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TESTING SINGLE AND MIXED RESINS FOR CONSOLIDATING MODERATELY WEATHERED LIMESTONE OF ARCHAEOLOGICAL SITES, NEW APPLIED TECHNIQUES

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Abstract

Weathering is one of the most aggressive processes acting on natural and artificial materials world-wide. So, this paper aims to examine the efficacy of three resins highly recommended as consolidating material for oolitic limestone. These resins are namely; Ethyl Silicate, Premal-AC33, and Paraloid-B80. Petrographic, mineralogical, geotechnical properties, and durability investigations have been conducted for this limestone before treatment with such resins. The treatment with these resins has been conducted through two regimes namely; repeated brushing, and total impregnation within each resin at each level of concentration. Samples' surface color, resin's penetration depth, rock's geotechnical and durability properties' limits are the main basis of examining these resins. The net result indicated that Paraloid-B80 dissolved in acetone, ethyl silicate "dissolved in ethyl alcohol" mixed with Paraloid-B80 "dissolved in acetone or toluene" verified the best results as stone consolidating material. Rock's pore size distribution is one of the main parameters controlling rock's durability before and/or after consolidation with a given resin. Resin's viscosity controls resin's penetration depth within a given rock.

***Keywords**: Oolitic limestone; Ethyl silicate; Primal-AC33; Paraloid-B80; Consolidation*

Introduction

The archaeological sites worldwide are remains of great value, from the historical and structural points of view, for a given nation(s) lived at a period that we did not live. Such remains attract our attention and act as one of the main economic resources to the countries through tourism. The constructional materials of the archaeological sites are of a wide variety (e.g. organic and inorganic component). Such components suffer weathering at rates and intensities based on the prevailing environmental conditions and building materials' properties [1, 2]. As the constructional materials of the archaeological sites are almost natural and/or artificial stones, then, several researchers have been concerned with such stones that present variable weathering forms and damage categories [1, 3, 4]. The weathering features are ranging from stone's surface discoloration, by salt efflorescence and/or dust accumulation, up to partial to total collapse of the whole archaeological site [1, 5]. The damage category of a given archaeological site is not only based on how much back weathering (volume of rock material had been lost) took place at the stone's surface but also on the percentage of loss of stone's surface inscriptions and/or paints [3, 6-8].

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Consequently, the current study aims to examine the capability of each of ethyl silicate, Primal-AC33, Paraloid-B80 resins to consolidate constructional blocks *particularly the oolitic limestone* of slightly to moderately weathered archaeological sites. This type of rocks act as the main building stone for a major sector of the archaeological sites in Lower Egypt that presents moderate damage category and require urgent decision of restoration [9]. Re-construction (replacement of the severely weathered blocks with new ones of the same dimensions and geometry as the original ones) is not highly recommended as we lose the originality of the archaeological site. So, strategy of consolidation with a suitable resin or mixture of resins following a planned protocol of such consolidating materials must be rapidly applied and followed up. The resins under consideration had been previously used as stone's surface consolidating materials for the lime-mud facies [10-12] and the net results indicated that Premal-AC33 verifies the maximum penetration depth up to 1.5mm, kept stone's surface breathability, increased rock's durability up to 15 cycles of artificial salt weathering with durability *class D*, increased stone's bulk density by the value 11.5% and reduced its total porosity by the value 6.9%.

For the current study, the three resins mentioned above have been tested following the protocol mentioned in the methodology section to arch-evaluation of them as a hardening material particularly for the *oolitic limestone* using advanced and non-destructive tools.

Materials and Methods

The resins (namely Paraloid-B80, Premal-AC33 and ethyl silicate) have been prepared using suitable solvents and prepared at definite levels of concentration, then, the efficacy of each resin has been examined based on the following points:

- improving the limits of rock's petrophysical parameters' limits after consolidation;
- reduction of Salt Susceptibility Index (SSI) of this limestone by changing its Pore Size Distribution (PSD); this is one of the main core points of resins' efficacy in rock's consolidation technique;
- keeping rock's surface color after consolidation as before consolidation;
- verifying the maximum penetration depth of the resins that can be measured using ultrasonic waves;
- keeping rock's breathability *by keeping a noticeable percentage of rock's porosity* after consolidation with each resin;
- verifying the ultimate rock's durability to weathering *particularly by salts* after consolidation compared with that before consolidation;

Sample's Preparation and its Testing

Before consolidation

The rock samples have been cut into cuboids of 7cm length, 5cm widths using a diamond saw to avoid using water during cutting that might alter rock's physical properties. The rock's texture and composition have been investigated using a transmitting polarizing microscope (TPM) and scanning electron microscope (SEM), not only that but also X-ray diffraction (XRD) has been used for rock's mineral identification. This is to find out if the rock under investigation has impurities, e.g. clays, that might affect its durability to slaking or not.

