sustainability

Article

Creating Mortars through the Alkaline Activation of Ceramic Waste from Construction: Case Studies on Their Applicability and Versatility in Conservation

Maura Fugazzotto [1,2], Paolo Mazzoleni [1,*], Antonio Stroscio [3] and Germana Barone [1]

1 Department of Biological, Geological and Environmental Sciences, University of Catania, 95125 Catania, Italy; maura.fugazzotto@unict.it (M.F.); germana.barone@unict.it (G.B.)
2 Department of Humanities, University of Catania, 95125 Catania, Italy
3 Department of Materials and Environmental Engineering, University of Modena and Reggio Emilia, 41124 Modena, Italy; astroscio@unimore.it
* Correspondence: pmazzol@unict.it

Abstract: This paper aimed to investigate the possibility of using alkaline-based binders made from the industrial waste produced by ceramic tiles in the field of conservation and the restoration of monuments and archaeological heritage. Geopolymer mortars, which are environmentally sustainable products obtained by chemical consolidation at room temperature, are studied for their versatility in applications as reintegration or bedding mortars and pre-cast elements, namely bricks, tiles or missing parts for archaeological pottery, as an alternative to traditional not sustainable products. Starting from a well-established formulation, the function of the product, meaning its technical characteristics and its workability, was optimized by changing the aggregates used, by adding a Ca-rich compound or by changing the liquid/solid ratio with the use of tap water. The possibility of tailoring the finishing of the obtained products was also evaluated. X-ray diffraction analysis showed the influence of adding the additive with the presence of newly formed phases, which positively affect the product's workability. On the contrary, no important variations were observed with the increase in the water content of the same formulation, opening up the possibility of managing it according to the required fluidity of the final product. Good results were observed, jumping above the laboratory scale and overcoming criticalities linked to the variabilities on site and the higher volume of materials used for industrial processes. The present research also demonstrates that ceramic-based geopolymers are suitable for application in a large variety of cultural heritage projects and with different purposes. Therefore, the paper encourages the use of alkali-activated mortars for green restoration, specifically given the wide range of ceramic materials.

Keywords: geopolymers; alkali activated materials; mortars; conservation; restoration; ceramic; construction waste; versatility; applications; cultural heritage

check for updates

Citation: Fugazzotto, M.; Mazzoleni, P.; Stroscio, A.; Barone, G. Creating Mortars through the Alkaline Activation of Ceramic Waste from Construction: Case Studies on Their Applicability and Versatility in Conservation. *Sustainability* **2024**, *16*, 1085. https://doi.org/10.3390/su16031085

Academic Editor: Syed Minhaj Saleem Kazmi

Received: 20 December 2023
Revised: 19 January 2024
Accepted: 24 January 2024
Published: 26 January 2024

1. Introduction

Nowadays, the high level of environmental pollution and the dangerous climatic conditions make it urgent for us to improve and promote the preservation of cultural heritage with the use of environmentally sustainable restoration materials [1]. Buildings and restoration materials, both now and in the future, must not further affect the already severely compromised environment. However, in the field of the conservation of buildings, non-environmentally friendly products such as cements, lime mortars and organic resins are usually and universally used [2]. All of these products have a dual responsibility. On the one hand, their manufacturing process involves high temperatures, resulting in a negative CO_2 footprint, and/or the use of non-renewable resources [3]. On the other hand, their apparent efficacy is invalidated by the significant negative drawbacks that have been discovered by the scientific community. Cements, lime mortars, gypsum and organic products, when used to repair stone monuments, architecture and cultural objects, generally show numerous disadvantages in terms of their compatibility and durability [4–11]. The use of inefficient products and methodologies makes these interventions unsustainable, both environmentally and economically, as well as philologically towards the substrate to be restored.

For this reason, research is being devoted to developing new materials that observe environmental sustainability principles while achieving high technological efficacy.

Alkali-activated materials, particularly geopolymers, have been extensively studied as potential alternatives to cement and ceramic materials due to their technical competitiveness and environmental sustainability. They are inorganic polymers obtained by mixing highly amorphous aluminosilicate powders with an alkaline solution [12]. The mixing and curing processes do not require high temperatures. On the contrary, consolidation often occurs more effectively at room temperature [13]. Furthermore, their eco-sustainability can be promoted by using local products or by recycling natural or industrial waste of aluminosilicate composition. This reduces CO_2 emissions linked to production and transportation. Additionally, the exploitation of virgin materials is significantly demolished.

Besides these general aspects related to the environment, in the field of cultural heritage conservation another issue becomes fundamental: restoration materials need to be compatible, at the chemical, physical, mechanical and aesthetical level, with the original materials constituting the monument/cultural object. Finally, the efficacy of the products must also be tested for their specific functionality and applicability. Indeed, the effectiveness of new products as an alternative to traditional ones is demonstrated by their successful application in case studies, bridging the gap between laboratory testing and real-word implementation in industry, construction and restoration sites.

In this context, a question arises: does a material exist that meets all of the indicated requirements? Meaning a restoration product that is sustainable towards the environment, compatible with the original substrates and versatile, meaning it can be easily tuned to the specific restoration intervention, and is easy to prepare directly on-site or suitable for industrial scale-up.

Several alkali-activated materials have been studied for cultural heritage conservation [4,5,14–19]. Using ceramic waste as the aluminosilicate precursors showed excellent feasibility results for the geopolymerization process [14,20–22]. It has also demonstrated good technical performance, particularly as mortars for the restoration of ceramic cultural heritage, with optimal compatibility. However, there is a lack of comprehensive research evaluating its applications and versatility. The aim of this research is to test the versatility of geopolymer mortars based on ceramic waste from construction, in order to ensure all-around sustainability and usability of new products. Geopolymer precursors, such as ceramic tile waste and brick waste, were used to create binders and mortars capable of restoring various types of ceramic products. The effectiveness and versatility of the materials were tested by applying them in various restoration contexts and adjusting the synthesis parameters to meet technical requirements on a case-to-case basis.

New binders, new mortars and pre-cast decorative and construction elements were improved, and critical procedural steps and solutions were studied. The paper also describes the operational steps taken to develop a material with easily tailored technical behavior according to its final application and on-site use.

The positive results obtained in the applications performed underline the sustainability and sustainable development of the proposed materials.

2. Materials and Methods

2.1. Materials

Geopolymer mortars were created by activating ceramic construction waste with a sodium-based alkaline solution. Two precursors of a ceramic nature were used, coming from local industries: ceramic tile waste (referred to as LBCa), supplied by La Bottega Calatina arl, in Caltagirone (CT—Italy) and ceramic brick waste (referred to as CWF), supplied by Laquattro srl, in Rometta (ME—Italy). Metakaolin (MK), specifically ARGICAL™ M–1000, supplied by IMERYS (Paris, France), was used as an additive at a weight of 10% in proportion to the solid precursors. Additionally, a commercial natural hydraulic lime called Prompt (P), supplied by Vicat Group (Paris, France), was added at a maximum weight of 20% in proportion to the solid precursor. The MK has a high amorphous content, consisting mostly of aluminosilicate species. This composition aids in the formation of the gel in ceramic-based alkali-activated materials. Moreover, the high Ca content of this natural cement can modify the viscosity of the synthesized products for specific applications. A solution of sodium hydroxide and waterglass, in equal weight proportions, was used as the liquid component. The sodium hydroxide was used to activate the aluminosilicate species in the powdered precursors, while the waterglass was used to strengthen the newly formed chemical network. Different kinds of aggregates were used: carbonate sand (SC), volcanic aggregates (VA) and marble powder (M). The amount of each aggregate type was determined based on the required intervention, starting with an aggregate-to-binder ratio of 1. The kind of aggregates used depended on the on-site availability and on the color and fineness, according to the requirements of that specific intervention. It is assumed that all the aggregates used are inert components. Hence, their use is justified in order to contrast the natural shrinkage of the alkali-activated slurries during the curing. Details on the starting binders are presented in Table 1. Further information is available in [14].

