

**THE PERFORMANCE OF AN INDUCED CALCIUM OXALATE  
SURFACE ON GLOBIGERINA LIMESTONE**

Tabitha Dreyfuss (tabitha.dreyfuss@gov.mt) and JoAnn Cassar  
(joann.cassar@um.edu.mt)

*Department of the Built Heritage, Faculty for the Built Environment,  
University of Malta, Malta*

**Abstract**

This paper contains the second set of results obtained from a research programme that consisted of an induced surface conversion of weathered Globigerina limestone from calcium carbonate to calcium oxalate and the prospects of it being used for the conservation of this stone. The first part of the research confirmed the formation of calcium oxalate even in salt (sodium chloride) contaminated samples. The second phase of the research showed that the production of calcium oxalate resulted in the formation of a more compact, more cohesive, and harder surface when compared to untreated samples, which showed no colour change, retained the original hydrophilic and wetting properties of the stone and also increased the stone's resistance to acid attack (acetic and hydrochloric acid), and to salt weathering (using sodium sulphate).

**Keywords:** oxalates, consolidation, protection, Globigerina limestone

**1. Introduction**

It is a long-standing and ever-present problem that salt-contaminated porous limestones are extremely difficult to treat successfully. In Malta, this is an especially serious problem since the locally available stone is highly porous and is usually heavily contaminated with marine salt (sodium chloride), and desalination is often not feasible. This stone, used for the great majority of the island's historic buildings, essentially consists of fine-grained limestone with few abundant fossils including planktonic and benthonic foraminifera especially Globigerinae, from which its name is derived. Globigerina limestone is a very porous stone (up to 41%) with mostly channel type pores (Cassar 2002). This allows suction of water by capillary action through the pore structure. Globigerina limestone used for building in the Maltese Islands is described by quarry workers to occur as two types: the more durable "franka" limestone, which usually weathers well, and, the "soll" limestone, which deteriorates badly, even in the same environment. It is believed that the majority of historical monuments were built with the "franka" type. A research programme, which commenced in 2004, consisted of an induced surface conversion of weathered Globigerina limestone from calcium carbonate to calcium oxalate, with the aim of using this conversion for the conservation of this stone. The first part of the research concerned the verification of the surface conversion, and the determination of its extent, using x-ray diffraction (XRD). The results confirmed the formation of calcium oxalate in all cases, and its extent, relative to the stone's surface texture and its salt (sodium chloride) content (Mifsud et al. 2006). Whewellite, as opposed to weddellite, was formed in all cases. The treated non-desalinated samples were found to form more whewellite than desalinated samples. This

was attributed, at least in part, to the increased surface area of the non-desalinated samples, which allowed for more contact with the ammonium oxalate poultice and thus resulted in more calcium oxalate being formed. This paper covers the second phase of the research, which was aimed at evaluating the performance of the induced calcium oxalate surface.

## **2. Samples and treatment**

The range of samples included fresh quarry samples, artificially weathered quarry samples (using sodium sulphate for the samples that were to be desalinated and sodium chloride for those that were not to be desalinated) and naturally weathered samples. All samples were of the “franka” Globigerina limestone type as indicated by quarry workers and confirmed through the insoluble residue test (Cassar 2002). These consisted of 5 cm cubes. Three samples were prepared for each of the tests. From each group of samples, both desalinated and non-desalinated samples were studied. The samples were subjected to a 5% ammonium oxalate poultice for 5 hours, after which testing took place on both treated and untreated samples.

## **3. Testing methodology**

Scanning Electron Microscopy (SEM) was carried out using a LEO 1430, Oxford Link microscope to look at the surface morphology and to make direct comparisons between treated and untreated samples. Any consolidation that may have developed as a result of ammonium oxalate treatment was evaluated through the Mohs hardness test in accordance with EN 101:1991 and the tape test. The tape test, which concerns the investigation of the superficial surface cohesion of the stone, was carried out as explained by Croveri, 2004. The protection from acid attack of the treated samples was examined through acid resistance tests using acetic acid at concentrations of 5% and 10%, and hydrochloric acid at concentrations of 0.5% and 2% (Matteini et al. 1994). The depth of calcium oxalate formation, and its distribution in the treated samples, was studied through acid etching following immersion in a 5% acetic acid solution and then drying. The resistance of the samples to salt crystallisation was examined by means of artificial weathering tests using sodium sulphate in accordance with EN 12370:2000, while the hydrophilic and wetting properties were investigated by means of water absorption tests through capillarity, as per NORMAL 11/85. The potential change in the appearance of the limestone following ammonium oxalate treatment was examined by visual inspection and direct comparison of treated and untreated samples, and their evaluation using the Munsell colour system.

