

Article

Design and Assessment of Pastes for the Reattachment of Fractured Porous Stones

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Abstract: Ancient stone masonry is a composite structure, mainly comprised of stone elements. During restoration, stone elements are sometimes found to present serious fragmentation, and their structural continuity must be re-established. In such cases, an adhesive material can be applied to reattach the detached fragment to its original position, with or without the use of pins or anchors, according to the size of the fragment and its position. However, many considerations must be taken into account regarding compatibility with the ancient material and the performance and longevity of the intervention. In the current study, a series of pastes are designed for the reattachment of stone fragments, with and without the concurrent use of titanium pins, aiming to re-establish the continuity of the porous stone elements of the Acropolis circuit wall. The designed pastes are examined in terms of physical and mechanical characteristics and assessed in relation to their compatibility with the original stone material, while their effectiveness as adhesive and/or anchoring materials is evaluated through a real-time and -scale pilot application on site at the Acropolis monument work site using fragments of the original ancient stone material. The natural lime–metakaolin paste presents the optimum results as an adhesive and anchoring material.

Keywords: acropolis; porous stone; pastes; titanium pins; compatibility; performance; reattachment; direct tension



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1. Introduction

After years in service, stone elements in ancient structures begin to deteriorate and are in need of conservation [1]. This is especially true in the case of porous stones, which exhibit a higher susceptibility to decay [2], especially when subjected to severe environmental loads, as in the case of outdoor monuments [3].

The deterioration of stone elements is the result of both intrinsic (stone characteristics) and extrinsic (climatic and anthropogenic) factors [4,5]. The effects of strong climatic variations and thermal and hygric fluctuations, in addition to the strong winds that exposed outdoor monuments are subjected to, enhance many decay processes [6]. The presence and transfer of water is an important decay factor affecting exposed stone monuments, as it is interlinked with most stone deterioration processes [7]; it facilitates the corrosive action of acidic pollution gases, such as SO_x and NO_x [8], its presence can lead to the

formation of internal cracks due to freeze–thaw cycles [9,10] and it allows for the transfer, accumulation and crystallization of water soluble salts [11,12], while it also affects and controls biodeterioration mechanisms [13]. In many cases, stone deterioration is further aggravated by interventions using incompatible materials; for example, salts migrating to calcarenite stones from incompatible materials such as Portland cement may enhance their deterioration by crystallization pressure, fatigue and shear stresses due to differential hygric and thermal expansions [6]. In addition to deterioration, static and dynamic stresses cause damage to stone elements when their mechanical strength is exceeded. Amongst the deterioration patterns observed in stone, the fracturing, detachment and loss of stone material are considered the most threatening, as they pose a risk to the structural integrity of the elements and the structure as a whole [6,14]. Thus, measures must be taken to re-establish the structural continuity of stone elements.

The reattachment of detached stone fragments to fractured stone elements, when necessary, demands the use of appropriate adhesive materials. A variety of materials have been tested as adhesives; amongst them, epoxy, acrylic and polyester resins are the most commonly used, while cement has also been extensively applied [15–17]. However, in recent years, attempts have been made towards the use of lime-based materials, which present a higher degree of compatibility with stone, especially in the case of soft, porous stone, and are considered preferable in terms of reversibility [18–20]. When dealing with monuments, the compatibility of an adhesive material is related to three aspects: physical, mechanical and chemical compatibility [21]. Lime- and hydraulic lime-based mortars are considered compatible adhesive materials on account of the moderate mechanical strength and high deformability they present, their chemical similarity with limestones, their high durability and the reversibility of their application [19,21].

Pins are commonly installed during the reattachment process, aiming to achieve better component alignment, redistribute loads and stresses and provide resistance to shear and tensile stresses [15,22]. The installation of pins requires drilling and is therefore an invasive intervention. Thus, specific considerations must be taken into account: (i) during drilling, care must be taken in order to ensure that no cracking is initiated, (ii) the pins and therefore the drilling points must be as few as possible (however, always more than one per fragment, in order to avoid the rotation of the fragment), (iii) the materials must be compatible with the original materials, and possible detachment on account of tensile stresses must not harm the original material [15]. Different pin materials have been tested in international research and the selection of the appropriate pin material is based on substrate characteristics, as well as on the environment in which the repaired unit will remain; thus, a corrosive outdoor environment demands the use of a durable material with high corrosion resistance (such as stainless steel or titanium [22,23]), while a controlled environment allows for a wider variety of pin material choices (including polycarbonate rods, fiberglass and carbon fiber) [24]. The pinning of marble fragments is discussed in the international literature, especially in relation to sculptures [24,25]; however, the use of pins in porous stones is a challenge which is yet to be addressed. In addition to the installation of the pin, an appropriate anchoring material must also be included to facilitate the adhesion of the pin to the fractured material.

The Acropolis masonry circuit wall is a large construction founded on the Acropolis hill in Athens, Greece. The Acropolis of Athens is one of the world's most recognizable and admired monuments, renowned for its archaeological, historical and touristic significance [26]. The circuit wall is of high historical significance, as it is a fortification monument of the classical era, embedding important architectural elements of archaic Acropolis temples [27,28]. Its geometrical properties (i.e., wall height and width) vary substantially around the Acropolis hill [29]. It is constructed mainly of Piraeus stone, classified as a porous sedimentary limestone with varying percentages of dolomitic, calcareous and alu-

minosilicate composition. This stone is present in the wall in different lithological types, as it presents a wide range of both composition and characteristics [28,30].

Visible interventions, additions and the presence of supporting structures indicate that the structure has presented static issues throughout the years [28], while today, it is in demand of conservation and restoration actions in order to maintain its structural integrity, as structural damage (cracks, gaps and severe deformations) is apparent in many areas not only of the ancient construction but also (and more so) in areas comprising later repairs [31]. The structural integrity of the Acropolis circuit wall is also interlinked with safety issues, as it retains the backfill materials that form the plateau around the Parthenon, the most important of the Acropolis monuments [29].

The conservation and restoration of the Acropolis circuit wall is an ongoing project of high importance which was initiated in 2000 AD. The stone elements are, in many cases, severely damaged and fractured, a result of harsh outdoor conditions and climatic variations, the use of incompatible restoration material in previous restoration interventions and natural aging.

In the current study, adhesive and anchoring pastes are designed, assessed and tested in situ, aiming to select the optimum material for the reattachment of the fractured porous stone elements of the circuit wall of the Acropolis. The materials are first assessed in the lab in relation to their physical and mechanical performance; based on the results, a compatibility assessment is performed in relation to the ancient stone's characteristics and finally, the mixes evaluated as optimum are tested on site as adhesive and/or anchoring materials regarding their performance in reattaching porous stone fragments with and without the concurrent use of titanium pins.

2. Materials and Methods

2.1. Materials Used in the Current Investigation

2.1.1. Raw Materials

Different binders were examined in the current study. Air lime ("L", CL90 type, in accordance with EN459-1:2015 [32]) and natural hydraulic lime ("NHL", NHL5 type, in accordance with EN459-1:2015 [32]) were selected, taking into account their compatibility with traditional materials as well as their reduced environmental footprint in relation to other binders [33–35], while white cement ("C", CEM I 52.5N in accordance with EN 197-1 [36]) was also tested as binding material; however, this was mainly for comparison reasons. It is noted that the Acropolis Restoration Service, taking into account the negative effects of cement mortars and pastes [37], has tried in recent years to substitute cement-based materials with more compatible lime- or hydraulic lime-based materials [19]. However, it was considered important to include this type of binder, as it is still used in many restoration projects.

The natural hydraulic lime used in this study (procured from Secil Martingança S.A., Portugal) presented a specific surface area of $4.14 \text{ m}^2/\text{g}$ (nitrogen absorption, through BET measurements [38]) and a bulk density of $0.65 \text{ g}/\text{cm}^3$, according to the manufacturer's datasheet. The hydrated lime (procured from CaO Hellas, Greece) presented a specific surface area of $13.6 \text{ m}^2/\text{g}$ (nitrogen absorption, -BET measurements) and a bulk density of $0.50 \text{ g}/\text{cm}^3$ [39]. The white cement binder CEM I 52.5N (procured from Aalborg white cement, Denmark) presented a specific surface area (Blaine Fineness) of $0.40 \text{ m}^2/\text{g}$ and a bulk density of $1.05 \text{ g}/\text{cm}^3$, according to the manufacturer's datasheet.

