54.74
Paraloid B 72 concentration 3 %	B	84.09
Paraloid B 44 concentration 3%	C	.9804
SILERS BS OH 100	D	67.83
Rammers KSE 300 E	E	98.14
NANORESTORE	F	88.83
Paraloid B 44 concentration 3 % + Nano Restore	G	82.62
Paraloid B 72 concentration 3 % + Nano Restore	H	93.61

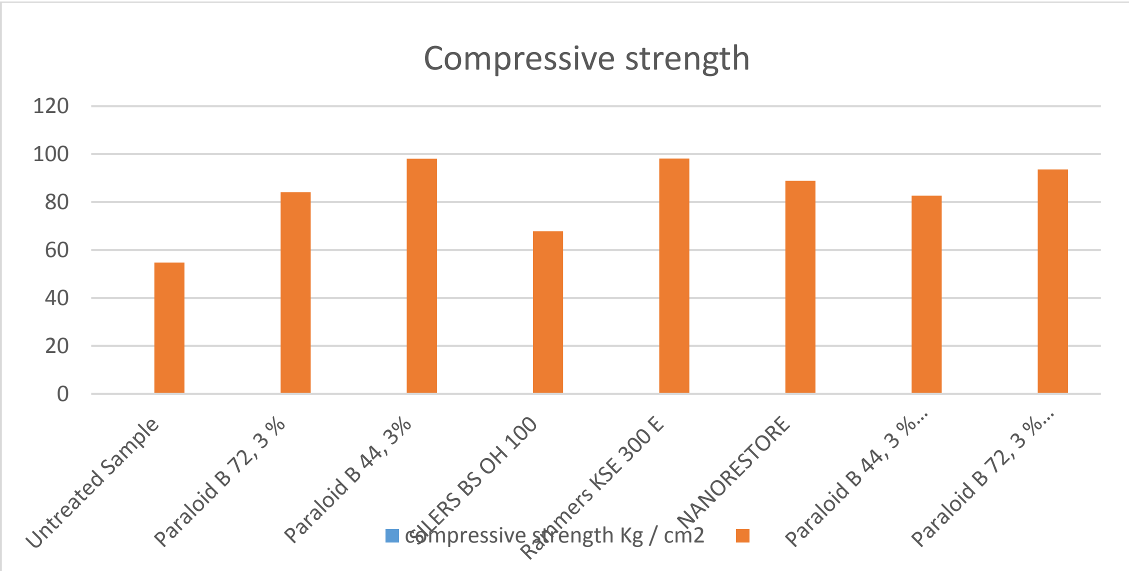

Fig.23 shows the values of compressive strength for untreated, treated limestone samples.

(6) Conclusion:

Hydroxide Calcium nanoparticles were added to Acrylic polymer to produce new Nanocomposite to improve its physicochemical and mechanical properties, the results showed how these materials achieve penetration of the dispersion, and how Nanocomposite improve physiochemical and mechanical properties compared to those treated with polymer without adding nanoparticles, such as paraloid B 72 concentration 3%, had achieved 84.09 Kg / cm^2,however, when added Nanorestore was achieved 93.61 Kg / cm^2 so its improve the mechanical properties, and the result of porosity and water absorption paraloide B 72 concentration 3% achieved after treatment 20.48%, 10.69%, but when samples treated with (paraloid B72 concentration 3%), and Ca

$(OH)_2$/polymer nanocomposites achieved 17.77%, 9.09%, in addition to density paraloid B 72 concentration 3%, had achieved after treatment 1.91 KG/CM^3, but when added Ca $(OH)_2$ nanoparticles achieved 1.95 $KG/CM^3$and about water repellent paraloide B 72 concentration 3%, Non-repellent water but it transfers to repellent water materials when added Ca $(OH)_2$ nanoparticles.
At the end of the research it̓s recommended to use calcium hydroxide nanoparticles and (paraloid B72 concentration 3%), and Ca $(OH)_2$/polymer nanocomposites to consolidate limestone according to its advantages that we came up with, in addition to not recommended to use Remmers KSE 300 E due to the result we reached as it̓s formation thick film and fill the pores of treated samples in addition to small and large cracks which clearly emergence.

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