TEOS BASED CONSOLIDANTS FOR MALTESE GLOBIGERINA LIMESTONE: EFFECT OF HYDROXYL CONVERSION TREATMENT

Sophie M. Briffa[1], Emmanuel Sinagra[2] and Daniel Vella[1]

[1] *Department of Metallurgy and Materials Engineering, Faculty of Engineering, University of Malta*
[2] *Department of Chemistry, Faculty of Science, University of Malta*

Abstract

Lime-based consolidants are widely used in Malta where the main building material is a sedimentary limestone. Over the past few years, commercial alkoxysilane consolidants have also infiltrated the local market, yet the effects of these materials on local Globigerina Limestone is still not well documented. Whereas it is well established that alkoxysilane consolidants form strong bridges between the deteriorating surface and healthy underlying stone in sandstones, the same is not necessarily true for porous limestone. A hydroxyl conversion treatment (HCT) has been proposed to improve bonding between silica-based consolidants and limestone (Wheeler 2005).

In this work, Globigerina Limestone test samples were treated respectively with a laboratory-prepared consolidant based on tetraethylorthosilicate (TEOS), and the same consolidant loaded with 35 nm silica particles. Another set of stone samples were first pre-treated with an ammonium tartrate solution known as HCT before application of TEOS and nanoparticle-loaded TEOS. The HCT converts the stone surface into calcium tartrate, offering a hydroxylated surface onto which the alkoxysilane can anchor. Ammonium tartrate was preferred to tartaric acid on grounds of conservation ethics. The effect of the surface conversion treatment was evaluated by an infra-red technique. Untreated limestone samples were employed for comparative purposes. Consolidant-stone interactions were observed at high magnification under the electron microscope. Alteration to stone colour was followed by a colorimetric technique. The physical properties of the consolidated stone were assessed by a hardness test, water absorption by capillarity and resistance to sodium sulphate crystallisation. Results showed that HCT improved the consolidation properties of the TEOS and possibly those of the alkoxysilane containing nanoparticles. The ammonium tartrate (AMT) pre-treatment was successful even though chemical formation of calcium tartrate was not favourable according to solubility equilibria. The tartrate treatment however led to some discolouration, probably resulting from mobilisation of intrinsic iron in the limestone.

Keywords: Globigerina Limestone, hydroxyl conversion treatment, alkoxysilane, sol-gel, ammonium tartrate

1. Introduction

The rock formation of the Maltese Islands consists of five main strata. These are listed in order of geological formation as follows: Lower Coralline Limestone, Globigerina Limestone, Blue Clay, Greensand and Upper Coralline Limestone (Spratt 1943; Murray 1890). Globigerina Limestone is exploited for its good building qualities. It can be described as fine-grained, full of foraminifera shells and visible fossils, and is primarily composed of calcium carbonate (Cassar 1999; Gatt 2006). The microstructure

consists of calcite crystallites cemented together by amorphous calcium carbonate, which may contain up to 12% clay minerals and 8% quartz (Cassar 1999; Cassar and Vannucci 2001). Globigerina limestone is very porous; the volume porosity ranges between 32% and 41% with the majority of pores having a size ≤ 4 μm (Cassar 1999; Cassar and Vannucci 2001). Globigerina limestone may be sub-divided into *franka* stone, which exhibits good weathering properties and changes to a pale yellow colour with a resistant surface and *soll*, which deteriorates rather easily by a process of cavitational weathering producing characteristic honeycombed structured erosional features (Vella et al. 1997). The *franka* limestone is the one chosen for building while the *soll* is primarily used in building foundations (Vella et al. 1997).

Commercial products containing alkoxysilanes, such as TEOS, are commonly employed as consolidants for stonework. An advantage of these materials is that they are applied in monomeric form and polymerise by hydrolysis and condensation reactions forming inorganic silica within the stone structure. Application viscosities are implicitly low and this minimises problems associated with consolidant penetration. Unfortunately, the unreacted monomer may be lost through evaporation (Brinker and Scherer 1990).