Before and after consolidation

The rate of water absorption for the control and consolidated limestone samples have been tested to rank them based on this parameter that affect rock's weathering susceptibility particularly by salts. Not only this but also the samples' petrophysical parameters (including total porosity, effective porosity, water absorption and bulk density) have been examined by impregnation method [13]. Then, the percentage of progress in limits of these parameters have been computed and ranked to find out which resin(s) verified the ultimate progress in such properties that also control rock's durability.

The rock's total volume of connected porosity (P_c), grain density and bulk density have been measured for such facies using mercury intrusion porosimetry *Auto-pore MIP-5900* then, the SSI has been computed using *S. Yu and C. Oguchi* [8] equation:

$$SSI = (I_{pc} + I_{pm0.1}) (P_{m5} / P_c) \quad (1)$$

where SSI is the rock's *Salt Susceptibility Index*, I_{pc} is the *Index of Connected Pores*; $I_{pm0.1}$ is the *Index of 0.1μm radius Micro-pores*; P_{m5} is the *Volume of the 5μm radius rock Micro-pores*, and P_c is the *Volume of the Connected Pores*.

The results of *Auto-pore MIP-5900* presenting the rock's SSI can be interpreted using the classification of *S. Yu and C. Oguchi* [8] listed in Table 1. This is to be compared with the PSD and SSI of the same facies after consolidation with resins under consideration. The end of this investigation aims to test the efficacy of each resin in increasing rock's durability to weathering (in particular salt weathering) that dominates in the Middle east [14, 15].

Table 1. Classification of salt susceptibility index limits and its interpretation (*Yu and Oguchi*, 2010)

SSI	Interpretation
$0 \leq SSI < 2$	Exceptionally salt resistant
$2 \leq SSI < 3$	Very salt resistant
$3 \leq SSI < 6$	Salt resistant
$6 \leq SSI < 12$	Salt prone
$12 \leq SSI < 16$	Very salt prone
$16 \leq SSI < 20$	Exceptionally salt prone

Resins' preparation for stone consolidation

The resins under investigation have been prepared at specific levels of concentration. Ethyl silicate has been prepared at two levels of concentration, one level has been prepared by mixing 100mL of this resin with 150mL of ethyl alcohol, and the other level by mixing 150mL of the same resin with only 100mL of ethyl alcohol. Premal-AC33 has been also prepared at two levels of concentration, one of them by dissolving 2g of this resin in 400mL distilled water, and the other by dissolving 6g of the same resin in 400mL distilled water. Paraloid-B80 has been prepared by dissolving 15g of B80 in 300mL acetone and dissolving 15g of B80 in 300mL Toluene.

Samples' treatment with resins

Two systems of treatments have been followed, namely; multiple-brushing and total Impregnation systems. The former one is to brush the sample with the resin till surface saturation over five separate days and the same period for the samples fully impregnated in the resin solution. Then, the samples have been left for three days for curing. After that, the different measurements for resins' evaluation have been conducted.

Resins Evaluation Techniques

The resin's maximum penetration depth within the consolidated rock

It is one of the main items of resin's evaluation to be used for consolidating the slightly to moderately weathered rocks. This can be conducted using different tools, but the ultrasonic waves are the easiest and cheapest tool to be used [16]. The samples' preparation for such test have been conducted following the method of *M. Montoto et al.* [17], *A. Punuru et al.* [18], *A. Maria et al.* [19], *S. Stefan and M. Anne* [20]. Then, measuring and computing the velocity of these waves C_p for each sample have been conducted, using the ultrasonic waves (Fig. 1), following the method and the equations of *P. Kapranos et al.* [21], listed below:

$$[(A_o + A_t)/(A_o - A_t)] = X \quad (2)$$

$$(\pi n/Qc) = \{\ln [2/(1 - X)]\}/(1 + X) \quad (3)$$

$$C_p = 2Lf/n \quad (4)$$

where: A_o is the magnitude of the initial waves and at is the magnitude of the waves at the steady state, Q_c is an internal friction at a given mode of measuring; C_p is the ultrasonic wave velocity (km/sec); L is the sample's length (cm); n is the mode at which we get the best echo-form of the waves; f is the frequency of the waves at the best echo-form.

