CHARACTERIZATION OF STONE WEATHERING :
A CASE STUDY FOR CHAMBORD CASTLE, FRANCE

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ABSTRACT

The aim of this study is the characterisation of spalling, main degradation of tuffeau, limestone used in
the castle of Chambord. The stone degradation is analysed by thermogravimetric analysis (TGA) and X-ray
diffraction (XRD). XRD analyses are carried out according to two processes: traditional XRD analysis on
the stone powder and original XRD analysis on the whole sample in order to detect mineralogical
modifications more precisely. First results show that stone presents biological degradations by the presence
of lichens. The result of mineralogical characterization reveals physico-chemical degradation with the presence
of gypsum content in the cracking zone.

INTRODUCTION

The “SACRE” project is based on the achievement of a health record from Chambord castle
(Loire Valley in France) and aims to provide a basis for scientific monitoring and planning of
restoration works using health and aesthetic criteria. The collected data (location of degradations,
weather measurements, architectural and historical archives) are used to reference all the
information necessary to establish a detailed diagnosis of the state of alteration of the monument.

Characterization of physico-chemical degradations of tuffeau, and understanding the
mechanisms of degradations are components of this project. These results provide thereby a basis
for a numerical simulation predicting the evolution of stone damage with time and environmental
conditions.

The white tuffeau is the main stone in the castle of Chambord and in the most of the
monuments built along the Loire valley in France. This highly porous limestone (porosity about
45%) is very sensitive to atmospheric conditions (pollution, salts, water movement) [1].

The main degradation of tuffeau is spalling of the stone: a plate of 1 or 2 cm stands out
gradually, and the surface under the plate is pulverulent. The degradation phenomenon is related
to the nature of the stone (mineral composition, morphology of the porous media), to the climatic
conditions (rain, cold, sun, wind, air pollution), the morphology of the building (sculptures,
facades, cornices, balconies, window frames) and to the exposure of the building (North, East,
South West for the weather, influence of soil) [2].

Samples of weathered stone have been carried out on the tower of “Chaudron”. The tower was
little restored and has a lot of degradations. Samples were collected from different places of the
tour, showing different facieses. The purpose of this study is to achieve a "mapping" of the
altered stone (spalling) with depth in order to observe precisely the mineralogical and textural changes generated by the weathering process.

**EXPERIMENTAL PROGRAM**

*Sedules*

Several areas of sampling were chosen in the most degraded part of the tower of “Chaudron”, in the north and the lower parts. Two of these samples were studied here: a fragment with a start spalling (zone A) has been studied and compared to a block of molded architectural element disassociated from the wall (zone B).

Zone A is located in the lower part of a pilaster, in a plate about to detach. The stone has a lapidary sign, thereby the date of its installation on the tower is about 500 years (Figure 1). Sample A-1 is a plate about 1 cm thickness with a hard outside surface, covered with lichen (A-1a), and a very pulverulent inside surface (A-1b). Between these two textures of stones, cracks can be observed, parallel to the surface area of spalling, which accentuate the separation of the two parts of the sample.

Samples were then collected in the area powder A-2 behind the plate. Sample A-2a was taken from the part between the powder surface and 5 mm deep. Sample A-2b, was taken from the part between 5 and 10 mm as the stone is considered to be undegraded for depth higher than 10mm.

Zone B is located at the top of the broken stylobate (molding along the tower) (Figure 2). A large fragmented block has been collected, numbered B-1. It is consistent throughout the thickness (about 5 cm). It was divided into several parts from the outside surface to the part in contact with the wall. The first five millimeters from the outer surface covered with lichen were rated B-1a and the first five millimeters from the area in contact with the wall were rated B-1b.

Finally, a small area (B-2) was selected under the block B-1 to take samples of powder into the wall at two different depths: sample B-2a between 0 to 5 mm, and B-2b between 5 to 10 mm.
The detachment of the plate A-1 has been at the bottom. The samples of powder made on the wall under the plate were therefore not directly subject to rain and runoff, in contrast to area B where the crack in the block B-1 has allowed the movement of water rain and runoff.

**Methods**

*X-ray diffraction (XRD)*

Analysis of crystalline phases was performed by X-ray diffraction. Two types of equipment were used: one for the analysis of the powder of the stone (Philips PW 3020), the other for the analysis of a solid sample, with a curved detector INEL CPS120.

The first method required a fine grinding of the sample. The measurement was carried out with an angle 2θ ranging from 1.5 to 60° with an exposure time of 6 seconds for a step of 0.025°. Diffractograms were obtained with the Kα line of copper (λCu = 1.5406 Å).

