KINETICS AND SURFACE ALTERATION OF LIMESTONE: IMPACT OF ACID SOLUTIONS ON THE SURFACE FINISHES OF MONUMENTAL STONES

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Abstract

Stone-cutting marks left on architectural stones are essential for preserving the authenticity of craftsmanship. These surface finishes, tangible witnesses of historical events, traditional construction practices and tooling techniques, embody cultural and technical aspects of intangible heritage.

Although stone is traditionally considered as a durable and permanent, it is not immune to deterioration and undergoes irreversible physico-chemical deterioration caused by environmental interactions. The Nara Document on Authenticity (1994) acknowledges that both natural and anthropogenic material alterations is part of the monuments' authenticity as well as the material itself, even if the most delicate aesthetic details gradually fade over time. The increasing impact of climate change, including acid rain and pollution, accelerates stone decay, raising concerns about heritage preservation. Acidic compounds from environmental and anthropogenic sources, like acid rain, maintenance products or biological colonisation, significantly contribute to limestone deterioration.

This study investigates the alteration of the Belgian Blue Stone, widely used in Belgian architectural heritage, under the influence of acidic conditions, focusing on three common surface finishes. Laboratory simulations assess weathering kinetics and material loss, initially assessing exposure to household acids to develop a controller system and refine the protocol. 3D optical profilometry quantifies surface roughness and specific surface areas. On saw-cut surfaces, the dissolution of the calcite matrix exposes fossils, increasing roughness, whereas initially rougher surface finishes (pitted, Antique) evolve differently. Comparing exposed and unexposed surface finishes using controller system provides insights into the long-term degradation processes and evolution of roughness, the role of initial texture and deterioration kinetics.

Keywords: Acid solutions, Belgian Blue Stone, Stone-cutting finishes, Acidic Reaction and Alteration Kinetics, Surface Roughness and Area

1 Introduction

Architecture and Built Heritage rely on a wide range of materials. Among these, stone has held a prominent place since at least 4700 BCE (Pereira and Marker, 2016) and remains a major structural element in many historical monuments. It is widely used in the construction of religious, civil, funerary, leisure, and military buildings all over the world. In architecture, the heritage value of an object is closely linked to its surface condition (Molina et al., 2020). However, monuments and the materials that compose them are exposed to weathering due to acid rains, a degradation phenomenon that has developed more intensively with industrial growth. Limestone, which is rich in calcium carbonate ($CaCO_3$), is particularly sensitive to these acidic conditions (Basu *et al.,* 2020). Water plays a fundamental role in the weathering of stone through its physicochemical interactions with the constituent minerals. Its acidity depends on the transport of atmospheric particles, such as SO_X, NO_X, dust, and carbon compounds. Today, the main source of acidification is carbon dioxide (CO_2) present in the atmosphere (IPCC, 2023). When dissolved in rainwater, these acidic compounds accelerate the dissolution of limestone materials, which are frequently used for façades, cornices, and sculptures. The origin of acidic agents varies: they can be atmospheric, biological – such as oxalic acid produced by lichens (Török *et al.,* 2010) – or result from the use of inappropriate maintenance products.

The interaction between the stone surface and these external agents alters its finish, affecting its physicochemical, mechanical, and aesthetic properties. This surface finish depends on the characteristics of the rock, its exposure to specific environmental weathering factors, and the type of marks left by stonemasons for functional or aesthetic reasons. The progressive weathering of stone-cutting finish surfaces presents a challenge for material conservation and raises questions about the authenticity and values attributed to the material, and by extension, to the monument to which it belongs. This notion of authenticity is widely debated in the field of heritage conservation. It is based on cultural and historical criteria

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(ICOMOS, 1994; Winter, 2014), notably with the case of the European vision. So, studying the evolution of weathering does not only allow the quantification of material loss through a before-and-after comparative approach (Jones and Yarrow, 2013) but also provides insights into the degradation processes that affect the legibility of traces left by craftsmen.

These imprints left by stonemasons on the surface testify to their craftsmanship and the use of tools on the stone surface (UNESCO, 2003). Preserving these marks is essential for transmitting traditional techniques to future generations and safeguarding the collective, social, and architectural memory of buildings (Jones and Yarrow, 2013; Yarrow and Jones, 2014; Kevat et al., 2024). Indeed, stone carving/cutting represents an intersection between tradition and innovation. As a traditional craft, stone cutting contributes to the authenticity of buildings, as highlighted in the Nara Document on Authenticity (ICOMOS, 1994). Furthermore, stone cutting serves as a temporal and spatial indicator of architectural practices, with each period and region associated with particular techniques (Doperé, 2018).

