Science and Art: A Future for Stone

Hughes, John; Howind, Torsten

Published: 01/01/2016

Document Version
Publisher's PDF, also known as Version of record

SCIENCE and ART: A Future for Stone

Proceedings of the 13th International Congress on the Deterioration and Conservation of Stone – Volume I

SC16

Edited by
John Hughes & Torsten Howind

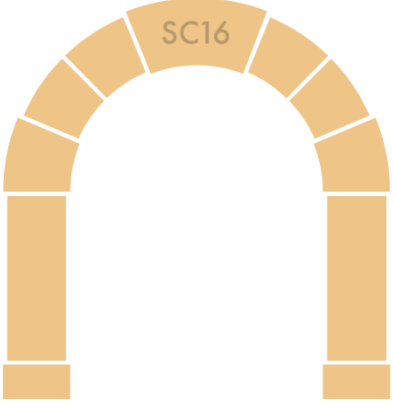
SCIENCE AND ART: A FUTURE FOR STONE

PROCEEDINGS OF THE 13TH INTERNATIONAL CONGRESS ON THE DETERIORATION AND CONSERVATION OF STONE

6th to 10th September 2016, Paisley, Scotland

VOLUME I

Edited by
John J. Hughes and Torsten Howind



UNIVERSITY OF THE WEST of SCOTLAND
UWS

ISBN: 978-1-903978-57-3
ISBN: 978-1-903978-54-2 (eBook)

ISBN: 978-1-903978-59-7 (Set: Volume 1&2)
ISBN: 978-1-903978-56-6 (eBook-Set: Volume 1&2)

Hughes J.J. and Howind T. (Editors), "Science and Art: A Future for Stone. Proceedings of the 13th International Congress on the Deterioration and Conservation of Stone", University of the West of Scotland, Paisley, September 6th to 10th, 2016.

Cover image: The front door of the Paisley Technical College building, now University of the West of Scotland. T.G. Abercrombie, architect 1898. Photograph and cover design by T. Howind.

EXPERIMENTAL STUDY OF THE AGEING OF BUILDING STONES EXPOSED TO SULFUROUS AND NITRIC ACID ATMOSPHERES

S. Gibeaux[1*], C. Thomachot-Schneider[1], A. Schneider[2], V. Cnudde[3], T. De Kock[3], V. Barbin[1] and P. Vazquez[1]

Abstract

During the last few decades, due to remediation procedures, SO_2 emissions in the atmosphere have decreased, unlike NOx. Air pollution has changed. Indeed, the aim of this research is to assess the effect of NOx and their interactions with SO_2 on stones, particularly on limestones used in Champagne-Ardenne (France) during the restoration processes. Three French building limestones (Courville, Dom and Savonnières) and one reconstituted stone were exposed during 28 days to four strong acid atmospheres i.e. two H_2SO_3 solutions with different concentrations and two mixed atmospheres with different proportions of HNO_3 and H_2SO_3. These tests produced an intensive acid attack on the stone, allowing the observation of short-term salt precipitation and the evolution of stone properties. Each day, one sample was removed from the acid atmosphere to measure the concentration of SO_4^{2-} and NO_3^- by ion-chromatography. The surface changes were assessed before and after the tests by 3D scanning and observations with electron microscopy. X-ray microtomography has been performed in the Centre for X-ray Tomography (UGCT) and the Department of Geology at Ghent University (Belgium) in order to observe the penetration of salts and the consequences in stones porosity. First observations showed that exposure to acid atmosphere, led to gypsum efflorescences. Obvious colour changes occurred in all tests. Salt crystallization entailed a change in the porous system, which was evidenced by 3D, mercury porosimetry and X-ray microtomography. Difference between weathered and fresh stone was highlighted by Ion chromatography analyses.

Keywords: acid atmosphere ageing tests, limestone, non-destructive testing (NDT), sulphates, nitrates

[1] S. Gibeaux* ,C. Thomachot-Schneider V. Barbin and P. Vazquez
GEGENAA, University of Reims, France
soizic.gibeaux@univ-reims.fr

[2] A. Schneider
IFTS, University of Reims, France

[3] V. Cnudde and T. De Kock
Dept. Geology and Soil Science, Ghent University, Belgium

*corresponding author

1. Introduction

The 21st century is known as a financial crisis period and an air pollution evolution era (CITEPA 2015). In this context we have to respect sustainability of our monuments choosing the best restoration processes while finding the cheapest solution. The two determining factors to take into account are the choice of the material and the type of environment. One of the most important weathering agent is the dry deposition of gaseous pollutants on stones which results in salt weathering (Török *et al.*, 2004; Charola *et al.*, 2007; Grossi *et al.*, 2007; Monna *et al.*, 2008). Crust formation, blackening, yellowing and carbonate dissolution are the consequences of this phenomenon (Grossi *et al.*, 2007; Monna *et al.*, 2008). Sulphur dioxide is particularly known as the main gaseous pollutant responsible for salt weathering but last decades, ratios in emissions of pollutants have changed with a SO_2 decrease and an increase in NOx). The consequences of these changes in atmospheric composition on the type of salt crystallization are scarcely investigated (Sikiotis and Kirkitsos, 1995; Camaiti *et al.*, 2007; Vazquez *et al.*, 2016) unlike the effects of NOx as catalysts for the SO_2 oxidation (Massey 1999).The alteration processes of the stones also depend on the material characteristics like chemical composition, porosity and texture (Massey 1999; Grossi *et al.*, 1995; Vazquez *et al.*, 2015). The goal of this study is to compare, quantitatively and qualitatively, the reactivity of fresh and weathered stones exposed to different acid atmospheres.

2. Material

2.1. Samples

Three natural stones and one artificial stone were tested. Samples of reconstituted stone and Savonnières limestone are not fresh because they stem from historical buildings, respectively from Orval Abbey (Belgium) and Saint-André Church (Reims, France), unlike the Courville and Dom samples which are fresh stones particularly used in the North of France and the South of Belgium (Fronteau 2000; Thomachot *et al.*, 2011; 2015). These stones present different composition and porosity detailed in Tab. 1.

Tab. 1: Characteristics and composition of the four studied stones.

Stone	**Limestone type**	**Colour**	**$CaCO_3$** wt.%	**SiO_2** wt.%	**Porosity** %	**Named as**
Reconstituted Stone	Lithoclastic	Orange	94.6	1.09	23	RS
Savonnières	Oolitic vacuolar	Grey	90.3	4.90	30	S
Courville	Micritic fine	Russet	86.9	6.64	16	C
Dom	Oolitic to bioclastic	Yellow ochre	96.3	0.68	20	D

2.2. Ageing tests

The dry deposition process was evaluated by means of accelerated ageing tests, based on the standard UNE-EN 13919:2003 procedures (CEN, 2002). They were performed with the atmospheres created by four solutions using nitric and/or sulphurous acids in different proportions (Vazquez *et al.*, 2016) as described in Tab. 2.

Tab. 2: Ageing tests solutions concentrations.

	HNO_3, mol l^{-1}	**H_2SO_3**, mol l^{-1}	**HNO_3/H_2SO_3 ratio**	**Named as**
Solution 1	$4.8\ 10^{-1}$	$1.7\ 10^{-1}$	3/1	$H_2SO_3 < HNO_3$
Solution 2	$1.4\ 10^{-1}$	$5.6\ 10^{-1}$	1/4	$H_2SO_3 > HNO_3$
Solution 3	-	$5.6\ 10^{-1}$	-	H_2SO_3 HC
Solution 4	-	$1.7\ 10^{-1}$	-	H_2SO_3 LC

The stock solution for nitric acid was Panreac 69% w/w M = 14.4 g mol^{-1}, and for sulphurous acid was Panreac 6% w/w M = 6 g mol^{-1}.

Tab. 3: Samples type in function of analysis.

Number of samples	**Size**	**Analysis**	**Analysis frequency**
28		Ion chromatography	One per day
7	1×1×0.4 cm	SEM/EDS	After 1, 3, 5, 8, 15, 22 and 28 days
1	 1×1×2 cm	Hg porosimetry	At the end of the experiment
1	 5×5×1 cm	Macroscopic evaluation Weight 3D scanning	At the end of the experiment
1	 Ø 0.4 cm	X-ray Microtomography	After 1, 10 and 28 days

3. Analytical methods

Dry deposition on stones lead to salt precipitation and stone dissolution. Different technics were used to assess change of the samples (Tab. 2). Photos and images of the upper face were taken with a Nikon Coolpix 4500 and a SEM Hitachi TM-1000 Tab. Top equiped with an EDS. The roughness change was assessed with the ZScan 700Cx device for the 3D scanning and the 3D Reshaper software for the processing of the point cloud with an accuracy of 0.05 mm and a resolution of 0.1 mm. Quantity of NO_3^- and SO_4^{2-} was determined by Ion Chromatography (IC) (Dionex ICS 2000). The high resolution X-ray Computed Microtomography was performed for RS and S tested with $H_2SO_3 < HNO_3$ using the in-house scanner HECTOR (Masschaele *et al.*, 2013) developed in the Centre for X-ray Tomography of Ghent University (UGCT). The tomographs were reconstructed with the Octopus Reconstruction software (Inside Matters, Belgium; Vlassenbroeck *et al.*, 2007), while the reconstructed images were subsequently analyzed using Octopus Analysis, formerly called Morpho+ (Brabant *et al.*, 2011). Porosity characterization was obtained using an Hg intrusion porosimeter (MIP) Micromeritics Autopore IV 9500.

4. Results

4.1. Visual and SEM observations

The observation showed a yellowing of every stone for every test. Only a located blackening of RS and D appeared in the H_2SO_3 < HNO_3 test and slightly in the H_2SO_3 LC test. In the former, white spots arise on C sample. The SEM images highlighted different salt crystal habits (Fig. 1) independently of the time of exposure. Moreover no evolution in the crystals shape or size was detected between the tests or the samples.

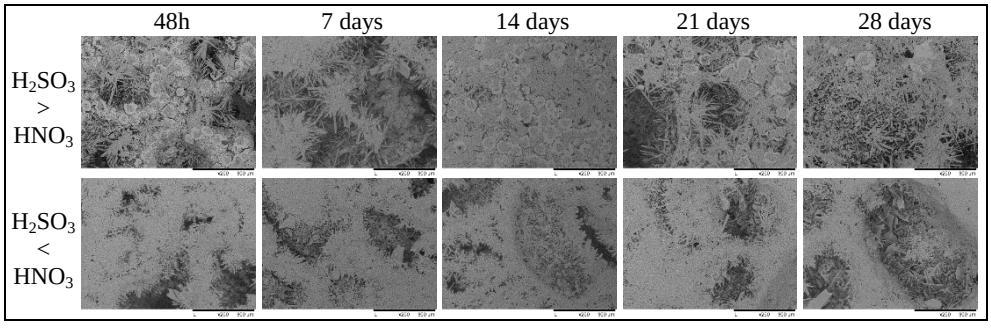


Fig. 1: SEM images of Savonnières sample during the mixed atmospheres tests.

4.2. Weight changes

After the H_2SO_3 < HNO_3 and H_2SO_3 LC tests, the weight gain did not exceed 0.5% with few differences between the stones. The weight gain was notable after the H_2SO_3 > HNO_3 and H_2SO_3 HC tests (from more than 0.5 to 2.0%), the latter with the highest values for all the stones except for S.

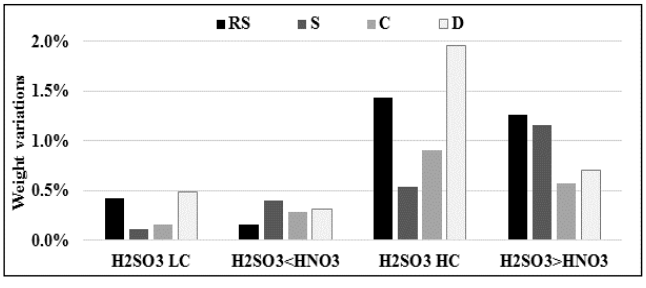


Fig. 2: Weight variations between initial and final states.

4.3. Roughness

Dry deposition created a new surface roughness. No spatial differences were observed among the tests. Fig. 3a showed the numerical subtraction of the surface before and after the tests. Green colour indicated that no change took place on the surface. Salt crystallized mainly in the sample's limits and in preexistent defects and pores (red colour). Dissolution occurred in carbonate grains in the case of RS (blue colour). In other stones, dissolution could be observed disseminated through the surface without a defined pattern.

4.4. X-ray Computed Micro tomography (µCT)

After solely one day of exposure to the H_2SO_3 < HNO_3 test, a homogeneous crust and some areas showing dissolution process appeared on RS and S. After 10 and 28 days, the growth crust was negligible. The fine crust large of around 50µm for RS and 100µm for S seemed to be mainly composed of needle-like crystals (Fig.3b).

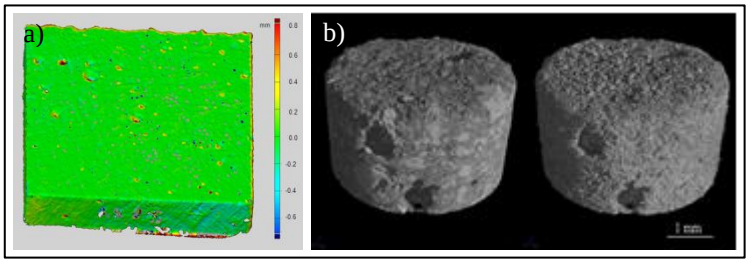


Fig. 3: a) Roughness measurements (subtractions between initial and after test states) on RS after H_2SO_3<HNO_3; b) 3D reconstruction of RS µCT scans before (left) and after 28 days (right) exposed to the H_2SO_3 < HNO_3 test.

4.5. Pore access radii

The total porosity varied slightly, between 0 and 6%, unlike the pore radius access (Fig.4). The volume of pore access radii could increase according to the stone and the test: C for every test except H_2SO_3 > HNO_3, S for H_2SO_3 > HNO_3 and H_2SO_3 HC tests, D for H_2SO_3 < HNO_3 tests. Some pore access radii could also disappear like the macropores of RS and S submitted to H_2SO_3 LC test and those of D submitted to H_2SO_3 LC and HC tests. The H_2SO_3 LC led to the closing of pore access radii of all stones except the Courville stone for which the pore access radii widened (H_2SO_3 > HNO_3).

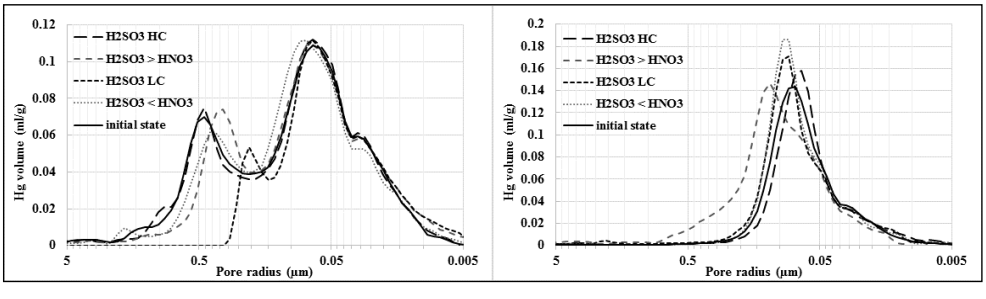


Fig. 4: Pore distribution of RS (left) and C (right) samples before and at the end of the tests.

4.6. Ion chromatography

S and RS were initially S-rich, because they were not fresh stones (from 5000 to 6000 mg/g, Fig. 5). In all tests, the NO_3^- concentration was less than 250 mg/g, therefore negligible if compared to SO_4^{2-} concentration which could reach up to 8000 mg/g. For C and D samples, there was a remarkable increase of the SO_4^{2-} concentration after the first

day, after which the concentration stabilized. The SO_4^{2-} concentration did not change during mixed atmospheres exposures for RS and S samples.

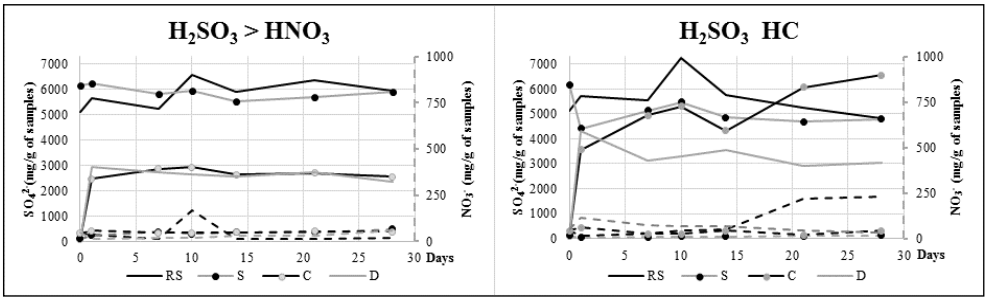


Fig. 5: SO_4^{2-}(solid lines) and NO_3^-(dotted lines) concentrations.

