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Hydrophobic Coatings' Efficiency and Limestones' Resistance to Salt Crystallisation

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Abstract: Stone deterioration is significantly influenced by the process of salt crystallisation. The expansion of salt crystals on a porous framework exerts pressure on the solid fraction, causing the stone to deteriorate when the internal pressure of salt surpasses the stone's strength. Protective coatings are employed to effectively hinder or substantially reduce the penetration of water and saline solutions. This study attempts to evaluate the effectiveness and long-term durability of limestones protected with hydrophobic coatings, focusing on their resistance to salt damage. The investigation followed the specifications set by the standard EN 12370:2019 and EN 14147:2003, which assesses the resistance of natural stone to salt crystallisation. The findings of this study indicate the conservation of physical–mechanical properties after ageing tests. In parallel, measurements of the static contact angle and the measurement of quality indexes revealed that the coatings maintained a certain level of hydrophobicity even after undergoing salt weathering tests, maintaining the good quality of the stones.

Keywords: stone durability; salt damage; stone protection; building pathology; slabs for cladding; mechanical resistance of limestones; efficacy of protective coatings; European standards

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1. Introduction

Salt crystallisation plays a significant contribution to the weathering of stones, with chloride and sulphate activities posing significant harm. All porous materials readily absorb saline solutions from various sources [1–3] (Figure 1). When these solutions evaporate under specific thermo-hygrometric conditions, salt tends to precipitate within the material. These conditions are unique to each salt or salt mixture, leading to their precipitation from a high supersaturated solution [4]. After nucleation, salt crystals grow and exert significant pressure within the porous framework, intensified by repetitive wetting–drying cycles [5,6] and, subsequently, cyclic salt dissolution and precipitation. The stone breaks down when the internal pressure from crystallisation surpasses the tensile strength of the stone. Several researches [7–10] state that this mainly happens if precipitation occurs in confined conditions. The specific deterioration forms and decay patterns depend on the characteristics of the lithologies, such as mineral composition, fabric, texture, and porous framework.

The application of hydrophobic treatments is a preventive maintenance practice to face the damaging effects of salt and ensure the longevity of construction materials. These coatings serve the following two important purposes, especially when stones are installed as cladding: first, to prevent the intrusion of aqueous solutions and their associated damage [11]; second, to safeguard metal fixings from corrosion in aggressive environments, thereby preventing instability and the potential collapse of slabs [12–14].

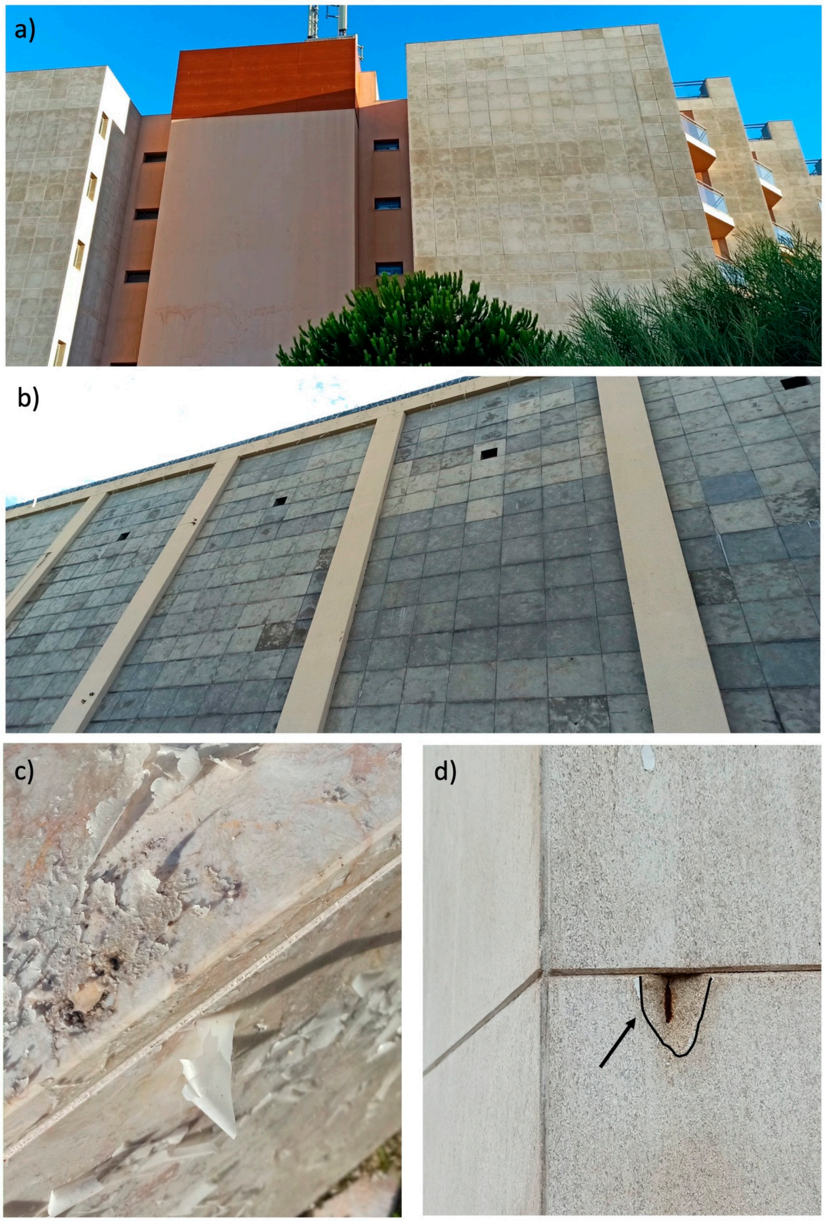

Figure 1. Common pathologies due to the presence of salt: (**a**,**b**) Stains on low-medium porous and low porous stone cladding caused by the weathering of adhesive bonding (Olhão and Coimbra, Portugal); (**c**) Peeling of the hydrophobic coatings applied on Lioz limestone (Lisbon, Portugal); (**d**) Corrosion of steel anchor due to the absorption of saline solutions through Branco limestone (Lisbon, Portugal).

This research deepens the relationship between salt crystallisation and stone weathering, shedding light on the harmful impact of the presence of soluble salts (mirabilite and halite). Additionally, the study analyses the effect of repetitive wetting–drying cycles, evidencing the repercussions of the internal crystallisation pressure exerted within the porous framework of stones. Moreover, the effectiveness of the application of hydrophobic coatings as a preventive maintenance measure in preventing the consequence of accidental saline solution absorption are explored. The novelty lies in the research design plan useful to understanding the stone durability and hydrophobic coatings efficiency by employing new laboratory salt weathering tests aligned with European standards, a modified version of EN 12370:2019 [15] and EN 14147:2003 [16] that are not mandatory but just recommended for stone heritage conservation. This study adopts a rigorous multi-analytical approach to assess the quality and performance of stones in aggressive environments. Beyond traditional assessments, it introduces a comprehensive procedure, including measurements of visual inspection, physical properties, the calculation of a static contact angle, and alterations in many mechanical properties that are not expressly required in the mentioned standards. In this context, the current study illustrates the significance of effectively driving through numerous standards and profiting from the most substantial principles to enhance the development of a more thorough and comprehensive study.

As highlighted in Table 1, silanes and siloxanes are used for stone material protection. Ethyl silicates in various molecular weights and fluorinated compounds are commonly included as small percentages in these formulations to optimise the hydrophobicity efficiency. All these products mixed in the right proportions impart different properties to the surfaces of stone materials and additional resistance to ageing.

Table 1. State-of-the-art EN 12370 and EN 14147 standards for natural stone affected by salt weathering were adopted by researchers to verify the durability of protective coatings. The substrate, chemistry of products, and application methods are also cited together with the outcomes of the specific studies. In this study, three types of hydrophobic coatings were used as follows: (i) aminopropyltriethoxysilane; (ii) aminefluorosilane; and (iii) methylmethoxysilane-based formulation.