Tetraalkoxysilane consolidants are reported to be very effective at consolidating sandstones (Wheeler 2005; Wheeler et al. 2000; Weiss et al. 2000). As consolidant precursors polymerise inside the stone, covalent siloxane bonds (≡Si-O-Si≡) readily form between silanol groups (≡Si-OH) present on the surface of sandstone and those on the surface of the growing silicate polymer by condensation reaction. The situation for limestone is reported to be less satisfactory due to silicate based consolidants having little affinity for calcite surfaces (Wheeler 2005; Wheeler et al. 2000; Weiss et al. 2000).

In an attempt to improve the adhesion of tetraalkoxysilane consolidants to limestone surfaces, Weiss and co-authors proposed a hydroxyl conversion pre-treatment (HCT) for limestone (Weiss et al. 2000). In the process, a pH-adjusted solution of tartaric acid is applied to the stone. This converts the surface of the stone into calcium tartrate; the acidity converts carbonate into CO_2 and H_2O, liberating Ca^{2+} ions. The latter combine with tartrate depositing calcium tartrate onto the surface. The alcoholic groups of the tartrate provide necessary anchorage for consolidant silanol groups, very probably by hydrogen bonding. The research group confirmed the presence of calcium tartrate tetrahydrate by microscopy and adhesion testing. Preliminary tests with TEOS consolidant showed that pre-treating limestone to the hydroxyl conversion led to a significant improvement in strength (Weiss et al. 2000). In this work, freshly quarried limestone specimens were treated with a solution of ammonium tartrate rather than pH-adjusted tartaric acid as a hydroxyl conversion pre-treatment. This was followed by the application of simple TEOS consolidants.

A problem that arises with TEOS consolidant films is that they tend to crack on drying (Brinker and Scherer 1990). As solvent evaporates from a consolidant film (the sol), a point is reached when the gel network is exposed; from this point onwards, further evaporation of solvent occurs from within the pores of the gel structure. As a result, a build-up of capillary forces occurs, which translate into tensile stresses and may lead to consolidant fracture (Kim et al. 2008). Yang and co-authors (1998, cited in Scherer and Wheeler 2009) showed that by adding silica particles to a silicate consolidant, drying shrinkage was observed to decrease while elastic modulus increased. Furthermore, the nanoparticle loaded consolidant material was still able to penetrate the

2

stone, despite an increase in viscosity. The dried gel was observed to remain porous (Kim et al. 2008; Yang et al. 1998). Another advantage of particle-modified consolidants (PMCs) is that they seem to perform better in salt-laden environments. Aggelakopoulou et al. (2002) compared the behaviour of Ohio Massilian sandstone treated with PMCs to those treated with a conventional silicate consolidant in a salt crystallisation test. Salt efflorescence in PMC treated stone was enhanced. Aggelakopoulou argues that this is probably due to the fact that the nanoparticles aid capillary flow towards the exterior surface of the stone. Other authors have experimented with PMCs achieving quite promising results (Escalente et al. 2000; Kim et al. 2008; Mosquera and de los Santos 2008).

2. Methodology
2.1 Materials

The following chemicals were used as received: ammonium tartrate dibasic (Aldrich, Fluka Analytical), tetraethylorthosilicate, TEOS (Aldrich, Reagent Grade), 98% absolute ethanol (Aldrich, Chromasolv) and dibutyltin dilaurate, DBTL (Aldrich, Fluka Analytical). Franka-type Globigerina Limestone specimens measuring 50x50x20 mm^3 were sourced from a quarry in the limits of Imqabba, a village situated to the southeast of Malta. The freshly cut surfaces were ground to achieve a flat surface and cleaned of excessive dust using filtered compressed air.