## **4. Results**

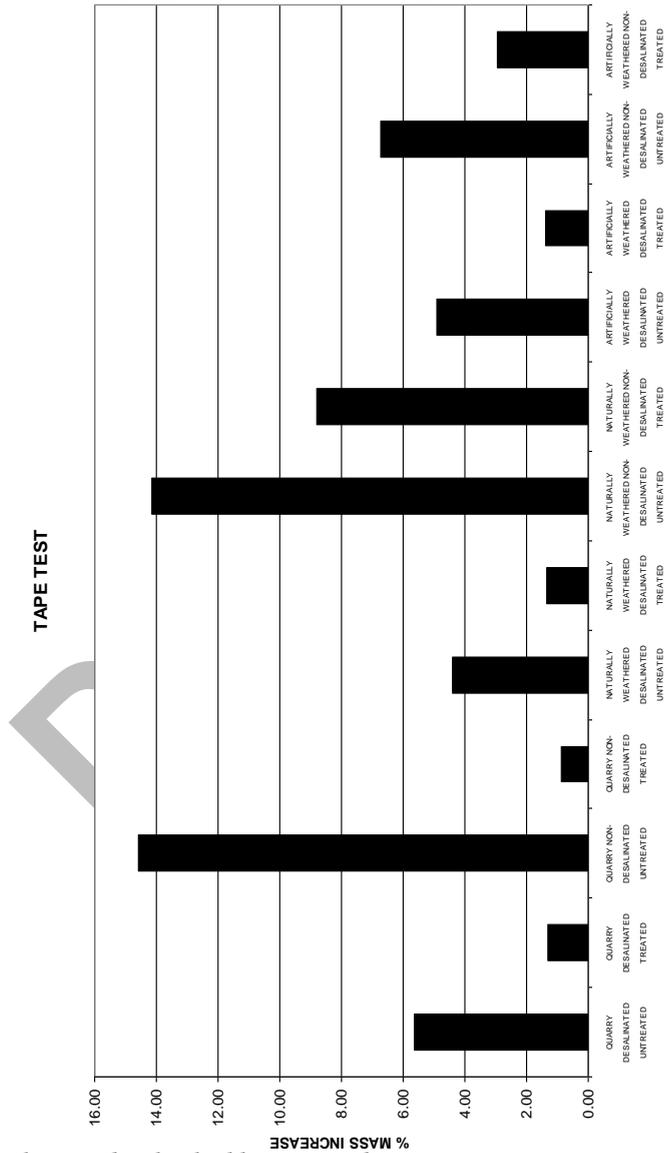
### **4.1 Visual analysis for colour change**

Following ammonium oxalate treatment and drying, the colour of the treated samples was not visibly different, from the untreated samples, to the naked eye. For each sample type, treated and untreated stones were directly compared to a Munsell colour chart and in all instances, treated and untreated samples corresponded to one specific colour only. The quarry non-desalinated samples corresponded to 5Y8/1, and all the other samples corresponded to 5Y8/2. Therefore, although different sample groups

differed in colour from each other, within each group, treated and untreated samples were the same colour.

