

# Assessment of Hydrophobic Coating on Porous Calcareous Rocks Surface Exposed in Urban Ambient Air Pollution

V Pelin<sup>1,2,3</sup>, O Rusu<sup>2</sup>, M M Cazacu<sup>2,4,\*</sup>, S Gurlui<sup>2</sup>, A V Sandu<sup>5,6</sup>, I Radinschi<sup>4</sup>,  
V Ciocan<sup>7</sup> and I Sandu<sup>6,8</sup>

<sup>1</sup> Department of Environmental Science, Faculty of Geography - Geology, Doctoral School of GeoScience, Alexandru Ioan Cuza University, Carol I Blvd, no. 20A, 700505, Iasi, Romania

<sup>2</sup> Atmosphere Optics, Spectroscopy and Lasers Laboratory - LOASL, Faculty of Physics, Alexandru Ioan Cuza University, Carol I Blvd, no. 11, 700506, Iasi, Romania

<sup>3</sup> Department of Concrete Structures, Building Materials, Technology and Management, Faculty of Civil Engineering and Building Services, Gheorghe Asachi Technical University, prof. Dimitrie Mangeron Blvd, no. 1, 700050, Iasi, Romania

<sup>4</sup> Department of Physics, Gheorghe Asachi Technical University, prof. Dimitrie Mangeron Blvd, no. 59A, 700050, Iasi, Romania

<sup>5</sup> Faculty of Materials Science and Engineering, Gheorghe Asachi Technical University of Iasi, prof. Dimitrie Mangeron Blvd, no. 41A, 700050, Iasi, Romania

<sup>6</sup> Romanian Inventors Forum, Sf. Petru Movila Street, no. 3, Iasi, Romania

<sup>7</sup> Department of Building Services, Faculty of Civil Engineering and Building Services, Gheorghe Asachi Technical University, prof. Dimitrie Mangeron Blvd, no. 1, 700050, Iasi, Romania

<sup>8</sup> Arheoinvest Interdisciplinary Platform, Alexandru Ioan Cuza University, Carol I Blvd, No. 11, 700506, Iasi, Romania

E-mail: marius.cazacu@tuiasi.ro

**Abstract.** Urban air quality has changed rapidly in recent years, that requiring new research focused on the effects of pollution, both on the environment and on human health, as well as on apparent changes in building surfaces, including historical ones. As is known, permanent exposure to the atmosphere in the urban environment causes degradation processes on the surfaces of natural stone monuments, especially on porous stone surfaces. In these investigations were used samples of porous calcareous rocks similar to the natural stone from the many historical monuments of the Iasi city - Romania. These samples were coating with various commercially hydrophobic solutions. Further, these samples were exposed in the immediate vicinity of a historical monument and an intense road traffic junction. After about six months of exposure, apparent changes in the treated surfaces were compared with untreated control surfaces but subjected to the same environmental conditions over the same time period in order to evaluate the effectiveness of the hydrophobic treatment.

## 1. Introduction

As it is known, there is a strong connection between the local geological setting and the old architectural surface [1, 2]. For objective reasons, in the metropolitan area of Iasi City - Romania, porous calcareous rocks have been used extensively, being extracted from the nearby pits, such as



those in the village of Paun, located on the plateau of Repedea Hill [3, 4]. Taking into account that any natural stone becomes predisposed to a series of physical and mechanical transformations, from the moment of extraction by the quarry or when it is used in a construction and becomes exposed to environmental conditions [5, 6], long-term research is required the length of time that such geomaterials [7] are aging over time [8]. Moreover, the pronounced carbonate and porous character of the Paun – Repedea stones [9] implies the adoption of a coating treatment that prevents or limits as far as possible the undesirable effects [10, 11]. Also, the presence of urban pollution factors, which has increased in recent years in the city of Iasi, has favored the surface alteration of building stones [6, 12-18], which gives special attention to the use of these lithic materials in construction civil or historical building.

Given the above, knowing at the same time that there is no universally valid hydrophobic product [19,20], this paper proposes the assessment of the impact of ambient air on hydrophobic indigenous rocks and subsequently exposed for a certain period of time, under the conditions of an urban environment [21, 22], with intense car traffic, having the main research technique CIE  $L^*a^*b^*$  colorimetry, useful in determining the total colour change on the investigated surfaces [23, 24].