X-ray diffraction carried out in transmission on stone samples having about 0.5 mm thickness. Samples were prepared (cut) with absolute ethanol and without water to avoid solubilization of the salts of the stone. The sample was mounted on a steel blade pierced in its center to allow X-rays through, to detector protected from direct beam by a lead "sink". The diffraction peaks measured were positioned over the channels, which established a calibration correspondence [3]. Measurements were performed for 2θ values ranging from 0 to 30° (Molybdenum Kα line: λMo = 0.70926 Å). Analyses were performed with a beam of 150µm in width and 3mm in height, with a displacement of 0.2 mm, and a pause of three hours. The sample located on a movable sample holder was moved perpendicular to the beam, by translation, allowing a very detailed analysis at the location of crystalline phases in the sample [4].

*Thermogravimetric analysis (TGA)*

Measurements of X-ray diffraction have been coupled with thermogravimetric analysis. The weight loss of sample due to the departure of water or chemical reactions is measured through an Electro Setaram TG-DTA 92-18, following the rise in temperature in a furnace swept with flow constant argon. The chosen heating program started with a level of 3 h at 60°C to remove free...
water sample without the risk of removing the water content of gypsum, possibly present in the sample. The temperature rise was then performed up to 1000°C with a speed of 3.33°C per minute.

RESULTS AND DISCUSSION

Mineralogic analysis by XRD on powder

Analyses of X-ray diffraction were carried out along with depth on the blocks, and on the powders collected from the wall under the fracture zone. Zone A has been divided into 4 samples: the hard zone and the pulverulent zone of the plate, and the two powders collected at 5 and 10mm under the plate. For the block B-1, analyses were performed on 10 samples (each 5mm) and on two samples of powder collected under the block.

XRD patterns are shown in Figure 3 for Zone A and in Figure 4 for zone B.

![Figure 3: Diffractograms of different stone powders of the zone A](image)

Figure 3: Diffractograms of different stone powders of the zone A
In both samples of tuffeau (A and B), XRD shows the presence of calcite, with the main peak at a 2θ angle of 29.4°, Silica as quartz at 26.6° and in a form of opal with broad peak characteristic of a mineral not entirely crystallized between 21° and 22°. The clay minerals are present in small angles, with the main peak of the glauconite to 8.8° for example.

In zone A, we observed that calcium oxalate is present on the surface of the plate. The other three samples contained gypsum. In zone B, we observed gypsum and calcium oxalate on the surface, and only gypsum powder in the sample taken from the wall in Block B-1. However, sample of the block in contact with the wall does not contained gypsum, like other 8 samples of block B-1 located between the surface and the area in contact with the wall. These last samples have no exogenous minerals and seem healthy.

The atmospheric sulphur may be carried by rainwater and reacts with calcite stone to form calcium sulphate. It may also be trapped in the epigenetic layer of stone, as can be supposed in the
case of the surface of the block B-1. The high solubility of gypsum compared to other crystalline phases of stone, could increase its migration in the stone along with cycles of imbibition-drying [5].

When the relative humidity decreases, gypsum crystallizes in the stone. When drying is very fast, the solution containing dissolved gypsum has no time to migrate by capillarity towards the evaporating surface. Therefore, the evaporation front is located within the stone, and the salts will crystallize inside [6]. This could be the mechanism of the spalling alteration process of the tuffeau, as we found gypsum located principally in the fracture zone of the stone. This could be also due to wetting and drying cycles of the stone. The particles of crystallized salt are accumulated in in the surface and water flow is not being more perpendicular to the surface, but parallel [7]. The gypsum can be formed and accumulated behind the surface after the formation of spalling of the stone.

The location of sampling probably influences the presence or absence of gypsum at the interface between the plate and the wall. Sample A-1 was taken from the vertical wall. Rainwater and runoff can not reach inside the plate at the area of spalling. In contrast, sample B-1 is a block that broke off diagonally along its entire height. Runoff therefore widely circulated and reached the part of the block that was previously in contact with the wall. One can suppose that the gypsum present at this location has been dissolved and transported elsewhere by leaching due to rainwater. This can explain the absence of gypsum in the sample B-1b. The diffractograms (Figures 3 and 4), shows also the presence of calcium oxalate with a characteristic peak around 14.4° on the surface of the plate A-1 within the first five millimeters, and on the surface of the block B-1.

**TGA**

Figure 5 presents the weight loss measured and the the derivative of the curve (DTG) in order to more easily visualize changes in slope caused by the weight loss during heating.

