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Hygric behavior of Portland sandstone as a function of the applied water repellent formulation

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SUMMARY: The study aimed to assess whether the moisture content of Portland sandstone at the time a water repellent was applied affected its subsequent behavior with regards to moisture adsorption and elongation. Two commercial water repellents were tested, a water dispersion and a solvent based formulation. The samples were preconditioned to 43% and 75% RH prior to the application of the water repellent. After treatment the samples were conditioned at increasing relative humidity (43%, 75%, 99%) as well as totally immersed in water for four days. The moisture content and the elongation were measured. Additionally, water vapor transmission was measured on ad hoc samples. Overall, the water based water repellent performed better.

KEY-WORDS: Water repellents, Moisture absorption, Hygric expansion, Portland sandstone

INTRODUCTION

Portland sandstone, also referred to as Brownstone, was one of the most popular construction stones for buildings and monuments in the principal cities along the Atlantic coastline during the mid- to late 19th century [1]. The stone did not weather well showing typical delamination and powdering deterioration which was caused by both freeze-thaw and salt crystallization cycles. The stone and its behavior have been the object of many studies [2-10]. Also the effect consolidation may have on it has been addressed [11; 4 pp. 65-69], however, to our knowledge, the application of water repellent has not been addressed. Though these products are not recommended in situations where soluble salts are present, they could prove useful to mitigate water absorption in areas of the building where the main problem may be water absorption and freeze-thaw.

The present study aimed to evaluate the hygric moisture adsorption and the consequent linear expansion behavior of the fine-grained variety of this clay containing sandstone when treated with a water repellent. For this purpose, two commercially available water repellents —a solvent based silane and alkyl silicate solution and an aqueous dispersion of an

oligomeric siloxane-silane mixture— were used to treat the sandstone. Furthermore, the influence of the sandstone moisture content at the time the water repellent was applied was also considered following the results of the study carried out on concrete by Johansson et al. [13].

MATERIALS AND METHODS

Portland Sandstone Sample Preparation

Portland sandstone, from a quarry of the Portland formation in the Connecticut Valley, is a reddish-brown sedimentary stone which exhibits variations in texture, color and chemical composition across layers. It consists mainly of quartz (~40 %), plagioclase feldspar (~30%), mica (~5%), iron oxides (~16%) and clays (~3%) (see pp. 7-8, 31-38 and 73-79 in [4]). The fine-grained variety ─apparent porosity ~2.8% (w/w); open porosity ~ 6.7% (v/v), was used in this study.

Eighteen prisms (25.4 x 25.4 x 127 mm) were cut perpendicular to the sedimentary bedding planes, where the expansion was expected to show the highest value. Two steel gauge studs were fixed to both ends of the prism with epoxy to fit into a length comparator. A drawing of the assembly with the dimensions is shown in Figure 1. Although the gauge length, which is the nominal length between the innermost ends of the gauge studs, is considered as the true length to be measured for the calculations, the total length of the setup, i.e., 168.275 mm, was adopted since the difference is a determinate error that will not affect the comparison of results.

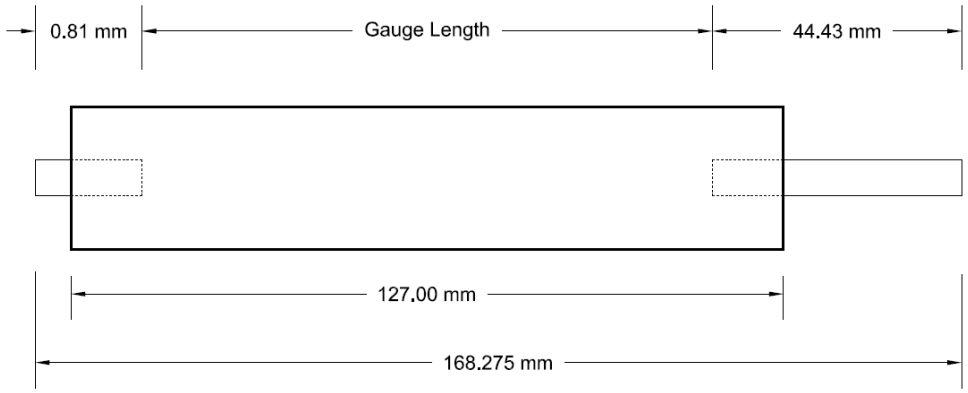

Figure 1. Prism assembly used for length measurement. The total length of the setup is 168.275 mm.

