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Hughes, John; Howind, Torsten

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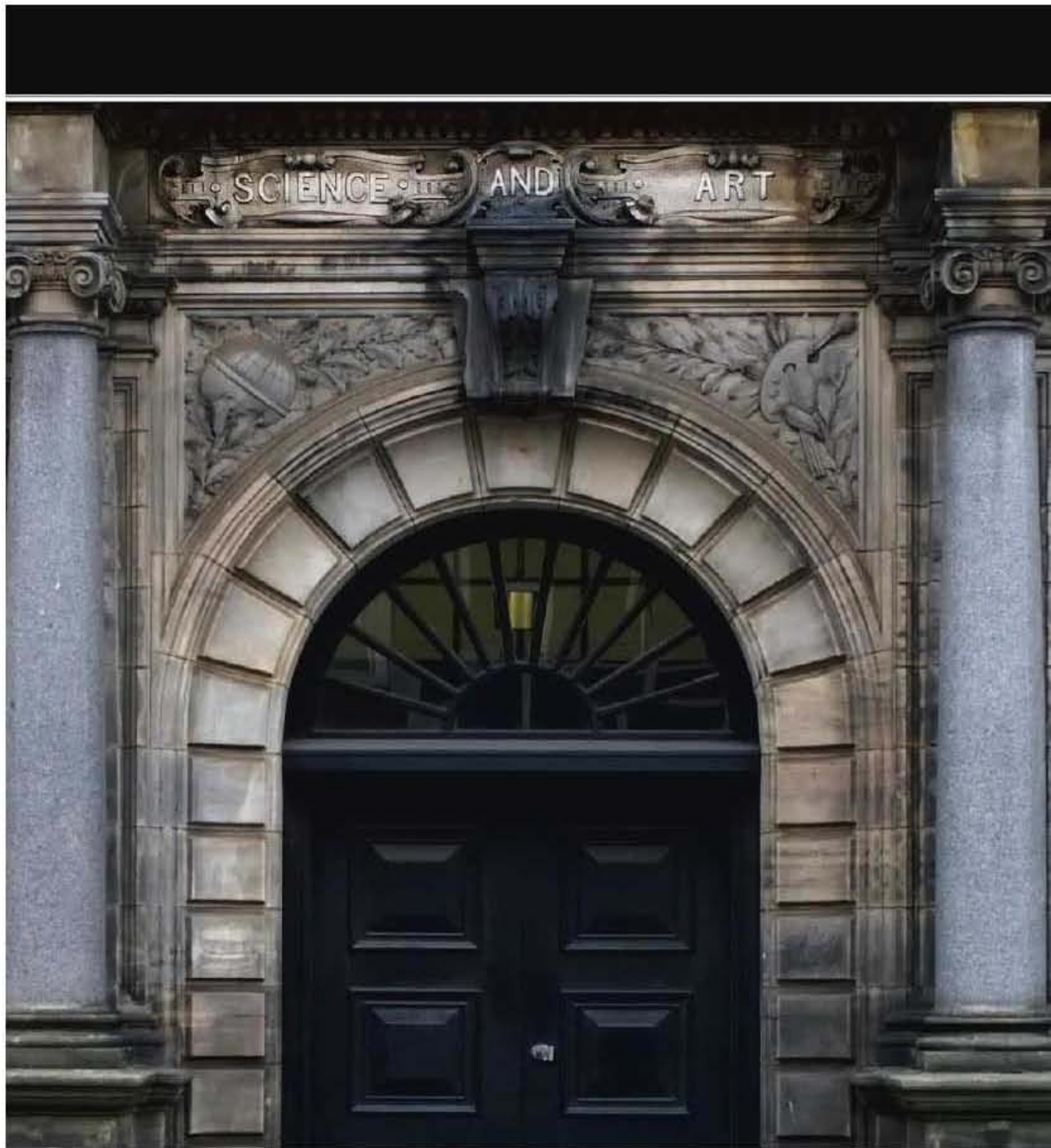
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SCIENCE and ART: A Future for Stone

