Local strain measurements during water imbibition in tuffeau polluted by gypsum

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Abstract

The research presented in this communication aimed to evaluate the mechanism of spalling generated by mechanical stresses and strains developed due to imbibition and the link with atmospheric pollution generating gypsum in the stone. Tests were carried out on a French limestone, called tuffeau. Local strains were measured using strain gage rosettes during water imbibition in polluted and unpolluted samples. Three rosettes were placed on a sample at different distances from the surface (1, 4, 7 cm) to measure locally the strain during water infiltration. These rosettes determine the strain in three directions 0°/45°/90°.
Results concerning the behaviour of polluted stone during imbibition are compared to unpolluted stone. Results concerning differential strains between the surface and the core of the stone due to water infiltration demonstrate unusual behaviour not restricted to expansion alone: a local contraction zone and expansion zone in each direction separately for the stone. Pollution by gypsum has an effect on the strain measurements mainly on the first few centimetres of the stone.

Keywords: gypsum, spalling, local strain, imbibition, tuffeau

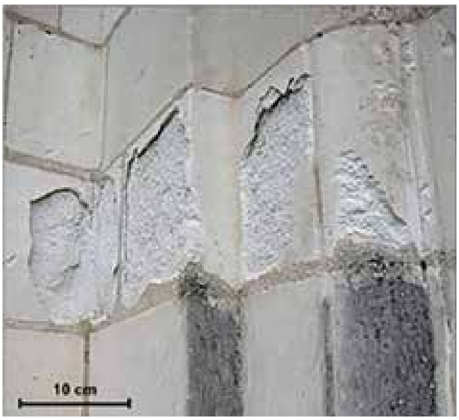
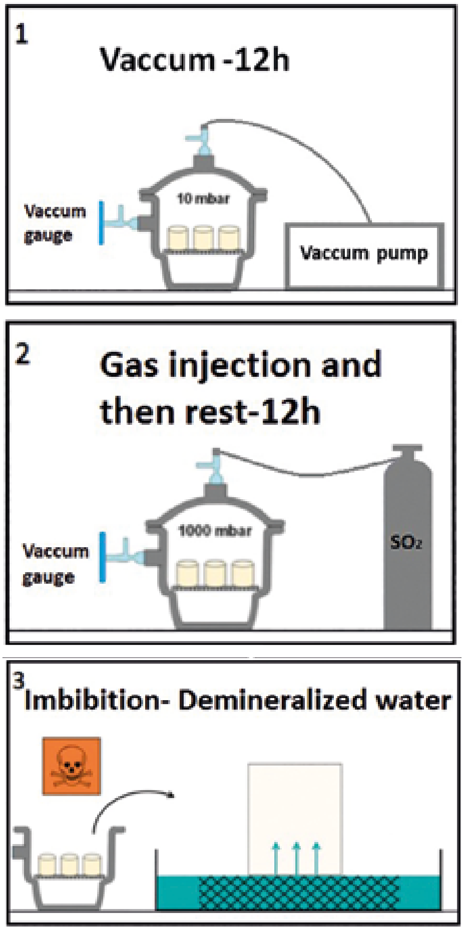


Figure 1: Example of spalling in tuffeau at the "Chateau de Chambord" (France)[3]

1. Research aim

Limestones constitute the main construction materials in historical monuments and are affected by several deterioration mechanisms, among which spalling.[1, 2] This decay is defined as a detachment of thick plates (1 to 3 cm thick) gradually formed on the surface of the stone *(Fig. 1)*. Once the plate falls off, the resulting stone surface turns to powder. Mineralogical analysis of the degraded stone, throughout its depth, shows the presence of gypsum ($CaSO_4.2H_2O$) located mainly within a crack network parallel to the surface at 1 or 2 cm depth.[3] Therefore, the study of the effects of pollution on these stones is one of main aims to understand the physico-chemical mechanism leading to spalling. There is also a consensus on the role of water, which is the source of physical changes and the dissolution/ crystallization of phases. In order to further our knowledge of the reaction of stones with respect to water migration and the effect of pollution, a



b

Figure 2: Sample pollution process (a), sample of tuffeau with strain gage rosettes (b)

this paper presents the results of an experimental campaign applied to a French limestone: tuffeau. The experiment consisted in subjecting stone samples (both polluted and unpolluted) to imbibition, and in monitoring strain at different heights in the samples. Pollution was generated in the laboratory with the precipitation of gypsum in depth within the fresh stone samples. The work presented aimed to assess the mechanism of spalling generated by mechanical stresses and strains developed due to imbibition and the link with atmospheric pollution.

