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Decay assessment approach of building stones from cultural heritage in freshwater reservoirs

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***Abstract* – Numerous cases of built cultural heritage that once were submerged in freshwater reservoirs are emerging in the last years due to increasing droughts. The DAMAGE project assesses the study of the specific degradation processes that occur in the building stones of this type of heritage subjected to constant immersion and emersion cycles. A real case of a Spanish old royal site, flooded in the 1950s, has been studied through portable non-destructive techniques to evaluate the state of conservation. The results have been combined with laboratory tests and a degradation simulation to fully characterize the main materials and determine the deterioration pattern.**

I. INTRODUCTION

Underwater cultural heritage has attracted the attention of numerous researchers over the last decades, and the interest in developing proper methodologies to protect it has increased especially since the international treaty of the 2001 UNESCO Convention [1]. However, most of these studies focus on the heritage that is permanently submerged, such as shipwrecks [2-4], and very few have studied the degradation processes that occur in cultural heritage that is cyclically submerged in inland waters like freshwater reservoirs [5]. This type of underwater heritage is particularly abundant in Spain, since it is one of the countries with the largest number of reservoirs in Europe and in the world, with more than 3,000 dams, mostly built since the 1950s [6]. Although these huge infrastructures are necessary due to the mostly Mediterranean climate of the Iberian Peninsula, they were built without considering the villages and cultural heritage that would be flooded. In recent decades, the increase in droughts has highlighted the number of unprotected cases that emerge every summer and submerge again in the rainy season.

The degradation processes in this type of heritage subjected to cycles of immersion and emersion are not the same as those in other underwater or aerial environments. To address the study of the deterioration pattern suffered by heritage in reservoirs, in 2020 the DAMAGE project was created and presented at the MetroArchaeo2020 conference [7].

Two case studies have been selected in this project, both are in reservoirs close to Madrid and belong to the Tagus River basin, however, in the present work only one of them will be assessed for clarity reasons: the submerged old town of The Royal Site of La Isabela, located in the Buendía reservoir in the province of Guadalajara.

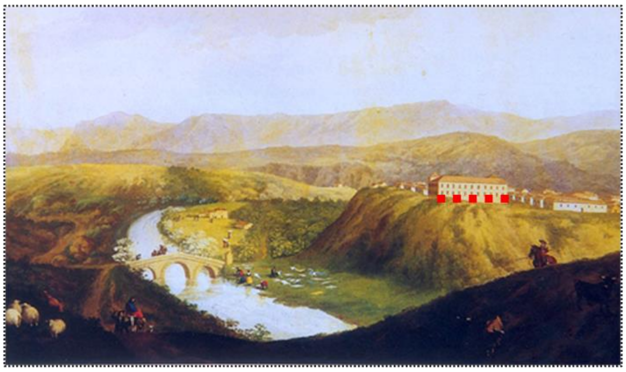

Fig. 1. View of the Royal Palace of La Isabela by Fernando Brambila (1763-1834). The red dotted line marks the Northeast façade of the palace, as a reference to better understand Fig. 2. B.

II. CASE STUDY

The Royal Site of La Isabela was founded by King Ferdinand VII of Spain, in honor of his wife Isabel of Braganza, conceived as a charitable entity, as a place of leisure and rest for the monarchs, and as a nucleus of economic activity, due to its exploitation of thermal waters and agriculture (Fig. 1). Construction began in 1817 and was completed in 1826. The existence of springs with curative properties, both for bathing in their waters and for the therapeutic use of their ingestion, has been known and exploited since ancient times by Romans, Arabs, and Christians alike. The buildings, apart from the baths and the palace, (organized in twenty-seven blocks, eleven streets, and two squares), were intended for the accommodation of bathers, a tavern, inn, hostel, oven, forester's house, offices, and houses for employees and settlers, barracks, smithy, slaughterhouse, tile factory, hospital, and hermitage [8, 9].