Table 1. Details of the starting binders.

Label	Precursor	Alkaline Solutions	Additive (MK)
LBCa 1/1 + 10MK	LBCa = ceramic tile waste	NaOH (8M)/Na_2SiO_3 (R = 3) = 1	10%
CWF 1/1 + 10MK	CWF = solid brick waste	NaOH (8M)/Na_2SiO_3 (R = 3) = 1	10%

The synthesis always occurred at room temperature by mixing the liquid and solid components for 5 min. The aggregates were then added to the resulting slurry, and water was added drop by drop as needed. On-site applications involved hand-mixing in a plastic bowl, while industrial processes utilized a planetary gear suitable for 5–10 kg of slurry before pouring it into extendable molds. For on-site applications, curing occurred without any protection. However, for pre-cast elements, a plastic bag was used to cover the samples throughout the entire 28-days curing period.

2.2. Test Methods

2.2.1. Application Test on Monuments: Reintegration Mortars

The Roman Odéon of Catania was chosen as the first case study for testing the application of ceramic-based AAMs, thanks to a scientific collaboration between the University of Catania and the Parco Archeologico. This monument holds significant historical importance for ancient Catania, dating back to the 2nd century A.D. and is located in the historical center of the city, behind the more recent Roman theatre. The two monuments are interconnected and belong to the Parco Archeologico e Paesaggistico of Catania. The Odéon consists of eighteen walls that create long and narrow covered areas. The structural integrity of the entire monument was compromised over time, requiring substantial restoration interventions during the 20th century. The interventions focused on the brick elements constituting the walls and involved replacing entire pillars. However, the restoration materials, both bricks and mortars, have not proven to be durable and are currently experiencing several types of decay, such as disintegration and scaling. The importance and uniqueness of the archaeological site determined the preliminary application of the synthetized materials on the damaged restoration bricks. Two tests were performed, applying LBCa 1/1 + 10MK SC in area 1 and CWF 1/1 + 10MK SC in area 2 (Figure 1). The geopolymer mortars were applied to two different pillars, one being partially sheltered on the side of the pillar (area 1—Figures 2 and 3), and the other directly exposed to the atmospheric agents (area 2—Figure 4). The surface of the CWF mortar was further finished by abrading it with a spatula to expose the aggregates. This was carried out to test the possibility of achieving an antique appearance. The applications were then visually monitored for three months.

Figure 1. Areas selected for the geopolymer mortars application tests. Area 1 is indicated in the up-right picture; area 2 is indicated in the bottom-left picture.

Figure 2. Geopolymer mortar application in area 1.

Figure 3. Geopolymer mortar applied in area 1—detail at time zero.

(**a**) (**b**)

Figure 4. Geopolymer mortar application in area 2: (**a**) area before the intervention; (**b**) area after the intervention.

2.2.2. Test of Industrial Scale-Up: Glazed Tiles

The case study chosen to evaluate the suitability of geopolymer products as replicas of three-dimensional objects is the famous staircase of Caltagirone, namely Santa Maria del Monte. It would be interesting to replicate a typical tile from the renowned "Ceramica di Caltagirone" and try to glaze it. In order to promote a true circular economy, this test utilized a formulation based on LBCa waste. New "ceramic" tiles made from geopolymer binders were produced in Caltagirone by recycling ceramic waste from the local company La Bottega Calatina. This process involves the company in a productive system reconversion. LBCa 1/1 + 10MK was used with local VA, and its L/S ratio was adjusted to pour the paste into molds with the actual dimensions of a typical tile on the Caltagirone staircase. The geopolymer paste underwent glazing by airbrush and was then fired at 800–900 °C to fix the glaze.

2.2.3. Test of Industrial Scale-Up: Brick Masonry Mock-Up

A small masonry structure was planned to resemble the pillars of the Odéon, which were already considered in the first test. The structure was designed entirely using alkali-activated materials, from the foundation to the top. The LBCa 1/1 + 10MK SC formulation was selected in order to create pre-cast bricks of standard dimensions (25 × 5 × 12.5 cm) and also the bedding mortar.

2.2.4. Application Test on Pottery: Reintegration Mortars, Fillers and Adhesives

Two reintegration mortars, made by using LBCa 1/1 + 10MK SC and CWF 1/1 + 10MK SC, were tested for the restoration of museum materials, specifically for the restoration of pottery such as dishware, pitchers, amphorae and other potsherds. The study was conducted at the restoration laboratory of the Parco Archeologico e Paesaggistico of Catania, located in the historical building of Manifattura Tabacchi. This case study was conducted in three steps. The first step involved applying the products to define their efficiency and pitfalls in this specific case. The second phase was laboratory work aimed at improving the formulations in order to achieve better mortars for the specific case. The third step was the application of the final products to the original remains. For the test, three original objects were selected: a terra sigillata dish, a vessel and an amphora that were excavated in Via Crociferi, in Catania. The first two fragmentary remains were reassembled based on the available fragments and used for phase I. The amphora was used for the final test (phase III), after preliminary reassembly.

Furthermore, LBCa 1/1 + 10MK SC was tested for creating three-dimensional pieces to reconstruct possible lacunae on small objects. The mortar was poured into a mold, and, once consolidated, attached to the original piece using the same LBCa 1/1 + 10MK binder. A modern pottery handle was intentionally broken with a hammer and used to create the mold.

2.3. Analytical Methods: X-ray Diffraction Analysis

The new alkali-activated binders developed for the mortars used to restore the pottery were investigated by means of X-ray Diffraction analysis. The instrument used is a PANalytical X'Pert PRO X-ray Diffractometer, with Cu Kα radiation and operating at 45 kV and 40 mA, with the following operative conditions: time 20 s, step 0.04 in a range of 3–70 2θ. High Score Plus software v.4.8 was used for the qualitative investigation. The quantitative data were obtained with the Rietveld method using Profex software, version 5.2.4. The amorphous abundance was calculated by means of internal corundum standard addition [23].

Details about the newly synthesized products are provided in Table 2.

Table 2. List of new formulations (ceramic-based alkali activated mortars and binders) and the case studies where they were applied. All the formulations are characterized by a ceramic-waste/MK = 9 and NaOH/waterglass (when waterglass is present) = 1. Only the synthesis parameters that could change with respect to the original binder are indicated within the table. L/S ratio changed within the range 0.36–0.55, according to the specific requirements directly during the applications. * The first line indicates the original binder, which was applied for adhesive purposes.

Label	Na_2SiO_3 (R = 3; R = 2)	P	Aggregates	Case Study	Function
LBCa 1/1 + 10MK *	R = 3	/	/	Pottery	Adhesive
LBCa 1/1 + 10MK SC	R = 3	/	SC	Odéon	Reintegration mortar
				Pottery	Reintegration mortar
					Pre-casted elements
CWF 1/1 + 10MK SC	R = 3	/	SC	Odéon	Reintegration mortar
				Pottery	Reintegration mortar
LBCa 1/1 + 10MK VA	R = 3	/	VA	Brick masonry mock-up	Pre-cast tiles
					Pre-cast bricks
					Bedding mortars
LBCa 1/1 + 10MK + 10P	R = 3	10%	/	Pottery	Reintegration mortar
LBCa 1/1 + 10MK + 10P M	R = 3	10%	M	Pottery	Reintegration mortar
CWF 1/1 + 10MK + 10P	R = 3	10%	/	Pottery	Reintegration mortar
CWF 1/1 + 10MK + 10P M	R = 3	10%	M	Pottery	Reintegration mortar
LBCa 1/1 + 10MK + 20P	R = 3	20%	/	Pottery	Reintegration mortar
LBCa 1/1 + 10MK + 20P M	R = 3	20%	M	Pottery	Reintegration mortar
CWF 1/1 + 10MK + 20P	R = 3	20%	/	Pottery	Reintegration mortar
CWF 1/1 + 10MK + 20P M	R = 3	20%	M	Pottery	Reintegration mortar
LBCa (NaOH) + 10MK	/	/	/	Pottery	Reintegration mortar
LBCa (NaOH) + 10MK M	/	/	M	Pottery	Reintegration mortar
CWF (NaOH) + 10MK	/	/	/	Pottery	Reintegration mortar
CWF (NaOH) + 10MK M	/	/	M	Pottery	Reintegration mortar
LBCa 1/1 + 10MK + 10P (R2)	R = 2	10%	/	Pottery	Reintegration mortar
LBCa 1/1 + 10MK + 10P M (R2)	R = 2	10%	M	Pottery	Reintegration mortar
CWF 1/1 + 10MK + 10P (R2)	R = 2	10%	/	Pottery	Reintegration mortar
CWF 1/1 + 10MK + 10P M (R2)	R = 2	10%	M	Pottery	Reintegration mortar
LBCa 1/1 + 10MK + 20P (R2)	R = 2	20%	/	Pottery	Reintegration mortar
LBCa 1/1 + 10MK + 20P M (R2)	R = 2	20%	M	Pottery	Reintegration mortar
CWF 1/1 + 10MK + 20P (R2)	R = 2	20%	/	Pottery	Reintegration mortar
CWF 1/1 + 10MK + 20P M (R2)	R = 2	20%	M	Pottery	Reintegration mortar
LBCa H_2O	R = 2	/	/	Pottery	Reintegration mortar
CWF H_2O	R = 2	/	/	Pottery	Reintegration mortar

3. Results

3.1. Results of the Applicability Tests

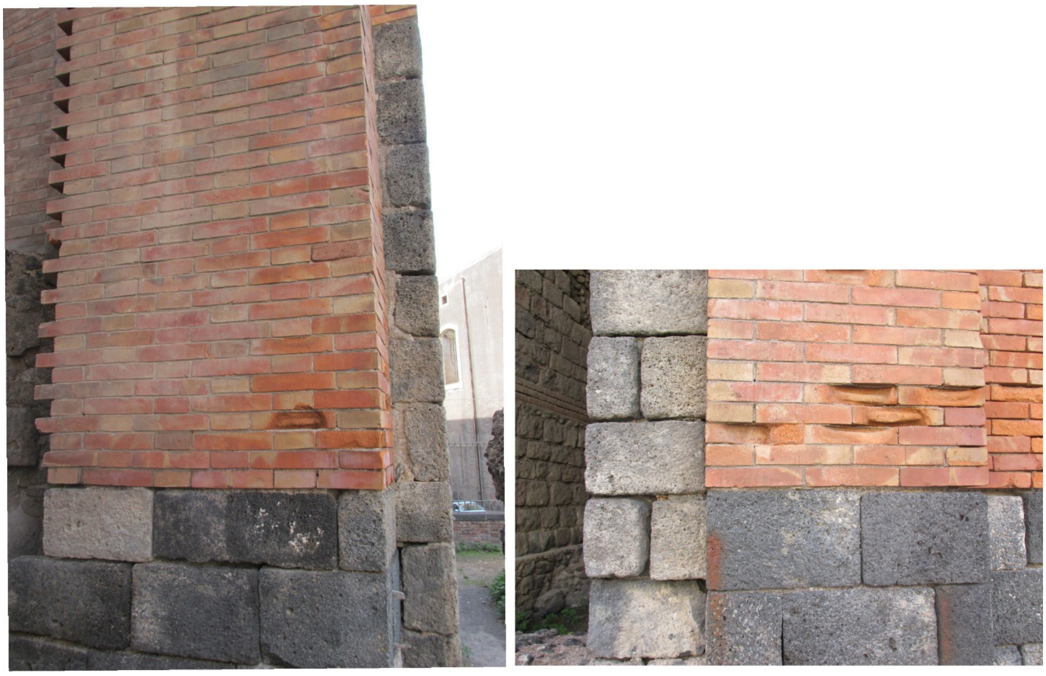
3.1.1. Application Test on Monuments: Reintegration Mortars

The discussion with the restorers was an important milestone in the research. It was productive in identifying the best application modes and requirements for optimizing on-site workability. Additionally, it addressed the need to treat the surface of a test application to create a finish similar to the substrate. It was useful to reconsider the mortars based on the impossibility to synthesize them using stoichiometric procedures while on-site. This required overcoming the need to weigh the solid and liquid components of the mortar. The optimized versions of the mortars now include approximate weights of each component, resulting in a recipe in parts instead of weights. After the solid and liquid components were mixed, the slurries were manually applied to the surface previously wetted with waterglass using a brush (Figure 2). This trick was employed to prevent the liquid components of the mortars from being preferentially absorbed by the porous substrate. This procedure becomes relevant when working on site where it is not possible to cover the surface of the fresh mortar. This results in faster drying, which is inevitable. Considering the natural tendency of these materials to fall off when applied to vertical surfaces, we decided to spread thin layers, pausing for approximately ten to fifteen minutes between each layer. This approach ensures that each layer has enough time to set and support the new layer without collapsing.

Figure 5 shows the monitoring results, that are satisfactory. Both mortars adhere well to the substrate and do not exhibit any efflorescence, shrinkage or visible cracks, except for a minor surface fissure on the LBCa mortar. This fissure was already present at time zero after the setting, likely due to the application procedure. During the monitoring phase, environmental conditions were controlled through direct observation of the data collected on the website of Catania Astrophysical Observatory. On average throughout the year, the temperature ranged between 25.5 °C and 27.5 °C, and relative humidity was at approximately 60% [24].

Figure 5. Monitoring of the two geopolymer mortars exposed on site over time.

Regarding color appearance, the CWF mortar achieved a high degree of similarity to the substrate. However, this type of intervention may not be considered ethical in terms of intervention recognizability. In such cases, creating lowered surfaces would be preferable. On the other hand, the LBCa test shows a more recognizable appearance, with a color that does not alter the overall aesthetic appearance. The lightness appears to be lower while maintaining the same hue. Figure 6 provides an overview of the monument with the applied interventions, demonstrating how the interventions are not immediately visible, but can be recognized upon closer inspection.



