

Colour change evaluation on UV radiation exposure for *Păun-Repedea* calcareous geomaterial

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Abstract. When talking about the preservation treatments that can be applied to natural stones used in different constructions, the surface hydrophobization plays an important part, especially when referring to porous surfaces like the calcareous oolithic stones specific to Repedea area, Iași County, Romania. The present paper presents a method that evaluates the hydrophobization efficiency of two types of pellicles, involving UV artificial ageing and colorimetric analysis of the treated surfaces. The evaluation was done through continuous colorimetric monitoring and by comparing the evolution of the chromatic modifications of the two treated surfaces with the original colorimetric values and with the witness area, which was exposed to UV radiations under the same conditions, but left chemical untreated. The techniques used during this experiment were: CIE $L^*a^*b^*$ colorimetry, OM, SEM-EDX, UV radiation exposure and Spectrum Irradiance Measurement.

1. Introduction

Geomaterial definition includes soils, rocks and minerals which are mostly used in the construction and structuring of buildings, in natural form or processed form but excludes the products fabricated through complex technological processes, based upon an advanced knowledge of engineering [1]. With the passing of time, any one of geomaterial can be subject to deterioration or degradation, through the influence of environmental factors, the main factor of aggression being environmental humidity, weathering and the presence of urban pollution [2-4]. The occurrence of urban/industrial aerosols type and their impact in the ambient air over the Iași area (Romania) is already proved by



specialized literature by changes of radiative forcing due to the properties of aerosols to absorb and scatter differently the optical radiation [5,6]. As a result, the sunlight radiation represents another factor of alteration, because it is able to generate undesired effects [4,7], especially in the case of hydrophobic treatments, through the chromatic variation of treated surfaces, due to UV radiation exposure. Thus, is necessary to apply a waterproofing and coating treatment with various chemical solutions, current commercially available. Therefore, this paper proposes presenting a collection of data that afford for the analysis of chromatic deviation and the accelerated aging from the lithic surface of the calcareous stone sample exposed to UV radiation, after carrying out hydrophobic treatments.

2. Materials and methods

The lithic material exposed to UV radiations is a sedimentary calcareous rock, form during the Sarmatian geological age, and was sampled from Păun – Repedea village, Iași County [8].

The two chemical products used for hydrophobization and tested are commercially available and known as LTP Mattstone[®] and LTP Mattstone H2O[®].

CIE $L^*a^*b^*$ colorimetry was done using a Lovibond[®] RT 300 spectrophotometer (Reflectance Tintometer D65/10°) which allowed the measuring of the chromatic modifications, in the exact same spots, for the entire duration of the investigation.

The porosity and the degree of permeability of the hydrophobized surfaces were studied using a Zeiss Axio Imager[®] A1m optic microscope, with an attached Axio Cam and specialized software. The **optical microscopy** (OM) was also used to evaluate the changes regarding the texture, morphology and chromatic modification that took place after the treatment of the investigated surfaces.

Scanning Electron Microscopy (SEM) coupled with **energy dispersive X-ray** (EDX) allowed the recording of the micrographic analyzed area and recording the spectrum based on which to determine elemental composition for lithic materials. A scanning electron microscope model Vega II LSH – Tescan[®], coupled with an EDX detector, model Quantax QX2 – Bruker - Roentec[®] was used.

UV radiation exposure was done with a predominant wavelength 300 - 365nm by using four high-pressure mercury vapour lamps (Osram Ultra Vitalux[®] 300W - 230V). The intensity of the light produces by these lamps was measured both analogically (TYPMDLx lux meter) and digitally (LX 1010B lux meter).

Comparative **spectrum irradiance measurement** have been studied by means of a high-resolution monochromator (Princeton Instruments[®] Acton SP2750i, 750 mm focal length) and an intensified CCD camera (Roper Scientific Princeton Instruments[®] PI MAX3-1003-UNIGEN2, 1024x1024 pixels, minimum gating time 2ns). The complete spectrum was obtained by using the “step-and-glue” procedure of the monochromator/camera software, which automatically increments the grating position once a given (8nm wide).

The humidity content of the sample surface was measured with a non-invasive technique, using a Gann Hydromette[®] (Compact B humidity meter) that works on the principle of measuring the dielectric constant, through high radio frequency.

The investigations were carried out in constant laboratory conditions, at a temperature of 21°C and relative humidity (RH) of 60%.

3. Experimental part

After probing, the sample of lithic material was cut into dimensions and divided into three areas of investigations, with equal surfaces (of around 6cm²). The three obtained areas were noted using the symbols C0, C1 and C2 (figure 1). After that, the stone sample was stored in desiccators for 48 h before chemical treatment. The two hydrophobic products were noted using the symbols S1 (LTP Mattstone[®]) and S2 (LTP Mattstone H2O[®]). Each product was used for one area as follows: S1 for C1 and S2 for C2. The area C0 is the witness area, left untreated, but exposed to the UV radiations, under the same conditions like the two treated areas.

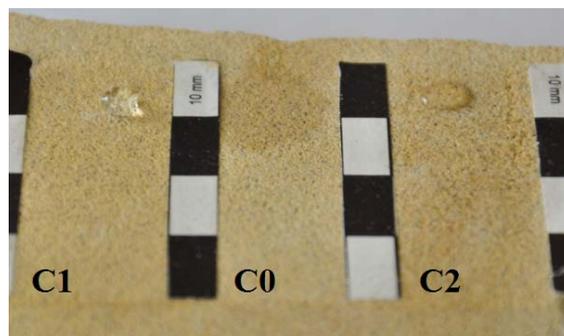


Figure 1. The dripping water test on the investigated and treated surfaces. Pictures taken at 24 h after the treatment.

After the three areas were delimited, a first set on initial colorimetric measurements was taken, in conditions of constant humidity of the lithic surfaces. According to the technical sheets, a quantity of 0.18 mL from each chemical product was applied using a soft brush on every investigated surface, in successive stages. In the case of the S1 solution, a pause of 2 hours was taken between applying the layers, while the S2 solution was applied wet on wet.

At 24h after treatment, distilled water was applied in droplets for the macroscopic evaluation of the hydrophobic degree of the surfaces being treated (figure 1). As can be observed in figure 1, the surface corresponding with the control area (C0) absorb the water instantaneously and stain the surface compared to the treated areas, where the drops of water do not reach the pores and also do not stain the surfaces. The volume of distilled water used was 0.05 mL for every area investigated.

In order to evaluate the hydrophobic efficiency of the two products on the surfaces C1 and C2, the evaporation time for the distilled water drops used to determine the degree of permeability was calculated: $t_1/C1 = 170$ minutes and $t_2/C2 = 135$ minutes.

Furthermore, the hydrophobic degree was also evaluated at a microscopic level (figure 2), using distilled water drops with a volume of up to 4 μL for each investigated surface.

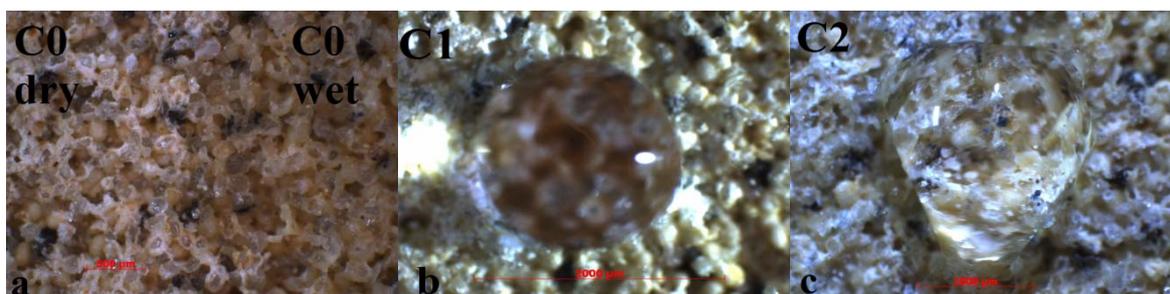


Figure 2. Optical microscopy (5X) from the porous surface of the investigated sample. Images taken during the dripping process of the distilled water over the three surfaces : (a) C0 – dry / wet; (b) C1; (c) C2.

The porosity of the investigated surfaces can be observed in figures 2(a), (b) and (c), and is influenced by the oolitic structure specific to the lithic material from Repedea area. The porosity was also analysed through SEM (figure 3), while the elemental composition of the sample was determined through EDX (table 1) thus confirming the presence of chemical elements specific to sedimentary calcareous rocks [9,10]. The presence of carbonate minerals was confirmed through a rapid drop test using HCl, the effervescent results specific to this chemical reaction being observed in figure 4.