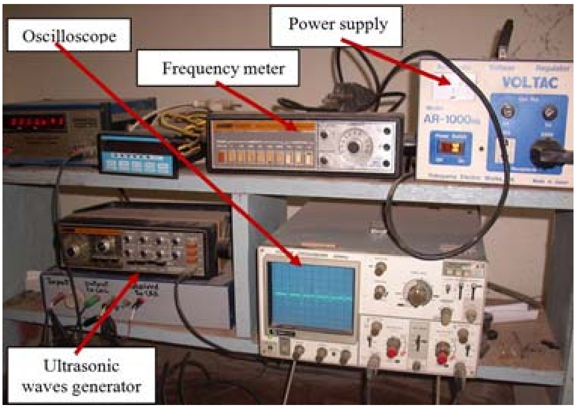

Fig. 1. Image of the Magneto-structive ultrasonic waves' tool used for the measurements in the current study

Rock's durability after treatment:

It is to be done using the artificial salt weathering to test the efficacy of each resin at each level of concentration. Salt solution of anhydrous sodium sulfate has been prepared by dissolving 71g of this salt in one liter of bi-distilled water to get salt solution of 0.5M concentration. Then, the samples have been immersed in this solution following the regime of CPI (Continuous Partial Immersion) as shown in Figure 2.

This salt, thenardite (Na_2SO_4), is hydrated to mirabilite ($Na_2SO_4 \cdot 10H_2O$) at temperature less than 32.4ºC and relative humidity more than 71% [22]. The test has been conducted using Age Accelerating Chamber (AAC) fixed for 12 hours at hydration conditions of this salt (i.e. temperature 20ºC and relative humidity 80%) and 12 hours at dehydration conditions of this salt (i.e. temperature 40ºC and relative humidity 30%). The 24 hours represent one complete cycle of hydration-dehydration, and the test has lasted out after 30 cycles. Photo-documentation of the weathering forms recorded on each of the resin-treated limestone sample as well as the resin un-treated (control) sample have been conducted for some representative cycles of this test. The weight loss percentage has also been computed at the end of this test for each of these samples. This is to numerically rank the efficacy of these consolidating resins where the most efficient one is that result in the lowest weight loss.

Results and Discussion

Before consolidation

The petrographic and mineralogic investigations, for the rock under investigation, revealed that it is oolitic limestone with packstone texture and bio-sparite in composition [23, 24]. The dominant mineral composition of this rock is calcite as shown in the X-ray diffractograph (Fig. 3).

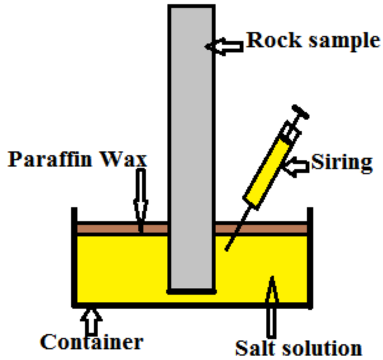

Fig. 2. Sketch presenting the artificial salt weathering through Continuous Partial Immersion (CPI) regime

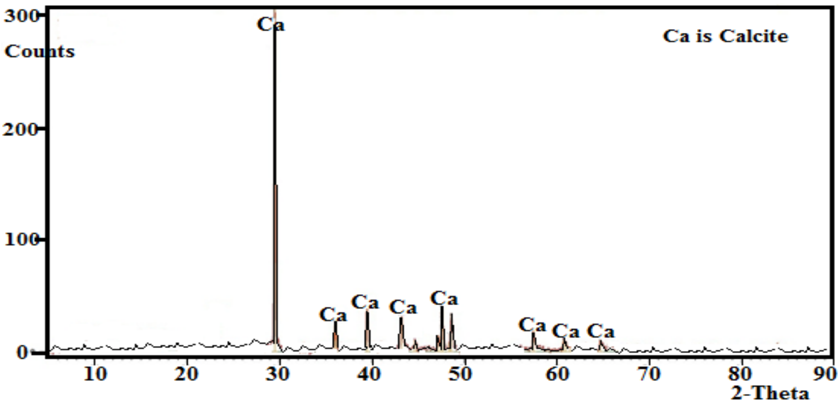

Fig. 3. X-ray diffractograph presenting the dominant mineral composition of the limestone used in the current study before consolidation.

Rock's pore size distribution *PSD* and its Salt Susceptibility Index (SSI) - it has been investigated for two samples using Mercury Intrusion Porosimetry (MIP) before treatment with any of the resins under investigation, the results are listed in Table 2. It has been indicated that this rock is classified as very salt prone with high tendency to the upper limit of salt prone class based on *S. Yu and C. Oguchi* [8] classification. The critical pore radius that results in this class, for this rock, is almost in the range of 2.5÷5.0μm (Table 2).

