

Conservation of Earthen Bricks in Architecture: An Experimental Campaign to Test Treatments on Vernacular Built Heritage

Original

Conservation of Earthen Bricks in Architecture: An Experimental Campaign to Test Treatments on Vernacular Built Heritage / Mattone, Manuela; Fratini, Fabio; Luvidi, Loredana; Rescic, Silvia. - In: HERITAGE. - ISSN 2571-9408. - 6:2(2023), pp. 1541-1566. [10.3390/heritage6020083]

Availability:

This version is available at: 11583/2975781 since: 2023-02-08T10:50:56Z

Publisher:

MDPI

Published

DOI:10.3390/heritage6020083

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)

Article

Conservation of Earthen Bricks in Architecture: An Experimental Campaign to Test Different Treatments on Vernacular Built Heritage

Silvia Rescic ¹, Manuela Mattone ^{1,2}, Fabio Fratini ¹ and Loredana Luvidi ^{3,*}

¹ Institute of Heritage Science (ISPC), National Research Council of Italy (CNR), Università degli Studi di Firenze, Polo Scientifico e Tecnologico di Sesto, Via Madonna del Piano, 10, Sesto Fiorentino, 50019 Florence, Italy

² Department of Architecture and Design (DAD), Politecnico di Torino, Viale Mattioli 39, 10125 Torino, Italy

³ Institute of Heritage Science (ISPC), National Research Council of Italy (CNR), Via Salaria Km 29, 300, Monterotondo S., 00015 Roma, Italy

* Correspondence: loredana.luvidi@cnr.it; Tel.: +39-0690672887

Abstract: Earthen architecture, by its nature, is a fragile because it has a poor resistance toward the action of weathering, which has also increased in recent years through the effects of climate change. The presence of interesting examples of earthen brick buildings, for example, in the Piedmont Region of Italy, is characterised by the absence of rendering, which reveals the need to test treatments for the protection and/or strengthening of the walls of these buildings. This action is of fundamental importance to improve its resistance to the aggressive action of atmospheric agents and avoid their disappearance. A testing campaign adopting protective products with sustainability characteristics and low environmental impact was carried out on earthen brick walls. Different products belonging to various categories (synthetic polymers, natural resins, nano-structured materials) and selected based on previous experiments or tested for the first time on earthen surfaces were selected. The performance assessment of the products was carried out by taking into account the standardised procedures in the field of cultural heritage conservation through the following tests: water absorption, water vapour permeability, drilling resistance, water erosion tests (Geelong and spray), contact angle measurements, colorimetric measurements, and ageing tests. Although the choice of the optimal protective product should be made on a case-by-case basis, where it is not sustainable to proceed in this way, the results of this experimental campaign—in the presence of materials and weathering conditions similar to those of the case study analysed—will provide indications in identifying of the most appropriate product.

Keywords: earthen architecture; earthen bricks; conservation issues; protective products; test methods

Citation: Rescic, S.; Mattone, M.; Fratini, F.; Luvidi, L. Conservation of Earthen Bricks in Architecture: An Experimental Campaign to Test Different Treatments on Vernacular Built Heritage. *Heritage* **2023**, *6*, 1541–1566. <https://doi.org/10.3390/heritage6020083>

Academic Editor: Maria Laura Santarelli

Received: 23 December 2022

Revised: 25 January 2023

Accepted: 28 January 2023

Published: 1 February 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Widespread in many countries worldwide, earthen construction not only represents a thousand-year tradition but, above all, constitutes a testimony of the peasant civilisations' knowledge, skills, and habits. Earth has been the most widely used material for constructing many historic villages over centuries [1–5], as evidenced in some examples ranging from monumental defensive structures to rural buildings and typical villages in the Middle East (Figures 1–3). In recent decades, the preference given to materials considered more reliable and durable such as reinforced concrete [6] has led to the progressive abandonment of earthen construction techniques and the deterioration and rapid extinction of earthen heritage—abandoned because they are considered unhealthy and unsafe, but above all, because they are incompatible with the concept of modernity that people

aspire to—which means that these buildings are today at risk [7–9]. These constructions can be widely found in many Italian regions, where different construction techniques are adopted such as rammed earth and earthen bricks in Piedmont, *ladiri* (earthen bricks) in southern Sardinia, and *massone* (unshaped earthen bricks) in Abruzzo and Marche [10]. Since the beginning of the 1970s, the spread of a renewed interest in earthen buildings has promoted the rediscovery of this traditional architectural heritage by encouraging the study of methodologies aimed at ensuring its conservation over time and fostering its protection.



Figure 1. Deshengbao fortress was built in 1539 (Ming Dynasty) near the Great Wall in Shanxi Province, China (by Luvidi, 2017).



Figure 2. Teresa’s house, the visitor centre of the “Centre for permanent documentation on earthen houses” in Abruzzo region, Italy (by Luvidi, 2021).



Figure 3. Corbelled dome dwellings in the Aleppo region, Syria (by Fratini, 2011).

The main decay factors of earthen architecture are intrinsic (structural defects, kind of earth, realisation), and external agents (raising damp and salt, atmospheric agents, use). The earth is particularly sensitive to the action of water either as erosive action due to the impact of rain on the surface or runoff at the base of the building, or through disintegration phenomena due to the capacity of water to make the earthen material plastic again with the loss of cohesion and consequently of the mechanical characteristics of strength and rigidity (phenomena of capillary rise, infiltration salts). The phenomena of decay can be grouped into the following categories: (1) surface degradation of a physical and biological nature; (2) damp patches; fracturing, swelling and exfoliation of plasters; biological patinas; and (3) loss of material through erosion and falling elements. The latter phenomenon develops in areas that have lost cohesion due to the action of water and can affect the stability of structures if the loss of material affects important construction elements. These phenomena are localised mainly at the base of the walls (due to poor drainage that causes capillary rise and masonry disintegration) and at the corners (exposure to rain and wind). These decay factors are usually interrelated. Therefore, it is important to understand the actual cause of the processes and not just intervene on a single phenomenon. In fact, only in this way is it possible to develop an adequate, non-damaging and preventive intervention with respect to the possible emergence of new decay phenomena. Since decay factors are essentially due to the action of water and structural problems, conservation intervention must act in these two directions. The lack of maintenance (infiltration from the roof, the capillary rise of water, etc.) resulting from both the end of use of the building and the lack of manpower capable of intervening or who intervenes in an inappropriate manner are further significant factors of decay.

Specific measures were and are still adopted to ensure adequate protection against the aggressive action exerted by atmospheric agents. It is a widespread practice to apply renders to guarantee protection, and several studies have been conducted to increase the durability of earthen plasters [11–16]. Aside from renders, protective treatments may be required where conservation needs and the necessity to ensure the legibility of the original

surfaces are urgent (as in the case of decorated or painted earthen surfaces) [17–19]. These treatments can significantly increase the weathering resistance and reduce maintenance interventions on surfaces without render.

However, an analysis of the literature concerning on-site conservative treatments has shown a greater interest in consolidation products rather than protective ones. The most frequently used product, probably due to its compositional affinity with the earth, is ethyl silicate, but organic polymeric products (synthetic and natural) have also been applied for the consolidation of earthen structures [20–28].

Mattone M. [29], in her work on the protection of earthen bricks, used products already on the market and products of natural origin with low environmental impact and in agreement with the sustainability requirements. Among the applied products, potassium silicate, Aleurites oil, Cagir oil, and corn oil can guarantee a good resistance of the earthen surfaces to the erosive action exerted by water and reduce its absorption. However, no studies on the breathability of the treatment have been performed.

Stazi et al. [16] investigated the effectiveness of several admixtures and surface treatments for earthen render protection that also included nanotechnological products. Ten different typologies of plasters were obtained by adding different admixtures such as silicon nanoparticles, titanium dioxide, silica nanoparticles, silane-siloxane, and beeswax. According to the results of the water-repellence and water erosion resistance tests, the earthen render treated with the silane-siloxane product was the best. The authors underline that the addition of a synthetic treatment such as silane-siloxane, unfortunately causes a slight worsening in the ecological and economic qualities of the plaster, even if this difference is not very significant because the final plaster is fully compatible.

According to all of the studies cited regarding the protection action against water access (which can cause swelling, dissolution, and biological growth), it is impossible to define a perfect treatment for earthen buildings, as this will vary according to the characteristics of the building and the environment. For this purpose, new experiments can increase the possibility of finding treatments that have positive results on several properties such as aesthetic, physical-mechanical ones (durability), and the compatibility/retractability of the treated surfaces. It is also true that every type of earthen material will behave differently towards the same treatment (applied with the same method and in the same conditions) due to its different composition.

Starting from the experiences shown above and in particular from Mattone M. [29], the authors decided to carry out a new experimental campaign during which synthetic protective products (commercial and innovative) belonging to different classes (fluoro-elastomers, silanes and siloxanes, and nano-silica) and natural products (oil of Aleurites) with a lower environmental impact than synthetic products were tested on earthen bricks from a rural building located near Alessandria (Piedmont region, Italy) (Figure 4). These types of architectures are not covered by render; therefore, a surface protection treatment could increase their resistance to water and, consequently, their durability, reducing their maintenance. However, it is obvious that these treatments cannot replace ordinary maintenance interventions such as making the roof and the base of the building safe, which must always be carried out periodically.



Figure 4. Vernacular earthen architecture in the Alessandria province, Piedmont, Italy (by Mattone, 2020).

It is essential to underline that the results of this experimentation could find helpful application not only in existing earthen architecture, but also in new earthen buildings, whose construction is improving nowadays thanks to the implicit, innate, and very significant features of the sustainability of the earthen material.

The rediscovery of knowledge and materials belonging to ancient building traditions, in addition to the experimentation of new products, might significantly improve the preservation of the existing heritage and the widespread use of this material in new buildings, which offers real advantages in terms of sustainability.

2. Materials and Methods

2.1. Earthen Bricks

The earthen bricks used for the experimentation were recovered from the demolition of an unlisted rural building constructed in the early 20th century, located in the countryside near the town of Sale, in the province of Alexandria (Italy). In this area, the earthen bricks are manufactured according to traditional methods with the local earth and formed by adopting wooden moulds.

The dimensions of the earthen bricks used for the experimentation were $26 \times 13 \times 6$ cm. Not fissured bricks with relatively regular surfaces were chosen. They were previously cleaned with a chisel stonemason and a brush, removing all traces of plaster, mortar, and any vegetal residues (Figures 5 and 6).



Figure 5. Earthen bricks: Specimens made with local earth (from Alessandria, Italy) and treated with a fluoroe elastomer (Tecnoflon N215).

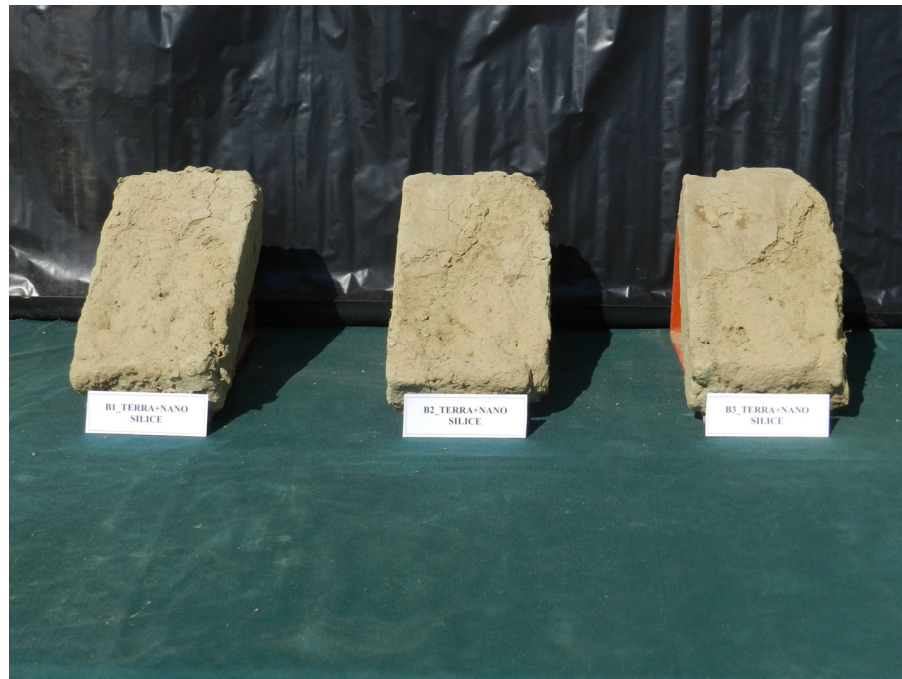


Figure 6. Earthen bricks: Specimens made with local earth (from Alessandria, Italy) and treated with nano-silica (Nano Estel).

The mineralogical characterisation of the earthen bricks was carried out through X-ray diffraction (XRD), and the granulometric distribution of the earthen material was also evaluated.

For the evaluation of the product performances (effectiveness, compatibility, and durability), reference has been made to, where present, to European standards on porous

inorganic materials constituting cultural heritage [30–33], but given the fragile nature of this building material, the standards of New Zealand legislation, specific for raw earth materials and related to water erosion resistance tests were also considered [34,35]

The performance evaluation of the conservation treatments was carried out through the following tests: (1) Protective efficacy with water surface erosion by the Geelong test and erosion spray test, water absorption by the Karsten pipe method, and hydrophobic behaviour by static contact angle test; (2) compatibility of the protective treatment with the evaluation of residual breathability by the water vapour permeability with the wet cup method, surface formation of crust by the Drilling Resistance Measurement System (DRMS), and colour change by the spectrophotometric measurements; (3) durability after thermo-hygrometric cycles through the evaluation of weight loss, hydrophobic behaviour, and colour change.

Three earthen bricks were used for each water erosion test and the absorption test by Karsten pipe. In order to carry out the colour measurements, water vapour permeability, contact angle, drilling resistance, and ageing tests, samples with standardised dimensions (5 cm × 5 cm × 2 cm) were prepared by cutting them from the earthen bricks (Table 1).

Table 1. Schematic list of the tests and sample sizes.

Test	Sample Size in cm	Number of Samples for Each Treatment	Number of Tests for Each Sample
Spray	26 × 13.5 × 6.5	3	1
Geelong	26 × 13.5 × 6.5	3	3
Karsten	26 × 13.5 × 6.5	3	3
Colour	5 × 5 × 2	12	3
Water vapour permeability	5 × 5 × 2	3	1
Static contact angle	5 × 5 × 2	3	10
DRMS	5 × 5 × 2	3	3
Ageing	5 × 5 × 2	3	1

2.2. Treatments

In this experimentation, products with hydrophobic properties that belonged to different categories such as synthetic polymers (fluoroelastomer, silane, and siloxane mixture), natural resins (Aleurites oil), and silica nanoparticles (nano-silica) were selected based on previous experiments by the authors [29] or tested for the first time on this kind of material (mixture of nano-silica + fluoroelastomer) [36].

Nano-silica is a consolidant that was tested combined with the fluoroelastomer to understand its contribution to the mixture in terms of its conservative performance. Thus, the product was also tested on its own to understand its contribution in terms of consolidation effectiveness, as investigated through the DRMS test.

A natural product such as Aleurites oil was used because in a previous experimental campaign, it showed good efficacy in terms of decreasing water absorption and increasing the resistance to water erosion [29].

Two different application methods of the products were adopted in this study: by spray through a nebulizer (fluoroelastomer, nano-silica, silane and siloxane mixture, nano-silica + fluoroelastomer) and by brush (Aleurites oil), applying them according to the procedure called “wet on wet”. It should be noted that during brush application, an earthy residue was visible on the brush. The products were applied on one face of the sample with the exception of the specimens dedicated to the ageing test, where the lateral faces were also treated.

Before applying the product, all of the samples were stored in the desiccator until they reached a constant mass, and then the initial mass was determined. After the treatment, the samples were left at room conditions (T = 23 °C, RH = 50%) for one month to allow for the evaporation of the solvent. Then, the samples were stored inside a desiccator

to reach the “dry” condition, typically a couple of weeks. The treatments were applied to all faces of the specimens.

The commercial products used as the fluoroelastomer (Tecnoflon N215, molecular weight around 132.000 g/mol and 66% fluorine content) and nano-silica (Nano Estel, particle size around 10–20 nm) were supplied by Solvay-Solexis, Milan, Italy and by CTS s.r.l., Vicenza, Italy, respectively. Wacker Chemie-Germany supplied the silane and siloxane mixtures (Silres® BS 4004). The Aleurites oil (olio fiorentino no. 337) marketed by Durga is a special quick drying formulation consisting of linseed stand oil, stand oil of Aleurites (tung), vegetable damar resin, beeswax, and carnauba wax, natural drying agents of manganese and zinc. A new formulation was obtained by mixing a 1.5% (*w/w*) solution of nano-silica particles (Nano Estel) in water and a 0.5% (*w/w*) of the fluoroelastomer (Tecnoflon N215) in acetone to obtain a ratio nano-silica:fluoroelastomer equal to 2.5. The mixture was developed under the co-funded project by the Tuscan Region PORCREO/FERS 2007-2013 Tecon@Bc [35].

Tecnoflon N215 was applied diluted in 1% acetone while Nano Estel, SILRES® BS 4004, and Aleurites were diluted at 1% *w/w* in water, isopropanol, and limonene, respectively. Table 2 shows the characteristics of the different treatments.

Table 2. Schema of the treatments.

Treatment	Brick	Original Concentration (% <i>w/w</i>)	Applied Concentration (% <i>w/w</i>)	Solvent	Amount Applied (L/m ²)	Method of Application
Tecnoflon N215	A	3	1	Acetone	2.20	Spray
Nano Estel	B	30	1	Water	1.28	Spray
Nano Estel+N215 *	C	1.5% Nano Estel +0.5% N215 *	1.5% Nano Estel +0.5% N215 *	Acetone/water	1.92	Spray
Silres BS 4004	D	50	1	Isopropanol	2.00	Spray
Aleurites high	E	37	37	-	2.12	Brush
Aleurites low	F	37	1	Limonene	2.12	Brush
Not treated	G	-	-	-	-	-

* With a nano-silica:fluoroelastomer ratio equal to 2:5.

2.3. Grain Size Distribution and Mineralogical Composition

The grain size distribution of the earthen sample was carried out through sieving in order to separate the following fractions: sand ($\varnothing > 63 \mu\text{m}$), silt ($4 \mu\text{m} < \varnothing < 63 \mu\text{m}$), and clay ($\varnothing < 4 \mu\text{m}$).

The mineralogical composition of the earth of the bricks was determined through X-ray diffraction with an X'Pert PRO diffractometer by PANalytical equipped with an X'Celerator detector and HighScore software for acquisition and interpretation of the data according to the following operative conditions: Cu $K\alpha_1 = 1545 \text{ \AA}$ radiation, 40 KV, 30 mA, $2\theta = 3\text{--}70^\circ$. The analysis of the clay minerals was performed according to Banchelli [37] and by utilizing a PHILIPS PW 1729 diffractometer according to the following operative conditions: CuK $\alpha_1 = 1545 \text{ \AA}$ radiation, 40 KV, 20 mA, $2\theta = 3\text{--}14^\circ$.

2.4. Water Surface Erosion Test

The erosion tests were conducted, according to Standards New Zealand NZS 4298 [34,35], in two different ways by the Geelong and spray tests.

The Geelong test is based on measuring the erosion of the sample caused by the repeated impact of a water drop on the surface tested, placed at an angle of nearly 30° to the horizontal to evaluate the durability performance of earthen materials against rainfall-induced erosion.

The erosion evaluation was done by measuring the cavity's depth caused by the impact of a water drop on the surface (erodibility index) (Table 3).

Table 3. Erodibility index according to New Zealand NZS 4298 Appendix E—Geelong test.

Depth of Erosion D [mm]	Erodibility Index
$0 < D < 5$	2 (no erosion)
$5 \leq D < 10$	3
$10 \leq D < 15$	4
$D \geq 15$	5 (fail)

According to NZS 4298-E [35], Standards Association of Zimbabwe [38] and Standards Australia [38], specimen failure occurs when the pitting depth is greater than 15 mm.

The erosion spray test involves the measurement of the erosion of the sample due to its exposition to a water jet projected from a distance of 470 mm and with a pressure of 0.5 bar. The test lasts up to one hour, or until complete erosion of the sample, and it is interrupted at intervals of 15 min to evaluate the depth of the erosion caused by the water jet. According to NZS 4298 Appendix D [34] and SAZS 724 [39], failure of the specimen occurs when the depth of erosion is greater than 20 mm. The erodibility index is calculated by the ratio of the erosion depth and time of erosion (mm/h) (Table 4).

Table 4. Erodibility index according to New Zealand Standard NZS 4298-D—Spray erosion test.

Depth of the Erosion D [mm/h]	Erodibility Index
$0 < D < 20$	1
$20 \leq D < 50$	2
$50 \leq D < 90$	3
$90 \leq D < 120$	4
$D \geq 120$	5 (fail)

2.5. Karsten Test

The water absorption tests were carried out with the pipe method [40] by measuring, for a maximum of 15 min and at regular intervals of time (one minute), the rate of water absorbed from a graduated pipe, known as a Karsten pipe. The water penetrates at low pressure into the porosity of the stone, and its quantity is recorded on the graduated scale, providing indications for the evaluation and monitoring of the protective treatments applied and the variation in the porosity of the treated material.

2.6. Static Contact Angle Test

The evaluation of the hydrophobic action induced by the products was carried out according to EN 15802 [30,31] by measuring the static contact angle. The earthen brick samples were placed on a pivoting support so that the surface of the specimen was always aligned with the optical axis of the digital camera reflex (Canon EOS 7D) equipped with a macro lens (Canon EFS 60 mm). Drops of 10 μL ($\pm 0.1 \mu\text{L}$) of distilled water were deposited on the surface of the stone sample with a micro-pipette and photographed after 15 s. The contact angle was obtained by measuring the dimensions of the drop [$\theta = 2\arctg(2$

h/a), where θ = contact angle in degrees; h = height of the drop; a = width of the drop at the base] performed directly on the macrophotography.

2.7. DRMS Test

The DRMS system was used to assess the compatibility of treatments by checking the possible formation of a hard surface crust and to assess the consolidation effectiveness in the case of the combined Nano Estel + Tecnoflon N215 treatment and Nano Estel alone treatment. The system also makes it possible to verify the depth of penetration of a product, in the event that it confers a re-cohesion, and is therefore more appropriate for consolidating treatments. For a protective treatment, it is not necessary for the product to penetrate deeply into the material, but it must have a good surface distribution [41–43]. The drilling resistance measurements were carried out under the following operating conditions: 200 rpm rotation speed of the bit, 10 mm/min forward speed of the bit, and 10 mm depth of the hole. A Fischer carbide-tipped masonry drill bit, for stone and concrete, with a 5 mm diameter was used.

2.8. Wet Cup Test

A key feature of plasters or earthen materials is their breathability. Inside the dwellings, this feature allows thermo-hygrometric conditions to be consistently stable and comfortable. Therefore, it is important to assess the compatibility of the applied treatments in terms of changing the breathability of surfaces. A test of the permeability to water vapour was carried out by the wet cup method, as defined by EN 15803 [32], which measures the mass of vapour flowing every 24 h up to 10 days when equilibrium is reached (e.g., when the difference between two successive weighings at an interval of 24 h is not greater than 0.1% of the specimen mass). The test chamber was maintained at a temperature of 23 °C and relative humidity of 50%. The barometric pressure was recorded every day. Test results are expressed as water vapour diffusion resistance (μ). The EN 15803 [32] standard for this test does not provide information on the acceptability range for the permeability variation to water vapour. According to Rescic et al. [44] and considering the 20% threshold proposed by Snethlage [45] and 10% by Delgado and Grossi [46], a prudent approach suggests using the second one in the interpretation of the results. The % variation referring to parameter μ is calculated as follows:

$$\Delta\mu(\%) = [(\mu_{\text{brick untreated}} - \mu_{\text{brick treated}}) / \mu_{\text{brick untreated}}] * 100.$$

2.9. Colour Test

The colour variation induced on the earthen bricks by the treatments is a key parameter to evaluate the compatibility of the protective treatment. This colour change should be minimised [31]. Fulfilling this requirement is even more important in the case of the integration of missing bricks. A Konica Minolta spectrophotometer CM 700d adopting the CIE $L^* a^* b^*$ method [47] was used to measure the colour parameters. According to this method, the colour of a surface is described by three parameters: L^* (0 to 100) represents the lightness, a^* is related to the impulse of the red-green colour, and b^* is related to the impulse of the yellow-blue colour [31–33].

The total colour change is summarised by the parameter ΔE^* calculated with the following equation:

$$\Delta E = \sqrt{((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)}$$

where

$$\Delta L^* = (L^* \text{ before treatment} - L^* \text{ after treatment});$$

$$\Delta a^* = (a^* \text{ before treatment} - a^* \text{ after treatment});$$

$$\Delta b^* = (b^* \text{ before treatment} - b^* \text{ after treatment}).$$

The measurements were performed with diffuse illumination (D65 standard source) on an area of 8 mm diameter, with specular components included and excluded.

2.10. Durability Test

Artificial aging tests through wet–dry [48,49], freeze–thaw [50,51] and thermo-hygrometric cycles help evaluate the durability of the earthen bricks when exposed to weathering. The first two ageing tests have been set up for materials such as cement and coatings, therefore, they are too severe for earthen materials, and many authors have modified them to allow for their application to different and more fragile materials [10]. Earthen bricks can be exposed to thermo-hygrometric cycles in a climatic chamber. It is known that the exposure of earthen materials to moisture and daily thermal variation may cause the swelling and shrinkage of clay minerals with an expandable lattice, causing physical decay over time (from a simple surface dusting up to the loss of considerable size fragments).

The not treated and treated earthen bricks were exposed to artificial ageing in an Angelantoni Challenge 500 Climatic Chamber. The thermo-hygrometric conditions were simulated experimentally based on the cycle represented in Figure 7. This cycle was carried out by reprocessing original data recorded by “Rete di Monitoraggio Meteoroidrografica” of ARPA Piedmont in the Alessandria Lobbi weather station over ten years. The data were averaged, and one-year behaviour was converted to an RH cycle of 35 h ranging from $-5\text{ }^{\circ}\text{C}$ to $30\text{ }^{\circ}\text{C}$ and from 40 to 90% RH. The cycle was repeated 50 times. Colorimetric change, weight, and contact angle measurements were performed before and after accelerated ageing.

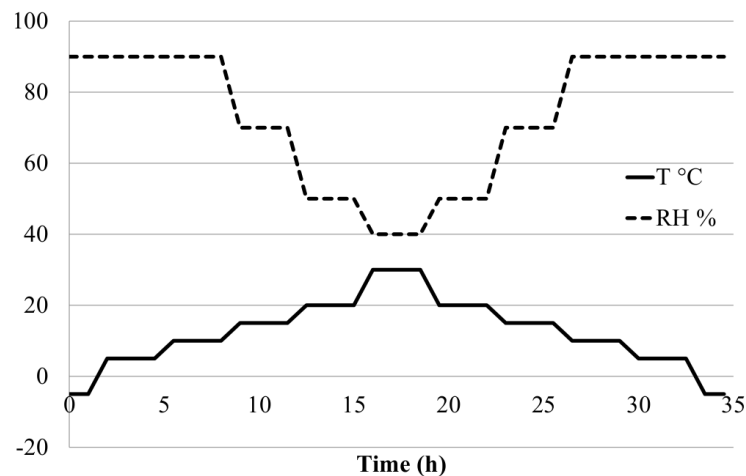


Figure 7. Diagram representative of the TH cycle (credit: Rescic).

3. Results

3.1. Material Characterization

The grain size distribution of the earthen material (sand 24%, silt 45%, clay 31%) taken from the farmhouse under demolition was obtained through sieving. The main mineralogical composition of the earthen bricks, performed by X-ray diffraction, is as follows: quartz, feldspars, calcite, micas, and clay minerals (Figure 8).

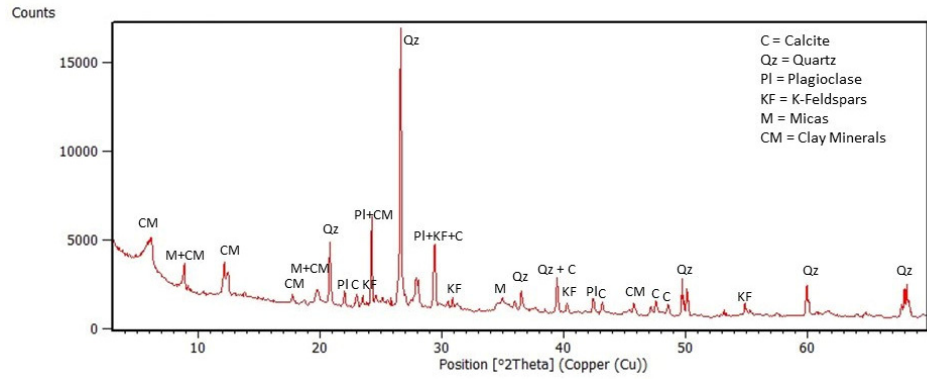


Figure 8. XRD diagram of the main mineralogical composition of the earthen not treated brick (credit: Rescic).

The semi-quantitative composition of the clay fraction was as follows: kaolinite 35%, illite 20%, and smectite 45% (Figures 9–11).

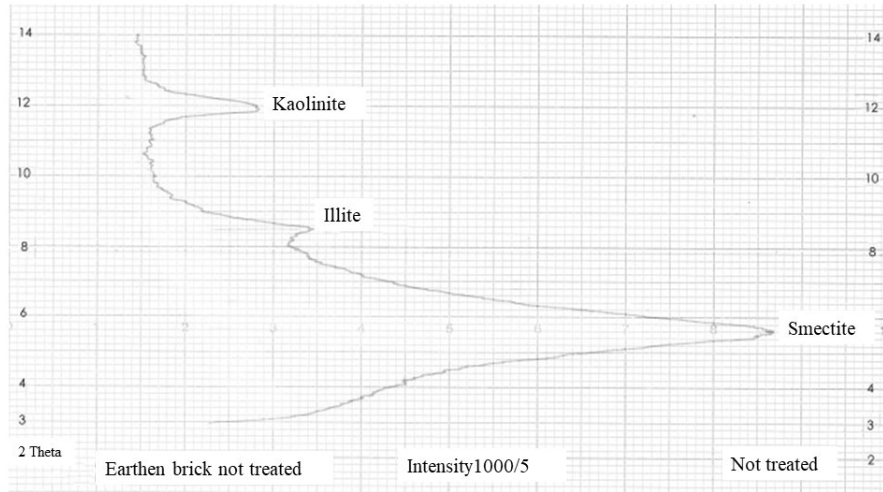


Figure 9. XRD diagram of the clay mineral fraction: Not treated sample.

