Limestone sourced from Salisbury Cathedral and Bath Abbey (UK) was treated with commercially available nanolime of concentration 25 g/l. The response of the stones to the treatment was studied using a variety of analysis techniques including optical microscopy, electron microscopy, drilling resistance measurement and mercury intrusion porosimetry. Weathered and non-weathered surfaces of both types of stones were compared. All the specimens were characterised before and after the treatment to determine any changes in their properties caused by their weathering and by the treatment itself. Results show that the degradation processes of the stones strongly affect their interaction with nanolime consolidation treatments. Drilling resistance measurements of treated and untreated samples were compared. After 20 days significant increases in sub-surface drilling resistance was observed in the non-weathered Bath stone and a small increase in the weathered Bath stone after 6 months was also noted. Both weathered and non-weathered Chilmark stone showed an increase in drilling resistance after 6 months, however at 20 days this was most evident in the samples treated with nanolime in isopropanol as opposed to ethanol.

1. Introduction

Many of the United Kingdom’s historic masonry buildings suffer damage and decay of their external surfaces caused by processes such as natural weathering, pollution and human contact (El-Turki et al., 2010). This means that intervention is often required to repair or stabilise damage; in severe cases, this might mean replacement of the stone but surface consolidation can also be an option. This is the process of strengthening the stone by applying consolidating treatments and has the advantage of retaining the stonework (which is important in buildings of architectural or historic interest). Although consolidation cannot completely prevent deterioration of the stonework, it can slow down the cycle of decay.

Consolidation can be achieved by several methods such as ethyl silicate, ethyl-methacrylate or epoxy resins (Ferreira Pinto and Delgado Rodrigues, 2012; Karatasios et al., 2009) but recently there has been some focus on the potential use of nanolime. This newly introduced product to stone conservation is based on the chemical synthesis of nanometre-sized particles of calcium hydroxide (Daniele and Taglieri, 2010; Dei and Salvadori, 2006; Giorgi et al., 2000). It has the potential to provide chemically compatible treatments with carbonatic materials and to produce improved consolidation compared to that achieved with traditional methods such as limewater and milk of lime. However, the exact response of weathered stone to nanolime treatment is currently uncertain and widely debated (López-Arce et al., 2010; Daniele and Taglieri, 2010; Karatasios et al., 2009). This is probably due to the fact that nanolime has been mainly developed for use on plaster (Giorgi et al., 2000), to conserve historic wall paintings, so much of the existing research has focused on this. Furthermore, some researchers also highlighted that different environmental conditions can affect the carbonation mechanism of nanolime producing less stable phases such as vaterite or a recrystallisation of portlandite (Lopez-Arce et al., 2010).
2011). Owing to their instability, these phases change over time and this can affect the result of the consolidation treatment.

Regardless of the mineral phases formed by the carbonation reaction, as the properties and characteristics of decay of lime-based materials and stones are very different, research specifically focused on nanolime use on weathered and non-weathered stone is needed.

Furthermore, accelerated decay of stonework has been observed previously after some consolidation treatments had been employed (Dei and Salvadori, 2006). To reduce the potential for these problems to occur with nanolime, in-depth research needs to be undertaken to obtain a detailed knowledge of the interaction between nanolime and the stone surface to which it is applied. This includes sufficient understanding of the optimal application methods, the environmental conditions during application and the consequence of the treatments on stone properties.

This paper reports the results from the first phase of a 2 year independent research programme funded by English Heritage, Engineering and Physical Sciences Research Council (EPSRC) grant EP/I001204/1. An Electrochemical Approach to Study Carbonation of Novel Lime Based Materials, has provided an important theoretical background to understand the behaviour of nanolime in conservation. It is hoped that, when combined with further on-site testing and laboratory trials, this work will contribute towards developing best practice guidance for those specifying and using nanolime.