The samples were conditioned in well-sealing cabinets where the desired RH was obtained by including pans containing saturated solution of appropriate salts. Potassium carbonate (K_2CO_3) was used for the 43% RH and sodium chloride (NaCl) for the 75% RH. The RH in all cabinets was checked by Traceable® Humidity-On-A-Card monitors [14].

Water Repellents

Two commercially available water repellents, henceforth WR, were used to treat the sandstone. One was a solvent based formulation (Weather Seal Natural Stone Treatment) while the other was an aqueous dispersion (Weather Seal Siloxane PD), both products being commercialized by PROSOCO. The active ingredients are a mixture of silanes and polysilicates (11%) for the solvent, and a mixture of silanes and siloxanes (7%) for the water based one. Table 1 gives the information as provided in the manufacturer's Material Safety Data Sheet.

Table 1. Tested water repellent specifications according to the manufacturer's Material Safety Data Sheet.

WR Type	Code	Diluent	Active Ingredient	Ingredients
Weather Seal Siloxane PD	SPD	Water	7 %	methyl hydrogen siloxane, alkyl alkoxysilane, ethyl alcohol (hydrolysis by-product)
Weather Seal Natural Stone Treatment	NST	Solvent	11 %	petroleum naphtha, isobutyltriethoxysilane, alkyl polysilicates, i.e., ethyl silicate, ethyl alcohol

The solvent based water repellent includes ethyl silicate in the formulation presumably to improve adhesion of the isobutyltriethoxy silane to the substrate, since longer alkyl chains show a steric effect and may not bond as well to the substrate as described by Oehmichen et al. [15]. As recommended by manufacturers, and proved by studies [16], consolidation prior to the application of a water repellent improves their behavior.

Application Method

The water repellents were applied by brushing on to all the surfaces of the prismatic samples (including the two ends where the pins were inserted with an epoxy) after they were conditioned to either 43% or 75% RH. The samples were then left to dry out for nine days at laboratory conditions (20ºC and 50% RH), followed by drying in the oven at 60ºC to determine their dry weights for the subsequent determination of moisture adsorption isotherms. The remaining amount of water repellent applied was negligible compared to the weight of the samples (less than 0.02%). Three specimens were prepared for each WR and conditioning RH and six control specimens were used. A total of 18 samples were tested and Table 2 summarizes all the specimens and their code names.

Moisture Content

The moisture content of the conditioned samples was measured gravimetrically using a Sartorius M-prove balance with a sensitivity of ±0.01 g. The samples were then exposed sequentially to 43% RH, then 75% RH and 99% RH, the latter being achieved using a saturated solution of gypsum ($CaSO_4.2H_2O$). Finally, the samples were totally immersed in water for 4 days.

Table 2. Number of specimens treated with each water repellent applied at the specified RH conditioning, as well as the control samples. N corresponds to the solvent based and S to the aqueous emulsion formulation while L corresponds to the low RH (43%) and H to the high RH (75%) conditioning.

Ident. code	Formulation	Specimens	RH Condit.	WR applied
NL	Solvent	3	43%	NST
SL	Water	3	43%	SPD
NH	Solvent	3	75%	NST
SH	Water	3	75%	SPD
CL	-	3	43%	-
CH	-	3	75%	-

Elongation Measurements

The linear elongation was measured with a HUMBOLT H3250 length comparator with a digital indicator having a sensitivity of ±0.002 mm. To measure the length, an adapter for 5" (127 mm) specimens was installed on the base. A reference bar was used to calibrate the length comparator to zero before each prism was measured. For each reading taken, the prisms were always placed in the same orientation in the length comparator to minimize changes in reading due to differences in contact surfaces.