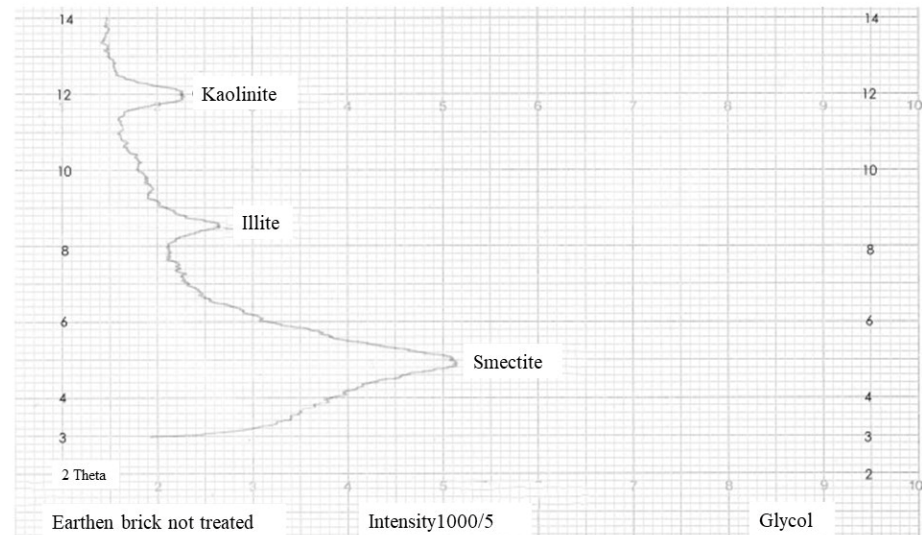


Figure 10. XRD diagram of the clay mineral fraction: glycol sample

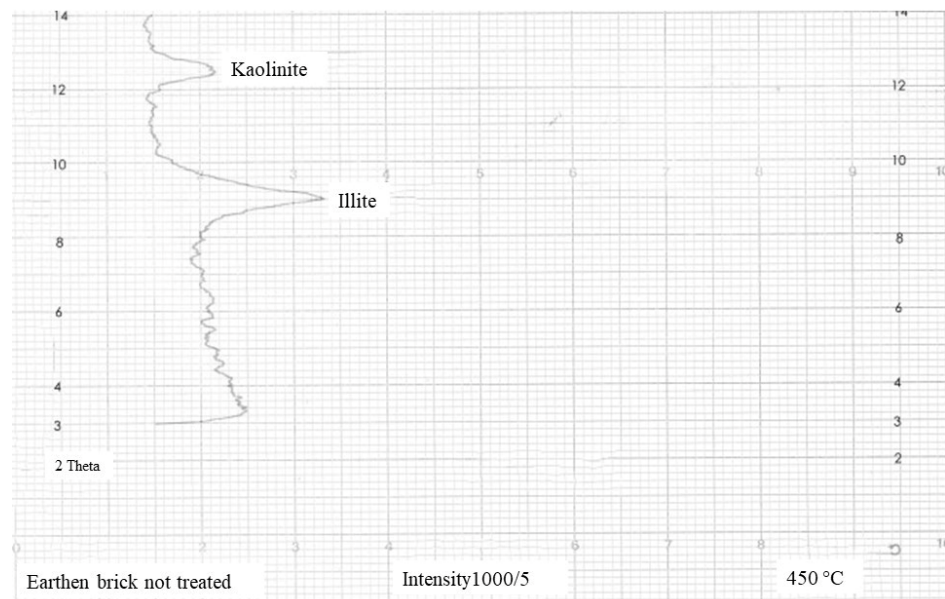


Figure 11. XRD diagram of the clay mineral fraction: sample at 450 °C

The comparison of the granulometric distribution of the earthen bricks of Sale (Alessandria) with those of the Piedmontese provinces of Cuneo, Turin, and Biella showed a greater affinity of the samples tested with those of the Cuneo area (Figure 12).

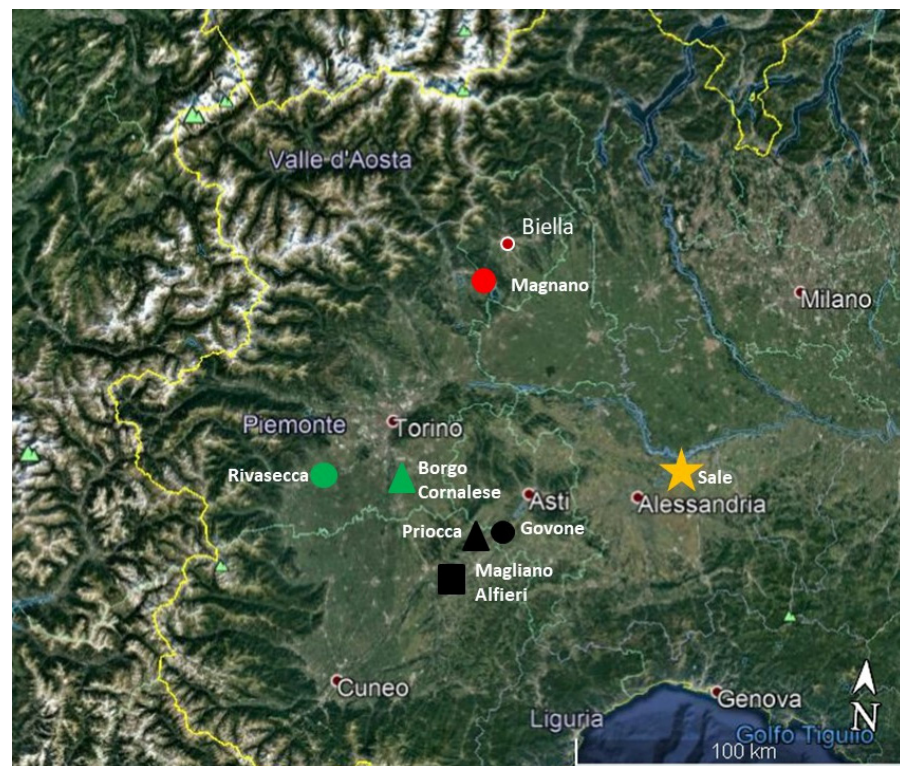


Figure 12. Map of areas where the earthen brick were sampled in Piedmont (from Google Earth Pro V 7.3.4, accessed on 14 December 2015, 44°54'44" N, 08°38'20" E, Videocamera alt 303 km, Google Landsat Copernicus data SIO, NOAA, U.S. Navy, NGA, GEBCO, modified by the authors).

In fact, these bricks were characterised by a greater presence of the finest fraction (silt), as can be seen from the diagram shown in Figure 13, where the optimal granulometric distribution area is indicated as defined by CRAterre (Figure 13) [52].

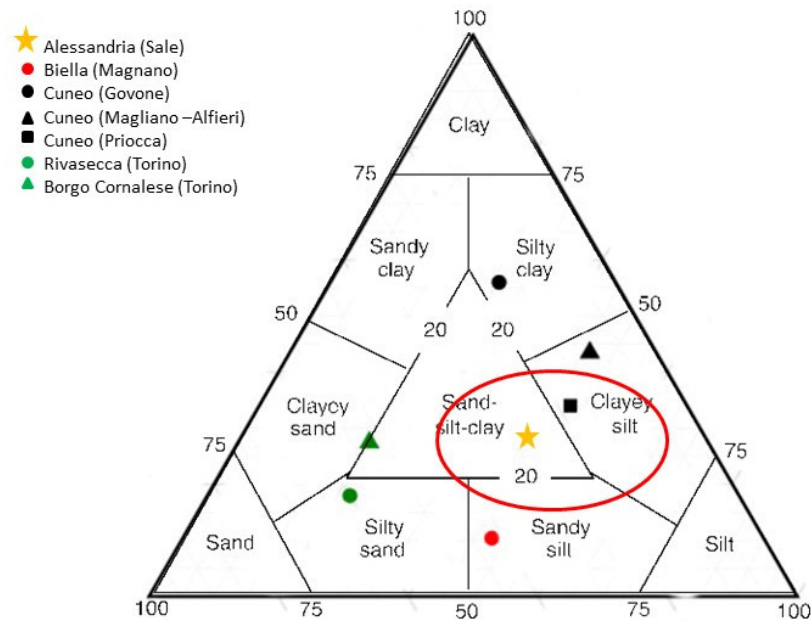


Figure 13. Diagram of the grain size composition of the earthen brick from Sale (Alessandria) compared with others from the Cuneo, Biella, and Turin provinces; within the red circle is the area of acceptability for adobe reported by CRAterre.

The bricks from Sale and Priocca (Figures 12 and 13) lie in this area, while those of Govone and Magliano-Alfieri are more clayey. Another similarity with the bricks from the Cuneo area concerns the mineralogical composition of the clay fraction with the presence of illite-smectite and smectite expandable lattice minerals [53]. These data suggest that the results obtained from the present experiment could also be useful for applications on bricks of earthen material from the Cuneo area.

3.2. Evaluation of the Performance of the Treated Earthen Bricks

The following paragraphs show the results of the performance tests on earthen bricks after the different treatments in terms of protective effectiveness against the action of water (Geelong and spray test, Karsten test, contact angle test), compatibility (DRMS test, cup wet method test, colour test), and durability (accelerate ageing through thermo-hygrometric cycles).

3.2.1. Geelong and Spray Test

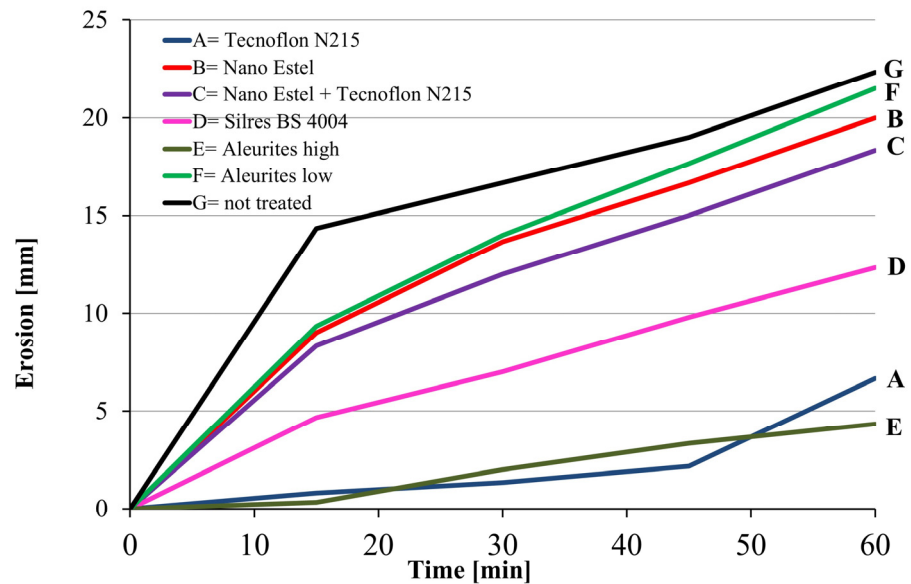
The results of the Geelong tests are reported in Table 5 as the average value of the depth of the holes and the relative index of erosion according to the New Zealand Standards [34,35].

The best results were obtained for bricks A (Tecnoflon N215) and E (Aleurites high) with an erosion index equal to 2, corresponding to no erosion at all (0 mm). In addition, brick D (Silres BS 4004) achieved an erosion index of 2, with an erosion depth of 0.16 mm. Bricks G (untreated) and F (Aleurites low) had an erosion degree of 3. As for bricks B (Nano Estel) and C (Nano Estel + Tecnoflon N215), they reached an erosion degree of 3, but it should be noted that the erosion depth exceeded even those of untreated brick (G).

Table 5. Results of the Geelong test.

Brick	Depth of Erosion (mm)	Index
Tecnoflon N215	0	2
Nano Estel	8.23 ± 0.20	3
Nano Estel + Tecnoflon N215	8.00 ± 0.20	3
Silres BS 4004	0.16 ± 0.10	2
Aleurites high	0	2
Aleurites low	4.00 ± 0.15	2
Not treated	5.34 ± 0.15	3

The results of the spray erosion tests are shown in Figure 14.

**Figure 14.** Spray erosion test diagram (credit: Mattone).

The results of the spray erosion test allow for the following considerations:

- All of the treatments except Nano Estel (B) and Aleurites low (F) improved the resistance to the spray erosion of the not treated brick;
- All of the bricks including the untreated ones and excluded those treated with Tecnoflon N215 (A) and Aleurites high (E) showed an erosion rate higher in the first 15 min, according to a lower cohesion of the surface layer of the bricks (possibly induced by the cleaning made before the treatments);
- The bricks treated with Tecnoflon N215 and Aleurites high showed a very low erosion rate in the first 45 and 15 min, respectively. However, the erosion rate grew very slowly even afterwards, and they generally had a higher resistance to all of the other treatments. In the case of these two treatments, the erosion at the end of the test reached about 5 mm.

3.2.2. Karsten Test and Static Contact Angle Test

The results of the water absorption test with the Karsten method are shown in Figure 15.

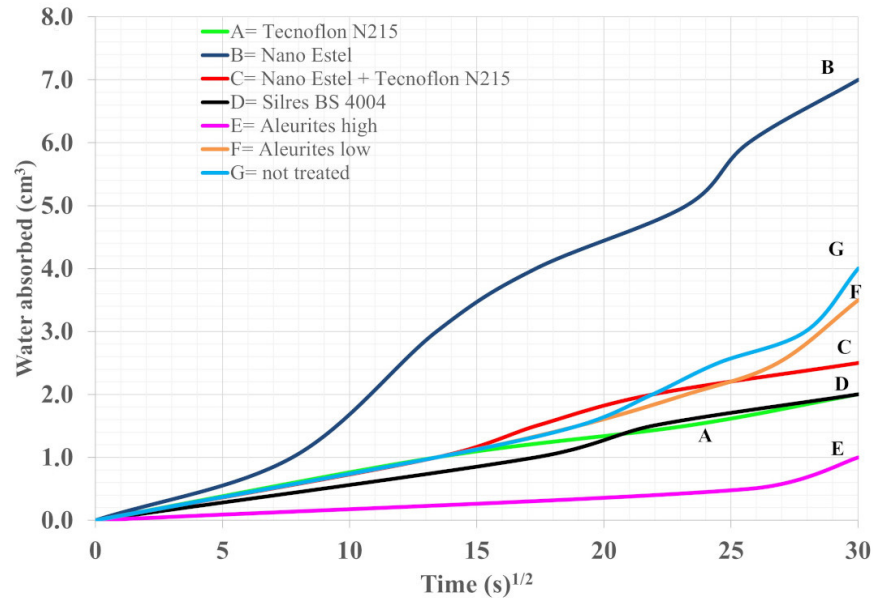


Figure 15. Water absorption diagram.

The results of the water absorption test allow for the following considerations:

- At the end of the test, only the brick treated with Aleurites high (E) absorbed an amount of water lower than the not treated brick (G). Moreover, brick E began to absorb water 10 min after the beginning of the test, demonstrating that the treatment significantly decreased the water absorption;
- Earthen brick B (Nano Estel) showed the worst results compared to the not treated brick (G). It absorbed the maximum amount of water (i.e., 7 cm³) and began to absorb from the first minute. This result is not unexpected for two reasons: nano silica is a consolidating but not a protective product, and second, it is applied in an aqueous solvent. The aqueous solvent could have caused partial melting of the earth with a reorganization of the matter that favoured the creation of a porous network more accessible to liquid water [47];
- Bricks A, C, and F began to absorb water like an untreated brick (G) (i.e., after 3 min), but while bricks A and C moderately reduced the water absorption to the untreated earthen brick (G), brick F reached a value of water absorption similar to that of the not treated brick G;
- Earthen brick D began to absorb water after 6 min, showing that the treatment decreased water absorption. Nevertheless, at the end of the test, the amount of absorbed water was similar to that of A and C, even if lower than the untreated brick.

The hydrophobic action of the treatments was also performed through an evaluation of the contact angle change. The results are shown in Figure 16 and Table 6.

Table 6. Results of the static contact angle test.

Treatment	Contact Angle θ°	Water Absorption Speed
Tecnoflon N215	110 ± 5	Very slow
Nano Estel	10 ± 2	Very fast
Nano Estel + Tecnoflon	120 ± 5	Very slow
Silres BS 4004	125 ± 5	Very slow
Aleurites high	93 ± 3	Slow
Aleurites low	40 ± 3	Medium slow
Not treated	20 ± 3	Fast

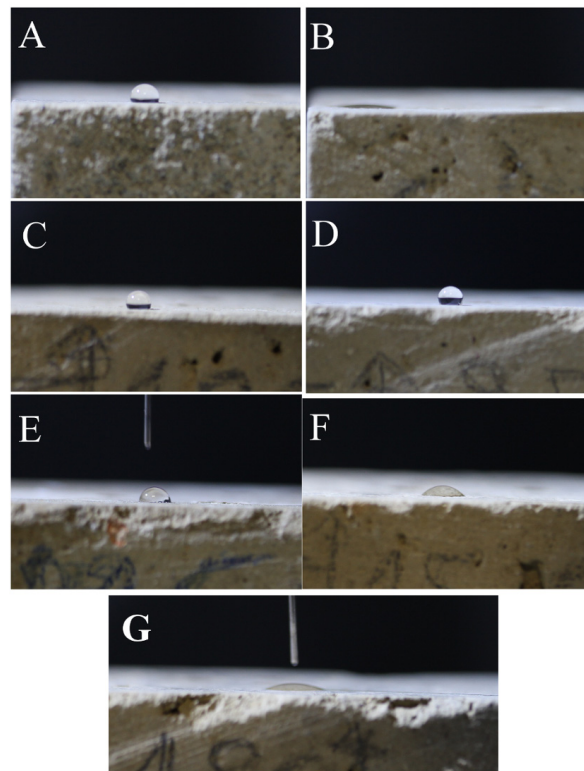


Figure 16. Contact angle of the earthen brick samples treated (A–F) and not treated (G). (A = Tecnoflon N215; B = Nano Estel; C = Nano Estel + Tecnoflon N215; D = Silres BS 4004; E = Aleurites high; F = Aleurites low; G = not treated) (credit: Rescic).

The conservative treatment products that performed best in this test were Tecnoflon N215(A), Nano Estel + Tecnoflon N215 (C), and Silres BS 4004 (D), namely, the products with well-known hydrophobic properties.

The samples treated with Aleurites oil low (F), and especially those treated with Aleurites oil high (E), showed medium hydrophobic properties. The bricks treated with Nano Estel (B) showed a rapid absorption, similar to the untreated bricks; this behaviour agreed with its mainly consolidating properties and the previous result of the water absorption test. When combined with Tecnoflon N215 (C), the latter was the product that provided the hydrophobic behaviour.

3.2.3. Wet Cup Test

Table 7 shows the mean values of the parameters calculated from the results of the water vapour permeability tests. The most interesting parameter is the resistance to water vapour diffusion μ ; the lower this value (the air has a value of 1), the more the vapour can pass through the material.

Data in Table 7 show that only two products (Aleurites high and low), respectively bricks E and F, determined an appreciable worsening of the μ parameter compared with the untreated earthen brick. This is probably due to the partial occlusion of the pores that allow for the passage of water in vapour form, with an increase in the vapour transmission resistance between 30% and 50% when compared with the untreated brick (see $\Delta\mu$ in Table 7).

For all of the other treated bricks, the variation of $\Delta\mu$ was relatively low, if not almost unchanged, compared to the untreated brick (Table 7). The slight decrease could have been caused by the action of the solvent, which can dissolve the earthen material and rearrange the porous network.

Table 7. The water vapour permeability results.

Parameter	Brick						Not Treated
	Tecnoflon N215	Nano Estel	Nano Estel + Tecnoflon N215	Silres BS 4004	Aleurites High	Aleurites Low	
μ (-)	9.0 ± 0.1	8.8 ± 0.1	8.7 ± 0.1	8.7 ± 0.1	14.2 ± 0.1	11.7 ± 0.1	9.1 ± 0.1
$\Delta\mu$ (%)	-0.9	-3.4	-4.6	-4.3	28.3	56.5	-

To evaluate the possible action of solvents used in the treatments, tests were carried out on the earthen bricks treated only with the solvent (water, acetone, isopropanol, limonene). The tests (Table 8) show that all of the solvents, except for limonene, probably due to its nonpolar characteristics, slightly reduced the resistance to water vapour transmission, $\Delta\mu$ 1–3%. This is probably due to the dissolving of the earth and reorganisation of the porous network, with an increase in the fraction of pores that allow for the passage of the water vapour [54,55].

Table 8. Solvent action: Water vapour permeability results.

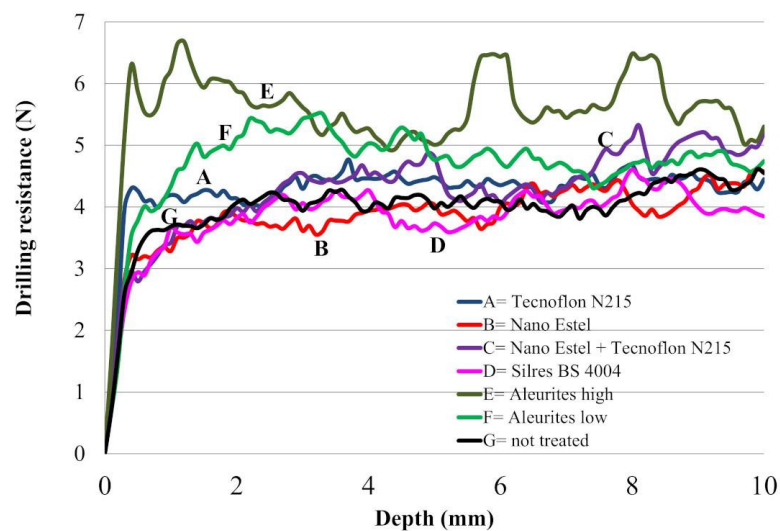
Parameter	Solvent			
	Water	Acetone	Isopropanol	Limonene
μ (-)	8.8 ± 0.1	9.0 ± 0.1	8.9 ± 0.1	9.1 ± 0.1
$\Delta\mu$ (%)	3.3	2.2	1.1	0

3.2.4. DRMS Test

The results of the drilling resistance tests are shown in Table 9 as average values in the depth ranges of 0.3–10 mm, 0.3–2 mm, and 2–10 mm, and in Figure 17 as the average profiles for all bricks. Therefore, by analysing these depth intervals, it is possible to assume the absence of a hard surface crust induced by the treatments. Usually, these data are supported by the interpretation of the drilling resistance profiles. The initial readings, when the force was growing (from 0 up to ~0.3 mm), were not considered since these values are not real.

