Consequence of the atmospheric pollution on the degradation to the coating facing of the Basilica of Saint Augustine in Annaba Algeria
Consequência da poluição atmosférica sobre a degradação do revestimento da Basílica de Santo Agostinho em Annaba, Argélia

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Abstract
In this study we aimed to determine the mechanisms of deterioration of the wall covering used in the construction of the Basilica of St Augustine in Annaba in Algeria. The wall coating is regarded as the outer skin of any construction, therefore most exposed to external aggression of environment especially if the latter is polluted. To determine the degree of deterioration of the wall covering with respect to its composition chemical and mineralogical, laboratory analysis (dry weight of the unit, water absorption, effective porosity, SEM imaging, X-ray spectrometry, microbiological analysis) were performed on samples taken from the building, these were supplemented by observations on site. The main cause of the observed deterioration is due to significant pollution presence of sodium chloride, its presence is particularly localized in an area rich in calcium carbonate. The porosity is locally very important, form of interconnected vacuoles. Thereof constitute a plane of weakness and may partially explain the uniform appearance of the coating.

Resumo
Neste estudo, buscamos determinar os mecanismos de deterioração da cobertura de paredes utilizadas na construção da Basílica de Santo Agostinho em Annaba, na Argélia. O revestimento da parede é considerado como a pele externa de qualquer construção, portanto, mais exposta à agressão externa do meio ambiente, especialmente se esta última estiver poluída. Para determinar o grau de deterioração do revestimento da parede em relação à sua composição química e mineralógica, foram realizadas análises laboratoriais (peso seco da unidade, absorção de água, porosidade efetiva, imagem SEM, espectrometria de raios X, análise microbiológica) em amostras colhidas do edifício, estes foram complementados por observações no site. A principal causa da deterioração observada é devido à presença significativa de poluição do cloreto de sódio, cuja presença está particularmente localizada em uma área rica em carbonato de cálcio. A porosidade é localmente muito importante, forma de vacúolos interligados. Constituem um plano de fraqueza e podem explicar parcialmente a aparência uniforme do revestimento.

Keywords
Basilica of St Augustine; air pollution; wall covering; degradation; degradation
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Introduction

The purpose of this work is the characterization of the coating facing of the Basilica of St Augustine in Annaba in Algeria, and to seek the origin of disorders affecting it, as well as to determine the nature of microbiological spoilage product developed on this building. The city of Annaba is located in the east of Algeria between north latitudes (36°30N) and (37°30N), and East longitudes (07°20E) and (08°40E), with 12 municipalities with a total area of 1411.98 km². She is bordered by the Mediterranean Sea to the north, the city of Skikda in the West, the city of Guelma in the South and El Tarf in the East, Fig 1[2].

Environmental settings

The city of Annaba is characterized by a Mediterranean type of climate, with sub-humid and humid bioclimatic floors. It is characterized by mild temperatures in winter, hot in summer with an annual average temperature of 17.89°C, a maximum annual average temperature of 23.78°C, and finally an annual minimum temperature of 12.76°C and abundant rainfall, annual rainfall is 654.64mm. The compass has enabled us to highlight a dominant wind direction North-East and South-West, Fig 2.

Context of the study

The building, located on the side two kilometers inland on a hill in the center of the plain of the river estuary Seybouse, is oriented South West. The swamps surrounding the hill, while a chemical plants (sulfur) and a large steel mill, are located a few kilometers into the plain. The building was completed in 1900, Fig3. Since then, routine maintenance was provided seriously especially inside, but not always along with sufficient means, in particular, to access the upper parts of the building. Some materials in their entirety, others follow their location, were severely degraded and need to be addressed, Fig4:
- To the east, coatings show no apparent disorder, except in areas in the shade, in which microbiological recoveries are highlighted;
- To the west, siding with microbiological colonization type disorders (R2), and a seepages “blackish”;
- At the base, this phenomenon is arrested again (E2);
- At the front of the porch, coatings are locally cracked (E1 and R1); 
- Finally, at the lantern tower, coated with and without disorders are highlighted.
After consideration of all pathological cases, investigations have focused on a coating sample more specifically representative of the oldest finishing phase siding, it is also affected by a characteristic pathology (E1).

