Xjenza Online - Journal of Malta Chamber of Scientists
http://www.mcs.org.mt/
Doi: http://dx.medra.org/10.7423/XJENZA.2013.2.07

Research Article

A Study of Nanoparticle-based Silane Consolidants for Globigerina Limestone

Sophie M Briffa[1], **Daniel Vella**[1] **and Maria J Mosquera**[2]
[1]Department of Metallurgy and Materials Engineering, University of Malta, Malta
[2]Department of Physical Chemistry, University of Cadiz, Spain

Abstract. This STEPS[1] funded study focuses on the application of hybrid and nanoparticle loaded hybrid silane consolidants for the treatment of 'Franka' Globigerina Limestone. Consolidants act by gluing deteriorated stone material to underlying healthy stone (Dukes, 1972; Gutt, 1973; Garrod, 2001). The consolidants evaluated were a laboratory prepared hybrid silane based on a mixture of tetraethylorthosilicate (TEOS) and 3-(glycidoxypropyl) trimethoxysilane (GPTMS), the same hybrid loaded with silica nanoparticles and loaded with GPTMS-modified silica nanoparticles. In addition, a consolidant based on the hydrolysis product of TEOS was also tested.

Prepared consolidants were applied to test blocks by complete immersion. Untreated stone block were used as benchmarks. Following application, half of the treated samples were subjected to accelerated weathering. All limestone blocks were then characterised by colorimetry and optical and electron microscopy. The pore size distribution was assessed by Mercury Intrusion Porosimetry. A water absorption by capillarity technique was also carried out to assess any changes in water uptake rate. The mechanical properties were assessed by resistance to sodium sulfate crystallisation.

Microscopy observations showed that penetration into the stone occurred to different extents depending on the consolidant. The hybrid consolidant led to yellowing of the limestone but the addition of nanoparticles to the hybrid (modified or not) appeared to help restore the original colour of the stone. The porosity of the limestone was only marginally affected by the different treatments but the somewhat hydrophobic nature of the consolidants led to a disruption in the capillary flow of water into the limestone.

Keywords Globigerina Limestone - Nanoparticles - Hybrid - Alkoxysilane - Sol-gel.

1 Introduction

The stratigraphic setting of the Maltese Islands consists of five main formations. They are listed in chronological order (from older to younger) 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 it 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 percent 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: 1) franka stone, which exhibits good weathering properties and changes to a pale yellow colour with a resistant surface and 2) soll, which deteriorates rather easily by a process of cavitational weathering producing characteristic honeycomb structured erosional features (Vella et al., 1997). The franka limestone is the one chosen for structural building while the soll is primarily used in building foundations (Vella et al., 1997).

---

[1] Strategic Educational Pathways Scholarships

Correspondence to: S. M. Briffa (sbri0012@um.edu.mt)

Natural deterioration and weathering of stone monuments and buildings is inevitable even if there is no human intervention to cause damage. Thus, the need arises for the protection of these structures and the conservation of cultural heritage features in particular.

When it comes to conservation methods several practices can be undertaken, one of which is consolidation. The purpose of an ideal consolidant is to link together the deteriorated stone material with the underlying healthy stone without blocking the pores of the stone while maintaining the aesthetic and physical properties of the stone (Dukes, 1972; Gutt, 1973; Alessandrini et al., 1975; Garrod, 2001). Due to its irreversible nature, consolidation is very often embarked on as a last resort to save the stone when it has reached an advanced stage of deterioration.

Consolidants act by gluing together the deteriorated stone material with the underlying healthy stone (Dukes, 1972; Gutt, 1973; Alessandrini et al., 1975). Depending on the state of the stone, this process can be carried out before or after a cleaning programme. Consolidation is very often an irreversible process. It involves the introduction of organic or inorganic polymeric material within the stone pores making it practically impossible to reverse (Briffa et al., 2012). However, one must appreciate that the consolidation step is the last attempt to save the stone from complete replacement and these drastic measures, in such a situation, are tolerated (Garrod, 2001).

Figure 1: Location of Mqabba (marked in red) [accessed from http://upload.wikimedia.org/wikipedia/commons/thumb/3/32/Mqabba-map.svg/550px-Mqabba-map.svg.png on 24/06/2013]

Due to the increasing popularity of consolidants their performance requirements are constantly being improved. Primary performance requirements stipulate the conditions that a consolidant must fulfil such as physical properties or appearance. Secondary performance requirements include those conditions which are compulsory for a specific use and which are imposed in addition to primary requirements due to specific problems encountered (Clifton, 2008).

Commercial products containing alkoxysilanes, such as tetraethylorthosilicate TEOS, are commonly employed as consolidants for stonework. An advantage of these materials is that they are applied in monomeric form and polymerise by undergoing the sol-gel process involving 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). One way to improve this could be through the use of coupling agents.