In March 2013 the EPSRC funded a mission to research institutions of excellence in Italy as part of the EPSRC LimesNet project. The mission entitled ‘Better utilisation of lime in sustainable buildings and conservation’ included visits to the University of Catania, the University of Venice and the Politecnico di Milano. Discussions held with researchers at these institutions included the application, characterisation and testing of nanolime materials in conservation. Of particular relevance to the subject of this paper was a meeting held with Professor Luigi Dei, the patent holder of nanolime, at the Department of Chemistry, University of Florence. This provided a great insight into the manufacture and use of the material. A further meeting, also in Florence, was hosted by Dr Fabio Fratini, Institute for the Conservation and Promotion of Cultural Heritage (ICVBC), Italian National Council of Researches (CNR). The drilling resistance measurement system (DRMS) used to characterise the Bath and Chilmark stone was developed by SINT Technology, Italy, together with ICVBC. Invaluable discussions were held concerning application of the technique and methodologies for interpretation of results.

2. Materials

2.1 Stone samples

This research describes the consolidation of Chilmark stone from Salisbury Cathedral (Salisbury, UK) and Bath stone from Bath Abbey (Bath, UK) with nanolime. The consolidation effects were studied on both, weathered and non-weathered surfaces.

Chilmark limestone is a fine-grained, dense glauconitic stone from the Portlandian formation (Jurassic; Gauri and Bandyopadhyay, 1999; Geddes, 2003). It is easy to carve and is often used in masonry buildings although it is susceptible to erosion by weathering.

Bath stone is an Oolitic limestone formed during the Jurassic period, 135 to 195 million years ago when the area where Bath now stands was under a shallow sea. It is comprised mainly of ooliths which are formed from spherical grains of concentric layers of lime (calcium carbonate) called ooids, formed as they rolled around the sea bed. In addition to the ooliths minute fragments of shell, rock and decayed skeletons of marine life are also commonly observed together with the ooliths all bonded by a sparry calcite (Gauri and Bandyopadhyay, 1999; Geddes, 2003). Although both stone types studied are classed as limestones, Chilmark stone has a higher silica content in comparison with Bath stone. This is an important factor to consider as it alters how the materials weather.

The Chilmark stone used in the tests was originally a corbel removed from the Chapter House at Salisbury Cathedral during recent conservation work between 2009 and 2012. The exposed surface was very friable around the edges of the carved areas and the surface was powdery to touch. Some of the weathered material fell off in transportation demonstrating how fragile the weathered surface had become. Samples and measurements were taken from the front exposed surface (weathered) and from the back of the stone (non-weathered). The back surface, in fact, had not been exposed until its removal from the building facade after which the stone was stored in the laboratory at a temperature of 20°C and relative humidity of 53%. Sampling locations were selected which exhibited visually similar weathering and stone surface texture. In some cases the geometry of the stone dictated the location and direction of the drill holes used during drilling resistance measurements.

The stone sample obtained from Bath Abbey was part of a sculpture removed from the West Front in 1991 and stored since then in an external environment (during which time a layer of biological material had grown on the surface) until being moved into the laboratory where it was kept under the same conditions as the Chilmark stone. Samples and measurements were taken from the exposed surface (weathered) and
from the inner part accessed through a fresh fracture (non-weathered).

2.2 Nanolime consolidants
Nanolime is a suspension of colloidal nano-sized particles of calcium hydroxide (Ca(OH)₂) in an alcohol such as ethanol, isopropanol or n-propanol. Its preparation is based on a precipitation process in supersaturated aqueous solutions of calcium chloride (CaCl₂) and sodium hydroxide (NaOH). Following precipitation, water is substituted with alcohol to improve stability by reducing coagulation and dissolution/re-precipitation. Concentrations between 5 and 50 g/l are typically used for stone consolidation applications (Daniele and Taglieri 2010).

In the present study CaLoSiL E25 and IP25, which are both produced by IBZ-Freiberg (n.d.) and supplied by Hirst Conservation were used. E25 contains 25 g/l calcium hydroxide in ethanol and IP25 contains 25 g/l calcium hydroxide in isopropanol. The products were used in the ‘as received’ condition from the producer with no dilution.

3. Experimental methods of analysis
3.1 Pre-treatment characterisation tests
Specimens were characterised using a variety of analysis techniques including the Karsten tube penetration test, the Scotch Tape test, optical microscopy, electron microscopy, DRMS and mercury intrusion porosimetry.

3.1.1 The Karsten tube penetration test
This is a simple method of measuring the rate of water penetration into (and hence permeability of) building materials such as concrete, stone and plaster. The test was performed using a clear plastic open-ended tube marked with a volumetric scale. The base of the tube was placed on the surface of the material to be tested, and the joint made watertight using modelling clay. The tube was filled with water, and the volume of water absorbed into the surface recorded at various time intervals. The data was used to plot curves to compare the absorption behaviour of the materials from the different stone areas.

3.1.2 Scotch tape test
The informally termed ‘Scotch tape test’ (STT) or, more precisely, the ‘Standard test methods for measuring the adhesion by tape test’ was carried out according to ASTM D3359 (ASTM, 2009).

3.1.3 Optical microscopy
Optical microscopy was performed on polished sections of representative stone fragments no more than 25 mm in length and 15 mm in depth. Samples were embedded in low-viscosity resin by vacuum impregnation before being subjected to a pressure of 0.34 MPa for 12 h during the curing period. The surface of each sample was subsequently ground using progressively finer silicon carbide papers to a 1200 grit size before polishing with, 6, 3 and 1 μm diamond paste. A final polish was achieved using colloidal silica suspension. Images of the polished sections were taken using a Zeiss ICM 405 metallurgical microscope.

3.1.4 Microstructure and chemical information
This information was obtained from surface fractures using a JEOL JSM6480LV scanning electron microscope (SEM) coupled with an Oxford INCA X-ray analyser. Samples were fixed on the holder with a carbon tape before application of a 30 nm thick layer of gold using an Edward Sputter S150B coater to reduce charging. Energy-dispersive X-ray (EDX) analysis data was collected and analysed using INCA Energy 350 software from Oxford Instruments. High magnification images of the nanolime were obtained using a JEOL JEM1200EXII transmission electron microscope (TEM) operating up to 120 kV with a Gatan DualVision Digital Camera.

3.1.5 Mercury intrusion porosimetry
Mercury intrusion porosimetry (MIP) was performed using a Micrometrics AutoPore III utilising ports for both low and high pressure. WIN9400 series (version 2.00) software from Micrometrics Instruments Corporation allowed analysis of data downloaded from the Micrometrics Interface Controllers. Penetrometers (pen and stem) for solid samples with 5 ml volume from Micrometrics were used.

3.1.6 Drilling resistance measurements
These were obtained using a SINT Technology s.r.l. drilling machine. All tests were undertaken using a rotational speed of 600 rpm and penetration rate of 10 mm/min. The force (in N) required to maintain these rates (i.e., the drilling resistance of the material) was plotted against depth of penetration, up to a maximum depth of 40 mm. A 5 mm dia. polycrystalline diamond-coated, flat-ended drill bit was used. Drill bit wear was monitored throughout the testing schedule using SINT Technology s.r.l. artificial reference stone (ARS) as a reference material. Initial tests on the stones studied highlighted the inhomogeneity of these natural materials. For this reason absolute values of drilling resistance must be considered with caution. In this case, the results were of greater significance when the shapes of the curve produced by plotting force against depth were considered, rather than the absolute values. The DRMS results presented in this paper were plotted using an average of three tests on an arbitrary force scale. The force curves of the treated stones were aligned to correspond with the resistance at a depth unaffected by the treatment, typically 30 to 40 mm. This allowed a meaningful comparison between weathered, non-weathered and treated samples to be made.
3.2 Application and curing of nanolime

Nanolimes of type E25 and IP25 were applied to the Chilmark stone (weathered and non-weathered) to compare the effects of the different products. E25 was applied to the Bath stone (weathered and non-weathered) to compare with the Chilmark E25 test and to evaluate the effect that the different physical and chemical characteristics of the stone had on the response to treatment.

