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EVALUATION DE DEPOT DES POLLUANTS SUR LES MONUMENTS HISTORIQUES (MAROC): Caractérisation des produits d'altération superficielle, premiers résultats et perspectives futures.

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Abstract

Air quality and climate quickly changed in the last years, requiring new researches focused on pollution effects, not only on environment and human health but also on outdoor historical heritage. As it is well known, daily exposure to atmosphere in urban and coastal areas causes degradation processes on the stone monument surfaces, being soiling, concretions, films and black crusts, and deposits the most diffused and investigated phenomena. The deposition of gaseous and particulate atmospheric pollutants known to have a destructive effect on the calcareous stones [Nava et al. 2010; Urosevic et al. 2012] seem to be originated from the contamination by atmospheric pollutants emitted by industrial sources and vehicular traffic, particularly sulfur dioxide and by the marine sprays.

The objective of this work is to analyze the composition and the morphology of the superficial weathering products on the stone of some monuments, located very close to the Atlantic Ocean (Morocco). The techniques used in the evaluation of atmospheric contamination of the decay products are the Ion Chromatography (IC), the Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), the X-ray diffraction and the Transmission Electron Microscopy coupled to energy dispersive X-ray spectrometer (TEM-EDX).

The investigated stones are a calcarenite with porous texture, rich in calcium carbonates. Results indicate the precipitation of soluble salts and revealed the presence of different kinds of atmospheric particles: Fe, Na, Mg, Al, Si, P, S, Cl, K, Ca and O. However, the test results demonstrated the decrease in the contents of Calcium and Oxygen. These particulates contribute to extensive stone deterioration.

Keywords: Moroccan historic building, superficial weathering products, atmospheric particles, soluble salts.
Résumé
La qualité de l'air et du climat a rapidement changé dans les dernières années, ce qui nécessite de nouvelles recherches axées sur les effets de la pollution, non seulement sur l'environnement et la santé humaine, mais aussi sur le patrimoine historique en plein air. Il est bien connu que l'exposition quotidienne à l'atmosphère dans les zones urbaines et côtières provoque des processus de dégradation sur les surfaces des monuments en pierre, en étant salissures, des concrétions, des films et des croûtes noires, et les dépôts sont les phénomènes les plus diffusés et étudiés. La déposition des polluants atmosphériques (gaz et particules) connus pour avoir un effet destructeur sur les pierres calcaires [Nava et al. 2010; Urosevic et al. 2012] semble être l'origine de la contamination par les polluants atmosphériques émis par les sources industrielles et par les véhicules, en particulier le dioxyde de soufre et par les pulvérisations marins.
L'objectif de ce travail est d'analyser la composition et la morphologie des produits d’altération superficielle de la pierre de quelques monuments, situés tout près de l'océan Atlantique (Maroc). Les techniques utilisées dans l'évaluation de la contamination atmosphérique des produits de désintégration sont la chromatographie ionique (IC), l'émission plasma à couplage inductif spectroscopie atomique (ICP-AES), la diffraction des rayons X et la microscopie électronique à transmission couplée à la dispersion d'énergie spectromètre rayons X (TEM-EDX).
Les pierres étudiées sont calcarénite avec une texture poreuse, riche en carbonates de calcium. Les résultats indiquent la précipitation des sels solubles et ont révélé la présence de différents types de particules atmosphériques: Fe, Na, Mg, Al, Si, P, S, Cl, K, Ca et O. Cependant, les résultats des tests ont démontré la diminution des teneurs en calcium et en oxygène. Ces particules contribuent à une importante détérioration de la pierre.
Mots-clés: Monuments historiques marocaines, produits d’altérations superficielles, particules atmosphériques, des sels solubles.

Introduction
Stone is widely recognized as an adaptable and sustainable construction material, with a low intrinsic carbon signature, and also as a repository of much of the world’s tangible cultural heritage. With this recognition of its value has come an increasing awareness that stone has a finite life, which can be drastically curtailed when it is placed in often-aggressive urban or coastal environments. The intensive development of industry during the last centuries led to the negative changes in the state of the environment in the cities. The air pollution, as a result of intensive traffic, industrial emission, dust deposition, thermal and humidity variation are the major deleterious factors that control the stone decay. The impact of these factors is very different all over the world.
depending on the region location and climate conditions. The effect and decay rate of the stone also vary significantly with the composition of building materials.