Aiming to enhance the properties of the lime pastes and taking into account the demand for faster carbonation and the early and adequate acquisition of mechanical strength, it was decided to examine the use of metakaolin ($\text{Al}_2\text{Si}_2\text{O}_5$), a highly reactive artificial pozzolan, as an additive [40–44]. The metakaolin selected and used in this study

(“MK”, Metastar 501, procured from Imerys Group, France) presents a pozzolanic reactivity of 1100 mg Ca(OH)₂ per 1000 mg metakaolin (through the Chapelle test [2]) and a high surface area of 13.8 m²/g (nitrogen absorption, through BET measurements), while its bulk density is 0.38 g/cm³ [40]

The chemical composition of the binders and the pozzolan is presented in Table 1.

Table 1. Chemical composition of binders [39,40,45].

Oxides	Chemical Composition (%)			
	NHL	L	MK	C
SiO ₂	10.83	0.17	51.70	21.91
Al ₂ O ₃	3.74	0.18	40.60	3.58
Fe ₂ O ₃	1.88	0.07	0.64	0.24
CaO	55.29	70.06	1.67	66.43
MgO	2.50	2.35		1.10
MnO	0.02	-	-	-
SO ₃	1.82	0.77	0.10	3.39
K ₂ O	0.92	-	2.31	0.43
Na ₂ O	0.18	-		0.04
TiO ₂	0.24	-		0.21
Cl	-	-	-	0.03
P ₂ O ₅	0.05	-	-	0.04
Cr ₂ O ₃	-	-	-	0.02
SrO		-	-	-
LOI	19.91	25.60	1.19	2.58

NHL: NHL5 type natural hydraulic lime; L: air lime; MK: metakaolin; C: white cement, LOI: loss of ignition.

2.1.2. Paste Mix Design, Mixing and Curing

In the present study, four paste mixes were designed with the aim of developing an appropriate mix design to be applied as an adhesive material on the fractured surfaces of detached porous stones, as well as an anchoring material in the drilled openings of titanium connection pins when applicable. In the cases where metakaolin was used as a pozzolanic additive, each main binder’s calcium hydroxide percentage was taken into account, in addition to the pozzolanic activity of the specific metakaolin, aiming to add the necessary amount of metakaolin required to fully bond the free calcium hydroxide for the pozzolanic reaction. Thus, in the case of the air lime binder, the ratio of lime/metakaolin was determined at 1/1, while in the case of the natural hydraulic lime binder, the NHL/metakaolin ratio was determined at 4/1 per weight. The paste mix design is presented in Table 2, along with the water added to each mix in order to achieve the same workability.

All pastes were prepared in a mortar mixer (Tonitechnik, Greece). First, the appropriate amount of water was added; then, the binders were gradually added to the water while mixing. Mixing was continued until homogenization. The same procedure was followed for pastes prepared in the lab and on site.

The pastes were poured into cylindrical molds (3 cm × 6 cm). All specimens were cured in stable conditions (in accordance with EN1015-11 [46]) with the aim of achieving their proper setting and hardening until the testing dates. Specifically, the specimens were kept within the mold in a high-humidity chamber at RH = 95 ± 5% and T = 20 ± 2 °C for

7 days. They were then demolded and kept in the high-humidity chamber until the testing date. A total of 18 cylindric specimens were prepared for each paste mix design.

Table 2. Paste and mortar mixes ($w/w\%$).

Mortar/Paste Mix	Mix Design (% per Weight)				W/T
	NHL	L	MK	C	
NHL100	100				0.42
NHLMK20	80		20		0.48
LMK50		50	50		0.70
C100				100	0.40

NHL: natural hydraulic lime type NHL5, L: air lime, MK: metakaolin, C: white cement; W/T: water percentage in relation to total dry mix.

2.1.3. Other Materials Used in the Investigation

The mix designs which exhibited the most appropriate characteristics were further tested on site, with and without the use of titanium pins, in order to assess their effectiveness in reattaching detached stone fragments. In order to achieve results as close as possible to the interventions the materials are designed for, permission was granted to use actual, naturally weathered ancient Piraeus stones deriving from the circuit wall. The porous stone of the circuit wall is a sedimentary limestone from the Piraeus peninsula, with varying percentages of dolomitic, calcareous and aluminosilicate composition, which presents a wide range of physicochemical (porosity: 4.6–29.2%; water absorption capacity: 1.6–16.4%; capillary rise coefficient: 1.4–43.9 mg/(cm²s^{1/2})) and mechanical characteristics (12.8–34.10 MPa) [28].

The stones were derived from an already restored area of the wall and were not to be reinstalled (Figure 1). Each stone was fragmented into two pieces manually to simulate natural fractures and was then reattached during the pilot application using the optimum mixes studied in the current research.

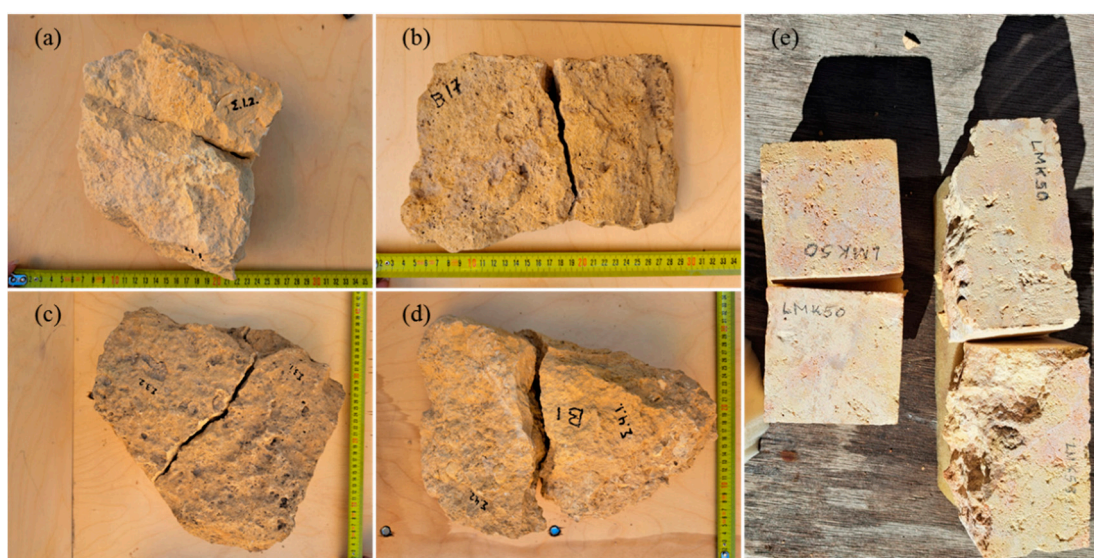


Figure 1. Ancient stone fragments used in the on-site investigation: (a–d) typical fragment systems S1–S4 used for the assessment of the materials as adhesive and anchoring materials in conjunction with titanium pins; (e) typical fragment systems used for the assessment of the materials as adhesive materials without titanium pins (Ss1, Ss2, Sr1, Sr2). Each system was of smaller size and consisted of fragments of the same stone member. Ss systems presented a smooth surface area (left part of Figure 1e), while Sr systems presented a rough fractured surface (right part of Figure 1e).

Larger fragments (S1–S4) were reattached with the concurrent use of titanium pins using the pastes assessed as optimum according to the results of this research as adhesive and anchoring materials, while smaller ones (Ss1, Ss2, Sr1, Sr2) were re-attached using the same paste mixes only as adhesive material on the fractured surfaces.

Titanium pins of 3 mm diameter, when applied, were used during the reattachment procedure as appropriate for small and medium fragments. The use of titanium (Grade 2, ASTM B348 και ASTM B265) was preferred on account of its high resilience [47] and optimum compatibility with traditional materials [48], especially in terms of thermal coefficient [22]; it has also been used successfully in Acropolis monument restoration interventions since 1979 [23,49]. In the current study, the titanium pins were set in place with the use of the pastes assessed as optimum in this research as anchoring material.

