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CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS
EVOLUTION AND DECAY PROCESSES IN THE VILLAMAYOR AND ZAMORA SANDSTONES

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ABSTRACT

In this paper, we report data on the nature, composition and behaviour of the Villamayor and the Zamora Sandstones under a semi-arid continental climate regime and the almost complete absence of air pollution. The main factors and mechanisms involved in the decay of the building sandstones are essentially related to the transport and later crystallisation of soluble salts from run-off and subsurface waters, sharp temperature changes (thermoclasy), freezing (gelification), filtration through roofs or capillarity in the lower parts of the buildings (wetting/drying). The Villamayor sandstone shows a more acute of decay than the Zamora sandstone owing to its greater porosity and high content in phyllosilicates (smectite and palygorskite).

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INTRODUCTION

Most ancient buildings of historical or cultural interest in the cities of Salamanca and Zamora (Spain) and their outlying zones were constructed with sandstones of different types. Appropriate conservation of these buildings requires in-depth study of the intrinsic properties of the stone used (mineralogical, chemical, physical, etc.), and also of the environment in which they are located and the damages to which they are subjected.

The term sandstone is applied to sedimentary rocks made of sand-sized detritic grains (6.25 μm-2mm in diameter) within a silty or clayey matrix that is more or less lithified by a cementing material (silica, iron oxides, carbonates, etc.). The classification of sandstones is mainly based on criteria such as grain size (textural), the ordering of the grains within the bulk stone (structural), and the mineralogical composition of both the skeleton and the intergranular material. As a function of the rock fragments involved, feldspars and quartz, it is possible to identify arkosic rocks (≥25% in feldspars), quartzarenites (≥95% quartz), greywacke (≥15% of pelitic matrix of less than 30 μm) (Aubouin et al., 1988).

In previous work (Vicente, 1983; Brufau, 1983; Vicente and Vicente-Hernández, 1985; Vicente and Brufau, 1986; Rives and Vicente, 1993; Vicente 1996) such rocks have been characterised as they appear in the quarry. The stones that have undergone important processes of decay on several representative buildings have also been analysed (Vicente, 1984; Serrano, 1988; Ortega, 1989; Rives et al., 1991; Vicente et al., 1993; Rives and Vicente, 1993; Vicente, 1996). The application of different consolidation and conservation treatments has also been aimed in many studies (Inigo et al., 1994; Vicente, 1996; García-Talegón et al., 1998; García-Talegón et al., 1999).

In the present paper, we report the most important data obtained in our studies of the evolution and decay of the Villamayor and the Zamora Sandstones, both subject to a semi-arid continental climate with a low degree of air pollution.

MATERIALS AND METHODS

In the provinces of Salamanca and Zamora there are several types of sandstones of different ages and composition, the best known being the Villamayor Sandstone in Salamanca and the Zamora Sandstone (Vicente, 1984; Añorbe, 1994).

VILLAMAYOR SANDSTONE

This sandstone comes from the quarries in Villamayor, located on the right bank of the River Tormes at about 6 Km from the City of Salamanca. It has been used for the construction and ornamentation of monuments from Roman times to the present. The quarries belong to the Cabrerizos Sandstone Formation (Alonso
Gavilán, 1981), comprising braided fluvial systems and paleosols at the top of each sequence. The sandstone is of Middle Eocene age (Jiménez, 1975).

The Villamayor sandstone is an arkosic stone whose skeleton comprises grains of quartz, microcline, plagioclase and rock fragments as major components and tourmaline, epidote, micas, staurolite and zircon as accessory minerals.

Its mineralogical composition (whole rock) is shown in Table 1, as determined by X-ray diffraction. Quartz is the most abundant mineral, followed by feldspars, layered silicates (smectite), fibrous silicates (palygorskite) and mica/filitte. Scanning electron microscopy reveals fibers of palygorskite lining pores and grains of quartz and feldspar (Fig. 1).

Table 1. Mineralogical compositions of the Villamayor and the Zamora Sandstones at the quarry.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Q</th>
<th>F</th>
<th>S</th>
<th>P</th>
<th>M/I</th>
<th>K</th>
<th>O</th>
<th>OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Villamayor</td>
<td>xxx</td>
<td>xx</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Zamora</td>
<td>xxx</td>
<td>t</td>
<td>t</td>
<td>t</td>
<td>x</td>
<td>xxx</td>
<td>t</td>
<td>t</td>
</tr>
</tbody>
</table>


Fig. 1. SEM micrographs of the Villamayor Sandstone showing fibers of palygorskite lining pores and grains of quartz and feldspar.

Table 2 shows the chemical analysis of its major elements. The percentage of SiO₂ is high, followed by Al₂O₃, K₂O, Fe₂O₃, as well as H₂O.