2. Studied stone and methodology

Tests were carried out on tuffeau, the stone used as building material in the construction of most cultural heritage buildings in the Loire Valley in France. It is of Turonian age (Upper Cretaceous period between 88-92 million years ago). It is mainly affected by spalling. Tuffeau is composed of a major calcite phase (50%), a high siliceous fraction (40%: opal Cristobalite-Tridymite and quartz) and a significant clay content (10%: glauconites, smectites, illite). It is very porous (45% of porosity), with a bi-modal (first peak at 8 µm; second peak at 0.01 µm) porous network.[4] The mechanical characteristics depend on the degree of water saturation and on the orientation with respect to the bedding plane.[5] The stone tested in this experimental campaign was extracted from the Usseau quarry, located in the Vienne department, in the Center-West of France. Two cylindrical stone samples, 40 mm in diameter and 80 mm in height, were cored in the direction parallel to the bedding plane (i.e. the cylinder axis is parallel to the bedding plane) *(Fig. 2)*. This direction was chosen to simulate a real in-situ imbibition process due to rain on the stonework.

For each sample, three strain gage rosettes were glued on the lateral surface of the cylindrical sample, at different heights: 10 mm (J1); 40 mm (J2); 70 mm (J3). Each strain gage rosette was composed of three strain gages, oriented at 0°, 45° and 90° depending on the eigenvectors of the loading, which correspond to the same directions as the axes of symmetry of the sample. The rosettes are „KFG 120“ type from Kyowa and were glued using a cyanoacrylate glue (CC-35A). The diameter of each rosette is 1 cm. The error of measurement is about 1E-06 m/m and the quantification limit is about 1E-08 m/m. Before testing, the samples were dried in an oven at 60°C during 92 hours. Then, they were cooled down in a desiccator with a drying salt that maintains an almost zero relative humidity. One of the samples was subjected to pollution by gypsum inside the stone. Pollution was generated in the laboratory by artificial ageing through an injection of dry gaseous SO_2 in the porous network of the stone followed by a partial imbibition of samples with water *(Fig. 2)*. For the creation of gypsum in the porous network, the following chemical equations were used:

$$SO_2 + H_2O \rightarrow H_2SO_3 \text{ THEN } H_2SO_3 + ½O_2 \rightarrow H_2SO_4 \quad (1)$$

$$SO_2 + ½O_2 \rightarrow SO_3 \text{ THEN } SO_3 + H_2O \rightarrow H_2SO_4 \quad (2)$$

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4.2H_2O + CO2 \quad (3)$$

The first two equations (1) and (2) are two possible reactions to obtain sulfuric acid and then the reaction of sulfuric acid, water and calcite (dissolved from the stone) makes it possible to obtain gypsum in the porous network inside the stone and not only at the surface (3). The injection of sulfur dioxide (SO_2) was carried out in the dry state in samples previously dried under vacuum for about 12 hours. The sample was therefore saturated with SO_2 gas (≈ 12 hours) and after opening of the desiccator, it was subjected to partial capillary imbibition (≈ 2 cm) of distilled water. Afterwards, the samples were stored in an oven at 50°C for 15 days. The stone sample, in the dry state, was placed on a plastic grid that allows demineralized water to be imbibed into the sample by a capillary process. During the test, the stone sample was subjected to imbibition in controlled conditions (20°C and 50% of relative humidity).

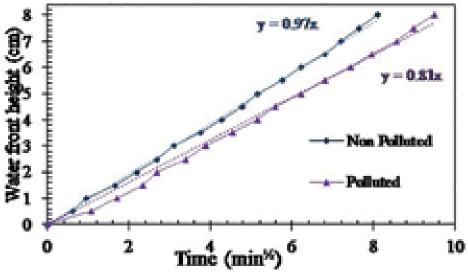


Figure 3: Imbibition curves of polluted and unpolluted tuffeau

3. Results

First, we present the well-known imbibition curves based on visual measurements of water front height and the time of capillary rise. The curve of water front height (cm) over square root of time (min½) is linear *(Fig. 3)*. The slope represents an intrinsic property of the material.

The imbibition curves show that the hydric properties of tuffeau changed due to the presence of gypsum. The slope of the curve decreased from 0.97 to 0.81. The imbibition rate decreased by 16%. This is the first evidence for the effect of pollution.

Figures 4.a and 4.b show respectively the results of strain measurements of vertical gages for unpolluted and polluted tuffeau. V10, V40, V70 refer respectively to the vertical strains of gages at 10 mm, 40 mm and 70 mm of height.

While the water penetrates into the stone, local vertical strains change. During the capillary imbibition and depending on the relative location of the water with respect to the rosette, the strain may be a contraction, an extena b

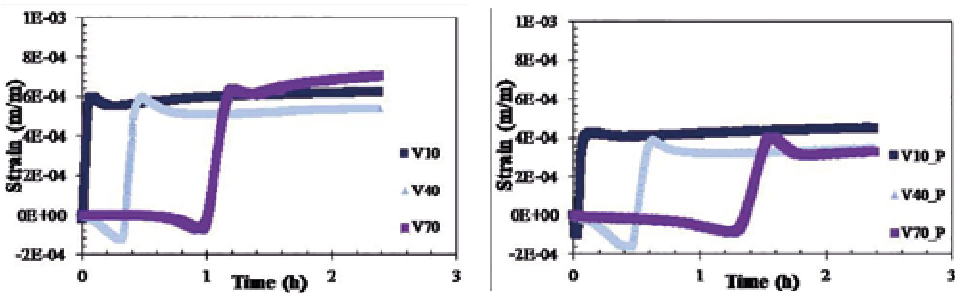


Figure 4: Vertical strains of unpolluted tuffeau (a) and polluted tuffeau (b)

sion, or a stabilization. When the water is below the rosette, the stone is locally contracted. The amplitude is estimated at 1.6E-04 m/m which represents 28% of total strain. Once the water reaches the rosette height, there is an abrupt extension up to a value of about 6E-04 m/m for unpolluted tuffeau and around 3.8E-04 m/m for polluted tuffeau. Then, a small contraction (relative to the amplitude of the extension) is measured, followed by a stabilization step. These stages are present for polluted and unpolluted tuffeau. Two differences were reported between the two states: The magnitude of total vertical strain was higher for unpolluted stone (around 6E-04 m/m against 4E-04 m/m), and the imbibition rate was higher for unpolluted stone. The pollution by gypsum decreased the total strain by 33%, which is significant.

Figures 5.a and 5.b show respectively the results of strain measurements of horizontal gages for unpolluted and polluted tuffeau. H10, H40, H70 refer respectively to the vertical strains of gages at 10mm, 40mm and 70mm of height. The horizontal strains show monotonous evolution in extension for polluted and unpolluted tuffeau. The same reasoning was adopted for the water front. When the water front is below the rosette, stone extension begins. Then, a sudden extension occurs when the water front reaches the rosette. A second stabilization plateau is obtained when the water front exceeds the rosette. Pollution has no real effect on the total horizontal strain value.

a b

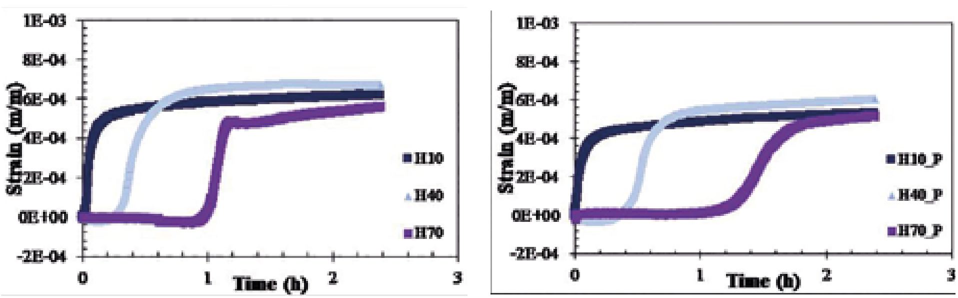


Figure 5: Horizontal strains of unpolluted tuffeau (a) and polluted tuffeau (b)

4. Discussion

As pointed out in the Results section, water has an effect on local strain changes. In vertical strains, four distinguishable stages are observed for tuffeau (polluted and unpolluted).

The first stage starts when the water front has not yet reached the rosette; there is vertical contraction and the onset of horizontal extension. This behaviour could be the consequence of the horizontal extension of the imbibed zone just under the rosette. Vertical contraction is due to the Poisson effect.[5] The horizontal tensile strain is accompanied by vertical compressive strain.