Elongation was measured after the samples had reached a stable moisture content at the conditioning RH (43%, 75% and 99%) and after 4-day total immersion in water. It was not the aim to evaluate the highest possible elongation but to determine differences between control and WR treated samples.

Water Vapor Transmission

Sixteen disks (⌀ 44.5 x 25.4 mm) were drilled out of a stone slab and were labeled using the same coding system as for the prisms, shown in Table 2. After conditioning at either 43 % RH or 75 % RH, the top surface of the disks (parallel to the sedimentary bedding plane) was treated with either of the two WR, NST and SPD, so that twelve treated disks, three controls and one dummy sample were used. These samples were air dried in the laboratory for several weeks. Following ASTM standard E96-05, the Water Method was used in which the disks were attached as covers on half-filled 50 ml tri-cornered polypropylene cups with the treated surface facing up. The sides of the disks as well as their attachment to the cups were sealed, and the assemblies were set into a 43 % RH environment. Loss in weight was measured every 24 hours and 13 valid data points were obtained. A dummy specimen over an empty cup was also prepared in the normal manner to compensate for variability in test conditions.

Results

Water Vapor Transmission

The overall weight change over time and the calculated Water Vapor Transmission (WVT) are presented in Table 3. Most of the samples exhibited similar water vapor transmission

properties (based on the standard deviation of the data), confirming that siloxane based water repellent agents do not "seal" the surface but allow water vapor to pass through. Figure 2 shows the points used to calculate the WVT and their corresponding linear regression, which had a minimum correlation factor of 0.995. From this graph it is clear that the moisture content at the time of application of the WR is more important than the type of WR used. Lower WVT was obtained for samples where the WR was applied at the lower moisture content although the value reported for NL in Table 2 appears to negate the statement. While the trend lines reflect the same pattern observed for the weight loss of the samples during the length of the experiment, the WVT slopes for the water based SPD samples diverge during the steady state while those for the solvent based NST samples converge.

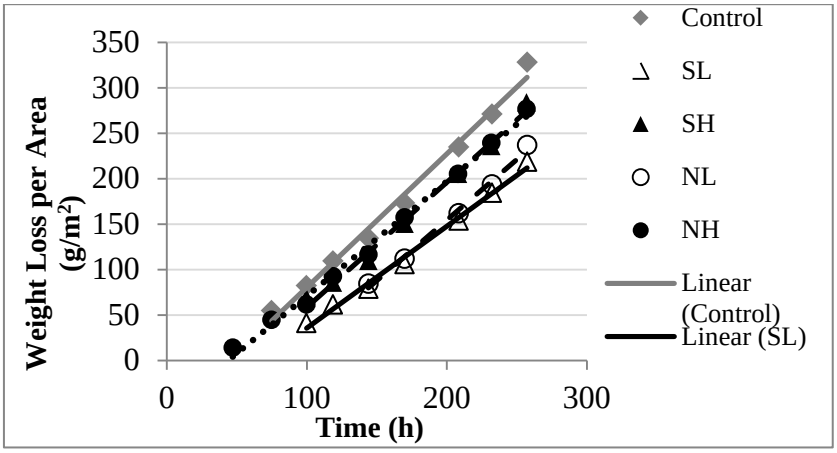

Figure 2. Data points for the weight loss over time during the steady state period and the calculated WVT slopes, where SL=SPD @43%; SH=SPD @75%; NL=NST @43%, and NH=NST @75%.

Table 3. The average weight loss over time for the length of the experiment and the Water Vapor Transmission results during steady state condition, where SL= SPD @43%; SH=SPD @75%; NL= NST @43%, and NH= NST @75%. Standard deviation between parentheses.

	Weight Loss (mg/h)	WVT (g/m^2h)
Control	1.83 (0.08)	1.47 (0.06)
SL	1.23 (0.08)	1.12 (0.04)
SH	1.60 (0.08)	1.37 (0.05)
NL	1.32 (0.08)	1.33 (0.06)
NH	1.61 (0.07)	1.26 (0.04)

Moisture Sorption

The moisture sorption isotherms obtained by conditioning at the three different relative humidity environments and including the 4-day total immersion absorption are shown in Figure 3 and the data presented in Table 4.