Table 9. The drilling resistance results.

Treatment	Drilling Resistance (N)		
	Depth Range (mm)		
	0.3–10	0.3–2	2–10
Tecnoflon N215	4.35 ± 0.36	4.17 ± 0.34	4.38 ± 0.49
Nano Estel	3.94 ± 0.68	3.52 ± 0.35	4.03 ± 0.83
Nano Estel + Tecnoflon	4.38 ± 0.65	3.51 ± 0.45	4.56 ± 0.53
Silres BS 4004	3.91 ± 0.61	3.44 ± 0.43	4.01 ± 0.59
Aleurites high	5.66 ± 0.71	6.05 ± 0.75	5.58 ± 0.37
Aleurites low	4.50 ± 0.74	4.82 ± 0.94	4.89 ± 0.96
not treated	3.66 ± 0.36	4.07 ± 0.49	4.15 ± 0.58

**Figure 17.** Drilling resistance profiles (A = Tecnoflon N215; B = Nano Estel; C = Nano Estel + Tecnoflon N215; D = Silres BS 4004; E = Aleurites high; F = Aleurites low; G = not treated) (credit: Rescic).

The results reported in Table 9 and Figure 17 show that:

- For all treatments, there were no relevant differences between the values of the drilling resistance calculated in the two depth ranges (0.3–2 mm and 2–10 mm) (Table 9). This suggests that there is no superficial crust due to a surface concentration of the product. This hypothesis was also confirmed by the drilling profiles shown in Figure 17;
- Only the two treatments with Aleurites oil, low (F) and high (E), showed an increase in the drilling resistance (Table 9) that was more evident in the case of the high concentration treatment, especially in the first few millimetres (Figure 17). This suggests a higher concentration of the product on the surface with the formation of a harder layer. However, it can be seen that the drilling resistance profile for both concentrations of the Aleurites treatment had higher values than that of the untreated one throughout the depth range. This would indicate that the product, through its porosity-filling action, also induced an increase in the surface cohesion of the earthen brick;
- The treatments with a consolidation action based on Nano Estel (B) alone and Nano Estel + Tecnoflon N215 (C) did not seem to have induced an increase in the drilling resistance compared to the untreated sample (G); this considered both the average value (Table 9) and the trends of the drilling profiles (Figure 17).

3.2.5. Colour Test

The results of the colorimetric measurements are shown in the Table 10 and Figure 18 as the differences (ΔL^* , Δa^* , Δb^*) of these values before and after treatment. The parameter ΔE^* is also shown.

Table 10. The average values of colour variation.

Treatment	ΔL^*	Δa^*	Δb^*	ΔE^*
Tecnoflon N215	2.56 ± 1.69	-1.35 ± 0.22	-5.10 ± 0.58	6.00 ± 1.00
Nano Estel	4.16 ± 2.89	-0.98 ± 0.45	-3.06 ± 1.46	5.70 ± 2.30
Nano Estel + Tecnoflon N215	5.51 ± 1.22	-1.35 ± 0.21	-4.17 ± 0.64	7.10 ± 1.20
Silres BS 4004	-4.07 ± 1.92	-0.32 ± 0.16	-1.78 ± 0.57	4.50 ± 1.90
Aleurites high	13.92 ± 3.73	-2.28 ± 0.33	5.51 ± 1.22	14.90 ± 3.10
Aleurites low	-2.04 ± 1.17	-0.24 ± 0.03	-0.65 ± 1.03	2.60 ± 1.50

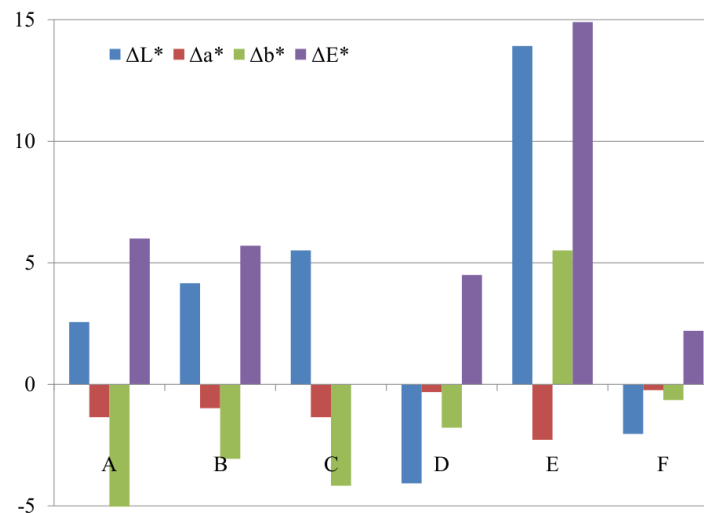


Figure 18. Average values of the variations in the chromatic parameters of the different treatments (A = Tecnoflon N215; B = Nano Estel; C = Nano Estel + Tecnoflon N215; D = Silres BS 4004; E = Aleurites high; F = Aleurites low; G = not treated) (credit: Luvidi).

All treatments, except for D and F, showed a total variation in colour perception (ΔE) appreciable with the naked eye ($\Delta E > 5$). In particular:

- Earthen bricks treated with Tecnoflon N215, Nano Estel, Nano Estel + Tecnoflon N215, and Aleurites oil high showed a decrease in brightness (L^*) and an increase in the a^* (redder) and b^* (more yellow) parameters. Therefore, the earthen bricks were darker brown than before the treatment;
- Earthen bricks treated with Silres BS 4004 showed an increase in brightness (L^*) and in a^* (redder) and b^* (more yellow) parameters. Therefore, for the treatment with Silres BS 4004, the earthen bricks were slightly lighter brown than before the treatment;
- Regarding the earthen bricks treated with the Aleurites oil low concentration, their colour remained almost unchanged, resulting in the variation $\Delta E < 3$.

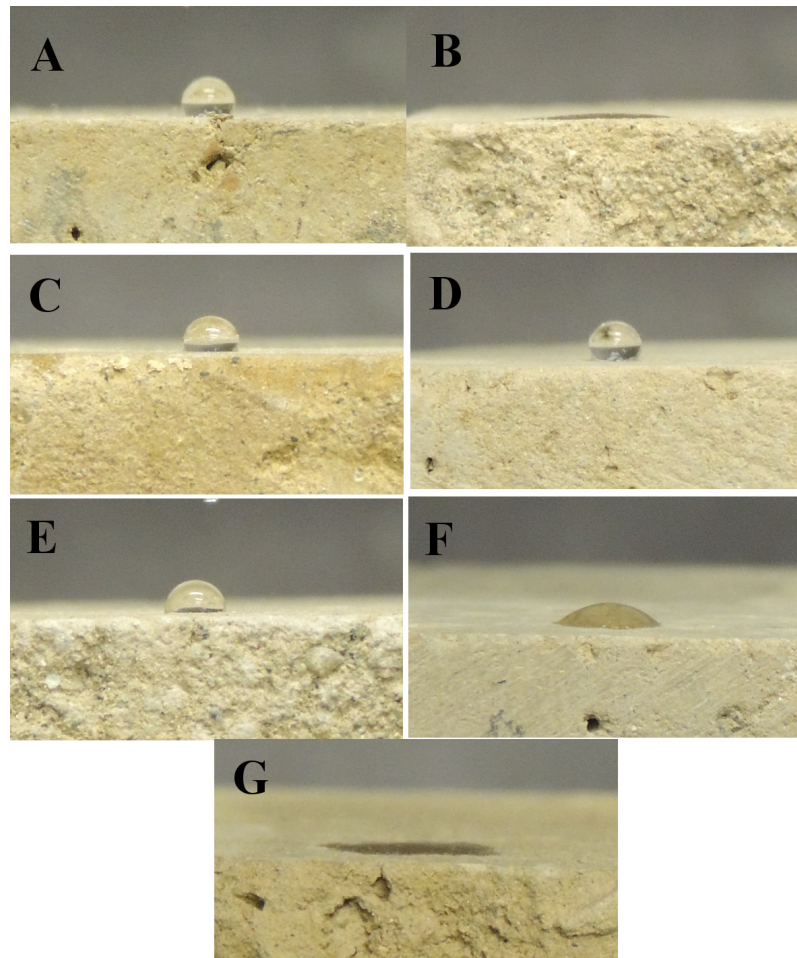
3.2.6. Durability Test

The effects on the durability after thermo-hygrometric ageing were evaluated by measuring the variations in colour, contact angle (Figure 19), and weight of the treated and untreated earth brick samples. These results are shown in Table 11.

Table 11. Changes in colour, contact angle, and weight on the treated and untreated earthen bricks after the accelerated ageing test.

Brick	Colorimetric Results				Contact Angle Result		Weight Results
	ΔL^*	Δa^*	Δb^*	ΔE^*	Contact Angle θ° Before	Contact Angle θ° After	# Weight Loss (%)
Tecnoflon N215	0.64 ± 0.74	-0.32 ± 0.20	-0.94 ± 0.50	1.25 ± 0.77	110 ± 5	108 ± 5	0.29 ± 0.10
Nano Estel	0.15 ± 0.41	0.00 ± 0.07	0.04 ± 0.17	0.37 ± 0.18	10 ± 2	10 ± 4	0.35 ± 0.12
Nano Estel + Tecnoflon N215	0.10 ± 0.09	-0.03 ± 0.00	-0.23 ± 0.08	0.26 ± 0.11	120 ± 5	118 ± 6	0.43 ± 0.12
Silres BS 4004	-0.15 ± 0.15	-0.03 ± 0.11	-0.07 ± 0.39	0.37 ± 0.17	125 ± 5	115 ± 7	0.42 ± 0.12
Aleurites high	-4.54 ± 2.54	0.58 ± 0.19	-0.97 ± 1.57	4.78 ± 2.75	93 ± 3	90 ± 3	0.31 ± 0.10
Aleurites low	-1.22 ± 0.50	-0.13 ± 0.05	-0.68 ± 0.28	1.40 ± 0.57	40 ± 3	37 ± 5	0.34 ± 0.10
not treated	-2.03 ± 0.08	-0.20 ± 0.07	-1.13 ± 0.16	2.33 ± 0.04	20 ± 3	10 ± 3	0.30 ± 0.10

Weight loss (%) = $[(\text{weight}_{\text{before ageing}} - \text{weight}_{\text{after ageing}}) / \text{weight}_{\text{before ageing}}] * 100$. $\Delta L^* = L^*_{\text{treated}} - L^*_{\text{aged}}$; $\Delta a^* = a^*_{\text{treated}} - a^*_{\text{aged}}$; $\Delta b^* = b^*_{\text{treated}} - b^*_{\text{aged}}$; $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$.