References	Methodology	Samples	Substrate	Coating and Application Method	Outcome
Striani et al., 2016 [17]	EN 12370	Cubic specimens of 4 cm sides	Lecce Stone: calcarenite	$HYBRID_{SUN}$: silane-based with acrylic component. Application using a brush on all surfaces of the cubes	Positive
Al-Dosari et al., 2016 [18]	EN 12370	Cubic specimens of 3 cm sides	Sandstones of Kharga Oasis in Egypt	SILRES® BS OH 100: silica/polymer nanocomposites. Application using a brushing on all surfaces of the cubes	Positive
Bergamonti et al., 2015 [19]	EN 12370	Cubic specimens of 4 cm sides	Noto Stone: biocalcarenite	Nanocrystalline TiO_2-based coatings. Application using a brushing on all surfaces of the cubes	Positive
Belfiore et al., 2012 [20]	EN 12370	Cubic specimens of 5 cm sides	Scicli calcarenite	Paraloid B72: acrylic resin ethylmethacrylate methylacrylate copolymer. Silo 111: organosiloxane oligomer. PVA K40: vinyl acetate homopolymer. Application via brushing on only one face of the cubes	Only Silo 111 was the most appropriate
Lisci et al., current study	Modified EN 12370 according to Lisci et al., 2021 [21]	3 Cubic specimens of 5 cm sides for each lithology and each treatment.	Branco, Lioz, Alpinina, Blue limestone: português limestones	Aminopropyltriethoxysilane, aminefluorosilane, methylmethoxysilane, Application via brushing on 5 faces of the cubes.	Positive

Table 1. *Cont.*

References	Methodology	Samples	Substrate	Coating and Application Method	Outcome
Di Benedetto et al., 2012 [22]	EN 12370	Cubic specimens of 4 cm sides	Neapolitan Yellow volcanic tuff; Vicenza Stone limestone	Tetramethylenediammonium dichloride. Application via immersion	Negative in terms of chemical compatibility with the tuff; Positive for Vicenza Stone
Di Benedetto et al., 2012 [22]	EN 14147	Cubic specimens of 5 cm sides	Neapolitan Yellow volcanic tuff; Vicenza Stone biodetrial carbonate	Tetramethylenediammonium dichloride. Application via immersion	Positive
Leal et al., 2011 [23]	EN 14147	Cubic specimens of 4 cm sides	Semi Rijo. Moleanos and Cinzento azulado: bioclastic limestones. Cinzento Monchique and Cinzento azulado de Alpalhão: coarse-grained nepheline syenite and fine-grained biotitic granite, respectively.	Silane and siloxane-based in water emulsion. Products are applied by manually spraying on the stone surface	Generally positive, mainly for silicate stones
Celik et al., 2019 [24]	EN 14147	Cubic specimens of 5 cm sides	Andesits of Afyonkarahisar region (Turkey)	Siloxane-based water repellent. Application via brushing	Positive
Lisci et al., current study	EN 14147	3 Cubic specimens of 5 cm sides for each lithology and treatment.	Branco, Lioz, Alpinina, Blue limestone: português limestones	Aminopropyltriethoxysilane. aminefluorosilane. methylmethoxysilane. Application via rolling on 5 faces of the cubes.	Positive

The measurement of open porosity and the calculation of the static contact angle were made to assess the water protection capabilities of the hydrophobics. Furthermore, the alteration of mechanical properties was evaluated by measuring the sound speed propagation and calculating the building material's quality and the compressive strength.

2. Materials and Methods

2.1. Building Stones and Coatings Application

Four types of Portuguese limestone widely used in the natural stone industry were selected for this investigation: Branco, Lioz, Alpinina, and Blue limestone (Figures 1 and 2), quarried from Leiria District, belonging to the Estremadura Calcareous Massif.

Branco was used in Portugal in urban architecture and in some important buildings like Park of the Nation (Lisbon) and the Warsaw Children's Hospital (Poland).

Lioz was used in Portugal for the construction of the Belem Tower and Jeronimos Monastery (UNESCO, Lisbon) and the modern Champalimaud Foundation in Lisbon which project received the Honorable Mention Valmor 2012 Award.

Alpinina is used mainly in modern architecture (interior design and exterior cladding), cobblestones and artistic artifacts and it is widely exported.

Blue limestone apart the use in Portugal, is highly demanded abroad, mainly in France, Spain.

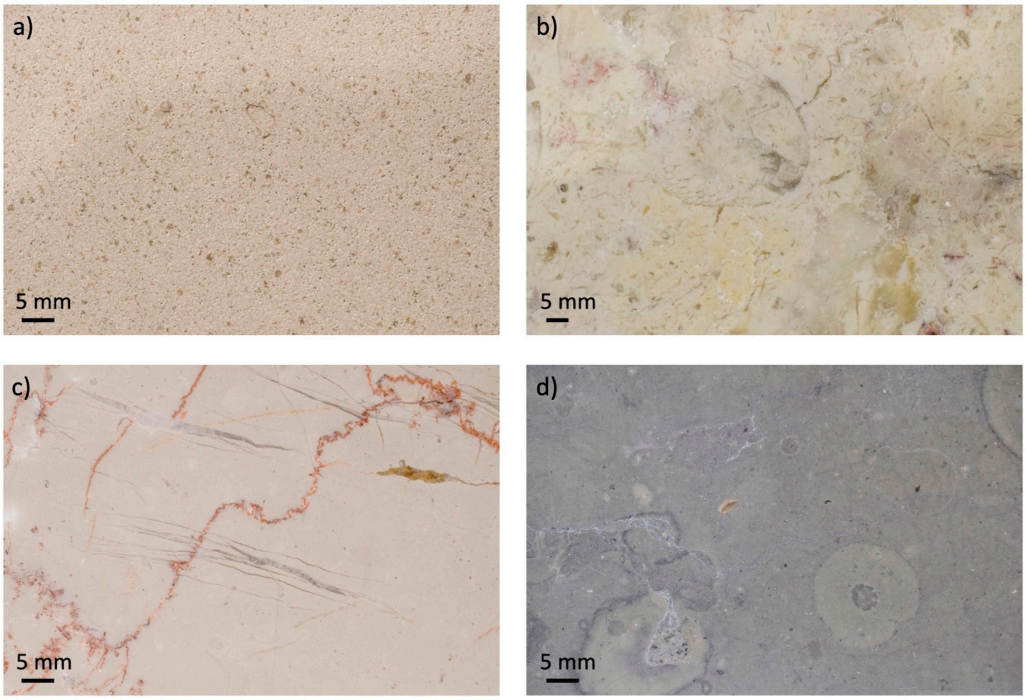

Figure 2. Macroscopic characteristics of the studied limestones: (**a**) Branco; (**b**) Lioz; (**c**) Alpinina; (**d**) Blue limestone.

Branco is a cream to light cream-coloured, soft, and pure limestone that is rich in bioclasts and oolites (Figure 2a). Lioz is a very compact light cream from coarse, bioclastic limestone. It is usually characterised by stylolithic joints with variable opening and spacing according to the facies (Figure 2b). Alpinina is a compact, beige colour and fine-grain limestone. It has closed and iron-rich stylolites and calcitic veins. The limestone is partially tectonised and recrystallised. Alpinina also contains bioclasts (Figure 2c). Blue limestone is a grey-blue compact calciclastic and bioclastic limestone. It contains organic matter and other impurities, mostly silicates and pyrite. It is characterised by the low frequency of closed stylolites (Figure 2d).

For each lithology, three bulk samples were untreated specimens, and three cubes for each hydrophobic treatment were used to compare the stones. The saturation of the substrate of the more porous Branco was ensured. Any excess of product on low porous Lioz, Alpinina, and Blue limestone was avoided. In this study, the samples were treated with aminopropyltriethoxysilane (COATING 1), aminefluorosilane (COATING 2), and methylmethoxysilane-based (COATING 3) (Table 2).

Table 2. Experimental plan design table.

Standard Reference	Modified EN 12370:2019	EN 14147:2003
Test type	Determination of resistance to salt crystallisation.	Natural stone test methods: determination of resistance to ageing by salt mist.
Type of salt	Saline solution of mirabilite ($Na_2SO_4 \bullet 10H_2O$)	Saline fog of sodium chloride (NaCl)
Number of specimens	i. 3 cubes * of untreated stone for each lithology ii. 3 cubes of each stone protected with the 3 coatings for each lithology *	i. 3 cubes * of untreated stones for each lithology. ii. 3 cubes of each stone protected with the 3 coatings for each lithology *

* is the minimum suggested by EN 16581:2014—Conservation of Cultural Heritage—Surface protection for porous inorganic materials—Laboratory test methods for the evaluation of the performance of water-repellent products [25].

Coatings were applied using a roll in five of the six faces of the cubes, leaving just the top surface. This procedure is designed to replicate a potential water penetration scenario involving saline solution or salt fog, which might occur in slabs for cladding or ashlars with protective coatings applied just on the top surface (Figure 3).

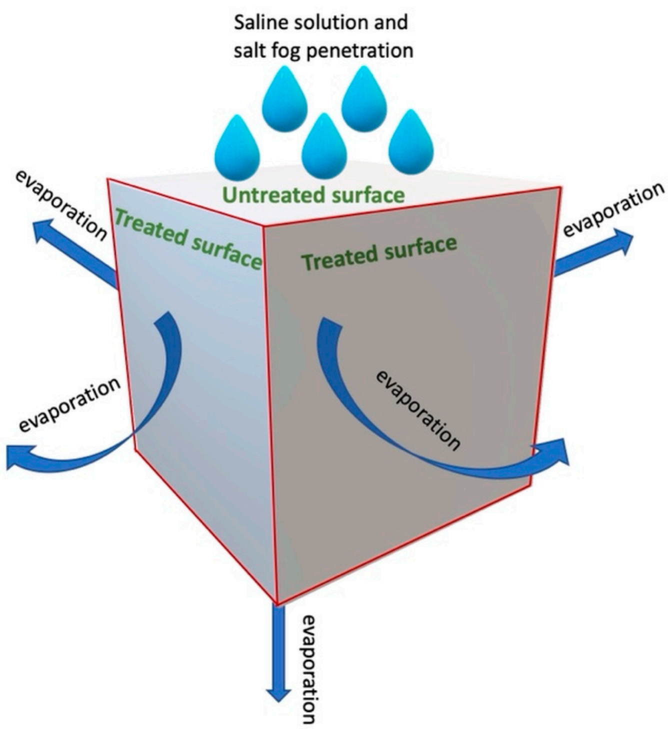

Figure 3. Representative scheme of specimen's treatment. The accidental ingress of saline solution/salt fog is supposed to occur through the untreated surface. The other hydrophobised five faces serve to investigate the durability of the treatments under salt crystallisation pressure after the evaporation of the saline solution.