A sample of each stone type and condition (weathered and non-weathered) was prepared for further testing. For each sample three applications of consolidant were applied with a brush until saturation was achieved. After the treatment, a white bloom formed on the surface of the stone due to accumulation of excess nanolime. Even though it is a common practice to remove the white bloom, in this case it was not sponged off in order to maintain an accurate record of the amount of consolidant applied each time. The applications were applied at 3-h intervals under laboratory conditions as described previously. To allow carbonation of the calcium hydroxide nanoparticles, the samples were stored after treatment for 2 weeks in the laboratory before characterisation.

3.3 Post-treatment characterisation tests

The tests used to characterise the stones were repeated to determine the effects of consolidation treatment. MIP analyses were performed 3 weeks after treatment. The STT and Karsten tube tests were carried out after 4 weeks. DRMS measurements were taken after 2, 4 and 24 weeks and the SEM imaging was performed at 5 weeks from the application of treatments.

The MIP, Karsten tube and SEM were carried out at different times as a consequence of equipment availability and scheduling of the experimental programme. A minimum period of 3 weeks was allowed before commencing these tests to ensure a significant proportion of the nanolime had carbonated, therefore giving representative changes. DRMS was performed at intervals over a 24-week period to allow changes to be monitored.

Where possible, the tests were repeated to improve statistical accuracy, and average values are reported. When removing samples for characterisation and identifying areas for drilling, similar positions were selected when the sample geometry allowed.

4. Results

4.1 Pre-treatment characterisation of stones

4.1.1 Chilmark limestone

Chilmark limestone samples were characterised using MIP as shown in Figure 1(a). Results indicated that weathering increased the total open porosity by 56% compared with non-weathered stone. The majority of the additional pores were around 12-5 μm in dia. However there was a smaller increase in all the pore volumes especially for those with diameters greater than 1-2 μm.

The SEM images of the samples shown in Figure 2(a) and (b) revealed silica grains bonded within a calcium carbonate matrix. The comparison of the images of weathered (Figure 2(a)) and non-weathered (Figure 2(b)) specimens suggests that the calcium carbonate component was more compact in the non-weathered sample.

Figure 3 shows EDX spectra of untreated Chilmark stone both in the weathered (Figure 3(a)) and non-weathered (Figure 3(b)) condition. The presence of a sulfur peak on the analysis taken from the weathered surface (Figure 3(a)) was attributed to the reaction of the stone with atmospheric sulfur dioxide. In comparison, the sulfur peak was not present on the spectra of the non-weathered stone (Figure 3(b)).

Water absorption characteristics determined using the Karsten tube test showed that the weathered stone surface adsorbed water around seven times faster in comparison with the non-weathered surface. The STT removed around 17% more material from the weathered stone compared to the non-weathered surface.

Drilling resistance force was lower for the weathered surface for almost the entire depth of the hole in comparison with the non-weathered stone (Figure 4). The non-weathered stone showed a relatively stable and constant resistance; however, the weathered stone exhibited a gradual increase in resistance with depth. The weathered resistance was closest to the non-weathered resistance at a depth of 30 mm after which the resistances for both stones were constant. The DRMS data between 17 and 26 mm has been omitted due to high variability.

4.1.2 Bath limestone

The structure of the Bath stone was characterised by examination of a polished cross-section taken from the surface to a depth of 19 mm. The section showed a layer of denser material located adjacent to the surface which was also visible with the naked eye as a whitened area. A 1.3 mm thickness of the outer stone edge is shown in Figure 5 with the outer crust identified as densely packed finer grained particles on the left-hand side of the image. Figure 5(a) shows a cross-section of the weathered stone at a depth of approximately 4 mm. The ooids in this section are slightly smaller and resemble those identified on the non-weathered stone Figure 5(b).

Samples were taken from the crust, from below the crust (still in the weathered zone, no more than 1 cm from the surface)
Figure 1. Pore size distribution of: (a) weathered and non-weathered Chilmark stone and (b) weathered (crust and below the crust) and non-weathered Bath stone.
Figure 2. SEM images of untreated Chilmark and Bath stone: (a) weathered Chilmark stone, (b) non-weathered Chilmark stone, (c) weathered Bath stone, (d) non-weathered Bath stone.