This study investigates the susceptibility to weathering of different limestone surface finishes subjected to an acidic environment. The research focuses on stones used in Belgian monuments and recognised by the Heritage Stone Task Group, namely Belgian Blue Stone (BBS, Kupper, 1975 ; Pereira et al., 2015). An experimental approach is developed to assess the evolution of surface finishes induced by weathering and to better understand the interactions between three surface finishes and their degradation processes.

2 Materials

Belgian Blue Stone (BBS) is a Carboniferous grey-bluish crinoidal limestone, mainly extracted in the Hainaut region and around the Ourthe valley in Belgium (Tournaisian-age). It is composed of 96% to 99% of microcrystalline calcite, fossils (crinoids) but also some quartz, dolomite, pyrite and other minerals in less proportion. The open porosity is less than 1% and its density is 2689 kg/m³ (Buildwise and De Barquin, 2001).

BBS is used in various configurations as well indoor and outdoor in different orientations, such as worktops, flooring, or vertical façades. Three common machine-finished surfaces were selected to highlight distinct behaviours (Figure 1):

- A saw-cut sample (A) in natural bed orientation and on which the stratification is highlighted by a stylolithic joint, a kind of natural discontinuity resulting from dissolution under pressure.
- A pitted cutting sample (B), which is a finer type of bush-hammering.
- An Antique cutting sample (C), where the surface exposed to acidic agent has vertically oriented bedding planes. The Antique cutting features randomly carved mechanical tool strokes, with stripes parallel or slightly inclined to the edges.

The samples were sourced directly from the quarry and not previously exposed to construction or atmospheric conditions. As a preliminary study, one representative sample per surface finish was selected and altered ten times, as detailed below.

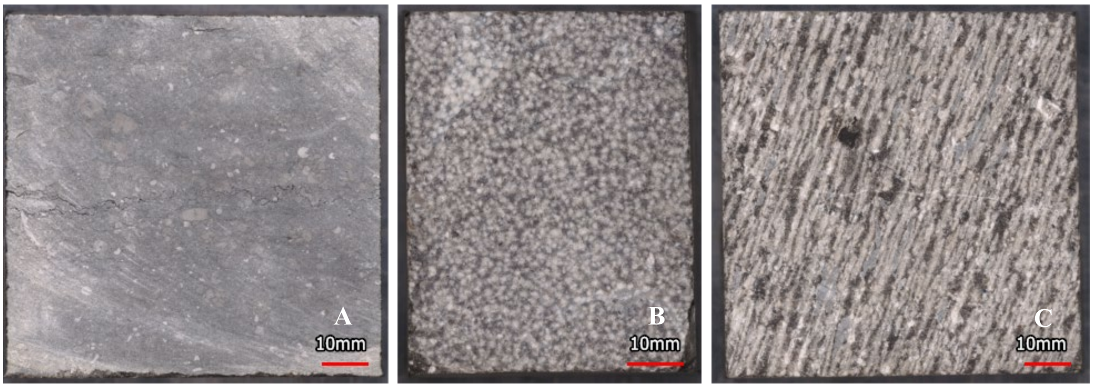

Figure 1 : (A) Saw-cut sample – (B) Pitted cutting sample – (C) Antique cutting sample carried out mechanically

3 Methodology

3.1 Weathering test - Partial immersion of a finished surface in acidic solution

Our weathering test is based on partial immersion of a finished surface in acidic solution (Figure 2). In order to understand the behaviour of a finished surface in contact with the acidic solution, only a portion of each sample surface is immersed (contact surface: ∅ =32mm) by means of a sealed tube and monitored during the test. This approach allows for the presence of a reference surface and an altered part on the same sample, enabling direct comparison.

Tests with an artificial acid rain solution require long exposure times and frequent solution replacement, as reported in previous studies (Molina-Piernas *et al.,* 2013; Eyssautier *et al.,* 2016; Vázquez *et al.,* 2016; Gibeaux *et al.,* 2018; Molina *et al.,* 2020). Before conducting such tests, in this study, the BBS is exposed to an acetic acid solution (7%, CH_3COOH, pH 2.44) to accelerate the weathering process and determine the sensitivity of the surface relief to acidic exposure. In addition, it allows to investigate the weathering kinetics of this stone and the effects of a different type of acid commonly found in maintenance products.

