COMPARISON OF POROUS SEDIMENTARY STONE CONSOLIDATION BY A NEW HYDROXYAPATITE-BASED TREATMENT AND BY TEOS

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Abstract
The effects of consolidating two sedimentary porous stones by a new hydroxyapatite-based treatment and by TEOS were compared, in terms of modifications in mechanical, physical and microstructural properties. Both treatments caused significant mechanical improvement, however TEOS also caused considerable alterations in pore size distribution and water sorptivity, which leads to identify hydroxyapatite as a more compatible material for stone consolidation.

Introduction
A new hydroxyapatite-based treatment for limestone consolidation has recently been proposed [1]. The treatment is based on the fact that, by impregnating the stone with an aqueous solution of di-ammonium hydrogen phosphate (DAP), hydroxyapatite (HAP) can be formed inside stone pores as the reaction product between DAP and the calcitic substrate. In this paper, the effects of the HAP-based treatment on two sedimentary stones with varying mineralogical composition and open porosity were investigated and compared to the effects of consolidation by ethyl silicate (TEOS).

Materials and Methods
Two stone were used: *Giallo Terra di Siena* (SS1), a porous stone containing calcite (84.3 wt%), quartz and Na-feldspar, and *Globigerina* limestone (SS2), a very porous limestone containing calcite (91.4 wt%) and quartz. Before any test, stone samples were artificially weathered by heating, according to [1, 2].
For the HAP-based treatment, a 1 M aqueous solution of DAP (Sigma–Aldrich) was applied by brushing until refusal. The samples were left reacting for 48 hours (impeding the consolidant evaporation) then dried at room temperature until constant weight.
For the TEOS-based treatments, a solution of 75% v/v TEOS (containing a 1% dibutyltin dilaurate catalyst) and 25% v/v organic solvent (isopropyl alcohol for SS1, white spirit for SS2, CTS s.r.l., Italy) was applied by brushing until refusal. The samples were left curing in laboratory conditions for at least 1 month before any test.
Samples were characterized in terms of dynamic elastic modulus (E_d) and tensile strength (σ_t), determined on cylindrical samples as described in [2]. Open porosity (OP) and pore size distribution were measured by mercury intrusion porosimetry (Fisons Macro185 pore Unit 120 and Porosimeter 2000 Carlo Erba). Water absorption by capillarity after 24 hours (WA) and sorptivity were measured on 5 cm cubic samples according to EN 15801.

Results and Discussion

After consolidation by DAP, both stones experienced remarkable increases in mechanical properties (Tab. 1), as a consequence of HAP formation inside pores, which leads to a more effective bonding among stone grains [1]. The HAP-based treatment performed better on SS1 than SS2, especially in terms of tensile strength, in spite of the higher carbonate content of the latter, presumably because of the different artificial deterioration produced by heating (cracks opening by heating was more effective in SS1 than in SS2 [2, 3]).

Tab. 1. Mechanical, physical and microstructural properties of untreated and treated samples

Sample	E_d [GPa]	σ_t [MPa]	OP [%]	WA [%]
SS1	22.7	4.1	21.5	4.5
SS1+HAP	28.4	5.0	20.3	4.5
SS1+TEOS	31.5	5.4	17.5	0.3
SS2	11.4	2.3	36.7	16.1
SS2+HAP	15.7	2.7	35.2	15.2
SS2+TEOS	18.5	5.2	27.6	0.6

TEOS made mechanical properties increase even more than HAP (Tab. 1), even if silicate consolidants are widely reportedly to be less effective on carbonate stones than on silicate ones [4]. However, in the present case, the good performance of TEOS can be explained considering that small amounts of quartz are present in both SS1 and SS2, so that some chemical bonding between the silica gel and the substrate can occur [5]. Consolidation by TEOS was more effective on SS2 than SS1 (Tab. 1) probably because of the different solvent used in the two cases [6].
TEOS-treated stones exhibited partial pore occlusion (Fig. 1) and a considerable OP decreases (Tab. 1). In terms of WA and sorptivity, both TEOS-treated stones exhibited dramatic reductions (Fig. 2 and Tab. 1), owing to residual ethoxy groups even 1 month after the treatment, leading to some not-permanent hydrophobic effect. On the contrary, HAP formation caused negligible alterations in pore size distribution, OP and stone transport properties (Fig. 1 and Fig. 2).
As pore occlusion and alterations in stone hydrophilic behavior are usually undesired [4], HAP can be regarded as a more compatible consolidating material with respect to TEOS.