Many buildings and monuments from the cultural heritage in Morocco are constructed of natural stone “calcarenite”. The last decades, however, we noticed that this eternal material started to decay more severely than during the previous centuries and urgent interventions were necessary. When exposed to coastal environments, stones become exposed to very different temperatures, pressures and moisture regimes, as well as to the actions of aqueous solutions, atmospheric gases and organisms. Under these conditions they become unstable and suffer micro-structural and mineralogical changes known as “weathering or deterioration”. This causes the mineralogical breakdown of their crystalline lattices, allowing ionic migration to produce new minerals with a tendency to enter thermodynamic equilibrium with their environment.

The high level of air pollution near industrial sites leads to significant increases in the deterioration rates of historical monuments. Burning fossil fuels increases the concentration of \( NO_x \) and \( SO^2 \) in the atmosphere, the agents most harmful to masonry [Rozniakowski et al. 2001; Bityukova 2006; Massey 1999]. A look into the literature enlightened how few are still known on the atmospheric aerosol impact on the built heritage, in particular on its content of metals coming from pollution [Hamilton et al. 1995; Schiavon et al. 1995; Rodriguez-Navarro and Sebastian 1996; Lammel and Metzig 1997; Primerano et al. 2000; Delalieux et al. 2001; Esbert et al. 2001; Brimblecombe and Grossi 2005; Rampazzi et al. 2011; Horemans et al. 2011; Ghedini et al. 2011; Dragovich and Egan 2011]. For decades, Heavy metals commonly found are lead (Pb), cadmium (Cd), copper (Cu), zinc (Zn), nickel (Ni) and chromium (Cr). They are the markers of traffic areas and there content in aerosol was the indicator of petrol vehicles.

The emission of these metals as particulate particles is a consequence of the degradation of catalytic converters, chemical and physical stresses caused by oxidation and reduction reactions, high working temperatures and mechanical abrasions, mainly the wear and tear mechanism of the external layer rich in the two catalysts [Smichowski et al. 2008; Wiseman and Zereini 2009] being the most important causes. With respect to other pollutants, monumental stones can be used as geochemical monitors of heavy metal fallout. Analyzing samples of different ages collected from old monuments can reveal the recent history of heavy metal pollution [Shrivastav et al. 1998]. Weathering processes occur in open systems in non-equilibrium conditions. Although the mechanisms can be studied separately, the physical, chemical and biotic reactions involved proceed concurrently.

In this work, the study of stone deterioration has been approached in order to evaluate the effects of marine salts and air pollution on four historical monuments located near the Atlantic coast (Morocco), and to relate these findings to their state of conservation. The characterization of
weathering traces in stones from historical buildings is a crucial task when conservation activities or cleaning treatments are planned. To avoid any further deterioration, appropriate surface cleaning machines and products must be chosen, appropriate for the specific chemical properties of the material to be treated.

With permission from the Moroccan Ministry of Culture, Cultural Heritage Directorate, measurements were made during the period from June 2011 to May 2012.

**Study areas**

*Location and historical background*

In this paper interest focuses on the stone weathering products of some of the most important historical monuments and old cities in Morocco (Figure 1), especially those settings in industrial and urban coastal areas (Atlantic Ocean). Table 1 shows the original locations and positions for the study sites. The investigated monuments are built with local calcareous stones. In 2004 and 2012, UNESCO inscribed respectively the Portuguese City and the Kasbah of Oudayas into the World Heritage List.

![Fig. 1 General map and aerial photographs showing the geographical location of the investigated monuments, Morocco (http://maps.google.com)](image)