## 2. Materials and methods

The lithic material exposed to urban environmental conditions is a sedimentary and oolitical calcareous and porous rock [9], form during in the Sarmatian geological age, and was sampled from Paun – Repedea village, Iasi County – Romania. This quarry was for many years an important source of natural geomaterials necessary for construction of local civil and historical buildings [4, 25].

The hydrophobization of porous calcareous surface samples were conducted used eight chemicals products, for lithic materials maintenance, with the following commercially names: LTP Mattstone H2O, LTP Colour Intensifier Stainblok Seal 2, Sikagard S700, Sikagard S703, Isomat Nano Pro-C, Isomat Nano-Seal, Isomat PS-20 and Tenax Ager.

CIE  $L^*a^*b^*$  colorimetric investigations were performed using a Lovibond® RT 300 (Reflectance Tintometer D65/10°) spectrophotometer, monitoring the chromatic deviation at the same measurement points in each specific work step. Colorimetric measurements were carried out in constant laboratory conditions, at a temperature of ~21°C and relative humidity (RH) of ~60%.

The meteorological parameters were monitored using a LSI LASTEM station which contains sensors and characteristics for wind and relative humidity recording data.

## 3. Experimental part

After taken calcareous rocks from a pit located on the outskirts of Paun - Repedea village, in southern part of Iasi city - Romania, these were cut using roughly rectangular shapes with two planar surfaces to facilitate fastening on support and to have a uniformity of the gravimetric deposition areas of the airborne particles while allowing for colorimetric measurements before and after exposure. After cutting ten porous calcareous samples, marked P0 to P9, was dried and stored in desiccators for 48h, preceding the first colour measurements and coating chemical treatments. The samples labelled P0 and P9 were used for witness test left untreated, but exposed under the same urban environmental conditions like the eight treated samples.

The hydrophobic solutions were grouped by producers and named S1 to S8, in according with the stone sample`s notation, from P1 to P8 (Table 1).

The hydrophobic coating was carried out under the conditions provided by the manufacturer`s technical sheets, respecting the working conditions and the hydrophobic solutions quantities for each of the eight porous lithic surfaces. After this step, the treated samples stored and dried in laboratory conditions for 96h to stabilize the surfaces moisture and then the colorimetric measurements were performed and labelled with *AT* symbol (by *after treatment* but before exposure to urban environment). Exposure period of all porous calcareous samples (the ten pieces) was performed between Oct. 10, 2017 and Apr. 05, 2018 (178 days). After the samples were withdrawn, these were dried for 96 hours under the same laboratory conditions. Final step was to measure results

colour coordinate for each sample which was noted with *ATE* symbol (after treatment and exposure), in accordance with Table 2. 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 ( $\Delta E_{ab}^*$ ) was calculated in accordance with the following equation [23,24,26, 27]:

$$\Delta E_{ab}^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

in which  $\Delta L^*$  is the change in light intensity in the respective point, at different time intervals, as compared to the initial value ( $\Delta L^* = L_n^* - L_{initial}^*$ ), where  $L^*$  means the lightness to darkness coordinate and varying from 0 (black) to 100 (white);  $\Delta a^*$  is the chromatic modification of the coordinates of axis  $a^*$  ( $+a^*$  indicating red and  $-a^*$  green), from the same point, at different time intervals, as compared to its initial value ( $\Delta a^* = a_n^* - a_{initial}^*$ ) and  $\Delta b^*$  is the chromatic modification of the coordinates of axis  $b^*$  ( $+b^*$  means yellow and  $-b^*$  blue), respecting the same method of calculation ( $\Delta b^* = b_n^* - b_{initial}^*$ ).

**Table 1.** The chemical products notation in accordance with producers grouping and samples labelling.

Producer	Chemical products		Stone samples notation
	commercially name	notation	
LTP	Mattstone H2O	S1	P1
	Colour Intensifier Seal 2	S2	P2
Sika	Sikagard 700S	S3	P3
	Sikagard 703W	S4	P4
Isomat	Nanopro-C	S5	P5
	Nano-Seal	S6	P6
	PS 20	S7	P7
Tenax	Ager	S8	P8