The main building materials used in the complex are stone from the surroundings (sandstone and limestone), bricks, and mortars.

From 1865 onwards, La Isabela passed through various owners, and the old palace was converted into a Casino and Dance Hall. The outbreak of the Spanish Civil War in 1936 led to its definitive closure. The town of La Isabela remained for a few more years, until 1955 when the construction of the Buendía Reservoir caused the waters to cover the town and the spa.

Buendía is the fourth largest reservoir in Spain in terms of total storage capacity (1,638 cubic hectometers), covering an area of 8,194 hectares, and forming part, together with other reservoirs, of what is known as the "Sea of Castile".

III. METHODOLOGY

Several walls of the Royal Site of La Isabela constructions have been selected to assess the state of conservation and study the deterioration processes they suffer, using non-destructive and portable characterization techniques. Results of in situ measurements are compared to laboratory tests done in the main building materials found.

A. In situ measurements

The case of La Isabela is not a single building but an entire submerged village, therefore, three walls have been selected to represent different conditions occurring at this site (Fig. 2. B). The proximity to the interior of the reservoir and the terrain's inclination has been considered, since some walls spend more time submerged than others, as well as the orientation of the façades. Thus, the North and South façades of three walls that are at different distances from the shore are being studied (walls named 3E, 4E, and 5E in Fig. 2. B). Wall nomenclature is based on their location on the map of the old town shown in Fig 2. B. The town streets form a grid layout of numbered rows (1 to 6) and lettered columns (A to E) corresponding to each block of the buildings' ruins. The selected walls, 3E, 4E, and 5E, were chosen because they are in the most accessible part of the town and share similar terrain elevations. In each wall, the different properties are measured at various heights.

Generally, each façade is divided into four distinguishable zones according to height, and measurements are taken along the entire line of ashlars corresponding to each of these zones (named a, b, c, d in order of height). Whenever possible, three measurements of a given technique are made on each ashlar to measure a specific property.

The measurement and sample collection campaigns are done at least annually at the same points, generally in the dry season, when the water level is lower, and the constructions have emerged and are more accessible. In the wet seasons, some technological adaptation tests to the underwater environment have been carried out recently, although those results are not discussed in this article.

The properties studied, the techniques applied in situ, and the respective equipment are the following:

- The detection of defects and cohesion degree by studying the propagation velocity of ultrasonic pulses (UPV) (C.N.S. Electronics PUNDIT).
- Leeb hardness by rebound with a micro-hardness tester (Proceq Equotip® 3).
- Chromatic parameters by spectrophotometry~~.~~ (Minolta® CM-700d/600D spectrophotometer). To analyze color Variations, the CIELAB 1974 color coordinate system was used, where the studied parameters are L* (brightness), a* (range from red to green), b* (range from yellow to blue), and C* (chroma or saturation).
- Surface moisture content (%) by electrical conductivity and capacitance measurements (Protimeter Surveymaster®) which provides values on a scale ranging from 70 to 999 (arb. units.).
- Detection of surface temperature to detect damp areas and hidden defects or structural elements through infrared thermography imaging (FLIR ThermaCAM™ B4).
- Surface micro-roughness of materials with an optical roughness meter (TRACEiT® roughness meter).
- Hydrophobicity by portable (water-stone substrate) contact angle analyzer (Krüss Mobile Surface Analyzer).
- Detail imaging by portable digital microscopy (Dinolite Edge Digital Microscope).