Another 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 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).

In order to incorporate both the concept of the use of the coupling agents and that of nanoparticles, a hybrid sol was prepared based on the Self-assembled Nanophase

Particle (SNAP) surface treatment.

The study aims to compare the consolidation effects of simple silane systems and hybrid silane systems that were doped with silica nanoparticles or modified silica nanoparticles.

2 Methodology

2.1 Materials

The following chemicals were used as received: tetraethylorthosilicate, TEOS (Aldrich, Reagent Grade), 98% absolute ethanol (Aldrich, Chromasolv), dibutyltin dilaureate, DBTL (Aldrich, Fluka Analytical), 3-(glycidoxypropyl)trimethoxysilane, GPTMS (Aldrich, Reagent Grade), acetic acid (Aldrich, Reagent Grade), Diethylenetriamine, DETA (Aldrich, Reagent Grade) and silica nanoparticles ˜≈ 10nm (Aldrich, Reagent Grade). Franka-type Globigerina Limestone specimens measuring $50 \times 50 \times 50\,\mathrm{mm}^3$ were sourced from a quarry in the limits of Mqabba, a village situated to the south-east of Malta, Fig.(1). The freshly cut surfaces were ground to achieve a flat surface and cleaned of excessive dust using filtered compressed air.

2.2 Preparation of Consolidants

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 hybrid sol was a mixture of TEOS and GPTMS in a mole ratio of 1:3 with the addition of 64.8mL of a 0.05M solution of acetic acid. This sol was allowed to mix for 3 days in a sealed container on a magnetic stirrer prior to the addition of 1% v/v DETA. DETA was added to act as the crosslinking agent. Once added the sol was then mixed with 4 volume parts water and immediately applied to the stone.

A mixture of the hybrid sol with the addition of 10% wt/v approximately 10nm silica nanoparticles was also applied as a consolidating system.

The final consolidating system tested was a mixture of the hybrid sol with the addition of 10% wt/v modified silica nanoparticles. The modified silica nanoparticles were prepared by means of the addition of GPTMS in a solution of water and acetic acid to 10nm silica nanoparticles. The quantities of these reactants were mixed in a ratio of 1 : 18.75 : 20 respectively. These values were obtained by calculating the ideal GPTMS ratio needed to react with the silica nanoparticles. The solution was left mixing overnight following which the solution was added to the hybrid sol and then immediately applied to the stone.

In addition to these treatments, a group of stone samples were left untreated to act as controls. This allowed for a comparison of treated stones with original untreated samples.

2.3 Mode of application

The consolidating treatments were applied by completely immersing the stone sample for 30 minutes in the consolidant to ensure an even application throughout. Whilst immersed the samples were wedged up from the base of the container using thin non-absorbent supports to act as point contacts. This was done so as to allow for better absorption through exposure of more surface area of the samples.

2.4 Drying

Treated samples were left to air dry for a period of 5 weeks prior to undergoing accelerated weathering. The samples that did not undergo accelerated weathering were left to stand and air dry for another 4 weeks until the accelerated weathering cycling was complete. Once this was done the treatment-sample interaction could be characterised and physical property testing could be carried out.