2.2 Preparation of the consolidant

The basic silicate consolidant or TEOS consolidant was prepared by mixing TEOS, deionised water and absolute ethanol in a mole ratio of 1:2:5 in a closed glass vessel. The catalyst DBTL (1% v/v) was added to promote the hydrolysis-condensation reactions. The final concentration of silica in ethanol, assuming complete conversion of TEOS to silica was 109.2 g/L.

20-50 nm silica particles were prepared in ethanol solvent by a modified Stöber process (Razink and Schlotter 2007). Particle size analysis (NanoZeta ZS, Malvern) showed the average size of the particles to be 35 nm. A volume of this sol was transferred into the TEOS consolidant prepared as described above to make 1% (w/v) nanoparticle loaded TEOS consolidant.

Consolidant pre-mixtures were applied to the limestone specimens as homogenous liquids by a full immersion method. The time between preparation of the consolidant pre-mixtures and application into the stone was less than 10 minutes. Treated stone specimens were left to dry in atmosphere for one week before characterization and testing. Untreated limestone specimens served as the controls.

Hydroxyl conversion of the limestone was carried out by capillary rise method. Globigerina limestone specimens were placed in contact with a 0.1M aqueous ammonium tartrate (AMT) solution for 1 hour. The development of the conversion treatment is presented separately in Section 2.5.

2.3 Characterization: limestone consolidant system

Colour alterations of the limestone specimens before and after treatment were measured with a Minolta CM-508i spectrophotometer. An electron microscope (Zeiss-Merlin Field Emission) was used to study the interaction of the consolidant with the interior stone pore surfaces. The interior of the treated stone was exposed by fracturing.

2.4 Testing: limestone consolidant system

A salt crystallisation test was carried according to EN12370:1999. It allowed for an indirect method of evaluating the mechanical strength of the limestone treated with the different consolidant systems. A test to determine water absorption by capillarity was carried out according to EN1925:1999. This test allowed the assessment of the flow of water into the stone after applying the different consolidant treatments. Stone surface hardness was determined by a Shore hardness test using the Shore DO indenter.

2.5 Developing the Hydroxyl Conversion Treatment

In this preliminary work, the concentration of the ammonium tartrate (AMT) and the contact time with the specimens needed to precipitate calcium tartrate were investigated. The formation of calcium tartrate on the stone surface was verified by infra-red spectroscopy. Globigerina limestone test specimens were first pre-treated with 0.1, 0.5 and 1M aqueous solution of AMT for one hour. The pH values of these solutions were measured to be between 6.2 and 6.5.

The corresponding infrared spectra of the limestone specimens are presented in Figure 1. The spectra are very similar suggesting that calcium tartrate forms on the limestone surface at all concentrations tested. The characteristic IR bands for calcium tartrate include two medium absorption bands at 3420 cm^{-1} and 3550 cm^{-1} attributed to OH stretching. A strong absorption band at 1600 cm^{-1} results from the C=O stretching vibration of the carbonyl group. A medium-to-low strength absorption band at 580 cm^{-1} indicates the formation of the Ca–O bond (Selvarajan et al., 1993).
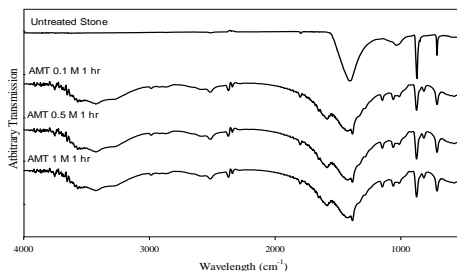

Figure 1. Infrared spectra of limestone treated with different concentrations of ammonium tartrate (0.1-1M AMT) for a fixed contact time of 1 hour.

The results of varying the contact time with fixed concentration of AMT are presented in Figure 2. Calcium tartrate was detected after 10 minutes of exposure to 0.1M AMT. The IR signal for calcium tartrate becomes progressively stronger as the exposure time is increased. The absorption bands at 3420, 3550, 1600 and 580 cm^{-1} are clearly defined after 1 and after 3 hours of exposure.