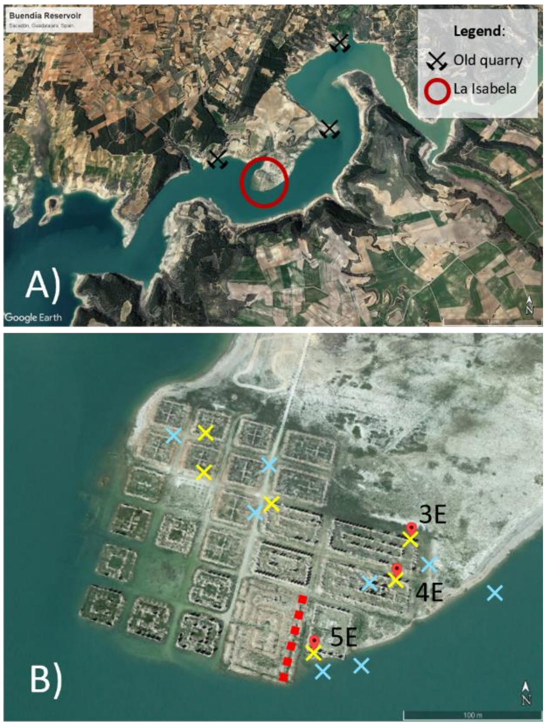

Fig. 2. A) General view from Buendía reservoir. B) Closer view of La Isabela. The red dotted line marks the palace's NE façade as in Fig. 1. Red pins indicate the studied walls 3E, 4E, and 5E. Crosses mark the sampling points, yellow for solid and blue for water samples. Each point may represent several samples in the same location.

B. Laboratory tests and sample analysis

A sampling of the main construction materials of La Isabela has been carried out, which are sandstone, brick, limestone, flint, lime mortars, and cement mortars, as well as periodic water sampling in different seasons. Each of the sampling locations in La Isabela is indicated in Fig. 2. B, where each point represents a small area where several samples have been taken. Samples of sandstone from nearby old quarries have also been taken to confirm the source of the constructive sandstone used in the study case.

In total, 40 samples have been taken. These materials have been analyzed and characterized using the following techniques:

- Analysis of the petrographic characteristics of the construction stones using petrographic slides and a transmitted light polarizing microscope.
- Powder X-ray diffraction (pXRD) was performed at the X-ray Diffraction Unit of the CAI of Chemical Techniques of the UCM (Bruker D8 ADVANCE A25 Diffractometer).
- FTIR-ATR (Attenuated Total Reflection) and FTIR-Reflection analysis were conducted using the Bruker FTIR Alpha II spectrometer with QuickSnap™ modules.
- Raman spectroscopy analysis was carried out using the portable i-Raman® Pro spectrometer from B&WTek.

Periodic sampling of the reservoir water is also carried out and analyzed using liquid ion chromatography (HPLC) with a Metrohm 761 compact IC chromatograph. Carbonate and bicarbonate titration is performed using the automatic 888 Titrando titrator.

In addition to the analyses mentioned in the previous points, laboratory tests have been carried out to characterize the main constructive materials (sandstone and brick) and sandstones from nearby quarries to study the following properties:

- Capillarity water properties: A capillarity test has been performed to observe the water absorption rate and the amount of water absorbed by each of the materials. The test is monitored by means of IR thermography images, to be able to appreciate the distribution of water in each case as it is absorbed.
- Other water properties: Vacuum saturation tests to study the water absorption capacity, open porosity to water, and apparent and real density, following the European EN 13755:2002 Standard.
- Porosity: Porosimetry by mercury intrusion (MIP) is performed to study pore size, distribution, macro and microporosity, tortuosity, and total porosity (%) accessible to mercury, which reaches smaller pores than water.

IV. RESULTS AND DISCUSSION

In La Isabela, there is a clear differentiation of the conservation status and deterioration agents based on the height within a wall, as well as in relation to the orientation of the façades (North or South) and the proximity to the reservoir's shore.

A. Material description and composition

The primary construction materials in La Isabela are sandstone masonry and bricks, often with lime mortars and occasionally cement mortars. In the noblest buildings like the old palace, limestone, and silex masonry were used for the foundation and plinth. However, not much remains of these buildings, precisely because their materials were relocated prior to the flooding for reuse. Therefore, the characterization tests and analysis results discussed here are mainly of sandstones and bricks.

