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"Structural Repair and Maintenance of Historical Buildings III"

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Structural Repair and Maintenance of Historical Buildings III

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SECTION 3: DETERIORATION, PROTECTION AND EVALUATION OF MATERIALS

Deterioration of ancient and modern buildings materials due to environmental factors

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ABSTRACT

Simulations of environmental damage processes were performed in the laboratory. Samples of carbonate stones and mortars were exposed at 25 °C temperature, 100% relative humidity, 3 ppm SO_2 concentration, using different types of carbonaceous particles. The exposed samples were analysed by x-ray diffraction (XRD) and infrared spectroscopy (FTIR) to identify the main chemical species and by ionic chromatography to quantify $SO_4^=$ and $SO_3^=$ concentrations.

INTRODUCTION

The effects of the deposition of atmospheric gas and aerosol on building materials constitute one of the main damage mechanisms affecting the cultural heritage. The study of environmental damage on stones, mortars and concretes is of fundamental importance in both the preservation of modern buildings and correct planning of conservation works on historical monuments, in which such materials are commonly used.

Alongside field work, where the main damage products are measured on historical buildings, laboratory simulations are necessary so as to gain an understanding of the reactions between atmospheric pollutants and building materials and their kinetics. Due to the simplifications necessary in the realization of physical models, the data obtained cannot be directly extended to real systems. However, useful indications can be deduced on the competitive effects of the various mechanisms concurring in the deposition of environmental pollutants and their interaction with building materials.

In the literature laboratory simulations are reported on the effects of gases, such as SO_2, NO_x and O_3 (Gauri *et al.* [1]; Johansson *et al.* [2]). However, little information is available with regard to the effects of atmospheric aerosol, particularly carbonaceous particles, which are the most abundant component found in the damage crusts generally observed on monuments in urban areas (Zappia *et al.* [3]). The aim of this work is to simulate the effects of carbonaceous particles on different types of building materials in SO_2-exposure experiments.

EXPERIMENTAL SECTION

APPARATUS SYSTEM — A chamber was designed and built in our laboratory in order to simulate the effects on different building materials in controlled atmospheres. The temperature, ranging between −5 and 50 °C, is measured by a thermocouple which pilots a partial-select output, connected to 4 filament lamps acting as hot sources and a refrigeration system which contains the whole chamber. The relative humidity, ranging between 10 and 100%, is controlled by a partial-select output which pilots a vapour production system, composed of a piezotite crystal oscillator that generates cold vapour from a film of bidistilled water. The dry air and different gases (SO_2, NO_x, O_3), controlled by flowmeters, are mixed in a pre-chamber and released into the chamber at fixed concentrations. A homogeneous distribution of the gases within the chamber is ensured by an external recirculation system. The sample support is set on the chamber floor (Zappia *et al.* [4]).

MATERIALS — Tests were performed on three carbonate rocks – Carrara marble, Travertine and Trani stone. Carrara marble has been widely used internationally as a statuary and architectural marble both outdoors and indoors. Travertine is a limestone utilized in numerous famous monuments, such as the Colosseum in Rome. Trani stone was chosen as a representative example of the limestones used in Southern Italy. A chemico-physical characterization of the three carbonate rocks was performed. The total porosity was 1.5, 4.3, 6.2%, the specific area 0.2, 1.3, 0.5 m^2g^{-1} and the sulphate ion concentration 27, 77, 52 $\mu g\ g^{-1}$, respectively. The three stones were cut into samples sizing 10×10×5 mm, which were cleaned in distilled water and then in a concentrated ethyl alchool solution. The samples were dried and preserved in an inert atmosphere dryer (UPP nitrogen).

Mortars – The three mortars studied are reported in Tab. 1. The following constituents were utilized: hydrated lime powder, natural pozzolana (Segni), Portland cement and siliceous sand. The constituents were added dry and mixed with water for 4 min. During setting the fresh mortar was cut into 10×10×5 mm sections and cured in air at 20 °C temperature and 50% RH for 28 days. After curing the samples were preserved in an inert environment (UPP nitrogen). The chemico-physical characterization of the lime, pozzolana and cement mortars showed a total porosity of 32.7, 26.1, 13.4%, a specific area of 1.5, 0.7, 0.3 m^2g^{-1} and a $SO_4^=$ concentration of 62, 86, 854 $\mu g\ g^{-1}$, respectively.

SAMPLES WITH CARBONACEOUS PARTICLES — Three types of carbonaceous particles were deposited on the stone and mortar samples (P1, P2 and P3). To use particles similar to those found on Italian monuments (Sabbioni [5]), aerosol samples were collected at the emissions of 3 fueled-oil combustion sources: one centralized domestic heating system (P1) and two electric generating systems (P2 and P3). The three particle samples (P1, P2 and P3) were analyzed using CHNSO Elemental Analyzer (EA1108 Carlo Erba): a carbon concentration of 86.3, 10.8 and 39.8% and sulphur content of 3.2, 17.4 and 11.7% were found, respectively. The morphology and elemental composition of the particles were analyzed by scanning electron microscopy – energy dispersive x-ray analysis (SEM-EDAX), showing spherical shape, porous surface and S and V as principal elements (Fig. 1).

The problem of applying the carbonaceous particles to the stone and mortar surfaces was studied. The dispersion of the particles in a liquid phase (such as water, acetone or organic solvents) was considered unsuitable, since a dissolution of the soluble species present in the particles could occur, leading to the growth of authigenic crystals (Del Monte *et al.* [6]). A number of tests were carried out with dispersed gas injection, but modifications in particle size and morphology were observed.

Finally, particles were scattered on the specimen surfaces and the samples exposed to air flow (higher than the flux operating in the chamber) so as to eliminate any excess and prevent phenomena of resuspension inside the chamber with the contamination among samples. The amount of particles

Table 1. – Mortars studied

Mortar	Constituents	Ratio	Water/Binder Ratio
LIME	Lime, sand	1:3	0.88
POZZOLANA	Lime, pozzolana, sand	1:1:6	0.85
CEMENT	Cement, sand	1:3	0.82

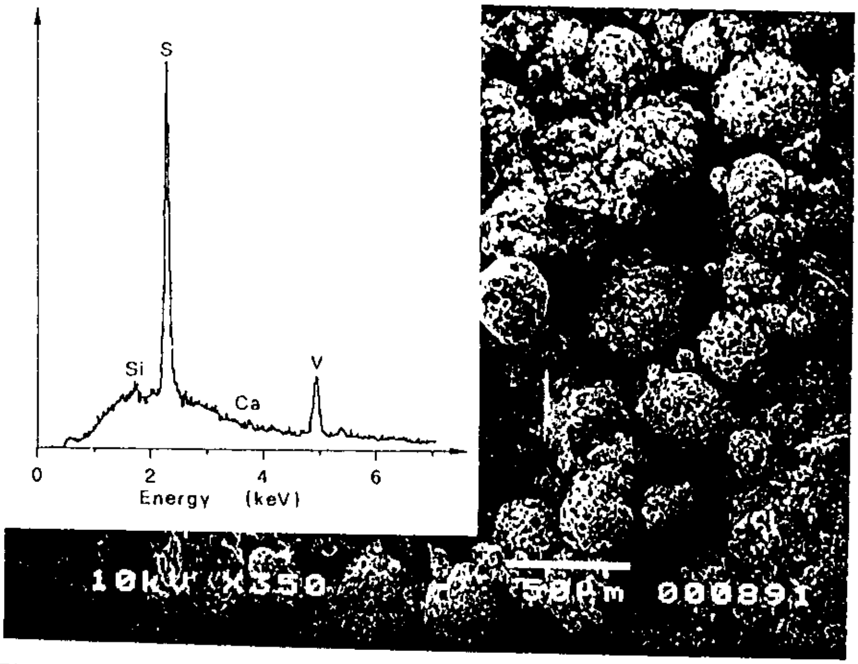

Fig. 1 SEM micrograph and EDS spectrum of the P2 carbonaceous particles utilized in our experiments.

measured on the specimens varied between 30-50 µg. The particle distribution of each stone and mortar specimen was recorded by optical microscopy, showing a homogeneous, low concentration, that does not mask the surface and reduce gas/material interaction.

TESTS — The tests were carried out at an SO_2 concentration of 3 ppm, 25 °C temperature, 100% relative humidity, 0.50 $l\ min^{-1}$ flow gas velocity. The Carrara, Travertine and Trani stones and the lime, pozzolana and cement mortars were exposed blank and with each of the three carbonaceous particles (P1, P2 and P3). The exposure times were 30, 60 and 90 days. After exposure the samples were preserved in an inert environment (UPP nitrogen).

ANALYSES — To quantify the reaction products, concentrations of sulphite and sulphate ions were measured by ion chromatography (HPLC Dionex 4500i). However, some difficulty was encountered in measuring sulphites due to their easy oxidation into sulphates, as confirmed in the literature (Dasgupta [7]).

In this regard a procedure was adopted for the quantification of both sulphite and sulphate ions by HPLC: a) after exposure the samples were preserved in dry N2 UPP; b) a pretreatment of the HPLC column was performed by injection of sodium sulphite solution at 200 ppm concentration; c) the stability of the sulphite solution was studied in order to check its stability range in relation to the total analysis time. The $SO_3^=$ and $SO_4^=$ concentrations in the samples, blank and with particles, for the Carrara, Travertine and Trani stone are reported in Fig. 2 and for the pozzolana mortar in Fig. 3.

The degree of hydration of the sulphur compounds was investigated by x-ray diffraction (XRD) using a Philips PW 1730 diffractometer and by infrared spectroscopy (FTIR) with a spectrophotometer Nicolet 20 SX. XRD peaks were found at 11.8° for S(IV) and 28.5° for S(VI). The characteristic FTIR band for $SO_4^=$ was recorded at 1120-1160 cm^{-1}, while two peaks at 980 and 640 cm^{-1} for $SO_3^=$ were found.

RESULTS AND DISCUSSION

As shown in Figs. 2 and 3, sulphite ion is present in many of the samples analyzed in a concentration which is generally lower although of the same order of magnitude as sulphates. However, our results indicate the importance of measuring sulphites alongside sulphates.

In many papers on laboratory exposure (Johansson *et al.* [2]; Haneef *et al.* [8]) quantifications of sulphite are not reported. In such cases the results should take into account that part of the sulphates derive from sulphite oxidation after exposure or during analysis.

In our tests the lime and cement mortars present an $SO_3^=$ and $SO_4^=$ concentration following a trend similar to the pozzolana mortar reported in Fig. 3. In most cases the three mortars show a higher reactivity compared to the stone samples.

The three types of carbonaceous particles deposited on the carbonate stones and mortars appear to increase SO_2 deposition and the formation of damage products determined as sulphite and sulphate. Furthermore, among the analysed samples, P2 particles present the highest reactivity.

Regarding the degree of hydration of the sulphur compounds found, the XRD and FTIR results agree in indicating the presence of calcium sulphite hemihydrate ($CaSO_3 \cdot 0.5\ H_2O$) and calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$).

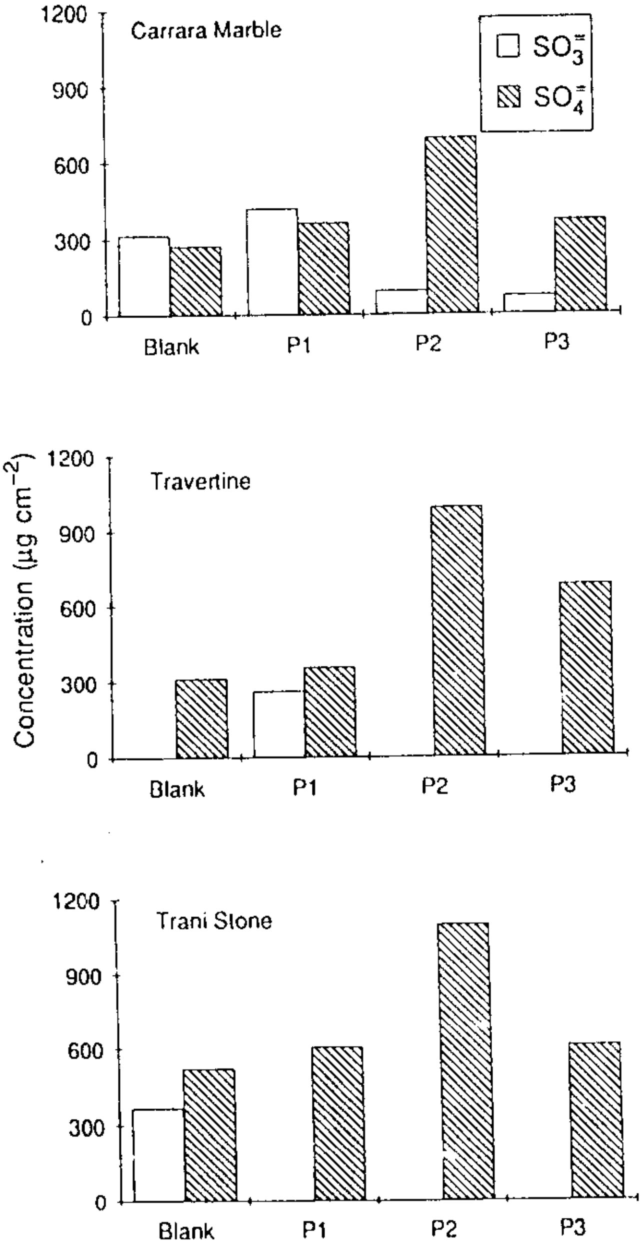

Fig. 2 Sulphite and sulphate ion concentrations (μg cm^{-2}) of the carbonate stones exposed at 3 ppm SO_2 for 90 days blank and with carbonaceous particles.