2.5 Accelerated weathering

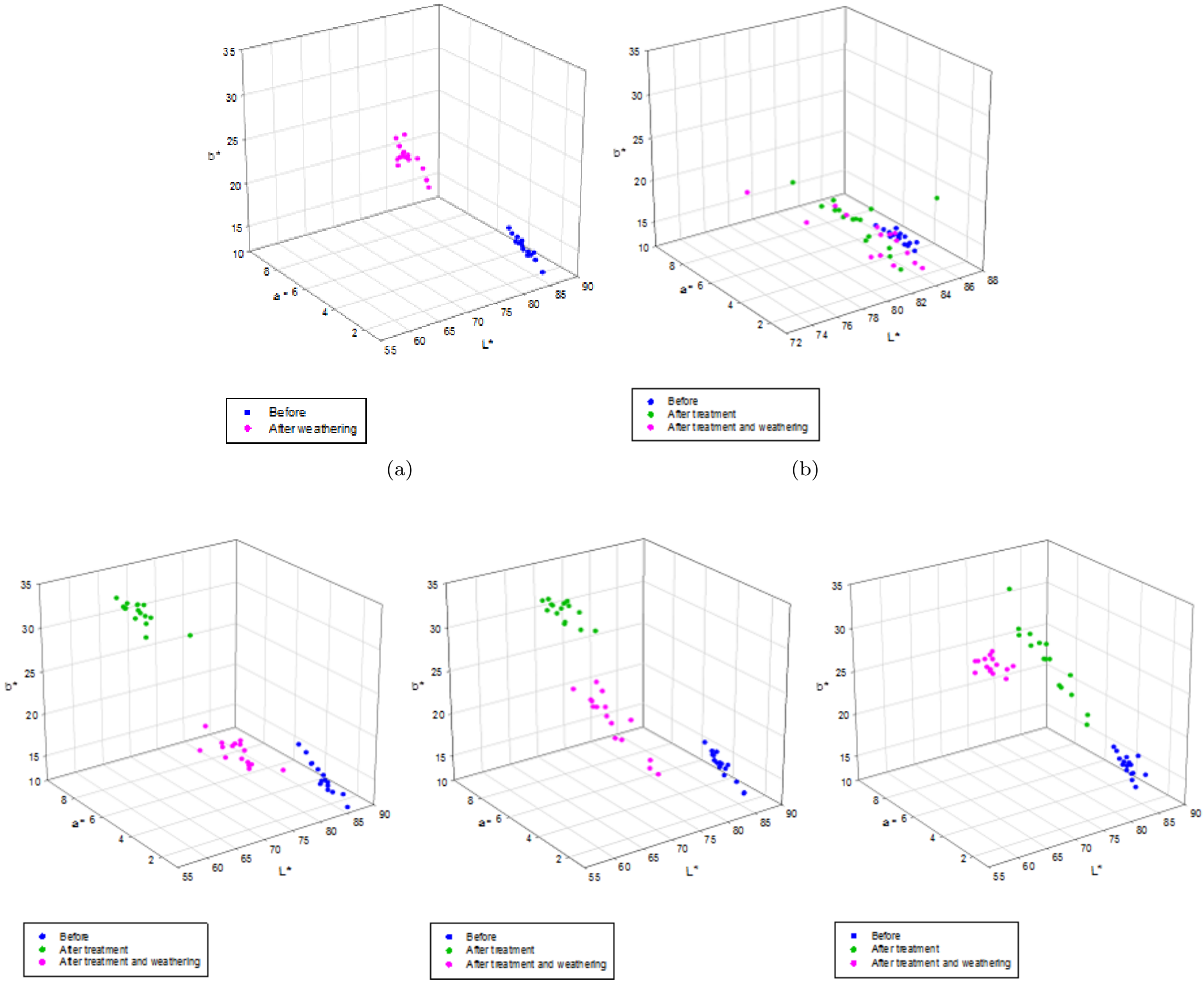
Accelerated weathering was carried out so as to see how the treatment would fare when exposed to rain. This was achieved through repeated 24 hour wet-dry cycles. The cycling involved 8 hours exposure to water vapour at 35°C in an accelerated corrosion test chamber CNS/500 and 16 hours drying at room temperature. During the 16 hours of drying the test chamber was switched off and the samples were left inside the chamber with the lid wide open. The cycling was repeated 28 times for trial period of 4 weeks.

2.6 Characterisation

Colour alterations of the limestone specimens before and after treatment were measured with a Minolta CM-508i spectrophotometer. The samples were observed on a microscopic level by means of a Remet SMZ-2T light microscope. 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. The pore size distribution of the samples and the total porosity was determined through Mercury Intrusion Porosimetry. This was carried out using a Quantochrome PoreMaster (PM-60+12) at the Department of Physical Chemistry at the University of Cadiz in Spain.

2.7 Testing

A test to determine water absorption by capillarity was carried out according to EN1925:1999 and assessed the



(a) (b)

(c) (d) (e)

Figure 2: Colour data for before treatment, after treatment and after weathering for stone samples treated with b. TEOS, c. hybrid, d. nanoparticle loaded hybrid by immersion and e. modified nano-particle loaded hybrid by immersion.

flow of water into the stone after applying the different consolidant treatments.

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.

3 Results and Discussion

3.1 Colorimetry

Fig.(2)(a-e) shows stone colour before treatment, after treatment and after treatment and weathering for the different consolidant treatments. The colour data are 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 to 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. This is in agreement with the results of an earlier study (Briffa et al. (2012) and the results of alkoxysilanes used in the field (Wheeler, 2005).

The largest discrepancy between the before and after L*, a* and b* values was noted for the samples treated with the hybrid by means of immersion (Fig.(2)(c)). The addition of nanoparticles also resulted in a large discrepancy whilst the addition of modified nanoparticles seems to result in a more spread out cluster that is closer to the original colour.

Weathering is seen to have an effect on the colour of the samples as even the untreated weathered sample showed a shift in the before weathering colour data results and the after weathering colour data results of the graph shown in Fig.(2)(a). The samples became slightly darker, slightly redder and mostly more yellow when compared to those that were not weathered. This is representative of what is reported in published literature regarding the weathering of 'Franka' type Globigerina Limestone. Cassar states that this type of stone withstands exposure well and changes into a honey-coloured stone upon ageing (Cassar, 2002).