2.2. Paste Examination and Assessment Methods and Techniques

2.2.1. In-Lab Paste Examination Techniques

During setting and hardening, the paste specimens were examined through the following techniques:

- Determination of bulk density: The bulk density of the specimens was determined by dividing the mass of each specimen (after drying) by the volume of the specimen (as calculated by its dimensions). Bulk density was determined at 12 months' curing in accordance with EN 1936 [50]. Measurements were conducted on three specimens for each mix. Bulk density, in addition to its importance as a building material characteristic, was also used for the estimation of the dynamic modulus of elasticity for each material through the ultrasonic pulse velocity measurements, as presented below.
- The characteristics of capillary rise coefficient, porosity accessible to water through capillary pores and water absorption through capillarity capacity percentage were determined in accordance with EN 15801 [51]. Tests were conducted on three specimens for each mix at 12 months curing.
- Determination of porosity accessible to water through total immersion and total water absorption capacity percentage: These characteristics were determined in accordance with EN 1936 [50] and EN 13755 [52]. Tests were conducted on three specimens for each mix at 12 months curing.
- Compressive strength tests: Specimens were subjected to uniaxial compression in accordance with EN1015-11 [46]. Tests were conducted at 1, 3, 6, 12 and 30 months' age on three specimens for each mix and age using a ToniTechnik DKD-K-23301 (loading rate: 0.01 KN/s).
- Ultrasonic pulse velocity measurements and estimation of dynamic modulus of elasticity: Measurements were conducted at 12 months' age (three specimens for each mix) using a CNS Farnell-Pundit 6 (transducers frequency: 54 KHz; probe diameter: 20 mm) in accordance with ASTM-C597-16 [53]. The measurements were conducted on the flat surfaces (upper top surface, lower bottom surface) of the cylindrical specimens using a direct method (transmitter on one surface and receiver on opposite surface). The following formula was applied for the estimation of the dynamic elasticity modulus:

$$E_{\text{dyn}} = \rho V_{\text{us}}^2 \frac{(1 + \nu) \cdot (1 - 2\nu)}{(1 - \nu)} \quad (1)$$

where E_{dyn} : dynamic elasticity modulus; V_{us} : ultrasonic pulse velocity through the direct method; ρ : density; ν : dynamic Poisson's ratio (taken as $\nu = 0.25$, in accordance with bibliographic values regarding the specific paste type materials [54]).

2.2.2. Paste/Ancient Stone Compatibility Evaluation Criteria

A compatibility assessment between the different pastes and the ancient stone was conducted based on the results of the in-lab paste examination and the stone's characteristics.

As a general rule, physical and mechanical compatibility is ensured when the characteristics of the paste are as close as possible to the characteristics of the stone it will be applied to, thus allowing the reattached system to act in a homogenous manner [55,56]. In the current study, the following criteria were set:

- The bulk density of the adhesive/anchoring material should be equal to or lower than that of the ancient stone;
- The porosity of the repair material should be equal to or higher than that of the ancient stone in order for the adhesive/anchoring material to play the role of a sacrificial material in terms of water uptake. The same applies for water absorption capacity;
- The capillary rise coefficient of the repair material should be as close as possible to that of the ancient stone in order to neither increase water uptake nor cause water to preferentially transfer to the ancient material;
- The mechanical strength of the repair material must be as close as possible to or lower than that of the ancient material in order for the repair material, and not the ancient material, to fail under compression; this applies to compressive strength and ultrasonic pulse velocity.

The compatibility assessment was conducted to select the two optimum paste mixes that would be used in in situ tests.

2.2.3. In Situ Paste Evaluation Techniques

Following the selection of the optimum paste mixes, the in situ application of the pastes as adhesive and/or anchoring materials for the reattachment of actual ancient weathered porous stone fragments was undertaken and assessed in terms of applicability, adhesion and direct tension.

The aim was firstly (i) to assess the effectiveness of the pastes as adhesive materials for reattaching small fragments (Ss1, Ss2, Sr1 and Sr2, see Figure 1) without the use of titanium pins and, following this, (ii) to test the applicability of the pinning technique on site and assess the effectiveness of the pastes as both adhesive and anchoring materials for reattaching medium-sized fragments (S1–S4, see Figure 1) with the use of titanium pins. In both cases, the fracture mode of the reattached stone systems when subjected to direct tension was evaluated.

In all cases, following the reattachment, digital microscopy was applied after 28 days of curing to examine the paste–stone interface, as well as the paste matrix, using an i-scope Moritex (magnification $\times 30$). The reattached fragments then underwent direct tension tests, where the applied weight was recorded through the use of a Bilatron digital crane scale with a maximum measurement capability of 12 tons.

3. Results and Discussion

3.1. In Lab Assessment of Paste Mix Designs

3.1.1. Determination of Physical Properties and Hygric Behavior During Setting and Hardening

Bulk Density Determination

Bulk density was determined at 12 months' curing (Table 3). The lime metakaolin paste (LMK100) presented the lowest bulk density, while the cement paste (C100) presented the highest. The natural hydraulic lime pastes (NHL100 and NHLMK20) presented intermediate values. The substitution of part of the natural hydraulic lime with metakaolin

resulted in a decrease in bulk density. It is noted that these results are in agreement with relevant international research [57].

Table 3. Bulk density of pastes.

Paste Mix	Bulk Density (g/cm ³)	
	Average	St. Dev.
NHL100	1.37	0.00
NHLMK20	1.34	0.01
LMK50	1.07	0.01
C100	1.76	0.02

These results are interconnected with (i) the different W/T ratios (see Table 2) of the mixes, as increased W/T (see Table 2) leads to a lower bulk density of the hardened material when the same binder is applied, (ii) the different bulk densities of the raw materials (see Section 2.1.1), as higher-bulk-density raw materials lead to a higher-bulk-density hardened material, and (iii) the type of binder, as well as the possible presence of pozzolanic additives and their interaction with the main binder. The latter also affects the bulk density of the hardened material on account of the hardening products of each mix: cement mainly generates hydrated calcium silicate compounds, C₃S and β-C₂S [58]; lime and metakaolin react through the pozzolanic reaction to form calcium silicate and calcium aluminosilicate hydrates, while calcium carbonate is also formed in these mixtures by the carbonation reaction of Ca(OH)₂ [59]; and in the case of NHL mixtures, C-S-H is mainly formed by the hydration reaction of C₂S [59], while in NHL–metakaolin mixtures, the hardening products present in NHL mixtures and lime–metakaolin mixtures are present.

Capillary Rise Coefficient, Porosity Accessible to Water Through Capillary Pores and Water Absorption Through Capillarity Capacity Percentage

The capillary rise coefficient (C.R.C.) is an important material characteristic, as it governs water transfer and the transfer of soluble harmful compounds within the material, which can negatively affect its long-term behavior and durability [60]. In order to avoid incompatibility between different materials, and especially the accumulation of salts in the pores of the ancient material, a homogenous hygric behavior is desired [61]. The pastes underwent water capillary rise tests at 12 months' curing (Figure 2 and Table 4).

Table 4. Physical properties and hygric behavior of pastes in relation to water capillary rise.

Paste Mix	C.R.C. * (mg/(cm ² s ^{1/2}))		P _{cap} ** (%)		W.A.C. _{cap} *** (%)	
	Average	St.Dev.	Average	St. Dev.	Average	St. Dev.
NHL100	29.9	0.6	46.0	0.3	33.1	0.3
NHLMK20	11.0	0.9	22.1	1.3	15.9	0.8
LMK50	125.9	8.3	51.7	0.7	47.9	0.9
C100	6.2	1.8	14.8	1.3	8.3	0.7

* C.R.C.: capillary rise coefficient. ** P_{cap}: porosity accessible to water through capillary rise. *** W.A.C._{cap}: water absorption capacity accessible to water through capillary rise. St. Dev.: standard deviation of measurement.

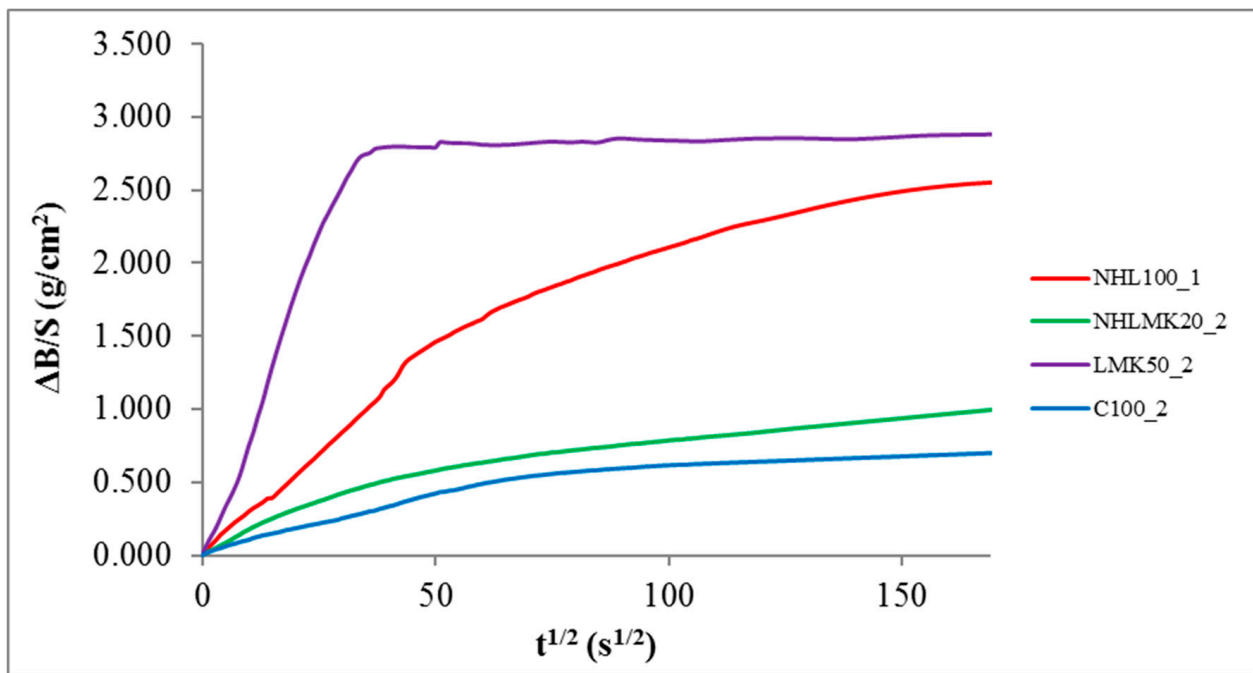


Figure 2. Typical capillary rise test results of each paste mix (ΔB : mass of water uptake; S : surface area in contact with water; t : time).