Before and after consolidation

Rate of water absorption for control and consolidated samples: the rate of water absorption has been tested, for the control and the consolidated limestone samples, by weighing the samples over ranges of time for 24 hours where stability in samples' weight have been achieved, the results are listed in Table 3. It is clear that the general trend of water absorption rate is high at the first few minutes of impregnation, then reduced on time progress with individual deviation from this trend for some consolidated samples. This deviation is expected to be a result of variation in rock's pore size distribution after treatment with each the prepared resins [12].

Using these data, the water absorption percentage for the control and consolidated samples has been computed, then, the samples have been ranked and graded based on their water absorption (%) to reflect in an indirect way the impact of these resins on progressing the rock's petrophysical parameters' limits (Table 3).

Table 2. Percentage of pore sizes and salt susceptibility index for two reference limestone samples before treatment with the resins under investigation

Sample No.	SSI		Percentage of each pore size						
	SSI Interpretation	SSI Value	> 5.0	2.5 - 5.0	1.0 - 2.5	0.5 - 1.0	0.1 - 0.5	0.05 - 0.1	less than 0.05
R	VSP	12.61	1.11	77.41	8.23	1.21	6.78	2.22	3.04
R	VSP	12.63	3.59	76.84	5.34	1.83	6.88	2.41	3.11

**R is reference sample; SSI is salt susceptibility index; VSP is Very Salt Prone*

After consolidation

The rock's surface color change after its treatment "consolidation" and curing is the first point to be recorded and considered. This point is of value particularly for the archaeological sites i.e. the resin that results in a noticeable change in stone's surface color must be rejected from the archaeological point of view. In the current study, it has been visually recorded that none of these resins resulted in change of stone's surface color.

Rock's petrophysical parameters' limits after consolidation: the petrophysical parameters including rock's porosity, effective porosity, water absorption, and bulk density have been measured for the control and consolidated samples (Table 4). The percentage of decrease in rock's porosity, effective porosity and water absorption on one hand, and increase in rock's bulk density have been computed and listed in table 4.

Then, the ranges of increase or decrease (%) of these parameters have been conducted (classifying them into five classes of equal ranges) to rank them with one of five grades starting from very bad (VB) to excellent (E) (Table 5).

Table 4. Limits of petrophysical parameters for the reference and consolidated limestone samples, the percentage of increase or decrease in these limits and grades of the treated samples

Sample code	W1 (g)	W2 (g)	W3 (g)	a (g)	V (cm^3)	Petrophysical parameters				Percentage of decrease in Φ	Percentage of decrease	Percentage of decrease	Percentage of increase in Ϭd	Grading of the treated
						(Φ) %	(Φe) %	(Wa) %	(Ϭd) g/cm^3					
R	327	375	194	4.2	R	25.5	26.0	14.7	1.77					
1	276	301	150	4.2	1	16.3	16.0	9.0	1.78	36.21	38.38	38.74	0.56	M
2	350	386	191	4.2	2	18.1	18.0	10.2	1.76	29.07	30.77	30.60	-0.57	VB
3	351	383	201	4.2	3	16.6	16.9	8.9	1.89	35.03	35.23	39.55	6.35	M
4	353	379	190	4.2	4	14.0	13.7	7.5	1.82	45.15	47.29	48.98	2.75	G
5	368	388	219	4.2	5	10.4	11.7	5.5	2.12	59.04	54.98	62.55	16.51	E
6	332	366	190	4.2	6	18.0	18.7	10.1	1.85	29.42	28.16	31.41	4.32	B
7	315	346	181	4.2	7	17.3	18.1	9.7	1.86	32.13	30.50	34.12	4.84	B
8	359	387	213	4.2	8	14.4	15.5	7.7	2.02	43.62	40.30	47.69	12.38	G
9	376	404	220	4.2	9	13.9	15.1	7.6	1.99	45.39	42.14	48.71	11.06	G
10	401	433	240	4.2	10	15.0	16.1	7.9	2.03	41.19	38.15	46.27	12.81	G
11	344	377	205	4.2	11	16.6	18.9	9.7	1.95	34.99	27.43	34.26	9.23	B
12	298	335	179	4.2	12	20.4	22.6	12.1	1.87	19.97	13.10	17.91	5.35	VB
13	302	320	177	4.2	13	10.8	12.3	6.0	2.05	57.59	52.63	59.16	13.66	E
14	359	384	211	4.2	14	12.1	13.7	6.7	2.03	52.41	47.48	54.34	12.81	E

W1, W2, W3, a, V are sample's weight at dry state, water saturated state, sample's apparent weight, thread suspension weight and sample's volume respectively; Φ, Φe, Wa and Ϭd are porosity, effective porosity, water absorption and bulk density respectively; GAPP is grading including All petrophysical parameters; VB, B, M, G, E are very bad, bad, medium, good, and excellent progress in petrophysical parameters.