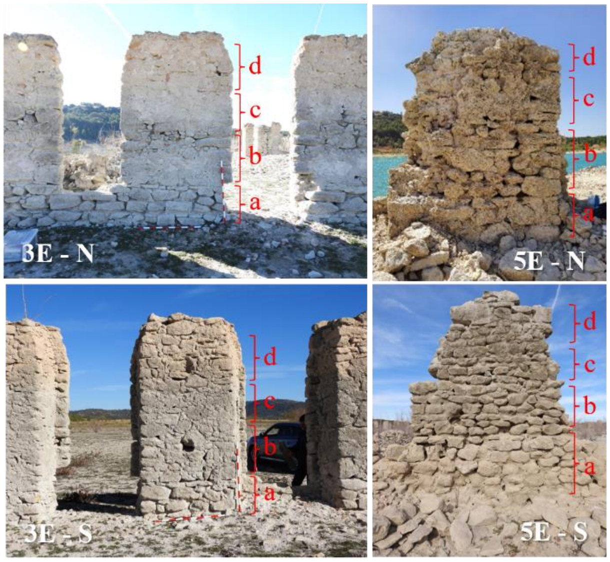

Fig. 3. On the left, the studied wall in the farthest part from the reservoir (3E - N and S façades). On the right, the wall from the closest part to the shore (5E - N and S façades). Height sections are marked in red (a, b, c, d). All pictures were taken in the dry season.

Analysis by XRD, Raman, and/or FTIR spectroscopy showed that sandstones were mainly composed of quartz, calcite, and feldspars, in proportions corresponding to those of nearby old quarries. Bricks' predominant components were calcite and quartz, and to a lesser extent, illite-muscovite, gehlenite, microcline, and gypsum. Lime mortars consist of calcite and quartz, while cement mortars contain quartz, calcite, and various cement-related minerals such as belite, alite, and celite. Crusts found on top of most of these materials are mainly composed of organic matter, mud, calcite, and calcium or magnesium sulfates.

Water analysis by HPLC showed that the main ions from highest to lowest concentration are sulfate, calcium, magnesium, chloride, and sodium. It is worth mentioning that the concentration of sulfate found in the same sampling areas differs significantly depending on the season. Samples taken in the wet season had an average of (268±9.87) mg/L, while those taken in the dry season had an average of (418±46.2) mg/L. The main reasons for this difference are that, firstly, evaporation during droughts makes the water more saturated in salts, and secondly, the geology of the area is rich in gypsum and clay.

Sulfated water and the dissolution of the walls' gypsum rendering is likely to be the reason why most efflorescences are sulfate salts. Another interesting phenomenon is that during the wet season, a common charophyte algae grows and spreads all over the surface of La Isabela's terrain. In the dry season, these algae dry out and tend to calcify, leaving only a fragile hollow structure that turns into dust and covers the site (Fig. 4B). Therefore, most of the crusts present a high content of calcite along with the sulfate salts.

Table 1. Results of Porosimetry by mercury intrusion, capillarity, and vacuum saturation tests to study the porosity and hydric properties of the main materials.

	Sandstones	Bricks
Hg-Porosity (%)	25,5	18,3
Micro <5µm (%)	15,8	93,1
Macro >5µm (%)	84,2	6,94
Average pore diameter (µm)	10,1	0,138
Tortuosity	5,35	8,94
Capillarity coeff. ($kg\cdot m^{-2}\cdot s^{-1/2}$)	$(87{,}7\pm30{,}6)\cdot10^{-3}$	$(52{,}6\pm1{,}33)\cdot10^{-3}$
Open porosity (%)	25,3	36,7
Absorbed water (m/m) (%)	12,7	22,2

Porosimetry analysis (MIP) obtained an average porosity of 25.5% for sandstones and 18.3% for bricks (Table 1). However, sandstones have 84.2% of macropores (>5 µm), with an average diameter of 10.1 µm, while bricks have 93.1% of micropores (<5 µm), with an average diameter of 0.14 µm. Tortuosity was higher in bricks than in sandstones. Both are porous materials but with different pore size and distribution. Moreover, capillarity tests resulted in a higher capillarity coefficient for sandstones than for bricks, while vacuum saturation tests showed both more absorbed water and open porosity to water (%) for bricks than for sandstones (Table 1). This means that sandstones absorb water faster than bricks when the level rises, but they have less capacity to accumulate water. Smaller-sized pores can also make bricks retain water for longer periods, which can promote the growth of efflorescence and microorganisms.

