Construction and Building Materials 168 (2018) 187–198

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Weathering assessment under X-ray tomography of building stones exposed to acid atmospheres at current pollution rate

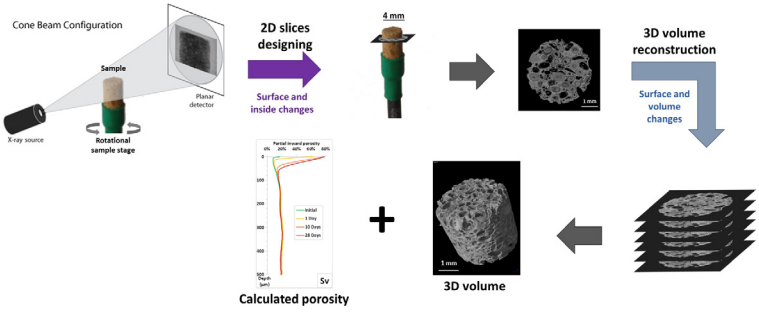
Soizic Gibeaux [a,*], Patricia Vázquez [a], Tim De Kock [b], Veerle Cnudde [b], Céline Thomachot-Schneider [a]

[a] Groupe d'Etudes sur les Géomatériaux et les Environnements Naturels, Anthropiques et Archéologiques (GEGENAA, EA 3795), Université de Reims Champagne-Ardenne, Reims, France
[b] PProGRess – UGCT, Dept. Geology, Ghent University, Gent, Belgium

HIGHLIGHTS

- HRXCT allows to observe the variation in the inner stone microstructure.
- Limestone shows uniform dissolution and artificial stone granular disaggregation.
- HRXCT highlighted the salt crystallization within the porous network.
- Salt crystallization on the surface and inside oolites.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 September 2017
Received in revised form 15 January 2018
Accepted 18 February 2018

Keywords:
Atmospheric SO_2/NO_x pollution
Acid atmosphere
Acid rain
Building stones
Artificial stone
Porosity
High resolution X-ray computed tomography

ABSTRACT

Interactions between the environment and the building stones lead to their alteration, besides water and air pollution play an important role. The link between air pollutants such as SO_2 and stone deteriorations are well known. Last decades the SO_2 emissions have decreased much more than those of NO_x and consequently the SO_2/NO_x ratio reversed until reaching a current proportion of 1/3. In this new environment, we have to adapt our knowledge on ageing and weathering of building stones, particularly to make restorations of historical monuments as sustainable as possible. The aim of this study was to assess the effect of this new ratio of SO_2 and NO_x on the weathering kinetics of building stones. For this purpose, laboratory aging tests were performed simulating acid atmosphere exposure and acid rain runoff. Weathering was assessed by high resolution X-ray computed tomography (HRXCT) on two building materials frequently used as restoration material in cultural heritage buildings in a.o. northern France and Belgium: the oolitic limestone Savonnières and an artificial reconstituted stone made of debris of limestone mixed with a cement in variable proportion. Acid deposition effects were assessed by exposing one sample of each stone to a strong mixed acid atmosphere. Acid rain was simulated by immerging one other sample of each stone type in a mixed acid solution at pH = 5. Each sample was scanned before and after 1, 10 and 28 days of testing. HRXCT allowed to visualize the first steps of acid pollutant attack on the stones' microstructure. The two tests led to different alterations, mainly salt crystallization for atmospheric exposure and dissolution for immersion. After only one day of test, HRXCT scans showed that exposure to mixed acid gas led to salt crystallization preferentially on sample surfaces for both types of stone. The thickness of this salt crust remained stable until the end of the test, after 28 days. The treatment of the reconstructed scans highlighted a dissolution stage which occurred before the crystallization stage. The dissolution produced by the immersion test happened immediately during the first day on the surfaces and the open porosity for both stones, although Savonnières dissolved homogeneously due to its pure calcitic composition, while the reconstituted stone showed granular disaggregation because of its mineralogical heterogeneity.

* Corresponding author.
E-mail address: soizic.gibeaux@univ-reims.fr (S. Gibeaux).

https://doi.org/10.1016/j.conbuildmat.2018.02.120
0950-0618/

1. Introduction

When stones are used outdoors as construction material in buildings or monuments, acid rain and deposition of airborne pollutants are well-known as the major factors in stone alteration processes [1–4]. Both of these processes are directly linked to the pollutants concentration, particularly sulfur dioxide SO_2 and nitrogen oxides NOx.

Pure rain shows an inherent pH around 5.5 and is considered as naturally acid [1]. Thus, rain water induces dissolution and therefore assists in the leaching of the stone surface. The resulting material loss leads to roughness variations and/or granular disintegration depending on the stone texture and composition [2,5,6]. The intensity of dissolution by rainwater depends on two parameters named karst and acidity effects [1]. The karst effect is due to the natural acidity of rainwater, depending on the amount of CO_2. The acidity effect is due to anthropological activities and mainly depends on the sulfuric acid H_2SO_4 and the nitric acid HNO_3 products of SO_2 and NOx oxidation respectively [2,7]. In urban environment, due to fossil fuels used in transports, industrial emissions and heating installations, sulfur dioxide SO_2 has been the main pollutant since industrial revolution and until the 1980s (Fig. 1) [8].