#### 4.2 Tape test

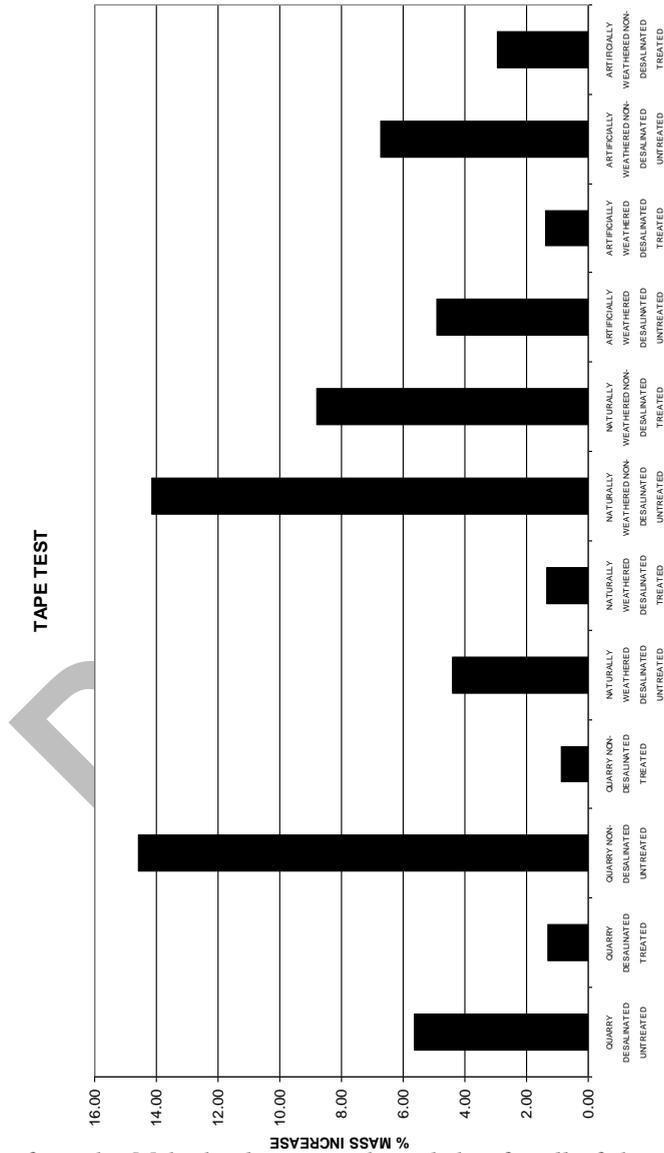
The results obtained from the tape test are illustrated in Figure 1. This shows that, in all cases though to varying degrees, the untreated samples left more material on the back



of the tape than the samples that had been treated.

Figure 1. Results of Tape test

4.3 Mohs hardness test



The results from the Mohs hardness test showed that for all of the samples, the treated stones exhibited an increased scratch resistance when compared to the untreated ones. The untreated samples had a scratch resistance that varied from 2 (gypsum) to 3

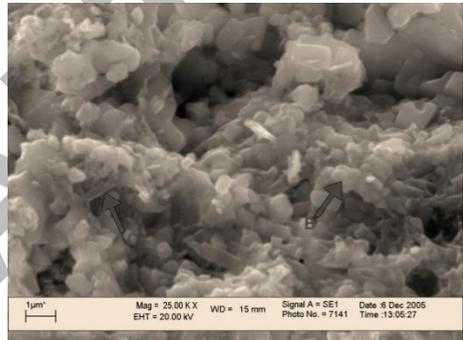
(calcite) whereas in all cases, the treated samples had a scratch resistance of 4 (fluorspar), which is the hardness of calcium oxalate.

#### 4.4 Scanning electron microscopy (SEM)

The treated and untreated samples of the same type were examined and photographed at identical magnifications using the scanning electron microscope. This facilitated direct comparisons. Magnifications ranged from 500x up to 25kx. In general, the untreated samples showed a surface with loose, individual rounded grains. These rounded crystals, probably calcite, may be observed in Figure 2. In the treated samples, these rounded grains are present as part of a larger mass/ cluster in Figure 3. In addition, in the treated samples, elongated/ extended grains were observed; these were not observed in any of the untreated samples. These elongated grains, which could be whewellite, are sometimes seen to be linking grains together (Figure 3). Figure 3 also shows arm-like formations branching between different parts of the treated surface. These again are not seen in the untreated samples.



**Figure 2.** Naturally weathered non-desalinated sample untreated (left)



**Figure 3.** Naturally weathered non-desalinated sample treated (right)

#### 4.5 Water absorption through capillarity

The results for the water absorption test through capillarity are expressed graphically in Figure 4. All the graphs are similar and are seen to contain two portions, an initial rapid amount of water absorbed per unit area in a given amount of time (within the first 1 hour 15 minutes), and the later, slower absorption of water following that (between the first 1 hour 15 minutes and one week).