To capture the alteration process induced by acetic acid, the immersion was performed in ten successive phases of 15 minutes each. During immersion, the pH evolution was continuously monitored to maintain a consistent acidic attack on the stone using a pump system, if necessary, managed by a 32-bit microprocessor Arduino UNO R4® (Figure 2). Between each phase, the samples were rinsed with distilled water to prevent salt crystallisation on the surface, which could affect roughness analyses. This also ensured a continuous alteration process.

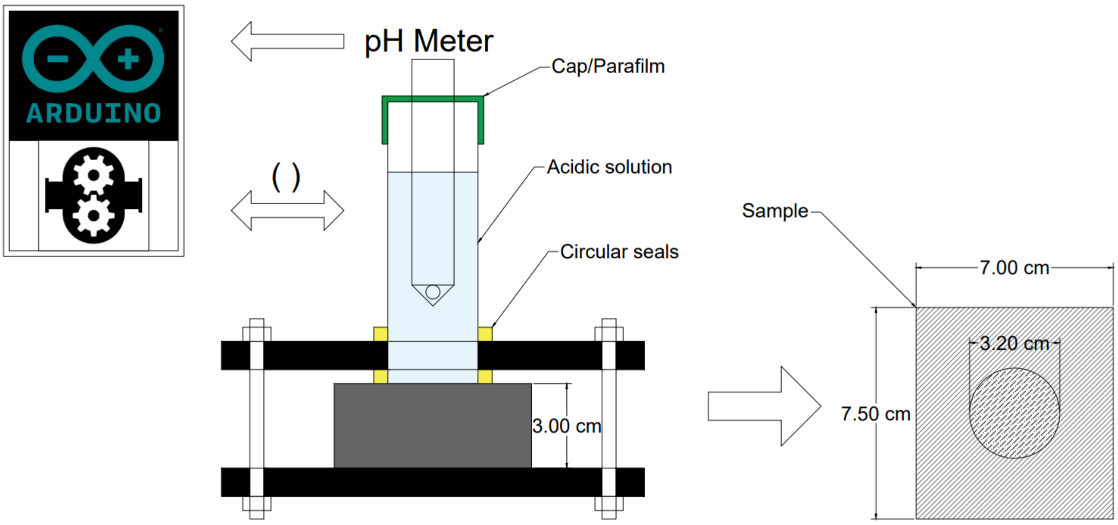

Figure 2 : Experiment configuration.

3.2 Weathering evaluation - Roughness and surface area

A 3D optical profilometer Keyence Serie VR-6200 provides 3D scans of the entire sample surfaces between each test phasis, without any surface modification. The profilometer has a resolution of ± 4µm in z and ±5µm in x and y directions. A linear light projection of fringes (LED) strikes the object diagonally (right/left to minimise errors) and reveals the height differences on the analysed surface, by deformation of the projected image of the fringes. The analysis module offers more than 30 statistical roughness estimators, most of which are proposed in the ISO 4287 (1997) and ISO 25178 standard.

S_a (Arithmetic Mean Surface Roughness) represents the mean absolute deviation of the measured surface profile from a reference mean surface [µm]. This parameter provides a general indication of the roughness level without distinguishing between extreme peaks and valley.

$$S_a = \frac{1}{A}\iint_A |Z(x,y)|dxdy \ [\mu m] \quad (1)$$

where:

A is the surface area considered

$|Z(x,y)|$ is the Z coordinates of each (x,y) point of the surface

S_z (Maximum Surface Roughness Height) represents the difference between the highest peak and the lowest valley within a given surface profile. This parameter is particularly useful for detecting depressions or raised features that may accelerate material degradation by increasing the surface area in contact with liquids, gases, or other environmental factors**.**

$$S_z = S_{Peak} + S_{valley} \ [\mu m] \quad (2)$$

where:

S_{Peak} is the maximum surface height

S_{valley} is the minimum surface height

Two other parameters are explored in this research: the **Surface Area** which is an indicator of the texture and roughness of a 3D surface [mm²] and represents the actual surface area in contact with liquids, gases, or other environmental factors; and the projected surface **Cross Sectional area (C.S area)** [mm²].