5. Discussion and conclusion

5.1. Type of atmosphere

Every test led to salt efflorescence growth on each stone. It formed a fine and homogeneous crust highlighted by the X-ray computed microtomography. Additionally, 3D measurements revealed the location of crystallization in the stone defects while dissolution occurred mainly at the contact with calcite elements. Weight variations showed the reactivity between stones and acid atmospheres seemed directly linked to the quantity of H_2SO_3 regardless pure or mixed with HNO_3. MIP showed that pure H_2SO_3 atmospheres led to the closing of pore access radii while the mixed atmospheres (H_2SO_3 combined with HNO_3) led to the widening of the pore access radii. The ion chromatography showed the maximum production of sulfates during the first day of exposure regardless the test and the stone. A low quantity of nitrates was measured in both mixed test because of their high instability in water and their hygroscopicity (Cheng *et al.*, 1987). Or nitrates play a catalytic role in the oxidation of sulfur compounds. The variations of SO_4^{2-} concentrations were similar from on test to another for each stone except for Courville limestone. The bad correlation between the weight variations and salts quantity can be due to the difference in size scale of samples.

5.2. Behaviour *of fresh stone and exposed stone*

The presence of sulphates in the initial state of the tested weathered samples did not differ in the degree or type of decay to the fresh ones. The only difference was found in ion chromatography analyses. The initial concentration of sulphates in the initially weathered stones (RS and S) is much higher than in the fresh ones (C, D). However, this high concentration in RS and S remained constant through the whole test, while in C and D sometimes an increase was observed after the first day, and then the concentration kept almost constant.

5.3. Suitable techniques in the study of stone decay by exposure to acid atmosphere

The exposure to an acid atmosphere enriched in SO_2 entailed the formation of a gypsum crust from the very first day of test. The different techniques to assess the evolution of the decay gave rich but varied information about the process. Visual observation gave

information about the general changes on the stone surface, such as colour changes or crystal formation. On one hand, visual observation resulted fast and suitable techniques to evaluate the decay (Vazquez *et al.*, 2015). On the other hand, SEM observations only showed the crystal shapes since the salt crust was formed during the first day. Weight variations give information about the new precipitated crystals. However, this information should be taken with care. Dry deposition in controlled atmosphere involves precipitation and dissolution, two processes that depend strongly on stone properties. A weight gain reflects that salt precipitation was more important than dissolution. To have detailed information about where precipitation or dissolution occurs, 3D measurements is an optimal technique to study the sample's surface (Vazquez *et al.*, 2016), MIP to assess the variation in the pore radii access and the µCT to observe exactly in which grain or pore the process took place (Dewanckele *et al.*, 2012). Ion chromatography gives a general idea about the anion quantity, however, only the strong changes in concentration must be taken into account due to the heterogeneous reactivity of each sample.

References

Brabant, L., Vlassenbroeck, J., De Witte, Y., Cnudde, V., Boone, M.N. and Dewanckele, J., 2011, Three-dimensional analysis of high-resolution X-ray computed tomography data with Morpho+, Microscopy and Microanalysis, 17, 252–263.

Camaiti, M., Bugani, S., Bernardi, E., Morselli, L. and Matteini, M., 2007, Effects of atmospheric NOx on biocalcarenite coated with different conservation products, Applied Geochemistry, 22, 1248–1254.

CEN (EUROPEAN COMMITTEE FOR STANDARDISATION), (2002), "EN 13919: Natural stone test methods. Determination of resistance to ageing by SO_2 action in the presence of humidity", CEN, Brussels.

Cheng, R.J., Hwe Ru, J., Kim, T.J. and Leu, S-M., 1987, Deterioration of marble structures - the role of acid rain, Analitical Chemistry, 59, 104A-106A.