(**a**) (**b**)

Figure 6. Final general appearance of the waste ceramic based-geopolymer mortars applied on brick masonries: (**a**) test 1 with LBCa formulation; (**b**) test 2 with CWF formulation and treated texture.

3.1.2. Test of Industrial Scale-Up: Glazed Tiles

Firstly, the geopolymer mortar LBCa 1/1 + 10MK SC, chosen for this test, was tested for its resistance to the high temperature used for the glazing. Ad hoc molds were realized in order to have the possibility to replicate the dimension of the tiles of the staircase of Santa Maria del Monte. The L/S ratio was modified in order to obtain a good workability even if a moderate amount (kilos) of the materials is used. Furthermore, it was modified to make it pourable. After 28 days of curing, the obtained tiles were glazed, with very good results. Figure 7 shows some operative steps and the final product, before the finishing of the surface. While Figure 8 shows the original tiles compared to the geopolymer ones.

3.1.3. Test of Industrial Scale-Up: Brick Masonry Mock-Up

The bricks used for the masonry mock-up were created using the same formulation as was optimized for creating the tiles for the staircase of Santa Maria del Monte. To prevent cracking during curing, a plastic net was placed inside each brick (Figure 9a). Ad hoc molds were used. Once the bricks were ready (Figure 9a), they were applied using LBCa 1/1 + 10MK VA mortar, which was directly prepared on-site and used as bedding mortar. To achieve a similar appearance to the pillars of the Odéon, which we aimed to replicate, it would be useful to soil the fresh mortar with powder. The geopolymer bricks were firmly attached to the geopolymer base thanks to the geopolymer mortar. In addition, well-defined layers of bricks/mortar were obtained. The final appearance of the masonry mock-up is shown in Figure 9b.

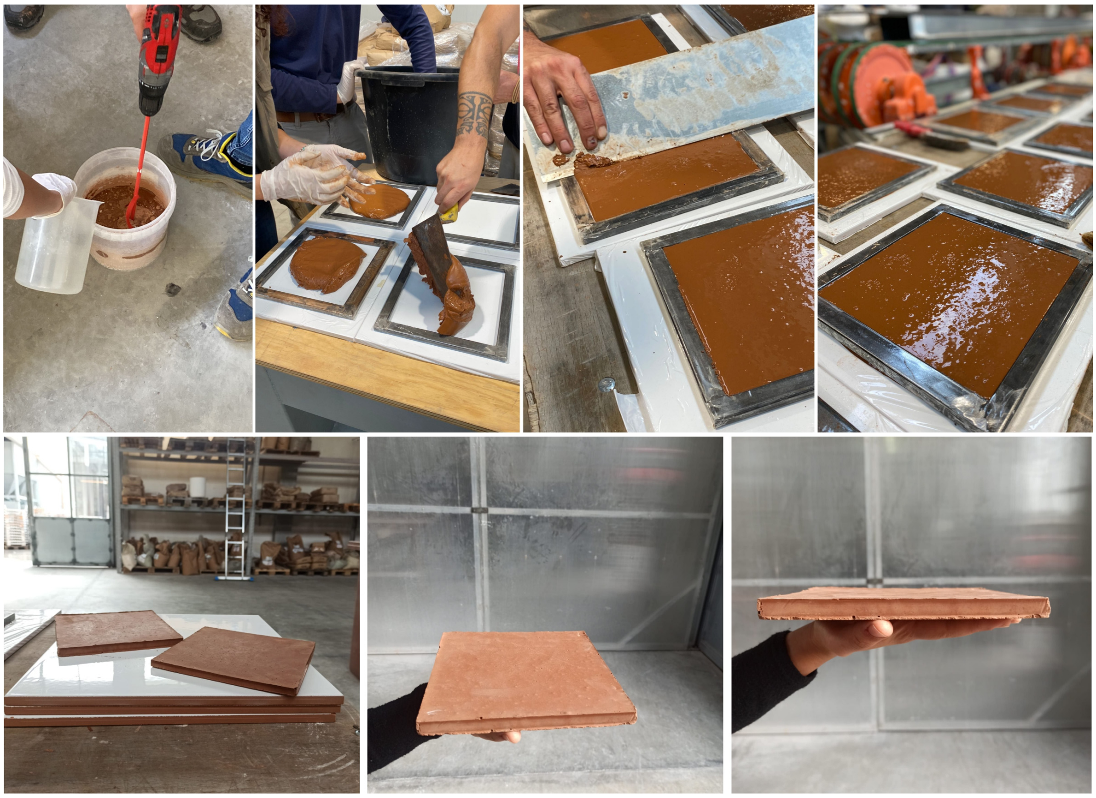


Figure 7. Geopolymer tiles realization process at La Bottega Calatina and the final raw product: in reading order mixing, pouring, surface leveling, curing, final products.

(**a**) (**b**)

Figure 8. (**a**) Staircase of Santa Maria del Monte in Caltagirone; (**b**) geopolymer glazed tiles.

3.1.4. Application Test on Pottery: Reintegration Mortars, Fillers and Adhesives

Phase I

During the first phase (Figures 10 and 11), we identified certain issues and specific requirements for the product's use. It was observed that the geopolymer material exhibits a thixotropic behavior that needs to be attenuated. Indeed, the product tends to adhere to the spatula, making it difficult to work with, specifically for creating three-dimensional parts, such as, for example, a small plinth for a dish. To replicate decorations and small molding, the product should be workable for at least 30 min and maintain its shape. However, it should not dry too fast to allow for eventual modifications during application. A more pliable material is, therefore, desired. Considering the tested formulations, after curing for one day under room conditions, the applied materials are completely dried and became very hard. It was difficult to work on them, even for surface leveling using abrasive papers. A certain visible shrinkage is also present. Positive results were, instead, linked to the color appearance. The hardened mortars were then removed by mechanical action with the help of hydrochloric acid in some instances.

(**a**) (**b**)

Figure 9. (**a**) Bricks during preparation, with the plastic net (**top**) and consolidated bricks (**bottom**); (**b**) brick masonry mock-up.

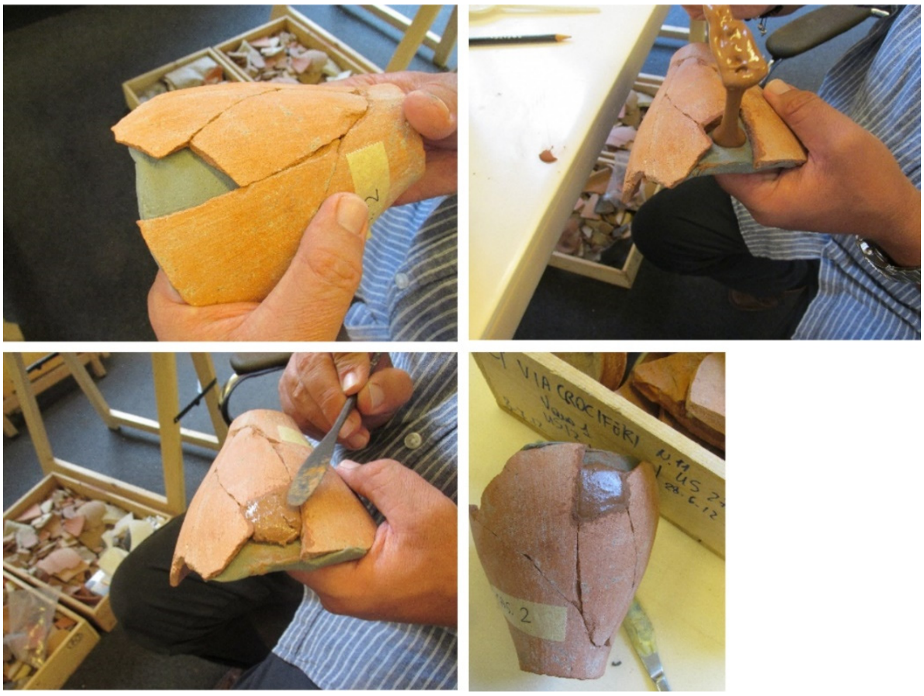


Figure 10. Application of LBCa geopolymer mortar on ceramic archaeological remains.

