Limestone resistance to sodium sulfate degradation after consolidation by hydroxyapatite and TEOS

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Abstract

The use of aqueous phosphate solutions to produce hydroxyapatite (HAP) inside weathered carbonate stones has recently been proposed as a new consolidating technique. In this paper, the resistance of HAP-treated stone to soluble salt crystallization was investigated. Globigerina limestone, a porous stone typically used in historic architecture in Malta and often severely affected by salt crystallization, was used. After preliminary artificial weathering by heating at 400 °C for 1 hour, aimed at producing micro-cracks opening in the stone, cylindrical samples (5 cm height, 2 cm diameter) were treated by brushing application of a 3 M aqueous solution of diammonium hydrogen phosphate, followed by application of a limewater-impregnated poultice. For comparison's sake, a similar set of samples was treated with a commercial TEOS-based product, while a third set was left untreated. After proper curing, HAP- and TEOS-treated samples, together with untreated ones, were subjected to sodium sulfate crystallization cycles, by partial immersion in a 14 wt% sodium sulfate decahydrate solution for 7 hours and then drying at 50 °C for 15 hours. After each cycle, damage evolution was monitored by visual assessment and weight measurement. Five cycles were carried out in total. From the results of the study, the performance of the novel phosphate treatment can be regarded as promising, as HAP-treated samples exhibited less micro-cracking and lower mechanical damage than untreated and also TEOS-treated samples.

Keywords: ammonium phosphate, inorganic consolidants, pore size distribution, calcite, ethyl silicate

1   Introduction

Limestone consolidation is still a very challenging task, as a commercial product that satisfies all the requirements that consolidants must meet [1] does not currently exist. In fact, the available treatments exhibit significant limitations when applied to carbonate stones, with regard to their effectiveness (e.g., nano-limes and silicate consolidants), compatibility (e.g., silicate and polymeric consolidants) and/or durability (e.g., polymeric consolidants) [2, 3].

To overcome such limitations, the use of aqueous phosphate solutions to produce hydroxyapatite (HAP) inside weathered carbonate stones has recently been proposed [3]. The idea is that HAP can be formed directly inside the stone, as the reaction product between the phosphate solution and the calcitic substrate, so that cohesion between grains can be restored and mechanical properties can be improved [3]. The HAP-treatment has been found to provide a remarkable consolidating action, leaving the total porosity of treated stone substantially unaltered and preserving stone hydrophilic behavior [3-5]. According to results obtained so far, the effectiveness and compatibility requirements can hence be considered as fairly satisfied.

With regard to the durability requirement, preliminary tests have shown a good resistance of HAP-treated stones to wetting-drying cycles [3] and some mitigating effect towards thermal weathering [6]. However, no specific study aimed at evaluating resistance to salt crystallization, which is one of the main causes of limestone deterioration in the field, has been reported so far. The importance of evaluating the resistance to salt damage further derives from the fact that HAP formation has been found to cause a slight shift of pore size distribution towards smaller pores [3, 7], which may eventually increase the susceptibility of treated stone to salt crystallization.

Therefore, in this paper a preliminary evaluation of the durability of HAP-treated limestone to salt crystallization was carried out, by means of accelerated sodium sulphate crystallization cycles in laboratory conditions. Moreover, the HAP performance was compared with that of TEOS, which is currently the most frequently used consolidant for carbonate stones in the on-site practice (notwithstanding its reduced efficacy on this kind of substrate), basically because of the lack of more suitable alternatives.

2   Materials and methods

2.1   Stone

Globigerina limestone from Malta was used for the experimental tests. This lithotype is often severely affected by salt crystallization, especially sodium chloride and sodium sulphate coming from marine aerosol and rising damp

from the ground [8]. From a slab provided by Xelini Skip Hire and High-Up Service (Malta), cylindrical samples (5 cm height, 2 cm diameter) were core-drilled perpendicular to stone bedding planes.