Table 3 shows the physical characteristics measured in water; the real density, between 2.65 and 2.66 g/cm³; the apparent density, between 1.66 and 1.86 g/cm³, and total porosity (between 30 and 37%). Of this porosity, between 66 and 85% is directly intercommunicated with the external surface.
Table 2. Chemical composition of major elements (%) of the Villamayor and Zamora Sandstones in the quarry

<table>
<thead>
<tr>
<th>OXIDES</th>
<th>VILLAMAYOR SANDSTONE</th>
<th>ZAMORA SANDSTONE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AVERAGE (%)</td>
<td>RANGE (%)</td>
</tr>
<tr>
<td></td>
<td>MINIMUM</td>
<td>MAXIMUM</td>
</tr>
<tr>
<td>S\textsubscript{2}O\textsubscript{3}</td>
<td>81.2</td>
<td>71.8</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>7.5</td>
<td>6.1</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>1.6</td>
<td>0.9</td>
</tr>
<tr>
<td>MnO</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>MgO</td>
<td>1.3</td>
<td>0.7</td>
</tr>
<tr>
<td>CaO</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>Na\textsubscript{2}O</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>K\textsubscript{2}O</td>
<td>2.4</td>
<td>1.8</td>
</tr>
<tr>
<td>TiO\textsubscript{2}</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>P\textsubscript{2}O\textsubscript{5}</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>LOI</td>
<td>3.6</td>
<td>2.0</td>
</tr>
</tbody>
</table>

The stone is very porous and contains swelling layered (smectites) and fibrous (palygorskite) silicates in its composition. All of them with a large specific surface area and high water ab-/adsorption capacity, govern its behaviour. In the wet state, the stone increases appreciably in volume and loses hardness and resistance. In the drying process it hardens and develops a nice golden patina. These features make it easy to work with and have allowed its use in the beautiful filigree stonework of the Plateresque style of Salamanca (sixteenth and seventeenth centuries) (Vicente, 1984; Rives and Vicente, 1993). However, they are also the main cause of its fragility and ready decay.

**ZAMORA SANDSTONE**

The Zamora sandstone corresponds to the Lower Unit of the Paleogene (Corrochano, 1979). It outcrops in a narrow N/S-oriented band in the province of Zamora, close to the western border of the Duero basin. According to Corrochano (1980, 1982), these silicified rocks are detritic levels of sandstones and conglomerates that reach a depth of up to 15 m. Grosso modo, the sandstone corresponds to a fluvial siderolithic series that discordantly fossilizes a kaolinitic weathering mantle.
Its age, according to its characteristics and its association with the Cretaceous outcropping in the Central Mountain System, is related with Mesozoic (Molina et al., 1989). This stone shows marked changes in colour due to the remobilisation of iron oxyhydroxides under ancient hydromorphic and acid conditions, with the local precipitation of sulphates of the allunite-jarosite group (García-Talegón, 1995; Molina et al., 1997).

Under the petrographic microscope, it is possible to visualise a skeleton formed mainly (more than 80%) of grains and fragments of quartz and quartzites. Accessory minerals are muscovites (more or less altered), feldspars, tourmaline, zircon and some opaques (Añorbe, 1994).

The mineralogical composition of the Zamora sandstone (Table 1) by X-ray diffraction of whole rock samples is essentially quartz and opal, with the presence of kaolinite and traces of feldspars, smectite, iron oxyhydroxides and mica/illite.

The results on the chemical composition of the major elements are shown in Table 2. There are high contents in SiO₂, together with the presence of Al₂O₃ and H₂O.

Table 3 shows that the real density of the material ranges between 2.57 and 2.61 g/cm³ and the apparent density between 2.26 and 2.37 g/cm³. Total porosity ranges between 9 and 12% and the saturation coefficient between 89 and 98%.

<table>
<thead>
<tr>
<th></th>
<th>VILLAMAYOR SANDSTONE</th>
<th>ZAMORA SANDSTONE</th>
</tr>
</thead>
<tbody>
<tr>
<td>RD</td>
<td>2.65 - 2.66</td>
<td>2.57 - 2.61</td>
</tr>
<tr>
<td>AD</td>
<td>1.66 - 1.86</td>
<td>2.26 - 2.37</td>
</tr>
<tr>
<td>TP</td>
<td>37 - 30</td>
<td>9 - 12</td>
</tr>
<tr>
<td>Coef. Sat.</td>
<td>66 - 85</td>
<td>89 - 98</td>
</tr>
</tbody>
</table>

RD: real density (g/cm³), AD: apparent density (g/cm³), TP: Total porosity in water (%), Coeff. Sat: Saturation coefficient (%).

In this work, the following techniques and methods were used to characterise the types of sandstone:

The mineralogical composition was studied on a PHILIPS PW-1740 diffractometer, using Cu Kα radiation (λ = 154.05 pm); the chemical characteristics were determined by X-ray fluorescence on a SIEMENS RS-200 device, and the petrophysical properties determined in water (real and apparent density, total porosity and saturation coefficient) were calculated according to the standard norms (NF, 1973a and 1973b).
RESULTS AND DISCUSSIONS

Environmental conditions

Salamanca and Zamora are situated on the Castilian plain at heights of 800 and 640 metres, respectively. These zones have a semiarid continental climate with low atmospheric pollution (Table 4). Climatological data were supplied by the Area Meteorological Service of the Duero Region, using data from meteorological observatories located in Salamanca and Zamora.

