



## Chemical Mechanism Involved in the Movements of Soluble Salts Inside Masonry: Different Affinity of Salts Toward the Brick's Components

M.P. Sammartino<sup>1</sup> and G. Visco<sup>2</sup>

<sup>1</sup>Chemistry Dept, La Sapienza University, p.le A. Moro 5, 00185 Roma

<sup>2</sup>Appointed Professor in the Degree Course "Technologies for Conservation and Restoration of Cultural Heritage"; La Sapienza University, p.le A. Moro 5, 00185 Roma

### Abstract

We here present a part of a wider research aiming to improve the understanding of the moving of soluble salts inside of masonries.

At this aim commercial bricks were used as substrate and solutions of chloride, nitrate and sulphate as salts. Three different approaches were adopted; by two of them we simulate the capillary rise and the entrance of salts by humid layers, i.e. mainly physic mechanisms, while by the third, that is object of the present communication, we looked for a chemical mechanism. An HPLC column was filled with finely ground powder and used as stationary phase for Ion Chromatography. Different eluents were tested in order to find a trend as function of their pH.

### Introduction

It is well known that water entering stone materials, such as and above all as saline solution, constitutes one of the main cause of degradation of such materials. A lot of physical, chemical and mineralogical-petrographical parameters play a role in the movement of soluble salts inside the stones; so, a modelling and, in turn, a prevision of damage it is not easy to be assessed [1] and, in fact, no Italian Norm that regulates interventions of desalinization exists.

Anyway, the inlet and exit mechanisms of the salts from masonries are known while what it is difficult to establish is how each of the above mentioned parameter influences the effect of the others; so, a study "case by case" is needed.

The transport of soluble salts through the capillary rise or diffusion driven by water present as humid layer on stone surfaces are enough studied; on the contrary the different chemical affinity of different salts toward the stone components is a new task that we are studying; here we present the first results that treat the behaviour of anions while for the one of cations the research is running.

### Materials & Methods

A Ionic Chromatograph [2] mod 716 compact IC, Metrohm (Switzerland), equipped with 2 modified YMC (4x150 mm) columns emptied and linked together, without guard column, were used. All reagents were of analytical grade and their solutions were obtained using deionized water (conductivity  $\leq 0.5 \mu\text{S}$ ). A SEM/EDS (LEO1450VP Scanning Electron Microscope (SEM) equipped with INCA300 X-ray Dispersive Energy detector (EDS) was used to determine the average size of the powdered brick and its elemental composition. The mineralogical composition was obtained by a Siemens D5000 X-ray diffractometer. About 100 g of a brick (dated in early 1900) were grinded by a blade mill and sifted between 50 and 65  $\mu\text{m}$ .

### Results

Data in Table 1 show that Chloride and Nitrate are not well separated during the chromatographic run using all the tested eluents; in fact, the differences of the Retention Times ( $t_r$ ) are of the same order of the single Standard Deviations obtained for the two anions. Sulphate is instead well separated from the previous two with the better separation in formic acid at pH 6.10; anyway, data obtained using water as eluent (see fig. 1 and Table 1) must be considered the better because of the better reproducibility and good separation (about ten times higher than the SD

obtained for all the three anions); more, the lower retention times allow a decreasing of the analysis time. Table 1 also shows an increase of the eluent pH starting from the slightly acidic eluents that can be imputed to the leaching of the carbonate present in the brick composition.

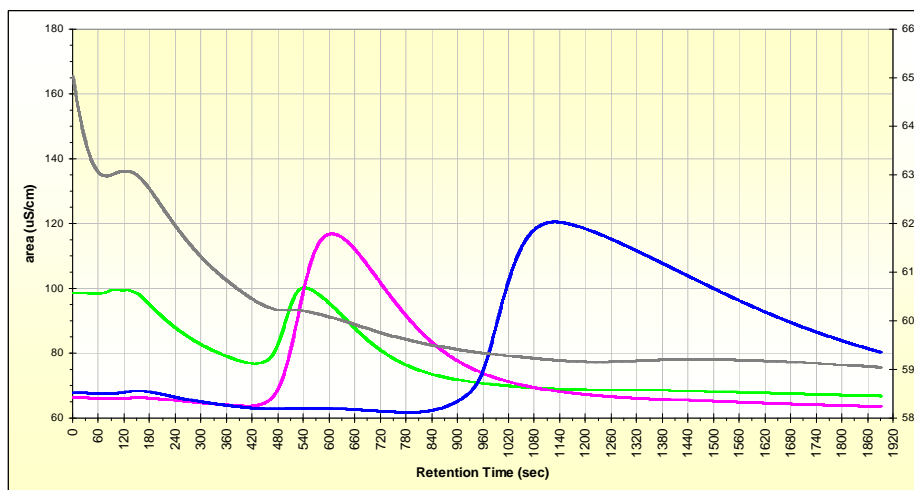


Fig.1; Chromatographic runs of Eluent (water), Chloride in green, Nitrate in purple and Sulphate in blue color.

	$t_r$ (min)			pH		$\Delta t_r$ (min)		
	Chloride (a)	Nitrate (b)	Sulphate (c)	inlet	outlet	a-b	c-a	c-b
formic acid	16.6±0.7	17.2±0.8	22.2±0.6	5.27	9.42	-0.5	6.9	6.4
formic acid	20.7±1.9	18.7±1.4	29.6±2.9	6.10	9.66	2.0	8.9	10.9
Water	8.9±0.9	9.8±0.8	17.8±1.1	6.64	9.81	-0.9	8.9	8.0
carbonate/bicarbonate	14.8±0.2	15.0±0.3	15.7±0.3	10.00	9.90	-0.2	0.9	0.7
carbonate	10.9±0.2	10.7±0.2	11.6±0.3	10.80	10.00	0.2	0.7	0.9

The SEM image evidences grains of low sphericity and variable roundness (ranging from angular to sub-rounded) with dimensions ranging from about 7 to about 15  $\mu\text{m}$ . EDS and XRD analyses, as expected, evidences the presence of silico-alluminate, Iron oxide and some Calcium carbonate.

## Conclusions

Even if the soluble salts movement inside stones is mainly bound to their concentration gradient as well as to the humidity gradient, the research here presented had demonstrated that, a different affinity of the single salts towards the constituents of the bricks also plays a role. Sulphate is surely more retained inside bricks; this must be considered a further reason for its well known dangerous effect because of the easier possibility to form sub-efflorescences. Nitrate and Chloride have instead a similar affinity toward the components of the brick that results very lower than the one of Sulphate; this could be imputed to both the higher charge and mass of the last. The best separation of the chromatographic peaks was obtained at slightly acidic pH with a decrease at both more acid and more basic values.

Other measures are running to test the cations behaviour and all data will be a part of a wider research aiming to evaluate all the physical and chemical driving forces involved in the movement of the soluble salts inside masonries. The capillary rise and the inlet by humid layers is also a subject of the running research; all the data will be treated by chemometrics tools trying to obtain some modelling.

## References

- 1) May-Fun Liou, A Numerical Study of Transport Phenomena in Porous Media, *PhD dissertation*, Case Western Reserve University, 2005
- 2) C. Borges, C. Caetano, J. Costa Pessoa, M.O. Figueiredo, A. Lourenco, M. Malhoa Gomes, T.P. Silva, J.P. Veiga, Monitoring the removal of soluble salts from ancient tiles by ion chromatography, *Journal of Chromatography A*, 770 (1997) 195-201