Before consolidant application, the stone was artificially weathered by heating at 400 °C for 1 hour, according to a methodology previously developed by the authors [9]. Salt crystallization cycles could have been alternatively used for artificial weathering (they are actually the main cause of on-site deterioration of Globigerina limestone), but in the present study thermal weathering was preferred, because applying DAP on salt-contaminated samples would have made the effects of the treatment too hard to be assessed, at this stage of research on HAP.

An application procedure consistent with those usually followed in the field was chosen. For each consolidant six samples were treated by brushing 10 times on the whole external surface. Six samples were left untreated for comparison.

2.2   Hydroxyapatite-based treatment

The procedure recently proposed in [7] was followed. Firstly, a 3.0 M aqueous solution of diammonium hydrogen phosphate (DAP) was applied by brushing and then left to react for 48 hours, evaporation being impeded by sample wrapping in a plastic film. Then, after drying, samples were treated with a poultice, prepared by mixing dry cellulose pulp and limewater with a weight ratio of 1:6. After 24 hours of poultice application and wrapping in a plastic film, samples were finally left to dry in contact with the poultice until constant weight.

2.3   TEOS-based treatment

A commercial product, composed of 75 wt% ethyl silicate oligomers (also containing 1% dibutyltin dilaurate as catalyst) and 25 wt% White Spirit D40 (ESTEL 1000 by CTS s.r.l., Italy), was applied by brushing.

The samples were then left to cure in laboratory conditions (T=20±2 °C, RH=50±5%) for 1 month. Even if this period is usually reported in commercial products technical data sheet as sufficient for TEOS hydrolysis-condensation reactions to be completed, TEOS-treated stone may exhibit hydrophobic behaviour for additional several months [2]. This may significantly alter the evaluation of TEOS-treated stone durability to salt crystallization, as stone temporary hydrophobicity hinders the salt solution ingress into the stone. For this reason, after 1 month curing in room conditions, TEOS hydrophobicity was eliminated according to a recently proposed novel methodology, which consists in boosting the curing reactions of ethyl silicate by water poulticing [10].

2.4   Salt crystallization cycles

A 14 wt% solution of sodium sulphate decahydrate and deionized water was used. According to the methodology reported in [11], each cycle consisted in: (i) sample impregnation by partial immersion in the salt solution for about 5 mm and soaking for 7 hours; (ii) drying at 50 °C for 15 hours; (iii) cooling to room temperature for 2 hours. In total, 5 cycles were carried out.

2.5   Characterization techniques

The mechanical effects of the consolidating treatments were evaluated in terms of dynamic elastic modulus (E_d, measured on cylindrical samples before and after consolidation by an ultrasonic instrument with 55 kHz transducers) and tensile strength (σ_t, measured by Brazilian splitting test on the same cylindrical samples as above). The microstructural alterations induced by the treatments were evaluated by mercury intrusion porosimetry (MIP), using a Porosimeter 2000 Carlo Erba with a Fisons Macropore Unit 120. Water sorptivity and water absorption after treatment (and after accelerated curing, in the case of TEOS) were determined on cylindrical samples subjected to capillary absorption for 24 hours, in the conditions described in EN 15801.

The effects of salt crystallization cycles were firstly evaluated by visually inspecting the samples and monitoring their weight after each cycle. Then, after the fifth cycle, for each condition two samples were taken by chisel (to avoid salt washing away by wet sawing) from the positions indicated in Figure 1. The two samples were: (i) a lower sample, coming from the bottom part of the cylinder directly immersed in the salt solution (labeled as "1") and (ii) an upper sample, coming from the top of the cylinder (labeled as "2"). During samples collection, particular care was given to avoiding the external surface, where efflorescences had grown.
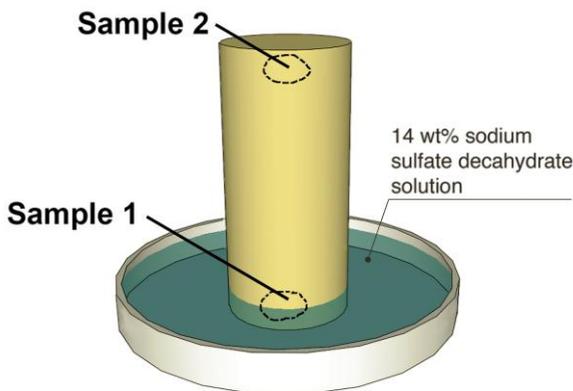
Figure 1:   Scheme illustrating the sampling points in cylinders subjected to salt crystallization cycles.