The concentration-time regime of 0.1M AMT and 1 hour was adopted as hydroxyl conversion treatment. The regime gave the most promising result within the experimental constraints set for this work.

Ammonium tartrate is applied to the stone as an aqueous solution. This results in some calcite dissolution within the water film (K_{sp} = 5.0 x 10^{-9} mol^2 dm^{-6}). Once Ca^{2+} is available in solution in the presence of ammonium tartrate, the potential for calcium

tartrate formation and precipitation appears slim based on a comparison of the K_{sp} values. The larger K_{sp} value for calcium tartrate ~ 7.7 x 10^{-7} mol^2 dm^{-6} means that it is more soluble than calcite and therefore less likely to precipitate. The situation however is more complex as calcite dissolution is driven forward by the ionisation of CO_3^{2-} in solution and the dissolution of calcite in water is actually enhanced. Furthermore, the slightly acidic nature of ammonium tartrate solution, pH value of 6.4 - 6.8 at 25 ºC, further enhances the formation of freely available Ca^{2+} ions.
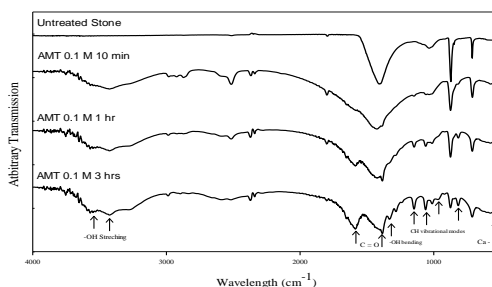
Figure 2. Infrared spectra of limestone treated with a 0.1M solution of ammonium tartrate with varying contact times.

3.   Results and discussion

3.1 Electron microscopy

The electron micrograph presented in Figures 3(a) shows limestone treated with TEOS and in 3(b) limestone pre-treated with hydroxyl conversion followed by TEOS. In both cases the consolidant material has penetrated the limestone interior forming consolidant films on the interior pore surfaces. Whereas direct deposition of TEOS result in relatively thick cracked films of deposited gel material, consolidant films appear to deposit more evenly over hydroxyl converted limestone surfaces.
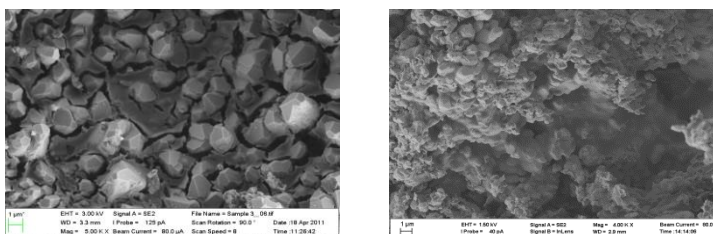

Figure 3. (a) TEOS treated limestone at x5k magnification and **(b)** TEOS applied to hydroxyl converted limestone x5k magnification.

Figures 4 (a) and (b) present electron micrographs of limestone treated with nanoparticle-loaded TEOS at different magnifications. The consolidant material appears to have deposited relatively thick films in some areas, see Figure 4(a). Unlike for the TEOS consolidant however, deposited films are relatively crack-free. The nanoparticles seem to have reduced cracking. This is in agreement with the work of Yang and co-workers (1998). Figure 5 shows the nanoparticle-loaded consolidant applied to hydroxyl converted limestone. The consolidant appears thickly applied.
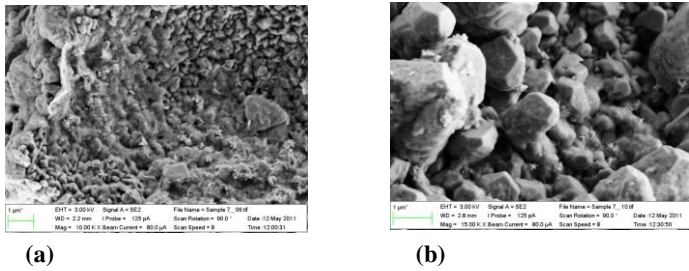
5