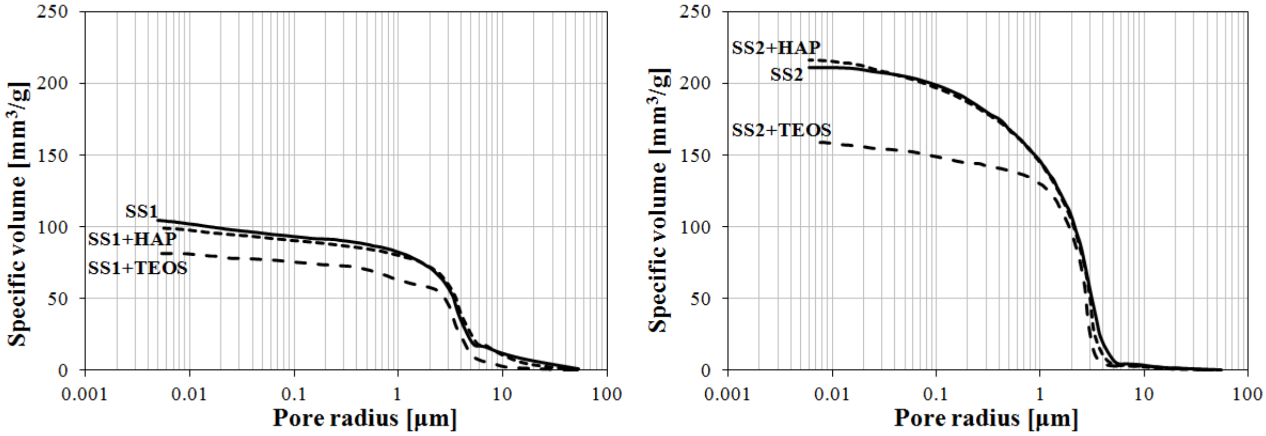

Fig. 1. Pore size distribution of untreated and treated samples

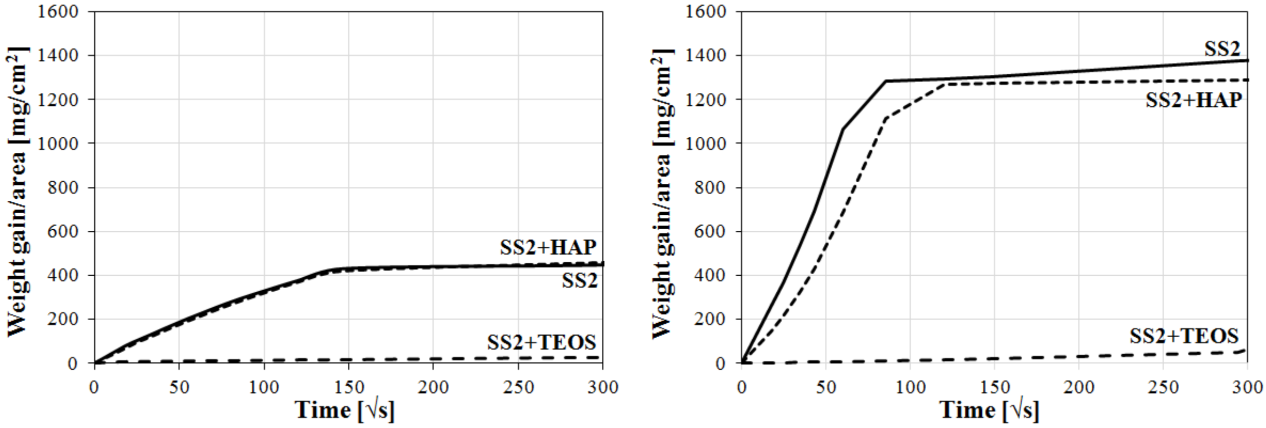

Fig. 2. Water sorptivity of untreated and treated samples

Conclusions

HAP appears as a promising material for the consolidation of porous mainly carbonate stones. Indeed, it was found to significantly improve stone mechanical properties, without occluding pores and causing dramatic alterations in water absorption and sorptivity. On the contrary, TEOS-based treatments, which however proved to be very effective in increasing stone mechanical properties, caused considerable pore occlusion and dramatic alterations in stone transport properties.

References

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