**Proceedings of the 13th International Congress on the
Deterioration and Conservation of Stone – Volume I**

**Edited by
John Hughes & Torsten Howind**

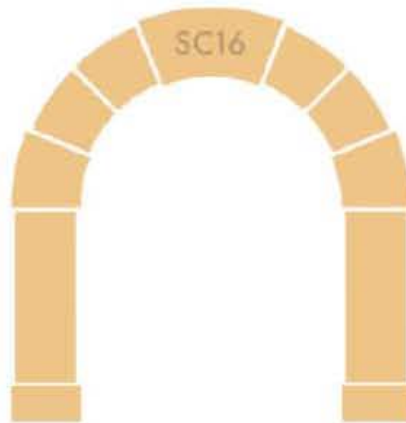
SCIENCE AND ART: A FUTURE FOR STONE

PROCEEDINGS OF THE 13TH INTERNATIONAL CONGRESS ON THE
DETERIORATION AND CONSERVATION OF STONE

6th to 10th September 2016, Paisley, Scotland

VOLUME I

Edited by
John J. Hughes and Torsten Howind



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Cover image: The front door of the Paisley Technical College building, now University of the West of Scotland. T.G. Abercrombie, architect 1898. Photograph and cover design by T. Howind.

THE NATURAL WEATHERING OF AN ARTIFICIALLY INDUCED CALCIUM OXALATE PATINA ON SOFT LIMESTONE

T. Dreyfuss^{1*} and J. Cassar¹

Abstract

This paper focuses on the effects of natural weathering on Globigerina Limestone (Malta) which was treated with ammonium oxalate to produce a calcium oxalate surface layer. This study includes the first two phases of a larger research programme. Laboratory samples were considered first. These were treated and tested in a controlled environment (Phase 1). Identical samples sets were prepared for Phase 2. These were treated *in situ* and exposed to site conditions for the period of one year. In an attempt to simulate site conditions, for both Phase 1 and Phase 2 samples, the limestone was contaminated with soluble salts before treatment took place. These included three separate types; sodium chloride, sodium sulfate and sodium nitrate. Desalinated samples were also included in the study. Scanning Electron Microscopy (SEM) was carried out on the Phase 1 samples while Drilling Resistance Measurement System (DRMS) was carried out on the samples of both phases. This paper focuses on the results from the SEM and correlates these with those results from the DRMS in light of the influence of natural weathering on an artificial calcium oxalate layer, induced in the presence of soluble salts.

Keywords: oxalates, consolidation, protection, limestone, treatment durability

1. Introduction

The Maltese Islands, a small island archipelago measuring 316 square kilometres and located 93km south of Sicily and 288km north of Africa have a large collection of historic limestone buildings and monuments that span the millennia. These are built in Maltese Globigerina Limestone - a highly porous calcareous stone which naturally deteriorates in an environment that is exposed to both water and soluble salts. These buildings and monuments inevitably require conservation action at certain points in their lifetime which may include consolidation and/or protective treatments. Many of the historic stone edifices (pre-1850s) in Malta and Gozo were built without the insertion of a damp proof course, thus allowing water entry in the form of rising damp together with any soluble salts present. Additionally, wall construction generally utilised soil infill, usually salt laden, between two masonry wall leaves. The island environment further enhances salt contamination through wind driven and aerosol borne salts. The context is therefore a porous limestone which has a continual supply of water and soluble salts.

¹ T. Dreyfuss* and J. Cassar
Department of Conservation and Built Heritage, Faculty for the Built Environment,
University of Malta, Malta
tdrey01@um.edu.mt

* corresponding author

Consolidation of exposed Globigerina Limestone which has lost cohesion, manifested as powdering/ granular disintegration, must therefore take this context into account. The aim must be to bridge the loose powder/ grains together and to the sound stone beneath with a compatible material that retains both the water and salt transport properties of the stone that is being consolidated. Ammonium oxalate treatment on calcareous stone has been studied as a surface treatment providing protection from acid attack together with possible consolidating properties (Matteini *et al.*, 1994; Matteini 2007), even on Globigerina Limestone (Croveri 2004; Mifsud *et al.*, 2006; Dreyfuss *et al.*, 2012 and 2013), which to date has revealed promising results suggesting its potential use in this respect. The actual study of ammonium oxalate treatment on Globigerina Limestone *in situ* and its relationship with soluble salts present in the stone was the next step. This was to take this research to a point where the actions and mechanisms of ammonium oxalate treatment are understood in terms of the parameters presented by a historical building. The two parameters identified here are the presence of salts and site exposure whilst stone pathology is considered in other parts of the larger research project (Phase 3). To this end, the parameters included here were desalinated versus salt contaminated conditions and controlled versus uncontrolled environments.