Figure 3 - The Basilica of St Augustine

Figure 4 - Deterioration of the wall coating, the front porch

Sample identification

Seven samples were collected, Table 1 gives the references and the main characteristics of the samples sent to the laboratory for analysis (LERM) [4].

Figure 5 - Implantation of samples, main facade.
Figure 6 - Implantation of samples, horizontal section of the building.

<table>
<thead>
<tr>
<th>Ref</th>
<th>Origin</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>Porch, East Tower, west face.</td>
<td>Microbiological Products: pretty fragmented lichen covering</td>
</tr>
<tr>
<td>R2</td>
<td>West facade, dome</td>
<td>Microbiological Products: collections of lichens and bryophytes</td>
</tr>
</tbody>
</table>
| E1  | Porch, East Tower, West Face | Wall coating with disorders. Two layers:  
- Body coating: meager character, rich in sand siliceous  
  fine to medium, 2 cm thick, fine texture, good cohesion  
- The top coat: fatter, fairly rich in binder, 5mm thick,  
  good overall cohesion, but presents a phenomenon of  
  alveolarization, fine texture.                          |
| E2  | Bedside, ground floor   | In this zone, the coating of finish presents different characteristics. It presents a coarse finish appearance. However, it was smooth. It comes from an area with disorders. |
| E3  | Arm of the transept     | Two layers:  
- Body coating: rich in binder, added with colored fine  
  sand, very compact, hard, contains an occluded porosity.  
- The top coat: beige matrix rich in colorful fine to  
  medium sand. Porosity fine, consistent. Smoother  
  surface                                                            |
| E4  | Porch, East Tower, West Face | Powder coating                                                                        |
| E5  | Bedside, ground floor   | Powder coating                                                                        |

Materials and methods

Sample preparation and sample analyses were performed on the different sample types using overlapping techniques in mineralogical and geochemical analyses whenever possible. Thin sections perpendicular to the exposed surface of the samples were prepared and textural analysis of thin sections was performed by different technical analyses.

Thermal analysis

The prepared samples are heated from room temperature to 1000°C with a speed of 25°C/min. The thermogravimeter used in this study is the Perkin Elmer Pyris 1 TGA model. The heating environment (oven) is maintained in a nitrogen gas atmosphere having a flow rate
of 15ml/min. The oven is rapidly cooled with water from 1000 °C to 100 °C. The sample holder used is ceramic. Before the beginning of the tests, the calibration of the device is carried out. The test is performed in accordance with ISO 9924-3, NF T 46-047. The Auto Step One software that equips the analyzer allows working in high resolution and thus better separate products that break down in the same temperature range.

Scanning electron microscopy and EDX analysis

To visualize the coating simple (E1) (body and top coating) and to detect elemental-mineralogical composition, SEM-EDX techniques were applied on thin sections as well as on small fragment samples. EDX-analyses were performed on a Quantra 200 with a field emission cathode with an initial voltage of 20kv. Detection limits are calculated from the error propagation of the two measurements of the background signals of each X-ray line and are given as a 2-sigma value. The element distribution of Mg, Al, K, Ca, Fe (WDS) and S, Si (EDS) was mapped using an acceleration voltage of 15kv and beam current of 30 nA. The acquisition time was set to 50ms per step. The scan grid was spaced at 0.5 lm per step, covering in total 400x400 steps. Simultaneous acquisition of the back-scatter signal in composition mode was performed.