**Table 2.** The chemical products notation in accordance with the producers grouping and the labelling of samples.

colorimetric variables		P0	P1	P2	P3	P4	P5	P6	P7	P8	P9
$\Delta L^*$	AT	0	-3.76	-2.22	-1.99	-3.98	-1.32	-4.19	-1.86	-12.21	0
	ATE	-8.38	-13.56	-13.94	-11.94	-12.76	-16.56	-16.38	-11.05	-14.76	-10.62
$\Delta E_{ab}^*$	AT	0	6.73	3.97	3.49	7.17	2.22	6.31	2.60	14.09	0
	ATE	8.43	13.64	13.96	11.95	12.78	16.88	16.47	11.16	14.99	10.97

The current urban environmental exposure area is located near a major and crowded road junction called *Stone Bridge (Podul de Piatra)*, in the immediate vicinity of a XIX<sup>th</sup> century historical monument with the same name: Stone Bridge. This exposure place is located over the Bahlui River and southern margin of mentioned intersection. Thus, the exposure place is located between the historic bridge and the south-eastern part of the intersection, with the following geographical coordinates: 47.158035 N, 27.575451 E (Figure 1).



**Figure 1.** Stone Bridge (Podul de Piatra) intersection/cross-road from Iasi city, Romania: (a) older bridge (historical); (b) newer bridge; (c) geographical position for exposure area. [24]; (d), (e) exposure sample and meteorological station.

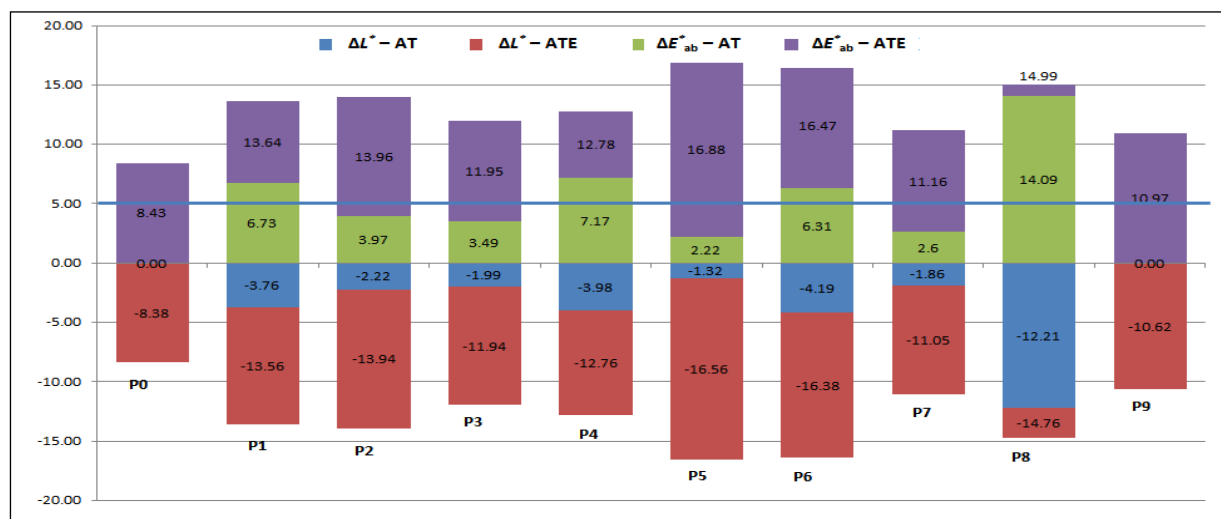
In the same area is placed LSI LASTEM meteorological station for daily monitoring and data recording at regular intervals of time.

#### 4. Results and conclusions

##### 4.1. Hydrophobic assessment by colorimetric measurements

As can be observe in Table 2 and in the graph of Figure 2, after chemical treatment, total color change value ( $\Delta E^*_{ab} - AT$ ) varies between 2.22 (P5 / S5) and 14.09 (P8 / S8). The samples P1, P4 and P6 have slightly above the minimum value in according with scientific literature:  $\Delta E^*_{ab} \geq 5$  [27]: P1 - 6.73, P4 - 7.17, respectively P6 - 6.31. The value of total color exchange for sample P8 confirms the manufacturer's specifications of the S8 solution in terms of obtaining the "wet" effect on the treated lithic surfaces, which is very important to note as it will major influence the aesthetics of any architectural surface treated with this chemical product.

For samples P2, P3 and P7, after coating (AT), the total color exchange values fall below the prescribed limit:  $\Delta E^*_{ab} \leq 5$  [27].