In practice, the parts of the material in contact with adhesives, mortars, or grouts of anchor systems typically remain uncoated to facilitate physical/chemical adhesion between the installation system and the stone. Therefore, the objective of employing this application method is to assess how well the hydrophobic coatings perform when exposed to salt crystallisation. This research involved the determination of the average and standard deviation values of three samples for each group of specimens, without and with treatments, for a total of 12 specimens for each lithology.

2.2. Natural Stone Test Methods: Determination of Resistance to Salt Crystallisation through Modified EN 12370:2019 and EN 14147:2003

EN 12370:2019 is the European standard for evaluating the resistance and durability of stones to salt crystallisation after immersion in a saline solution. The standard defines the following specific tasks:

(i) The immersion of 4 cm sides cubes in a 14% solution of sodium sulphate decahydrate (mirabilite) for 2 h;
(ii) Drying at a temperature of 105 ± 5 °C for at least 15 h;
(iii) Cooling at room temperature for 2 ± 0.5 h before re-immersion in mirabilite solution;
(iv) After the 15th cycle, the specimens are stored for 24 ± 1 h in fresh water at (23 ± 5 °C); Finally, they are washed thoroughly with flowing water.

Modified EN 12370:2019 is an internal protocol proposed by the authors in a previous study [21]. The guidelines for testing cubes with 5 cm sides (instead of 4 cm) with any degree of porosity are as follows:

(i) Soaking in a 14% solution of sodium sulphate decahydrate (i.e., Mirabilite mineral) for 2 h;
(ii) Drying in an oven at a temperature of 40 °C for 22 h instead of the excessive 105 ± 5 °C imposed by EN 12370;
(iii) Cooling at room temperature for 30 min before soaking in fresh mirabilite solution;
(iv) After the 15th cycle, the specimens are removed from the oven and stored for 24 ± 1 h in water at (23 ± 5 °C). Finally, they are washed thoroughly with flowing water.

EN 14147 is the European standard for evaluating the resistance and durability of stones to salt crystallisation under NaCl salt fog in specific saline-fog climatic chambers. In this research, the authors used a C100/400B (CO.FO.ME.GRA company, Milan, Italy). This standard defines specific tasks. After the preparation of specimens (cubes of 5 cm side), it consists of the following:

(i) Spraying the NaCl salt fog for 4 h ± 15 min at 35 °C;
(ii) Drying the specimens at 35 °C in the chamber for 8 h ± 15 min.

After completing the test, the specimens are taken out of the chamber and placed in deionised water to eliminate any deposited salt.

As described in EN 12370, the standard focuses only on natural stones with an open porosity greater than 5%, and it recommends testing cubes of 4 cm in length. However, this investigation went beyond these specifications to comprehensively understand the stone/hydrophobic durability. This caused lithologies with an open porosity lower than 1.6% to be included in the modified EN 12370. This choice aimed to examine the impact of structural heterogeneities such as stylolites, impurities, and low-absorbent surfaces on stone and stone/hydrophobic longevity.

In contrast to measuring mass variation, as mandated by EN 12370 and EN 14147, this study adopted a more comprehensive methodology. To assess the damage caused by salt crystallisation, cubes of 5 cm side were employed, enabling a multi-analytical approach. This approach comprises the investigation of various parameters, including mass and porosity variation, ultrasound speed propagation calculations, and the measurement of uniaxial compressive strength. All the tests require cubes of 5 cm side. While they are not explicitly required by EN 12370 and EN 14147. The incorporation of these procedures into the research provides insights into how salt crystallisation affects the long-term durability of the stone and the efficacy of protective coatings.

2.3. Stone Characterisation and Damage Assessment

Petrographic analyses were made using a Hirox-01 digital microscope (HIROX company, Limonest, France) on 30 µm thickness thin section.

SEM-EDS analyses were performed with a scanning electron microscope HITACHI S3700N (Hitachi High-Technologies Corporation, Tokyo, Japan). This technique allowed us to obtain the elemental composition of the stones.

Mass fluctuations were indicated by the relative mass difference of ΔM, represented as a percentage of the initial dry mass (Md) or as the number of cycles needed to cause failure in cases where the specimen disintegrated or broke into two or more pieces. Open porosity before and after the salt tests' ageing was measured following the standard EN 1936:2008 [26]. Specimens were subjected for 2 h ± 24 m to a vacuum of 2.0 ± 0.7 kPa, and they were saturated with distilled water under a vacuum, remaining immersed for 24 ± 2 h.

The non-destructive ultrasonic test was conducted to assess the dynamic indices and structural integrity of the limestone both before and after the salt crystallisation tests. Employing a PUNDIT PL200 from Proceq (Screening Eagle Technologies, Schwerzenbach, Switzerland) equipped with 54 kHz transducers, the velocity of the longitudinal wave (Vp) was determined in accordance with EN 14579:2007 [27]. Starting from these values, the calculation of the Velocity Ratio Index (VRI) was possible (Equation (1)):

$$VRI = (Vpf/Vpi)^{0.5} \quad (1)$$

where Vpf is the final velocity value after the test, while Vpi represents the initial value of Vp for the intact specimens. The VRI allowed the Quality of Building Materials to be measured (Table 3), as proposed by Kahraman [28], and also adopted by other researchers specialised in NDT-integrated techniques on building stones [29,30].

Table 3. Quality of Building Materials according to the Velocity Ratio Index (VRI) proposed by Kaharaman [28].

Quality of Building Materials
VRI < 0.25 Very poor
0.25 < VRI < 0.50 Poor
0.50 < VRI < 0.75 Fair
0.75 < VRI < 0.90 Good
VRI > 0.90 Very good

The compressive strength value (σc) was calculated via the uniaxial compression test following EN 1926:2008 [31]. A PEGASIL EL200 (CEI by Zipor, São João de Madeira, Portugal) hydraulic press with a capacity of 1200 kN was used. The rupture load was applied perpendicular to the stratification planes or other discontinuities.

The static contact angle was measured according to EN 15802:2010 [32] using a goniometer/tensiometer Ramé-hart 210-U4 (Ramé-hart Instrument Corporation, Succasunna, NJ, USA) with an optic fibre illuminator and 520 frames/second SuperSpeed digital camera. DROPimage Pro software version 2.1 (Ramé-hart Instrument Corporation, Succasunna, NJ, USA) digitally measures the value of the static contact angle.

3. Results

3.1. Stone Characterisations by Petrographic Investigations

Branco is characterised by a grain-supported texture and the presence of bioclasts, oolites and peloids with interstitial sparite. Based on the Folk classification [33], it is an intermediate bio-ool-pelsparite (Figure 4a).

Lioz presents a microcrystalline grain-supported texture. It has a 52% vol. of sparite and about 48% of bioclasts. The rock is classified as biosparite (Figure 4b).

Alpinina has a mud-supported matrix, which is about 80% of the thin section. In total, 10% belongs to recrystallised calcite (sparite) veins. Their openings vary from 0.1 mm up to 5 mm with variable spacing. Bioclasts and peloids are the other 10%. Iron oxides as impurities are also detectable. According to Folk classification, Alpinina limestone is classified as Pel-biomicrite-sparite (Figure 4c).

Blue limestone has a >90% vol. of a micritic matrix, also containing clay minerals (<2% vol). Allochems as quartz (0.4% to 1.8% vol.) are present. The organic matter is up to 7% in vol. The bioclastic component is also abundant. According to Folk classification, the stone is classified as biomicrite (Figure 4d).

3.2. Damage Assessment by Visual Inspection

Regarding Branco samples (Figure 5), decohesion, flaking, and contour scaling are more pronounced after subjecting the material to the modified EN 12370 test conditions. The severity of the decay can be attributed to the higher concentration (14%) of mirabilite saline solution that is absorbed through total immersion compared to the 10% NaCl salt fog used in the EN 14147 test. Despite the standard attempts to wash the samples, the stone still exhibits a yellowing effect, primarily due to the presence of thenardite (Na_2SO_4) in the inner matrix, which is highly sensitive to relative humidity changes [34]. The degree of hygroscopicity of salt and the resulting visible colour change are responsible for the yellowing, as documented in a previous study conducted by the authors [21]. Also, in this case, the yellowing is more substantial in Branco after modified EN 12370.

