



## Study of the Migration of the Anions in Historic Masonry by Three Complementary Approaches

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### Abstract

The presence of soluble salts inside built heritage is among the most important degradation factors; so, a better understanding of the salts migration process can help in identifying the sources and the entry mechanisms and, consequently, allow to suggest the best approach for the maintenance. This research work treats the migration of soluble salts inside new and historical bricks.

At this aim, three different approaches were planned: the first two simulating a capillary rise or an horizontal inlet from the wall, the last is an attempt to evidence eventual differences in the salts migration due to their chemical difference. First of all the bricks samples were carefully washed in order to eliminate, or at least know, the content of salts already present. This purpose was pursued by total immersion in deionized water or by shorter washings helped by ultrasound.

### Introduction

Moisture plays a key role in the degradation of porous materials, being directly or indirectly responsible for several degradation processes, such as freeze-thaw cycles, biological growth, chemical attack from acid rain and cycles of crystallization-dissolution from soluble salts [1].

In recent years, the research has given particular attention to the study of the mechanisms of degradation caused by the attack of salts. Various aspects were taken into consideration, but few studies have been aimed to understand the mechanisms of the migration of salts within the masonry structures [2]; such knowledge is instead essential to identify their possible sources so being of help in planning solutions for restoration or routine maintenance. The most abundant salts commonly found inside masonries are chloride, nitrate and sulphate i.e. those that commonly rise by capillarity because always present in waters, or bound to the presence of marine aerosol and acid gases in the atmosphere that solubilize in the moisture veil of the wall.

### Materials & Methods

For the test 1, regarding the capillary rise, we used an home-made polystyrene chamber simulating a semi-confined environment, hosting the brick on one of the walls and resting on a layer of cellulose pulp saturated by a standard anionic multi-element solution; the thermo hygrometric monitoring inside and outside the chamber is foreseen. Just on end of the capillary rise samples must be drilled, according to a sampling design, and analysed for the salts content.

The test 2, for salts migration across the brick, was simulated using the apparatus in Fig.1: a Rilem pipette, filled with the same standard solution, and a glass cell with an input on the top are positioned on the opposite sides of the brick; just when the side hosting the cell appear wet, it is filled with deionised water that, at prefixed times, is replaced and analysed for the salts content.

The affinity of the salts toward the brick components (test 3), was studied by packing a steel HPLC columns (4x300mm, by joining two columns of 150 mm) with brick powder (grain size ranging from 50 to 63  $\mu\text{m}$ ). The column was used as stationary phase for anionic IC and tested with eluents of different pH: dilute HCOOH, deionised water, NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>-NaHCO<sub>3</sub>. Anions content was determined by Ion Chromatography (IC) using a Metrohm 761-IC (Switzerland) equipped with AS9+AG9 columns (by Dionex USA). Cations were determined by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) using a Vista RL-CCD (by Varian USA).

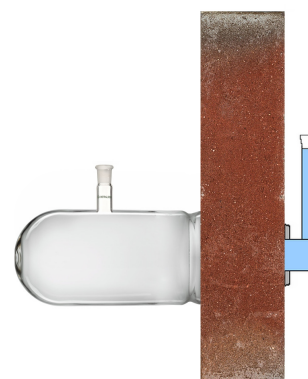


Fig. 1: Apparatus for test 2

Anion multi-element standard ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ), type II, CertiPUR, HC607686, from Merck was used for IC and ICP-AES analyses. Bench-top instruments were used for pH and conductivity measurements. Deionised water ( $\Lambda < 0.5 \mu\text{S}$ ) and high purity reagents were used in all the experiment. Commercial terracotta bricks 210x110x55 cm in size and about 2.8 Kg in weight were used.

## Results

Tests 1 and 2 are running and up-today we worked on the modeling and preliminary tests aimed to establish the time needed for the capillary rise (test 1) and horizontal crossing (test 2) in different thermohygro-metric conditions; the first resulted at least one week while the second about 12 hours. In test 1, the rise front looks more or less concave upward marked also by a consistent white efflorescence band even if only deionised

water was used; this reveals the presence of not negligible amount of salts inside the brick. In test 2 a very low lateral diffusion was observed without preferential direction, i.e. the water stain observed at the end of crossing remained perfectly circular even if a little wider; no efflorescence are evident. The content of salts already present in the brick samples had been already evaluated through analyses of solutions coming from successive washings. In figure 2 results obtained using ultrasound are reported.