B. State of Conservation

The advanced deterioration of La Isabela is remarkable, the degradation processes are developing rapidly, worsening seasonally. The fluctuation in water conditions, caused by the constant submersion-emersion cycles related to the reservoir floods, causes an aggravated alteration process of the materials.

In general terms, the main processes and mechanisms of alteration are the following:

- Loss of construction material, mainly in the crowns and sides of the walls (the original openings of the windows and doors), related to the loss of joint mortars and the movement of water during the phases of total submersion, which causes the displacement of elements (Fig. 3).
- Cracks and fractures, both across the sandstone ashlars and vertically along the walls (Fig. 3).
- Severe granular disaggregation and rounding of the sandstone ashlars (Fig. 3 and 4. A).
- Formation of heavy crusts of salt efflorescence and mud (Fig. 4. A).
- Peeling and scaling on the surface of stone ashlars.

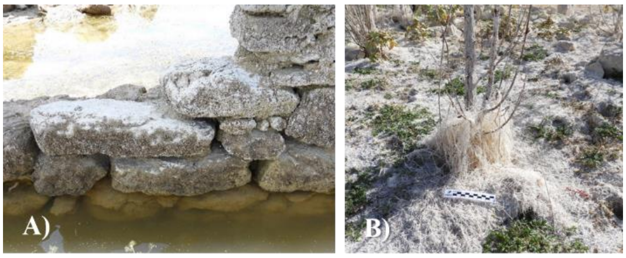

Fig. 4. A) Formation of salt efflorescence on the top of sandstone ashlars during the emersion period. Mud crust and bio-colonization can also be observed. B) Calcified algae during the dry season.

- Biodeterioration, lacustrine vegetation, and algae growing on the surface of the walls and inside the structures (Fig. 4).

C. Degradation Pattern: Preliminary Results

The preliminary overview of the results obtained in the 2022 campaign and in the laboratory has allowed us to advance a series of conclusions on the specific forms of degradation in the context we are dealing with, as well as the identification of trends related to the deterioration evolution. Nonetheless, more campaigns of in situ measurements are left to do by the time this article is being published. Changes in the petrophysical properties of the materials, such as surface hardness, internal cohesion, chromatic parameters, water absorption capacity, etc., have been evaluated in different campaigns over the last two years to quantify the decay evolution and its different forms. All the results discussed below are presented as $(\bar{x} \pm StD)$ either of each façade (e.g., 3EN for wall 3E with N orientation) or of each height section (a, b, c, d), as shown in Fig. 3.

The ultrasound pulse velocity (UPV) results in Fig. 5 show that the walls furthest from the shore and the North-facing façades of each wall mostly obtain higher average values of propagation velocity Vp (m/s) than the walls closer to the reservoir and the South-facing façades. The maximum value is obtained from the North-facing façade of wall 3E with (1715±352) m/s, and the minimum is from the North-facing façade of wall 5E with (762±148) m/s. It is worth noting that the differences between the North and South orientation of each wall are more pronounced the further they are into the reservoir; walls 3E and 4E differ by 18% and 6% respectively between their North and South façades, while wall 5E differs by 31%. These data indicate that, on the one hand, the longer the walls are submerged (like 5E), the lower their average Vp, and therefore, the worse their state of preservation in terms of internal material cohesion. Furthermore, wall 5E is more exposed to the action of water as it is the last line of buildings from La Isabela. Similar to what happens in coastal areas, during low tides, water drags sediments and destabilizes the terrain, which here is predominantly sedimentary and clayey, potentially leading to structural alterations in the walls. On the other hand, orientation influences the deterioration caused by increased exposure to solar radiation and higher temperatures.