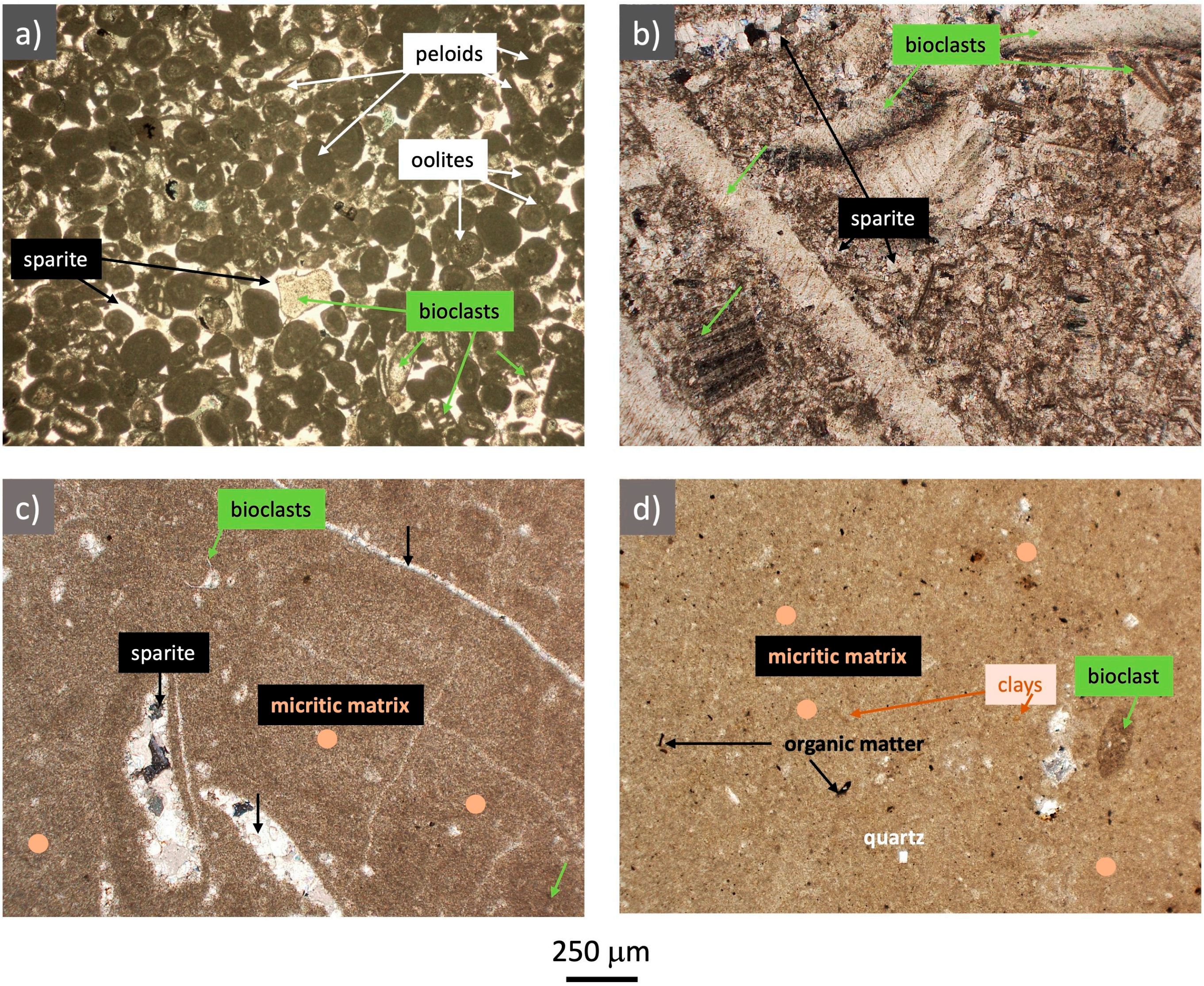

Figure 4. Thin sections of (**a**) Branco (bio-ool-pelsparite); (**b**) Lioz (biosparite); (**c**) Alpinina (pel-biomicrite-sparite); and (**d**) Blue limestone (biomicrite).

In Lioz, colour changes were not so evident, but material detachment along the stylolites arose after modifying EN 12370. The diverse structure, resulting from stylolites with varying spacings and openings, supported the absorption of a saline solution containing mirabilite. As the drying phase at 40 °C ensued, a remarkable cyclic process of salt nucleation and growth exerted a compelling internal crystallisation pressure, resulting in the expansion of the stylolites [35,36], with consequent detachments of stone portions.

Regarding Alpinina, a yellowing phenomenon because of modified EN 12370 and EN 14147 tests was observed. This discolouration can be attributed to iron oxides, which are sensitive to leaching in saline solutions. These conditions also contribute to the stone's susceptibility to alterations and corrosion [37]. However, it is essential to highlight that despite these effects, Alpinina maintained its original geometric and morphological features due to very low porosity.

The blue limestone experienced slight contour scaling following the two standards, particularly towards the conclusion of the modified EN 12370. After EN 14147, there was a substantial chromatic alteration and partial sub-millimetric detachments that exhibited film-like characteristics (peeling). These detachments could be attributed to the coatings applied on the surfaces [38] and also to the peeling of the untreated stone.

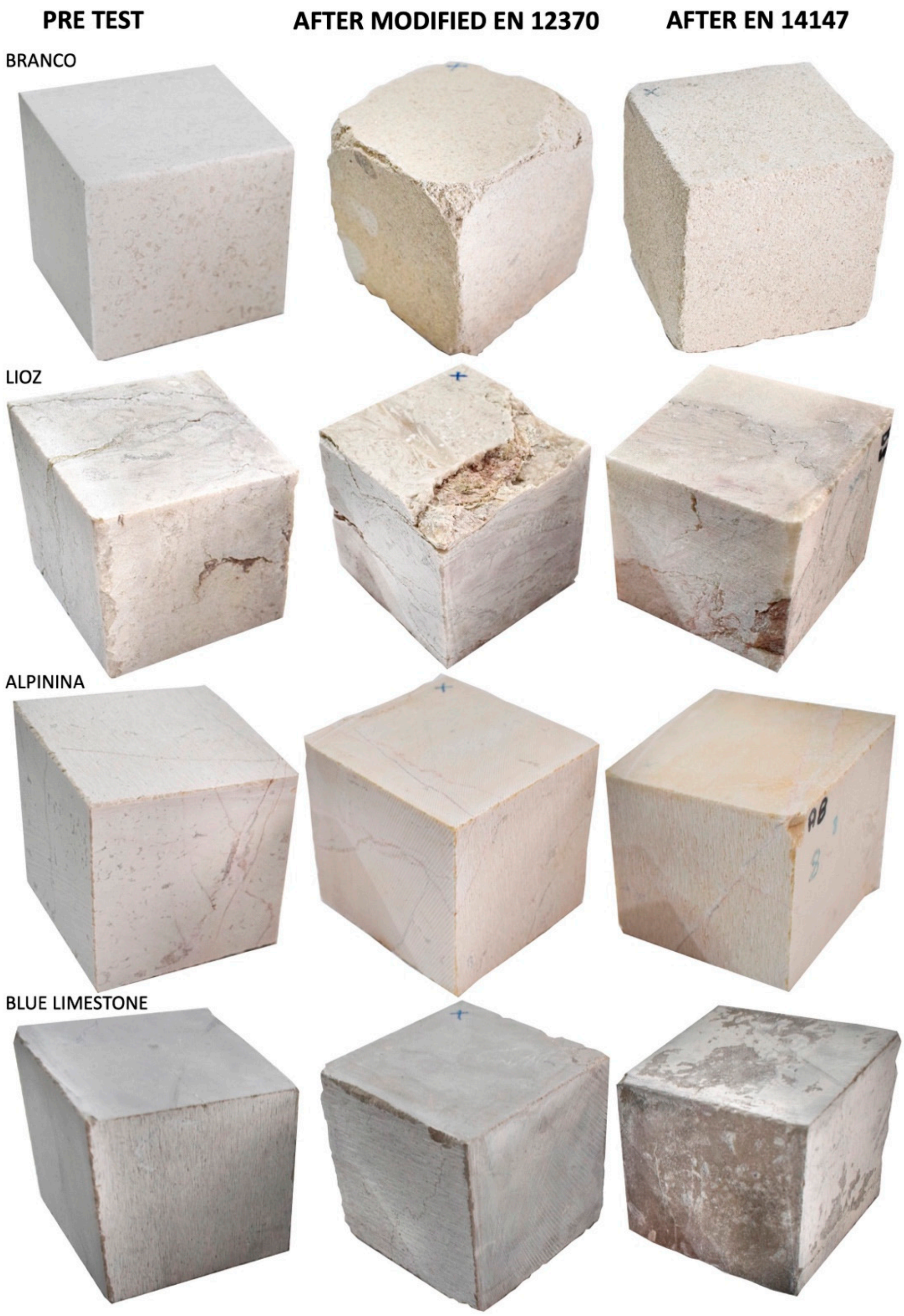

Figure 5. Morphological changes in Branco, Lioz, Alpinina, and Blue limestone after modified EN 12370 and after EN 14147. Discolouration occurred mostly on Branco, Alpinina, and Blue limestone. Contour scaling is more pronounced on Branco and Blue limestone. Only Lioz suffered from detachment after modified EN 12370 along the stylolites. Peeling occurred in Blue limestone after salt crystallisation tests.