4 Results

The tested samples have different initial surface finishes that can be quantified by the roughness estimates described in section 3.2. Before exposure, the surface area of A is very close to its projected cross-section area, approximately 804 mm². The surface area of B and C is initially slightly higher than A (about 6%). (A) being the least rough surface, its parameter $S_{a\ init\ mean}$ (A) is lower than the two others initial surfaces (B) and (C) (Figure 5).

Tableau 1 : Sa and Sz parameters for the initial phase

	Sa Average (std.DV) [µm]	Sz Average (std.DV) [µm]
Sawn (A)	3,85 (0,92)	58,25 (15,66)
Pitted (B)	67,52 (7,44)	503,54 (33,16)
Antique cutting (C)	91,51 (12,33)	664,71 (122,73)

Figure 3 shows, for each stone finish, the evolution of the surface between the initial situation and up to 10 phases of partial immersion. The dissolution process of calcite by acetic acid follows the reaction:

$$CaCO_3 + 2CH_3COOH \rightarrow Ca(CH_3COO)_2 + CO_2 + H_2O \quad (3)$$

All samples dissolve progressively, and their average surface lowered approximately by 0.3mm after 10 phases (Figure 4). In Figure 3, the dissolution seems more rapid for (A) with 0.04mm depth of loss between P0 and P1 than for the other two surface finishes (B) and (C) because of their initial roughness. A progressive change was really observed after P2-P5, followed by the exposure of fossils and a subsequent textural change at P10. For (B) and (C), Figure 4 provides typical profiles after 10 phases. They seem to include a higher frequency content that superposes on the overall lowering of the immersed surface.