Water total porosity technique

The water total porosity is measured after water saturation following the standard recommended by the AFPC-AF- REM [5] which consists of drying the samples at a Temperature of 60 °C for 48h, until their mass becomes constant. After a degasification step, under a primary vacuum for 24h, the samples were submerged in water until the saturation. The samples are weighed dry, after saturation and in hydrostatic condition. Total porosity, \( N_t \), is calculated as:

\[
N_t = \frac{M_2 - M_s}{M_2 - M_1} \times 100
\]

Where \( M_1 \) is the hydraulic weight of the sample, \( M_2 \) is the weight of the sample saturated with water, \( M_s \) is the Weight of the dry sample.

Identification of biological material

Biological material taken from several locations on the exposed surface of the wall was identified by polarizing microscopy [6].

Research and dosage of soluble salts

The various assays of the soluble salts (SO\(_4^{2-}\), Cl\(^-\), NO\(_3^{-}\)) were carried out, after aqueous extraction of the solid samples, and then subjected to an analysis by infrared spectroscopy. The spectrometer used is the IRAffinity-1S model.

Results and discussion

Examinations under scanning electron microscope

This part gathers the results of the examinations and analysis carried out under a scanning electron microscope (SEM) on polished section and fracture of the sample (E1). They allowed highlighted the following key points [4]:

*The top coat:* Figures 7 to 10, comprises a matrix of carbonated airy lime, associated with a sand silico-limestone, predominantly limestone, of fine to coarse crushed granulometry. The porosity is abundant, fine and has numerous vacuoles. A few millimetres deep, these are interconnected to form a weakness plane. This can eventually cause the detachment of the epidermis of the coating.
The presence of these vacuoles is not related to method of production of the coating and could be correlated with water circulation, which led to the dissolution of the limestone matrix. However, there was no evidence of blunt facies, nor the presence well-identified of mineral neoformation. Diffuse traces of sulfur are however attested in the matrix. The presence of microbiological filaments is highlighted in the porosity of the coating, indirect witnesses of the presence of moisture.

**Body coating.** Figure 11 to 18, for its part consisting of a heterogeneous matrix of a carbonated lime of a hydraulic character, locally associated with a past containing sulphates and an internal horizon carbonated. A Sand silico limestone is added. It has the same size characteristics as the top coat. Finally, it is reported that, a sodium chloride salt efflorescence formed after sample inclusion in resin, flush of the carbonated internal horizon. This phenomenon reflects the state of pollution of this layer and its location in the upper part of the coated body.
Thermal analysis

The results of the thermogravimetric analysis at 1000°C under nitrogen, coupled to the differential thermal analysis, expressed in weight percentages and are shown in Table 2[4].

<table>
<thead>
<tr>
<th>Component</th>
<th>Sample (F1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>open water (&lt; 105°C)</td>
<td>0.3</td>
</tr>
<tr>
<td>bound water (from 105°C to 630°C)</td>
<td>1.4</td>
</tr>
<tr>
<td>loss (from 580° to 1000°C)</td>
<td>38.7</td>
</tr>
<tr>
<td>whose CO₂ from CaCO₃</td>
<td>37.2</td>
</tr>
<tr>
<td>whose CO₂ from MgCO₃</td>
<td>1.4</td>
</tr>
<tr>
<td>Total loss</td>
<td>40.4</td>
</tr>
</tbody>
</table>

The interpretation of these results allows highlighting the species grouped in Table 3 [4]
Table 3 - Estimation of the composition of the top coat

<table>
<thead>
<tr>
<th>Constituent</th>
<th>(E1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCO₃</td>
<td>2.7</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>84.5</td>
</tr>
</tbody>
</table>

According to Table 3, the thermal analysis confirms the presence of a cementitious matrix rich in carbonates, resulting from the carbonation of an aerial lime. The presence of magnesium carbonate can be considered an impurity.