Figure 11. Application of CWF geopolymer mortar on ceramic archaeological remains.

Phase II

Several attempts were made to improve the workability and reduce shrinkage while enhancing adhesion. To achieve the desired plasticity for shaping the formulation to suit various restoration scenarios and prevent rapid hardening, additives were visually monitored during the process. A Ca-based additive (Prompt) was used to control the plasticity of the mixture by reducing the liquid limit and increasing the plastic limit [25].

The tests foresaw:

(A) The addition of a Ca-rich additive at 10 and 20% in proportion to the weight of the original formulations;
(B) The modification of the original formulation by excluding waterglass;
(C) The addition of a Ca-rich additive in 10 and 20% in weight to the modified original formulation where R = 3 waterglass was substituted with a less concentrated one (R = 2);
(D) All the previous tests were replicated with the addition of powdered marble in a 4/1 binder/aggregate ratio.

With the aim of reducing the shrinkage due to water evaporation, the mortars were cured inside a sealed plastic bag. These tests were performed on modern ceramic fragments.

Both the use of a Ca-rich additive and reducing the concentration of waterglass in the mixture improved its workability properties. However, excluding waterglass from the formulation led to the appearance of efflorescence, which was not observed in the test with less-concentrated waterglass. Additionally, test A resulted in a very hard consolidated product after only a few hours, making it difficult to work with over time. A compromise between the first two attempts (case C) seems to be the best solution. This involves using both Prompt and reducing the concentration of the waterglass (Figure 12). The workability improved with the addition of 20% of Prompt. Furthermore, the best results were obtained when aggregates were added, which also allowed for the control of shrinkage [8].

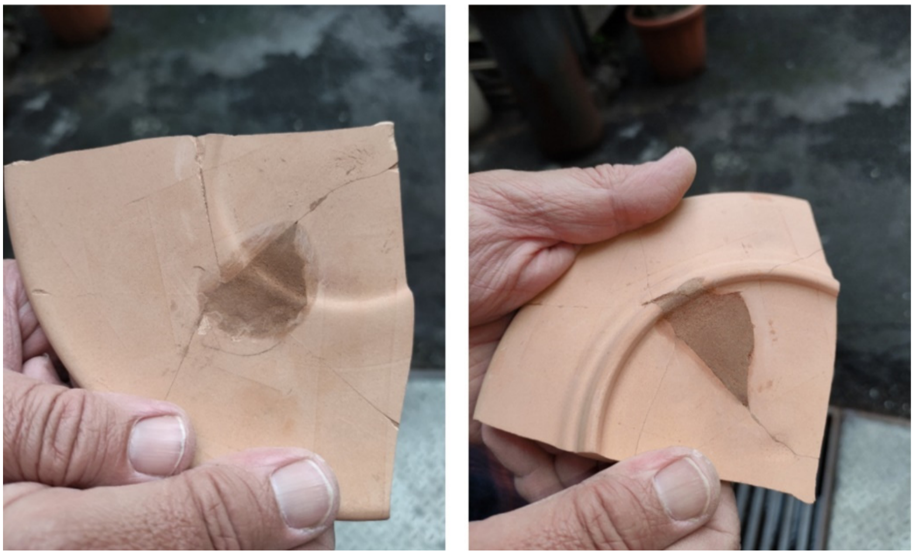


Figure 12. Optimization of the LBCa geopolymer mortar and application on modern ceramic.

These observations apply to both LBCa and CWF mortars, even though the workability seems to be better for LBCa-based products.

Starting with the best results, obtained with LBCa 1/1 + 10MK + 20P M and CWF 1/1 + 10MK + 20P M, diluted binders were used to fill the fissures, where little shrinkage occurred. In cases where the reintegration was performed using LBCa-based mortars, the fissures were filled with the binder LBCa 1/1 + 10MK + 20P diluted with tap water (labeled LBCa H_2O). Conversely, when reintegration was performed using CWF-based mortars, the fissures were filled with the binder CWF 1/1 + 10MK + 20P diluted with tap water (labeled CWF H_2O).

Phase III

After monitoring the applied products for one month, no efflorescence crystallization was observed and good adhesion was achieved (with no more shrinkage). The products were then applied to the ancient amphora (Figure 13) with successful results.

Figure 13. Application of the optimized geopolymer mortars on original archaeological support.

LBCa 1/1 + 10MK SC was used to replicate the handle of a small piece of pottery by pouring it into a mold that was created specifically for this purpose. The consolidated material perfectly replicates the shape of the handle and attaches well to the original piece by using the binder LBCa 1/1 + 10MK (Figure 14). The system also allows the object to be picked up with the attached handle.

(**a**) (**b**)

Figure 14. Modern amphora (**a**) before and (**b**) after the intervention.

3.2. Analytical Results

X-ray Diffractometry

Figure 15 shows the mineralogical comparison between the filling product, LBCa H_2O, its respective formula without water (LBCa 1/1 + 10MK + 20P) and the original binder (LBCa 1/1 + 10MK), and Figure 16 shows a mineralogical comparison between the filling product CWF H_2O, its respective formula without water (CWF 1/1 + 10MK + 20P) and the original binder (CWF 1/1 + 10MK). The qualitative mineralogical composition of the samples with and without water does not change, while comparing the samples with and without Prompt some new peaks appear. In LBCa samples with Prompt, the peaks centered at 17.15° and 17.96° could be attributable to pirssonite ($Na_2Ca(CO_3)_2 \cdot 2H_2O$), and are mostly visible in the sample without water; peaks centered at 29.40°, 47.50° and 48.58° are instead attributed to calcite. In CWF samples with Prompt, a new peak attributable to calcite appears centered at 35.96°, probably denoting an increase in this already present phase. In support of this hypothesis, is the increase in the peak centered at 29.3°, still linked to calcite. Furthermore, the peak attributable to diopside and positioned just below 30° quite disappears in the samples with Prompt. All of the changes which occurred could be attributed to the reaction of the Ca-rich phases of the used additive during the geopolymerization process. The presence of pirssonite is probably due by an excess of Ca and Na within the slurry, which reacting with the CO_2 of the atmosphere determines the mineral formation, probably in form of efflorescence.