**Table 1** Studied sites lists, with indication of their historical details (Morocco)

<table>
<thead>
<tr>
<th>Building(s)</th>
<th>Built</th>
<th>Situation</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kasbah of Mehdiya</td>
<td>5th, 900, 1515, 1614 and 1795</td>
<td>Rural (overlooking the sea)</td>
<td>Kenitra</td>
</tr>
<tr>
<td>Kasbah of Oudayas</td>
<td>17th Century</td>
<td>City center (overlooking the sea)</td>
<td>Rabat</td>
</tr>
<tr>
<td>Old Medina</td>
<td>3rd, 11th, 14th, 15th, 16th Centuries</td>
<td>Town center (overlooking the sea)</td>
<td>Azemmour</td>
</tr>
<tr>
<td>Portuguese City</td>
<td>1514 and 18th Century</td>
<td>City center (overlooking the sea)</td>
<td>El Jadida</td>
</tr>
</tbody>
</table>
Climatology
Located along the Atlantic Ocean, with a Mediterranean climate character, the studied region has a mild, temperate climate, shifting from cool in winter to warm days in the summer months. Characterized by the alternation of a wet season from October to April which the average temperatures reaches 14 °C and a hot dry season from May to September which the average temperatures reaches 24 °C. The mean air temperature varies between 16.3°C (with mean minimum of 10.0°C and mean maximum of 23.8°C) at Kenitra, 16.3°C (with mean minimum of 10.0°C and mean maximum of 23.8°C) at Rabat and 20.2°C (with mean minimum of 14.5°C and mean maximum of 25.8°C) at El Jadida.

The opening of the region on the Atlantic Ocean earned him abundant precipitations that are around an average of 450mm per year in recent 30 years, with 450mm per year at Kenitra, 450mm at Rabat and 450mm at El Jadida. Pluviometry is concentrated between October 15 and April 15 at 90%, the predominant winds come from the north-west (Figure 2).

Pollution levels
High demographic growth and constant socio-economic development have put pressure on natural resources and caused environmental degradation. Sources of air pollution are the industrial and mining, transport, and agriculture sectors. Industrial activity in Morocco is mostly concentrated around the study area, the biggest factories and plants are located in this region. At the same time the number of cars and trucks has increased very rapidly (with more than three times last ten years) and this trend is expected to continue which would lead to the significant increase in emission of volatile organic compounds, NOx, SO2 and CO in cities air. The impact of atmospheric pollutants on the investigated monuments, associated to coastal weather, led to apparition of superficial weathering forms on the calcarenite stones, such as black crusts, granular disintegration, and alveolization.

For example, in Rabat city, fine particulates (less than 3μm in diameter) have an annual average of 243μg/m³ (World Bank 2003; National Environment Observatory of Morocco 2001). CO₂ concentrations reach 144μg/m³, SO₂ concentrations vary between 8 and 144μg/m³ depending on the region inside the city [Chaaban].

![Fig. 2 Climatographs](http://www.marocmeteo.ma)
Materials and methods

Materials and sampling conditions

The materials used in these historical sites are numerous. In this study, we were interested on calcarenite, it is a coarse bioclastic limestone resulting from a littoral drawstring of plioquaternary age [Akil 1990; Azouaoui et al. 2000; Zaouia et al. 2005] and that constitutes the basement of the whole region. Four different samples have been studied and discussed in this paper as representative of different kind of weathering products and they are described in details in Table 2. The samples have been collected as a result of archaeological excavations carried out at the study sites, the samples from the damaged stones collected from the external facades of the studied monuments were taken from the surface 2-5 cm layer of building stones from the height of approximately 1,5-1,8m from the foundation of the buildings. These powder samples have been collected by dry drilling, then kept in a plastic bag and stored until the analysis was carried out.

Table 2 Origin of the sampled superficial crusts

<table>
<thead>
<tr>
<th>Case study</th>
<th>Samples</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Reference (altered stones) Natural weathering product</td>
<td>RCM NWPCM Kasbah of El Mehdiya</td>
</tr>
<tr>
<td>II</td>
<td>Reference (altered stones) Natural weathering product</td>
<td>RCO NWPCO Kasbah of Oudayas</td>
</tr>
<tr>
<td>III</td>
<td>Reference (altered stones) Natural weathering product</td>
<td>RCA NWPCA Old Medina of Azemmour</td>
</tr>
<tr>
<td>IV</td>
<td>Reference (altered stones) Natural weathering product</td>
<td>RCP NWPCP Portuguese City (Mazagan) of El Jadida</td>
</tr>
</tbody>
</table>

Analytical techniques

The powdered samples studied in this research program are characterized and compared with the careful and synergic employ of traditional analytic techniques, in order to evaluate various elements both qualitatively and quantitatively. These techniques include Ion Chromatography (IC), Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), X-ray diffraction (XRD) and Transmission Electron Microscopy coupled to energy dispersive X-ray spectrometer (TEM-EDX).