3.2 Microscopy

3.2.1 Light Microscopy

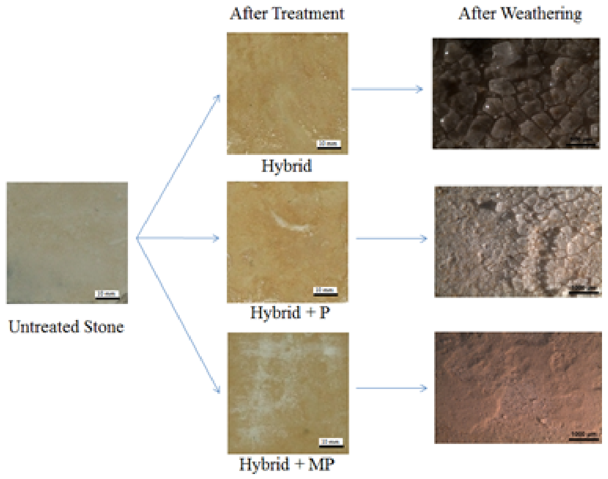


Figure 3: Surface appearance effect of hybrid based treated samples.

Observing the samples under low magnification revealed interesting features, some of which were unfortunately undesirable.

For the untreated sample surface, it is clearly seen that no treatment is present on the surface. The flow chart depicted in Fig.(3) shows the surface of the hybrid linked treatments after treatment and after treatment and weathering. It can be seen that that the addition of the nanoparticles or modified nanoparticles improved the surface colour of the sample when compared to the surface colour of the hybrid.

Although cracking was not seen for the non-weathered samples, the hybrid based treatments all cracked upon weathering. This was not desirable as it is probably interfering with the consolidating effect of the treatment. However, the degree of cracking, that was visually analysed, seemed to vary depending on whether the consolidating system applied contained nanoparticles or modified nanoparticles or neither.

3.2.2 Scanning Electron Microscopy

The relatively smooth and often flat surfaces of the foraminifera chambers offered ideal areas for observing the consolidant – limestone interactions. These can be clearly seen in the image of the untreated sample, Fig.(3.1). The distinctive, clear cut stone features observed for the untreated sample are not always seen for the treated samples due to surface cover by the treatment (Fig.(4)(b-e)). For the treated samples a layer of treatment material can clearly be seen on the surface of the stone.

TEOS based consolidants experience cracking during drying as a result of capillary forces. This is reported by a number of researchers (Kim et al., 2009) and was observed by means of the SEM in this work. The degree of cracking seen for the TEOS treated samples was not as extensive as that of an earlier study performed by the author (Briffa et al., 2012). This is possibly due to the difference in ambient temperature when the limestone samples were treated for the different projects.

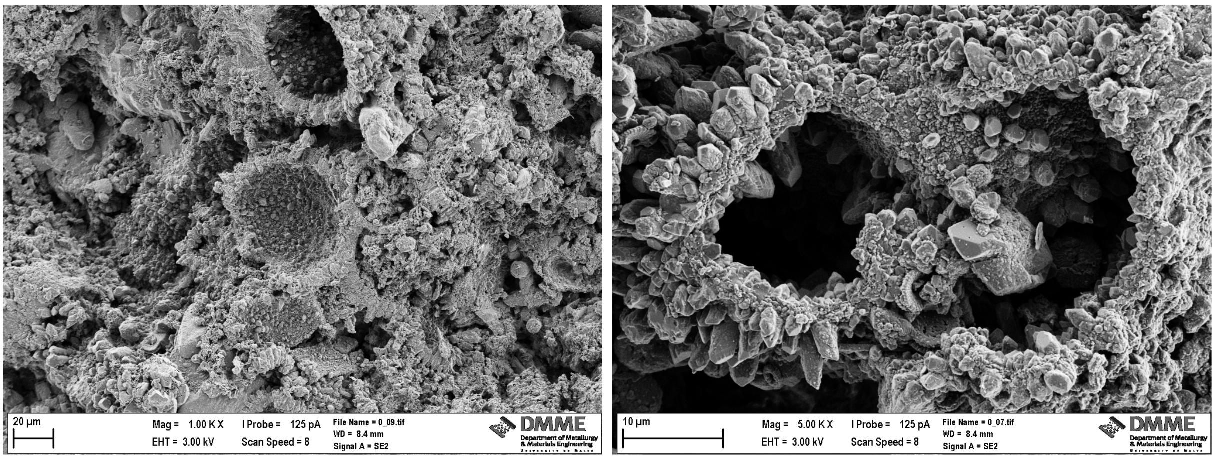
When compared to the TEOS treated micrographs, those of the hybrid based treated samples seem to show that there is more treatment present on the surface of the stone and the treatment layer is thicker.