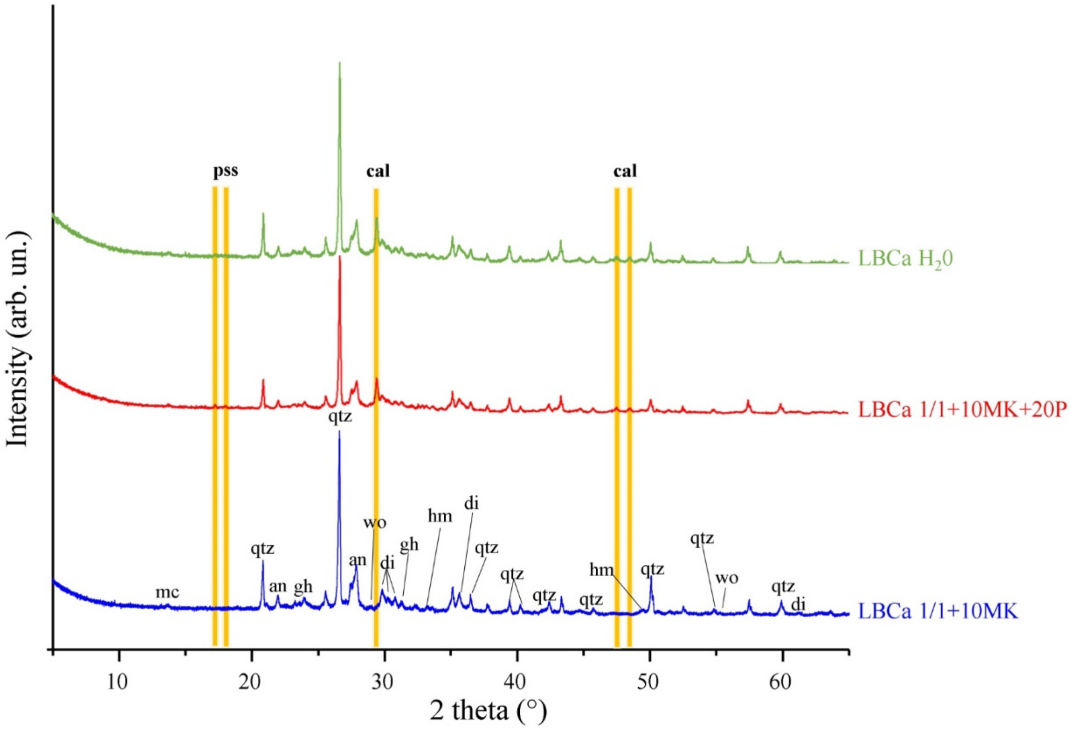


Figure 15. XRD pattern of LBCa 1/1 + 10MK (in blue), LBCa 1/1 + 10MK + 20P (in red) and LBCa H_2O (in green). an = anorthite; cal = calcite; di = diopside; gh = gehlenite; hm = hematite; mc = microcline; pss = pirssonite; qtz = quartz; wo = wollastonite; the new phases are indicated with a yellow line.

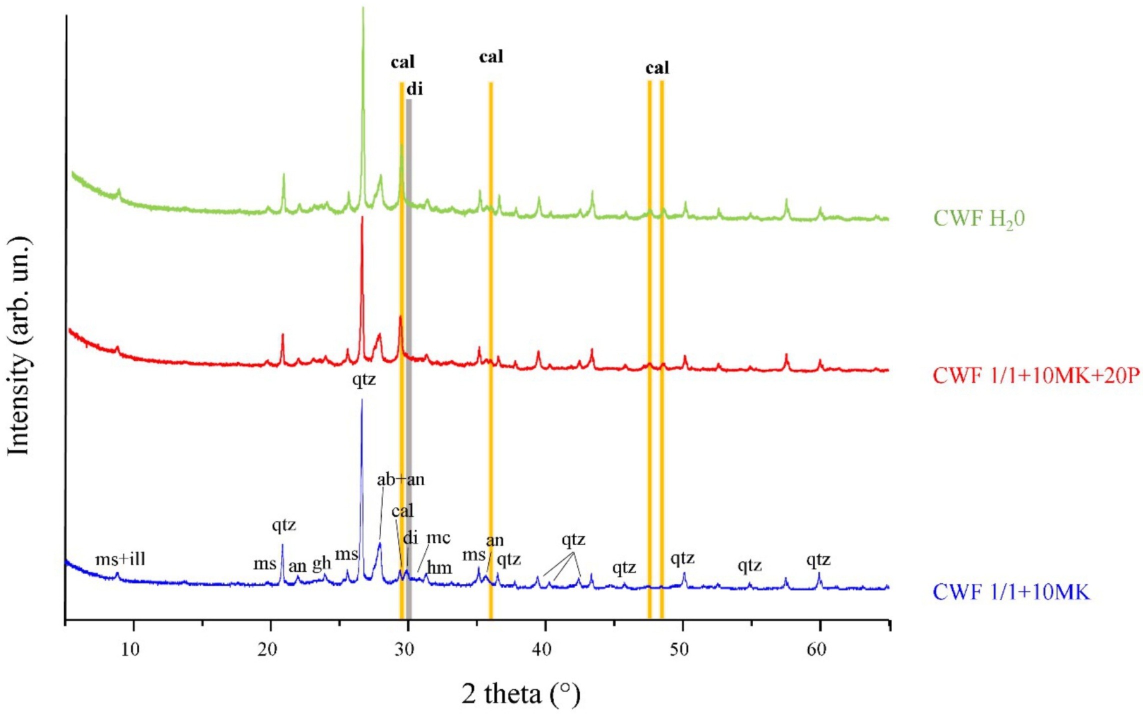


Figure 16. XRD pattern of CWF 1/1 + 10MK (in blue), CWF 1/1 + 10MK + 20P (in red) and CWF H_2O (in green). an = anorthite; cal = calcite; di = diopside; gh = gehlenite; hm = hematite; ill = illite; ms = muscovite; qtz = quartz; the new peaks or increasing peaks are indicated with a yellow line; the peak which decreases in intensity is indicated with a grey line.

All the described results are also confirmed by the quantitative data. Considering the amorphous phase, it is interesting to note that the samples with added water are those samples which show the higher percentage.

The entire mineralogical composition and the respective quantitative analysis of the analyzed samples is exposed in Table 3.

Table 3. XRD phases in the LBCa samples and CWF samples, where ab = albite; an = anorthite; cal = calcite; di = diopside; gh = gehlenite; hm = hematite; ill = illite; mc = microcline; ms = muscovite; pss = pirssonite; qtz = quartz; wo = wollastonite; am = amorphous phase.

ID Samples	ab %	an %	cal %	di %	gh %	hm %	mc %	ms/ill %	pss %	qtz %	wo %	am %
LBCa 1/1 + 10MK	/	16.78	/	6.27	1.39	0.79	6.71	/	/	15.38	2.15	50.52
LBCa 1/1 + 10MK + 20P	/	7.29	4.37	3.84	1.47	0.86	1.56	0.82	4.11	10.83	2.02	62.83
LBCa H_2O	/	6.28	5.09	2.27	1.13	0.97	2.10	4.05	3.21	10.47	1.93	62.5
CWF 1/1 + 10MK	3.58	14.02	2.10	3.66	2.95	0.91	3.34	1.99	/	15.34	/	52.11
CWF 1/1 + 10MK + 20P	3.24	10.02	9.42	2.87	2.07	1.33	1.7	5.08	/	12.09	/	52.00
CWF H_2O	2.55	6.31	7.47	1.17	2.37	0.94	1.86	3.93	/	7.9	/	65.5

4. Discussion

The applicability tests were conducted in various contexts and for different types of interventions. These tests allowed us to verify the feasibility of tailoring the formulation, assessing the functional efficacy, workability and final appearance of geopolymers synthetized using ceramic waste and local aggregates. The case studies provided insight into the potential challenges that may arise during work on a conservation/construction site or in industry during a scale-up process. Although preliminary, the study facilitated the improvement of these products.

The positive outcomes achieved in all the case studies presented were due to the optimization of products based on specific requirements. This was achieved by defining the best application mode for each case.

For the Odéon case study, it was crucial to apply the product layer by layer, ensuring good adhesion between each layer to prevent the product from collapsing under the force of gravity [9]. The tested materials proved to be efficient and compatible. Efficiency was assessed for both tests (in both the areas). The absence of efflorescence, despite the very harsh climate of Catania (humidity and temperature cycles during the summer, succession of rainy and sunny days during the autumn) [26], is one of the most important outcomes. Indeed, efflorescence is a strict limitation in the application of these materials [27]. When the chemical balance of formulations is not perfect, it often results in an excess of alkaline ions that are free to move. These ions react with atmospheric CO_2, leading to the formation of salts that can have negative visible and structural effects. In the end, a significant achievement is linked to the preparation of the geopolymer components in parts. This method of preparation eliminates the needs for precise on-site weighing, which is a time-consuming task. This aspect alone could enable restorers to make a practical choice in favor of geopolymers.

For the Caltagirone case study it was necessary to make the mortars more fluid to allow for easy and fast pouring, as well as to create materials that could receive glazing or other decorations without being broken.

In terms of industrial scale-up, the collaboration with the company was essential to understand the requirements of an industrial system, and the suitability of these products for the industrial process. Materials with different functions, such as bricks and mortar, were confirmed to be obtainable by making small adjustments to the same formulation.

In the last case study, instead, it was important to obtain a more malleable material that could be applied in excess and then flattened with abrasive papers once consolidated. In this way it can properly adhere to the interfaces without any discontinuities. This is a usual technique in the restoration field, to avoid the tendency of the liquid components to form a meniscus, determining difficulties to obtain planar surfaces [9]. In this case, it is a positive result also the possibility to remove the excess with hydrochloric acid.

The research highlighted that small adjustments can significantly affect workability and fluidity, without messing up the mineralogical composition of the gel. According to the mineralogical analysis performed on the latest formulations, no new phases are linked to degradation products, or zeolites, even though the formulations are so deeply modified. The only phases appearing are linked to the addition of the new additive rich in calcium. This probably affects the kind of geopolymer gel formed, in terms of chemistry (NASH or CASH, or more probably a hybrid). In this context, the role of water seems to be strictly associated with the workability change, but without evident effects on the mineralogical composition.

Conversely, a different microstructure and chemistry of the geopolymeric gel surely affect its property. For example, the typical thixotropic behavior of geopolymers is counteracted by the use of a Ca-rich additive, which facilitates the creation of a hybrid geopolymeric network. It increases the plasticity of the slurry, making it easier to be shaped for longer periods of time, as requested by the restorers. However, for the applicative purposes of this research, no deeper microstructural or chemical investigations are needed.

To summarize, the formulations that satisfied the applicability requirements best are listed here:

- Restoration mortars for monuments: LBCa 1/1 + 10MK SC and CWF 1/1 + 10MK SC;
- Restoration mortars for pottery: LBCa 1/1 + 10MK 20P M (R2) and CWF 1/1 + 10MK 20P M (R2);
- Pre-cast elements: LBCa 1/1 + 10MK VA and LBCa 1/1 + 10MK SC;
- Adhesive: LBCa 1/1 + 10MK;
- Filler: LBCa H_2O and CWF H_2O.

5. Conclusions

Starting from the same geopolymer formulation (1/1 + 10MK), it was possible to create a plethora of restoration products, including reintegration mortars for intervention on monuments, bedding mortars for masonries, restoration mortars for finer interventions, fillers, adhesives, three-dimensional materials for substitutions in structural interventions (bricks) or for decorative purposes (glazed tiles), as well as three-dimensional plastic elements for interventions on statues or objects (the handle of the amphora). The original formulation was replicated by using two different types of ceramic waste (tiles LBCa and bricks CWF) as precursors; they were optimized as mortars by using different kind of aggregates (carbonate sand SC, volcanic aggregates VA or marble M), optimized for workability case by case, adding small amount of an additive (natural hydraulic lime P) where necessary. All of these tests showed very good results, both in terms of feasibility for on-site or industrial synthesis, as well as in terms of appearance in accordance with restoration rules or recommendations. The formulations studied have been confirmed to be highly versatile. Being easy to prepare, highly performing, consolidating at room temperature, involving the recycling of natural and industrial wastes, these materials could be considered eco-friendly and suitable for the application in the field of conservation-restoration as alternative to the traditional restoration materials. They could be functionalized by changing the type and/or proportions of the precursors or by the use of specific additives, being optimized according to the finality of their application. This aspect is of primary importance in order to underline the intervention efficacy. This research, finally, allowed to assess by the use of alkali-activated mortars the improvement of suitable restoration products which promote a green restoration. We created ad hoc materials which were compatible with the substrate being restored, and at the same time, were efficient, durable and eco-friendly.

Author Contributions: Conceptualization: M.F., G.B. and P.M.; Data curation: M.F., G.B., P.M. and A.S.; Funding acquisition: M.F., G.B. and P.M.; Investigation: M.F.; Methodology: M.F., G.B. and

P.M.; Project administration: G.B. and P.M.; Resources: G.B. and P.M.; Supervision G.B. and P.M.; Validation: G.B. and P.M.; Visualization: M.F.; Roles/Writing—original draft: M.F., G.B., P.M. and A.S.; Writing—Review and Editing: M.F., G.B., P.M. and A.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Ph.D Grant PO FSE Sicilia 2020 (CUP E64F18000430009) and the Advanced Green Materials for Cultural Heritage (AGM for CuHe) project (PNR fund with code: ARS01_00697; CUP E66C18000380005).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data are contained within the article.

Acknowledgments: The authors wish to thank the partners of the AGM for CuHe project involved in this research; specific thanks goes to La Bottega Calatina arl who supplied tiles waste and contributed to the realization of the industrial scale-up, SB Engineering srl for planning the masonry mock-up and Megares srl for its realization on site; thanks to Piacenti srl for the restoration interventions on the Odéon pillars. The authors further thank Marco Patrì and Daniela Carella, restorers of the Parco Archeologico e Paesaggistico of Catania for their fruitful suggestions regarding the interventions on pottery. For all the study we are kind to thank Gioconda Lamagna and the Parco Archeologico e Paesaggistico of Catania for the permissions to work at the archeological site. Thanks, furthermore, to Roberta Occhipinti and Claudio Finocchiaro, both from the Department of Biological, Geological and Environmental Sciences of the University of Catania, for their support in the scale-up activities within the framework of AGM for CuHe project. We thank Giuseppe Cultrone of the University of Granada (Spain) and the Centro de Instrumentacion Cientifica (CIC, University of Granada) for their assistance with the XRD analyses.