Samples 1 and 2 were analyzed for determining their salt content and pore size distribution. The salt content was determined by ion chromatography (IC), using a Dionex ICS 1000, after sample grinding, salt extraction by deionized boiling water and filtering. The pore size distribution of the upper samples ("2") was evaluated by MIP immediately after the salt crystallization cycles and after removing the salts from the samples by poulticing (cellulose pulp and distilled water). Finally, the salt crystallization effect on sample integrity was evaluated by measuring E_d of cylindrical samples after salt removal by poulticing.

3　Results and discussion

Both treatments caused remarkable increases in dynamic elastic modulus and tensile strength, as reported in Table 1. Even if TEOS caused a higher improvement, the consolidating effectiveness of HAP is remarkable, being ΔE_d = +40% and $\Delta\sigma_t$ = +40%. The very good performance of TEOS can be explained considering that Globigerina limestone naturally contains small amounts of quartz, that can allow some chemical bonding between the formed silica gel and the stone [12].

Neither of the two treatments was responsible for dramatic pore occlusion, even if TEOS caused a non-negligible 13% decrease in open porosity (Table 1). In terms of pore size distribution (Figure 2), HAP caused an increase in the amount of pores with radius 0.01-0.1 µm, whereas TEOS (and to a smaller extent HAP) led to a slight increase in the pores with radius < 0.01 µm. These increases in the relative percentage of the finest pores occurred mainly at the expense of the pores with radius 0.1-1 µm.

In terms of physical properties (Table 1), HAP caused only minor modifications in stone sorptivity and water absorption, consistent with previously obtained results [3, 7]. In the case of TEOS, a very little modification in water transport properties was found as well, which can substantially be ascribed to the good efficacy of the accelerated curing procedure, able to cause complete TEOS hydrolysis-condensation in a much shorter period of time than experienced on site [10].

Table 1:　Mechanical, microstructural and physical properties of untreated and treated samples, before salt crystallization cycles (E_d = dynamic elastic modulus; σ_t= tensile strength; OP = open porosity; AC = absorption coefficient; WA_{24} = water absorption after 24 hours).

	E_d [GPa]	σ_t [MPa]	OP [%]	AC [mg/(cm^2√s)]	WA_{24} [%]
UNTR	11.6	2.5	37.1	20.5	14.6
HAP	16.3	3.5	34.7	19.3	13.9
TEOS	18.9	5.6	32.1	19.6	14.1
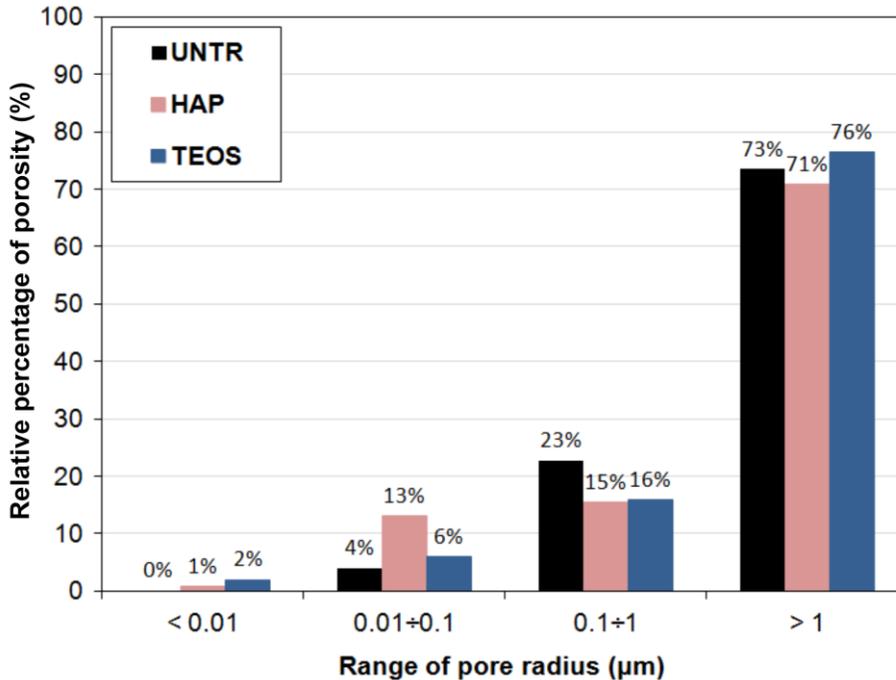
Figure 2:   Distribution of pore size in untreated and treated samples.