The main aim of adding the nanoparticles was to reduce the major problem of gel cracking associated with alkoxysilanes. Literature has shown that the addition of particles seems to promote the production of a crack-free gel (Scherer and Wheeler, 2009; Mosquera and de los Santos, 2008).This was also seen with the addition of silica nanoparticles to a TEOS sol in an earlier project (Briffa et al., 2012).However in this case, at a microscopic level, no cracking was noted for the hybrid based treatments and the nanoparticles therefore had little or no effect on this property. The organic groups incorporated into the hybrid material render the consolidant more plastic and less prone to cracking. The addition of the nanoparticles to the hybrid sol led to the deposition of a thick layer of consolidant on the surface of the stone as seen in Figs.(4)(d,e) for the nanoparticle loaded and modified nanoparticle loaded hybrid treated samples respectively.

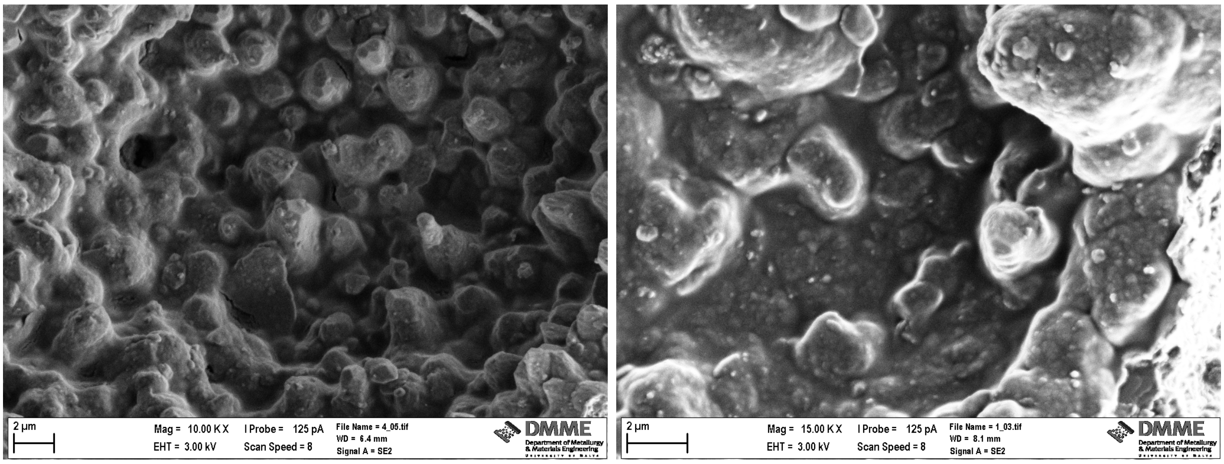
3.3 Mercury Intrusion Porosimetry

Mercury Intrusion Porosimetry (MIP) results show the effect of the treatment on the percentage porosity and the pore size distribution of the limestone samples treated by immersion compared to the untreated samples. A minimum of two repeated readings were carried out for each specimen treatment system and the pore size distribution and the percentage porosity for the repeats are very close. Therefore the results can be considered to be repeatable. This also shows that the treatment is evenly applied to each of the samples tested (Mosquera, 2012).

The percentage porosity of the untreated limestone ($\approx 39.29\%$) is in agreement with 32 -41% range values obtained by Cassar (Cassar, 2002). Indeed, even the

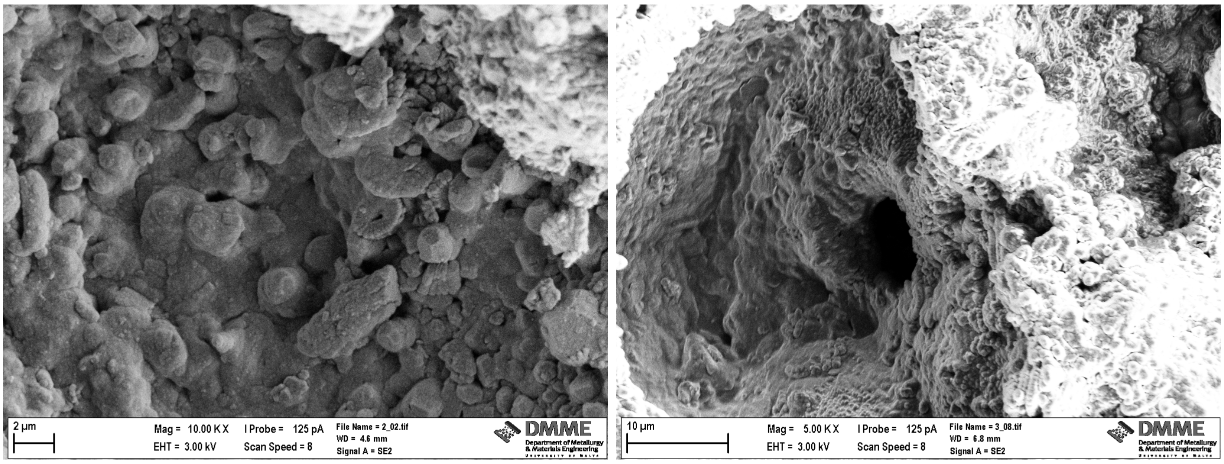


(a) Untreated stone at ×500 and ×5000 magnification.