Determination of densities and porosity

The porosity accessible to water and the real and apparent densities soaked of the top coat sample (E1) was measured by soaking in vacuo, followed by hydrostatic weighing. The results obtained are presented in Table 4[4]

Table 4 - Volumetric mass and porosity

<table>
<thead>
<tr>
<th>Réf</th>
<th>Real density in kg/m³</th>
<th>Bulk density in kg/m³</th>
<th>Porosity accessible to water in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E1)</td>
<td>2080</td>
<td>1750</td>
<td>32.7</td>
</tr>
</tbody>
</table>

Research and determination of soluble salts

The determination of the soluble salts (SO₄²⁻, Cl⁻, NO₃⁻) was carried out by infrared spectroscopy on the samples taken from different zones at different depths, to more than 1.50m from ground level. Results are expressed in weight percentages, in Table 5 [4]

Table 5 - Assay results ions (wt%)

<table>
<thead>
<tr>
<th>Réf</th>
<th>Horizon</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>Na⁺</th>
<th>K⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>E4</td>
<td>bell, tower</td>
<td>0.22</td>
<td>0.04</td>
<td>0.12</td>
<td>0.29</td>
<td>0.04</td>
</tr>
<tr>
<td>E5</td>
<td>bedside</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.03</td>
<td>0.05</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The analyzed samples reveal different results. With regard to the (E5) sample, the contents are negligible, whereas for the (E4) sample, a high chlorides and sodium content is attested, this results confirms the pollution state of the sample (E1), which comes from the same area as sample (E4).

The presence of sulfate, which is a salt of sulfuric acid H₂SO₄. Originates from air pollution. In this case the sample (E4) was taken on the main facade of the building Fig 5, this facade is oriented in the direction NE-SO. This direction is the trajectory that leads us to the industrial area of the city of Annaba. Furthermore to the abundant presence of CaCO₃ in the coating facing, and in contact with SO₄. This results in the transformation of the mortar into a crust formed of CaSO4, this crust is very alterable with water therefore degradable [7].

Identification of microbiology products.

The microorganisms responsible for the degradations can be separated into two groups. Those that cause the formation of visible deposits, such as algae, fungi, lichens. Those, more insidious which, like certain bacteria, cause a decohension of the material through their metabolic reactions without forming a visible deposit. [8]. For this purpose and in order to determine the biological load on a sample suspected of being damaged by a biological type attack. We realized at the laboratory of molecular biology of the department of biology of the university of Souk Ahras, Algeria, an identification by visualization with the microscope.

Microscopic observation and chemical tests have identified the following strains:

- Four crustose lichens on the sample (E1): Caloplaca maritima, Candelariella medians, Lecanora muralis and Squamarina gypsacea.
- Two foliose lichens: Xanthoria parietina and Physconia grisea, and two bryophytes: Tortula muralis and Orthotrichum diaphanum on the sample (E2).
Conclusion

Investigations have been undertaken on a sample from the porch on the east tower, this coating being characteristic of the oldest coating work phase, implementation on the Basilica. We can conclude that the top coats and the coating body, their constituents are characterized by:
The coating body comprises a hydraulic lime matrix, whose the carbonation is heterogeneous in heart. The presence of calcium sulphate is also highlighted. It should be noted that a significant pollution of sodium chloride is identified, its presence being more particularly located in an area rich in calcium carbonate. Silico-calcareous sand is associated with this matrix.
The top coating consists of a rich matrix carbonated lime, associated with limestone sand domination, containing some siliceous grain. It is little affected by the presence of pollution, or at least in traces (sulphates, chlorides), but its porosity is locally very high in the form of interconnected vacuoles. These constitute a plane of weakness and may partially explain the uniform aspect of this coating. This situation is most likely the result of circulating water, leading locally a solubilising of the matrix.
The porosity of a top coating sample (E1) shows a characteristic porosity of a lime mortar. Regarding research and dosing salts, it turns out that in the sampling area of this same coating sample, we have confirmed a significant sodium chloride concentration, phenomenon corroborated by microscopic examination.
Regarding the biological organisms that colonize the north side of the basilica, lichens and bryophytes (foam) are identified. The dominant species in the (E1) sample is Candelariella medians.

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References


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