**Figure 2.** Comparative graphical representation of the colorimetric data  $\Delta E^*_{ab}$  and  $\Delta L^*$  obtained after chemical treatment (AT) and exposure in urban ambient air from Stone Bridge area (ATE).

At the same time,  $\Delta E^*_{ab} - AT$  values for samples P1, P5 and P6 can be compared with the results of similar treatments with the same chemicals (S1, S5 and S6) used on the same type of lithic material (from Paun - Repedea pit) and in the same laboratory conditions, the results identified in the literature are as follows: S1 - 9.58 (vs. 6.73), S5 - 1.27 (vs. 2.22) and S6 - 6.26 (vs. 6.31) [23,28]. Therefore,

these solutions may have predictable results in case of coating of the porous calcareous material with the same source.

#### 4.2. Hydrophobic assessment by colorimetric measurements after exposure in urban ambient air

After exposure to the urban climate in the *Stone Bridge* area, all ten samples significantly exceed the minimum threshold of notable total color change ( $\Delta E^*_{ab} \geq 5$ ), with remarkable increasing value for P5, P6 and P9 samples,  $\Delta E^*_{ab} - ATE$  having 16.88, 16.47 and 14.99 units, respectively. Also, the control samples (P0 and P9) showed significant color shifts, with values of 8.43 for P0 and 10.97 for P9.

On the other hand, after exposure in the urban environment, all samples have a change in the apparent color (from shade term, in natural light, by authors evaluation) from ashen yellow and grey yellowish to blackening (Figure 3). This is explained through:

- the high porosity of the samples [9] may cause a *receptivity* of them to retain on the lithic surface the air borne and the particles from the atmosphere and
- by corroborating *wet* and *dry deposition* processes, depending on various meteorological parameters from different periods of the year [5, 26,29].



**Figure 3.** Calcareous porous sample: **left** – at 96h after chemical treatment (AT); **right** – testing hydrophobization efficiency after exposure period (178 days) in ambient urban air (ATE) and dried in 96h, in laboratory conditions.

According to the data from Table 2 and the graphical representation in Figure 2, it is observed that all  $\Delta L^* - ATE$  luminescence values are sensitively equal with  $\Delta E^*_{ab} - ATE$ , meaning that the other colorimetric parameters are involved,  $\Delta a^* - ATE$  and  $\Delta b^* - ATE$  (see eq.1), have an insignificant influence (see eq.1). In scientific literature, this phenomenon is explained by the *blackening* process, which is assimilated to the major fluctuation of luminescence,  $\Delta L^*$  having only negative values, by lowering the  $L^*$  in values comparing to the initial value. (see eq. 1) [26]. This is the case for all samples after the 178 days of exposure in the urban environment from *Bridge Stone* area, that case can confirming in the preliminary way the receptivity of the porous geomaterials for retaining air borne or particles in suspension from the atmosphere, even if they were chemically treated for protection against the undesirable effects of wetting, the priority role of these treatments being exclusively the periodic maintenance of the apparent architectural surfaces [22].

An example for this situation can be represented by the colorimetric variation, after chemical treatment of the P2 sample, which has the lowest value of the total colour change, between the treated sample ( $\Delta E^*_{ab} - AT = 2.22$ ) and after exposure in the urban environment, when increases significantly, reaching the limit of 16.88, this value being the maximum between the obtained results for  $\Delta E^*_{ab} - ATE$ . From this point of view, at the opposite of the results of the P2 sample, there is the colorimetric variation of the sample P8 which seems to have a lower *receptivity* (or *susceptibility*) to retain the atmospheric