(a)   **(b)**

Figure 4: electron micrographs showing limestone treated with nanoparticle loaded **(a)** x10K and **(b)** x15K magnification.
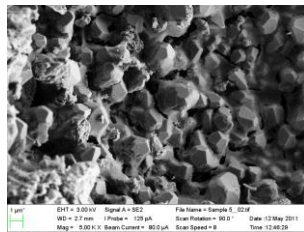

**Figure 5:** Electron micrograph showing AMT+ nanoparticle loaded TEOS, x5K magnification.

3.1 L*a*b* colour

Figures 6 (a-d) present stone colour before and after the different consolidant treatments. The colour data is plotted on 3-d graphs of L* a* b* where L* represents lightness (0% black, 100% white), a* redness-greenness, and b* yellow-blueness. Of more importance for this work are the values of a* > 0 and b* > 0, which represent the colours red and yellow respectively. The colour of untreated Globigerina limestone falls within the range: L* 77-82%, a* 0.8-1.4 and b* 16-18.5. In general, consolidant treatments led to a darkening of the limestone surfaces. For TEOS consolidant treatment for example, the L* dropped by 5-10% while for nanoparticle loaded TEOS 1-5%.

The colour of limestone specimens treated with TEOS were observed to altered slightly after the treatment, average ΔE ~ 7.3, see Figure 6(a). For TEOS applied onto limestone specimens pre-treated with AMT, a clear change in surface colour was observed visually (ΔE ~ 14.5). The average b* and a* values increased and the stone appears red-orange coloured after the treatment. This discolouration very probably results from the mobilisation and oxidation of iron originally contained in minerals naturally present in the limestone. Tartrate anions chelate Fe^{2+} promoting their dissolution in the aqueous film. Once displaced in solution, Fe^{2+} ions are easily oxidized to Fe^{3+} by atmospheric oxygen, precipitating as iron oxyhydroxides and giving the characteristic red-brown colour of rust. Perhaps the addition of a very mild reducing agent such as citrate anions to the AMT might help minimize the discolouring effect without interfering with the tartrate. Colour data for limestone treated with nanoparticle-loaded TEOS presented similar results, see Figures 6 (c) and (d).
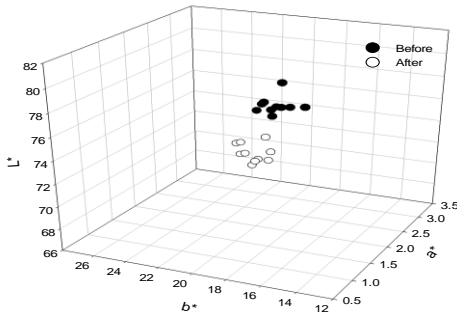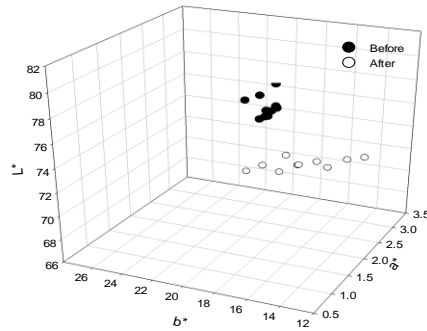
(a)
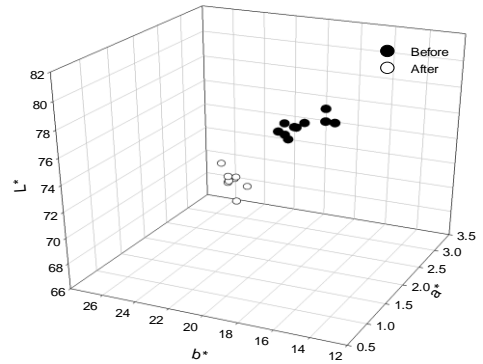
(b)
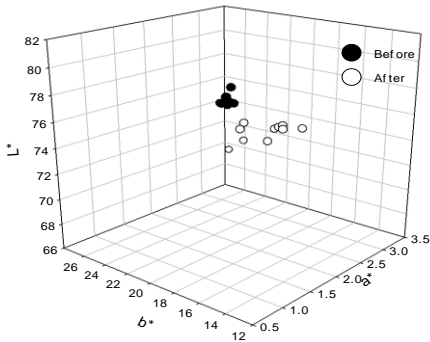
(c)

(d)

Figures 6. Colour of Globigerina limestone surface before and after treatment with **(a)** TEOS consolidant **(b)** AMT+ TEOS consolidant **(c)** nanoparticle loaded TEOS consolidant **(d)** AMT+ nanoparticle loaded TEOS consolidant.

3.2 Water capillarity test

The results of the water absorption by capillary test are presented graphically in Figures 7(a) and (b) for limestone treated with TEOS and nanoparticle-loaded TEOS respectively. In general, consolidant treated limestone specimens absorbed less water than the untreated specimens, irrespective of whether or not they were pre-treated to a hydroxyl conversion. The consolidant material appears to disrupt the free passage of water into the masonry material. In a local context where salt crystallization is an issue, maintaining a degree of water permeability after a consolidation treatment is deemed

imperative for the structural integrity of the limestone. If a limestone is unable to freely exchange water and dissolved electrolytes with the atmosphere, salt inflorescence will be favoured with consequent damage to the stone pore structure.
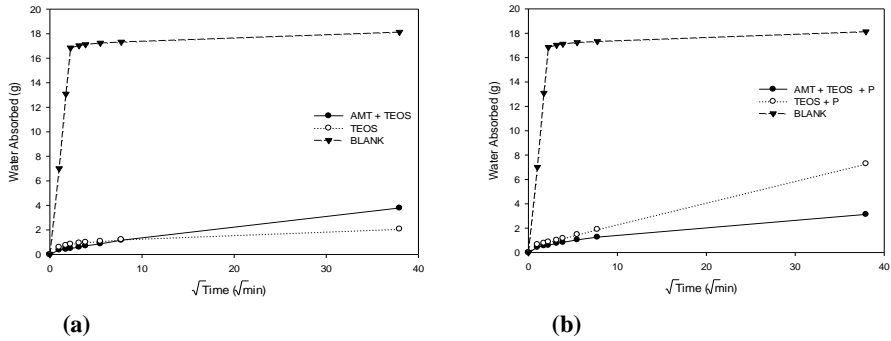

(a)   (b)

Figure 7. Results of the water capillary test **(a)** untreated limestone (blank), TEOS and AMT + TEOS **(b)** untreated limestone, nanoparticle loaded TEOS and AMT + nanoparticle loaded TEOS.

3.4 Salt crystallisation test

The % loss of limestone versus the number of sodium sulphate crystallisation cycles for specimens treated with TEOS and nanoparticle-loaded TEOS consolidants are presented in Figures 8 (a) and (b) respectively. The % weight loss of untreated limestone is also presented for comparative purposes. As expected, a loss in weight was recorded for both treated and untreated limestone specimens with an increase in the number of crystallisation cycles. Whereas a mass loss accompanied by visual damage was observed on untreated specimens after cycle 2, consolidated limestone resisted damage until cycle 4.

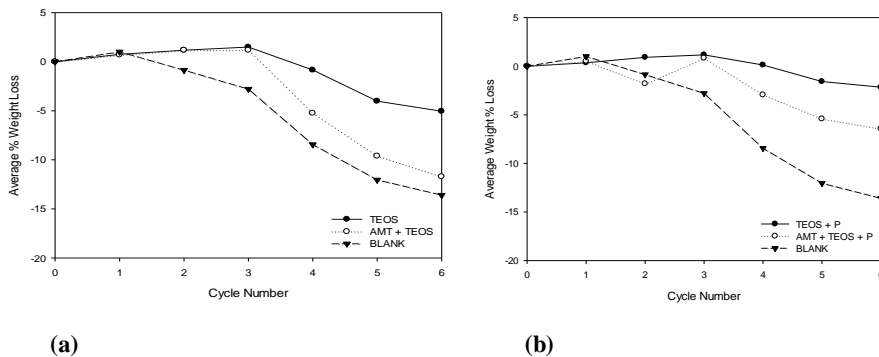(a)   (b)

Figure 8. The results of the salt crystallisation test **(a)** comparison of untreated limestone, TEOS and AMT+TEOS **(b)** comparison of untreated limestone, nanoparticle loaded TEOS and AMT + nanoparticle loaded TEOS.

Following cycle 4, the consolidant system comprising AMT+TEOS deteriorated at a slightly faster rate than limestone treated with TEOS only. Indeed, the % loss in weight for AMT treated stone was comparable to that of untreated, unconsolidated limestone. The consolidant systems comprising particle loaded-TEOS and AMT + particle-loaded TEOS followed a similar trend. Limestone treated with particle loaded TEOS lost less material than the same treatment applied onto AMT treated stone.

The improved resistance of consolidated limestone to the salt crystallisation test can be explained by an improved strength of the stone resulting from the consolidant application. Alternately one can also argue that the applied consolidants partially block liquid ingress and therefore the passage of sodium sulfate solution into the stone, thereby reducing the negative effects of the said salts. A combination of the two effects is probably more likely.

3.5 Surface Hardness

The Shore DO hardness results are presented in Table 1. Differences in surface hardness values were minimal between the different treatments, but some trends were noted. In all cases, the hardness results of treated specimens increased over those of untreated limestone. Stone specimens treated with TEOS showed slightly higher average hardness values than those of nanoparticle-loaded TEOS. Hardness values of the TEOS and nanoparticle loaded-TEOS consolidants applied directly to limestone and those applied to AMT treated stone showed very similar hardness values.

Sample Coating	Average Hardness
Untreated Limestone	94.88 ± 0.94
TEOS	97.46 ± 0.79
TEOS + P	96.62 ± 1.03
AMT + TEOS	97.91 ± 1.13
AMT + TEOS + P	96.76 ± 0.92

Table 1. Shore DO Limestone Surface Hardness Results

4. Conclusions

The treatment of limestone with ammonium tartrate solution resulted in the successful conversion of calcite into calcium tartrate as confirmed by the infra-red study.

Cracking of consolidant films were observed when TEOS consolidant was applied directly to Globigerina limestone. This is in agreement with other literature studies on sandstone (Scherer and Wheeler 2009). On the other hand cracking was not observed when TEOS was applied to a hydroxyl converted limestone surface. In the latter case, electron micrographs showed the consolidant to be more evenly applied; the HCT possibly aided consolidant spreading and enhanced adhesion to the limestone. Consolidant cracking was also subdued in the nanoparticle loaded TEOS consolidant.

The salt crystallization tests show that there is an improved resistance to salt crystallization damage with the application of the TEOS based consolidants over untreated limestone. Arguably this can be seen as an improvement in the strength of the limestone. The reduced uptake of water in the water capillarity test for both TEOS and nanoparticle TEOS consolidant application however show that the application of these consolidants have somewhat suppressed the free passage of water into the limestone

albeit partially. This reduced water uptake could also have contributed to the improvement observed in the salt crystallization test.

On the downside the hydroxyl conversion treatment gave rise to a degree of stone discolouration very probably due to mobilization and oxidation of intrinsic iron(II) compounds to Fe(III). Perhaps this effect can be discouraged by addition of a mild reducing agent which limits iron(II) oxidation without affecting the tartrate.

References

Aggelakopoulou, E., Charles P., Acerra, M. et al. 2002. 'Rheology Optimization of Particle Modified Consolidants'. *Materials Research Society Symposium Proceedings,* **712** (II):1-6.