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

References

1. Sesana, E.; Bertolin, C.; Gagnon, A.S.; Hughes, J.J. Climate change impacts on cultural heritage: A literature review. *Wiley Interdiscip. Rev. Clim. Chang.* **2019**, *90*, e710. [CrossRef]
2. Caroselli, M.; Ruffolo, S.A.; Piqué, F. Mortars and plasters—How to manage mortars and plasters conservation. *Archaeol. Anthropol. Sci.* **2021**, *13*, 188. [CrossRef]
3. Benito, P.; Leonelli, C.; Medri, V.; Vaccari, A. Geopolymers: A new and smart way for a sustainable development. *Appl. Clay Sci.* **2013**, *731*, 1. [CrossRef]
4. Geraldes, C.F.M.; Lima, A.M.; Delgado-Rodrigues, J.; Mimoso, J.M.; Pereira, S.R.M. Geopolymers as potential repair material in tiles conservation. *Appl. Phys. A Mater. Sci. Process.* **2016**, *122*, 1–10. [CrossRef]
5. Sassoni, E.; Pahlavan, P.; Franzoni, E.; Bignozzi, M.C. Valorization of brick waste by alkali-activation: A study on the possible use for masonry repointing. *Ceram. Int.* **2016**, *42*, 14685–14694. [CrossRef]
6. Fiori, C.; Lorusso, S.; Pentrella, R. *Restauro, Manutenzione, Conservazione Dei Beni Culturali: Materiali, Prodotti, Tecniche, I. Beni Culturali e l'Ambiente*; Pitagora Ed. Bol.: Jalisco, Mexico, 2003; pp. 1–280.
7. Lazzarini, L.; Laurenzi Tabasso, M. *Il Restauro Della Pietra*; CEDAM: Padova, Italy, 1986; p. XVI–320.
8. Pecchioni, E.; Fratini, F.; Cantisani, E. *Le Malte Antiche e Moderne Tra Tradizione ed Innovazione*; Pàtron Ed. Bol.: Jalisco, Mexico, 2008; pp. 1–238.
9. Matteini, M.; Moles, A. *La Chimica Nel Restauro. I Materiali Dell'arte Pittorica*; Nardini Editore: Firenze, Italy, 2007.
10. Warscheid, T.; Braams, J. Biodeterioration of stone: A review. *Int. Biodeterior. Biodegrad.* **2000**, *46*, 343–368. [CrossRef]
11. Favaro, M.; Mendichi, R.; Ossola, F.; Russo, U.; Simon, S.; Tomasin, P.; Vigato, P.A. Evaluation of polymers for conservation treatments of outdoor exposed stone monuments. Part I: Photo-oxidative weathering. *Polym. Degrad. Stab.* **2006**, *91*, 3083–3096. [CrossRef]
12. Palomo, A.; Maltseva, O.; Garcia-Lodeiro, I.; Fernández-Jiménez, A. Portland Versus Alkaline Cement: Continuity or Clean Break: "A Key Decision for Global Sustainability". *Front. Chem.* **2021**, *9*, 1–28. [CrossRef] [PubMed]
13. Lancellotti, I.; Catauro, M.; Ponzoni, C.; Bollino, F.; Leonelli, C. Inorganic Polymers from Alkali Activation of Metakaolin: Effect of Setting and Curing on Structure. *J. Solid State Chem.* **2013**, *200*, 341–348. [CrossRef]
14. Fugazzotto, M.; Cultrone, G.; Mazzoleni, P.; Barone, G. Suitability of ceramic industrial waste recycling by alkaline activation for use as construction and restoration materials. *Ceram. Int.* **2023**, *49*, 9465–9478. [CrossRef]
15. Barone, G.; Caggiani, M.C.; Coccato, A.; Finocchiaro, C.; Fugazzotto, M.; Lanzafame, G.; Occhipinti, R.; Stroscio, A.; Mazzoleni, P. Geopolymer production for conservation-restoration using Sicilian raw materials: Feasibility studies. *IOP Conf. Ser. Mater. Sci. Eng.* **2020**, *777*, 1–9. [CrossRef]

16. Clausi, M.; Tarantino, S.C.; Magnani, L.L.; Riccardi, M.P.; Tedeschi, C.; Zema, M. Metakaolin as a precursor of materials for applications in Cultural Heritage: Geopolymer-based mortars with ornamental stone aggregates. *Appl. Clay Sci.* **2016**, *132–133*, 589–599. [CrossRef]
17. Hanzlíček, T.; Steinerová, M.; Straka, P.; Perná, I.; Siegl, P.; Švarcová, T. Reinforcement of the terracotta sculpture by geopolymer composite. *Mater. Des.* **2009**, *30*, 3229–3234. [CrossRef]
18. Ricciotti, L.; Molino, A.; Roviello, V.; Chianese, E.; Cennamo, P.; Roviello, G. Geopolymer Composites for Potential Applications in Cultural Heritage. *Environments* **2017**, *4*, 91. [CrossRef]
19. Elert, K.; Bel-Anzué, P.; Monasterio-Guillot, L.; Pardo, S. Performance of alkaline activation for the consolidation of earthen architecture. *J. Cult. Herit.* **2019**, *39*, 93–102. [CrossRef]
20. Alhawat, M.; Ashour, A.; Yildirim, G.; Aldemir, A.; Sahmaran, M. Properties of Geopolymers Sourced from Construction and Demolition Waste: A Review. *J. Build. Eng.* **2022**, *50*, 104104. [CrossRef]
21. Reig, L.; Tashima, M.M.; Borrachero, M.V.; Monzó, J.; Cheeseman, C.R.; Payá, J. Properties and microstructure of alkali-activated red clay brick waste. *Constr. Build. Mater.* **2013**, *43*, 98–106. [CrossRef]
22. Robayo, R.A.; Mulford, A.; Munera, J.; Mejía de Gutiérrez, R. Alternative cements based on alkali-activated red clay brick waste. *Constr. Build. Mater.* **2016**, *128*, 163–169. [CrossRef]
23. Gualtieri, A.F.; Zanni, M. Quantitative determination of crystalline and amorphous phase in traditional ceramics by combined rietveld-RIR method. *Mater. Sci. Forum* **1998**, *278–281*, 834–839. [CrossRef]
24. INAF. Osservatorio Astrofisico di Catania. Available online: https://www.oact.inaf.it/ (accessed on 16 January 2024).
25. Tajaddini, A.; Saberian, M.; Sirchi, V.K.; Li, J.; Maqsood, T. Improvement of mechanical strength of low-plasticity clay soil using geopolymer-based materials synthesized from glass powder and copper slag. *Case Stud. Constr. Mater.* **2023**, *18*, e01820. [CrossRef]
26. Beck, H.E.; Zimmermann, N.E.; McVicar, T.R.; Vergopolan, N.; Berg, A.; Wood, E.F. Present and future Köppen-Geiger climate classification maps at 1-km resolution. *Sci. Data* **2018**, *5*, 180214. [CrossRef] [PubMed]
27. Lloyd, R.R.; Provis, J.L.; van Deventer, J.S.J. Pore solution composition and alkali diffusion in inorganic polymer cement. *Cem. Concr. Res.* **2010**, *40*, 1386–1392. [CrossRef]