a) Ion Chromatography method

The weathering products were submitted to ion chromatography analysis, using an ICS-3000 System (Reagent FreeTM, RFICTM, DIONEX), for determining their content on soluble salts (anions). The soluble salts measured by this method are Cl⁻, NO₃⁻ and SO₄²⁻, following the procedure described in NF EN ISO 10304-1 standard.

b) Inductively coupled plasma-atomic emission spectroscopy (ICP-AES)

Heavy metals (Cd, Pb, Zn, Cu, Ni, Cd, and Cr) were analyzed by this technique using an Ultima 2 spectrometer from Jobin Yvon. ICP-AES is an emission spectrophotometric technique, in which
excited electrons emit energy at a given wavelength as they return to ground state. The characteristic of this process is that each element emits energy at specific wavelengths. The intensity of the energy emitted at the chosen wavelength is proportional to the amount of that element in the analyzed sample. Thus, by determining which wavelengths are emitted by a sample and by determining their intensities, the analyst can quantify the elemental composition of the given sample relative to a reference standard. Since ICP-AES analysis requires a sample to be in solution, samples were dissolved by a combined attack employing HNO₃ and HCl acids.

c) X-ray diffraction (XRD)
This method was selected for the identification of minerals composition. Such analysis was performed with an X’Pert Pro MPD (Panalytical) powder diffractometer. The samples were ground, introduced in a diffractometer and analyzed. The components were identified with the percentages (semiquantitative analysis).

d) Transmission electron microscopy observations and EDX analysis (TEM–EDX)
The samples were also characterized by this microscopic method, in order to study the morphology and chemical composition of the weathering traces. Powdered samples were examined by a TEM (TECNAI G2/FEI) using back-scattering electrons. Some particular areas of the samples were analyzed for chemical composition on major and minor elements (Fe, Na, Mg, Al, Si, P, S, Cl, K, Ca and O) using EDX. The X-ray peak intensities for each element were converted into relative weight percentages using the EDX software.

Results and discussion
The results of weathering products analyze are presented in tables and figures. Results of XRD analysis and its mineralogical composition are displayed in Table 3; the X-ray diffractograms are shown in Figure 3. Table 4 shows the results of atmospheric contamination by soluble salts. In Table 5 the results of the ICP-AES analyses are shown, with the average contents of heavy metals. Figure 4 presents TEM micrographs of traces of chemical weathering, such as the corrosion-dissolution of calcite crystals. The EDX diffractograms are presents also in Figure 4. Its chemical contents of weathering traces elements are given in Table 6.

Case study I: Kasbah of El Mehdiya
The X-ray diffraction analysis (XRD) identified two components as essential minerals in the superficial crusts powder sampled: calcite (75%), quartz (25%) and none component as salts. Sulfate concentration (9936,6 ppm) were determined to be higher than nitrate (3700,5 ppm) and chlorite (2070,8 ppm) concentrations in this sample. Results indicate that this building is highly affected by Zn (55,885 ppm), Cr (22,308 ppm) and Pb (21,388 ppm) as heavy metals.
Under the TEM, observations reveal noticeable morphological differences between the altered stones and their superficial weathering products. The images are extraordinarily clear and show how the weathering products are overrun with prismatic gypsum crystals and halite crystals. The EDX data have confirmed that Ca is the main component, and minor proportion of Si. The High contents of Fe, Na, Al, P, S, Cl and K traces in the weathering product are also remarkable in comparing with the altered sample (up to 7.4%, 6.8%, 2.3%, 7.5%, 1.0%, 12.1%, 4.3% and 1.8% respectively). The EDX results indicate also the decrease in the contents of Ca and O (up to 26.2% and to 18.0% respectively).

**Case study II: Kasbah of Oudayas**

The X-ray diffraction (XRD) patterns suggest that the mineralogical composition of the superficial crusts powder sampled is primarily: calcite (65%), quartz (25%) and one component as salts: halite (10%). Chlorite concentration (19344 ppm) were determined to be higher than nitrate (8577.6 ppm) and sulfate (7663.5 ppm) concentrations in this sample. The highest contribution on heavy metals into weathering crust was estimated for Ni (57.611 ppm), Zn (55.357 ppm) and Cr (19.287 ppm).

By observation of the micromorphology, TEM micrographs show the presence of altered calcite grains. Calcite grains, corroded by well dissolution development are visible (gypsum crystals formation). Moreover, the image confirmed the presence of a halite deposit. The analysis carried out by EDX for this sample, are mainly made up of high contents of calcium and oxygen with low contents of silicon and aluminum. However, other elements were detected but with small proportions such as iron, sodium, manganese, potassium, phosphorus and sulphur. The High contents of Na, S, Cl and K in the weathering product are remarkable (up to 8.6%, 2.9%, 9.6% and 2.0% respectively) in comparing with the altered sample. The results indicate also the decrease in the contents of Ca and O (respectively up to 47.2% and 10.6%).

**Case study III: Old Medina of Azemmour**

The X-ray diffraction analysis of the superficial crusts powder sampled identified two components as essential minerals: calcite (32%), quartz (62%), 6% unidentified phase; and none component as salts. The IC analyses show the existence of a considerable amount of soluble salts mainly chlorides and sulphates. Nitrate concentration (12734.16 ppm) were determined to be higher than chlorite (11605.5 ppm) and sulfate (1955.4 ppm) concentrations in this sample. The highest concentrations of Zn (48.012 ppm) and Pb (21.263 ppm) were established.

Noticeable morphological differences between the altered stones and their superficial weathering products are revealed after TEM observations. The images show how the weathering products are overrun with prismatic gypsum crystals and halite crystals. For this monument case’s, the EDX analysis on the surface shows that the weathered products are mainly made up of low contents of
oxygen and calcium in comparing with the altered sample (decrease from 70,6% to 32,7% and from 19,0% to 18,5% respectively). The EDX data have indicated the High contents of Fe, Na, Al, S, Cl and K traces in the weathering product (up to 1,8%, 7,7%, 1,5%, 26,1%, 4,4% and 2.6% respectively), in comparing with the altered sample.

Case study IV: Portuguese City (Mazagan) of El Jadida

The XRD analysis identified tree components as essential minerals in the superficial crusts powder sampled: calcite (47%), quartz (15%) and Dolomite (38%); and none component as salts. Chlorite concentration (8624,3 ppm) were determined to be higher than nitrate (4938,7 ppm) and sulfate (4028,3 ppm) concentrations in this simple. Results indicate that this building is highly affected by Zn (66.884 ppm) and Pb (27.506 ppm).

TEM enables to understand the deterioration mechanisms and gave more detail of the features of the stone surfaces. The TEM micrographs present various decay forms, image shows the presence of altered calcite grains testifying to an unbalanced medium favorable to the dissolution. Moreover, the image shows the presence of a halite deposit. The studied altered stones had a content of Ca up to 57,7% and they are characterized by very weak dolomitization. The EDX data demonstrated that the contents of Fe, Na, Mg, Al, P and Cl in weathering products in values increase, in comparing with the altered sample and close to 1,0%, 7,5%, 8,9%, 2,1%, 1,4% and 9,2% respectively. However, the EDX results indicate the decrease in the contents of Ca and O (up to 48,1% and to 16,0% respectively).

Fig. 3 X-ray diffractograms of the altered stones (reference) and their natural weathering products obtained from the surface
Table 3 Results of XRD phase analysis

<table>
<thead>
<tr>
<th>Case study</th>
<th>Samples</th>
<th>Minerals</th>
<th>Essential Salts and weathering products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Compound Name</td>
<td>Chemical Formula</td>
</tr>
<tr>
<td>I</td>
<td>RCM</td>
<td>Calcite</td>
<td>CaCO$_3$</td>
</tr>
<tr>
<td></td>
<td>NWPCM</td>
<td>Calcite</td>
<td>CaCO$_3$</td>
</tr>
<tr>
<td>II</td>
<td>RCO</td>
<td>Calcite</td>
<td>CaCO$_3$</td>
</tr>
<tr>
<td></td>
<td>NWPCO</td>
<td>Calcite</td>
<td>CaCO$_3$</td>
</tr>
<tr>
<td>III</td>
<td>RCA</td>
<td>Calcite</td>
<td>CaCO$_3$</td>
</tr>
<tr>
<td></td>
<td>NWPCA</td>
<td>Calcite</td>
<td>CaCO$_3$</td>
</tr>
<tr>
<td>IV</td>
<td>RCP</td>
<td>Calcite</td>
<td>CaCO$_3$</td>
</tr>
<tr>
<td></td>
<td>NWPCP</td>
<td>Calcite magnesian</td>
<td>(Mg,Ca)CO$_3$</td>
</tr>
</tbody>
</table>