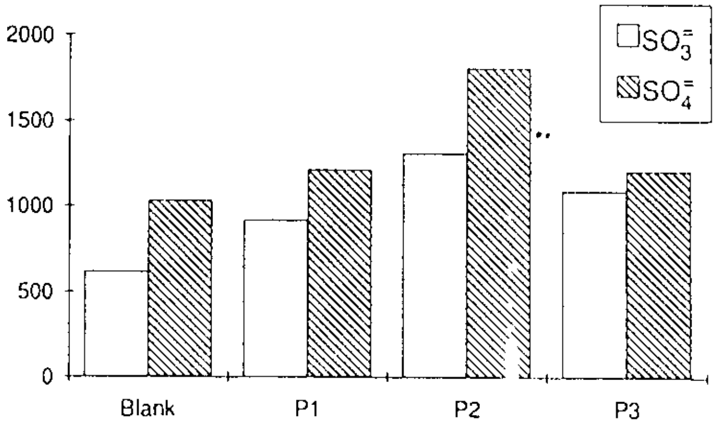

Fig. 3 Sulphite and sulphate ion concentrations ($\mu g\ cm^{-2}$) *of the pozzolana mortar exposed at 3 ppm* SO_2 *for 90 days blank and with carbonaceous particles.*

Gauri [9] and Amoroso and Fassina [10] report calcium sulphite dihydrate ($CaSO_3 \cdot 2H_2O$) as an intermediate product of interaction between SO_2 and $CaCO_3$: this compound was never found on our samples.

According to our results the reactions occurring at the building material surfaces are:

$$CaCO_3 + SO_2 + 0.5H_2O \rightarrow CaSO_3 \cdot 0.5H_2O + CO_2$$

$$2CaSO_3 \cdot 0.5H_2O + O_2 + 3H_2O \rightarrow 2CaSO_4 \cdot 2H_2O$$

Moreover, in the case of cement mortars, concretes and hydraulic mortars in general, the formation of calcium sulphate dihydrate (gypsum) can produce further damage processes. In specific microclimatic conditions the interaction between the original constituents of the hydraulic binders and gypsum leads to the formation of two salts after material consolidation: ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), which produces spalling and cracking (Metha [11]) and thaumasite ($CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O$) causing decohesion of the cement matrix (Crammond [12]).

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REFERENCES

1. Gauri, K.L., and Gwinn, J.A. 'Deterioration of marble in air containing 5-10 ppm SO_2 and NO_2' *Durability of Building Materials*, Vol. 1, pp. 217-223, 1982/1983.
2. Johansson, L.G., Linqvist, O. and Mangio R.E. 'Corrosion of calcareous stones in humid air containing SO_2 and NO_2' *Durability of Building Materials*, Vol. 5, pp. 439-449, 1988.
3. Zappia, G., Sabbioni, C. and Gobbi, G. 'Carbonaceous aerosol on marble and limestone monuments' *J. Aerosol Sci.*, Vol. 22S, pp. 581-584, 1991.
4. Zappia, G., Sabbioni, C., Pauri, M.G. and Gobbi, G. 'Effects of SO_2-enriched atmosphere on ancient and modern building materials' *Materials Engineering*, Vol. 3, pp. 445-458, 1992.
5. Sabbioni, C. 'Characterization of atmospheric particles on monuments by scanning electron microscopy/energy dispersive x-ray analyses' Vol. 2, pp. 773-776, *Proceeding Electron Microscopy EUREM 92*, Granada, Spain, 1992.
6. Del Monte, M., Sabbioni, C., Ventura, A. and Zappia, G. 'Crystal growth from carbonaceous particles' *The Science of the Total Environment*, Vol. 36, pp. 247-254, 1984.
7. Dasgupta, P.K. 'On the ion chromatographic determination of S(IV)' *Atmospheric Environment*, Vol. 16, pp. 1265-1268, 1982.
8. Haneef, S.J., Johnson, J.B., Dickinson, C., Thompson, G.E. and Wood, G.C. 'Effect of dry deposition of NO_x and SO_2 gaseous pollutants on the degradation of calcareous building stones' *Atmospheric Environment*, Vol. 26A, pp. 2963-2974, 1992.
9. Gauri, K.L., Doderer, G.C., Lipscomb, N.T. and Sarma, A.C. 'Reactivity treated and untreated marble specimens in an SO_2 atmosphere' *Studies in Conservation*, Vol. 18, pp.25-35, 1973.
10. Amoroso, G.G. and Fassina, V. *Stone Decay and Conservation* Elsevier, Amsterdam, 1983.
11. Metha, P.K. 'Mechanism of expansion associated with ettringite formation' *Cement and Concrete Research*, Vol. 3, pp. 1-6, 1973.
12. Crammond, N.J. 'Thaumasite in failed cement mortars and renders from exposed brickwork' *Cement and Concrete Research*, Vol. 15, pp. 1039-1050, 1985.