ATG curves for samples A-1b, A-2a, A-2b, B-2a and B-2b are similar to that presented in Figure 5. Weight loss $\Delta 1$ corresponds to the loss of free water in the sample when the temperature of 60°C was maintained constant during three hours. Weight loss $\Delta 2$ is due to the water loses during the decomposition of gypsum. Finally, weight loss $\Delta 3$ around 800°C corresponds to the transformation of calcite into calcium oxide due to the departure of CO2.

![Figure 5](image)

*Figure 5*: Thermogravimetric analysis, zone A, outer surface of the sample
In contrast, the part on surface of the plate A-1 and the block B-1 have a different profile as shown in Figure 6. In addition to the weight loss due to the departure of free water ($\Delta 1$) and that related to the transformation of the calcite ($\Delta 4$), two weight losses can be noted around 120°C and 450°C ($\Delta 2$ and $\Delta 3$). They could be correlated with the presence of calcium oxalate detected in the X-ray diffraction on powder.

Therefore, thermogravimetric analyses confirmed the results obtained by XRD on powder samples.

![Thermogravimetric analysis, zone A: sample under the plate (0 to 5 mm)](image)

**Figure 6**: Thermogravimetric analysis, zone A: sample under the plate (0 to 5 mm)

**XRD in solid sample**

The X-ray diffraction on solid consisted of a mineralogical analysis of the plate A-1 and B-2 block, according to the depth: every 0.2 mm starting from the surface covered with lichen to the fine particle zone of spalling.

Diffractograms in Figure 7 confirm the results obtained in XRD on the powder samples: no gypsum in the first few millimeters on the surface of the plate A-1. This figure shows also, the presence of calcium oxalate in the surface layer of the sample including the first 200 microns of the surface. The calcium oxalate was not detected beyond this thickness (depth). These results confirm and specify the location of calcium oxalate in the first five millimeters analyzed by X-ray diffraction on powder. Similarly, an accurate analysis of the surface of the block B-1 helped to highlight the presence of calcium oxalate in the first millimeters of the surface.
The location of the oxalate layer on the surface of the stone seems in compliance with the work of B. Brunet-Imbault, 1999 [4]. Oxalate is even generally located in the first 50 microns of the skin of the stone [8]. It is known that the presence of calcium oxalate at the surface of the stone can be due to the development of lichen on the stone. Lichens are multicellular organisms composed of fungi and cyanobacteria. It is unclear which of these two components is responsible for the production of oxalic acid, which reacts with the calcite of the stone [5]. The oxalate layer formed reduces the surface porosity and so the penetration of water into the stone is limited but the transpiration (diffusion) continued [6]. These data seem consistent with the presence of lichens on the surface of samples.

**Studies in progress**

Gypsum was very difficult to locate in the samples. Results show that it is not always present in surface samples and in the part of the block or the plate in contact with the wall. In contrast, the presence of gypsum is attested in the powders collected on the wall, between the fracture zone and 10mm of depth. The X-ray maps of SEM-EDX were carried out and continued. Similarly, analysis of chromatography and atomic emission spectrometry coupled to induced plasma (ICP-AES) are planned to quantify the gypsum with depth. Measurements of mercury porosimetry will complete this study to analyse the pore size distribution and the porosity of the tested samples.

The absence of gypsum occasionally observed on the zone in contact with the wall may be due to a too small amount of gypsum present in the sample, or even a loss of material during sampling operation. Other sampling procedures are considered for the studies in progress.
CONCLUSIONS

The aim of this study was to analyse the mineralogical and textural changes due to spalling. Preliminary results were presented in this communication.

The first experimental results obtained on degraded samples obtained from the tower of “Chaudron”, show the presence of exogenous minerals. Sample surfaces present an alteration of biological origin, composed of calcium oxalate. The pulverulent (powder) fracture zone contains gypsum, a destructive salt to the stone. Chemical measurements, that allow precise quantification of gypsum with depth, have not yet been achieved. The analysis of solid samples throughout the depth seems essential for better localization of gypsum and to demonstrate its contribution in the phenomenon of spalling.

However, it’s well known the environmental conditions including water transfers, are involved in the process of spalling. To better understand this process and factors implied spark off these in the degradation, a meteorological station was placed on the tower of “Chaudron”. Moreover, temperature and relative humidity sensors were arranged at two locations of the tower, north and south, at two different heights and three different depths in the stone framing the current sampling zone. The data collected will help to refine the hypotheses on the weathering processes, and provide a basis for accelerated aging protocols performed in the laboratory. Indeed, it will be interesting to try to reproduce the damages observed and analyzed, to understand their formation process and the kinetics of degradation.

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