- absence

Table 4 Atmospheric contaminants in decay products determined by Ion Chromatography (ppm)

<table>
<thead>
<tr>
<th>Case study</th>
<th>Samples</th>
<th>Cl</th>
<th>NO$_3$</th>
<th>SO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>NWPCM</td>
<td>2070.8</td>
<td>3700.5</td>
<td>9936.6</td>
</tr>
<tr>
<td>II</td>
<td>NWPCO</td>
<td>19344</td>
<td>8577.6</td>
<td>7663.5</td>
</tr>
<tr>
<td>III</td>
<td>NWPCA</td>
<td>11605.56</td>
<td>12734.16</td>
<td>1955.4</td>
</tr>
<tr>
<td>IV</td>
<td>NWPCP</td>
<td>8624.3</td>
<td>4938.7</td>
<td>4028.3</td>
</tr>
</tbody>
</table>

Table 5 Measurements of heavy metals of decay products by ICP-AES (ppm)

<table>
<thead>
<tr>
<th>Case study</th>
<th>Samples</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>NWPCM</td>
<td>2.300</td>
<td>22.308</td>
<td>5.060</td>
<td>7.819</td>
<td>21.388</td>
<td>55.885</td>
</tr>
<tr>
<td>II</td>
<td>NWPCO</td>
<td>2.505</td>
<td>19.287</td>
<td>6.763</td>
<td>57.611</td>
<td>14.779</td>
<td>55.357</td>
</tr>
<tr>
<td>IV</td>
<td>NWPCP</td>
<td>1.979</td>
<td>7.322</td>
<td>11.477</td>
<td>6.134</td>
<td>27.506</td>
<td>66.884</td>
</tr>
</tbody>
</table>
Fig. 4 Representative TEM photographs and corresponding EDX spectra

Table 6 Particles (weight %) observed by TEM and detected by EDX

<table>
<thead>
<tr>
<th>Case study</th>
<th>Samples</th>
<th>Fe</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>RCM</td>
<td>0.4</td>
<td>2.3</td>
<td>1.2</td>
<td>1.1</td>
<td>0.8</td>
<td>0.6</td>
<td>0.6</td>
<td>0.4</td>
<td>0.5</td>
<td>58.9</td>
<td>33.2</td>
</tr>
<tr>
<td>II</td>
<td>RCO</td>
<td>3.3</td>
<td>3.9</td>
<td>2.1</td>
<td>4.5</td>
<td>6.0</td>
<td>1.1</td>
<td>0.6</td>
<td>0.9</td>
<td>0.8</td>
<td>52.8</td>
<td>24.0</td>
</tr>
<tr>
<td>III</td>
<td>RCA</td>
<td>1.4</td>
<td>2.4</td>
<td>1.6</td>
<td>0.7</td>
<td>1.4</td>
<td>1.0</td>
<td>0.4</td>
<td>0.4</td>
<td>1.1</td>
<td>70.6</td>
<td>19.0</td>
</tr>
<tr>
<td>IV</td>
<td>RCP</td>
<td>0.3</td>
<td>4.7</td>
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Conclusion

First results: Evaluation of atmospheric contamination and composition of weathering products

Carbonate stones used in construction of the following Moroccan building monuments have been investigated with regard to mineral and chemical content on weathering traces: (1) the kasbah of El Mehdia, (2) the Kasbah of Oudayas, (3) the Old Medina of Azemmour and (4) the Portuguese City (Mazagan) of El Jadida. They derive from three distinct areas, Kenitra, Rabat and El Jadida cities. It was shown that these materials are subject to atmospheric contamination. From the experimental results outlined earlier, the following conclusions can be drawn:
1) X-ray diffraction analysis (XRD) of superficial crusts powder sampled from these monuments show no significant differences between them and demonstrated the predominance of calcite (calcium carbonates) the original main content of these stones and which gives them a high susceptibility to acid attack by gaseous atmospheric pollutants and to hydrous marine sprays charged with various salts, the minor phase is Quartz. Crust obtained from the Portuguese City, shows the presence of Dolomite;

2) In additional, crystalline phase for halite NaCl was detected only at the Kasbah of Oudayas weathering products. Halite is, however, believed to be the main salt responsible for the observed damage. The XRD of the powdered crust sample and the analysis of soluble salts by IC showed concordant results for the Kasbah of Oudayas. The new formation of sodium chloride represented by crystals of halite, more or less developed, is the main mechanism of stone weathering in this part of the Kasbah very near to the ocean. Curiously, in contrast to halite, gypsum is not detected in any monuments, a fact which we attribute to the high solubility of these compounds;