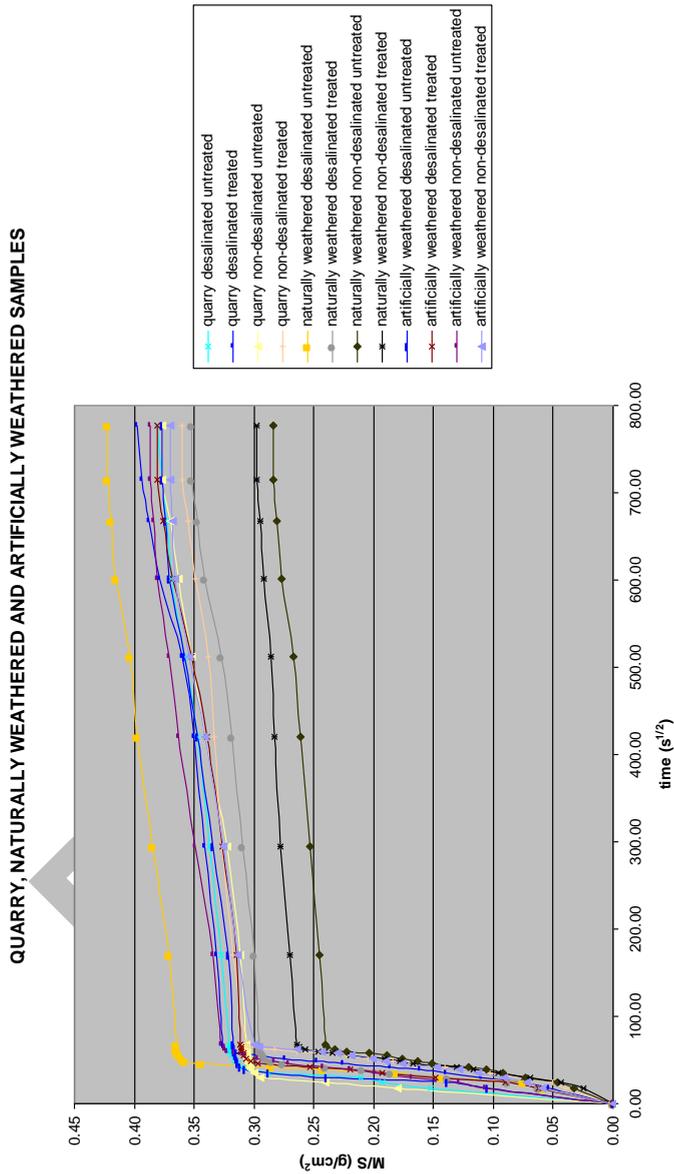


Figure 4. Water absorption through capillarity for all the samples

#### 4.6 Sodium sulphate crystallisation test

The results for the sodium sulphate crystallisation test showed that in all cases, the treated samples had a greater resistance to damage than the untreated samples. This was evaluated through the weighing of material lost. Following the salt weathering tests, the surfaces of the samples were visually observed. While the untreated samples had a

powdery rough texture, the treated samples all had a smoother surface with less deterioration visible.

#### **4.7 Acid resistance tests**

The resistance to acid attack was evaluated through the determination of the percentage of mass lost in the samples, which were placed in contact with acetic and hydrochloric acids at different concentrations. The percentage mass lost in the samples after 5 minutes was calculated. In all instances, the samples that were treated with ammonium oxalate showed more resistance to acid attack. This was seen as a smaller percentage of mass of sample lost in the treated samples than in the untreated samples of the same type.

#### **4.8 Depth of oxalate formation**

The unexpected whitening effect produced when the treated samples were placed in contact with a 5% acetic acid solution was used to determine the depth of calcium oxalate formed, as this appeared to outline the areas that were treated and distinguished them from untreated areas. The change in colour from yellowish to white in the top faces and the top part of the sides was seen in all of the treated samples. None of the untreated samples became whiter on contact with the acid. The average depth of the white part and the maximum depth observed on the sides of the treated samples are shown in Figure. 5. These depths may not necessarily be representative of the depths achieved throughout the sample internally, but are a representation of the depths achieved on the perimeter of the sample. The samples were treated on the top face only, but migration into the stone could be easier on the external perimeter than internally.

### **5. Discussion**

The lack of a visible colour change in the samples of Globigerina limestone following ammonium oxalate treatment is an encouraging sign. It also suggests that little or no free iron was present, at least in these particular samples that could be mobilised by the treatment. Further testing on other samples is needed to confirm that this is generally the case.

A consolidating action, at least on the surface of the samples, as a result of ammonium oxalate treatment has been confirmed by the fact that less material came away during the tape test in all cases of the treated samples. This conclusion is supported by the consistent increase in hardness to grade 4 (fluorite) in all of the treated samples. Also, the SEM image comparisons showed that the surfaces of the untreated and treated samples differed in their surface morphology. In general, the treated samples showed a surface that was more compact, with a reduction in loose surface grains visible. This observation, together with the formation of clusters of grains and the bridging between clusters observed in the treated samples, suggests that a consolidation action has in fact occurred. In addition, on visual observation and on handling of the samples, all the treated samples had a smoother texture with a smaller amount of loose grains present on the surface. Even though a change in surface porosity

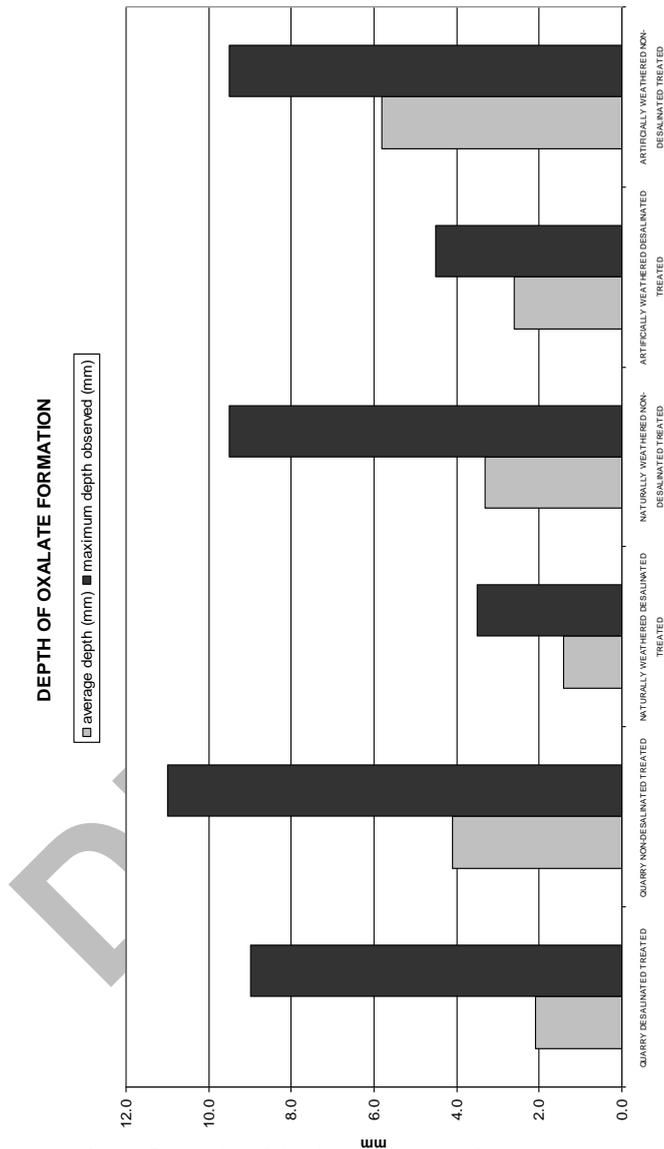


Figure 5. Results of the depth of oxalate formation

and pore size probably takes place with ammonium oxalate treatment, the hydrophilic properties of the stone, and thus the water absorption patterns of the stone, are seen to be preserved in all cases as seen in the water absorption tests. The reduced loss in material following sodium sulphate weathering of the treated samples, when compared with the untreated samples, also signifies that protection from deterioration by salt crystallisation takes place following treatment. The greater damage occurring in the untreated samples confirms this. Resistance to acid attack in the treated samples was seen as a smaller

percentage of mass of sample lost than in the treated samples. The amount of protection from acid attack achieved is directly comparable to the amount of calcium oxalate formed, which was obtained through XRD analyses (Mifsud and Cassar 2006).

The whitening observed in the treated samples only during testing with the 5% acetic acid solution may be explained by the fact that this acid is corrosive to calcium carbonate, while calcium oxalate remains undamaged. The calcium carbonate, together with its colour impurities, thus erodes, leaving behind the calcium oxalate, which is white in colour. This outcome, which was used to determine the depth of calcium oxalate formation in the treated samples, showed that in all instances the samples that were seen to have the greatest average depth of formation of calcium oxalate were again the non-desalinated (sodium chloride) samples. The whiter surface observed in the treated non-desalinated samples suggests that the formation of calcium oxalate in these samples is more uniform and better distributed than in the treated desalinated samples. This is in keeping with the results obtained from XRD analysis, where the treated non-desalinated samples were seen to have developed more calcium oxalate than the treated desalinated samples of the same type. This has already been explained as being possibly due to the increased surface area that the non-desalinated samples possessed, and which the desalinated samples lost during the desalination process (Mifsud and Cassar 2006). The deeper calcium oxalate formation in the non-desalinated samples also suggests that ammonium oxalate treatment in non-desalinated “franka” limestone results in a deeper penetration of the treatment. This observation merits further investigations.

## 6. Conclusions

These promising results present ammonium oxalate treatment of “franka” Globigerina limestone in a positive light. This treatment results in some surface consolidation, which is manifest as a smooth surface texture with a reduced amount of loose surface material as well as an increased hardness and scratch resistance of the surface of “franka” limestone, an increased resistance to salt crystallisation and to acid attack. Additionally, it has been seen that the hydrophilic and wetting properties of the treated stone are not disturbed, and no colour changes are observed. The results have also shown that the non-desalinated samples developed a deeper average formation of calcium oxalate than the desalinated samples. Further research is being planned and is also to include the evaluation of the porosity and pore-size distribution of the surfaces of treated and untreated samples. This will allow for the better understanding of the differences in behaviour of treated samples when compared with untreated ones. The study of the use of different concentrations of ammonium oxalate, as well as different duration times and different modes of application, together with an evaluation of the depth of calcium oxalate formed inside the stone, may lead to an optimum method for treating exposed naturally weathered “franka” Globigerina limestone. The practical in situ application of the treatment to vertical surfaces, such as those found in buildings is also to be researched, as well as the ongoing monitoring of treated monuments and buildings. In practical terms, it can in fact be concluded that this treatment can potentially be used in the field of conservation as a protective treatment, possibly with some consolidating properties, on historic buildings and monuments built with this stone in the Maltese Islands.

## References

- Cassar, J., 2002. 'Deterioration of the Globigerina Limestone of the Maltese Islands'. In *Natural Stone, Weathering Phenomena, Conservation Strategies and Case Studies* Geological Society Special Publication, 205. Siegesmund, S., Weiss, T., and Vollbrecht, A. (eds.) 33-49. London: Geological Society London
- Croveri, P., 2004. Metodologie di consolidamento di materiali lapidei nell'area Mediterraneo: La Globigerina Limestone maltese – degrado e consolidamento. Dottorato di Ricerca in Scienza per la Conservazione dei Beni Culturali XVII ciclo, Università degli Studi di Firenze. Unpublished
- EN 101:1991: Ceramic floor and wall tiles. Method for determination of scratch hardness of surface according to Mohs
- EN 12370:2000: Natural stone test methods – Determination of resistance to salt crystallisation
- Matteini, M., Moles, A., Giovannoni, S., 1994. 'Calcium oxalate as a protective mineral system for wall paintings: methodology and analyses'. In *3rd International Symposium on the Conservation of Monuments in the Mediterranean Basin, Venice*. Fassina, V., Ott, H., and Zezza, F. (eds.) 155-162. Venice: Soprintendenza ai Beni artistici e storici di Venezia
- Mifsud, T. & Cassar, J. 2006. 'The treatment of weathered Globigerina limestone: the surface conversion of calcium carbonate to calcium oxalate'. In *Heritage, Weathering & Conservation*. Fort, R., Alvarez de Buergo, M., Gomez-Heras, M., & Vazquez-Calvo, C. (eds.) 727-734. London: Taylor & Francis Group
- NORMAL 11/85, 1986: Assorbimento d'acqua per capillarità. Coefficiente di assorbimento capillare. CNR – ICR