Figure 3. EDX analysis of untreated Chilmark stone both (a) weathered and (b) non-weathered.
Figure 4. Drilling resistance measurements of Chilmark stone. Response of untreated stone shown by grey line and treated stone by black line: (a), (b), (c), (d) weathered stone and (e), (f), (g), (h) non-weathered stone.
Figure 5. Polished section of the Bath stone (magnification 50 ×, scale bar 30 μm): (a) weathered stone with, on the left, the superficial crust and (b) non-weathered stone.

Figure 6. Drilling resistance measurements of Bath stone. Response of untreated stone shown by grey line and treated stone by black line: (a), (b), (c) weathered stone and (d), (e), (f) non-weathered stone.
and from a non-weathered area and the porosity of each of these samples was determined using MIP. Results are presented in Figure 1(b) and show that total porosity was reduced in the weathered crust by around 6% while just below the crust the total porosity was virtually the same as the non-weathered stone, albeit with different pore size distributions. The most apparent difference in pore dia. range was between 0-1 and 10 μm. In this range the weathered stone had significantly fewer pores with diams. between 1 and 6 μm. Beneath the weathered crust a distinct peak was observed corresponding to pores of 8 μm dia., whereas in non-weathered stone the peak corresponded to pores of 2 μm dia.

The SEM image in Figure 2(c) shows that the crust of the weathered stone consisted of smaller particles which were more densely packed together. Absorption tests showed no significant difference in the initial absorption rate (in the first 2 s) of weathered and non-weathered stone, although, following the initial absorption, an increase in rate was observed for the non-weathered stone. The absorption rate in the weathered zone below the crust was approximately half that of the non-weathered stone.

The STT showed that 7% more material was removed from the non-weathered surface in comparison with that of the crust.

Drilling resistance of the non-weathered specimen in Figure 6 showed a relatively steady resistance which was independent of the depth. However, the crust on the weathered surface was clearly observed as a distinct peak at the surface which was followed by a rapid decline in force as the drill broke through the crust into the weaker underlying stone. A gradual increase in resistance was then observed to a depth of 20 mm where the average non-weathered resistance value was reached.

4.2 Characterisation of stones following consolidation with nanolime

4.2.1 Weathered Chilmark limestone

The particle size of E25 was evaluated by TEM and found to be in the range 50 and 300 nm (Figure 7). As IP25 only differs from E25 by the carrier solvent, which is added after the crystals are formed, it is reasonable to assume that the particle sizes of these two products are similar.

Results from MIP after treatment clearly showed a modification of the pore size distribution greater than 3 μm for the weathered sample treated with E25 (Figure 8). Most notably the number of pores with a dia. of 12.5 μm had decreased by 38% (largest peak) and there had also been an increase in the number of pores of dia. 6-6 μm. The effect of the white bloom can be clearly observed by comparing the SEM images of the stone before (Figure 9(a)) and after treatment (Figure 9(b)).

The MIP results for the IP25 treatment showed a different response (Figure 8). Whereas the E25 treatment did not affect all the pores at 12.5 μm, the IP25 produced a new peak at a pore dia. of 10 μm resulting in a total porosity decrease of 20%.

The SEM images of the surface suggest a blooming effect similar to that produced by the E25 treatment.

The DRMS results for the E25 suggest that the treatment did not add additional resistance to drilling after 20 days from the treatment whereas a clear increase was noticeable after 6 months. Use of IP25, on the contrary, allowed an increase in the resistance starting from 20 days but no further increases were noticeable at 6 months after the treatment (Figure 4).

4.2.2 Non-weathered Chilmark limestone

The MIP plot of E25 treatment suggests that the consolidant affected pores with diams. ranging between 0.9 and 3.0 μm and not larger pores of 12.5 μm (Figure 10). An SEM image of the untreated stone is shown in Figure 9(c).
MIP showed that treatment of the stone with IP25 shifted the modal pore dia. from 12-5 to 10 μm (Figure 10). The graph of the non-weathered specimen treated with IP25 showed similar results to that of the weathered stone treated with the same consolidant.

The DRMS results shown in Figure 4 for the non-weathered samples indicate that the E25 treatment had no effect on the drilling resistance of the stone after 20 days and only a small effect after 6 months.