The fact that both treatments left water transport properties basically unchanged and that open porosity was only slightly decreased after treatments allows to expect that also soluble salt-containing solutions will be able to exit from the treated stone, without causing sub-efflorescences formation and consequent stress inside the stone. However, the modifications in the pore structure induced by HAP and TEOS (Figure 2) may potentially be responsible for higher crystallization pressures inside the treated stone (the smaller the pore, the higher the crystallization pressure [13]). Therefore, the need of specifically evaluating resistance to salt crystallization after consolidation is confirmed.

When subjected to sodium sulphate crystallization cycles, untreated and treated samples underwent the weight changes reported in Figure 3. At the end of the fifth cycle, accelerated weathering was stopped as the samples exhibited marked visible decay and the appearance of untreated and treated samples, after salt washing away, was that illustrated in Figure 4. The untreated samples exhibited the most pronounced surface alteration, due to considerable flaking and pulverization, while HAP-treated samples apparently underwent the lowest deterioration.
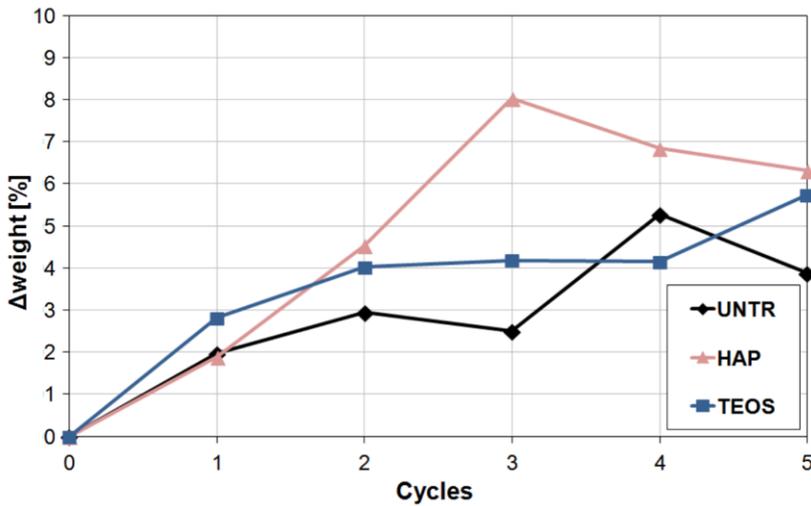
Figure 3: Percentage weight change of untreated and treated samples as a function of salt crystallization cycles.
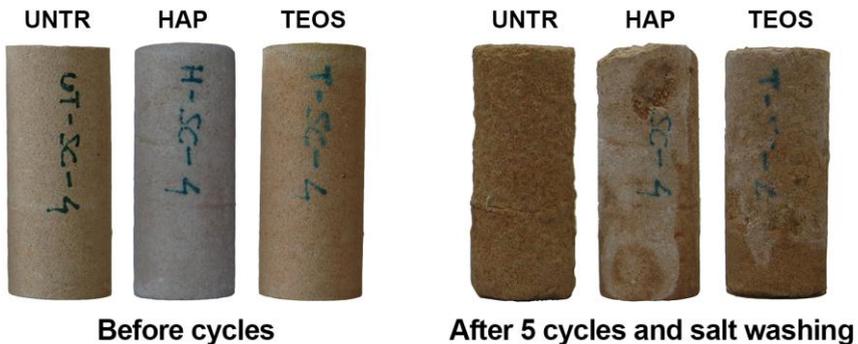
Figure 4: Appearance of untreated and treated samples, before and after 5 cycles and salt washing away.

