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Influence of surface finish and composition on the deterioration of building stones exposed to acid atmospheres

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HIGHLIGHTS

- Acid atmospheres may cause damage to all types of stones.
- In calcitic stones, the effect of acid atmospheres is related to porosity.
- Intensity of colour change depends mainly on the inherent stone colour.
- Artificial finish influences the acid atmosphere's attack.
- HNO_3/H_2SO_3 ratio controls whether nitrogen compounds react with the stone or acts only as a catalyser.

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ABSTRACT

Six stone types with differences in composition and texture were exposed to four strong acid atmospheres formed from different acids: H_2SO_3, HNO_3, and two mixed solution with different proportions of H_2SO_3 and HNO_3. The changes on the surface were assessed by weight, colour, roughness and microscopic observation. Exposure to the atmosphere formed by HNO_3 hardly affected the stone, whereas these formed from H_2SO_3 produced evident alterations. Depending on the HNO_3/H_2SO_3 ratio, the nitrogen compounds may react with the stone and precipitate nitrates or nitrites or may only act as a catalyser of SO_2 and enhance the formation of gypsum. Colour and roughness are efficient non-destructive approaches to evaluating the damage produced by acid atmospheres.

1. Introduction

Weathering of natural building stones exposed to the environment is a field of study in constant development. The main reason is that the agents of decay, climate and pollution are changing due to technical progress and political choices. One of the remediation procedures for global warming involves the modification of combustibles, producing a different air pollution that leads to different stone weathering processes [1]. In the last century, SO_2 concentrations in the atmosphere have decreased, and thus, the proportion of nitrogen oxides and volatile organic compounds increased in the atmosphere. This also led to an increase in the ozone production in urban air and consequently to oxidation products such as nitrogen dioxide or nitric acid [2]. SO_2 has been the main pollutant involved in the decay of building stones, giving rise to crust formation, yellowing and carbonate dissolution [1,3–7]. In recent times, there has been a strong decrease from high levels of sulphate deposition. Currently, the deposits are dominated by diesel soot and nitrogen compounds that may act as catalysts for the SO_2 oxidation [8].

Stone decay generated by mixed gases has been demonstrated to be faster than decay induced by a single gas [9–11]. Stones exposed to a mixture of NO_2, SO_2, O_3 and H_2O show higher degradation rates than those exposed to SO_2 and NO_2 individually [8,12]. The role of metal oxides in the oxidation reactions is, however, under discussion [8–11,13]. On a dry surface exposed solely to

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SO_2, the gas phase oxidation from SO_2 to SO_3 is slow, whereas for a surface exposed only to NO_x, the conversion from NO_2 to NO_3 is fast. On a dry surface exposed to the mixed gases $SO_2 + NO_2$, the oxidation of SO_2 to SO_4^{2-} is 10 times greater than that for exposure to only SO_2, whereas the oxidation of NO_2 to NO_3^- is 0.4 times less than that of exposure to single NO_2. This confirms that the reaction with stone is dominated by the oxidation of SO_2 compared with the oxidation of NO_2. However, NO_2 can enhance SO_2 absorption without producing nitrates, acting as catalysts and increasing the decay produced by SO_2 pollutants [14]. Nitrogen oxides have been mainly studied from the point of view of their action as SO_2 oxidants. The interaction between NO_x and the stone surface is less known [15,16].

The effect of pollutants on stone decay is related to its nature and the inherent characteristics of the stones such as composition, texture or porosity [8,11,17–20]. Moreover, artificial features such as surface finish lead to different surface topographies and consequently to different decay characteristics [17,21,22]). There are also differences between the SO_2 absorption in calcite and dolomite [16,23,24]. Calcareous stone reacts with acid pollutants via dissolution. Sulphur and nitrogen salts crystallise on the surface [17,21,23]. Sandstones with carbonate as fragments, cement or clays are also vulnerable to acid attack. The texture of the stone, especially the grain boundaries, may enhance the crystallisation process [24] or the weight loss when exposed to acid rain [25]. Sandstones are vulnerable to air pollutant attack due to their porosity, even if they have low or negligible carbonate contents. Open porosity allows the airborne particles and gazes (SO_2, O_3, NO_x) to enter within the stone and interact with its components. Pore distribution and specific surface area influence the uptake of moisture from the air. High specific surface area implies high moisture content, which will favour dry deposition. Dry deposition could be important in the case of NO_2 deposition, as NO_2 is less soluble than SO_2 [26].

Acid atmospheres produce chemical and physical changes on the stone surface, potentially reaching depths of a few millimetres. As a result, surface properties such as colour and roughness will provide precious information about the degree of the decay. Colour is one of the most representative features of an ornamental stone. Consequently, the colour variations produced by chemical reactions during pollutant exposure have a priority over the evaluation of the decay [e.g., 27–29]. The contaminants studied to date produce yellowing or blackening of the stone. However, the effect of the new proportion of pollutants is less well known, and consequently, so is the colour change. Another parameter closely related to surface decay is roughness. Surface roughness varies due to erosion, dissolution and/or precipitation, providing information about the intensity and the types of decay [30–34], and this is sometimes also related to colour [35]. In addition, surface roughness increases the exposed surface area, trapping more gas and particles [22], and the deterioration process may be enhanced by the increase in surface roughness [17,21].