The STT results show that less material was removed from the surface after consolidation. The percentage difference of material removed before and after treatment (ΔM) is presented in Table 1. Comparing ΔM values for the different samples showed a greater reduction for the weathered samples for both types of treatment compared with non-weathered. For weathered stone, the results also showed a slightly better response for E25 in comparison with IP25.

Results of the absorption test are given in Table 2. ΔQ is the percentage difference in water absorption rate for before and after treatment and was calculated considering the absorption rate of the untreated stone as a reference. Similar to the STT results, the weathered samples exhibited a greater reduction in comparison with the non-weathered samples. For weathered stone, IP25 appears to have been more effective at reducing the absorption rate than E25.

Absorption curves for the weathered and non-weathered stones, both treated and non-treated, are given in Figure 11. In the weathered stone both IP25 and E25 behaved in the same manner whereas in the non-weathered stone E25 exhibited a greater effect than IP25.

### 4.2.3 Weathered Bath stone

The pore size distribution after treatment in the crust of the weathered Bath stone showed changes in the range 0-1 to 0-6 μm (Figure 12). The pores at 8-0 μm were reduced by 75% and there was no increase in percentage of pores with diameters less than this.

The SEM images shown in Figure 13 show a penetration of the consolidant through the material from the surface. This figure in particular, shows the deposit of nano-particles on the surface that created a layer of very dense material 15 μm thick.

The DRMS results in Figure 6 suggest that after 6 months from the treatment E25 affected only the weak stone behind the crust whereas after 20 days no significant change in resistance could be detected.
4.2.4 Non-weathered Bath stone

The consolidation treatment showed very little effect on the pore size distribution of non-weathered stone as shown in Figure 14. There were a few reductions in pore numbers: the graph suggests that treatment affected pores at sizes 0.4, 3.0 and 200 μm.

According to the previous findings, the SEM images of the weathered Bath stone showed the fine particle surface coating formed on the exposed surface of the stone, while tests with the DRMS showed the most distinctive result of the treatment applications. Resistance of the stone appears to have been increased to a depth of 1.5 mm above the untreated average (Figure 6). All STT results showed a positive response to treatment. In particular, Table 1 shows the treatment on the non-weathered sample of Bath stone had a greater cohesion improvement after consolidation.

All the absorption test results indicate a reduction in absorption after the treatment. Table 2, in particular, suggests that the absorption test was correlated to the STT as a greater change in ΔQ corresponded to a greater change in ΔM value. The reduction in absorption rate for the non-weathered Bath stone after consolidation was 82%.

5. Discussion

5.1 Effect of weathering on the tested stones

From the characterisation of the two limestones some of their similarities and differences have been highlighted. The effect of weathering on the Chilmark stone was an increase in total open porosity (nearly double) and in particular in the pore size around 12.5 μm dia., thus producing a material with reduced mechanical properties, much more absorbent and with less...
The depth of affected stone was estimated to be as much as 37–5 mm from the exposed surface.

Results suggest that in the Chilmark stone tested, weathering had dissolved the carbonatic binder surrounding the glauconite particles, increasing the porosity and in some cases allowing attack from sulfates with a general reduction of mechanical properties.

The degradation process of the Bath stone had resulted in the formation of a surficial crust with different physical and mechanical characteristics compared with the zone beneath. SEM images, MIP and DRMS results suggest that some of the carbonatic binder contained in the area just beneath the crust was dissolved by acidic rainwater and re-precipitated close to the surface to form a crust. The crust depth was between 2 and 7 mm, while below the crust where the binder had been dissolved a weak zone between 15 and 20 mm from the surface was identified.

The crust was, then, characterised by a lower porosity compared with the other parts of the stone and higher mechanical resistance. The stone just beneath the crust was characterised by a higher porosity (in particular in the region around 8 μm pore dia.) and lower mechanical resistance.