The cement paste (C100) presents the lowest capillary rise coefficient, while the lime–metakaolin paste presents the highest C.R.C. in relation to the other pastes. The natural hydraulic lime pastes present intermediate values, while the substitution of part of the natural hydraulic lime with metakaolin leads to a decrease in the water uptake rate through capillaries. All of the above results are interconnected with the developed microstructure, which is influenced by the binder (and pozzolanic additive, where applicable), as well as by the W/T content [62]. Porosity accessible to water through capillary pores presents a similar trend; thus, in the case of the examined pastes, higher capillary rise coefficients are also interlinked with a higher pore volume accessible to water through capillary rise. The water absorption capacity of the pastes also follows the same trend, as expected.

Total Water Immersion Results

Porosity accessible to water through total immersion (Table 5) presents the same trend as porosity accessible through capillary rise; however, it presents slightly higher values, as more pores are accessible.

Table 5. Physical properties and hygric behavior in relation to total water immersion.

Paste Mix	Porosity * (%)		Water Absorption Capacity * (%)	
	Average	St. Dev.	Average	St. Dev.
NHL100	46.4	0.4	33.4	0.3
NHLMK20	40.8	0.3	29.5	0.1
LMK50	51.9	0.7	48.1	0.9
C100	23.8	0.2	13.4	0.3

* Accessible to water through total immersion. St. Dev.: standard deviation of measurement.

The lime–metakaolin paste presents the highest porosity accessible to water through total immersion in comparison with the other binders; this is associated with the specific

binder and pozzolanic additive, as well as the higher W/T. The cement paste presents the lowest porosity; this is interlinked with the microstructure developed in cement-based materials and is associated with the low W/T as well [58,59]. Natural hydraulic lime pastes present intermediate values, and the substitution of part of the natural hydraulic lime with metakaolin leads to a lower pore volume accessible to water through total immersion, as well as a lower water absorption capacity.

It should be noted that the difference between the porosity accessible to water through total immersion values is within the standard deviation of the porosity accessible to water through capillary rise for the lime–metakaolin paste and the natural hydraulic lime paste, indicating that capillary pores are almost exclusively responsible for moisture transfer, in agreement with relevant research [57]. However, in the case of the cement-based paste (C100) and the natural hydraulic lime–metakaolin paste (NHLMK20), the porosity accessible to water through total immersion is much higher than the porosity accessible to water through capillary rise, indicating the development of a different microstructure and specifically the presence of smaller pores, $<1\ \mu\text{m}$, which are associated with absorption and diffusion water transfer mechanisms rather than capillary absorption [63]. The same exact trends are noticed regarding the water absorption capacity percentage; the lime–metakaolin paste and the natural hydraulic lime paste (LMK50 and NHL100) present the same water absorption capacity, whether water is transferred through capillary rise or total immersion; however, the cement-based paste (C100) and the natural hydraulic lime–metakaolin paste (NHLMK20) present a much higher water absorption capacity when totally immersed in water in comparison to the effect of capillary rise.

3.1.2. Determination of Mechanical Properties During Setting and Hardening Compressive Strength

Compressive strength measurements were conducted at different paste ages, aiming to examine the acquisition of compressive strength over time (Figure 3).

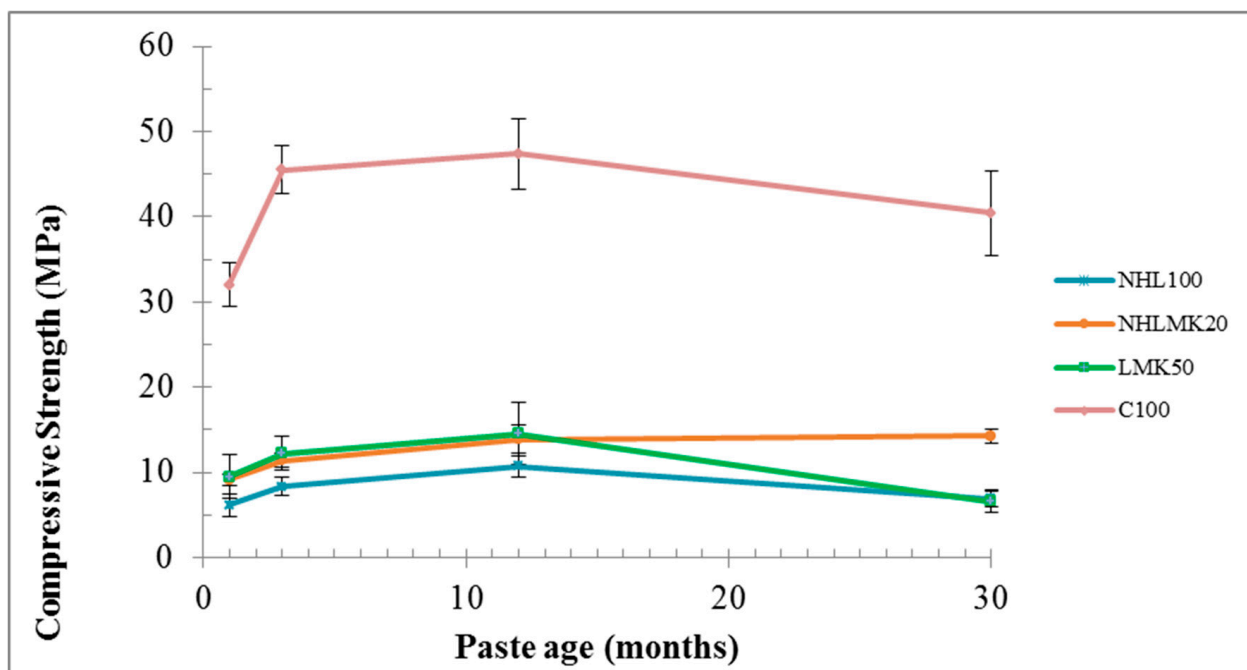


Figure 3. Compressive strength of pastes.

Regarding the pastes, the cement paste (C100) presents much higher compressive strength values and a very high standard deviation in relation to the other hydraulic pastes.

The addition of metakaolin to natural hydraulic lime seems to be beneficiary in terms of compressive strength at all paste ages. Thus, NHLMK20 presents an enhanced mechanical behavior in relation to NHL100, an effect also noticed by other researchers [64]; furthermore, in the current study, it is revealed that the beneficiary effect is also noted, and is even greater, at higher ages.

The lime–metakaolin paste, LMK50, presents compressive strength values similar to the natural hydraulic lime–metakaolin paste, NHLMK20, up to 12 months. Thereafter, a sharp decrease is noticed, and at 30 months, LMK50 presents similar values to the natural hydraulic lime paste without metakaolin. This decrease in mechanical strength has been noticed by other researchers and is an issue under investigation. Researchers have attributed this decrease at higher ages to the instability of calcium–aluminum hydrated compounds formed through the pozzolanic reaction [43,65]; however, this decrease has also been interlinked with possible microcracking on account of shrinkage [41], which is more possible in the case under investigation, as capillary cracks were noticed on the surface of these specific specimens. The difficulty in pinpointing the reason behind this decrease is interlinked with the complexity of the different hardening mechanisms developing at the same time in lime–metakaolin and natural hydraulic lime–metakaolin pastes, which involve carbonation, hydration and pozzolanic reactions [66]. It is noted that the compressive strength measured in this study regarding the lime–metakaolin paste at early ages (1 and 3 months) is similar to that measured in previous studies [57].

The long-term mechanical behavior of mortars and pastes is an interesting issue which demands further investigation. In the current study, certain mixes present differentiations in relation to their mechanical behavior from 12 to 30 months of curing, which could be interlinked with the formation of microcracks during hygrometric shrinkage and/or the instability of formed compounds, as aforementioned.