Table 4. Relative moisture content (% w/w) of the various samples upon conditioning at different RH and after 4 days of total immersion in water, where SL= SPD @43%; SH=SPD @75%; NL= NST @43%, and NH= NST @75%. Standard deviation indicated between parentheses.

Conditioning	0%RH	43% RH	75% RH	99% RH	Total immersion
Control	0	0.124 (0.005)	0.226 (0.004)	0.64 (0.09)	2.57 (0.03)
SL	0	0.121 (0.003)	0.219 (0.006)	0.54 (0.04)	1.7 (0.2)
SH	0	0.115 (0.001)	0.209 (0.004)	0.59 (0.06)	1.9 (0.3)
NL	0	0.119 (0.003)	0.211 (0.005)	0.63 (0.05)	1.11 (0.03)
NH	0	0.124 (0.001)	0.219 (0.004)	0.53 (0.03)	1.19 (0.01)

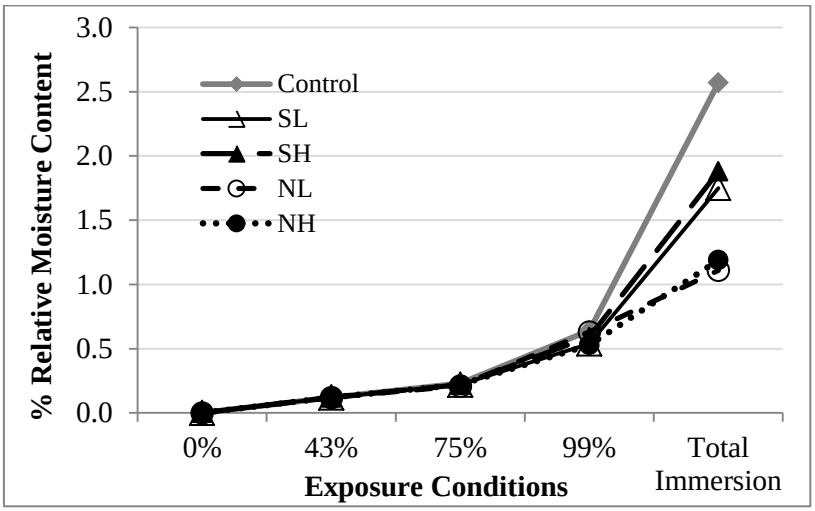

Figure 3. Relative Moisture content isotherms for the various samples, where SL=SPD @43%; SH=SPD @75%; NL=NST @43%, and NH=NST @75%.

At both 43% and 75% RH there appears to be no significant difference (~ 7%) between the control and the treated samples. However, by 99% RH the moisture sorption of the WR treated samples (except NL which as in the case of WVT is out of line) was significantly

lower than for the control and unaffected by their conditioning prior to treatment. This was even more evident for the water immersed samples where a clear trend could be established depending on the type of WR, the solvent based NST showed the lowest absorption of water (55% less than the control average), while the water dispersed SPD showed only around 30% less. The standard deviation for the latter measurements is nearly tenfold higher reflecting the greater data dispersion. There is no significant difference in the data dispersion as a function of their conditioning prior to treatment.

Elongation Measurements

The elongation measured on the samples conditioning at the three different relative humidity environments and after 4 days total immersion in water are shown in Figure 4, while the data is given in Table 5.

Table 5. Elongation (μm/m) for the samples conditioned at different RH and after 4 days total immersion in water, where SL= SPD @43%; SH=SPD @75%; NL= NST @43%, and NH= NST @75%. Standard deviation indicated between parentheses.