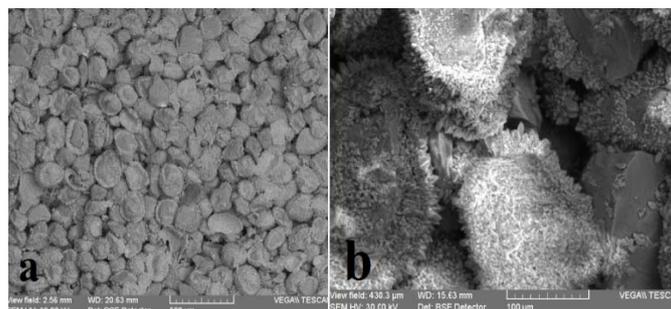


Figure 3. SEM micrographic images for oolitic calcareous sample: a) 100X image ; (b) 500X image.

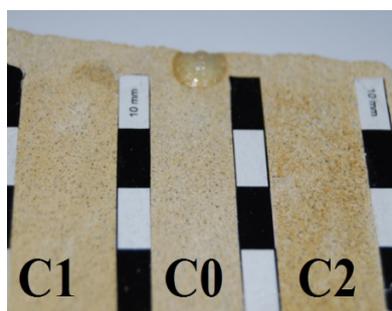


Figure 4. HCl dripping rapid test.

Table 1. The elemental composition for calcareous sample, obtained through EDX spectrum.

Element	[norm. wt.- %]	[norm. at.- %]
Calcium	47.41	31.47
Silicon	18.39	17.42
Aluminium	1.63	1.60
Magnesium	0.90	0.98
Iron	1.55	0.74
Potassium	2.40	1.63
Carbon	0.12	0.27
Oxygen	27.60	45.89
Total	100	100

After 48h of chemical treatment, the surfaces were exposed to UV radiation in laboratory conditions, total period of exposure being on 24h for each surface. In this case, the colorimetric variation was monitored every two hour, taking into consideration the reference values after the application of chemical treatment, for areas C1 and C2. At the same as the colorimetric measurements, the surfaces humidity of each area investigated was also monitored, so as to evaluate its possible influence upon colorimetric radiation.

The four UV lamps were distributed in a radial pattern, in half a circle with a radius on 40 cm, the centre being the place where the lithic sample is fixed. Two of the lamps were centrally positioned, while the other two lamps were fixed on the sides, all at an angle of 36° reporting to the planar surface of the sample.

4. Results and discussions

Concerning the colorimetric evolution, the colour change was measured for each coordinate (L^* , a^* and b^*), as compared to its initially value, on the same sample and in the same point, whereas the total change of colour (ΔE^*_{ab}) was calculated in accordance with the following equation [11-13]:

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2},$$

where L^* represent the lightness /darkness coordinate and varying from 0 (black) to 100 (white), a^* is the red/green coordinate ($+a^*$ indicating red and $-a^*$ green), and b^* means the yellow/blue coordinate ($+b^*$ indicating yellow and $-b^*$ blue).

The results of the colorimetric measurements carried out at 24h after the chemical treatments are presented in table 2. In the case of measurements carried out simultaneously with the UV radiation exposure the colorimetric variations for control and treated areas are presented in table 3 and figure 5.

Also, in table 2 and table 3 are presented the humidity from investigated areas on all experimental procedure's phase.

Table 2. Total colour change after chemical treatment and the moisture content from the surface of the material (h%).

Investigated area	before treatment	after treatment	
	h%	ΔE^*_{ab}	h%
C0	0.22	-	-
C1	0.18	7.06	0.19
C2	0.17	9.58	0.18

Table 3. Total colour change after UV exposure and the moisture content from the surface of the material (h%).

hours	area C0		area C1		area C2	
	ΔE^*_{ab}	h%	ΔE^*_{ab}	h%	ΔE^*_{ab}	h%
0	0	0.22	0	0.19	0	0.18
2	0.57	0.18	1.05	0.18	1.19	0.17
4	0.68	0.20	1.10	0.19	1.24	0.19
6	0.62	0.18	1.17	0.16	1.27	0.16
8	0.69	0.18	1.30	0.17	1.44	0.16
10	0.75	0.17	1.47	0.16	1.58	0.15
12	0.81	0.18	1.51	0.16	1.65	0.16
14	0.84	0.18	1.57	0.16	1.80	0.16
16	0.86	0.17	1.67	0.16	1.84	0.15
18	0.87	0.18	1.75	0.16	1.91	0.16
20	0.88	0.17	1.81	0.15	1.93	0.16
22	0.92	0.17	1.81	0.15	2.04	0.16
24	0.99	0.17	1.88	0.15	2.17	0.16

It should be mentioned that, throughout all the investigations stage, the water content from each surface of the sample varied insignificantly (table 2 and table 3). In this case, the humidity of surfaces did not influence the chromatic deviation of the areas being investigated. In the case of the two treated areas of studied geomaterial, the chromatic aspect is influenced by the way in which the treatment solutions interact with the porous surfaces of samples [14]. So, it can notice the colour tendency to accentuate more on the surface C2, treated with the product S2 (figure 1). This fact is also evidenced by the data represented in table 2, where it can be clearly seen that treatment with the solution S2 determined notable value of total colour change, in accordance with the specialized literature in this

domain [11,12]. The C1 area treated with S1 product, also experienced a colour change, but of a smaller value ($\Delta E^*_{ab} = 7.06$), in comparison with that of C2 area, where $\Delta E^*_{ab} = 9.58$.