(b) TEOS treated sample at ×10,000.

(c) Hybrid treated limestone at ×15,000.



(d) Nano-particle loaded hybrid at ×10,000.

(e) Modified nano-particle loaded hybrid at ×5000.

Figure 4

porosity results of the treated samples fall within this range. The total porosity values obtained for the different treatments are altered slightly to lower values. This is in agreement with literature (Ksinopolou, 2012, Wheeler, 2005). The slight decrease in porosity indicates that the treatment has penetrated within the samples and supports the electron microscopy observations. The slight decrease in porosity noted could show that the treatments are lining the stone pores rather than blocking them. This conforms to the SEM observations.

No significantly large changes were observed in the porosity and pore size distribution of the limestone samples following treatment application and weathering. Table 1 lists the values for the total percentage porosity of the limestone samples upon treatment with the different consolidant systems. The percentage porosity after weathering is also given.

Table 1: Total porosity percentage of non-weathered and weathered samples.

Treatment	Total % porosity after consolidation	Total % porosity after weathering
Untreated	39.29	38.39
TEOS	35.83	42.00
Hybrid	36.17	39.15
Hybrid + Nano-particles	34.76	38.62
Hybrid + Modified nano-particles	32.87	35.94

It appears that the presence of the nanoparticles within the hybrid treatment decreases the porosity when compared to the hybrid treatment. This is probably due to the presence of more solid material within the treatment. The addition of the modified nanoparticles further reduces the porosity of the sample. This may be due to the modified particles possibly being larger than the particles that are not modified since the modified nanoparticles are surrounded by functional groups attached to the surface.

In the case of all the treated samples, weathering seems to have increased the total porosity when compared to the non-weathered samples. On the other hand, weathering has little effect on the pore size distribution of the treated limestone samples. A possible reason for the increase in porosity is that the weathering might have broken down the consolidants washing them out of the stone.

Weathering of the untreated sample resulted in a marginal decrease in the total porosity. In addition, it resulted in a decrease in the number of larger pores and an increase in the number of smaller pores. This could be due to calcite dissolution and re-precipitation on the surface of the stone sample during the accelerated weathering.

3.4 Water Capillarity

The results for the water absorption by capillarity test carried out according to EN 1925:1999 are shown in Figs.(5.1, 5.2) for non-weathered and weathered samples respectively. Each plotted point is the average of 3 readings obtained from 3 different limestone samples.

In general water absorption in the stone sample increases over time reaching a plateau. The plateau occurs around 500gm^{-2} depending on the treatment. The only samples that fail to reach this plateau during the stipulated time are the TEOS, hybrid and nanoparticle loaded hybrid samples.

The untreated samples absorb the largest amount of water. The hybrid, nanoparticle loaded hybrid and TEOS treated samples all absorb a very little amount of water in the first half of the graph, absorbing slightly more in the second half of the graph but not as much as the untreated or modified nanoparticle loaded hybrid treated samples.

Weathering (Fig.(5.2)) causes the rate and in some cases even the amount of water absorption to increase especially in the case of the hybrid and hybrid and nanoparticles treated samples.

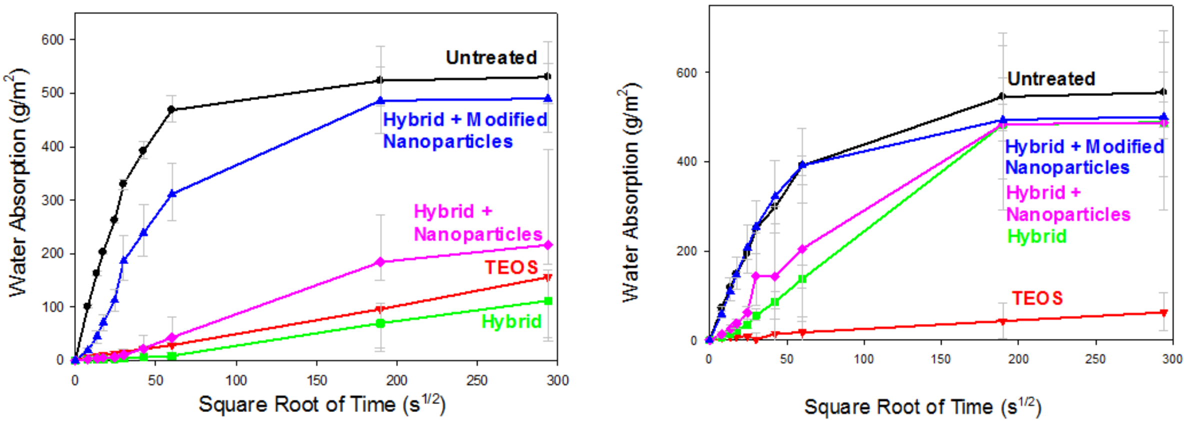
The presence of the silica nanoparticles within the hybrid solution showed an improvement in the water absorption when compared to the hybrid solution on its own, as can be seen particularly for the non-weathered samples. The addition of modified nanoparticles further improves the water absorption properties of the samples.

Yang et al. (1998) showed that, by addition of silica particles to the silicate consolidant, dried gel remained porous. Although in this work the hybrid was also produced from GPTMS, which has a tendency of making the treatment more hydrophobic, the silica particles probably had the same effect on this hybrid treatment as they did on the silicate consolidant.

3.5 Salt Crystallisation

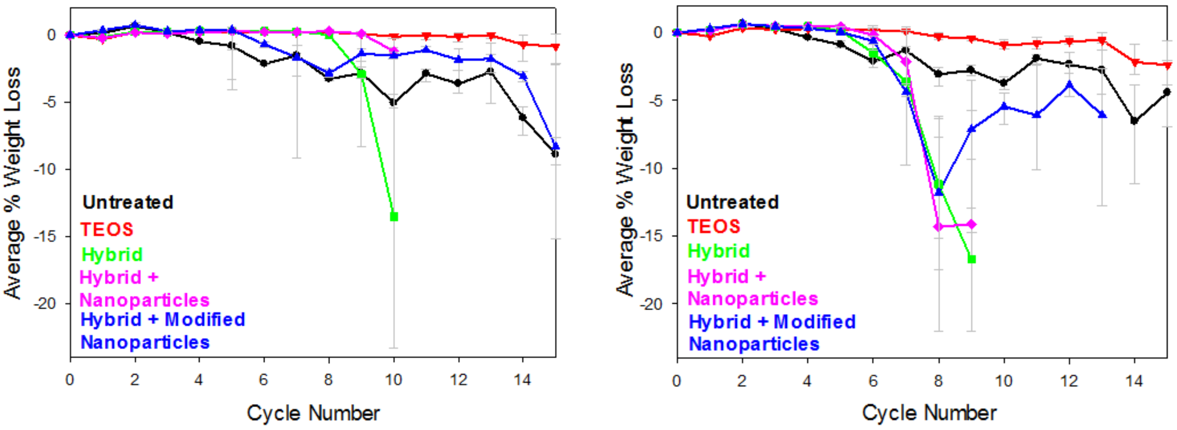
The salt used in this test was sodium sulfate decahydrate (Na2SO4.10H20) as recommended in the European Standard EN12370:1999. This test mimics an accelerated real-life situation that involves the deterioration of stone by exposure to repeated sodium sulfate crystallisation. The results of the resistance to salt crystallisation test are presented in Figs.(6)(a, b). Each point in the graphs is the average of 3 readings obtained from 3 different samples. Not all the limestone samples survived the 15 cycles of salt crystallisation.

In both graphs it can be seen that the TEOS treated samples are those that performed best in this test. The untreated samples closely followed. It is interesting to see that the untreated stone behaves so impressively well and hardly seems to be affected by the salt crystallisation.



(a) (b)

Figure 5: Graph of water absorbed(g/m^2) plotted against square root time (s$^{1/2}$) for all of stone samples treated by immersion and for the untreated stone samples and for all of the samples treated by immersed and weathered and for the untreated weathered stone samples.



(a) (b)

Figure 6: Graphs of salt crystallisation test of immersed (left) and immersed and weathered (right) samples representing average percentage weight loss vs. cycle number.

For the immersed samples shown in Fig.(6)(a) initially the nanoparticle loaded hybrid treated samples looked very promising. These however broke into smaller pieces (spalled) unexpectedly after cycle 10.

When comparing the data for the immersed and immersed and weathered samples, one can see that weathering had a significant effect on the nanoparticle and modified nanoparticle loaded hybrid treated samples and their rate of weight loss. The weathering decreased these samples' resistance to the salt crystallisation test.

Compared to the untreated and TEOS treated samples all the hybrid based samples do not fare so well and large decreases in mass occur. A possible reason for this could be that the hybrid consolidating treatments are efficiently consolidating the limestone hence making it harder for the stone to be deteriorated by the salt and when it is, large pieces are broken off at a time.