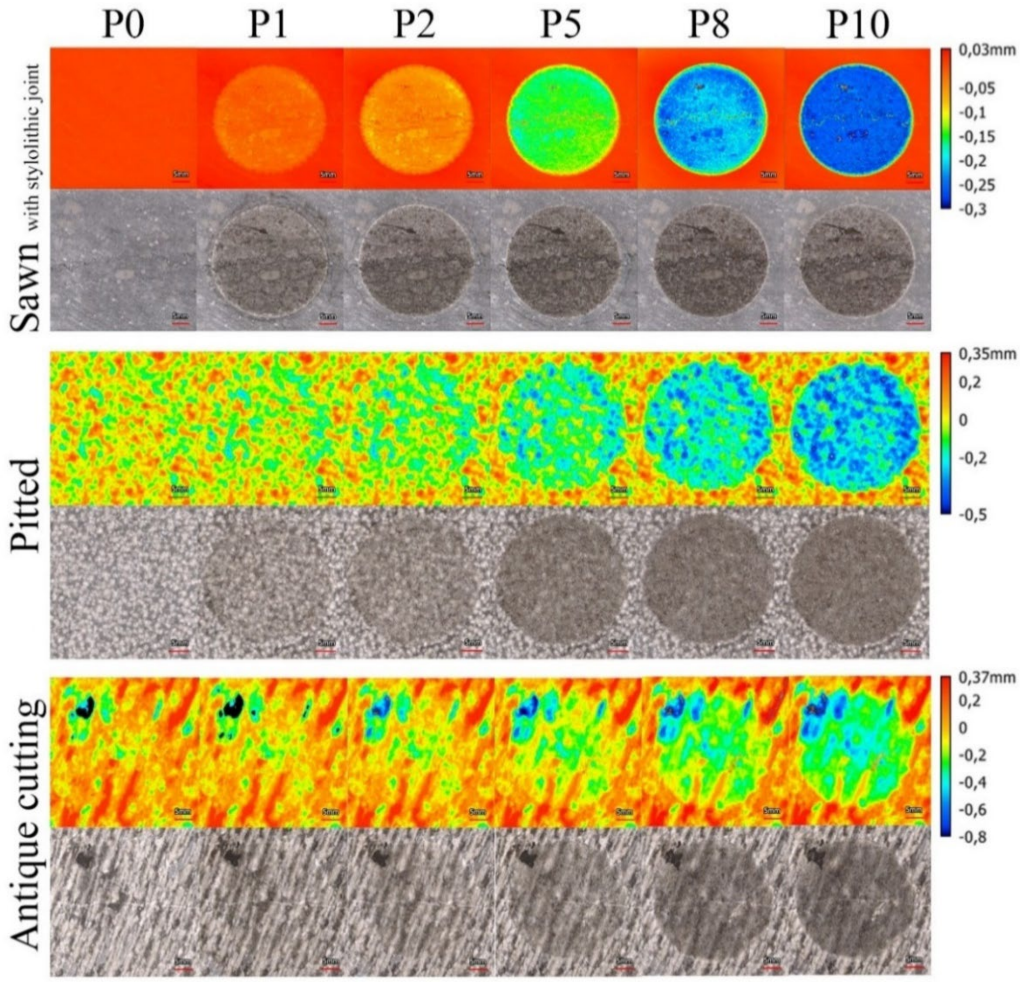

Figure 3 : Height range and optical image of each type of finished surfaces obtained with 3D optical profilometer (Sawn (A), Pitted (B), Antique cutting(C)). The diameter of the tested area is 32mm.

An increase in the surface area was observed for all three samples over successive alteration phases (Figure 3). Upon contact with acetic acid, the (A) sample becomes rougher, and its area increases, with peaks and valleys becoming more pronounced. The ratio of surface roughness $S_a/S_{a\ init}$, (Figure 5), follows a linear trend y = 0.581x + 1 (R^2=0.9636). The evolution of (B), though less exacerbated, also follows an increase of Sa with time. Sample (C) shows an opposite trend: its surface area does not really change during the tests, but its roughness Sa decreases (Figure 4). It is due to the stripes which are affected by the acidic action and tend to vanish.

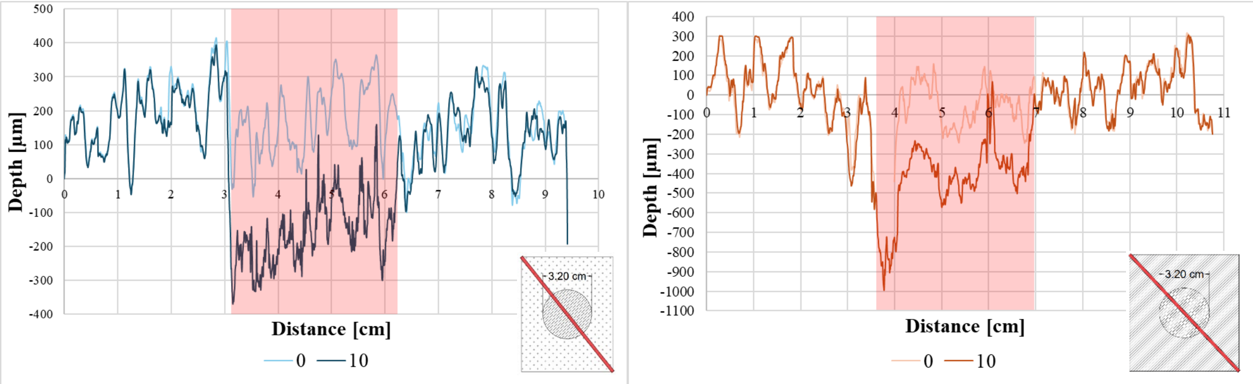

Figure 4 : Comparison of initial (P0) and final (P10) profiles for Pitted cut (left - B) and Antique cutting (right - C)