The natural susceptibility of Blue limestone to alterations is documented in other studies [39]. This susceptibility is primarily attributed to the following two factors: (i) the presence of organic matter that induces stone discolouration; (ii) the existence of highly reactive framboidal pyrite (Figure 6a). It reacts with oxygen and water leadings to the formation of sulphuric acid. Consequently, this process causes the sulphation and chalking of the stone [40] (Figure 6b).

The alteration reaction is as follows:

$$2FeS_2\ (s) + 2H_2O\ (l,g) + 7O_2\ (g) \rightarrow 2H_2SO_4\ (l) + 2FeSO_4\ (s)$$

$$CaCO_3\ (s) + H_2O\ (l,g) + H_2SO_4 \rightarrow CaSO_4{\cdot}2H_2O\ (s) + CO_2\ (g)$$

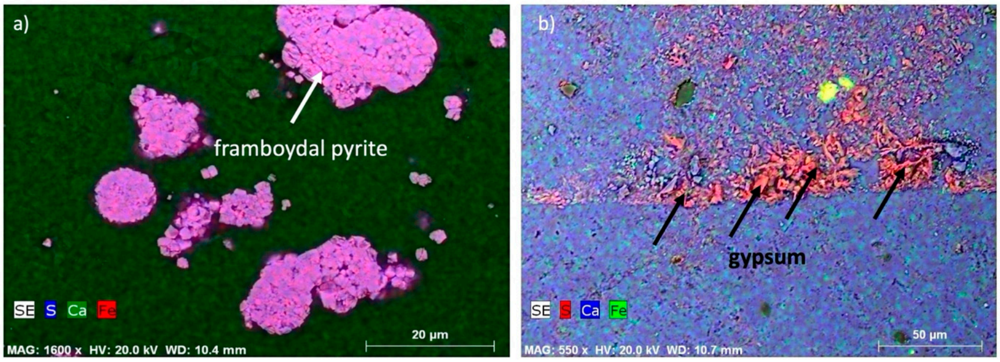

Figure 6. Elemental mapping under SEM-EDS of Blue limestone. (**a**) Framboidal pyrite inclusion; (**b**) Gypsum efflorescence formation occurred as a secondary product resulting from the reaction between the calcite and sulphuric acid generated during the oxidation of iron sulphides.

3.3. Wettability and Static Contact Angle

The wettability of a solid surface is a characteristic that defines how a liquid spreads on it, and this is assessed through the measurement of the contact angle in sexagesimal degrees [41]. The angle between the interfaces of solid/liquid and liquid/vapor is referred to as the equilibrium angle when the three phases (solid, liquid, vapor) are in equilibrium. The equilibrium angle is known as the Young contact angle [42]. The wettability of a surface is influenced by both cohesive forces within the liquid and adhesive forces between the liquid and the solid surface. Protective coatings are applied with the goal of reducing electrostatic attraction between the polar molecules of water and the electronegative components of stone, such as silicates and carbonates. As hydrophobicity rises, the liquid's surface tension also increases, leading to heightened cohesive forces. Simultaneously, the solid surface seeks to minimise its surface-free energy, making the solid more resistant to facilitating adhesive forces between the liquid and solid [43].

Table 4 documents the minimum and maximum contact angle ($\Theta°$) values for each lithotype, both for untreated stone and those with coatings. Untreated samples exhibit hydrophilic behaviour, meaning that water drops tend to spread rapidly on their surfaces, resulting in a contact angle of $\Theta = 0°$.

Branco results

This stone has complete wettability, with $\Theta° = 0$. Samples treated with COATING 1 showed a contact angle pre-test ranging from 98° to 105° and from 0° to 84° after modified EN 12370. The results are coherent with the salt attack triggered by the modified EN 12370 by total immersion in mirabilite solution, as shown previously in Figure 5. Since Branco has an initial open porosity of ~12–14%, the combination of the stone's open porosity, salt absorption, crystallisation pressure, and the subsequent breakdown of the stone matrix can all contribute to a reduction in hydrophobicity. COATING 2 and COATING 3 resist the salt attack better after modified EN 12370 with contact angle values ranging from 60° to 75° (COATING 2) and from 64° to 84° (COATING 3). After EN 14147, the products maintain their hydrophobicity, showing a contact angle ranging from 93° to 104° (COATING 1), from 81° to 94° (COATING 2) and from 91° to 96° (COATING 3).

Table 4. Minimum and maximum contact angle values expressed in sexagesimal degrees (Θ°) for each lithotype, both for untreated stones and those with coatings. COATING 1 = aminopropyltriethoxysilane; COATING 2 = aminefluorosilane; COATING 3 = methylmethoxysilane-based formulation.

	Pre-Test (Θ°)		**After Modified EN 12370 (Θ°)**		**After EN 14147 (Θ°)**	
Sample	**Min.**	**Max.**	**Min.**	**Max.**	**Min.**	**Max.**
Branco Untreated	0	0	0	0	0	0
Branco COATING 1	98	105	0	84	93	104
Branco COATING 2	122	125	60	75	81	94
Branco COATING 3 Sample	130	137	64	84	91	96
Lioz Untreated	0	0	0	0	0	0
Lioz COATING 1	99	103	89	100	85	102
Lioz COATING 2	123	125	97	108	104	107
Lioz COATING 3 Sample	130	134	107	112	72	76
Alpinina Untreated	0	0	0	0	0	0
Alpinina COATING 1	110	116	77	109	85	87
Alpinina COATING 2	124	127	83	125	102	115
Alpinina COATING 3 Sample	133	137	106	117	101	105
Blue limestone Untreated	0	0	0	0	0	0
Blue limestone COATING 1	110	115	70	78	42	70
Blue limestone COATING 2	120	126	102	116	53	91
Blue limestone COATING 3	132	135	120	123	96	120

Lioz results

The static contact angle Θ° ranges from 99° to 103° on unweathered stone surfaces treated with COATING 1. After modified EN 12370, the static contact angle decreases a little, with the minimum value (89°) on the limit of hydrophobicity (that is 90°). The maximum value calculated is Θ° = 100. After EN 14147, the minimum value is 85°, and the maximum angle is 102°. A good efficiency is still preserved. Regarding the use of COATING 2, after both salt resistance tests, it sustained its hydrophobicity, with Θ° values from 97° after modified EN 12370 up to 107° after EN 14147. In specimens treated with COATING 3, the contact angle varied from 130° to 134° before performing the tests. After

EN 12370, the static contact angle varied from 107° to 112°, showing a good performance. After EN 14147, it was included from 72° to 76°.

Alpinina results

After modified EN 12370, samples treated with COATING 1 suffered from lowering the minimum static contact angle value with respect to the initial values, from 110° to 77°. In some portions of the samples, the product still conferred good protection with Θ° = 109. After EN 14147, the contact angle was 85° < Θ° < 87°, which is slightly below the limit of hydrophobicity. Concerning COATING 2, the results are also quite good for Alpinina protection. After both salt crystallisation tests, the treatment showed a range of contact angles of 83° < Θ° < 125°. After EN 14147, the water protection conferred by the coating was well retained, as demonstrated by the contact angle measurement (102° < Θ° < 115°). Concerning COATING 3, in all cases, it provided great resistance to the salt attack, with a value of 105° < Θ° < 117° regarding both salt crystallisation tests.

Blue limestone results

The static contact angle Θ° measured in COATING 1 samples decreased from 110–115° to 70° < Θ° < 78° after modified EN 12370 and 42° < Θ° < 70° after EN 14147. Concerning COATING 2, the degree of hydrophobicity was relatively high, and the contact angle was 102°< Θ° < 116° after modified EN 12370. Considering that the pre-test values were 120–126° and the salt damage induced by the test, the results were satisfactory. After EN 14147, the minimum contact angle value measured on some surfaces was 53°. This marked a reduction in the contact angle in relation to the peeling of the limestone due to the interaction of the matrix with the salt fog. In Blue limestone, only COATING 3 succeeded in avoiding the stone surfaces being hydrophilic, with values of the contact angle at 120° < Θ° < 123° after EN 12370 and 96° < Θ° < 120° after following EN 14147, respectively.

3.4. Mass Variation and Open Porosity Variation

Regarding Branco and Blue limestone, the minimal or negligible alteration of the original porosity and mass were traced even for the incidence of decohesion and detachment (as seen in previous Figure 5). This was due to the accumulation of salt deep inside the porous matrix that often compensates for the loss of mass.