Charola, A.E., Pühringer, J. and Steiger, M., 2007, Gypsum: a review of its role in the deterioration of building materials, Environmental Geology, 52, 339–352.

CITEPA, (2015), "Inventaire des émissions de polluants atmosphériques et de gaz à effet de serre en France", Ministère de l'Écologie, du Développement durable et de l'Énergie. http://www.citepa.org/fr/activites/inventaires-des-emissions/secten.

Dewanckele, J., De Kock, T., Boone, M.A., Cnudde, V., Brabant, L., Boone, M.N., Fronteau, G., Van Hoorebeke, L. and Jacobs, P., 2012, 4D imaging and quantification of pore structure modifications inside natural building stones by means of high resolution X-ray CT, Science of The Total Environment, 416, 436–448.

Fronteau, G., 2000, Comportements télogénétiques des principaux calcaires de champagne-ardenne, en relation avec leur faciès de dépôt et leur séquençage diagénétique, Ph.D. thesis, University of Reims Champagne-Ardenne, France.

Grossi, C. M., Murray, M. and Butlin, R. N., 1995, Response of porous building stones to acid deposition, Water, Air, and Soil Pollution, 85, 2713–2718.

Grossi, C.M., Brimblecombe, P., Esbert, R.M., Alonso, F.J., 2007, Color changes in architectural limestones from pollution and cleaning, Color Research & Application, 32, 320–331.

Masschaele, B., Dierick, M., Loo, D.V., Boone, M.N., Brabant, L., Pauwels, E., Cnudde, V. and Hoorebeke, L.V., HECTOR: A 240kV micro-CT setup optimized for research, Journal of Physics: Conference Series, 463, 1-4.

Massey, S.W., 1999. The effects of ozone and NOx on the deterioration of calcareous stone. Science of the total environment 227, 109–121.

Monna, F., Puertas, A., Lévêque, F., Losno, R., Fronteau, G., Marin, B., Dominik, J., Petit, C., Forel, B. and Chateau, C., 2008, Geochemical records of limestone façades exposed to urban atmospheric contamination as monitoring tools? Atmospheric Environment, 42, 999–1011.

Reddy M.M., 1988, Acid rain damage to carbonate stone: a quantitative assessment based on the aqueous geochemistry of rainfall runoff from stone, Earth Surface Processes and Landforms, 13, 335-354.

Sikiotis, D. and Kirkitsos, P., 1995, The adverse effects of nitrates on stone monuments. Science of the Total Environment, 171, 173–182.

Thomachot-Schneider, C., Gommeaux, M., Fronteau, G., Oguchi, C.T., Eyssautier, S. and Kartheuser, B., 2011, A comparison of the properties and salt weathering susceptibility of natural and reconstituted stones of the Orval Abbey (Belgium), Environmental Earth Sciences, 63, 1447–1461.

Thomachot, C., Gommeaux, M., Vazquez, P., Lelarge, N., Conreux, A., Mouhoubi, K. and Bodnar, J.-L., 7-11 September, 2015, Relationship between Na_2SO_4 concentration and thermal response of reconstituted stone in the laboratory and on site, Proceedings of The WORLD Multidisciplinary Earth Sciences Symposium, Prague, Czech Republic, 456.

Török, A. and Rozgonyi, N., 2004, Morphology and mineralogy of weathering crusts on highly porous oolitic limestones, a case study from Budapest, Environmental Geology, 46, 333-349.

Vazquez, P., Carrizo, L., Thomachot-Schneider, C., Gibeaux, S. and Alonso, F.J., 2016, Influence of surface finish and composition on the deterioration of building stones exposed to acid atmospheres, Construction and Building Materials, 106, 392-403.

Vázquez, P., Menéndez, B., Denecker, M.F.C. and Thomachot-Schneider, C., 2015, Comparison between petrophysical properties, durability and utilisation of two limestones of Paris region, Geological Society of London, Special Issue, 416.

Vlassenbroeck, J., Dierick, M., Masschaele, B., Cnudde, V., Van Hoorebeke, L., Jacobs, P., 2007, Software tools for quantification of X-ray microtomography, Nuclear Instruments and Methods in Physics Research A, 580, 442-445.