**Figure 19.** After ageing, contact angle of the earthen brick samples treated (A–F) and not treated (G). (A = Tecnoflon N215; B = Nano Estel; C = Nano Estel + Tecnoflon N215; D = Silres BS 4004; E = Aleurites high; F = Aleurites low; G = not treated) (credit: Rescic).

The untreated earthen brick appeared to be the only one with a slight worsening in its natural capacity of hydrophobicity, with a contact angle reduction and an increased absorption rate. The contact angle and the corresponding water absorption rate for all other treatments remained practically unchanged.

The amount of material lost after ageing was low for all bricks and compatible with their handling during the execution of the tests. Regarding the colour change, except for the Aleurites high sample, the variations were not perceptible to the naked eye ($\Delta E < 3$). For the samples treated with Aleurites high, the thermo-hygrometric cycles probably induced ageing of the oil, mainly causing its darkening (decrease in the L^* parameter).

4. Discussion

Based on the test results obtained for the various treatments, the following considerations can be summarised:

- Tecnoflon N215 (A) showed good behaviour in the tests in both the resistance to the erosive action of the water and in the evaluation of the hydrophobic properties, guaranteeing excellent characteristics of permeability to water vapour. However, a change in colour was evident ($\Delta E > 5$). The drilling resistance also did not show a significant increase in the first millimetre excluding the formation of a hard crust;
- Nano Estel (B) showed poor results concerning the resistance to water erosion, water absorption, hydrophobicity, and drilling resistance. The poor result of the drilling resistance test in this case was not expected since the product is a consolidating agent. The main causes could be related to the difficult penetration of the nanoparticles inside the porosity of the material due to the application method (spraying); a low percentage of the applied product that is therefore unable to provide cohesion back to the material; and a negative action of the aqueous solvent on the earthy material that caused it to disintegrate. This last hypothesis seems confirmed by the water vapour permeability test performed on brick samples on which solvents were applied (see Table 7) [54]. It was observed that, in general, the solvents, polar and nonpolar (water > acetone > isopropanol > limonene) [56], interacted with the earth material, in particular with the clay fraction, triggering absorption/desorption phenomena (swelling/contraction), particularly in expandable lattice minerals such as smectite and vermiculite [57–59]. The result is a reorganisation of the structure and probably a lower “compactness” of the material. A role can also be played by the rate of evaporation of the solvent, namely, how long the material remains wet (solvent vapour pressure increasing: limonene > water > isopropanol > acetone) [55–57]. The colour variation was not relevant;
- The combined product Nano Estel + Tecnoflon N215 (C) showed promising results with respect to water absorption and hydrophobic tests, and is connected to the presence of a fluoelastomer in the mixture, which can preserve the permeability to water vapour. As in the case of Nano Estel alone, the resistance to water vapour transmission was decreased, probably due to the disaggregation power of the solvent or to experimental error/data dispersion. As for the resistance to both the action of water by spray and the Geelong tests and to drilling, no positive effects were observed. It was positively assessed that the drilling resistance did not show significant increases in the first millimetre excluding the formation of a hard crust. The colour changed perceptibly, that is $\Delta E > 3$;
- Silres BS 4004 (D) showed a behaviour similar to that of Tecnoflon N215 with excellent results both for the tests of resistance to the erosive action of water and for the hydrophobic properties, guaranteeing the excellent characteristics of water vapour permeability with a change in colour below that perceptible to the naked eye ($\Delta E < 3$). The resistance to the transmission of water vapour was decreased, and also, in this case, the reason can be attributed to the action of the solvent or to experimental error/data dispersion. The drilling resistance did not show significant increases in the first millimetre excluding the formation of a hard crust;

- Aleurites high (E) showed excellent results concerning the action against water ingress and the increase in the surface hydrophobicity. Unfortunately, the DRMS test seemed to indicate the formation of a surface hard layer, although such ‘hardening’ was also observed within the brick up to the investigated depth (10 mm). In agreement with the presence of this harder layer, there were also the very poor results of the water vapour permeability test, where it seems that the product caused occlusion of the pores. A possible reason is the product application as supplied by the seller, without dilution, which is therefore of a higher concentration with respect to the others. Additionally, the results of the colour tests were very poor;
- Aleurites low (F) seems to have occluded the material’s pores with an increase in the resistance to the water vapour transmission. There was a slight increase in the drilling resistance, showing that the treatment did not induce the formation of a hard surface layer in this concentration in the first millimetres but did not even confer the characteristics of protection against water, as evidenced by the tests of resistance to erosion, water absorption, and surface hydrophobicity, with results similar to those of the untreated brick. There were small colour changes but considering all of the performances, the treatment did not induce positive effects.

5. Conclusions

The results obtained from the experimentation on local earth bricks recovered from a farmhouse in the province of Alessandria (Italy) are interesting in several aspects such as the method of application of the products and the type of solvent used:

- Application by brush could guarantee a good distribution of the product, but the best results were obtained by spraying because the “mechanical” interaction between the earth’s surface and the brush, which could cause the removal of material from the surface, is avoided;
- The type of solvent is undoubtedly a critical parameter when the material to be protected is earth. Indeed, a water solvent should be preferred for lower toxicity, but water has a bad effect on the earthen material, especially in the presence of swelling clay minerals. Therefore, solvents with low polarity and high vapour pressure should be used. However, the action of the solvent on the earthen material would need to be investigated with even more in-depth experimentation.

In general, among the applied products, the synthetic ones (Tecnoflon N215 and Silres BS 4004), having specific water-repellence characteristics, performed very well on the earthen bricks, delaying the penetration of water considerably and increasing the resistance to the erosive action of water, but nevertheless maintaining a good transmission of the water vapour.

Finally, we remember that each type of “earthen material” has a particular composition and, consequently, a different response to treatment. When intervening in monumental heritage, it is therefore necessary to carry out specific experimental campaigns to identify the products that, in compliance with the compatibility criterion, are capable of guaranteeing adequate protection of earthen surfaces. On the other hand, as far as interventions to conserve and recover vernacular architectural heritage are concerned, it is not possible to evaluate the most suitable products on a case-by-case basis. It will be necessary, from time to time, to refer to the results of experimental campaigns carried out on similar materials and in similar contexts, conducting the experimentation on a single artefact, taken as a case study, whenever possible.

Author Contributions: Please note that all authors of this paper should be considered principal authors. All authors shared the concept of the research. M.M. performed the water erosion tests and the water absorption test. F.F. cut the samples and carried out the grain size distribution and XRD analysis. S.R. performed the DRMS measurements, water vapour permeability tests, static contact angle, and artificial ageing tests. L.L. carried out the colorimetric measurements and the evaluation of the ageing effect on the treatments. All authors contributed to the discussion of the results and

the drafting of the article. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data presented in this study are available within the article.

Acknowledgments: Leonardo Borgioli (CTS-Italy) kindly supplied Nano Estel; Wacker Chemie-Germany and Solvay-Solexis-Italy kindly supplied Silres® BS 4004 and Tecnoflon N215. We thank Mara Camaiti (CNR-IGG, Florence, Italy) for her support in the realisation of the treatments and for the important suggestions in discussing the results.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Mattone, M. Earthen Architectures: History, Typologies and Construction Techniques. In *Past and Present of the Earthen Architectures in China and Italy*; CNR Edizioni: Roma, Italy, 2021; pp. 11–22. ISBN 978 88 8080 470 3.
2. Minke, G. *Building with Earth: Design and Technology of a Sustainable Architecture*, 4th ed.; Birkhauser: Basel, Switzerland, 2021. ISBN: 9783035622539.
3. Costi de Castrillo, M.; Philokyprou, M.; Ioannou, I. Comparison of adobes from pre-history to date. *J. Archaeol. Sci. Rep.* **2017**, *12*, 437–448.
4. Guillaud, H.; Houben, H.; Dethier, J. *Traité de Construction en Terre*; Parenthèses Editions: Marseille, France, 2015. ISBN: 9782863641613.
5. Steen, A.; Steen, B.; Komatsu, E. *Built by Hand: Vernacular Buildings around the World*; Gibbs Smith Publishers: Layton, UT, USA, 2003. ISBN: 9781586852375.
6. Mecca, S. From disregard to innovation. In *Earth/Lands. Earthen Architecture of Southern Italy*; Mecca, S., Boti Briccoli, S., Forlani, M.C., Germanà, M., Eds.; Edizioni ETS: Firenze, Italy, 2011; pp. 89–95. ISBN: 9788846721464. Available online: <https://is-suu.com/dida-unifi/docs/earth-lands> (accessed on 18 January 2023).
7. Frenda, A. Earthen architecture in the agricultural heritage system: Sustainable development, restoration, and continuity of tradition. *J. Mater. Environ. Sci.* **2016**, *7*, 3614–3622.
8. Baglioni, E.; Rovero, L.; Toniatti, U. Drâa valley earthen architecture: Construction techniques, pathology and intervention criteria. *J. Mater. Environ. Sci.* **2016**, *7*, 3499–3508.
9. Mileto, C.; Vegas, F.; Llatas, C.; Soust-Verdaguer, B. A Sustainable Approach for the Refurbishment Process of Vernacular Heritage: The Sesga House Case Study (Valencia, Spain). *Sustainability* **2021**, *13*, 9800. <https://doi.org/10.3390/su13179800>.
10. Achenza, M. Historical Earthen Architectures in Italy. In *Past and Present of the Earthen Architectures in China and Italy*; CNR Edizioni, Roma, Italy, 2021; pp. 39–56. ISBN 978 88 8080 470 3.
11. Aloiz, E.M. New Investigations into a Historic Treatment: The Efficacy of Gelatin as an Adhesive for Earthen Finishes at Mesa Verde National Park. Master's Thesis, University of Pennsylvania, Philadelphia, PA, USA, 2011.
12. Eires, R.; Camões, A.; Jalali, S. Ancient Materials and Techniques to Improve the Earthen Building Durability. *Key Eng. Mater.* **2014**, *634*, 357–366.
13. Gomes, M.I.; Goncalves, T.D.; Faria, P. Earth-based repair mortars: Experimental analysis with different binders and natural fibers. In *RESTAPIA 2012, Valencia, 21–23 June 2012. Rammed Earth Conservation*; Mileto, C., Vegas, F., Cristini, V., Eds.; Taylor & Francis Group: London, UK, 2012; pp. 661–668.
14. Mattone, M.; Ibnoussina, M.; Rescic, S.; Fratini, F.; Magrini, D.; Mecchi, A.M.; Nocairi, M. Stabilization of earthen plasters: Exchange of knowledge and experiences between Italy and Morocco. *J. Mater. Environ. Sci.* **2016**, *7*, 3647–3655.
15. Mattone, M.; Rescic, S.; Fratini, F.; Manganelli Del Fa, R. Experimentation of Earth-Gypsum Plasters for the Conservation of Earthen Constructions. *Int. J. Archit. Herit.* **2017**, *11*, 763–772.
16. Stazi, F.; Nacci, A.; Tittarelli, F.; Pasqualini, E.; Munafò, P. An experimental study on earthen plasters for earthen building protection: The effect of different admixtures and surface treatments. *J. Cult. Herit.* **2016**, *17*, 27–41.
17. Ferron, A. The Consolidation of Earthen Surface Finishes: A Study of Disaggregating Plasters at Mesa Verde National Park. Master's Thesis, University of Pennsylvania, Philadelphia, PA, USA, 2007.
18. Ferron, A.; Matero, F.G. A Comparative Study of Ethyl-silicate-based Consolidants on Earthen Finishes. *J. Am. Inst. Conserv.* **2011**, *50*, 49–72. <https://doi.org/10.1179/019713611804488964>.
19. Pacheco, G.; Pozzi-Escot, D.; Cappai, M.; Malpartida, S.; Petrick, S. Productos orgánicos para la conservación de pintura mural. In *Proceedings of the XII World Congress on Earthen Architecture Terra 2016, Lyon, France, 11–14 July 2016*; Craterre: Villefontaine, France, 2016; pp. 133–137. ISBN 9791096446117.
20. Li, Z.; Zhao, L.; Sun, M. Deterioration of earthen sites and consolidation with PS material along Silk Road of China. *Chin. J. Rock Mech. Eng.* **2009**, *28*, 1047–1054.
21. Chiari, G. Chemical surface treatments and capping techniques of earthen structures: A long-term evaluation. In *Proceedings of the 6th International Conference on the Conservation of Earthen Architecture, Las Cruces, NM, USA, 14–19 October 1990*;