2. Methodology

2.1. Globigerina Limestone

The material considered, Globigerina Limestone, of the *franka* type (Cassar 2004), is a fine-grained limestone, sedimentary in origin with few to abundant fossils including planktonic and benthonic foraminifera especially globigerinae which is from where it gets its name. It is primarily composed of calcium carbonate in the form of calcite crystals cemented together by non-crystalline calcium carbonate. Besides calcite, Globigerina Limestone also contains clay minerals, quartz, feldspars, apatite and glauconite. A large part of the clay minerals consists of kaolinite with smectite, illite-smectite, illite and vermiculite also being present (Cassar 2002). The porosity is high and varies between 24% (Cassar 2004) and 41% (Cassar *et al.*, 2001) whilst the majority of pores $\leq 4 \mu\text{m}$ (Vannucci *et al.*, 1994).

2.2. Sample preparation

The samples were prepared as $50 \times 50 \times 10 \text{ mm}^3$ (for the SEM samples) and $50 \times 50 \times 50 \text{ mm}^3$ (for the DRMS samples) cut from stone blocks (approximately $w=410 \text{ mm} \times D=230 \text{ mm} \times H=267 \text{ mm}$) obtained from the quarry area known as *Ta' l-Iklin* in Qrendi (coordinates 51,500; 66,500) at a depth of 12 m below ground level. The horizontal (downward facing direction) bedding plane was noted in all cases and retained as the treatment and testing surface for all samples.

The samples consisted of quarry samples with different salt contents, namely desalinated samples, samples contaminated respectively with saturated solutions of sodium chloride, sodium sulfate and sodium nitrate. Desalination was carried out by immersion of the samples in distilled water, repeatedly changing the water until its conductivity revealed that soluble salts were no longer present ($\leq 3 \mu\text{S/cm}$). All of the samples were thus desalinated and then oven dried for 24 hours at a temperature of 105°C then cooled in the laboratory to constant mass at 20°C room temperature. One fourth of the samples were then retained to represent the desalinated type samples, while the remaining samples were divided into three sets and each set was salinated with a saturated solution of sodium chloride, sodium sulfate

and sodium nitrate respectively by immersion for 2 hours. Following immersion, the samples were air dried.

2.3. Ammonium oxalate treatment

Treatment was carried out to all sides of the samples using a 5% ammonium oxalate monohydrate solution applied in a cellulose pulp poultice for 24 hours at 20°C; conditions were 74% RH in the case of the laboratory samples and at 26°C, 70% RH on site. Following treatment the poultice was manually removed and the samples left to air dry. The excess pulp was brushed off with a soft nylon brush. Untreated samples were prepared for all treated sample types.

2.4. Site exposure

The one-year site exposure of the Phase 2 samples included temperatures ranging from 5.6°C to 37.5°C, a total rainfall of 350.7 mm, 3059.4 hours of sunshine, an average Relative Humidity of 72.4%, 35 days with thunderstorms, 12 days with hail, 4 days with fog and 4 days with "dust haze". The samples were retrieved after one year for DRMS testing which was carried out in a laboratory.

3. Testing

The Scanning Electron Microscopy (SEM) samples measured 10×10×10 mm³ and were cut out of the larger 50×50×10 mm³ samples using a surgical blade. The treated and untreated samples were examined under identical magnifications for each sample type, for direct comparison at ×100 and ×2000. The surface morphology, surface topography, surface features, surface texture, and crystal arrangement were analysed.

Drilling Resistance Measurement System (DRMS) was carried out on the 50×50×50 mm³ cube samples. The depth of the calcium oxalate layer was evaluated through the Drilling Resistance Measurement System (DRMS). Desalination was carried out before DRMS testing for all samples that were treated with ammonium oxalate in the presence of a soluble salt. In the case of untreated samples however, salt free and salinated types were tested.

4. Results & discussion

The DRMS results for the Phase 1 samples revealed a treatment depth of up to 1.60 mm for samples treated in a salt free environment and 0.70 mm - 1.00 mm in the case of samples treated in the presence of the soluble salts considered. The depths for the Phase 2 samples were 0.80 mm in the first instance and 0.70 mm - 0.90 mm in the second (Dreyfuss *et al.*, in preparation). Therefore, while salt-free conditions induced deeper formations with treatment (1.60 mm) when compared to salinated conditions (0.70 mm-1.00 mm), this depth was reduced (from 1.60 mm to 0.80 mm) over the year of site exposure which indicates that the calcium oxalate formed in this sample type was being weathered away. Conversely, the depths achieved with treatment in salt-contaminated conditions (0.70mm-1.00 mm) were still maintained one year after exposure (0.70 mm-0.90 mm), possibly suggesting improved durability.

The maximum drilling resistances at the corresponding depths of treatment were also recorded. The results showed that the increased depths of 1.60 mm in the samples treated in a salt-free environment were coupled with reduced values of drilling resistance (13.52 N) when compared to those samples treated in the presence of soluble salts which had

shallower treatment depths (0.70 mm-1.0 mm) but a greater drilling resistance (14.79 N-21.62 N), (Dreyfuss *et al.*, in preparation). This implies that the newly formed calcium oxalate in the salt contaminated samples has improved strength characteristics when compared to the calcium oxalate formed in salt-free environments. These DRMS results were further analysed and correlated to SEM observations as discussed below.

For SEM analysis a Merlin FESEM with Carl Zeiss optics and Gemini II column (s/n: 4216) was used. In the SEM images of the desalinated untreated samples at $\times 100$, individual calcite crystals/granules were observed together with globigerinae and other fossils. In the treated samples, the microfossils were still visible and the previously individual crystals/granules were seen to be more compact. These findings suggest that treatment results in an improved and more compact surface texture without blocking the globigerinae/fossils. At higher magnifications ($\times 2000$) the desalinated untreated samples showed that individual crystals/granules (A) were clearly distinguishable, (Fig. 1). In the treated samples (Fig. 2), the newly formed calcium oxalate was observed to take the form of flat crystals/plates which were arranged in a layered arrangement/stacked parallel to the sample surface (B). This arrangement is schematically illustrated in Fig. 4.

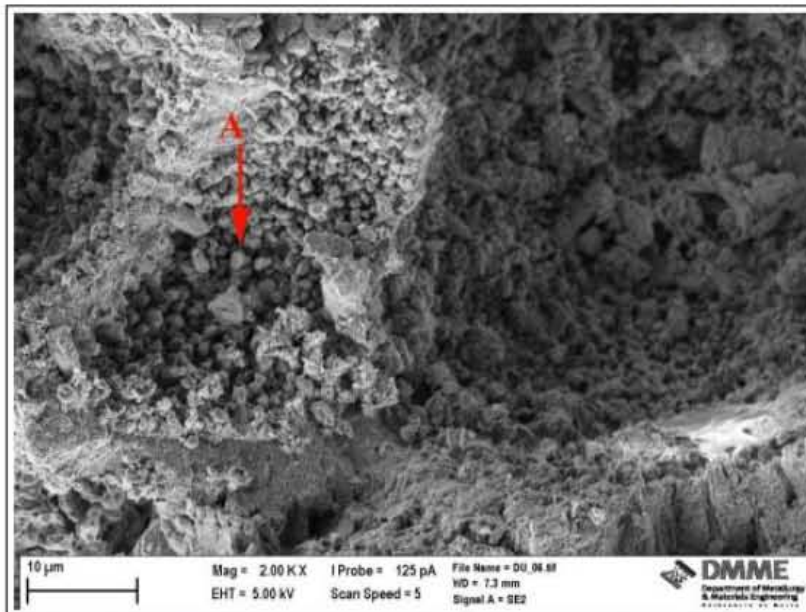


Fig. 1: SEM image ($\times 2000$) for desalinated untreated laboratory sample.