3) Results indicate that the products of degradation tested of these historic buildings are highly affected by air pollution. Several pollution compounds were detected such as Cl\(^-\), NO\(_3\)\(^-\), SO\(_4\)\(^{2-}\) and some trace elements like Cd, Cr, Cu, Ni, Pb and Zn;

4) The IC analysis carried out on samples showed that chlorite is the most abundant ion, with mean concentrations up to 10411,165 ppm, followed by nitrate (7487,74 ppm) and sulphate (5895,95 ppm). Also, it can be noted that there is an evident difference in the deposition level of sulfur compounds between the Kasbah of El Mehdiya, the Kasbah of Oudayas and the Old Medina of Azemmour sites. The Kasbah of El Mehdiya and the Kasbah of Oudayas show a significant higher deposition of sulfur compounds compared to the Old Medina of Azemmour. The classification of the Old Medina of Azemmour City corresponded to a rural place, a small city with 0.036 million inhabitants;

5) About chloride deposition, the levels are the same for the Kasbah of Oudayas and the Old Medina of Azemmour. It should be taken into account that both monuments are located close to the seashore. Under these conditions, the influence of airborne salinity in degradation phenomena of historic building in both monuments should be very similar. Although, the Kasbah of Oudayas and the Old Medina of Azemmour presents a significantly higher chloride deposition rate compared to the Kasbah of El Mehdiya, due to the influence of the surrounding buildings and the location close to the bay and not to the open sea. About nitrate deposition, there is a different situation. Highest nitrate concentrations belong to the Old Medina of Azemmour weathering products;
6) ICP-AES analysis view highlighted that the powdered samples are characterized by very variable contents of trace elements and were enriched in Cd, Cr, Cu, Ni, Pb and Zn. The mean values of Zn, Pb, Ni and Cr are approximately in 2-3 times higher relatively to Cu and Cd. The accumulation of these trace elements is caused by anthropogenous pollution from different sources (industrial pollution, emission from plants, combustion of fuel oil and gasoline, exhaust of vehicles etc.);

7) The TEM photographs qualitatively show the modifications of the morphology and also the topology between the altered samples and the weathering products for the all stone types. The images are extraordinarily clear and show how the weathering products are overrun with prismatic gypsum crystals and halite crystals. This can be of use when making choices concerning cleaning agents and treatments;

8) The microanalysis EDX throw light on the chemistry of the surfaces of the superficial crusts, and revealed the presence of different kinds of particles: Fe, Na, Mg, Al, Si, P, S, Cl, K, Ca and O. The EDX data demonstrated that the contents of Fe, Na, Mg, Al, P and Cl in weathering products in values increase, in comparing with the altered sample. However, the EDX results indicate the decrease in the contents of Ca and O. Calcium can be related to carbonates, sulphur can be connected to gypsum. Silicon, magnesium, aluminium and potassium indicate the presence of clays, iron is associated to iron oxides and phosphorous is associated to organic matter.

**Future prospects**

Further work is needed to extend the chemical/mineralogical characterization of the investigated calcarenitic stones. From a conservation point of view, the goal of this future research will be twofold: (a) a more precise identification of the source clay quarries originally used for historical brickmaking; the results will be of paramount importance in order to be able to reproduce the same stones for restoration purposes; (b) because of this, it is essential that the conservation of decaying stone (and indeed the choice of new and replacement stone) is underpinned by a detailed knowledge of stone behavior: how different stone types decay in specific environments, what factors trigger and control decay processes, and what strategies may be appropriate in managing decay or delaying its initiation in the first place.

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References

• Akil M. 1990. “Les depots quaternaires littoraux entre Casablanca et cap Beddouza: Etudes Geomorphologiques et Sedimentologiques (Littoral quaternary deposits between casablanca and beddouza: geomorphological and sedimentological studies).” These de Doctorat Es- Science, Universite Mohamed V Rabat, Maroc : 419 ;


• Chaaban F. b. “arab environment: future challenges, chapter 4 air quality”: 52;


Michelozzo’s Courtyard in Florence (Italy).” Science of the Total Environment 408 (6): 1403-1413;