Ultrasonic Pulse Velocity and Dynamic Modulus of Elasticity

The ultrasonic pulse velocity of the pastes was measured at 12 months' age. The measured values, as well as the calculated dynamic moduli of elasticity, are presented in Table 6.

Table 6. Ultrasonic pulse velocity and dynamic moduli of elasticity of pastes.

Paste Mix	Ultrasonic Pulse Velocity (m/s)		Dynamic Modulus of Elasticity (GPa)	
	Average	St. Dev.	Average	St. Dev.
NHL100	2755	177	8.7	1
NHLMK20	2260	186	5.8	0.9
LMK50	2293	115	4.7	0.5
C100	3905	101	21.4	1.1

St. Dev.: standard deviation of measurement.

The ultrasonic pulse velocity presents similar values amongst lime-based mortars, with the natural hydraulic lime–metakaolin paste (NHLMK20) presenting an almost identical value with the lime–metakaolin paste (LMK50). The natural hydraulic lime paste, NHL100, even though it presents lower compressive strength than the aforementioned pastes at 12 months, nonetheless presents a slightly higher velocity value, perhaps on account of the different microstructure developed on account of the absence of pozzolan in the mix. This is also in coherence with the slightly higher bulk density and lower porosity it presents.

The cement mortar (C100), on the other hand, presents a much higher ultrasonic pulse velocity, which is coherent with its higher compressive strength and is related to the much

higher density of the paste in comparison with the lime-based pastes, as well as its much lower porosity.

Regarding the dynamic modulus of elasticity, the cement paste, C100, presents a remarkably higher dynamic modulus of elasticity in relation to the other pastes, indicating its much lower ductility, a disadvantage discussed widely in the literature in relation to the use of cement in monument restoration actions [67]. The other paste mixes present adequate values for restoration purposes.

The lime–metakaolin paste presents the lowest modulus of elasticity, 46% lower than the natural hydraulic lime paste without metakaolin, thus confirming international research regarding the high elasticity of air lime-based materials [68]. The addition of metakaolin to natural hydraulic lime increases ductility, as indicated by the lower modulus of elasticity; the natural hydraulic lime–metakaolin paste NHLMK20 presents a ~33% lower dynamic modulus of elasticity in relation to the natural hydraulic lime paste without metakaolin, even though it presented a ~30% higher compressive strength at the same age (12 months), thus indicating an enhanced behavior in terms of mechanical characteristics (higher ductility and higher compressive strength).

3.2. Compatibility Evaluation of Pastes with Ancient Porous Stone

As aforementioned, the Acropolis circuit wall is a complex structure, constructed mainly of Piraeus coastal stone. Piraeus stone presents intense variations regarding its physicochemical and mechanical characteristics [19,28,30] on account of its sedimentary nature [69]. In order to evaluate the compatibility of the designed pastes with the stone elements comprising the Acropolis circuit wall, the whole range of the stone's characteristics was taken into account [28,30]. Table 7 summarizes the main characteristics of the ancient stone of the Acropolis circuit wall (given as a range, min-max) and the respective characteristics of the designed mixes.

Table 7. Summarized characteristics of ancient stone members of Acropolis circuit wall [28] and designed pastes.

Material		Bulk Density (g/cm ³)	Porosity (%) *	W.A.C. (%)	C.R.C. (mg/(cm ² s ^{1/2}))	Fc ** (MPa)	U.P.V. (m/s)
Piraeus stone	Min	1.8	4.6	1.6	1.4	12.80	2401
	Max	2.5	29.2	16.4	43.9	34.10	4567
NHL100		1.4	46.4	33.4	29.9	10.73	2755
NHLMK20		1.3	40.8	29.5	11.0	13.90	2260
LMK50		1.1	51.9	48.1	125.9	14.50	2293
C100		1.8	23.8	13.4	6.2	47.36	3905

W.A.C.: water absorption capacity through total immersion; C.R.C.: capillary rise coefficient; Fc: compressive strength; U.P.V.: ultrasonic pulse velocity. * Accessible though total immersion. ** Final strength at 30 months.

In accordance with the criteria set in Section 2.2.2, the main characteristics assessed are bulk density, porosity, water absorption capacity, capillary rise coefficient and mechanical characteristics (compressive strength and ultrasonic pulse velocity).

The cement paste presents the worst degree of compatibility, as it fails most set criteria; its use would distribute water differentially to the ancient stone, while the ancient stone would fail before the failure of the repair material under static and dynamic stresses, as the cement paste presents higher values of compressive strength, even in relation to the maximum stone value.

The other pastes do not present percentages which could indicate damage to the ancient material but would rather either act in a homogenous manner or even in a sacrificial one. NHLMK20 presents the closest values to the ancient stone, its compressive strength only slightly exceeding the lowest value of the wide range the ancient stone presents. Therefore, it was selected to be tested in the pilot application. LMK50 was selected as the other paste to be tested in the pilot application, taking into account its compliance with most set criteria and also taking into account the use of lime–metakaolin-based mortars for other interventions at the Acropolis monuments [19].

3.3. On-Site Pilot Application and Assessment

The compatibility assessment indicated that the most appropriate mixes, in terms of mechanical performance and physicochemical characteristics, are the lime–metakaolin and natural hydraulic lime–metakaolin pastes. We therefore decided to test pastes LMK50 and NHLMK20 as possible adhesive and/or anchoring materials in the pilot applications and select the paste with the optimum behavior.

Thus, the experimental procedure described in Section 2.2.3. was carried out on site in order to assess the applicability and effectiveness of each paste in real conditions (Table 8).

Table 8. Experimental procedure for assessment of fragment reattachment.

Paste Mix	Fractured Stone System	Prominent Pins	Hidden Pins	Pin Diameter	Pin Length
LMK50	Sr1	N.A.	N.A.	N.A.	N.A.
LMK50	Ss1	N.A.	N.A.	N.A.	N.A.
LMK50	S1	X		3 mm	11.5 cm
LMK50	S3		X	3 mm	18 cm
NHLMK20	Sr2	N.A.	N.A.	N.A.	N.A.
NHLMK20	Ss2	N.A.	N.A.	N.A.	N.A.
NHLMK20	S2		X	3 mm	11 cm
NHLMK20	S4	X		3 mm	21.5 cm

N.A.: Not applicable. The fragment systems are presented in Figure 1. Prominent pins were installed after reattachment from the outer surface of one fragment and recess 30 mm from the outer surface of the other fragment, while hidden pins were installed prior to the reattachment and recess 30 mm from the outer surface of both fragments.

The above pastes were applied on the fragmented surfaces and were also used as anchoring material during the application of the pins, thus securing them in place in the respective fractured stone system when the pins were applied.

3.3.1. Reattachment Without Titanium Pins—Small Fragments

The first part of the pilot application involved the reattachment of small fragments (Sq1, Sq2, Sf1, Sf2) for which reinforcement with metal elements is not necessary and/or not possible on account of the size of the fragments. The fractured surfaces were cleaned, humidity was provided in order to avoid the loss of humidity from the paste to the stone during application and the pastes were applied as adhesive material on the fractured surfaces (Figures 4 and 5).

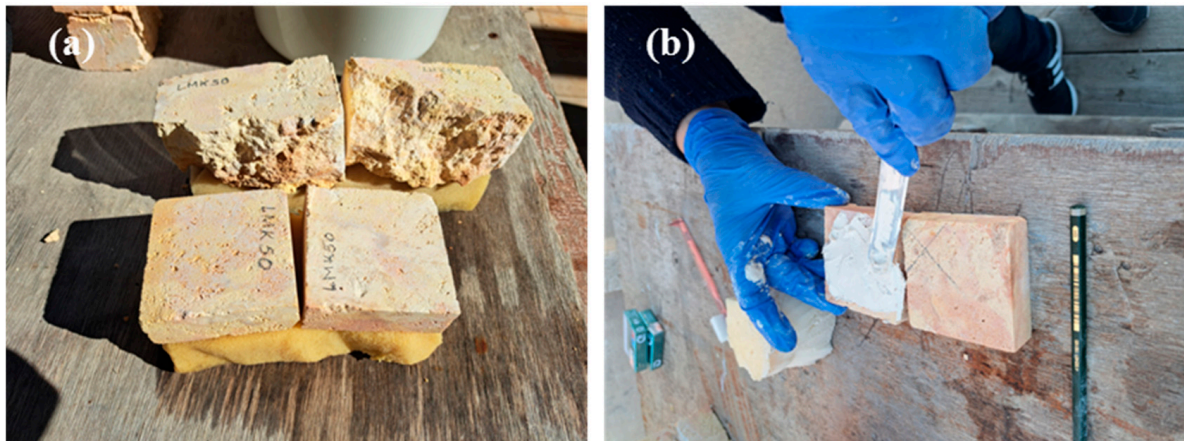


Figure 4. Use of wet sponges to provide humidity to the fractured surfaces prior to the application of the pastes (a); application of paste on the fractured surface (b).