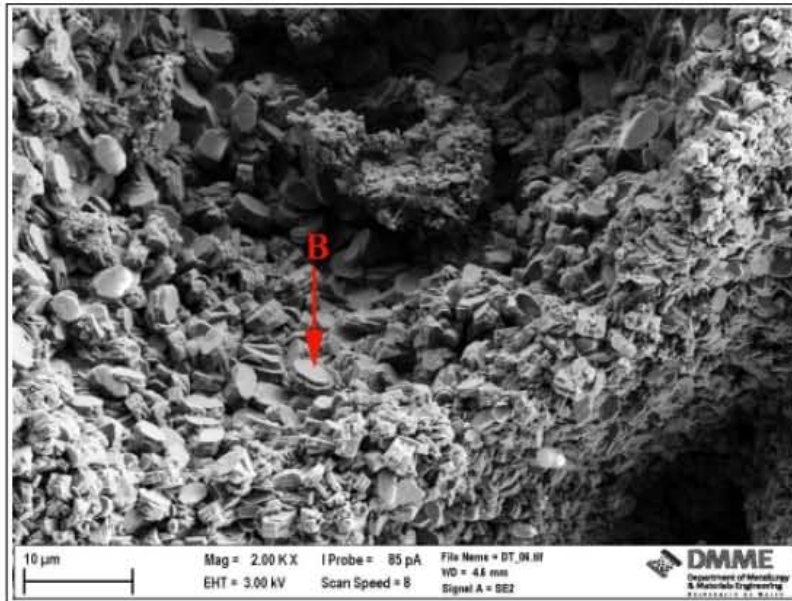


Fig. 2: SEM image (x 2000) for desalinated treated laboratory sample.

In the untreated salt contaminated samples, salt crystals were seen to completely cover the sample surface in the sodium chloride and sodium nitrate contaminated samples respectively. Sodium sulfate was also seen to substantially cover the sample surface although to a lesser extent since globigerinae were still visible after salt contamination. These findings confirm that salt contamination has a “pore blocking/coating” effect which probably inhibits the ammonium oxalate from penetrating deeper resulting in shallower calcium oxalate formations as observed in the DRMS results above.

After treatment, the amount of surface salt was seen to be greatly reduced in the sodium chloride and sodium sulfate contaminated sample types. The reduction in surface salt in the sodium nitrate contaminated samples was seen to occur to a lesser extent (C in Fig. 3) confirming the blocking/coating behaviour of this salt, also seen in the results from the DRMS where surface salt concentrations were still present after one year of site exposure (Dreyfuss *et al.*, in preparation). These conclusions indicate a reduction in salt content during treatment probably through the water-based poultice.

The morphology observed in the treated, salt contaminated samples showed calcium oxalate to be formed in a different configuration to that developed in the desalinated samples. The calcium oxalate was observed as individual crystals (not layered) which were organised in a vertical arrangement (not horizontal), predominantly perpendicular (not parallel) to the sample surface (D in Fig. 3). This configuration, which is schematically illustrated in Figure 5 may be understood to withstand erosion and natural weathering better than the arrangement of calcium oxalate formed in salt-free conditions (Figure 4), where the configuration may be more susceptible to erosion. The difference between the newly formed calcium oxalate crystal orientation in relation to the salt conditions during treatment

is currently being investigated further. This physical difference in calcium oxalate crystal orientation may account for the reduced depths, the increased drilling resistance and the improved durability achieved in salt laden samples.