<table>
<thead>
<tr>
<th>Stone type</th>
<th>Condition</th>
<th>Product</th>
<th>Untreated material removed: g/mm²</th>
<th>Treated material removed: g/mm²</th>
<th>ΔM: %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chilmark</td>
<td>Weathered</td>
<td>E25</td>
<td>1.521</td>
<td>1.242</td>
<td>-18.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IP25</td>
<td>1.521</td>
<td>1.275</td>
<td>-16.2</td>
</tr>
<tr>
<td></td>
<td>Non-weathered</td>
<td>E25</td>
<td>1.304</td>
<td>1.246</td>
<td>-4.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IP25</td>
<td>1.304</td>
<td>1.250</td>
<td>-4.1</td>
</tr>
<tr>
<td>Bath</td>
<td>Weathered</td>
<td>E25</td>
<td>1.358</td>
<td>1.263</td>
<td>-7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IP25</td>
<td>1.450</td>
<td>1.279</td>
<td>-11.8</td>
</tr>
</tbody>
</table>

Table 1. Scotch Tape Test results for the Bath stone and Chilmark stone before and after treatment. Values include the weight of tape.
It is probably for this reason that the degradation process often involves the detachment (and falling) of large stone laminations from the surface of worked stone found in historic buildings. The crust itself seems to be the limiting factor of the degradation process which slows down when the crust is formed but starts again when, for some reason such as freeze-thaw or thermal cycling, the crust detaches and exposes new, non-weathered stone to weathering processes.

5.2 Effect of nanolime on the stones

Nanolime tends to form a white dense layer on the surface of the stones that can be sponged off immediately following application in order to prevent any change in the natural colour of the stone that can affect the perception of the building after the treatment.

MIP results suggest the porosity of the non-treated stones was affected in different ways by the two products: IP25 tended to reduce (weathered sample) or maintain constant (non-weathered sample) the porosity of the Chilmark stone, as in both cases a slight shift in the position of the main peak was observed. E25, on the contrary, tended to change the porosity of the stone, reducing the volume of bigger pores with a consequential increase in the volume of smaller pores (non-weathered Chilmark stone, weathered Bath stone).

Differences caused by the degradation process led to variations in the results of the absorption test between the Bath stone and Chilmark stone. The most significant changes in Chilmark stone were observed in the weathered stone which was more porous in comparison with the non-weathered one, while in the Bath stone the main changes in absorption were found in the non-weathered stone, probably because of the role played by the crust in the weathered stone.

In the Bath stone, it is interesting to note that the three sections (crust, weathered and non-weathered part) showed an absorption capacity that increased from the external surface to the inner part. According to the MIP results, this suggests that the main limiting factor in the absorption was the crust.

The absorption rate of the Chilmark stone (both treated and non-treated) showed that, even when the weathered stone was treated, it tended to absorb water faster than the non-weathered stone.

<table>
<thead>
<tr>
<th>Stone type</th>
<th>Condition</th>
<th>Product</th>
<th>$Q$: ml/s untreated material</th>
<th>$Q$: ml/s treated material</th>
<th>$\Delta Q$: %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chilmark</td>
<td>Weathered</td>
<td>E25</td>
<td>0.113</td>
<td>0.036</td>
<td>−68.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IP25</td>
<td>0.113</td>
<td>0.032</td>
<td>−71.7</td>
</tr>
<tr>
<td></td>
<td>Non-weathered</td>
<td>E25</td>
<td>0.016</td>
<td>0.008</td>
<td>−50.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IP25</td>
<td>0.016</td>
<td>0.011</td>
<td>−31.3</td>
</tr>
<tr>
<td>Bath</td>
<td>Weathered crust</td>
<td>E25</td>
<td>0.023</td>
<td>0.014</td>
<td>−39.1</td>
</tr>
<tr>
<td></td>
<td>Weathered</td>
<td>E25</td>
<td>0.013</td>
<td>0.007</td>
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</tr>
<tr>
<td></td>
<td>Non-weathered</td>
<td>E25</td>
<td>0.028</td>
<td>0.005</td>
<td>−82.1</td>
</tr>
</tbody>
</table>

Table 2. Absorption test results for the Chilmark and the Bath stone before and after treatment