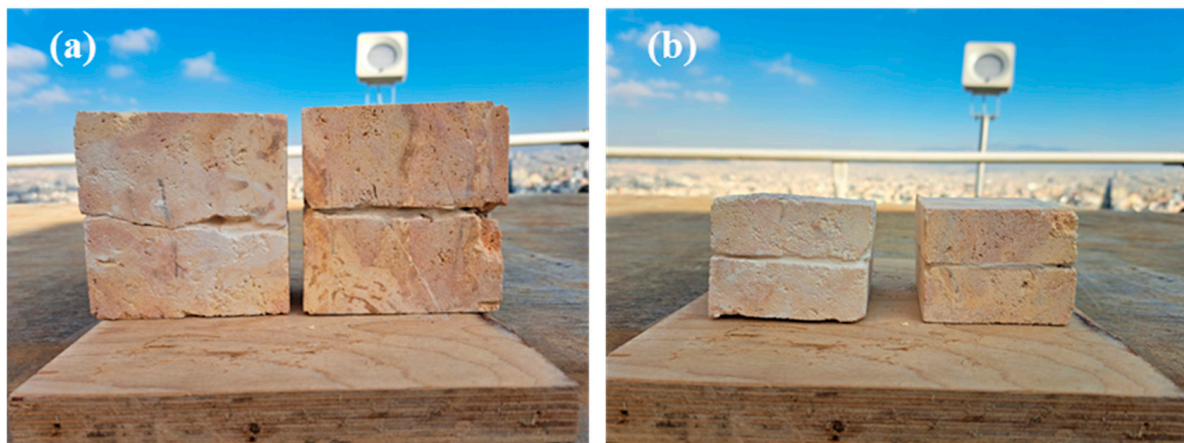


Figure 5. Reattached fragments with rough fractured surfaces ((a): Sr1, left; Sr2, right specimen) and smooth fractured surfaces ((b): Ss1, left; Ss2, right specimen).

After one month of curing, digital microscopy indicated excellent adhesion between the pastes and the stone surface, without the development of micro-cracks or indications of detachment at the paste–stone interface (Figures 6 and 7 for LMK50 and NHLMK20, respectively).

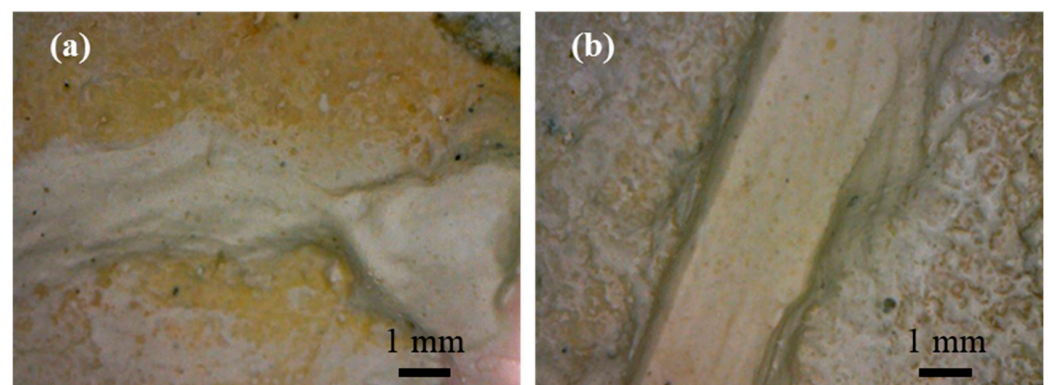


Figure 6. Digital microscopy images of the stone fragment–paste–stone fragment interface of reattached fragment systems (a) Sr1 and (b) Ss1.

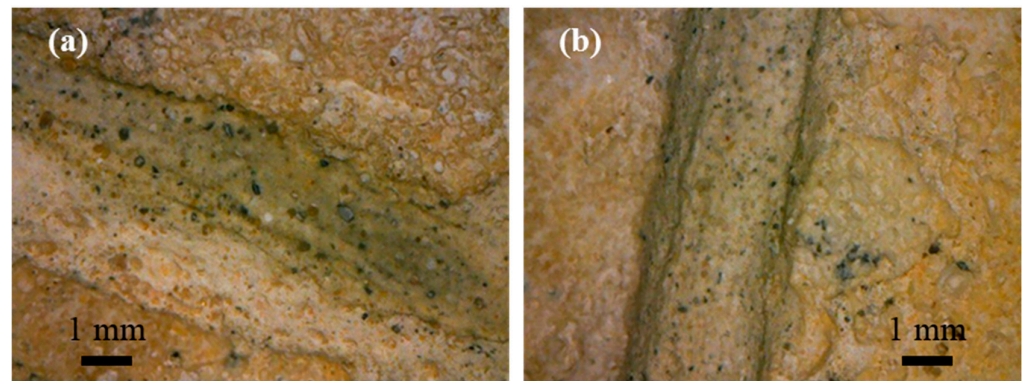


Figure 7. Digital microscopy images of the stone fragment–paste–stone fragment interface of reattached fragment systems (a) Sr2 and (b) Ss2.

At this point, the stone systems underwent direct tension in order to assess the effectiveness of reattachment with the different materials. One fragment of each stone system was attached to a steady position and the other fragment of each stone system was attached to a digital crane scale (Bilatron, max measurement capability: 12 t), as presented in Figure 8.

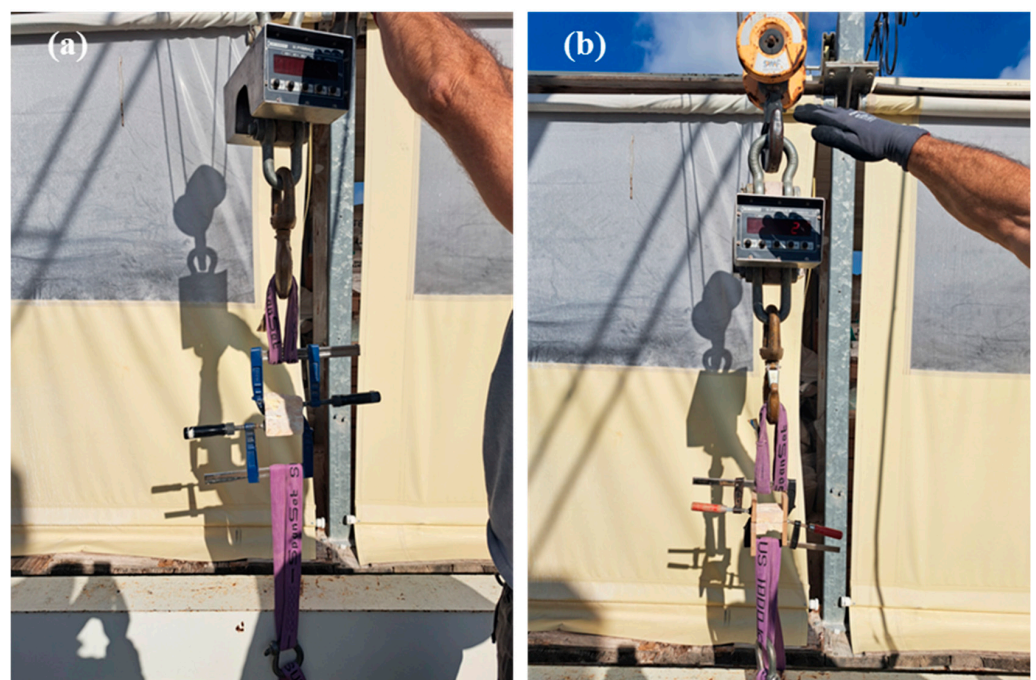


Figure 8. Direct tension system setup: (a) Sf1; (b) Ss2.

Each reattached stone system detached at a different weight application, which, taking into account the fragmented surface where the adhesive material was applied, was then converted into strength. Detachment occurred in the optimum manner, as the paste was ruptured without damaging the ancient material (Figures 9 and 10). The results are summarized in Table 9.