Table 5. Classes and grades of decrease or increase in percentage of the petrophysical parameters measured for the consolidated limestone samples

Classes range of percentage of decrease in Φ	20 - 27.8	27.8 - 35.6	27.8 - 35.6	43.4 - 51.2	51.2 - 59
Grades of Φ	VB	B	B	G	E
Classes range of percentage of decrease in Φe	13.1 - 21.5	21.5 - 29.9	21.5 - 29.9	38.3 - 46.7	46.7 - 55.1
Grades of Φe	VB	B	B	G	E
Classes range of percentage of decrease in Wa	17.9 - 26.9	26.9 - 35.9	26.9 - 35.9	44.9 - 53.9	53.9 - 62.9
Grades of Wa	VB	B	B	G	E
Classes range of increase of Ϭd	0.6 - 3.9	3.9 - 7.2	3.9 - 7.2	10.5 - 13.8	13.8 - 17.1
Grades of Ϭd	VB	B	B	G	E

VB, B, M, G, E are very bad, bad, medium, good, and excellent grades respectively, in petrophysical parameters.
Φ, Φe, Wa and Ϭd are porosity, effective porosity, water absorption and bulk density respectively.

Then, these grades and classes of the parameters have been used in combination to rank the samples consolidated with each resin regarding its impact in progressing the petrophysical limits of this limestone (Table 6).

Table 6. Grading of the consolidated limestone samples based on the classification in Table 5.

			Grades and Classes of Porosity							
			E	*G*	*M*	*B*	*V.B.*			
			51.2 - 59	43.4 - 51.2	35.6 - 43.4	27.8 - 35.6	20 - 27.8			
Grades and Classes of	*V.B.*	0.6 - 3.9	*B*	*B*	*V.B.*	*V.B*	*V.B.*	13.1 - 21.5	*V.B.*	Grades and Classes of effective
	B	3.9 - 7.2	*M*	*M*	*B*	*B*	*B*	21.5 - 29.9	*B*	
	M	7.2 - 10.5	*G*	*G*	*M*	*M*	*B*	29.9 - 38.3	*M*	
	G	10.5 - 13.8	*G*	*G*	*G*	*M*	*M*	38.3 - 46.7	*G*	
	E	13.8 - 17.1	*E*	*E*	*G*	*G*	*G*	46.7 - 55.1	*E*	
			53.9 - 62.9	44.9 - 53.9	35.9 - 44.9	26.9 - 35.9	17.9 - 26.9			
			E	*G*	*M*	*B*	*V.B.*			
			Grades and Classes of Water Absorption							

VB, B, M, G, E are very bad, bad, medium, good, and excellent grades tespectively, in petrophysical parameters

This ranking has been listed in Table 4 for each one of the treated rock samples. Grouping of the consolidated samples (Table 7) facilitates an understanding the impact of the resins under investigation on progressing of the rock's petrophysical limits that plays an effective role in its durability to weathering particularly to salts.

Table 7. Grouping of the consolidated samples based on grade of each sample achieved from all their petrophysical parameters

	VB	**B**	**M**	**G**	**E**
Sample code	2	1	3	8	5
	12	6	-	9	13
	-	7	-	10	14
	-	11	-	4	-

VB, B, M, G, E are very bad, bad, medium, good, and excellent grades tespectively, in petrophysical parameters

The rock's PSD has been measured and the SSI has been computed for all samples treated with each resin (Table 8). This is to find out which resin results in reduction of rock's susceptibility to salt weathering i.e. increasing rock's durability. It has been noted that Paraloid-B80 dissolved in Acetone (samples code 3 and 4), at the level of concentration mentioned in table 8, verified better results than others where the limestone is altered from very salt prone to salt prone and close to the Salt resistant limit on its consolidation with this resin. The highest percentage of pore radii that verified the lowest rock's salt susceptibility is 0.05÷1.00µm.

Regarding to rock's breathability; all resins under investigation keep rock's breathability as it kept a considerable percentage of total connected porosity as indicated from the MIP results (Table 8). Deviation of rock's PSD, towards smaller radii ranges, results in decreasing rock's SSI i.e. the consolidated samples became salt prone and salt resistant (Table 8) compared with the control (untreated) samples that are Very salt prone one (Table 2) but all still have a considerable percentage of total porosity.