- Agnew, N.; Taylor, M.; Balderrama, A.A.; Houben, H.; Grimstad, K.; The Getty Conservation Institute: Los Angeles, CA, USA, 1990; pp. 267–273.
22. Bourguès, A.; Colas, E.; Vissac, A.; Fontaine, L.; Anger, R.; Gandreau, D.; Joffroy, T. Similarities and differences in evaluation methods for stone or Earthen surfaces. In Proceedings of the International Conference on Conservation of Stone and Earthen Architectural Heritage, Gongju, Republic of Korea, 20–23 May 2014; pp. 165–171.
 23. Elert, K.; Sebastian, E.; Valverde, I.; Rodriguez-Navarro, C. Alkaline treatment of clay minerals from the Alhambra Formation: Implications for the conservation of earthen architecture. *Appl. Clay Sci.* **2008**, *39*, 122–132.
 24. Elert, K.; Pardo, E.S.; Rodriguez-Navarro, C. Alkaline activation as an alternative method for the consolidation of earthen architecture. *J. Cult. Herit.* **2015**, *16*, 461–469. <https://doi.org/10.1016/j.culher.2014.09.012>.
 25. Elert, K.; Bel-Anzué, P.; Monasterio-Guillot, L.; Pardo, S. Performance of alkali activation for the consolidation of earthen architecture. *J. Cult. Herit.* **2019**, *39*, 93–102. <https://doi.org/10.1016/j.culher.2019.03.004>.
 26. Lohnas, D.E. Evaluating the effectiveness of calcium hydroxide nanoparticle dispersions for the consolidation of painted earthen architectural surfaces. Master's Thesis, University of California, Los Angeles, CA, USA, 2012.
 27. Lanzón, M.; Madrid, J.A.; Martínez-Arredondo, A.; Mónaco, S. Use of diluted Ca(OH)₂ suspensions and their transformation into nanostructured CaCO₃ coatings: A case study in strengthening heritage materials (stucco, adobe and stone). *Appl. Surf. Sci.* **2017**, *424*, 20–27.
 28. Camerini, R.; Chelazzi, D.; Giorgi, R.; Baglioni, P. Hybrid nano-composites for the consolidation of earthen masonry. *J. Colloid Interface Sci.* **2019**, *539*, 504–515.
 29. Mattone, M. Prevenire il degrado: La protezione delle costruzioni in terra cruda. In Proceedings of the XXVI Convegno Internazionale Scienza e Beni Culturali-Pensare la Prevenzione, Bressanone, Italy, 13–16 July 2010; Arcadia Ricerche: Venice, Italy, 2010; pp. 141–150. ISBN 978-88-95409-14-6.
 30. European Standards EN 15802: 2009; Conservation of Cultural Property—Test Methods—Determination of Static Contact Angle. UNI: Milan, Italy, 2009.
 31. European Standards EN 16581:2014; Conservation of Cultural Heritage—Urface Protection for Porous Inorganic Materials—Laboratory Test Methods for the Evaluation of the Performance of Water Repellent Products. UNI: Milan, Italy, 2014.
 32. European Standards EN 15803: 2010; Conservation of Cultural Property—Test Methods—Determination of Water Vapour Permeability (δ_p). UNI: Milan, Italy, 2010.
 33. European Standards EN 15886: 2010; Conservation of Cultural Property—Test Methods—Colour Measurement of Surfaces. UNI: Milan, Italy, 2010.
 34. NZS 4298-D; Materials and Workmanship for Earth Buildings, Appendix D. Standards New Zealand: Wellington, New Zealand, 1998.
 35. NZS 4298-E; Materials and Workmanship for Earth Buildings, Appendix E. Standards New Zealand: Wellington, New Zealand, 1998.
 36. Camaiti, M.; Benvenuti, E.; Paciulli, L. Formulati a base di poliammidi parzialmente fluorurate e fluoroelastomeri per la protezione e il consolidamento di manufatti lapidei. *Arkos Sci. Restauro* **2011**, *28*, 29–33.
 37. Banchelli, A.; Fratini, F.; Germani, M.; Malesani, P.; Manganelli Del Fa, C. The sandstones of the Florentine historic buildings: Individuation of the marker and determination of the supply quarries of the rocks used in some Florentine monuments. *Sci. Technol. Cult. Herit.* **1997**, *6*, 13–22.
 38. *The Australian Earth Building Handbook*; Standards Australia International: Sydney, Australia, 2002.
 39. SAZS 724; Rammed Earth Structures. Standards Association of Zimbabwe: Harare, Zimbabwe, 2001.
 40. EN 16302: 2013; Conservation of Cultural Property—Test Methods—Measurement of Water Absorption by Pipe Method. UNI: Milan, Italy, 2013.
 41. Papamichos, E.; Papanicolopolus, S.A.; Larsen, I.; Alnæ, L.; Rescic, S. Method for in situ, quasi non-destructive diagnosis of mechanical properties and damage of natural building stones. In Proceedings of the Gulf Rock 2004, the 6th North America Rock Mechanics Symposium, Houston, TX, USA, 5–9 June 2004; paper n. ARMA-04-583.
 42. Valentini, E.; Benincasa, A.; Tiano, P.; Fratini, F.; Rescic, S. On Site Drilling Resistance Profiles of Natural Stones. In Proceedings of the International Workshop In Situ Monitoring of Monumental Sufaces, Florence, Italy, 27–29 October 2008; pp. 195–204.
 43. Rescic, S.; Fratini, F.; Tiano, P. Onsite evaluation of the mechanical properties of Maastricht limestone and their relationship with the physical characteristics. *Geol. Soc. Lond. Spec. Publ.* **2010**, *331*, 203–207.
 44. Rescic, S.; Mattone, M.; Fratini, F.; Luvidi, L. Earthen Plasters Stabilized through Sustainable Additives: An Experimental Campaign. *Sustainability* **2021**, *13*, 1090. <https://doi.org/10.3390/su13031090>.
 45. Snethlage, R. Stone Conservation. In *Stone in Architecture*, 5th ed.; Siegesmund, S., Snethlage, R., Eds.; Springer: Berlin, Germany, 2014; pp. 512–520.
 46. Delgado Rodrigues, J.; Grossi, A. Indicators and ratings for the compatibility assessment of conservation actions. *J. Cult. Herit.* **2007**, *8*, 32–34.
 47. CIELAB. *Commission Internationale de l'Eclairage*; Wien CIE: Vienna, Austria, 1976.
 48. ASTM D4141/D4141M; Standard Practice for Conducting Black Box and Solar Concentrating Exposures of Coatings. ASTM International: West Conshohocken, PA, USA, 2014.
 49. ASTM D559/D559M; Standard Test Methods for Wetting and Drying Compacted Soil-Cement Mixtures. ASTM International: West Conshohocken, PA, USA, 2015.

50. ASTM D560/D560M; Standard Test Methods for Freezing and Thawing Compacted Soil-Cement Mixtures. ASTM International: West Conshohocken, PA, USA, 2015.
51. Internal Damage of Concrete Due to Frost Action. In *Final Recommendation Test Methods of Frost Resistance of Concrete: CIF-Test: Capillary Suction, Internal Damage, and Freeze Thaw Test—Reference Method and Alternative Methods A and B in RILEM TC 176-IDC (2004)*; RILEM Publications, Champs-sur-Marne, France.
52. Houben, H.; Guillaud, H. *Traité de Construction en Terre de CRATerre*; Parenthèse Editions: Marseille, France, 1989.
53. Mattone, M.; Fratini, F.; Rescic, S.; Rovero, L. Analysis of the earthen architectural heritage in Piedmont (northern Italy): Typologies, construction techniques and materials. *Rev. Grem.* **2021**, *7*, 41–52.
54. Bourgès, A.; Tiennot, M.; Mertz, J.D.; Liégey, A.; Bouquillon, A. Review of earthen materials consolidation with ethyl silicate. In Proceedings of the 22th World Congress on Earthen Architecture, TERRA, Lyon, France, 11–14 July 2016; pp. 104–107.
55. Barsottelli, M.; Fratini, F.; Giorgetti, G.; Manganelli Del Fa, C. Microfabric and alteration in the Carrara marble: A preliminary study. *Sci. Technol. Cult. Herit.* **1998**, *7*, 109–120.
56. Sadek, P.C. *The HPLC Solvent Guide*, 2nd Ed.; Wiley-Interscience: New York, NY, USA, 2002; 644p. ISBN: 0-471-41138-8.
57. Madsen, F.T.; Müller-Vonmoos, M. The swelling behaviour of clays. *Appl. Clay Sci.* **1989**, *4*, 143–156.
58. Houben, H.; Guillaud, H. *Earth Construction: A Comprehensive Guide*; Practical Action Publishing: Rugby, UK, 1994, 376p. ISBN 10: 185339193X.
59. Rodriguez-Navarro, C.; Sebastian, E.; Doehne, E.; Ginell, W.S. The role of sepiolite-palygorskite in the decay of ancient Egyptian limestone sculptures. *Clays Clay Miner.* **1996**, *46*, 414–422.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.