Table 4. Climatological data concerning the cities of Salamanca and Zamora

<table>
<thead>
<tr>
<th></th>
<th>SALAMANCA</th>
<th>ZAMORA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual precipitation (mm)</td>
<td>420.0</td>
<td>365.5</td>
</tr>
<tr>
<td>Average annual temperature (°C)</td>
<td>12.5</td>
<td>12.3</td>
</tr>
<tr>
<td>Absolute maximum temperature (°C)</td>
<td>40.0</td>
<td>39.0</td>
</tr>
<tr>
<td>Absolute minimum temperature (°C)</td>
<td>-17.0</td>
<td>-13.4</td>
</tr>
<tr>
<td>Average of maximum temperatures (°C)</td>
<td>18.4</td>
<td>18.1</td>
</tr>
<tr>
<td>Average of minimum temperatures (°C)</td>
<td>6.7</td>
<td>6.6</td>
</tr>
<tr>
<td>Thermal amplitude over 24 h (°C)</td>
<td>30.0</td>
<td>29.4</td>
</tr>
<tr>
<td>Days of the year with minima &lt;0 (°C)</td>
<td>60</td>
<td>57</td>
</tr>
</tbody>
</table>

Decay process

The decay process of stone materials depends on the mineralogical composition, texture and structure of the stone, its location on the building and environmental conditions.

The key to the alterability of the Villamayor sandstone lies in the content and nature of its clay minerals (Fig. 1) and its high porosity (30-37%). The presence in this stone palygorskite (a fibrous silicate that adsorbs large amounts of water) and above all of smectite (a swelling clay whose volume varies on passing from the dry to wet state and vice-versa) means that the wetting/drying processes generate strong stresses inside the stone, thereby contributing to its decay.

In the Zamora sandstone, the most labile mineralogical component is opal CT, followed by phyllosilicates (smectite and kaolinite) and iron oxyhydroxides, which show strong surface reactivity and are susceptible to changes due to the conditions of the medium (pH, redox potential, etc) and the pore system of the stone. In the micropores of the pore network, closed systems (pF > 4.2) are developed and the main process controlling water dynamics in the pore system is diffusion instead of convection. Geochemical gradients occur in these systems and are manifested in
mineralogical changes in the closest immediacy of the least soluble component (Pedro and Delmas, 1980; Pedro, 1993).

As with other building stones, other factors to be taken into account as regards the decay of Villamayor and Zamora sandstones are their location (orientation and situation) and environmental conditions. In this sense, the decay of the outwards and higher parts of the buildings (dome, cornices and balustrades) is the result of phenomena of thermoclastic and gelifraction (Fig. 2). These processes lead to fissuring and above all surface arenization, which give rise to the erosion of exposed areas. However, in the lower parts of the buildings, as well as this type of decay there are also problems of salt crystallization in zones affected by the capillary

Fig. 2. The upper part of the Dome of the Cathedral of Zamora. Decay of the Zamora Sandstone by processes of thermoclastic and gelifraction.
damping of groundwater that contain saline species (Fig. 3). This in turn leads to a synergic effect between these phenomena, thereby considerably accelerating the degradative effect.

Inwards of the building, the most extensive and commonly observed decay is due to the presence of salts in microenvironments (Fig. 4), which crystallize inside the pore network (subeflorescences) or on the outside of it (eflorescences). The source of salts on the high parts of the buildings is due to infiltration by rain off, which dissolves the soluble species of mortars, while on the lower parts the source of salts come from capillary damping (polluted urban groundwater).
CONCLUSIONS

The Salamanca and Zamora cities are under a semi-arid continental climate and low atmospheric pollution, the evolution of the Villamayor and Zamora Sandstones is governed on one hand by their intrinsic characteristics and, on the other, by the climate of the study zones, the microenvironments generated at different parts of the buildings (upper and lower parts, inwards and outwards) and sources of pollution.

One of the most important decay process, generalised and degradative is salt crystallization in the pore network. This origin is mainly related to either dissolution of mortars by run-off and subsurface waters, or by capillary damping in lower parts of the monuments from subsurface contaminated water with soluble salts.

On the exposed exteriors of the buildings, thermoclasty and gelifraction are responsible for the decay. Additionally, outwards areas on the lower parts of the buildings, affected by capillary damping of polluted water are subject to a synergic effect between these factors and salt crystallization.

All these processes (salt crystallization, thermoclasty and gelifraction) occur both in the Villamayor and the Zamora Sandstones. In the former, the decay processes are more pronounced owing to its high content in clay minerals. Strains due to swelling-contraction in smectites give rise to the breakdown of palygorskite fibres.
ACKNOWLEDGMENT

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REFERENCES