<table>
<thead>
<tr>
<th>Stone type</th>
<th>Condition</th>
<th>Product</th>
<th>Total open porosity: ml/g</th>
<th>Peak pore size: µm</th>
<th>Absorption rate: ml/s</th>
<th>Cohesion: g/mm²</th>
<th>Average drilling resistance: N</th>
<th>Zone of influence (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chilmark</td>
<td>Weathered</td>
<td></td>
<td>0.220</td>
<td>12,500</td>
<td>0.113</td>
<td>1.521</td>
<td>0.50</td>
<td>−37.5</td>
</tr>
<tr>
<td></td>
<td>Non-weathered</td>
<td></td>
<td>0.141</td>
<td>12,500</td>
<td>0.016</td>
<td>1.304</td>
<td>2.3</td>
<td>−</td>
</tr>
<tr>
<td>Bath</td>
<td>Weathered crust</td>
<td></td>
<td>0.134</td>
<td>500</td>
<td>0.023</td>
<td>1.358</td>
<td>18.5</td>
<td>−2–7</td>
</tr>
<tr>
<td></td>
<td>Weathered</td>
<td></td>
<td>0.157</td>
<td>8,000</td>
<td>0.013</td>
<td>–</td>
<td>1.6</td>
<td>−19</td>
</tr>
<tr>
<td></td>
<td>Non-weathered</td>
<td></td>
<td>0.160</td>
<td>2,500 and 500</td>
<td>0.028</td>
<td>–</td>
<td>4.9</td>
<td>−</td>
</tr>
</tbody>
</table>

Table 3. Characterisation of sound stone and weathered stone: summary
Figure 11. Absorption rates for the Chilmark stone before and after treatment with E25 and IP25; weathered and non-weathered areas

Figure 12. Pore distribution for the crust in the weathered Bath stone before and after the treatment with E25
stone. As already suggested by other researchers, the absorption rate was related to the porosity (Lopez-Arce et al., 2010).

Results from the STT were in agreement with the absorption tests. The biggest differences in the material removal from the surface of the stones before and after the treatments were found in the weathered Chilmark stone and in the non-weathered Bath stone.

As already reported in other research, carbonation of nanolime is strongly affected by the environmental conditions and in particular by the humidity from the time of application and during curing (Dheilly et al., 2002; El-Turki et al., 2007). It is noteworthy that relative humidity values between 75 and 90% facilitate the growth of amorphous calcium carbonate and monohydrocalcite as well as calcite, aragonite and vaterite. These conditions also allow fast carbonation and larger particle size with higher crystallinity. In comparison studies at lower relative humidities between 33 and 54% by Lopez-Arce et al. (2011) concluded that mainly portlandite and vaterite with low crystallinity are formed as a result of slower carbonation and smaller particle size.

In the case of Bath stone, the nanolime appeared to be more effective for the consolidation of higher porosity non-weathered stone. The IP25 exhibited a better performance than E25 for non-weathered stone. However, this was not observed for the weathered stone.

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Figure 13. SEM Bath stone weathered sample with visible surface layer and nano-particles

Figure 14. Pore size distribution for non-weathered Bath stone before and after the treatment with E25
6. Conclusion
The following conclusions can be drawn from this study.

1. Variations in the mechanical and chemical characteristics of different limestone types have been shown to not only strongly affect their degradation process but also their interaction with nanolime consolidation treatments.
2. The natural weathering on some types of limestone surface can influence nanolime consolidation treatments through changes such as penetration into the surface.
3. The solvent carrier (isopropanol or ethanol) did not significantly influence the transport of nanolime particles into the Chilmark stone pore network.
4. The drilling resistance measurement system successfully measured changes in mechanical properties with depth into the stone surface. Variations in the penetration force were attributed to both the effect of weathering, most notably by the hard crust on the Bath stone surface. Changes in drilling resistance were also attributed to the nanolime treatments applied.
5. Techniques including MIP, absorption using a Karsten tube, the STT and microstructural evaluation using SEM were all sensitive to changes attributed to nanolime treatments and confirmed penetration into the surface. Changes in sub-surface porosity, absorption rate and surface friability were evaluated.

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REFERENCES

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