When the water front crosses the zone of the rosette, the extension is in all directions due to pore saturation. This phenomenon is the expected reaction of stone due to imbibition.[6–8] The total vertical strain of tuffeau is higher than the total vertical strain due to the high quantity of clays in tuffeau (10%).[7] The presence of gypsum salt has an effect on the extension of tuffeau and reduces the maximum strain value by 33%. In polluted sample, the gypsum which replaced the calcite acted as a local reinforcement of the stone structure. Gypsum is a soluble salt with a low solubility (2 g/l) but moves slightly during an imbibition. The main problem during partial imbibition is the accumulation zones of gypsum due to tidal effect with the movement of water. In these zones, gypsum content could be very high, and this effect of reduction of strain could be higher.

Then, the third stage begins when the water front is above the rosette. There is a slight contraction in vertical strain and a continuity of horizontal extension. This effect is due to two phenomena: the continuity of capillary imbibition in capillary pores and the slower saturation of small pores which decrease the saturation of the capillary pores. This stage is restricted because of the bi-modal porosity network of tuffeau as explained by Hassine.[5] The stone has the same behaviour even in the presence of gypsum. The final stage concerns the stabilization of strain in all directions, so all porosity is fully saturated by water. *Table 1* sums up the main phenomena affecting tuffeau stone during imbibition.

The main interesting feature of the results concerns the effect of pollution during imbibition on the local vertical strain. As shown by Hassine et al.[5], the effect of imbibition is not limited to monotonous extension, as was previously thought.[7, 8] Firstly, the existence of vertical contraction with significant amplitude may contribute to spalling. Secondly, the presence of salt (gypsum) in the stone stiffens the skeleton and creates a difference in stiffness between polluted and unpolluted areas. Subsequently, the polluted zone (the most rigid one) creates restraint stresses and a shear plane between the two zones. By comparison with in situ conditions of stones in a wall submitted to a rain event where pollution is located on the first few centimeters, the vertical contraction observed during the experiments corresponds to hori-

Vertical strain	- No effect on contraction phase
	- Decreases the maximum strain value by 33%
Horizontal strain	- No effect on strain changes
Imbibition kinetics	- Slows the imbibition rate

Table 1: Effect of gypsum pollution on tuffeau behaviour during imbibition

zontal contraction perpendicular to the surface of the stone. This contraction is restrained by the polluted area, resulting in tensile stress, situated just after the water front, i.e. around 1 to 2 cm depth. The amplitude of this tensile stress is not negligible compared to the low tensile strength of tuffeau. This could be the origin of a crack parallel to the surface at 1 to 2 cm depth, which corresponds to the description of spalling.

5. Conclusion

This paper evaluated the effect of pollution during water migration on the strain of a French limestone, tuffeau, and proposed an interpretation for the degradation process causing spalling. The local strains were measured by using strain gage rosettes. On tuffeau, which is a homogeneous stone, the strain measurements during an imbibition on several samples of unpolluted tuffeau showed reproducible results.[5] The evaluation of strain measurements in a sample polluted and unpolluted is reproducible. The tests have been repeated 3 times in each case and the error is about 1E-06 m/m.

Gypsum does not affect the contraction phase in the vertical direction, and decreases the maximum vertical strain value by 33%. However, no change is detected horizontally. The imbibition kinetics of the tuffeau are slowed down.

The presence of vertical contraction just above the water front can contribute to the discussion about the cause of spalling. This vertical contraction may correspond to horizontal contraction for in-situ stones in a wall exposed to rain. If the displacement of the stone in the direction of depth is restrained by harder stone (polluted area), it could result in significant tensile stress, able to generate a crack parallel to the surface. As the typical depth of water imbibition during a rain event in tuffeau is between 1 and 2 cm, the depth of the crack would be around those values. Hence, the presence of gypsum and the presence of vertical contraction observed on a sample submitted to imbibition could be a key element in the clarification of the origin of spalling. Indeed, this study is the first step for understanding the mechanisms of spalling of tuffeau and this hypothesis must be supported by further tests.

This work will be pursued on a second stone, Richemont stone, used as a replacement stone during restoration work at the end of the 20th century. The behavior of the two stones will be compared in order to understand the effect of gypsum pollution during imbibition and to explain why no degradation by spalling is observed on Richemont stone. Finally, research on both tuffeau and Richemont stone will be extended to investigate cycles of water imbibition – drying with and without gypsum pollution to better understand their long-term behavior.

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