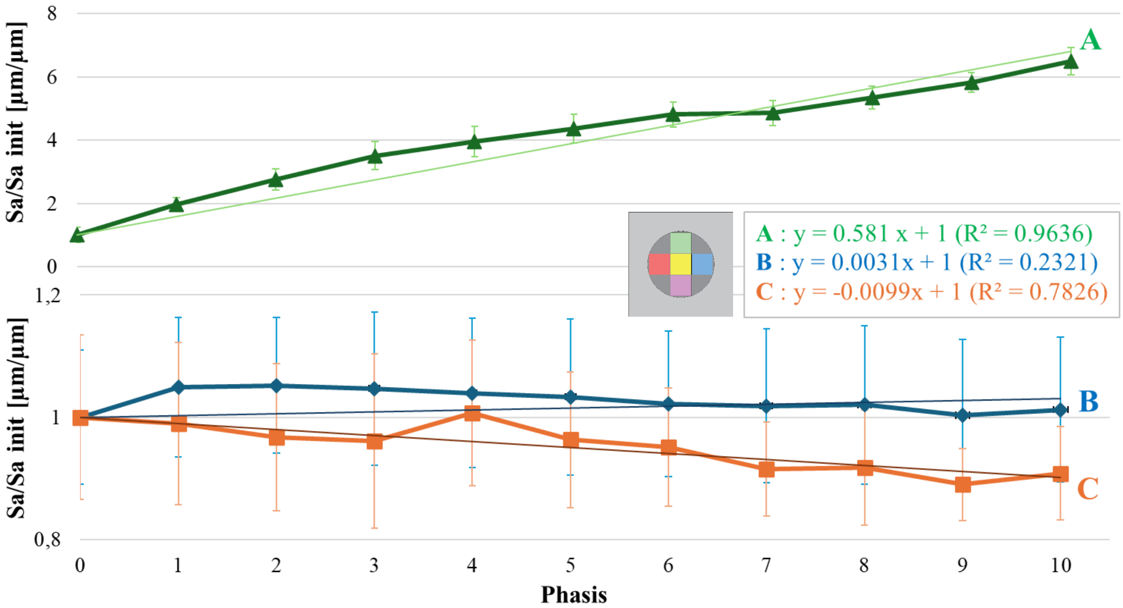

Figure 5: Evolution of surface roughness, normalised to the initial surface roughness, for each cut type, with variability shown across five equally sized surfaces (coloured squares) per sample. (A: Saw-cut/B: Pitted cutting/C: Antique cutting)

5 Discussion

The evolution of roughness differs among the surface finishes and micro-texture. The initially less rough saw-cut (A) and pitted (B) surfaces exhibit an increase in roughness and increased surface area exposed to acids. While the Antique cutting (C), which had a more developed initial texture, tends to reduce its average roughness after exposure. A hypothesis regarding the differential evolution of surface roughness between (B) and (C), we might observe a threshold between the two where roughness transitions from more to less rough. This suggests that once the original finish is altered, the surface stabilises to reflect the intrinsic characteristics of the stone. Stylolites and fossils emerge more prominently on (A) surface, indicating differential attack depending on the stone's microstructure and micro-texture in contact with acid solutions. The observed degradation also appears to correlate with stratification and bedding orientation, particularly in the saw-cut (A) sample. In (A), a stylolithic joint remains almost unaffected due to its mineralogical and chemical composition. Indeed, styloliths are enriched in clays, iron oxides, and organic matter, making them less prone to dissolution. Differences in mineralogical composition and compaction on either side of the stylolithic joint, as indicated by colour variations.

A particular attention must be paid to the 3D scan, an increase in S_z parameter and surface area significantly across successive alteration phasis suggests a progressive disparity between the highest and lowest points of the surface. This evolution can be attributed to several factors, including the non-dissolution of the stylolithic joint or the localised crystallisation of soluble salts observed on the saw-cut (A) surface despite rinsing with demineralised water. These crystallised deposits contribute to the surface relief, amplifying roughness variations.

6 Conclusion

This research contributes to assessing the behaviour of different surface finishing techniques under acidic conditions and evaluating whether initial roughness influences long-term resistance to weathering. The results highlight the role of surface finishings, texture, rock's anisotropy and heterogeneity in the alteration process, demonstrating that the exposure of the stone's texture significantly affects its degradation dynamics.

Although the material loss remains relatively low, around 0.3mm after 10 phases, this loss has a great impact on the stone's surface state and authenticity. Indeed, the finishing marks, originally shaped by the tools, progressively fade and are replaced by a profile dictated by alteration rather than craftsmanship. This compromises the readability of the original cutting techniques and modifies the stone's historical and aesthetic value.

Future tests will involve different acid solutions and surface finishes to refine the understanding of alteration mechanisms. Experiments with nitric and sulfuric acid, as present in synthetic acid rain, indicate similar reactions; however, the nature and solubility of the reaction products differ. The study will also extend to manually carved surfaces and historical stone finishes to assess their long-term behaviour.

References

Basu, A., Ram, B., Nanda, N., and Subhadeep Nayak, S., 2020, Deterioration of shear strength parameters of limestone joints under simulated acid rain condition, International Journal of Rock Mechanics and Mining Sciences, 135, available: https://doi.org/10.1016/j.ijrmms.2020.104508.

Buildwise and De Barquin, F., 2001, La pierre bleue de Belgique dite petit granit d'âge géologique tournaisien. NIT 220, 58p., available: https://www.buildwise.be/fr/publications [accessed 25 Jan 2024].

