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# Thermal behaviour of building stones contaminated with $Na_2SO_4$

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## Abstract

The Orval Abbey (Belgium) was rebuilt from 1928 to 1936 using the two original limestones of the previous Abbey and a reconstituted stone produced by mixing debris of the two natural stones with cement. These three materials have different resistance towards salt crystallisation; especially the reconstituted stone is highly salt-prone. The major salt found in the walls and at the surface of walls is thenardite (Na<sub>2</sub>SO<sub>4</sub>).

A previous study [1] showed that sulphates originate from the reconstituted stone itself. Active infrared thermography (IRT) recorded on parts of the Abbey show that the thermal response of salt-weathered part of walls is different from that of unweathered ones (Gommeaux et al., actual proceedings). This method is commonly used in heritage to detect thermal anomalies due to for example the presence of moisture or cracks or material change.

In this study, we applied the technique in the laboratory on samples of the three building materials used in the Orval Abbey. The aim was to understand the different behaviour of these materials and to see if there could be a relation between the extent of salt contamination and thermal response.

Keywords: infrared thermography, wetting-drying cycles, Na<sub>2</sub>SO<sub>4</sub>, limestone

## Materials

The two natural stones are limestones from the surroundings of the Abbey: one from the Bajocian (BJ) and one from the Sinemurian (SN), while the reconstituted stone (RS) is composed of debris of SN and BJ mixed with cement [1]. The last was made on site during the last-century reconstruction; the recipe is unfortunately not known.

The natural and reconstituted materials are quite similar in visual aspect, except that the reconstituted stone often shows bubbles. Its russet colour is intermediate between those of the BJ and the SN.

The BJ limestone is a calcareous limestone rich in bioclasts and with very low silica content while the SN is a siliceous limestone. The reconstituted stone has a composition that is intermediate between the two natural stones and contains besides elements typical for cement, such as aluminium and iron.

Although porosity and water transfer properties of the RS are similar to the BJ limestone, its pore access distribution is centred at 0.1  $\mu$ m which is the main pore access family of the SN (Figure 1). These three materials are similar but different enough to be distinguished through their porous network and transfer properties.

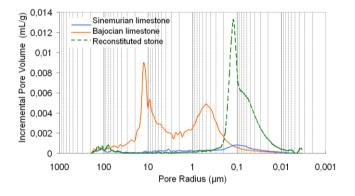


Figure 1: Pore size distribution of the three stones obtained by mercury porosimetry.

## Salt ageing tests

45 disk-shaped samples (diameter: 30 mm; height: 5 mm) of each material were submitted to immersion-drying tests in  $Na_2SO_4$  solutions of different concentrations: 7, 14 and 26 w%. 15 cycles of 24 h each were performed, consisting of 2 h immersion and 22 h of drying in boxes with silica gel.

The weight of the samples and the surface colour were recorded after each cycle. The samples were observed under a binocular magnifier.

After 1, 5, 10 and 15 cycles, 3 samples of each stone were selected for infrared thermography measurements.

# Active infrared thermography

Active IRT was conducted by means of a FLIR infrared thermography camera SC655 operating in the long-wave infrared spectra range 7.5-14 µm] and providing images of 640 x 480 pixels. Two flash lights were placed at 45° of the sample, symmetrically along the axis of the camera (Figure 2), producing light of 4800 J during 5 ms. The flux of photons emitted by the flash excites the sample leading to an increase of its temperature. Part of the heat is absorbed while the other part is emitted back and recorded by the camera. The emitted infrared radiation depends on the physical parameters of the material: density, porosity and pore structure, specific heat, thermal emissivity, thermal conductivity and thermal diffusivity, as well as on the surface properties (rugosity, color) and mineralogical composition. To minimize the effect of the surface aspect of the samples on the thermal response, samples were covered with a black high-temperature resistant paint layer. The thermal effusivity b (indicating the stones' ability to exchange thermal energy with their surrounding) was computed from the thermal curves (in  $J.K^{1}.m^{2}.s^{1/2}$ ).

Images were recorded each 10 milliseconds (100Hz), further treated and analysed with the ThermaCAM Researcher 2.10 software (FLIR).



Figure 2: Scheme and picture of the setting of active IRT measurements.

## Results

The salt crystallization at the surface of the samples of the three stones led to whitening that increased with the salt solution concentration. At the end of the  $15^{\text{th}}$  cycle, the color change  $\Delta E$  was about 25 for the SN using a salt solution of 26w%, while about 20 for the BJ and the RS at the same concentration.

The weight change of the samples is a balance between salt uptake and loss of stone debris due to salt damage. While very little change in weight was noticed on SN for all three salt concentrations, related to a low salt uptake and damage, the BJ showed a weight increase up to 3% using the 14 and 26w% solutions. However, sanding of the BJ occurred all over the experiment. From cycle 12 on, important loss of material (and in some cases, complete collapse) occurred. The salt uptake of RS was higher than for the other stones (maximum weight increase between 2% for the 7w% salt solution to 7% for the 26w% solution). This was likely due to the high porosity of the RS consisting of a high content of micropores (0.1 µm) which favor salt crystallization. Sanding on the edges and surface of the occurred samples over the entire experiment: some samples disaggregated completely from cycle 13.

For each of the three stones, the changes in thermal properties were very similar for all three salt concentrations. The thermal effusivity of the BJ and the RS was similar over the course of the experiment (initial value close to  $2300J.K^{-1}.m^{-2}.s^{-1/2}$ , constant until cycle 5, increase to  $4000J.K^{-1}.m^{-2}.s^{-1/2}$  after cycle 10 and little decline up to cycle 15). The evolution of the thermal effusivity of the SN showed a very different pattern. Yet after cycle 1, there was a large increase in thermal effusivity (from 3900 to 7000 J.K^{-1}.m^{-2}.s^{-1/2}) that showed a further decreasing trend.

## Conclusions

The results of IRT confirm that the properties of the RS are close to those of the BJ limestone. The initial purpose of making a RS suitable to replace the natural stones to complete the building of the Abbey was thus mostly fulfilled. However, the RS has properties closer to the BJ (which is used as freestone) than to the SN (used as rubblestone).

Furthermore, this study showed a clear link between salt uptake and a change in thermal properties of the stones. Although the relationship needs to be refined, this confirms that active IRT may be a valuable tool to distinguish similar-looking materials and for the diagnosis of salt accumulation in building materials.

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### References

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