4 Conclusions

Electron microscopy carried out in this work confirmed that the consolidants are present within the stone. Furthermore the pores of the stone, although altered, are not blocked. The results of the mercury porosimetry, carried out on the immersed non-weathered samples, seemed to confirm this.

The addition of the nanoparticles improved the surface colour of the hybrid treated limestone by better maintaining the original surface colour and the modified particles improved the surface colour even further. The nanoparticles and modified silica nanoparticles also decreased the amount of cracking of the weathered treatment as evident from the light microscopy work.

The water absorption by capillarity test showed that water flow into the consolidated stone has slowed down compared to untreated limestone. Given that the reduction in water absorption is not caused by a decrease in the porosity of the treated limestone, one possible reason for the drop in water uptake could be an increase in hydrophobicity of the surfaces by the different consolidants. This varies to different extents depending on the consolidating system.

The results obtained for the salt crystallisation test and those obtained for the water test do not follow the same trend. It would have been thought that the results would do so because if water is able to flow through the pores of the stone, so would a solution of salt, and conversely so.

The results obtained from salt crystallisation do not follow those obtained from the mercury intrusion porosimetry. The ability to withstand damage by salt crystallisation is not caused by decreasing the pore size and / or the porosity of the sample similarly to water absorption.

This proves that the salt test does not only depend on the hydrophobicity and the porosity of the stone but is far more complex and is also affected by the mechanical properties of the consolidant.

5 Acknowledgements

The authors would like to thank STEPS for funding the research and ERDF (Malta) for the financing of the testing equipment through the project: ”Developing an Interdisciplinary Material Testing and Rapid Prototyping R&D Facility (Ref. no. 012)”.

References

Aggelakopoulou, E., Charles P., Acerra, M. et al. (2002). Rheology Optimization of Particle Modified Consolidants, In: Materials Research Society Symposium Proceedings, 712, II.2.6.1-II.2.6.6.

Alessandrini, G., Del Fa, C. M., Rossi-Doria, P., Tabasso, M. and Vannucci, S., (1975), Treatment of Stone in Monuments. A Review of Principles and Processes, In: Proceedings of the International Symposium on Conservation of Stone I, 635-650.

Briffa, S. M., Sinagra, E. and Vella, D., (2012), TEOS based consolidants for Maltese Globigerina Limestone: Effect of Hydroxyl Conversion Treatment, In: Proceedings of the 12th International Congress on the Deterioration and Conservation of Stone.

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

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, In:Malta Archaeological Review, 5: 40-45.

Cassar, J., (2002) Deterioration of the Globigerina Limestone of the Maltese Islands, In: Natural Stone, Weathering Phenomena, Conservation Strategies and Case Studies, Ed: S. Siegesmund, T. Weiss and A. Vollbrecht, A., London, Geological Society London.

Clifton, J. R., (2008). Stone Consolidating Materials: A Status Report 2008. [online]. Available http://cool.conservation-us.org/byauth/clifton/stone/stone4.html.

Dukes, W. H., (1972), Conservation of Stone: Chemical Treatments, In: The Architects’ Journal Information Library, pp.433-438.

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

Garrod, E. (2001). Stone Consolidation. Halts decay and promotes life. [on-line]. Available: http://www.buildingconservation.com/articles/stoneconsol/stoneconsol.htm.

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.

Gutt, W. H., (1973), Conservation of Stone. The Next Steps, London, Stone Industries, 1973.

Kim, E.K., Won, J., Do, J. et al. (2008). Effects of Silica Nanoparticle and GPTMS addition on TEOS-Based Stone Consolidants. *J. Cult. Herit.*, 10: 214-221.

Ksinopoulou, E., Bakolas, A. and Moropouloum, A., (2012), Particle modified consolidants in the consolidation of porous stones, 12th International Congress on Deterioration and Conservation of Stone.

Mosquera, M.J., de los Santos, D.M.(2008). New Water-Repellent Nanomaterial for Protecting and Consolidating Stone, In: Paper presented at 11th International Congress on Deterioration and Conservation of Stone, Torun, Poland.

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

Rodrigues, (2011), Personal comm. with Profs Rodrigues, September 2011.

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

Spratt, T. (1943), On the geologv of the Maltese Islands. Proceedings of the Geological Society (London). 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 a Conversion Treatment for Calcareous Stone. In: Paper presented at 9th International Congress on Deterioration and Conservation of Stone, Venice, Italy.

Wheeler, G., Mendez-Vivar, J., Goins, E.S. et al. (2000). Evaluation of Alkoxysilane Coupling Agents in the Consolidation of Limestone. In: Paper presented at 9th International Congress on Deterioration and Conservation of Stone, Venice, Italy.

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

Yang, M., Scherer, G.W., Wheeler, G.S. (1998). Compatible Materials for the Protection of European Cultural Heritage, 201-208.