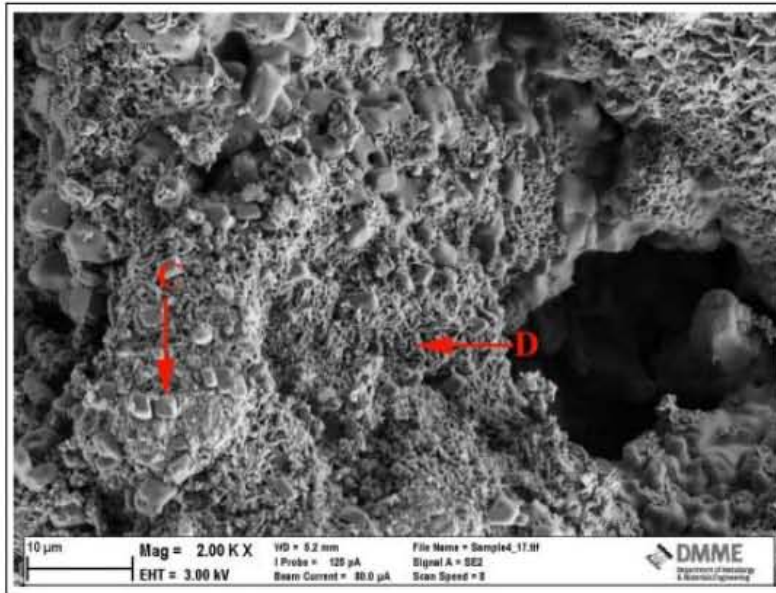


Fig. 3: SEM image (x 2000) for sodium nitrate contaminated treated laboratory sample.

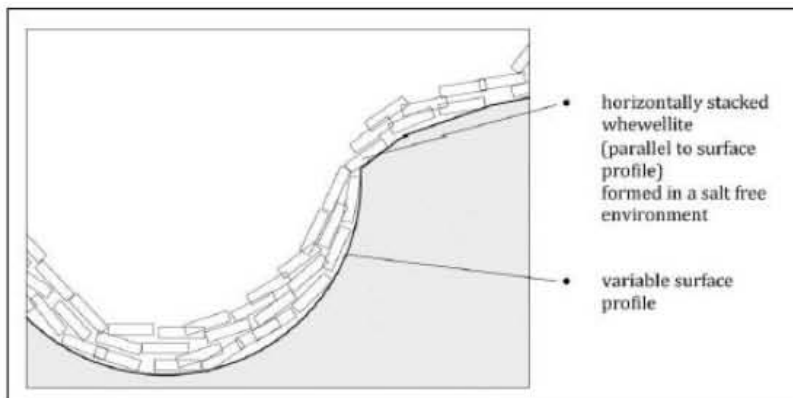


Figure 4: Schematic illustration of the whewellite formed in salt free environments.

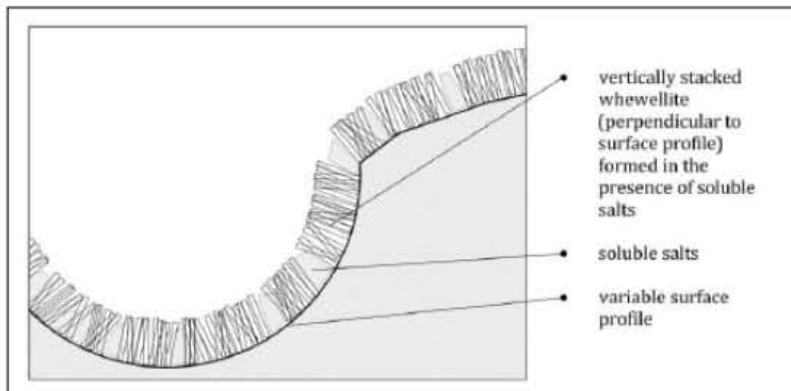


Figure 5: Schematic illustration of the whewellite formed in the presence of soluble salts.

5. Conclusions

When compared to treated desalinated samples of the same type, the treated salt contaminated samples recorded shallower calcium oxalate depths and higher values for the drilling resistance. This resulted in an increased durability during the one year of site exposure, after which the depth of induced “hardness” decreased from a range of 0.70 mm to 1.0 mm to a range of 0.70 mm to 0.90 mm. In the desalinated samples this decreased from 1.60 mm to 0.80 mm. This difference was explained through the SEM images where calcium oxalate was seen to form in horizontally stacked layers, parallel to the sample profile, in the desalinated samples, the physical configuration of which is probably differently susceptible to erosion. The calcium oxalate formed in the presence of soluble salts was arranged in a vertical manner, perpendicular to the sample profile, creating an interlocked network of whewellite crystals. Further research into the reasons for this varying orientation, as well as treatment and testing of exposed historic limestone is currently ongoing.

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