Conditioning	0%RH	43% RH	75% RH	99% RH	Total immersion
Control	0	2.4 (1.4)	5.9 (1.7)	13.7 (2.2)	33.5 (1.4)
SL	0	2.4 (0.2)	6.7 (0.7)	13.9 (0.7)	29.7 (2.4)
SH	0	2.0 (0.7)	5.5 (0.7)	15.0 (0.7)	29.7 (2.1)
NL	0	3.2 (0.7)	6.7 (1.3)	17.4 (1.8)	25.0 (0.2)
NH	0	2.8 (1.4)	7.5 (1.8)	15.4 (1.2)	25.3 (0.6)

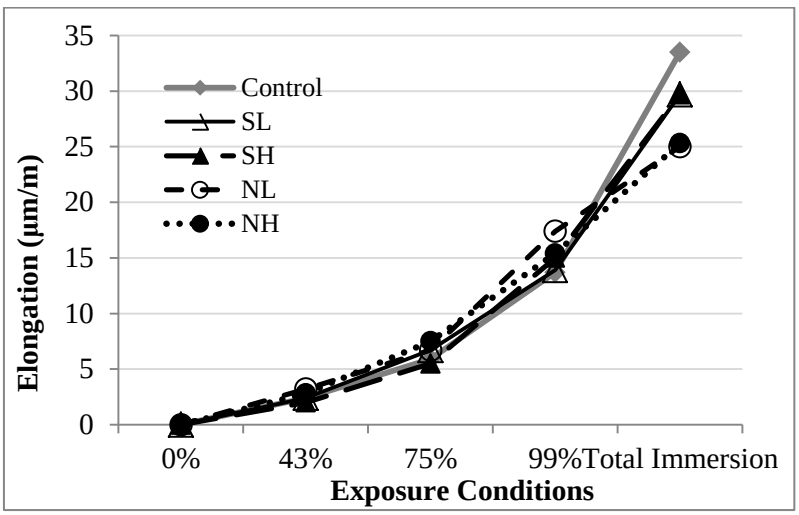

Figure 4. Elongation (μm/m) for the samples conditioned at different RH, where SL= SPD @43%; SH=SPD @75%; NL=NST @43%, and NH=NST @75%.

The hygric elongation is generally higher for WR treated samples as compared to the control ones and increases with increasing RH. Note that again at 99% RH, the NL sample shows the highest elongation (this apparent anomalous behavior could presumably be explained by the presence of silicate ester in the WR competing in the hydrolysis reaction with the alkoxysilane when applied at the lower moisture content). However, when samples were totally immersed in water, the hydric elongation of the control was significantly higher than that for any of the WR treated sample. The water based SPD showed a higher elongation (and greater data dispersion as indicated by the standard deviation) than the solvent based NST, following the same trend observed for their hydric moisture absorption.

Discussion and Conclusions

The WVT data show that the moisture content at the time of the water repellent application has a greater influence than whether the WR is solvent or water based. While all WR treated samples show a lower WVT than the control, those treated at the higher moisture content show a corresponding higher WVT (Figure 2). Contrary to this, the moisture sorption data (hygric and hydric) obtained appear to be influenced by the type of WR rather than the moisture content at application time —particularly when totally immersed in water— with the solvent based WR showing the lowest moisture absorption (Figure 3). For the hygric elongation, the solvent based NST shows slightly higher elongations than the control or the water based SPD with increasing RH. This trend inverts upon total immersion in water with the NST showing a significantly lower elongation than either the water based SPD or the control, which, as expected shows the highest elongation (Fig. 4).

Plotting the elongation as a function of the ad- or absorbed moisture, as shown in Figure 5, it is clear that the two types of water repellents behave similarly, the solvent based NST reducing the amount of sorbed moisture more than the water based SPD. However, the elongation at any given moisture content is higher for the solvent based NST, followed by the SPD and then the control.

If, however, the ratio of elongation/moisture content is plotted as a function of the exposure conditions, as shown in Figure 6, a different picture becomes apparent. In the first place, the maximum elongation per moisture content was observed for all samples around 75% RH indicating that this amount of moisture is the most “efficient” in inducing an expansion, which may be attributed to the formation of organized water layers along mineral surfaces, in particular, clays [17]. Under total immersion, although the amount of water absorbed is comparatively higher, it is less effective in inducing expansion.