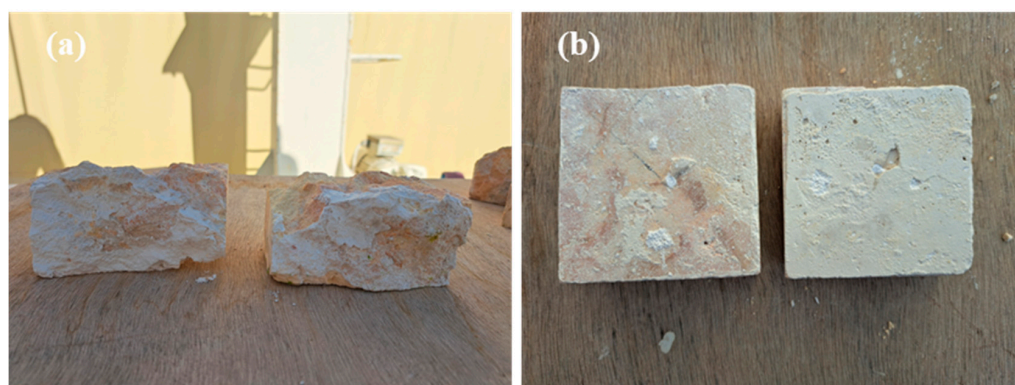


Figure 9. Image of reattached surfaces after failing under direct tension. Systems reattached with LMK50: (a) Sr1, (b) Ss1.

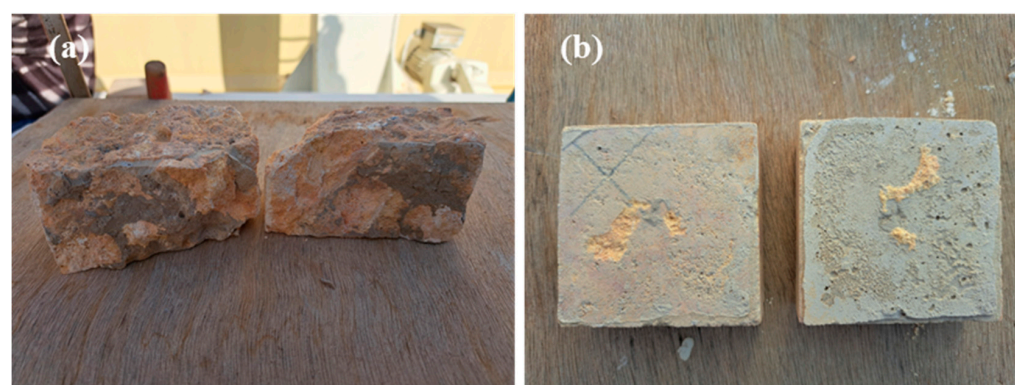


Figure 10. Image of reattached surfaces after failing under direct tension. Systems reattached with NHLMK20: (a) Sr2, (b) Ss2.

Table 9. Summarized results of direct tension tests—small fragments without pins.

Adhesive and Anchoring Material	Fragment System	Maximum Applied Weight (kg)	Reattached Surface (cm ²)	Force (N)	Direct Tension (MPa)	Manner of Detachment
LMK50	Sr1	32	55.00	313.92	0.06	Rupture of the paste No damage to the ancient stone
	Ss1	10	42.25	38.10	0.02	Rupture of the paste No damage to the ancient stone
NHLMK20	Sr2	250	48.00	2452.5	0.51	Rupture of the paste No damage to the ancient stone fragments
	Ss2	46	46.24	451.26	0.10	Rupture of the paste No damage to the ancient stone

NHLMK20 presented a better behavior under direct tension, especially in the case of the reattached system with natural fragmentation and a rougher surface.

3.3.2. Reattachment with Titanium Pins—Medium Fragments

Following the reattachment of small fragments without pins, medium-sized fragments were reattached with the concurrent use of titanium pins and the use of the pastes as adhesive materials (on the fractured surfaces) and as anchoring materials (for the installation of the pins).

It is noted that the stone fragments were drilled successfully in order to install the pins, as no crack initiation was caused on account of the drilling process (Figure 11), confirming the applicability of the pinning technique, even in ancient weathered porous stones. The diameter, the length, location and number of holes were chosen to suit the size, scale and type of stone fragment [70]. On account of the size of the fragments, two pins were used for each system. The reattached fragments were frequently sprayed with water and covered with a film in order to maintain high humidity conditions for 28 days, with the concurrent use of a wet sponge (Figure 12).

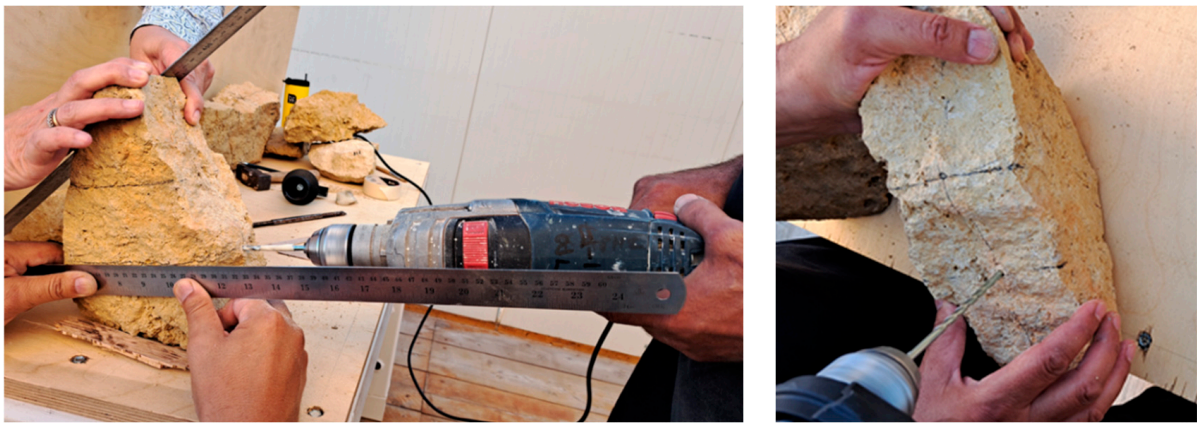


Figure 11. Drilling the ancient stone fragments.

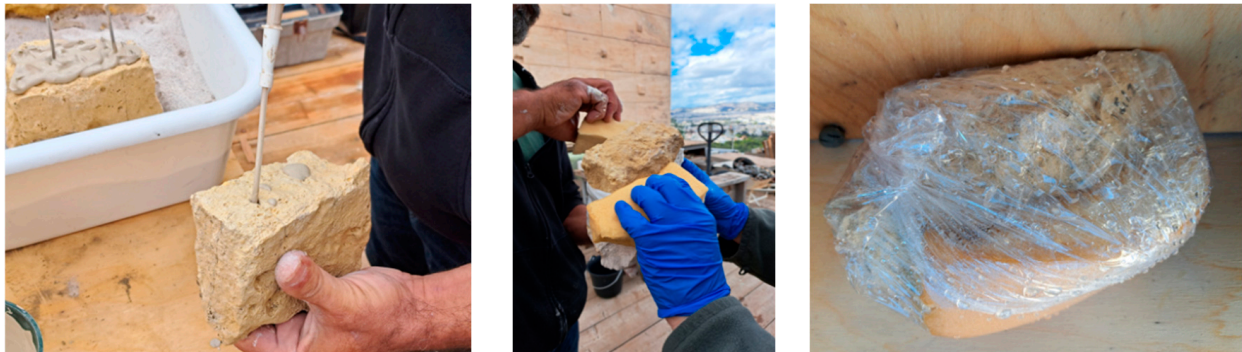


Figure 12. Application of anchoring paste right before reattachment (**left**); ensuring high humidity conditions during curing (**middle and right**).

After one month of curing, digital microscopy indicated excellent adhesion between the pastes and the stone surface, without the development of micro-cracks or indications of detachment at the paste–stone interface (Figure 13).