In analysing and interpreting the results of Lioz and Alpinina, the minimal, unrepresentative mass variation and open porosity observed in the samples deserve attention (Table 5).

Table 5. Values of mass difference and open porosity after modified EN 12370 and EN 14147. COATING 1 = aminopropyltriethoxysilane; COATING 2 = aminefluorosilane; COATING 3 = methylmethoxysilane-based formulation.

Sample		**ΔMass (%)**		**Δ Open Porosity (%)**	
		Modified EN 12370	**EN 14147**	**Modified EN 12370**	**EN 14147**
Branco Untreated	*average*	−0.35	0.22	0.01	−0.12
	st.dev.	1.04	0.10	0.02	0.06
Branco COATING 1	*average*	0.52	0.01	0.31	−0.09
	st.dev.	±0.51	±0.12	±0.08	±0.09
Branco COATING 2	*average*	−0.57	−0.11	0.07	−0.03
	st.dev.	±1.36	±0.06	±0.08	±0.05
Branco COATING 3	*average*	−0.05	−0.21	0.08	−0.05
	st.dev.	±0.45	±0.12	±0.06	±0.02
All Branco samples	*average*	−0.11	−0.02	0.12	−0.07
	st.dev	±0.89	±0.19	±0.13	±0.06

Table 5. *Cont.*

Sample		**ΔMass (%)** Modified EN 12370	**ΔMass (%)** EN 14147	**Δ Open Porosity (%)** Modified EN 12370	**Δ Open Porosity (%)** EN 14147
Lioz Untreated	*average*	−0.55	−0.03	0.08	0.13
	st.dev.	±0.91	±0.02	±0.21	±0.14
Lioz COATING 1	*average*	−0.02	−0.02	0.31	0.14
	st.dev.	±0.04	±0.01	±0.08	±0.11
Lioz COATING 2	*average*	−0.65	−0.02	0.15	0.32
	st.dev.	±1.08	±0.01	±0.16	±0.35
Lioz COATING 3	*average*	0.01	−0.03	0.03	0.67
	st.dev.	±0.01	±0.04	±0.20	±0.48
All Lioz samples	*average*	−0.30	−0.02	0.14	0.32
	st.dev	±0.68	±0.02	±0.18	±0.35
Sample		**Δ Mass (%)** Modified EN 12370	**Δ Mass (%)** EN 14147	**Δ Open Porosity (%)** Modified EN 12370	**Δ Open Porosity (%)** EN 14147
Alpinina Untreated	*average*	−0.004	0.003	0.12	0.05
	st.dev.	±0.01	±0.02	±0.11	±0.13
Alpinina COATING 1	*average*	0.005	0.004	0.08	0.13
	st.dev.	±0.01	±0.02	±0.15	±0.06
Alpinina COATING 2	*average*	0.01	−0.005	0.08	0.10
	st.dev.	±0.01	±0.01	±0.03	±0.08
Alpinina COATING 3	*average*	<0.001	−0.01	−0.004	−0.03
	st.dev.	±0.01	±0.01	±0.09	±0.04
All Alpinina samples	*average*	0.001	0.001	0.07	0.06
	st.dev	±0.01	±0.02	±0.10	±0.11
Sample		**Δ Mass (%)** Modified EN 12370	**Δ Mass (%)** EN 14147	**Δ Open Porosity (%)** Modified EN 12370	**Δ Open Porosity (%)** EN 14147
Blue limestone Untreated	*average*	0.13	−0.08	0.04	0.43
	st.dev.	±0.03	±0.01	±0.13	±0.14
Blue limestone COATING 1	*average*	0.13	−0.04	0.07	0.43
	st.dev.	±0.005	±0.04	±0.04	±0.22
Blue limestone COATING 2	*average*	0.16	−0.10	−0.004	0.50
	st.dev.	±0.02	±0.01	±0.02	±0.08
Blue limestone COATING 3	*average*	0.12	−0.03	−0.03	0.49
	st.dev.	±0.01	±0.12	±0.12	±0.20
All Blue limestone samples	*average*	0.14	−0.06	0.02	0.46
	st.dev	±0.02	±0.06	±0.09	±0.15

Considering the above, the significance of the results and reliable findings must be ensured.

3.5. Ultrasound Propagation, Velocity Ratio Index, and Quality of Building Materials

The evaluation of the change in longitudinal pulse velocity (ΔVp %) was utilised to measure the structural integrity of the limestone and the quality of the building materials (QBM) both before and after conducting salt crystallisation tests (Table 6).

Table 6. Value of the velocity of longitudinal waves Vp (m/s) and their difference ΔVp (%) before and after modified EN 12370 and EN 14147. COATING 1 = aminopropyltriethoxysilane; COATING 2 = aminefluorosilane; COATING 3 = methylmethoxysilane-based formulation. QBM—quality of the building materials.

		MODIFIED EN 12370				EN 14147			
Sample		**Vp Pre Test (m/s)**	**Vp Post Test (m/s)**	**ΔVp (%)**	**QBM**	**Vp Pre Test (m/s)**	**Vp after Test (m/s)**	**ΔVp (%)**	**QBM**
Branco Untreated	*average*	4196	3572	−14.8	0.92	4017	3704	−7.8	1
	st.dev	±382	±332	±4.11	±0.02	±104	±70	±1.86	±0.01
Branco COATING 1	*average*	4056	3594	−11.4	0.94	4041	3745	−4	0.96
	st.dev	±261	±309	±4.1	±0.02	±279	±159	±2.81	±0.01
Branco COATING 2	*average*	4026	3627	−9.92	0.95	4254	3785	−11	0.94
	st.dev	±108	±94	±0.73	±0.004	±89	±63	±0.38	±0.002
Branco COATING 3	*average*	3807	3377	−11.2	0.94	4012	3754	−6.4	0.97
	st.dev	±134	±60	±4.16	±0.02	±59	±80	±3	±0.01
All Branco samples	*average*	4021	3543	−12	0.94 QBM = very good	4081	3747	−8.2%	0.96 QBM = very good
	st.dev	±256	±224	±4		±176	±94	±5	
Lioz Untreated	*average*	4904	4855	−1	0.99	5825	4792	−17.7	0.91
	st.dev	±5	±54	±1.02	±0.01	±83	±98	±1.63	±0.01
Lioz COATING 1	*average*	4988	4910	−1.58	0.99	5763	4779	−17.1	0.91
	st.dev	±57	±77	±0.92	±0.005	±28	±77	±1.39	±0.01
Lioz COATING 2	*average*	5170	4951	−4	0.98	5443	4703	−13.6	0.93
	st.dev	±355	±115	±5.45	±0.03	±82	±34	±1.84	±0.01
Lioz COATING 3	*average*	5008	4908	−2	0.99	5759	4704	−18.3	0.90
	st.dev	±44	±64	±1.92	±0.01	±73	±89	±2.54	±0.01
All Lioz samples	*average*	5018	4906	−2.1	0.99 QBM = very good	5698	4744	−16.7	0.91 QBM = very good
	st.dev	±184	±77	±2.79		±168	±80	±3	
Alpinina Untreated	*average*	5152	5136	−0.31	0.99	5915	5104	−13.72	0.93
	st.dev	±37	±41	±0.51	±0.003	±47	±187	±2.48	±0.01
Alpinina COATING 1	*average*	5118	5122	0.08	1	5914	5148	−12.96	0.93
	st.dev	±141	±140	±0.05	±0.003	±28	±5	±0.49	±0.003
Alpinina COATING 2	*average*	5212	5158	−1.04	0.99	6111	5094	−16.45	0.91
	st.dev	±17	±24	±0.71	±0.004	±347	±44	±5.10	±0.03
Alpinina COATING 3	*average*	5169	5168	−0.01	1.00	6045	5124	−15.23	0.92
	st.dev	±21	±13	±0.19	±0.001	±90	±47	±0.57	±0.003
All Alpinina samples	*average*	5163	5146	−0.32%	0.99 QBM = very good	5996	5118	−14.7%	0.92 QBM = very good
	st.dev	±41	±36	±1		±178	±87	±3	
Blue limestone Untreated	*average*	4919	4853	−1.33	0.99	5616	4885	−13.01	0.93
	st.dev	±5	±23	±0.40	±0.002	±32	±31	±0.64	±0.003
Blue limestone COATING 1	*average*	4957	4894	−1.27	0.99	5641	4863	−13.79	0.93
	st.dev	±50	±67	±0.89	±0.004	±33	±23	±0.19	±0.001
Blue limestone COATING 2	*average*	4902	4896	−0.12	0.99	5604	4906	−12.44	0.93
	st.dev	±55	±25	±0.66	±0.003	±105	±29	±1.13	±0.006
Blue limestone COATING 3	*average*	4926	4796	−2.64	0.99	5619	4890	−12.97	0.93
	st.dev	±27	±137	±2.68	±0.01	±14	±41	±0.52	±0.003
All Blue limestone samples	*average*	4926	4860	−1.34%	0.99 QBM = very good	5620	4886	−13%	0.93 QBM = very good
	st.dev	±28	±78	±2		±51	±31	±1	

Branco results

After modified EN 12370 testing, the ΔVp of untreated samples is −14.8%. The associated QBM is equal to 0.92, which represents a "very good" quality for the untreated samples. After EN 14147 testing, QBM was also "very good," with a lower decrease with a ΔVp = −7.8%. Branco samples treated with COATING 1 showed a decrease in Vp of −11.4% after modified EN 12370 testing and −4% after EN 14147 testing. Similarly, Branco treated with COATING 2 showed a higher decrease in Vp with ΔVp = −11% after EN 14147 and close to −10% after modified EN 12370. COATING 3 samples also had ΔVp = −11.2% after EN 12370 testing and −6.4% after EN 14147 testing. After EN 14147 testing, the QBM for all samples was classified as "very good." Data suggest that the treatments with COATING 1 and COATING 2 did not significantly modify the quality of Branco. Still, the quality of the stone remained "very good" according to the QBM values after both testing conditions.

