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Investigating a method to limit damage in Globigerina Limestone, a soft porous stone widely used in historic buildings

S. Sammut^{1*}, J. Cassar¹, A. Marrocchi², C. Russo², L. Sommei² and M.L. Santarelli³

¹Department of the Built Heritage, Faculty for the Built Environment, University of Malta, Malta

²Department of Chemistry, Biology and Biotechnology, Università degli Studi di Perugia, Perugia, Italy

³Centro di Ricerca in Scienza e Tecnica per la Conservazione del Patrimonio Storico-Architettonico, Università di Roma La Sapienza, Rome, Italy

*svetlana.sammut.00@um.edu.mt

Abstract

A programme of studies is ongoing to investigate the action of environmentally-friendly functionalized polycarboxylates as organic crystallization modifiers on salts on two types of Globigerina Limestone of Malta, to compare their action and behaviour. This was mainly done to verify the potential of such compounds to control, and therefore, limit damage on this locally unexplored territory. The main thrust of the research, at this stage, was to observe modifications to solution transport and salt crystal growth induced in two varieties of the stone by treating under controlled laboratory conditions; work under uncontrolled conditions has also commenced, but will not be discussed here. In this paper, indications of the modifications obtained are discussed, in the context of former trials, the fact that they are still under investigation and with a view on way forward. A discussion establishing a classification for damage limitation is postulated.

Keywords: Globigerina Limestone conservation, salt damage, crystallization modifiers

1 Research aims

Research relating to the conservation of the built heritage, and in particular, behaviour of materials, stone conservation practices and possible environmental effects, has acquired great importance, also in Malta. The unsuitability of currently available treatments for conservation was often only understood following their application, in turn encouraging a generation of new research for the development of new materials and procedures, also with respect to salt weathering [1, 2].

As one of the most common causes of deterioration, salt damage in porous materials remains not yet fully understood, and hence has been the subject of study by many authors (examples are [3-8]). The crystal pressure against pore walls and volumetric changes during the growth of crystals during de/hydration and crystallization cycles under variable environmental conditions, are amongst the most investigated modes of damage for porous materials [1, 4, 9].

It is in this context of an incomplete understanding of damage, as well as the ever-present water (containing soluble salts) in porous building materials in the built heritage, that studies which directly target salt damage within porous building materials, are being undertaken.

The main aim of the research has been to observe, and compare, modifications to salt crystal growth induced in two varieties of Globigerina Limestone by the application of crystallization modifiers. This was done with a focus on the potential of such compounds to control, and therefore, limit damage. This study on this locally unexplored territory, has primarily focused on the damaging action of sodium sulphate, as one of the most damaging salt types [9-12], but also on sodium chloride, sodium nitrate and binary mixtures of the first two.

In this paper, the results obtained using this still experimental method of limiting salt damage on local stone are outlined. Indications on any effect on deterioration and changes to the crystallization habit of contaminant salts, following the application of salt crystallization modifying products on the stone systems, have also been visually and microscopically observed. The way forward is also anticipated.

2 The materials

The Globigerina Limestone under study originates from the geological sequence of the Maltese Islands consisting of four major and one minor sedimentary formations [13]. This archipelago, lies in the middle of the Mediterranean Sea, between Sicily and North Africa and is limited to circa 316 square kilometres. The Globigerina formation has been the primary building stone used for construction, for well over 5000 years [14]. It primarily consists of high purity calcite (>92%) with a fine grain and contains trace amounts of other minerals [15-17]. The porosity is very high

and can be up to 40% [12]. Its colour is mainly cream, with occasional inclusions of hard shell fragments, bioturbation and other variations in an otherwise generally homogenous matrix.

There are two basic classifications (by quarry owners) of this stone, namely the *franka* (freestone) 'good quality' and 'bad quality' *soll*, which generally lie at the extreme ends of the different 'grades' of this natural material. The latter type is generally less resistant when exposed to weathering, generally varying in geochemical and mineralogical composition and having a lower overall porosity with a higher degree of small pores [12, 15, 18-20]. The pores of *franka* are both inter- and intra-granular, with fossil chambers generally empty, while those of *soll* pores are mainly inter-granular, with parts of the fossil chambers often lacking voids [15]. The different stone types can hardly be distinguished visually on fresh material; however, the difference becomes evident on exposed surfaces showing different weathering patterns.