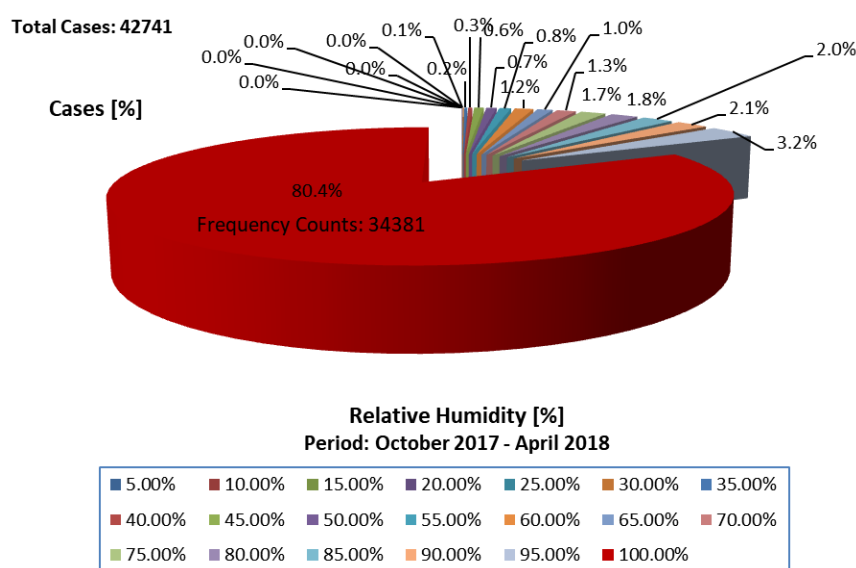


particles, because after the chemical treatment with S8 the value  $\Delta E^*_{ab} - AT$  reaches at 14.09 (maximum  $AT$  value) and after exposure the value  $\Delta E^*_{ab} - AT$  is very close to  $\Delta E^*_{ab} - AT$ : 14.99 units.

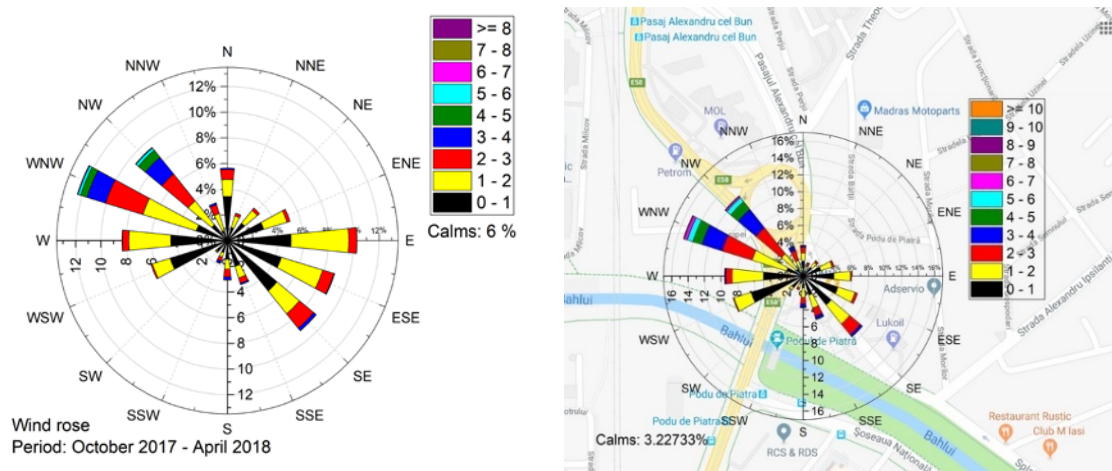
Certainly, this type of *receptivity* of porous lime coated hydrophobic surfaces should be investigated and studied in a larger manner in order to obtain a generally valid conclusion for porous lithic surfaces treatments.

#### 4.3 Environmental conditions over hidrophobised porous surface

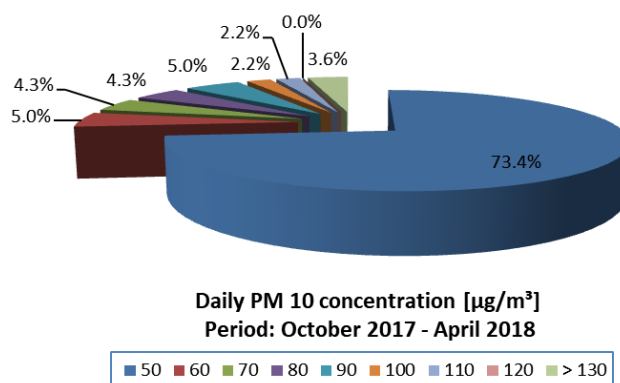
As it is known, the major influences on the apparent architectural surfaces are represented by various environmental factors [5,6,29]. Thus, during the period of exposure of samples P0 ÷ P9, the environmental parameters monitored in the *Bridge Stone* area were the wind, humidity and the presence of PM10 particles, according to the data presented in Figures 4, 5 and 6.



**Figure. 4.** Relative humidity during the exposure period - Oct. 2017 ÷ Apr. 2018, in *Stone Bridge* intersection. Data averages at 5 minutes, from 42,741 total cases.



**Figure 5.** Wind rose in *Stone Bridge* intersection: **left** – exposure period for P0 ÷ P9 samples: Oct. 2017 ÷ Apr. 2018; **right** – another wind action in the same area, in a previous period: Oct. 2016 ÷ Aug. 2017, shown in Google street mapping.



**Figure 6.** Statistics of daily PM10 concentration during the exposed period, in *Stone Bridge* area – Iasi, Romania [30].

The presence in over 80% of cases of a 100% *humidity* (Figure 4), a *total precipitation* of 136.40mm during the exposure period [31], alongside the predominant *wind action* from the WNW and NW to SE and SSE sectors (Figure 5) and the *presence of PM10* particles (Figure 6) on a *cold-season temperature* background [31] along with the auto traffic values in increasing, confirms the opinion of numerous authors regarding the influence of these parameters in the progressive change and alteration of urban ambient air, ultimately favoring the undesirable *blackening effect* previously presented [26,29,32-35].

Along with these factors, the *geomorphology* of the Iasi metropolitan area, to get her with the *local climate* factors, generates the effects of the *thermal inversion* specific of the cold season [36], blocking the dispersion of atmospheric pollutants or "*pushing*" them to the soil, which in time influences the quality of the apparent lithic surfaces of the built environment. This fact is also confirmed by the color full appearance (*blackened*) of the porous limestone samples P1 ÷ P9, after the exposure of approximately 180 days, in the low altitude zone at the *Stone Bridge* intersection in relation with surroundings of Iasi City, Romania.

## 5. Conclusions

In according to CIEL\*a\*b \* colorimetry measurements, applied to the ten porous limestone samples, a number of aspects could be assessed, such as:

- color evolution before and after chemical treatments allows first assessment of an aesthetic impact for investigated or maintained surfaces;
- the predisposition (or *receptivity*) of porous surfaces (including those that are hydrophobized) to retain particles or pollutants from the atmosphere;
- the direct influence of some parameters in the urban climate in the unwanted change of porous lithic surfaces, resulting in undesirable effects such as *blackening*.

The responsiveness of some local lithic materials to keep the particles in the atmosphere together with the *blackened appearance* of the samples after about six months of exposure near an important road junction in Iasi confirms also that a number of geomaterials in the architectural surface (including historical construction) become witnesses of the way in which atmospheric pollution takes place over time, especially in the urban environment.

Of course, this article represents a preliminary assessment of the impact and the relation between the porosity of some lithic surfaces, hydrophobization surfaces and various environmental factors. Last but not least, it is worth mentioning that for a complete technical evaluation it is also necessary to measure successively the contact angle after chemical treatments and after exposure of lithic porous samples under various urban environment conditions.

## 6. References

- [1] Di Benedetto C, Cappelletti P, Favaro M, Graziano S F, Langella A, Calcaterra D and Colella A 2015 *Eng Geol* **193** 310-319
- [2] Morra V, Calcaterra D, Cappelletti P, Colella A, Fedele L, de' Gennaro R, Langella A, Mercurio M, de' Gennaro M 2010 *Journal of the Virtual Explorer* **36** 26
- [3] Branzila M and Stefan P 2009 *Sci Ann Cuza Univ Jassy, Sect Geol* **LV(2)** 5-18
- [4] Badarau D and Caprosu I 2007 *The Old Masonry from Iasi City: until 1821* Demiurg Publisher, Iasi, Romania
- [5] Camuffo D 1995 *Sci Total Environ* **167** 1-14
- [6] Watt J, Tidblad J, Kucera V and Hamilton R 2009 *Effects of Air Pollution on Cultural Heritage* Springer, New York, United States
- [7] Fookes P G 1991 *Q J Eng Geol* **24(1)** 3-15
- [8] Bellopede R, Castelletto E and Marini P 2016 *Eng Geol* **211** 19-26
- [9] Chelarescu A, Nichita O, Paunel E, Mihul A, Tudoraş A, Dumitrescu I, Ciubotaru V and Constantinescu F 1956 *Bull. Polytech. Inst. Jassy* **II(VI)** 351-388
- [10] Bell F G 1993 *Environ Geol* **21** 187-200
- [11] Corcione C E, De Simone N, Santarelli M L and Frigione M 2016 *Prog Org Coat* **103** 193-203
- [12] Cazacu M M, Timofte A, Balin I, Dimitriu D G and Gurlui S 2011 *Environ Eng Manag J* **10(1)** 139-145
- [13] Banica A, Bobric E D, Cazacu M M, Timofte A, Gurlui S and Breaban I G 2017 *Environ Eng Manag J* **16(9)** 2147-2163
- [14] Cazacu M M, Timofte A, Unga F, Albina B and Gurlui S 2015 *J Quant Spectrosc Ra* **153** 57-64
- [15] Unga F, Cazacu M M, Timofte A, Bostan D, Mortier A, Dimitriu D G, Gurlui S and Goloub P 2013 *Environ Eng Manag J* **12(2)** 297-303
- [16] Cazacu M M, Tudose O G, Rusu O, Scripa A E and Radinschi I 2017 *Bull Polytech Inst Jassy, Sect Math Theor Mech Phys* **63(67)** 43-60
- [17] Breaban I G and Paiu M 2016 *Int Multi Sci Geoco* **II** 79-86
- [18] Pelin V, Breaban I G, Sandu I and Gurlui S 2017 *Rev Chim-Bucharest* **68(6)** 1333-1340
- [19] Boutin F 2001 *Proceedings of Hydrophobe III - Third International Conference on Surface Technology with Water Repellent Agents*, Aedificatio Verlag, Freiburg, Germany 233-244
- [20] Luvidi L, Mecchi A M, Ferretti M, Sidoti G 2016 *Int J Conserv Sci* **7(1)** 311-322
- [21] Comite V, Álvarez de Buergo M, Barca D, Belfiore C M, A. Bonazza A, La Russa M F, Pezzino A, Randazzo L and S.A. Ruffolo S A 2017 *Constr Build Mater* **152** 907-922
- [22] Vleugels G, Fobe B, Dewolfs R and Van Grieken R 1994 *Sci Total Environ* **151** 59-69
- [23] Pelin V, Sandu I, Munteanu M, Iurcovschi C T, Gurlui S, Sandu A V, Vasilache V, Branzila M and Sandu I G 2016 *IOP Conf Ser-Mat Sci* **133** 012061
- [24] Pelin V, Rusu O, Sandu I, Gurlui S, Sandu A V, Cazacu M M and Sandu I G 2017 *IOP Conf Ser-Mat Sci* **209** 012080
- [25] Ratoi B, Pelin V, Sandu I, Branzila M and Sandu I G 2018 *Int J Conserv Sci* **9(1)** 151-164
- [26] Grossi C M, Brimblecombe P, Esbert R M and Alonso F J 2007 *Color Res Appl* **32(4)** 320-331
- [27] Schanda J 2007 *Colorimetry. Understanding the CIE System* Wiley-Interscience Hoboken, New Jersey, United States of America
- [28] Pelin V, Sandu I, Gurlui S, Branzila M, Vasilache V and Sandu I G 2016 *Rev Chim-Bucharest* **67(12)** 2568-2572
- [29] Grossi C M and Brimblecombe P 2007 *Building Stone Decay: From Diagnosis to Conservation* Geological Society Special Publications **271** 117-130
- [30] \* \* \* [http://calitateaer.ro/public/home-page/?\\_\\_locale=ro](http://calitateaer.ro/public/home-page/?__locale=ro)
- [31] \* \* \* <https://www.wunderground.com>
- [32] Xie X, Semanjski I, Gautama S, Tsiligianni E, Deligiannis N, Rajan R T, Pasveer F and Philips W 2017 *Isprs Int J Geo-Inf* **6(12)** 389
- [33] Nazarenko Y, Kurien U, Nepotchatykh O, Rangel-Alvarado R B and Ariya P A 2016 *Environ*



*Sci-Proc Imp***18** 190-199

- [34] Buttini P and Pereg G 2003 *Structural Studies, Repairs and Maintenance of Heritage Architecture VIII*, Transactions on the Built Environment, WIT Press, **66** 221-228
- [35] Gill P S and Graedel T E 1983 *Rev Geophys Space Ge***21(4)** 903-920
- [36] Sfica L, Ichim P, Apostol L and Ursu A *Theor Appl Climatol* doi.org/10.1007/s00704-017-2305-4

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