Overall, the average decrease in Vp for all Branco samples after modified EN 12370 testing was −12%, while after EN 14147, the decrease was −8.2%. The immersion in saline solution caused more severe damage due to the strong salt crystallisation pressure. However, the average QBM for both testing conditions was classified as "very good".

Lioz results

After modified EN 12370, the velocity variation ΔVp (%) ranged between −4% (in COATING 2) and −1% (for untreated samples). However, after EN 14147, ΔVp (%) was higher, ranging from −18.3% to −13.6% for COATING 2 and COATING 3-treated samples, respectively. All Lioz samples presented ΔVp (%) at −16.7% on untreated samples. The salt fog test was observed to be more aggressive for Lioz, with negative ΔVp (%) being approximately 16.7% and −2.1% after modified EN 12370, respectively. Despite this, the measured QBM remained "very good", with a QBM = 0.99 after modified EN 12370 and 0.91 after EN 14147. Overall, the data suggest that Lioz underwent a change in velocity after EN 14147, but the general quality of the stone remained good. The use of different treatments (COATING 3 and COATING 1) also affected the behaviour of the stone in the test.

Alpinina results

Regarding this lithology, the results of Vp are unexpected. After modified EN 12370, the ΔVp (%) varied between ~1% and 0.08%, with the average ΔVp % of all samples equal to −0.32%. Some unexpected results were obtained after EN 14147, where a decrease of 14.7% ± 3 took place, considering both untreated and treated samples. Moreover, Alpinina exhibited exceptional resistance to salt crystallisation tests, maintaining its "very good" quality rating. This remarkable performance indicated a minor reduction in velocity following the test, hinting only at possible superficial or subtle alteration arising from its initially low porosity. Specifically, after EN 14147, −12.96 (COATING 1) < ΔVp (%) < −16.45 (COATING 2), the latter had a much higher standard deviation. COATING 3 presented an intermediate value of −15.23%, and the untreated samples had a value of ΔVp (%) −15.23%.

It is a significant difference if compared to the previous test and could indicate a greater degree of alteration or decay. Despite these results, the data state that a "very good" quality is preserved after the tests, and the difference in mass and open porosity also confirmed this. It suggests that even though some degree of alteration or damage occurred during the tests, the building materials still met the necessary quality standards. Overall, these data provide a central insight into the behaviour of this stone when exposed to saline solution absorption or salt fog. It is important to remark that variations in lithology constituent and different manufacturing processes can greatly impact the performance of the stone when installed as a construction element.

Blue limestone results

The higher negative ΔVp % obtained on samples treated with COATING 2 (−0.12%) after modified EN 12370 indicates that this treatment provides better resistance to salt crystallisation compared to the other treatments. On the other hand, the variation ΔVp % = −2.64 detected on samples coated with COATING 3 suggests that this treatment may not have the same resistance to salt crystallisation. The intermediate values of ΔVp % = −1.27 and ΔVp % = −1.33 were obtained using COATING 1 and on untreated specimens, respectively.

After modified EN 12370, the average of ΔVp % was −1.34%, while after following EN 14147, the average of ΔVp % of all specimens was equal ~13%. This suggests that all chemicals provide better resistance to salt crystallisation in the first test. QBM is classified as "very good."

A comparison with the value of the static contact angle (Θ°) completes the interpretation of the Blue limestone results. Except for COATING 1 (70° < Θ° < 78°), COATING 2 and COATING 3 maintained a good degree of hydrophobicity after modified EN 12370 1 (102° < Θ° < 116° and 120° < Θ° < 123°). After EN 14147, the values were lower, and the range between the minimum and maximum was quite wide: 42° < Θ° < 70° (COATING 1); 53° < Θ° < 91° (COATING 2); 96° < Θ° < 120° (COATING 3). These results confirm that, in the case of Blue limestone, the salt mist of EN 14147 is more harmful to the lithotype because of its composition (the presence of sulphides and organic matter, Figure 6). Also, the peeling documented in Figure 5 suggests that the salt mist was more severe to the stone.

3.6. Uniaxial Compressive Strength

Destructive testing with uniaxial compressive strength, integrated with the other techniques, aims to evaluate the effective integrity of the stones and the actions of the decay factors. Measuring the values before and after salt crystallisation tests (Table 7) serves as a parameter for assessing the resistance to environmental degradation and the longevity of the stone as a load-bearing element.

Branco results

The uniaxial compressive strength (σ_C) of pre-test Branco bulk samples was 40 ± 6 MPa. After modifying EN 12370, a general decrease in mechanical resistance took place in all the specimens. The minimum value of σ_C in the untreated samples was detected (30 ± 3 MPa). This indicates that the untreated samples were more susceptible to salt absorption, and the pore occlusion via sodium chloride could make the stone more compact and resistant to stresses. The lower value of Rc among the treated samples was calculated on COATING 3 (34 ± 3 MPa). This was followed by COATING 2 (36 ± 6 MPa). Finally, COATING 1 seemed better at protecting the stone (38 ± 3 MPa). The average of σ_C for all Branco samples was 34 ± 5 MPa after modified EN 12370.

In general, the results suggest that the application of protective coatings can limit salt damage, apparently improving the compressive strength of Branco stone, with COATING 1 showing the highest performance among the coatings tested.

After modified EN 14147, increased values of σ_C were observed in all samples compared to the modified EN 12370. On untreated samples, σ_C = 57 ± 2 MPa. It indicates that the untreated samples were more susceptible to salt absorption, and the pore occlusion by sodium chloride could apparently make the stone more compact and resistant to stresses. Regarding the protective coatings, a range in σ_C values was noticed. The higher value of σ_C was calculated on COATING 1 (53 ± 6 MPa), followed by COATING 2 (50 ± 7 MPa) and COATING 3 (42 ± 6 MPa). The average of σ_C for all Branco samples was 51 ± 8 MPa.

The results of the tests suggest that exposure to salt can apparently increase the resistance of stone to stresses, even if the salt mist of EN 14147 seems to be less damaging to the stone. Additionally, the protective coatings tested had varying levels of effectiveness in preventing salt absorption, with COATING 1 showing the highest level of durability, followed by COATING 2 and COATING 3. This interpretation is also confirmed by the values of the contact angle Θ°, where COATING 1 is 93° < Θ° < 104°. Regarding COATING

2 and COATING 3, they tabled similar maximum values of Θ°, 94° and 96°, respectively, while the minimum values detected were 81° and 91°, respectively.

Table 7. The value of uniaxial compressive strength (σc) and its difference Δσc (%) before and after modified EN 12370 and EN 14147. COATING 1 = aminopropyltriethoxysilane; COATING 2 = aminefluorosilane; COATING 3 = methylmethoxysilane-based formulation.