The *franka* can be further sub-classified, namely, the *bajda* (whitish) and *safra* (pale yellow variety). This paper only presents data relating to *bajda*. Studies on *safra*¹ are ongoing and are not reported in this paper. All types of stones have been identified by the respective quarry owners at this stage of the study, based on their experience in their own quarry.

2.1 General material physical properties

The porosity of Globigerina Limestone can reach values up to 40%, depending on location/depth, however, it generally varies between 24 and 37% [21]. The total porosity of the *Bajda* variety used in this research is 37% [22]. Pore radii lie in the range 0.001-6 μm , with smaller pore sizes not being detectable.

With respect to pore size distribution, the major part of pores (about 70%) has a size $>1\mu\text{m}$. The remaining pore volume corresponds mainly to smaller pores. On the other hand, the proportion of small pore sizes for *soll* generally lies in a 40% range, with a much higher proportion of smaller (less than $1\mu\text{m}$) pores, of the order of 60% [20, 22].

2.2 The crystallization modifiers

The types of modifiers selected for this study are functionalized polycarboxylates, as part of a broader research project on a range of materials, on different porous materials [12, 23-27]. To date, the use of these compounds has resulted in positive effects in inhibiting salt

¹ Results on *safra* are consistently similar to those of *bajda*, both in terms of physical properties, as well as those obtained to date with crystallization inhibitors (Cassar et al. 2008)

crystallization. Citrate ($C_6H_8O_7^{-3}$) and phosphocitrate ($C_6H_8PO_7^{5-}$), hereinafter referred to as CA and PCA respectively, are the principal systems used in conjunction with porous materials contaminated with sodium sulphate (Na_2SO_4), sodium chloride (NaCl), sodium nitrate ($NaNO_3$), and binary mixtures of the first two, in these tests.

Both modifying compounds were applied at very low concentrations, between 1 and 100 ppm, for reasons of their application on calcite, but possible because of the positive chemical affinity between the molecule structures in the system, enabling an interaction with the mineral surface even when present in trace amounts. Previous studies have shown that a concentration between 1 and 10 seems the most effective to induce crystallization inhibition [12, 22-27].

The pH of the solution ranges between 6 and 7.

Salt concentrations were kept to realistic levels of 0.35M, which, in comparison to most reported experiments in literature, are quite low; consequently, dramatic results as reported elsewhere [3, 28-30] were not obtained. Here, an incremental approach has been designed.

3 Experimental section

Sodium sulphate, with the addition of sodium chloride and sodium nitrate, was applied in simple and binary mixtures (binary mixtures were only used with the former two salts), in conjunction with treatments with salt crystallization modifying compounds, in three concentrations.

The development of the initial tests with sodium sulphate, particularly in binary mixtures, aimed at giving indications on the possible action of these modifiers in more complex, closer to in-situ situations, where the presence of different types of salts is ubiquitous.

Solution transport behaviour, general macro scale crystallization patterns/efflorescences and modifications to surface morphology of the stone, indicating salt crystallization damage, have been studied, in conjunction with microscopy. Other observations such as quantity of material disaggregation and efflorescence formation have also been noted.

3.1 Methodology

The work carried out to date was performed under controlled laboratory conditions. A methodology explored here is related to the treatment on sound stone, followed by a salt contamination, and related to the one on salt contaminated stone, so as to analyse any differences consequent to the alteration of the sequence in the modes of application/contamination. Such a sequence also enabled observation of any possible effects on sound stone.

The test combinations undertaken are outlined in Table 1 which indicates treatment/contaminant types, as well as environmental conditions.