The amounts of salts deposited in the untreated and treated samples are reported in Figure 5. As expected, the untreated samples exhibited a higher salt amount than treated samples, especially in the upper part (sample 2), where evaporation is more pronounced. TEOS-treated samples exhibited a similar trend in salt distribution, even if lower amounts were registered, whereas in the case of HAP no significant difference in salt content between the lower and upper parts was detected. The fact that untreated samples exhibited the highest salt content but, at the same time, the lowest weight increase (Figure 3) can be explained considering that these samples underwent the most severe flaking and material loss.
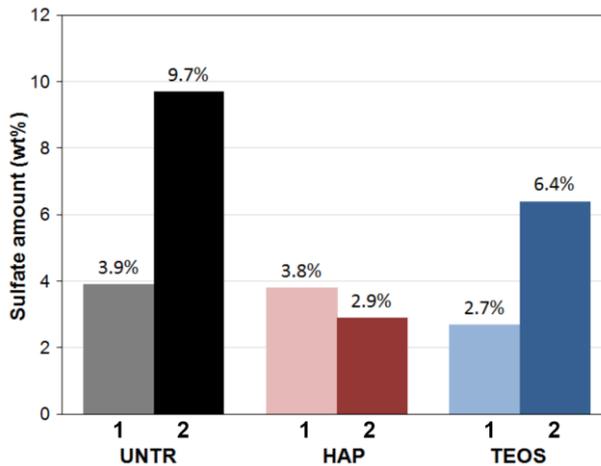
Figure 5:   Sulfate content of untreated and treated samples after 5 cycles.

The effect of salts on sample microstructure was evaluated by MIP. In the case of salt-laden samples (dashed lines in Figure 6), some pore clogging was found for all the conditions. After salt removal by poulticing (dotted lines in Figure 6), remarkable differences in the pore size distribution were found. In particular, all the samples subjected to salt removal exhibited a higher open porosity than the corresponding salt-containing samples (according to IC results, salt content decreased from that reported in Figure 5 to about 0.2-0.3 wt.%). In the case of the untreated sample and, to a lower extent, of the TEOS-treated sample, after salt removal the open porosity was found to be even *higher* than the corresponding salt-free references. This can be attributed to the opening of new micro-cracks, as a consequence of stress exerted by growing salt crystals inside the pores. Notably, in the case of the HAP-treated sample, after salt removal, the resulting open porosity was however *lower* than that of the HAP-treated reference. This seems to suggest that no micro-cracking of the consolidated stone occurred (the difference with respect to the salt-free reference being owing to some residual salts retained in the pores).