Penetration depth of the resins: besides improving rock's geotechnical properties, resin's penetration depth is one of the most important items that must be considered for the efficacy evaluation of a given resin as stone consolidating material. The more the penetration depth of a given resin in the rock, the better of its consolidation capability is expected. It has been measured, in the current study, for the resins under investigation using the ultrasonic waves (Table 9). The maximum penetration depth has been recorded to be 4.98mm for the samples treated with Paraloid-B80 dissolved in 300mL acetone particularly applied by brushing technique than impregnation technique. This is followed by the samples treated with mixture resins (samples number 13 and 14) that show penetration depth around 4.0mL (Table 9).

Table 8. Pore size distribution and rock's salt susceptibility index for the limestone samples treated with the resins under investigation

Sample No.	Pore size distribution *micron*							SSI	
	> 5.0	2.5 - 5.0	1.0 - 2.5	0.5 - 1.0	0.1 - 0.5	0.05 - 0.1	< 0.05	SSI Value	SSI Interpretation
1	3.85	1.55	27.10	22.49	25.08	9.44	10.49	10.37	SP
2	2.99	2.24	33.47	18.42	21.33	11.00	10.55	11.27	SP
3	0.78	0.04	5.05	23.64	29.90	33.08	7.51	4.51	SP ~ SR
4	5.75	0.05	1.35	39.00	25.05	21.86	6.94	4.32	SP ~ SR
5	5.75	15.06	6.35	39.00	25.98	3.75	4.11	11.63	SP
6	19.89	19.53	16.10	19.02	14.25	7.73	3.50	10.75	SP
7	5.72	24.16	1.28	20.27	36.55	3.45	8.57	11.04	SP
8	7.18	21.11	18.86	16.46	26.69	5.03	4.67	10.45	SP
9	3.61	27.23	19.84	13.94	22.84	9.31	3.23	10.3	SP
10	8.34	21.43	19.25	15.49	26.01	7.45	2.03	9.88	SP
11	3.49	2.24	37.30	21.14	20.94	9.84	5.05	11.2	SP
12	4.39	10.70	31.46	17.04	23.88	3.41	9.12	10.03	S.
13	8.04	10.53	27.50	14.67	19.76	10.65	8.85	9.49	SP
14	3.51	23.22	15.62	14.06	29.64	7.72	6.23	10.99	SP

SSI is salt susceptibility index, SP is salt prone and SR is salt resistant.

Table 9. The penetration depth of each of the resins under investigation within the limestone samples using the ultrasonic waves

Sample No.	Resin type and its preparation	Method of rock sample's treatment	Max. penetration depth (mm)
1	15g of Paraloid B-80 in 300mL Toluene	Impregnation	2.021
2	15g of Paraloid B-80 in 300mL Toluene	Brushing	2.121
3	15g of Paraloid B-80 in 300mL Acetone	Impregnation	4.651
4	15g of Paraloid B-80 in 300mL Acetone	Brushing	4.978
5	150mL Ethyl silicate in 100mL Ethyl Alcohol	Brushing	1.103
6	150mL Ethyl silicate in 100mL Ethyl Alcohol	Impregnation	1.026
7	100mL Ethyl silicate in 150mL Ethyl Alcohol	Impregnation	2.104
8	100mL Ethyl silicate in 150mL Ethyl Alcohol	Brushing	2.131
9	2g of Premal in 400mL distilled water	Brushing	2.011
10	2g of Premal in 400mL distilled water	Impregnation	2.001
11	6g of Premal in 400mL distilled water	Brushing	3.221
12	6g of Premal in 400mL distilled water	Impregnation	3.218
13	150mL Ethyl silicate in 100mL Ethyl Alcohol mixed with 15g of Paraloid B80 in 300mL Acetone	Impregnation	3.997
14	150mL Ethyl silicate in 100mL Ethyl Alcohol mixed with 15g of Paraloid B80 in 300mL Toluene	Impregnation	3.957

Artificial weathering results: it is among the most comprehensive and expressive techniques for resins' efficacy evaluation as a consolidating material for a given rock. The mechanism is to expose the consolidated rock sample to repeated cycles of artificial salt weathering. The best resin is that verifying the least weight loss percentage at the end of this test. The results of the treated samples indicated that the samples with codes 3, 4, 13 and 14 verified the least weight loss percentage (Table 10). Photo-documentation has been conducted before and throughout test progress for both Control and resin-treated samples to visually document what has happened for all these samples on one hand, and for each resin-treated sample on test progress on the other hand (Figs. 4, 5 and 6).