The pollutants emissions are of high importance as it will come in contact and react with the building materials. On the rain sheltered surfaces, water vapor from mists and fogs or condensation can occasionally wet the stone. Thus, the deposition of gaseous pollutants on limestone entails acids production which react with carbonate compounds [7,9–10]. The SO_2 also interacts directly with the moisture on the stone surface and reacts with calcite to produce gypsum which then potentially accumulates in crusts [12,13]. On sheltered and wet surfaces, crusts thickness reaches several millimeters or even centimeters making the underlying rock pulverulent [9].

Gypsum crusts may acquire a black color in urban environment [14–16] and a spongy or cauliflower shape due to the agglomeration of organic compounds [17] and atmospheric particles (soot and fly ash) [16,18,19]. Thus black crusts pattern are frequently observed in urban areas because of the anthropogenic activities and relict of the last century pollution, leading to higher emissions of SO_2, NO_x and particles [20].

The effects of SO_2 on stones has been extensively studied, from early gypsum crystallization [15] to black crusts formation [14], the protective effect of these crusts passing by the aesthetic appearance and the necessity or not of removing them [16]. In the black crust formation, the NO_x present in the environment was considered acting mainly as catalyst and not producing its own reaction with calcite leading to salt crystallization [21].

Last decades, due to the implementation of pollutant emission limitations, the SO_2 emissions decreased highly (Fig. 1) and entail the NOx emissions linked to SO_2 from industrial processes, the NO_2 also appeared during the combustion in diesel motors [9]. The ratio between both pollutants reversed and the NO_x concentration in the atmosphere is now two to four times higher than SO_2 [22].

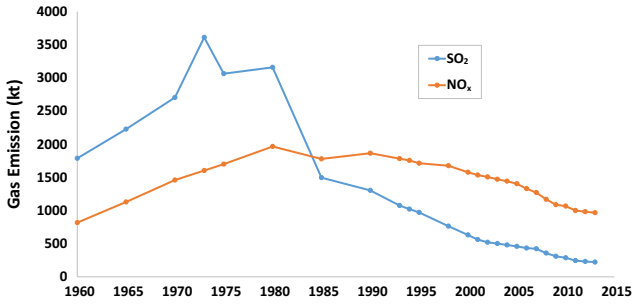


Fig. 1. Atmospheric emissions of the sulfur dioxide SO_2 and the nitrogen oxides NO_x in France from 1960 to 2013. Data from SECTEN national reports [22].

Nitrogen oxides (NO_x) are known mainly as catalysts for SO_2 oxidation [8,21], the oxidation in the gas phase being less important than in the moisture film on stone surface. Moreover the oxidation of SO_2 in the moisture film is more significant than that of NO and NO_2 [10]. Gypsum tends to remain on the stone surface during this substitution reaction [11,12], while nitrates are soluble salts prone to migrate inside the stone [23,24]. Indeed when they crystallize on the surface, Morillas et al. [25] suggest that nitrates come from atmospheric aerosols and in a lesser extent from the NOx oxidation.

Standard ageing tests exist to simulate, control and accelerate the processes of stone decay such as carbonate dissolution and salt formation. Even if these tests do not simulate the conditions of the real environment, they reflect the weathering processes, the type and degree of weathering and they allow to compare the behavior between different stones. In this case, with a changing pollution ratio this kind of test would predict the interaction of the new atmospheres with the stones and could be compared to the results of standard SO_2 ageing tests.

During the exposure to NO_2 or to HNO_3 in laboratory, some studies indicate nitrate salts might crystallize on the stone surface [26] similarly to the salts found in some natural environments [25,27]. In addition, some nitrates could be found in depth within the stone during pure NO_2 and mixed HNO_3/H_2SO_3 atmosphere exposures [4,23]. Vázquez et al. [23] showed that nitrates were also systematically detected after the exposure to a mixed atmosphere, occurring above a mixed acid HNO_3/H_2SO_3 solution, and Haneef et al. [10] revealed that alterations appear faster with mixed acids than with a single component.

If the presence of black crusts may protect the stones from new pollutant decay and limit the access to weathering agents in the porous network [28], fresh stones and recently cleaned ones are more prone to pollution weathering because their surfaces are completely exposed to the environment, and consequently their porous system open to new decay. Currently, the treatment of carbonated stones with hydrophobic products is often not a satisfactory protection toward pollutants [24] that highlighted the crucial need to anticipate their effects on stones.

The aim of this study is to show the effects of the current pollutant ratio (SO_2/NO_x ratio around 1/3) on the stone's degradation paying special attention in the evolution of its microstructure (dissolution, crystallization and decay distribution).

For that purpose, two stones were tested in laboratory conditions: the Savonnières limestone, and the reconstituted stone, an artificial alternative to the natural limestones. These two building materials have been commonly used over the last years for restoration purposes in the north of France and Belgium, mainly as substitute of other weathered Savonnières or other limestones with similar aspect. These stones were exposed to ageing tests based on the EN 13919 standard [29] and other researches [6,23] with modifications to adapt current pollutant ratios. Stone changes were assessed over time by visual observation, SEM assessment and High Resolution X-ray Computed Tomography (HRXCT). The HRXCT is a non-destructive technique that allows to visualize both the decay on the surface as well as within the stone at high resolution.

This technique had been proved to be a powerful tool to investigate a lot of various qualitative and quantitative characteristics such as: (i) shape and sphericity of material components [30], pore infilling, microcrack initiation, dissolution processes [31,32], (ii) porosity (open, closed and partial porosity) and the equivalent