It is evident a discontinuous trend of both conductivity and pH with peaks not ruled by periodicity; more, even after 50 washings the absence of salts cannot be stated. A comparing with the salts content has evidenced that conductivity must be imputed to a generally low concentration of chloride and nitrate while the peaks in fig. 2 correspond to a more or less huge increase of sulphate. In order to understand such trend we analysed some white grains visible in the brick body that were identified as gypsum. Even if it was not an aim of the washing treatment, we obtained a useful information, i.e. that gypsum coming from the brick production process is an inner source of sulphate very difficult to eliminate. Further, taking into account results from test 1 and 2, it can be stated that, as expected, a slower migration of water corresponds to a quicker dissolution of the gypsum grains.

Figure 3 shows the chromatograms obtained, for chloride, nitrate and sulphate, using the brick powder as stationary phase. A good separation was obtained for sulphate with respect to the other two that, in turn are only slighter separated. Tests performed with the other eluents have

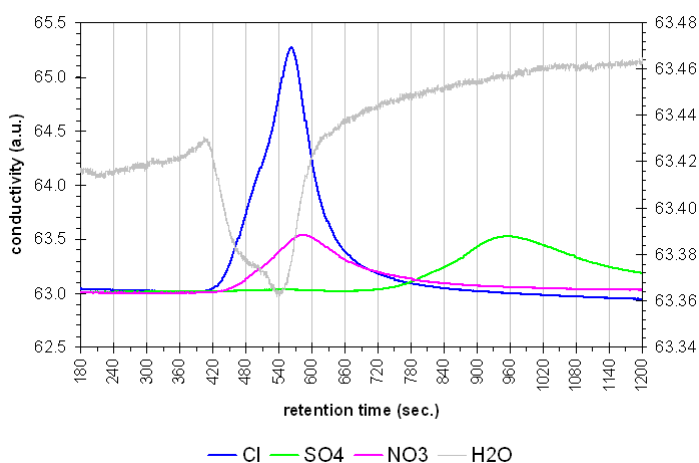


Fig.2; Chromatograms of salts obtained using the brick powder as stationary phase and deionised water as eluent

Nobile. Effect of salt crystallisation on the shear behaviour of masonry walls: An experimental study, *Construction and Building Materials*, 37 (181-189), (2012)

2) A.V. Turkington, B.J. Smith. Observations of three-dimensional salt distribution in building sandstone, *Earth Surf. Process. Landforms* 25 (1317-1332), (2000).

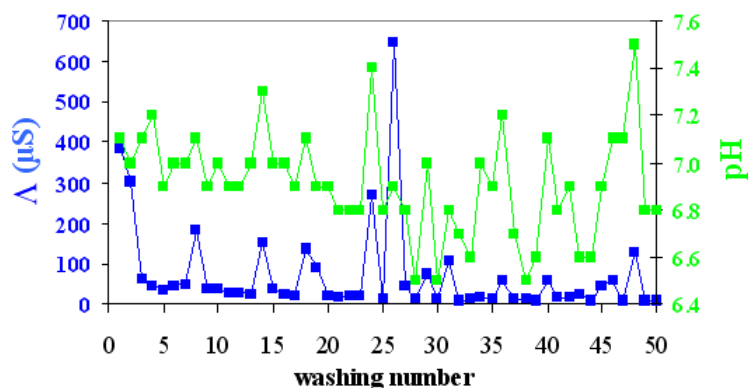


Fig.1; Trend of conductivity and pH during the brick washing

demonstrated that the separation depends on the pH being higher in neutral medium.

## Conclusions

This research work, although still running, already furnished some interesting information. The analyses of the washing solutions joint to the results obtained by test 1 and 2 suggest to ask for a more accurate production process of the bricks. Terracotta shows a higher affinity for sulphate with respect to chloride and nitrate, also depending on the eluent pH

## References

1) C. Gentilini, E. Franzoni, S. Bandini, L.