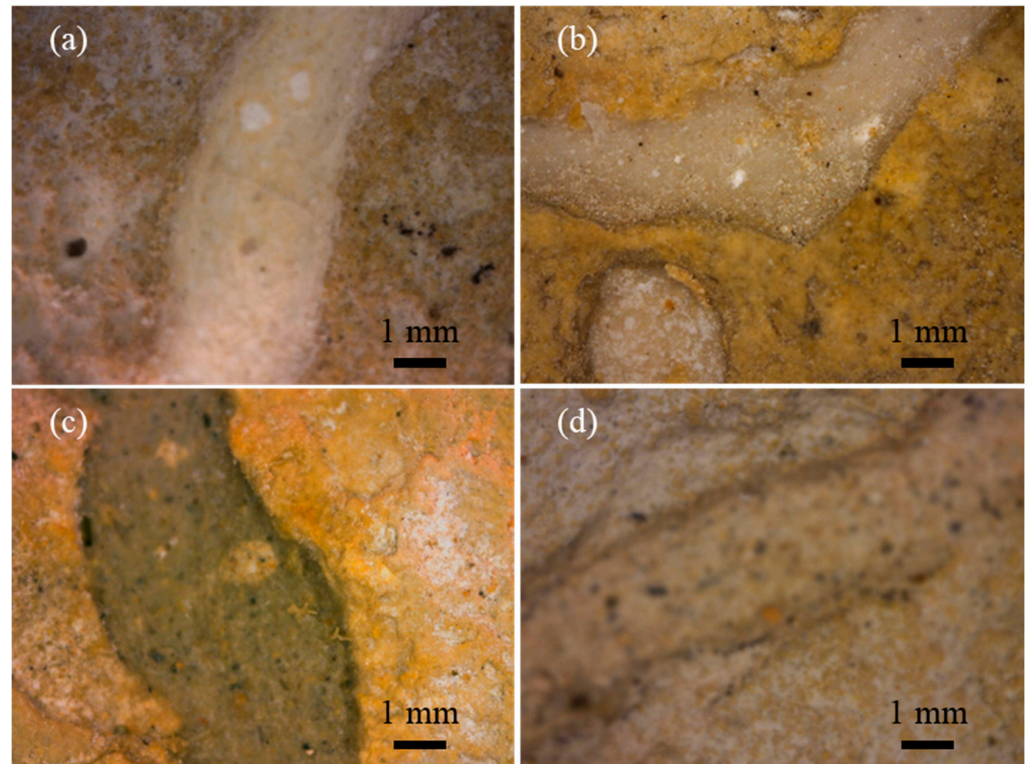


Figure 13. Digital microscopy images of the stone fragment–mortar–stone fragment interface of reattached fragment systems (a) S1, (b) S3, (c) S2 and (d) S4.

At this point, the stone systems underwent direct tension in order to assess the effectiveness of reattachment with the different materials. One fragment of each stone system was attached to a steady point and the other fragment of each stone system was attached to a digital crane scale (Bilatron, max measurement capability: 12 t), as presented in Figure 14.

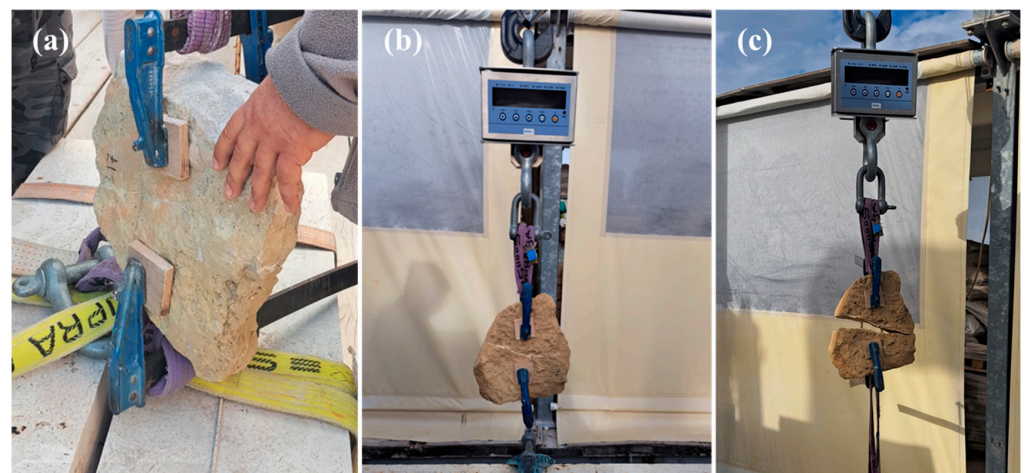


Figure 14. Direct tension system setup: (a) attaching stone fragments; (b) reattached system undergoing direct tension; (c) at the moment of detachment.

Each reattached stone system detached at a different weight application, which, taking into account the fragmented surface where the adhesive material was applied, was then converted into strength. Detachment occurred in the optimum manner, as the paste was ruptured, without damaging the ancient material (Figures 15–18). The results are summarized in Table 10.



Figure 15. Detached stone fragment system S1 where LMK50 was applied.



Figure 16. Detached stone fragment system S3 where LMK50 was applied.

Table 10. Summarized results of direct tension tests.

Adhesive and Anchoring Material	Fragment System	Maximum Applied Weight (kg)	Reattached Surface (cm ²)	Force (N)	Direct Tension (MPa)	Manner of Detachment
LMK50	S1	90	108.94	883	0.08	Rupture of the paste No damage to the ancient stone
	S3	680	378.87	6374	0.17	Rupture of the paste No damage to the ancient stone

Table 10. Cont.

Adhesive and Anchoring Material	Fragment System	Maximum Applied Weight (kg)	Reattached Surface (cm ²)	Force (N)	Direct Tension (MPa)	Manner of Detachment
NHLMK20	S2	300	78.96	2942	0.37	Rupture of the paste No damage to the ancient stone
	S4	340	198.94	3334	0.17	Rupture of the paste No damage to the ancient stone fragments



Figure 17. Detached stone fragment system S2 where NHLMK20 was applied.

The results indicate that the materials (pastes and titanium pins) were successful in reattaching the stone fragments without causing harm to the ancient stone and are thus an excellent choice for the case of medium fragments (indicatively up to 15 cm dimensions) which have detached from the original stone members.

NHLMK20 proved to provide a more reliable adhesion and anchoring material, as the fragments withstood a similar tension before detachment, and is thus considered a better choice.



Figure 18. Detached stone fragment system S4 where NHLMK20 was applied.

3.4. Discussion Regarding the Results of the Applied Methodological Approach in Relation to the Literature

Contrary to the reattachment of detached marble fragments [24,25], the reattachment of fractured porous limestones has not been extensively studied. Few studies are available in the international literature [18–20] and present limitations in relation to the methodology presented herein in terms of the curing time of adhesion and anchoring materials (regarding the in-lab assessment) and in terms of real-condition on-site tests, as well as in terms of the use of pins for the reinforcement of fragment reattachment.

In terms of the effect of curing time, it proved important to evaluate the materials (especially when dealing with lime-based materials) at higher ages, at least 12 months, and ideally higher, up to even 30 months, as the properties alter significantly with age, thus, in the long term, affecting the compatibility and performance assessment and the reliability of the final selection.

In terms of the compatibility assessment, when dealing with highly inhomogeneous sedimentary porous stones which are naturally weathered, it is important to take into account the whole range of the stone's characteristics, as the use of a median may result in misleading results in relation to the real situation addressed.

Regarding the use of pins for the reattachment, the on-site test confirmed the applicability of the technique, even in the case of weathered porous limestones; this is an important result, as until now, (i) the pinning of fragments has only been studied and assessed in relation to compact stones, such as marble [24,25], and (ii) the reattachment of porous limestone fragments has only been approached in a limited manner regarding reattachment without pins [18–20].

Finally, no study related to this issue has examined the on-site application of materials and the assessment of their effectiveness using naturally weathered original fragments. This is an important step, as otherwise the applicability of the reattachment method and materials is evaluated on a theoretical level, which may not be applicable in real conditions and in relation to the actual materials that are to be conserved. Thus, the on-site pilot application and assessment is considered a necessary step of the proposed methodological approach for the design, assessment and final selection of the appropriate materials.

4. Conclusions

The reattachment of ancient stone fragments is a demanding task which requires an appropriate reattachment procedure, as well as the selection of both performing and compatible repair materials.

In the present study, different paste mixes were designed and evaluated in terms of their physical and mechanical behavior and assessed in relation to their compatibility with the ancient stone of Piraeus, the main building material of the Acropolis circuit wall, and in terms of their performance as adhesive and/or anchoring materials with or without the use of titanium pins.

It seems that the use of white cement as the sole binder results in a rigid material, incompatible with ancient Piraeus stone in terms of both hygric and mechanical properties. Lime- and natural hydraulic lime-based materials, however, present a higher degree of compatibility. The addition of metakaolin to natural hydraulic lime enhances the performance of the paste, resulting in a stronger yet more ductile material with an enhanced hygric behavior. Lime–metakaolin-based materials present the advantages of air lime in terms of elasticity and hygric behavior, with enhanced mechanical performance.

The pilot application conducted on site in real conditions showed that both the lime–metakaolin and the natural hydraulic lime–metakaolin pastes are effective adhesive and anchoring materials. At one month of curing, the paste–stone interface presented excellent adhesion, as investigated through digital microscopy; furthermore, on-site tests revealed an optimum fracture mode under direct tension, as the paste was ruptured and the pins, when applied, were extracted without damaging the ancient stone material.

The direct tension test results indicated that, although both materials were successful in reattaching the fragments, both with and without the use of titanium pins, the natural hydraulic lime–metakaolin paste (NHLMK20) seemed to present a higher degree of reliability as an adhesive and anchoring material and is thus considered the optimum choice to be used in the Acropolis circuit wall restoration project.

The three-stage methodological approach—(i) material design and assessment, (ii) compatibility evaluation and (iii) pilot-scale application and assessment—proved to be valuable in the selection of the optimum material, especially taking into account the multiple variables and uncertainties which characterize monument materials and protection interventions.

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