Brinker C.J., Scherer G.W. 1990. *Sol-gel Science: The physics and chemistry of sol-gel processing.* Boston: Academic Press.

Cassar, J.,1999. 'Geochemical and mineralogical characterisation of the Lower Globigerina Limestone of the Maltese Islands with special reference to the "soll" facies'. Ph.D. dissertation. University of Malta.

Cassar, J., Vannucci, S. 2001. 'Petrographic and chemical research on the stone of the megalithic temples'. *Malta Archaeological Review*, **5**:40-45.

Escalente, M.R., Valenza, J., Scherer, G. W. 2000. 'Compatible Consolidants from Particle-Modified Gels'. Paper presented at 9th International Congress on Deterioration and Conservation of Stone, Venice, Italy.

Gatt, P. 2006. 'Model of limestone weathering and damage in masonry: Sedimentological and geotechnical controls in the Globigerina Limestone Formation (Miocene) of Malta', *Xjenza,* **11**:30-39.

Kim, E.K., Won, J., Do, J. et al. 2008. 'Effects of Silica Nanoparticle and GPTM addition on TEOS-Based Stone Consolidants'. *Journal of Cultural Heritage,* **10**(2009):214-221.

Mosquera, M.J., de los Santos, D.M. 2008. 'New Water-Repellent Nanomaterial for Protecting and Consolidating Stone'. In *Proceedings of the 11th International Congress on Deterioration and Conservation of Stone, 15-20 September 2008, Toruń, Poland.* J. W. Lukaszewicz and P. Niemcewicz, (eds.) 837–46. Poland: Nicolaus Copernicus University.

Murray, J., 1890 - Murray J (1890) 'The Maltese Islands with special reference to their geological structure'. Scottish Geographical Magazine (Edinburgh), **6**:325 - 34 1.

Razink, J.J., Schlotter, N.E. 2007. 'Correction to "Preparation of monodisperse silica particles: Control of size and mass fraction" by G. Tracy and C.F. Zukoski IV, Journal of Non-Crystalline Solids 104(1988) 95-106'. In *Journal of Non-Crystalline Solids,* **353**:2932-2933.

Scherer, G. W., Wheeler, G.S. 2009. 'Silicate Consolidants for Stone.' *Key Engineering Materials*, **391**(2009):1-25.

Selvarajan, P., Das, B.N., and Gon, H.B. 1993. 'Infrared spectroscopic and thermal studies of calcium tartrate single crystals grown by silica-gel technique'. *Journal of Materials Science Letters,* **12**:1210-1211.

Spratt, T. 1943, 'On the geology of the Maltese Islands'. *Proceedings of the Geological Society,* **4**:225 - 232.

Vella, A., Testa, S. and Zammit, T. 1997. 'Geochemistry of the Soll Facies of the Lower Globigerina Limestone Formation, Malta.'*Xjenza*, **2**(1): 27-33.

Weiss, N.R., Slavid, I., Wheeler, G. 2000. 'Development and Assessment of Conversion Treatment for Calcareous Stone'. In *9th International Congress on Deterioration and Conservation of Stone*. V. Fassina (ed.) 533-540. Amsterdam: Elsevier.

Wheeler, G., Mendez-Vivar, J., Goins, E.S. et al. 2000. 'Evaluation of Alkoxysilane Coupling Agents in the Consolidation of Limestone'. In *9th International Congress on Deterioration and Conservation of Stone*. V. Fassina (ed.) 541-546. Amsterdam: Elsevier.

Wheeler, G. 2005. *Alkoxysilanes and the Consolidation of Stone,* Los Angeles: Getty Publications.

Yang, M. Scherer, G.W., Wheeler, G. 1998. 'Compatible Consolidants'. In *Compatible Materials for the Protection of European Cultural Heritage*. G. Biscontin, A. Moropoulou, M. Erdik, J. Delgado Rodrigues (eds.) 201-208. Athens: Tech. Chamber Greece.