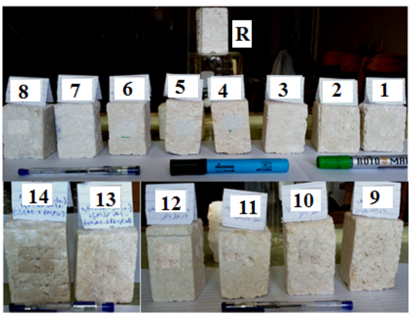

Fig. 4. Photo-documentation for the control *R* and fourteen limestone samples treated with the resins under investigation *before artificial weathering* with anhydrous Na_2SO_4

Fig. 5. Photo-documentation for the control "R" and fourteen limestone samples, treated with the resins under investigation, after 6 cycles of *artificial weathering* with anhydrous Na_2SO_4

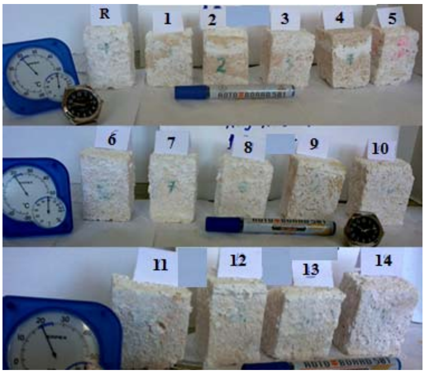

Fig. 6. Photo-documentation for the control R and fourteen limestone samples, treated with the resins under investigation, after 10 cycles of *artificial weathering* with nnhydrous Na_2SO_4

Table 10. Weight loss percentage for the reference and resin consolidated limestone samples using Anhydrous Sodium Sulfate for 30 cycles of artificial weathering

Sample No.	Resin type and Concentration	Weight loss %	Method of rock sample's treatment	Weight loss %
R	Untreated (Control or Reference) sample	19.98	untreated	19.98
1	15g of Paraloid B-80 in 300mL Toluene	5.5	Impregnation	5.5
2	15g of Paraloid B-80 in 300mL Toluene	5.32	Brushing	5.32
3	15g of Paraloid B-80 in 300mL Acetone	1.12	Impregnation	1.12
4	15gm of Paraloid B-80 in 300mL Acetone	1.04	Brushing	1.04
5	150mL Ethyl silicate in 100mL Ethyl Alcohol	7.87	Brushing	7.87
6	150mL Ethyl silicate in 100mL Ethyl Alcohol	8.33	Impregnation	8.33
7	100mL Ethyl silicate in 150mL Ethyl Alcohol	5.93	Impregnation	5.93
8	100mL Ethyl silicate in 150mL Ethyl Alcohol	5.66	Brushing	5.66
9	2g of Premal in 400mL distilled water	9.53	Brushing	9.53
10	2g of Premal in 400mL distilled water	9.48	Impregnation	9.48
11	6g of Premal in 400mL distilled water	8.73	Brushing	8.73
12	6g of Premal in 400mL distilled water	8.69	Impregnation	8.69
13	150mL Ethyl silicate in 100mL Ethyl Alcohol mixed with 15g of Paraloid B-80 in 300mL Acetone	1.27	Impregnation	1.27
14	150mL Ethyl silicate in 100mL Ethyl Alcohol mixed with 15g of Paraloid B-80 in 300mL Toluene	1.43	Impregnation	1.43

The evaluation of a given resin for treatment of a moderately weathered rock is not an easy job to be conduct as it must pass by series of investigations to get a satisfactory and accurate confirmation of the resin's efficacy for consolidation. Previous literatures in this field appear to be mainly based on testing stone's surface color before and after consolidation as well as rock's durability to salt weathering by complete impregnation, rather than continuous partial immersion, in salt solution(s) of single and/or salt mixtures [25]. So, the current study has been conducted based on a detailed and systematic protocol for such evaluation applied for oolitic limestone that had been widely used for the Greco-Roman archaeological sites in Egypt.

The first step to be considered in resins' evaluation is to check the stone's surface color after treatment compared with its color before this treatment. The visual investigation indicated that no obvious stone's surface color change had been occurred on using any of these single or combined resins at all levels of concentration mentioned in the current study (Fig. 4).

The limestone under investigation has high limits of petrophysical parameters (mainly porosity and water absorption, and low limits of bulk density) before treatment with any of these resins (Table 4). So, it presents high limits of weathering particularly by salts on its use for construction/re-construction of the archaeological sites in lower Egypt. This is confirmed on measuring its pore size distribution (Table 2) as it presents very salt prone tendency with pore radii almost within the range of 2.5÷5.0μm. The pore radii as well as the total connected porosity of the control (unconsolidated) limestone sample has been noticeably reduced (Tables

2, 4 and 8) on rock's treatment with the different resins under investigation, and so does its salt susceptibility index. Simply, moving downward in pore radii than that of the control one i.e. to the range of 0.1 to 1.0 micron, the rock's resistance "durability" to salt weathering is increased as noted for almost the treated samples particularly those treated with B80 (Table 8).

The B80 dissolved in acetone has been able to deeply penetrate in this rock and reduces the pore radii to the range of 0.05 to 1.0 micron lowering rock's SSI down to 4.4. So, they became salt prone to salt resistant rock rather than very salt prone for its control one. Continuing with the rock's petrophysical parameters and grading of their water absorption percentage, it can be noted that the samples code 5, 13 and 14 followed by samples code 4, 8, 9 and 10 have better petrophysical parameters limits i.e. low percentage of total porosity, water absorption and higher limits of bulk density compared with other samples treated with other resins (Tables 3 and 4). The worst are those with code 2 and 12. The samples code 3 and 4 that are treated with B80 doesn't come in the first order of this sequence although they are salt prone to salt resistant regarding to their SSI. So, this confirms that the pore size distribution is the main controller for rock's durability to weathering.

Although the resins always record an improvement of the geotechnical properties' limits of a given rock but this is sometimes a surficial progress, consequently, the penetration depth of each resin has been considered using quick, cheap, non-destructive tool (ultrasonic waves) and the results have been listed in table 9. A noticeable difference in penetration depth of the resins under investigation has been recorded (Table 6). The maximum penetration depth has been recorded for the samples treated with Paraloid-B80 dissolved in 300ml acetone i.e. samples code 3 and 4 as it reached 4.98mm (Table 9). This is followed by the samples treated with mixture of two resins (samples code 13 and 14) reaching 4mm (Table 9). The main reason behind that might be the resin's viscosity. Above that, it has been noted that for all the resins, the penetration depth is greater for those treated through brushing method than impregnated ones (Table 9). This might be explained as the brushing method enables resin penetration than impregnation method where the former method enables gradual resin replacement for air within rock's pores than the impregnation method. The difference in penetration depth of a given resin is not only based on pore radii of a given rock (otherwise the samples code 2, 6 and 12 with low progress in their petrophysical parameters' limits would present the greatest penetration depth of the resins applied for them) but also on the resin's physical properties (mainly its viscosity) [11, 26].

Another point that must be addressed is that, some resins might verify the greatest penetration depth and the noticeably enhance the limits of rock's geotechnical parameters as well as rock's salt susceptibility index but practically the rock still not resistant to weathering. the main reasons behind these can be explained as follows; the resin might penetrate deeply within a given rock but still not be able to cohere its components hardly together. The resin also might be able to reduce rock's total porosity, water absorption and increases rock's density (all as a geotechnical parameters) but still not be able to cohere rock's components hardly together [27]. Above that, the resin might modify rock's PSD to better (e.g. salt resistant or higher) limits but on rock's exposure to salt weathering in the field, a reverse situation might occur where the practical weathering conditions are the actual view for rock's durability rather than the computed ones. Consequently, the artificial salt weathering over 30 cycles has been conducted for the control and the treated limestone currently in use for this study. The salt behavior on each sample has been recorded (Fig. 4 and 5), and the weight loss percentage has been computed at the end of this test for the whole samples (Table 10). It has been indicated that the samples code 3, 4, 13 and 14 present the lowest weight loss percentage at the end of this test (Table 10). This numerical testing of resin's capability to consolidate this rock gives with high confidence the validity of Paraloid-B80 and the mixture resins as a rock consolidating material at aggressive environmental conditions that almost dominate in the Middle-East.

Conclusion

The current study dealt with a critical point of view regarding checking the efficacy of three resins for consolidation of moderately weathered limestone based on numerical measurements of treated samples using MIP, Ultrasonic waves, and immersion method. Not only that but also based on actual testing and imitating the aggressive environments using age accelerating chamber for artificial weathering test. The net results clarified the following points: either of Paraloid B-80 dissolved in acetone, or ethyl silicate dissolved in 100mL ethyl alcohol and mixed with 15g of Paraloid-B80 dissolved in 300mL acetone or toluene verified the best results of stone consolidation and this is recommended in the field of restoration of the weathered archaeological sites. It has also been concluded that pore radii are one of the main factors controlling rock's durability, the resin's viscosity controls resin's penetration depth. The artificial weathering test is one of the main and expressive tests for numerical and quantitative resin's evaluation.

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