The colour tendency to change simultaneously with the exposure at UV for a period of 24h (figure 5) is also greater in the case of area C2 ($\Delta E^*_{ab} = 2.17$), in comparison with the area C1 ($\Delta E^*_{ab} = 1.88$) and the witness area C0 ($\Delta E^*_{ab} = 0.99$).

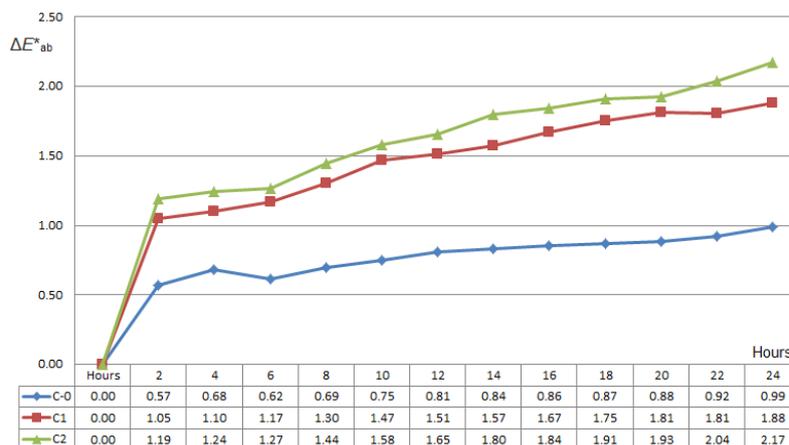


Figure 5. The graphic of ΔE^*_{ab} evolution on the hydrophobised surfaces exposed 24h to the UV radiations.

Concerning the dripping process on optical microscopy, figure 2a shows how the distilled water drop is instantly absorbed in smaller surface, from untreated zone C0, and this small area becomes wet and darker. In figure 2c, we can observe the distilled water drop tendency to flatten on area C2, process observed also in macroscopic mode (figure 1 – area C2). This indicates a lower hydrophobic capacity of the S2 product [13], in comparison with the hydrophobic effect obtained in area C1, treated with S1 (figure 1 and figure 2b).

The differences between the two water drops shapes that come in contact with the treated surfaces were confirmed by the evaporation times. The distilled water drop applied on C2 has a faster evaporation time (135 minutes) due to its flatter surface, while the distilled water drop applied on C1 has a more spherical shape, which result in a longer evaporation time (170 minutes). By correlating the way the distilled water drop flattens on the treated area C2 (figure 1 and figure 2c) with the higher values of chromatic modifications (ΔE^*_{ab}) after the chemical treatment and after the UV exposure, we can certainly state that the solution S2, while is eco-friendly, has some disadvantages in comparison which the effects and results obtained by using the S1 solution (obtained by mixing organic compounds that pose a threat to the environment).

In order to evaluate the UV exposure efficiency, the Osram Ultra Vitalux[®] lamps wavelengths were determined and compared to those of the solar spectrum using Princeton Instruments[®]. Figure 6 shows solar wavelengths measured at noon, around the laboratory, which is located on this coordinate: 47°1736'N latitude and 27°5713'E longitude.

Also, figure 6 present the UV lamps spectrum which allowed us to calculate the intensity rapport between the two sources and for each wavelength. Thus, in figure 7 it is shown the ratio between both spectrum and it can observed the UV lamps radiation have an intensity of 250 to 2700 higher than solar light radiation, for the spectral domain of 290 to 380nm. By analyzing the chromatic modification values (C1 - $\Delta E^*_{ab} = 1.88$ and C2 - $\Delta E^*_{ab} = 2.17$), obtained after 24h exposure to UV lamps radiations (with approximately 30×10^3 lux - intensity light) we can determine the fact that the two solutions, S1 and S2, have a certain UV resistance.