Ageing tests are used in research to simulate stone decay. These tests do not allow a real comparison between the decay produced in the laboratory and in the real environment. Nevertheless, they are extremely helpful for comparing the durability between different stones and to determine which stone characteristics influence the type and degree of decay, as well as which types of interactions between the stone and the weathering agent take place. In relation to the study of stone decay by pollutants, the standard UNE-EN 13919 [36] is an optimal test for research aims. This test produces an intensive acid attack on the stone, allowing observation in the short-term of the precipitation of salts [28,34] and the evolution of stone properties [37].

The general aim of this research is to evaluate the impact of mixed acid atmospheres on the surfaces of different stones by colour and roughness measurements. Six porous stones with different compositions (three limestones, two sandstones and one dolostone), commonly used as ornamental stones, were tested. The samples were prepared with two different finishes, one smooth (polished) and another rough (bush hammered). The strong atmospheres were obtained from single H_2SO_3, single HNO_3, and two mixed atmospheres with different proportions of H_2SO_3 and HNO_3. This study is intended to shed light on (i) the impact produced by new mixes of pollutants, (ii) the effect of different acid atmospheres on stones with different mineralogies and textures, and (iii) the influence of surface finish on the deposition of pollutants on the surface.

2. Materials and methods

Six stones were selected in relation to their composition and texture. Three of them were pure calcareous stones, showing differences in their textures: Albox travertine (AT), Fraga limestone (FL) and Santa Pudia limestone (SPL). The other three stones, which exhibit differences in composition, were Boñar dolostone (BD), Uncastillo sandstone (US), and Villaviciosa sandstone (VS). For future explanations in terms of composition, the three limestones were named "pure calcitic stones", and the group formed by the dolostone and the two sandstones was called "other sedimentary stones". Two surface finishes were selected in this study: polished and bush hammered finish.

2.1. Methods for the characterisation

The characterisation consisted of a petrographic description of the materials and a surface evaluation by means of colour and roughness measurements. Mineralogy and texture were studied using polarised optical microscopy (Zeiss Jenapol POM). Pore system parameters were obtained using a Hg intrusion porosimeter Micromeritics AutoPore III 9410, which reaches 414 MPa pressure and can measure pore radius sizes from 0.003 to 360 µm. All of the data were extracted from previous studies [38,39].

Colour was measured and quantified with a MINOLTA CR-200 colourimeter using the illuminant D65, a beam of diffuse light of 8-mm diameter, and a 0° viewing angle geometry, with a specular component included and the spectral response closely matching the CIE (1997) standard observer curves. Measurements were expressed following the CIE L^* a^* b^* systems (EN ISO 105-J03: 1997) [40]. L^* is the lightness that goes from black (value 0) to white (value 100), a^* goes from red (values up to +60) to green (values up to −60), b^* goes from yellow (values up to +60) to blue (values up to −60). ΔE^* is introduced as the total colour change, to compare the variations before and after the tests as follows: $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$. The determination of the colour in a heterogeneous material requires a previous study of the number of measurements needed, which is related to the colour of each mineral, grain size and heterogeneity [33,34]. The number of data points was determined by calculation of the cumulative average until the stabilisation of the values. In this study, 15 data points were the minimum required in each stone group (i.e., 5 measurements × 3 slabs).

Surface topography and roughness were measured using a stereomicroscope Leica MZ16A and the associated software Leica Stereo Explorer 2.1. The resolution is 840 Lp/mm, which provides enough accuracy to detect small surface variations. The maximum vision diameter is 57.5 mm, so a representative surface of the stone can be measured. This equipment uses visible light, which attenuates the irregular reflections and refractions of lasers in the presence of quartz. Prior studies determined an optimal area of measurement of 25 × 18 mm. Area roughness parameters were computed from an average of three areas in which twenty 2D profiles, with a spacing of 1.25 mm were measured, following the standard EN 4287 [41]. A cut-off length Gaussian filter was applied to evaluate only the roughness wavelengths. This cutoff allows focusing the analysis on the deterioration and not on the slab shape. The following parameters were selected to define surface roughness.

– Ra: *Arithmetical mean deviation*. Arithmetical mean of the absolute values of the deviations (Zi) from the mean line.
– Rp: *Maximum peak height*. The maximum value of the deviations (Zi) from the main line.
– Rv: *Maximum valley depth*. The absolute value of the minimum value of the deviations (Zi) from the mean line.
– *Bearing area curve*. Cumulative height distribution curve from the mean profile. The curve is plotted with a normalised abscissa from 0 to 100% of the profile length. The ordinate indicates the percentage of area analysed from the highest peak to the deepest valley.

A parameter that takes into account the whole surface, without the application of the filter, was also obtained: