

Efficiency of laboratory produced water repellent treatments on limestone

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Abstract

A number of cultural and architectural heritage structures all over the world are built with natural stone. Although this material is considered to be one of the most durable geomaterials, many existing stone buildings and monuments show clear evidence of decay and weathering. The deterioration of stone is strongly related to the presence and movement of water within its pore network. Therefore, hydrophobic surface treatments are usually adopted to protect existing or new stonework. Such treatments, however, should not affect the breathability of stone; else, there is a risk of enhancing possible decay mechanisms, such as salt crystallization.

Natural limestones appear to have a degree of inherent water repellency. This has been confirmed through multiple measurements of capillary absorption at different temperatures, using water and organic liquids. The measurements were carried out on several building and decorative limestones, showing in each case an anomalously low water sorptivity. This natural water repellency of limestones was attributed to the presence of organic contaminants, such as fatty acids, in the pore network of the materials under investigation.

In this paper, the natural water repellency of Cypriot limestones is exploited to develop several water repellent surface treatments, based on oleic acid. The aforementioned laboratory produced treatments were applied on a Cypriot calcarenite with proven poor durability cha-

racteristics. The results suggest that all treatments can permanently reduce the wettability of the stone under investigation, without modifying its composition or appearance.

In order to investigate the durability of the treated stone, wetting/drying cycles were performed. The results provide strong evidence that treatment with oleic acid positively affects the durability of the stone under study. Consequently, the aforementioned surface treatment may be potentially used in practice to protect stone facades in buildings and cultural heritage sites.

Keywords: limestone, oleic acid, water repellency, wetting, drying

1. Introduction

The decay and weathering of historical stone masonries is one of the most common and severe problems the construction industry is facing all over the world. Although natural stone is considered to be one of the most durable geomaterials, stone structures are susceptible to water-mediated decay processes, such as salt crystallization, induced by alternate cycles of wetting and drying.

Salt weathering is, in fact, considered to be one of the most important degradation mechanisms that a porous stone may undergo at or near the Earth's surface.¹ The slow process of absorption of water into a porous structure and its subsequent evaporation may lead to the

gradual deposit of salts in a wall. The masonry acts as a filter system for impure water into a structure, as the various soluble salts are drawn into the wall and then left behind.^{2,3} Upon changes in the environmental conditions, salts can crystallize either at the surface (efflorescence) or inside the pores (subflorescence) of a material.^{4,5} Crystallization of salts into a porous stone causes loss of coherence between the grain and the matrix. Weight loss, changes in the size of grains and pores, splitting and visible surface deterioration can therefore be produced by salt dissolution-crystallization cycles. Thus, salt crystallization may modify the properties of the affected porous stone, leading to the reduction of the lifetime of a stone building or monument.⁶

The need to protect existing stonework in buildings and cultural heritage sites from decay and weathering mechanisms, such as salt crystallization, has led several scientists to use hydrophobic surface treatments.⁷ Those treatments usually include alkyl silicone products (i.e. alkyl siliconates, alkyl silanes, silicone resins), water-based fluoralkylsiloxane, polydimethyl siloxanes, phosphoric and poly-maleic acid products.⁷⁻¹⁰ However, when applied, they may restrict the breathability of the treated material by suppressing stage I drying, thereby affecting its microstructure by inducing pore clogging.⁴ Thus, suitable alternative surface treatments need to be developed; these must confer hydrophobicity without affecting the breathability of the material.⁸

Limestones have an unpredictable behavior when water repellents are applied to them.¹¹ Furthermore, despite the fact that calcite surfaces are naturally hydrophilic¹², many researchers¹³⁻¹⁴ state that when carbonate minerals are exposed to natural environments, they acquire organic contaminants, which induce to them a degree of natural resistance to capillary water absorption. In fact, these organic contaminants reduce the affinity

of calcite for water, and therefore modify its wettability. Ioannou et al.¹⁴ confirmed the partial wettability of limestones to water through a series of measurements of capillary absorption at different temperatures, using water and organic liquids.

The most severe modification of calcite surfaces is due to the absorption of carboxylic and especially fatty acids.¹⁵ As quoted in the literature, the strongest affinity for carbonate surfaces is shown by medium-to-long chain fatty acids and carboxylate polymers.¹⁵ Consequently, surface treatments using fatty acids can modify the wettability of calcium carbonate surfaces, without affecting their inherent composition. In this paper, the efficiency of three laboratory produced water repellent surface treatments based on oleic acid is thoroughly investigated.

2. Experimental Work

In the experimental study, three light grey (according to Munsel Soil-Color charts) freshly quarried Cypriot limestones were used. They originate from the area of Agios Theodoros in Cyprus, which belongs to the Pachna Geological Formation. Those stones are packstones or poorly washed biosparites, with microsparry calcite and a small portion of micrite as their intergrain cementing material.¹⁶ They also have a complex mineralogy; they show a rather high percentage of calcite, with significant amounts of quartz, aragonite, zeolites (analcime), pyroxenes (augite), plagioclases (anorthite, andesine, orthoclase, albite) and clay minerals (chlorite, montmorillonite). *Table 1* summarizes the mineralogical composition of the stone variety under study.

Initially, the sorptivity (S) of all three specimens was measured at different temperatures using both water and organic liquids (i.e. ethanol, 2-propanol, n-heptane) in accordance with EN 1925.¹⁷

Stone variety	Petrological family	Colour (Munsell Chart)	Mineralogy (XRD)
Agios Theodoros	Calcarenite	5Y 7/2 Light Grey	calcite (65-69%), quartz (6-7%), clinopyroxene (4-5%), chlorite (4-5%), plagioclase (5-6%), K-feldspar (1-2%), aragonite (9-11%), montmorillonite and analcime (traces)

Table 1: General details and mineralogical composition of Agios Theodoros stone.

The results were plotted against $(\sigma/\eta)^{1/2}$, where σ [Nm^{-1}] is the surface tension and η [Nsm^{-2}] the viscosity of the wetting liquid at each temperature. From the graphs and using equation (1), the so-called intrinsic sorptivity (S_i) and the water wetting index (β) of each sample was estimated.¹⁸

$$S = S_i (\beta * \sigma/\eta)^{1/2} \quad (1)$$

Following the initial sorptivity measurements, the surface of each sample was treated with a different in-house developed water repellent treatment, aiming to control its wettability. All treatments were based on oleic acid (i.e. a fatty acid with 18 carbon atoms in a chain). As quoted in the literature¹⁹, when oleic acid is used as an organic additive, it can control the nucleation and growth of calcium carbonate (CaCO_3), and it can modify the wettability of its surface. In fact, back in 2012, in a research carried out by Walker et al.⁸, the use of oleic acid induced additional hydrophobicity to the calcite surface of the York Minister Cathedral.

The first treatment included an ethanol solution of oleic acid (concentration 0.5% w/w). The second treatment was performed using an aqueous solution of sodium oleate (concentration 0.5% w/w). Sodium oleate is the unsaturated metal soap of oleic acid; it has an equally high affinity for carbonated mineral surfaces and has been shown to act as a kind of

surfactant/plasticizer in renders applied on limestone substrates.²⁰ During the setting of the render, a reaction with calcium ions in limestones takes place and the oleate is transformed to a hydrophobic metal soap. Because of this reaction, sodium oleate is considered a 'Reactive Hydrophobic Agent'. It is worth noting that sodium oleate shows no gelling effect, due to its high content of unsaturated fatty acids.²⁰ The third treatment was performed using calcium oleate (i.e. the calcium soap of oleic acid), produced by mixing sodium oleate and calcium carbonate in an aqueous solution. Once again, the concentration of calcium oleate solution was 0.5% w/w. The three solutions were applied to the top surface of the specimens by brushing. Following this, the samples were allowed to dry at room temperature. In order to observe the effect of the treatment, the sorptivity of the treated samples was again determined through capillary absorption experiments at different temperatures using water and organic liquids.

The durability of the aforementioned surface treatments was investigated by subjecting the test specimens to wetting/drying cycles. Wetting was performed using vacuum saturation, while drying took place in an oven at 105°C, until constant weight was reached. Ten cycles of wetting/drying were performed. After each cycle, the sorptivity of the sample was determined through water capillary absorption tests.

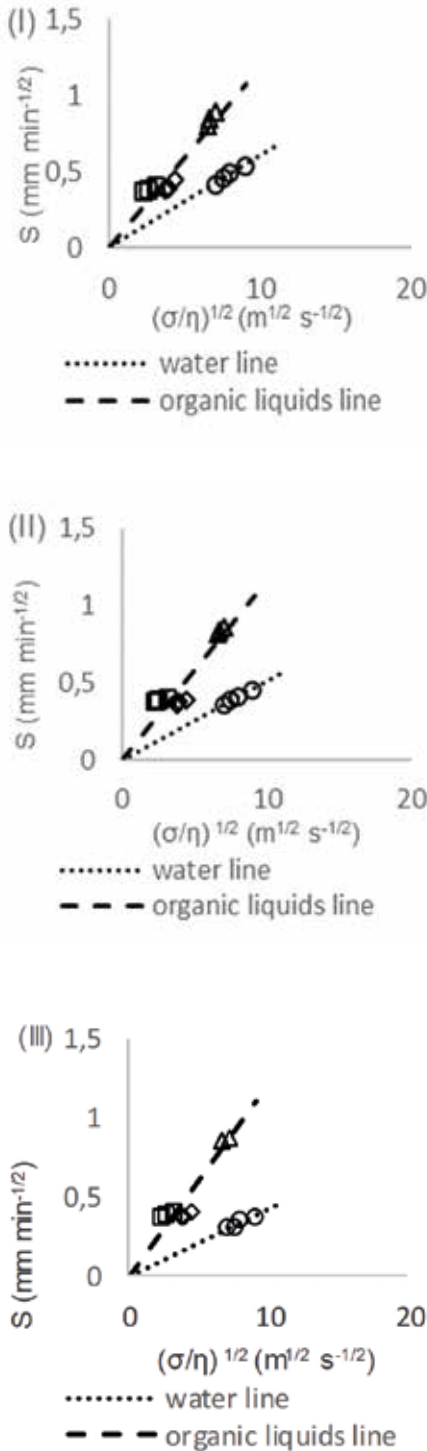


Figure 1: Sorptivity values S versus $(\sigma/\eta)^{1/2}$ for the three limestones under study. (I): Agios Theodoros I, (II): Agios Theodoros II, (III): Agios Theodoros III.

3. Results and Discussion

3.1. Capillary Absorption Measurements before the Treatments

The results of capillary absorption measurements before the treatments showed a linear correlation between the cumulative absorption per unit surface area i and the square root of time $t^{1/2}$, as expected. Consequently, the sorptivity S ($=i/t^{1/2}$) of each sample under study was derived from the slopes of the respective graphs. When the sorptivity values were plotted against $(\sigma/\eta)^{1/2}$, the data points fell into two groups, which lied on separate straight lines (Fig. 1 I, II, III). Despite the fact that both the organic liquids and the water sorptivity values increased linearly with $(\sigma/\eta)^{1/2}$, the water data lied on a line with a lesser slope. This is in line with previous relevant work¹⁴ and confirms the partial wettability of limestone specimens, which is attributed to natural organic contamination, due to the presence of a low-energy adlayer on the specimen's surface.^{14, 18} From the results of Fig. 1, the water wetting indices of each specimen were calculated using equation (1) (Table 2).

3.2. Capillary Absorption Measurements after the Treatments

The results of the capillary absorption experiments after the application of the surface treatments are shown in Figure 2 for each specimen. A linear behavior between the sorptivity S and $(\sigma/\eta)^{1/2}$ is once again noted. The organic liquids line remains generally unchanged after all treatments (an indication that no significant chemical or structural changes have occurred in the test specimens¹⁴), whereas the water line has an even lower slope. This, strongly indicates that oleic acid and its by-products adsorb well on the calcite surface of the samples under

Treatment	Intrinsic Sorptivity ($\times 10^{-4} \text{ mm}^{1/2}$)	Specimen Water Wetting Indices		
		Original	After surface treatment	After 10 cycles of wetting/drying
Oleic acid	4.83	0.26	0.004	0.03
Sodium oleate	4.74	0.19	0.10	0.04
Calcium oleate	5.84	0.13	0.02	0.01

Table 2: Water wetting indices of test specimens before (original) and after each treatment.

study and induce to them additional hydrophobicity. The latter is attributed to the deposition of the resulting $\text{Ca}(\text{C}_{17}\text{H}_{33}\text{COO})_2$ onto the calcite (CaCO_3) surface of the test specimens.

3.3. Capillary Absorption Measurements after the Wetting/Drying Cycles

The results of the sorptivity tests carried out on each specimen after the completion of the ten wetting/drying cycles are also shown in Figure 2. Tests with pure organic liquids were further performed after the completion of the wetting/drying procedure.

From the results, it is evident that the organic liquids line, and consequently the intrinsic sorptivity of the samples, continues to remain unchanged. The results also indicate that the samples were not affected by the wetting and drying cycles. In fact, in the cases of sodium and calcium oleate, there is a further significant reduction (ca. 50-60%) in the water wetting index of the samples after the wetting/drying procedure (Table 2). Whilst for sodium oleate this may be attributed to enhanced diffusion of the treatment into the sample, for calcium oleate the reason is not clear and needs to be further investigated.

It is worth noting that sodium oleate chemically adsorbs on the CaCO_3 surfa-

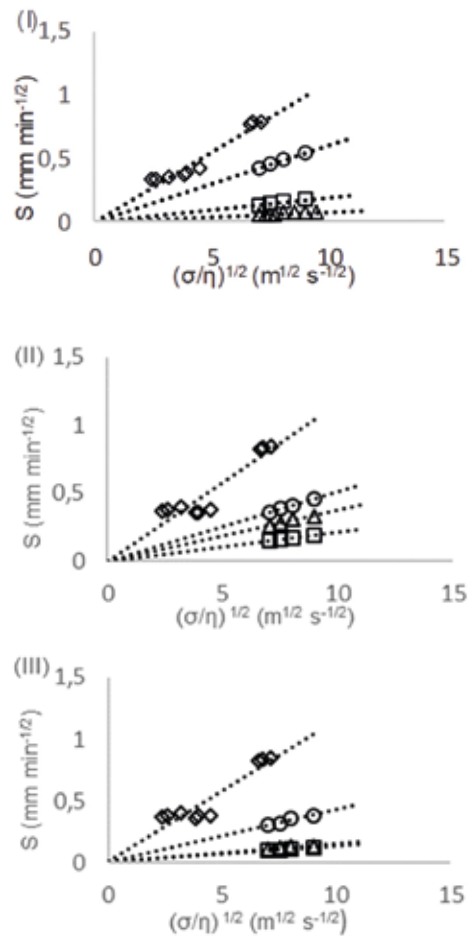


Figure 2: Sorptivity values S versus $(\sigma/\eta)^{1/2}$ for water and organic liquids before and after all treatments. (○) water before treatments, (◇) organic liquids before and after all treatments, (△) water after water repellent surface treatments, (□) water after 10 cycles of wetting and drying. (I): Agios Theodoros I, (II): Agios Theodoros II, (III): Agios Theodoros III.

ce of the stone, which interacts in itself with the oleate anions, thus producing a calcium oleate product. Since the latter is water insoluble, it remains on the CaCO_3 surface, thus inducing further water repellency.

Even in the case of oleic acid, where there appears to be an increase in the water wetting index of the sample after the ten wetting cycles (Table 2), the surface of the stone is still nearly water repellent at the end of the experimental procedure ($\beta=0.03$). These results, therefore, provide strong evidence that oleic acid and its by-products (sodium and calcium oleate) adsorb well on calcite surfaces, without modifying their chemical/structural composition or appearance (Figure 3). Hence, the aforementioned treatments may be adopted in conservation projects for the protection of stone masonries.

4. Conclusions

The inherent water repellency of limestones originating from the Agios Theodoros area in Cyprus has been confirmed by the experimental work presented in this paper. When the samples were subjected to capillary absorption experiments with water and organic liquids, at different temperatures, a significant differentiation in the respective S vs $(\sigma/\eta)^{1/2}$ graphs was observed; the water data consistent-

ly fell on a line of lesser slope, compared to the organic liquid data. This was attributed to the presence of a hydrophobic natural organic contaminants adlayer below the specimen's surface, inducing a degree of inherent water repellency to the stone.

The natural water repellency of the Agios Theodoros stone has been exploited through chemical modification of the surface of three test specimens using different treatments based on the use of oleic acid. All three surface treatments (i.e. oleic acid, sodium oleate, calcium oleate) proved successful in further reducing the water wetting index of the limestones under study.

The efficiency of the aforementioned treatments was further investigated through wetting/drying cycles. Data from capillary absorption measurements after these cycles revealed that oleic acid and its salts and soaps adsorb very well on the calcite bearing surface of the limestone under study. Despite the fact that, there was an increase in the water wetting index of the sample treated with oleic acid after wetting/drying, the stone retained its hydrophobicity. The other two samples showed a further reduction in their water wetting indices after ten cycles of wetting and drying.

This work has practical significance, since the durability of stone masonry is largely controlled by processes mediated

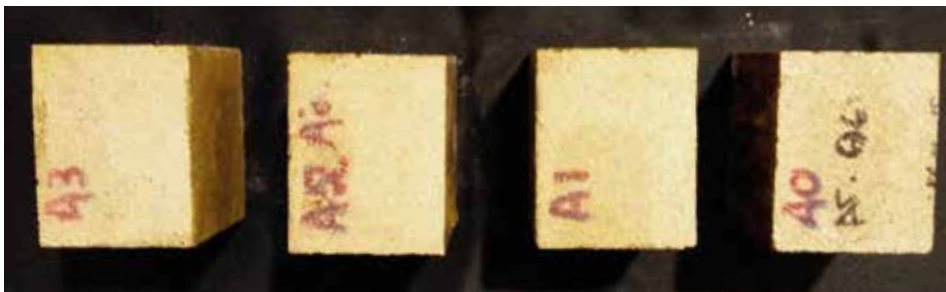


Figure 3: Physical appearance of the stone surfaces before/after each treatment. A0: Untreated stone, A1: Oleic acid treated stone, A2: Sodium oleate treated stone, A3: Calcium oleate treated stone

by water, such as salt crystallization. The results strongly suggest that the in-house developed water repellent treatments with oleic acid, sodium and calcium oleate not only manage to reduce the water absorption of the treated stone, but they are also durable against wetting/drying cycles. Therefore, the aforementioned treatments may be potentially used in conservation projects for the protection of stone facades in buildings and cultural heritage sites.

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