Sample		Rc (MPa) Modified EN 12370	σ_C (MPa) According to EN 14147	σ_C (MPa) and $\Delta\sigma_C$ (%) after Modified EN 12370 and after EN 14147	Sample		σ_C (MPa) Modified EN 12370	σ_C (MPa) According to EN 14147	σ_C (MPa) and $\Delta\sigma_C$ (%) after Modified EN 12370 and after EN 14147
Branco Untreated	*average*	30	57	37 ± 10 $\Delta\sigma_C$ = −7% after modified EN 12370 $\Delta\sigma_C$ = 37% after EN 14147	Lioz Untreated	*average*	112	101	80 ± 19 $\Delta\sigma_C$ = 30% after modified EN 12370 $\Delta\sigma_C$ = 26% after EN 14147
	st.dev	±3	±2			*st.dev*	±17	±7	
Branco COATING 1	*average*	38	53		Lioz COATING 1	*average*	88	107	
	st.dev	±3	±6			*st.dev*	±6	±1	
Branco COATING 2	*average*	36	50		Lioz COATING 2	*average*	106	94	
	st.dev	±6	±7			*st.dev*	±15	±2	
Branco COATING 3	*average*	34	42		Lioz COATING 3	*average*	108	101	
	st.dev	±3	±6			*st.dev*	±13	±12	
All Branco samples	*average*	34	51		All Lioz samples	*average*	104	101	
	st.dev	±5	±8			*st.dev*	±15	±8	
Sample		**σ_C (MPa) Modified EN 12370**	**σ_C (MPa) According to EN 14147**	**σ_C (MPa) and $\Delta\sigma_C$ (%) after Modified EN 12370 and after EN 14147**	**Sample**		**σ_C (MPa) Modified EN 12370**	**σ_C (MPa) According to EN 14147**	**σ_C (MPa) and $\Delta\sigma_C$ (%) after Modified EN 12370 and after EN 14147**
Alpinina Untreated	*average*	135	154	100 ± 16 $\Delta\sigma_C$ = 30% after modified EN 12370 $\Delta\sigma_C$ = 36% after EN 14147	Blue limestone Untreated	*average*	170	229	133 ± 27 $\Delta\sigma_C$ = 35% after modified EN 12370 $\Delta\sigma_C$ = 50% after EN 14147
	st.dev	±18	±30			*st.dev*	±40	±36	
Alpinina COATING 1	*average*	123	159		Blue limestone COATING 1	*average*	194	194	
	st.dev	±28	±30			*st.dev*	±53	±49	
Alpinina COATING 2	*average*	130	113		Blue limestone COATING 2	*average*	185	137	
	st.dev	±31	±48			*st.dev*	±39	±89	
Alpinina COATING 3	*average*	133	118		Blue limestone COATING 3	*average*	139	202	
	st.dev	±27	±59			*st.dev*	±70	±38	
All Alpinina samples	*average*	130	136		All Blue limestone samples	*average*	172	190	
	st.dev	±23	±43			*st.dev*	±49	±60	

Lioz results

The low porous and heterogeneous Lioz experienced was σ_C = 80 ± 19 MPa before the test. The structural heterogeneity of the material is reflected in its standard deviation, which is attributed to the varying occurrence of stylolites. After modified EN 12370, higher values of σ_C were obtained on untreated samples, with a similar standard deviation (112 ± 17 MPa). It indicates that the compressive strength of the untreated samples increased following the test. The results also confirmed that stylolites in Lioz govern the saline solution penetration through the stone, ending in the occlusion of discontinuities and an apparent improvement in the stone quality [21,37]. The compressive strength of the Lioz samples may be further weakened as they undergo wetting–drying cycles.

Samples treated with COATING 1 showed values close to the initial one (80 ± 19 MPa) but with a minor standard deviation (88 ± 6 MPa). COATING 2 and COATING 3 samples resulted in higher compressive strengths, with average σ_C values of 106 ± 15 MPa and 108 ± 13 MPa, respectively.

After EN 14147, higher values of σ_C were generally achieved compared to the pre-test, with 101 MPa as the average of all Lioz samples. The standard deviation was just $\pm$ 8. In COATING 3, where the standard deviation was $\pm$12, the remaining samples had a standard deviation between $\pm$1 (COATING 1) and $\pm$7 (untreated samples).

Overall, these results demonstrate that different types of saline solution (mirabilite or NaCl salt mist) trapped in discontinuities and the efficiency of different treatments can significantly affect the overall compressive strength of Lioz samples, altering the quality of the material.

Alpinina results

In these samples, compressive resistance was enhanced. The average pre-test value was $\sigma_C = 100 \pm 16$ MPa. Also, in this case, after modified EN 12370, samples revealed higher values. Regarding the untreated samples, $\sigma_C = 135 \pm 18$ MPa. Furthermore, the results of the treated samples pointed to an increase in porosity, along with an increase in mechanical strength values and the standard deviation. Specifically, the samples treated with COATING 1, COATING 2, and COATING 3 had σ_C values of 123 $\pm$ 28 MPa, 130 $\pm$ 31 MPa, and 133 $\pm$ 27 MPa, respectively. By comparing the contact angle values (Table 4) with these results, it can be noticed that lower values of the contact angle refer to lower values of σ_C: 77° < Θ° < 109° (COATING 1), 83° < Θ° < 125° (COATING 2) and 106° < Θ° < 117° (COATING 3).

Regarding EN 14147, mechanical strength and standard deviation values are even higher when compared with the increase obtained after the modified standard EN 12370. A similar σ_C was acquired for untreated sample and COATING 1 samples, 154 $\pm$ 30 MPa, and 159 $\pm$ 30 MPa, respectively; the latter had a contact angle of 85° < Θ° < 87°. COATING 2 and COATING 3 had lower values of compressive resistance but higher standard deviation with $\sigma_C = 113 \pm 48$ and 118 ± 59 and contact angle values of 102° < Θ° < 115° and 101° < Θ° < 115°, respectively. Consequently, this trend is opposite to what emerged after the modified EN 12370.

In conclusion, the results confirm that Alpinina has apparently improved its compressive resistance despite its initial low porosity and low absorption of saline solutions. The experience outlined the ability of Alpinina-treated Alpinina to also be subjected to the effect of absorption and contact with saline solutions in the long term. This consideration is important in the evaluation of its longevity as building stones in harsh environments.

Blue limestone results

After both performances of modified EN 12370 and EN 14147, σ_C generally increased. The results ranged from 133 $\pm$ 27 MPa (pr-test) to 172 $\pm$ 49 MPa after modified EN 12370 and to 190 $\pm$ 60 MPa after EN 14147, considering both the untreated and treated samples.

In detail, untreated samples showed a σ_C average = 170 $\pm$ 40 MPa after modified EN 12370 and 229 $\pm$ 36 MPa after EN 14147. Regarding the samples protected with the hydrophobics, COATING 1 samples gave $\sigma_C = 194 \pm 53$ MPa (with a static contact angle of 70° < Θ° < 78°), with COATING 2 samples σ_C of 185 $\pm$ 39 (102° < Θ° < 116°) MPa and 139 $\pm$ 70 (120° < Θ° < 123°) MPa after modified EN 12370. It can be noticed that a decrease in the static contact angle corresponded, in this case, to a higher σ_C.

Vice versa, after EN 14147, COATING 1 obtained $\sigma_C = 194 \pm 49$ MPa (with 42° < Θ° < 70°), COATING 2 obtained $\sigma_C = 137 \pm 89$ MPa (53° < Θ° < 91°), while COATING 3 samples exhibited $\sigma_C = 202 \pm 38$ MPa (with 96° < Θ° < 120°). Following EN 14147, it was not possible to find a correlation between σ_C and the value of Θ°.

The increased standard deviation observed in the salt tests signifies a higher degree of variability in the mechanical performance and mechanical quality of Blue limestone to salt-induced damage. This outcome also suggests a certain level of variability in the effectiveness of hydrophobic treatments. The variability in the results is influenced by several factors, including the presence of impurities, organic matter, fossils, and micro-discontinuities within the stone structure.

4. Conclusions

Natural stones' durability and efficiency of hydrophobic coatings on limestone with varying characteristics under salt exposure performing modified versions of EN 12370:2019 and EN 14147:2003 was ascertained. Major findings indicate that lithotype composition, structure, and aesthetic characteristics significantly impact the salt crystallisation effect. The coatings demonstrated proficient resistance to salt crystallisation with static contact angles indicating a generally good level of protection, albeit below the 90° hydrophobicity limit.

It was found that the building stones investigated maintained the necessary performance requirements and met the quality standards for their installation in buildings even after salt exposure. Despite this, salt deposition within porous frameworks was not completely lost during the final washing at the end of the tests, which could enhance the bulk stones' compactness, promoting apparent integrity and, consequently, more longevity. In this regard, the multi-analytical approach was pivotal for a reliable understanding of the materials' behaviour. An evaluation of hydrophobic durability through salt crystallisation tests, or, in general, after ageing tests, is not mandatory but just recommended according to EN 16581 for inorganic materials of cultural heritage (EN 16581:2015—Conservation of Cultural Heritage Surface protection for porous inorganic materials—Laboratory test methods for the evaluation of the performance of water repellent products) [38]. Before salt tests, COATING 3 (methylmethoxysilane-based formulation) exhibited the best protection, followed by COATING 2 (aminefluorosilane) and COATING 1 (aminopropyltriethoxysilane). Performance variations were observed across stones and coatings after salt exposure. This study highlights the collaborative efforts between academia and industry, emphasising the necessity to evaluate the treatment efficiency for material protection. The goal was to encourage appropriate material selection for real-world projects, incorporating sustainability criteria to foster innovation in the industry and construction sector. The importance of selecting suitable protective treatments based on stone characteristics and intended uses in aggressive conditions was pointed out with an emphasis on the significance of preventive/corrective actions for building envelope durability. This research expresses a desire to evaluate the efficiency of treatments created to protect a specific material, with the goal of incentivising the appropriateness of materials for real-world projects. This includes integrating sustainability criteria to foster innovation within the industry and construction sector.

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