Regarding the variation in height within each façade, the areas with lower average Vp values are the intermediate ones (zone c, followed by b). These are the heights where the water level spends more time throughout a hydrological year, as they are transitional states between cycles of immersion-emersion (1 cycle per year), where the walls are semi-submerged. In the hydrological year 2022/2023 it has been observed that the external walls spent a total of approximately 5 months completely emerging, 7 months semi-submerged, and none submerged. In contrast, the walls deeper into the reservoir spent approximately 4 completely emerged, 4 months semi-submerged, and 4 submerged. During the time they are semi-submerged, the intermediate level of each wall is subjected to a continuous flow of water, which promotes deterioration through physical, chemical, and biological processes. This favors capillary water rise, disaggregation of stone materials, dissolution of mortar joints, growth of efflorescence, deposition of mud crusts, and biological colonization of plants, insects, and microorganisms, generally in the form of biofilms.

The preliminary results of the Leeb micro-hardness test align with those of UPV, showing a similar trend where the walls furthest from the shore and the North-facing façades of each wall have higher average values. The highest value is found in the North-facing façade of wall 3E (221±59 HLD), while the lowest is in the South-facing façade of wall 5E (163±43 HLD). The differences between the North and South façades of each wall are also similar, with a 22% difference in wall 3E, 6% in wall 4E, and less than 1% in 5E. There is no significant variation in hardness with height within a wall, and no conclusive trends are observed in this aspect.

Moisture content results do not show significant variation between different walls, likely because the measurements were taken during the dry season when temperatures can reach values above 40°C. The maximum value is in the North-facing façade of wall 5E (220±145 a.u.), while the minimum is in the South-facing façade of the same wall (153±27 a.u.). The other walls range between 173 and 187 a.u., with low StD without showing significant differences between North and South orientations. The high value in the North-facing façade of wall 5E is mainly due to the presence of visible efflorescence in some ashlars of the lower area, which can increase capacitance and electrical conductivity.

Overall, the results obtained by spectrophotometry show a* and b* coordinates in the color space of ochres and browns, being slightly more intense in the North façades than the South façades. L* and C* values are also slightly higher in the North façades, indicating greater brightness and color saturation when exposed to less solar radiation. Nevertheless, these values were not that significant, and therefore in Fig. 6 coordinates a* and b* are represented for a given average L*. The color of the graphic is the area in the CIELAB space color that corresponds to our data.

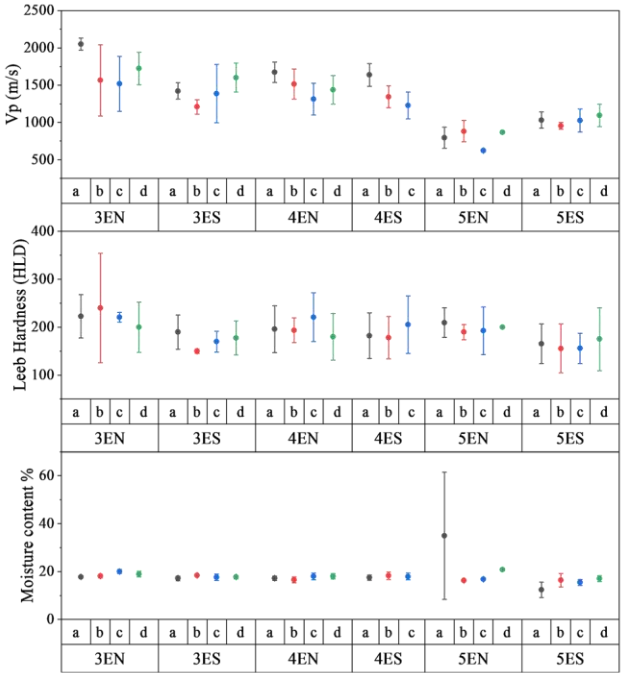

Fig. 5. Results of onsite measurements of ultrasound Vp (m/s), Leeb hardness (HLD), and moisture content (%). Displayed data are the mean values of each height section within each wall and orientation and error bars are the Standard Deviation.