To have a confirmation of this, dynamic elastic modulus measurement was repeated on two samples for each condition after salt removal. In agreement with indications obtained by MIP, remarkable decreases in E_d with respect to the condition before salt crystallization cycles were found for the untreated ($\Delta E_d = -15\%$) and TEOS-treated samples ($\Delta E_d = -20\%$). In the case of HAP, a much smaller decrease was found ($\Delta E_d = -3\%$), which seems to confirm that HAP-treated samples actually underwent less degradation than the other samples. Hence, since both TEOS- and HAP-treated samples exhibit similar E_d values after salt crystallization cycles (respectively, 15.7 and 15.5 GPa), any substantial advantage, in terms of mechanical properties, deriving from using TEOS rather than HAP seems to be lost after accelerated salt weathering.
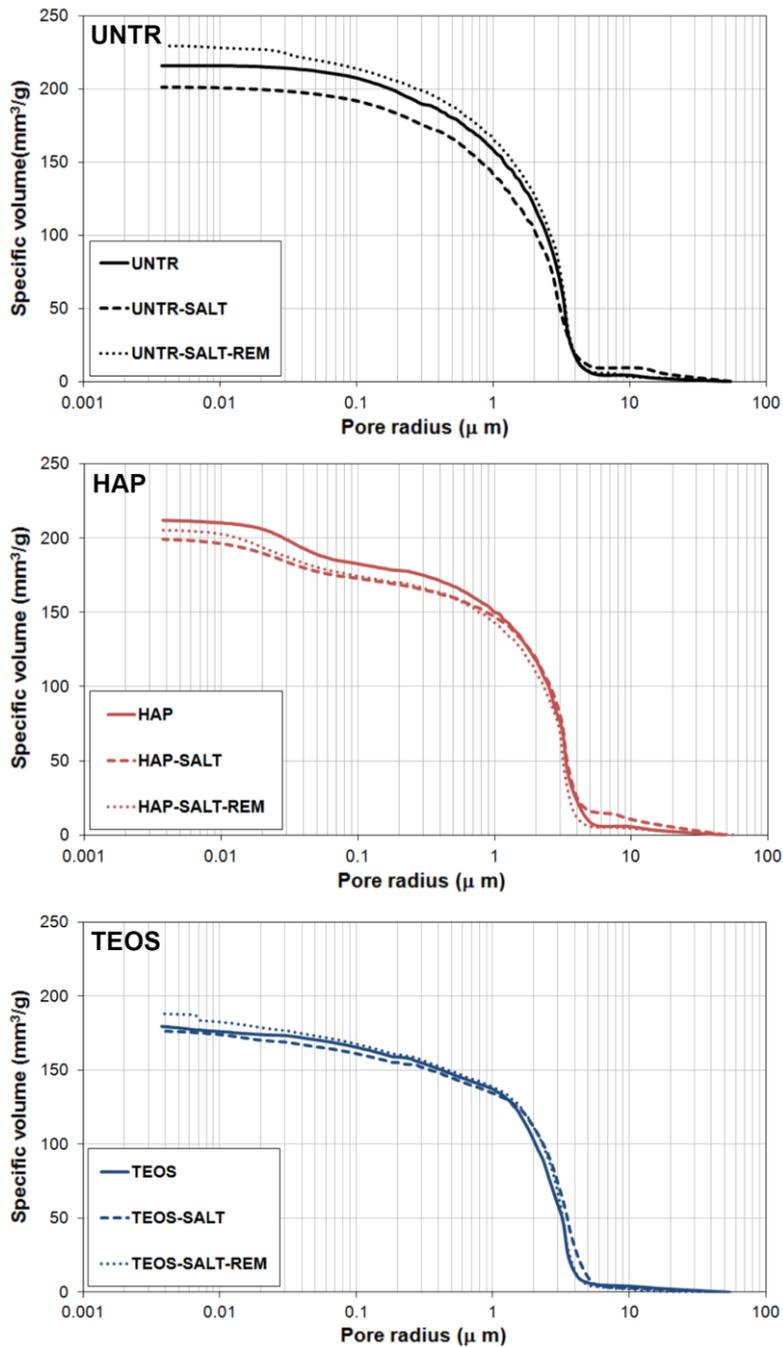
Figure 6: Pore size distribution of untreated and treated samples before, after 5 crystallization cycles ("-SALT" samples) and after salt removal ("-SALT-REM" samples).

4   Conclusions

In this paper, the durability of limestone samples consolidated by a novel phosphate-based consolidant was evaluated and compared to that of samples consolidated with a commercial TEOS-based product. Based on the results obtained in this study, by accelerated sodium sulphate crystallization cycles in laboratory conditions, a promising performance of the novel HAP-based consolidant was found. Indeed, HAP-treated samples exhibited less micro-cracking and lower mechanical damage than untreated and also TEOS-treated samples. In order to evaluate whether the HAP treatment may be responsible for sub-efflorescences formation at the interface between the unconsolidated substrate and the consolidated layer additional experimental tests are currently in progress. Future work will be also dedicated to evaluate the treatment performance when applied on already salt-contaminated substrates.

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