Doperé, F., 2018, Dater les édifices du Moyen Âge par la pierre taillée, Collection Précisions, Bruxelles: Éditions Safran.

Eyssautier, S., Marin, B., Thomachot-Schneider, C., Fronteau, G., Schneider, A., Gibeaux, S., and Vázquez, P. (2016) Simulation of acid rain weathering effect on natural and artificial carbonate stones, Environmental Earth Sciences, 75, available: https://doi.org/10.1007/s12665-016-5555-z.

Gibeaux, S., Thomachot-Schneider, C., Eyssautier, S., Marin, B., and Vázquez, P., 2018, Simulation of acid weathering on natural and artificial building stones according to the current atmospheric SO2/NOx rate, Environmental Earth Sciences, 77, available: https://doi.org/10.1007/s12665-018-7467-6.

ICOMOS, 1994, Document de NARA sur l'authenticité (1994), available: https://www.icomos.org. [accessed 30 Jan 2025].

IPCC, 2023, Climate Change 2023: Synthesis Report, IPCC, Geneva, Switzerland: Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, H. Lee and J. Romero (eds.)], 35–115, available: https://doi.org/10.59327/IPCC/AR6-9789291691647.

Jones, S. and Yarrow, T., 2013, Crafting authenticity: An ethnography of conservation practice, Journal of Material Culture, 18, 3–26, available: https://doi.org/10.1177/1359183512474383.

Kevat, R., Patel, A., Solanki, J., and Patel, C., 2024, Comparative Analysis of Human vs. Machine Stone Polishing Techniques: A Comprehensive Study on Cost, Productivity, Health, and Risk Management, International Research Journal on Advanced Engineering and Management (IRJAEM), 2, 2488–2490, available: https://doi.org/10.47392/IRJAEM.2024.0358.

Kupper, M., 1975, Recherches dans la région liégeoise (Belgique) sur l'altération des pierres calcaires exposées à l'air libre, Annales de la Société Géologique de Belgique, T. 98, 165–176.

Molina, E., Arizzi, A., Benavente, D., and Cultrone, G., 2020, Influence of Surface Finishes and a Calcium Phosphate-Based Consolidant on the Decay of Sedimentary Building Stones Due to Acid Attack, Frontiers in Materials, 7, available: https://doi.org/10.3389/fmats.2020.581979.

Molina-Piernas, E., Cultrone, G., Sebastián, E., and Alonso, Fco.J., 2013, Evaluation of stone durability using a combination of ultrasound, mechanical and accelerated aging tests, Journal of Geophysics and Engineering, 10, 035003, available: https://doi.org/10.1088/1742-2132/10/3/035003.

Pereira, D. and Marker, B., 2016, The Value of Original Natural Stone in the Context of Architectural Heritage, Geosciences, 6 (1), 13, available: https://doi.org/10.3390/geosciences6010013.

Pereira, D., Tourneur, F., Bernaldez, and Garcia-Blaquez, A., 2015, Petit Granit: A Belgian limestone used in heritage, construction and sculpture, Episodes, 38, 85–90, available: https://doi.org/10.18814/epiiugs/2015/v38i2/003.

Török, Á., Licha, T., Simon, K., and Siegesmund, S., 2010, Urban and rural limestone weathering; the contribution of dust to black crust formation, Environmental earth sciences, 63, 675–693, available: https://doi.org/10.1007/s12665-010-0737-6.

UNESCO, 2003, UNESCO - Savoir-faire liés à l'artisanat traditionnel, available: https://ich.unesco.org/fr/artisanat-traditionnel-00057 [accessed 26 Feb 2025].

Vázquez, P., Carrizo, L., Thomachot-Schneider, C., Gibeaux, S., and Alonso, Fco.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, available: https://doi.org/10.1016/j.conbuildmat.2015.12.125.

Winter, T., 2014, Beyond Eurocentrism? Heritage Conservation and the Politics of Difference, International Journal of Heritage Studies, 20, available: https://doi.org/10.1080/13527258.2012.736403.

Yarrow, T. and Jones, S., 2014, Stone is stone: Engagement and detachment in the craft of conservation masonry, Journal of the Royal Anthropological Institute, 20, available: https://doi.org/10.1111/1467-9655.12103.