Tests A02 and A05 relate to samples first contaminated with salts followed by a treatment. The application method of the modifiers in A03 was then changed to the brush type, but also introduced that of the poultice application of the crystallization inhibitor treatment.² The aim of these modifications in the test routines was the creation of a 'model' which is more realistic, in terms of any eventual in-situ application. Repeat sets of tests were also performed to confirm previous obtained results.

3.1.1 Crystallization tests

Two basic methods were adopted for the crystallization/drying tests. Sound cubes, initially 5x5x12.5cm, then reduced to 2.5x2.5x12.5cm (to manage more samples), were used. These stones were cleaned and dried to constant weight and then either:

1. treated with the modifiers in question, using either capillarity, brush or paper pulp application, followed by drying to constant weight and then contamination with the respective salt solution via capillarity in both controlled and uncontrolled laboratory conditions (the latter conditions in a closed room with a ceiling mounted extraction facility provided variations in relative humidity by circa $\pm 15\%RH$ and at times also up to $20\%RH$), or
2. contaminated with the saline solution, dried to constant weight and cleaned to remove efflorescence deposit, followed by treatment with modifying compounds in solution in both controlled and uncontrolled laboratory conditions.

Following the above procedures, a set up similar to that described elsewhere in literature [12] with sealed containers to promote capillary rise through the specimens, was adopted. The evaporative weight loss was measured and plotted in relation to the exposed surface area of sample to extrapolate a direct relationship. In all tests, a minimum of three samples was used per treatment type, with the equivalent control/blank samples.

The initial drying/crystallization tests were carried out with sodium sulphate, considering that this particular salt has proved to be the most damaging under laboratory controlled conditions [9-12]. Further tests and observations were then carried out with sodium chloride and sodium nitrate. Controlled conditions for the tests, including the single salts and binary mixtures, were those carried out at 20 and 23°C and an established

² This type of application was preferred over the partial immersion method, since it is more applicable to the in-situ situations.

50% relative humidity in a climatic chamber³ (Weiss Technik Sr. no.:201982-8-0001).

The formation of efflorescences and eventual limestone damage, were photographically recorded for all samples and the debris weighed to obtain the amount of material loss and efflorescence formation on the samples. The crystal formation and damage were viewed by optical (Nikon Microscope Optiphot – 100 in conjunction with Leica Digital camera DFC290) and digital microscopy (Dino-Lite Pro series AD413T). Elemental analyses of the samples were also performed using a Scanning Electron Microscope (SEM) Merlin FE-SEM by Carl Zeiss with enhanced Gemini II column in conjunction with EDS Edax having an SDD Apollo X detector, for blanks and samples showing the most positive results in terms of increase in evaporative water loss.

³ It must be noted that the controlled conditions in the climatic chamber are maintained by the operation of a rotating blade at the back of the chamber, thus increasing air flow around the samples and influencing evaporation rate. This has been noted to lead to the formation of efflorescences at a faster rate than in ambient, lower air velocity conditions, irrespective of the humidity levels.

Table 1: Actual comprehensive list of drying tests. A01-A04 and (part of) A05, B01, B03, C01 & C03 were carried out in controlled conditions, whereas (part of) A05, B02, B04, C02 & C04 in uncontrolled laboratory conditions

Test ref.	Stone type	Treatment type		Contaminant salt			Conditions		Application method		
		CA (ppm)	PCA (ppm)	Na ₂ SO ₄	NaCl	NaNO ₃	Ambient Av. Temp(°C)/RH(%)	Controlled	Capillary	Brush	Paper pulp
A01	bajda, soll	1	10	0.17M				23/50	✓		
A02*	bajda	1	10	0.35M				20/50	✓	✓	
A03	bajda, soll	1	10	0.35M				20/50		✓	✓
A04	bajda, soll	10	100	0.35M				20/50		✓	✓
A05*	bajda	10	100	0.35M			20/70			✓	✓
B01	soll	1	10		0.35M	0.35M		20/50		✓	✓
B02	soll	1	10		0.35M	0.35M	24/50			✓	✓
B03	bajda	1	10		0.35M	0.35M		20/50		✓	✓
B04	bajda	1	10		0.35M	0.35M	20/60			✓	✓
C01	soll	10	100	0.35M (1:1 & 1:2)				20/50		✓	✓
C02	soll	10	100	0.35M (1:1 & 1:2)			17/70			✓	✓
C03	bajda	10	100	0.35M (1:1 & 1:2)				20/50		✓	✓
C04	bajda	10	100	0.35M (1:1 & 1:2)			20/70			✓	✓

*Contamination followed by treatment was applied in these tests, otherwise, treatment, followed by contamination with saline solution of the types was adopted.

Specific areas studied were those in the upper 8mm, produced by chipping pieces (with a chisel and hammer) from the 'crust'. This zone appeared most affected by salt accumulation towards mid-height of the exposed part of the cubes (circa 3cm from the upper surface). No grinding was carried out so as to limit modifications incurred to the stone sample following such an operation.

4 Results

4.1 Crystallization tests

The initial results obtained for the two varieties of stone, utilizing various application methods indicated, included those for treatment by partial immersion, by brush and via paper pulp. These methods generally indicated a positive tendency of increase in evaporative water loss in the presence of the crystallization modifiers under study (Fig. 1). In general, the use of higher concentrations of CA, as well as the highest concentration of PCA (10 ppm) gave the most positive results, especially on the 'weaker' *soil* stone variety. This means that the crystallization modifiers used tend to influence the rate of transport of saline solutions within Globigerina Limestone, which is being taken as a sign of the effectiveness of the treatment. These compounds generally act as crystallization inhibitors, particularly in the first days following the application of treatment.

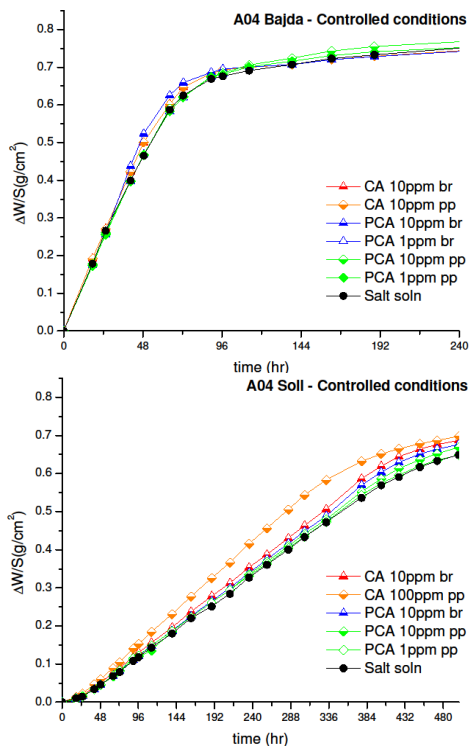


Figure 1: Evaporative weight loss results - Test run A04 using 0.35M Na₂SO₄, on both *bajda* and *soll*

4.1.1 Observations on the effect of the treatment compounds

The effects of the treatment, which varied widely, appear to primarily depend on the material type, but also on the treatment/contamination sequence, the salt type and environmental conditions, confirming observations by other studies [28, 31], whereas they appear to be less dependent on the mode of application of modifying products, as well as the presence or otherwise of a phosphate group in the inhibitor skeleton (over 450 samples have been tested under controlled conditions).

In the *bajda* type, an improved inhibiting effect of CA over PCA is observed in most conditions. Nevertheless, no particular pronounced efficacy was observed with varying mode of application. In the *soll* type, the presence of both CA and PCA indicates inhibiting properties, but, again, without a significant influence with respect to the application method.

It was also noticed that the most pronounced differences observed in evaporation graphs relate to those treated prior to contamination. In this case the drying is delayed; besides a generally reduced distinction between treated and reference samples is observed. This effect is probably due to precipitated salt crystals occluding pores.

The quantity of material disaggregation and efflorescence formation have also been measured, however, the differences obtained in various conditions were too small to draw conclusions, mainly as a consequence of the limited size of sample being used, unlike results reported in [12]. Table 2 (below) summarizes the results obtained so far.

Table 2: Summary of results relating to tests carried out with pure sodium sulphate under controlled conditions

Observations	<i>Bajda</i>	<i>Soll</i>	Remarks
General variance of enhancement in evaporative water loss within executed tests	Distinction between modes of application ranges from: insignificant to 0.2g/sqcm	Distinction between modes of application ranges from: 0.1 to 0.3g/sqcm	<i>Soll</i> exhibits a wider variability, possibly due to composition/pore size distribution
Influence of salt type – macroscopic and evaporative weight loss observations	Primarily filamental strands over exposed part of samples, 'extending' pore structure. This layer eventually crumbles to a powder	Primarily filamental strands, 'extending' pore structure, eventually crumbles to powder in the lowest exposed part of the sample	- Enhancement in evaporation rate is more pronounced with single salt types. - A variance in formation of efflorescence type could be observed macroscopically, with <i>bajda</i> , more readily allowing solution flow, reflecting prevalent larger pore size
Damage to stone	Surface damage generally limited to light superficial disaggregation, sometimes, more pronounced in the corners of the cuboid samples.	Concentrated in lower (exposed) parts of samples. Most pronounced with pure Na ₂ SO ₄ & results in 'peeling/lifting' effect of outer layer exposing a weaker disaggregated surface. Horizontal splits of base of stone observed.	- Damage mainly limited to specific exposed parts. - Appears to be heavily dependant on salt type, other than treatment. - Varies widely between the two stones tested - Least damage observed with salt mixtures.

4.1.2 Crystal morphological changes

Observations to date on representative stone samples⁴, were carried out by optical and digital microscopy⁵ but more importantly SEM, particularly on those samples showing a highly enhanced evaporation rate. Modifications in crystallization patterns and habits, in comparison with unconfined crystal formation have been noted. Crystal morphology generally appears to be far from the regular habit, especially in the presence of inhibitors. Indications are that crystals are more skeletal (especially for NaCl), with prevalent preferential development of specific faces.

A comprehensive SEM investigation of the tested samples to confirm these positive indications are planned, particularly for comparison with untreated, but salt-laden samples. This information shall be studied in the context of interpreting any changes vis-à-vis the modification solution transport and eventually contributing to data for building a mathematical model to understand the trends of action of crystallisation modifiers in question. The latter is deemed to be essential considering the heterogeneity of these natural materials, which broadens the scope in establishing a model of action.

5 Discussion and conclusions

The actual results obtained using the local stone, Globigerina Limestone, both 'good' and 'bad' qualities, confirm the need for the further deepening of the study of the action of the crystallization modifiers as inhibitors, particularly with respect to modification of evaporation rate as well as crystal habit modification.

The following observations and conclusions can be made at this point:

- The most significant modification of evaporation rate is observed in the initial period of the test, particularly when the solution within the pores is uninterrupted;
- The action of the inhibitors is very much dependent on the substrate type, but also on the solution composition and environmental factors, especially relative humidity levels which

⁴ Chippings from the outer 8mm of the stone cuboids were analysed.

⁵ Difficulties obtaining a clear image at various depths of the stone have been experienced, due to the limited aperture variation of available equipment (Nikon Microscope Optiphot – 100 in conjunction with Leica Digital camera DFC290). Such observations merit further investigations to obtain a better picture of changes; these will be reported in future.

appear to influence evaporation rate, but more importantly efflorescence patterns;

- Given the range of tests carried out, it can be concluded that a precise mode of action cannot be pre-determined, mainly due to the nature of the substrate, which in this case, is a heterogeneous natural material. Other variables come into play when dealing with such situations, particularly the more complex salt/environmental conditions in-situ type. A larger sample set is therefore recommended at this stage in conjunction with further analysis, also using statistical tools such as Cluster Analysis and Principal Component Analysis to identify trends.
- The application methods tested are also considered to limit the damage incurred to replacement fresh stone in the context of the presence of salts in existing structures.

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