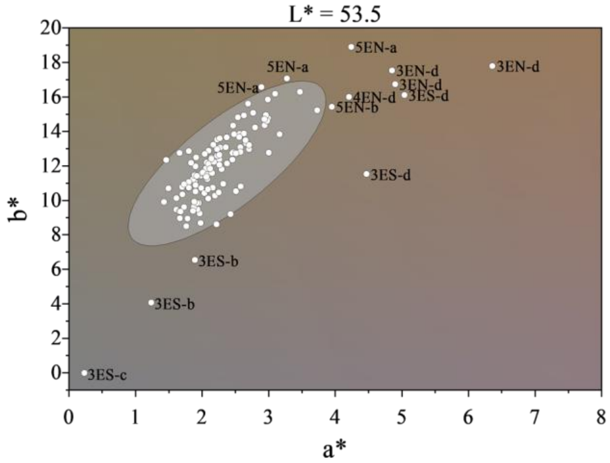

Fig. 6. Representation of color coordinates a and b* for a given average L* value using the CIELAB 1974 system. The ellipse indicates the centroid of most results which are quite homogeneous. The labeled points are the most scattered ones that indicate significant color changes.*

There is a noticeable color zoning by height within each façade that can be appreciated in Fig. 3. The walls furthest from the shore, which tend to spend more time semi-submerged and never fully submerged, there is greater contrast in color between heights, especially in the crowning. However, in the walls that spend more time submerged, the lower areas are the most saturated in color, likely due to the mud crust that deposits and the longer time they spend submerged and therefore protected from sun radiation.

It is important to note that, without more data from further measurement campaigns, we cannot draw definitive conclusions yet. Future measurement campaigns will help us to better understand the deterioration patterns, observing the evolution of the processes already described. The current variability in results may be due not only to the state of preservation of the materials, but also to factors like mud deposits on the façades, especially in heights a and b, or the appearance of efflorescence in heights c and d. These factors should be studied in the next campaigns to determine whether they are punctual, cyclical, or cumulative. Furthermore, to partially mitigate this variability in results and to contrast the observed trends so far, an accelerated deterioration simulation under controlled conditions is currently being carried out. Prismatic specimens of sandstone from quarries near La Isabela are being subjected to water level fluctuations, simulating the immersion-emersion cycles that the walls experience in the reservoir. This simulation has not yet concluded, as it is set to last for a whole year with several cycles. The results will be discussed in future publications.

V. CONCLUSIONS

The archaeological sites and cultural heritage that emerge every year during the increasing drought seasons in freshwater reservoirs have often been ignored by the heritage science community and government institutions. Very few interventions have been carried out at these sites and there is little information available regarding the specific degradation processes that this heritage suffers. Even if these sites cannot be preserved or restored because they will always be subjected to the fluctuations of the reservoirs in which they are located, it is important to keep a record of the valuable information they can provide, both historical and scientific.

The DAMAGE project is addressing this issue by running both in situ and lab tests to study deterioration patterns that occur in a real case, the submerged old town of The Royal Site of La Isabela. This study is performed through detailed analysis and characterization of the main building stones, which allows us to determine the state of conservation in each campaign. The applied techniques are mostly portable and non-destructive, and the preliminary results show that there is a wide variety of deterioration agents that must be evaluated and considered. The studied walls already show differences in the orientation of the façade, the height sections, and the periods they spend underwater. Nonetheless, the results obtained from the lab tests are coherent with those observed at the site, showing a surprisingly advanced state of deterioration due to the constant immersions and emersions.

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