The ΔE^*_{ab} value (0.99) of the witness area C0, exposed to the UV radiations in the same conditions for 24h, is lower than the ΔE^*_{ab} values for the other two areas, already mentioned. When comparing the same ΔE^*_{ab} value for area C0 with the ΔE^*_{ab} value of 2.94, registered on another witness area from

another old calcareous rock exposed to UV radiations for 24h [15], we can state that the artificial aging rate can vary accordingly with the age of the sample rock, with the time period between sampling and testing. By analyzing this aspect, we can deduce that a new lithic material, recently extracted, could have a reduced colour change at UV radiation exposure in laboratory conditions, than a similar geomaterial, that has already been aged through long time exposure in a natural microclimate, before being sampled and investigated in the same laboratory conditions.

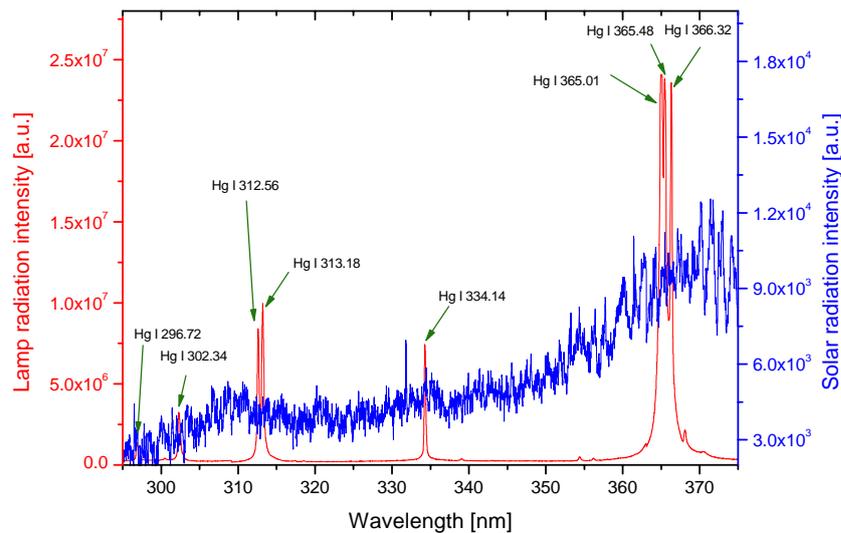


Figure 6. Lamps and solar radiation intensity.

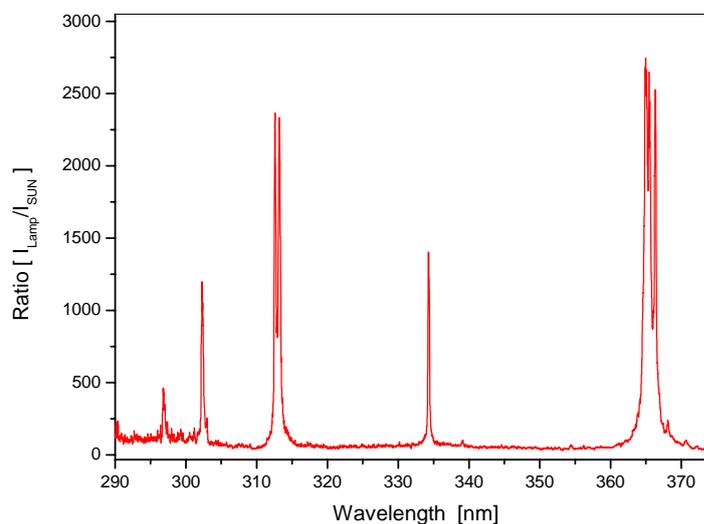


Figure 7. Ratio radiation intensity (wavelength lamps / wavelength Sun).

5. Conclusions

Due to the porous nature of the calcareous rocks from Păun-Repedeia area, Iași County, any surface hydrophobization action through pellicles is both necessary and welcomed, especially when this geomaterial was used in building and/or restoration processes of constructions that have historical and cultural value. The investigations have confirmed the hydrophobic capacity of the two selected

products, S1 and S2, with the notice that although they have a certain resistance to UV radiation, the samples treated changed colour in a significant manner, especially the LTP Mattstone H20[®] product, aspect also confirmed by the technical sheet provided by the manufacturer.

Taking into consideration the principles of scientific conservation of stone historical monuments, which require a minimal colour change during any kind of intervention [12,16], the use of S2 is not recommend in the case of constructions with historical value.

For any other maintenance process of porous calcareous rocks like those from Păun-Repedea area, the final decision, on which product to use from the two presented in the paper, belongs directly to the beneficiary and/or the involved specialists.

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