Secondly, it shows that the solvent based NST induced the highest elongation, with the water based SPD applied at the lower moisture content causing only a slightly lower expansion, and when applied at the higher moisture content it resulted in the lowest expansion of all —up to 75% RH— the difference disappearing when under total water immersion. The plot also shows, that the WR treated samples suffer a relatively higher elongation, the solvent based one (NST) showing the highest values. Even considering absolute expansion, this water repellent has the highest values for hygric expansion but the lowest ones for hydric expansion.

In conclusion, moisture content of Portland sandstone at the time the water repellent is applied appears to have a significant influence only for the WVT, but a slight effect on

moisture adsorption and elongation. For these parameters, the type of water repellent formulation, whether solvent or water based, had a larger effect. The results obtained show that for buildings, which suffer more from relative humidity changes than from long term water immersion, the environmentally friendly water based SPD performs better than the solvent based NST water repellent. To be taken into account is that all the variations observed are minimal and that therefore the conclusions may be considered hypothetical.

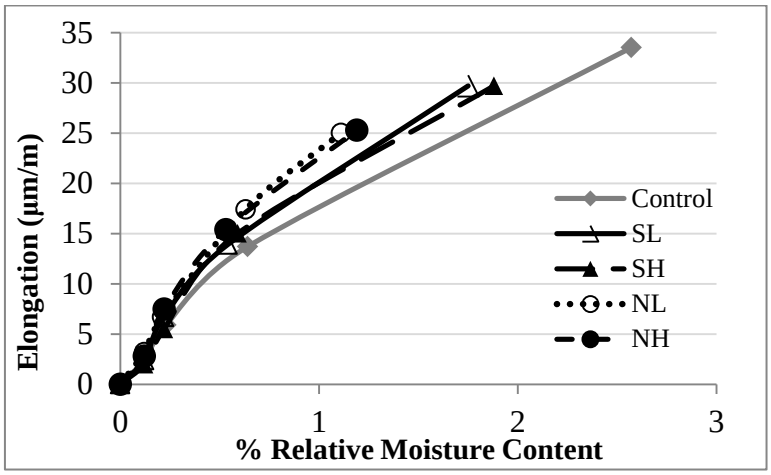

Figure 5. The average elongation of the samples as a function of their moisture content, where the three measured points corresponding to hygric adsorption and the last one corresponds to the hydric absorption.

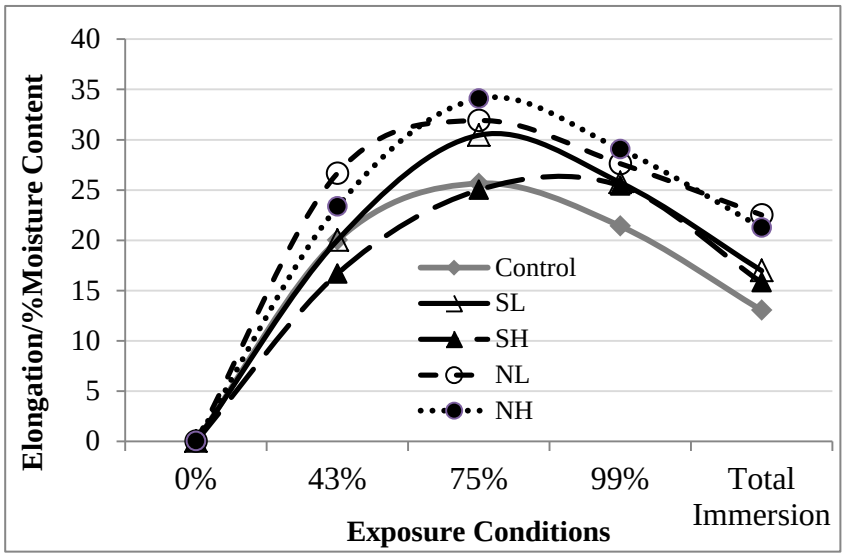

Figure 6. Ratio of the elongation and % moisture content as a function of the exposure conditions.

The results obtained are applicable only to the products tested and these particular formulations, provided that the manufacturer does not change them. This is one of the problems professionals in the field of architectural conservation have to face, as discussed elsewhere [18]. Further studies are required to elucidate the contribution that the different components in the formulation may have in the overall performance of the product.

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