SOLUCIONES INNOVADORAS DE GEOPOLÍMEROS PARA LA CONSERVACIÓN DEL PATRIMONIO CULTURAL

INNOVATIVE GEOPOLYMER SOLUTIONSFOR THE CONSERVATION OF CULTURAL HERITAGE

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RESUMEN

En las últimas décadas, la aplicación indiscriminada de materiales incompatibles en la restauración de estucos históricos ha provocado daños considerables al patrimonio cultural, comprometiendo la integridad de los sustratos originales y contraviniendo los principios fundamentales de la conservación. En respuesta a estos desafíos, el proyecto PhD tiene como objetivo desarrollar morteros innovadores basados en geopolímeros, materiales con base alumino-silicatada, diseñados específicamente para garantizar la compatibilidad fisicoquímica con los sustratos pétreos históricos.

Esta investigación forma parte de una red internacional entre los grupos de investigación ACLabs (Universidad de Nápoles Federico II) y TEMA (Universidad Politécnica de Madrid), en asociación con la Superintendencia de Nápoles para vincular la innovación en laboratorio con la aplicación práctica, probando los materiales desarrollados en sitios reales para apoyar su adopción futura en prácticas de restauración operativas. El enfoque metodológico adoptado es multidisciplinario, integrando profesionales de los campos de la ingeniería de materiales y de la construcción, arquitectura y ciencia de la restauración.

Las actividades experimentales incluyeron la caracterización fisicoquímica de materiales originales del Centro Histórico UNESCO de Nápoles y la formulación de nuevos morteros geopoliméricos obtenidos a partir de materias primas naturales (metacaolín) y materiales de desecho de excavación (tufo y ladrillo). Las pruebas de laboratorio incluyeron la absorción de agua, porosidad abierta, absorción capilar, resistencia mecánica, con especial atención a la compatibilidad entre los materiales desarrollados y los sustratos históricos. Los resultados preliminares confirman el potencial de los morteros geopoliméricos como una alternativa sostenible y eficaz para la restauración, ofreciendo un rendimiento comparable al de los materiales tradicionales y la ventaja de un impacto ambiental significativamente reducido.

La investigación pretende contribuir a la innovación en el campo de la conservación del patrimonio cultural, promoviendo una transición hacia materiales y tecnologías más sostenibles, respetuosos con el patrimonio y orientados hacia la gestión circular de los recursos.

Palabras clave: *conservación del patrimonio cultural, geopolímeros, materiales de aluminosilicato, materiales circulares*

ABSTRACT

Over the past decades, the indiscriminate application of incompatible materials in the restoration of historic plasters has resulted in considerable damage to cultural heritage, compromising the integrity of original substrates and contravening the foundational principles of conservation, such as compatibility and *reversibility. In response to these challenges, the PhD research project aims to develop innovative geopolymer-based binders, materials with an alumina-silicate base, specifically designed to ensure chemical-physical compatibility with historic stone substrates, while markedly reducing environmental impact compared to conventional restoration materials.*

This research is part of an international network that involves close collaboration between the research groups ACLabs (DICMaPI-University of Naples Federico II) and TEMA (Polytechnic University of Madrid), in partnership with the Superintendence of Archaeology, Fine Arts and Landscape for the Municipality of Naples. The objective is to bridge laboratory innovation and practical application, testing the developed materials on real sites to support their future adoption in operational restoration practices. The methodological approach adopted is multidisciplinary, integrating professionals from the fields of materials engineering, building engineering, architecture, and restoration science. The experimental activities involved the chemical-physical characterization of historical construction materials from the UNESCO-listed Historic Centre of Naples, as well as the formulation of new geopolymer binders obtained from natural raw materials (metakaolin) and excavation waste materials (tuff and cocciopesto).

Laboratory tests include water absorption, open porosity, capillary absorption, mechanical strength, with particular attention to the compatibility between the developed materials and the historic substrates. Preliminary results confirm the potential of geopolymer binders as a sustainable and effective alternative for restoration, offering comparable performance to traditional materials and the advantage of a significantly reduced environmental impact.

The project aims to contribute to innovation in the field of cultural heritage conservation, promoting a transition towards more sustainable materials and technologies, respectful of heritage and oriented towards circular resource management.

Keywords: *Cultural Heritage conservation, geopolymers, alumino-silicate materials, circular materials*

1. INTRODUCTION

In recent years, the construction sector has drawn growing attention from both the scientific community and regulatory institutions, as it is recognized as one of the primary contributors to global environmental impact. This sector is among the leading sources of greenhouse gas emissions, the depletion of natural resources, and the generation of solid waste.

Recent data indicate that primary resource extraction reached approximately 70 billion tonnes in 2020, with a substantial share allocated to the building industry (Schandl et al., 2024). Furthermore, a study published in Nature Scientific Data highlights that as early as 2010, the construction sector was already responsible for nearly 50% of global material extraction, with a consumption of about 40 billion tonnes projected to double by 2050 (Fishman et al., 2024). The extracted resources —such as sand, gravel, clay, and limestone— are being increasingly exploited, causing significant ecological damage, including soil erosion, land degradation, and biodiversity loss. In parallel, waste management represents a major challenge. In Europe, construction and demolition (C&D) waste accounts for more than 30% of the total solid waste generated, corresponding to around 850 million tonnes annually (European Commission, 2012). Although a portion of these materials is theoretically recyclable, practical reuse is hindered by contamination, compositional heterogeneity, and the lack of established recovery streams.

In response to these challenges, a dual pressure has emerged: on the one hand, regulatory pressure expressed through initiatives such as the European Green Deal and the Renovation Wave strategy, which aim to reduce emissions from the building stock by 55% by 2030 (European Commission, 2020); on the other hand, social and cultural pressure driven by growing environmental awareness, with a growing public demand for low-impact buildings made from recycled, local, and non-hazardous materials. In this context, public procurement systems have also evolved: many countries, including Italy, have introduced mandatory Minimum Environmental Criteria (CAM), requiring the use of low-carbon materials and the recovery of inert waste.

Within this framework, the adoption of alternative binders such as geopolymers —formulated from industrial by-products, chemically activated sediments, or natural pozzolanic materials— represents not only a technologically advanced solution but also a tangible response to the goals of ecological transition. Recent studies have shown that these materials can provide high mechanical performance, chemical resistance, and compatibility with conservation requirements, while simultaneously reducing the overall environmental impact of the construction cycle (Duxson et al., 2007) (Fernández-Jiménez et al., 2005) (Rovnaník, 2010).

The integration of scientific innovation and environmental sustainability now constitutes one of the most urgent and strategic challenges for the future of architectural design and conservation, as exemplified by these novel formulations. In particular, the use of geopolymers in the field of cultural heritage conservation has become an area of growing interest, particularly due to their ability to meet essential criteria such as mechanical and physical compatibility with original substrates, reversibility, and long-term durability. The possibility of tailoring the rheological, mechanical, and chromatic properties of geopolymers through the use of inert fillers, natural pigments, or local aggregates makes them particularly well-suited for architectural restoration applications, where visual and material compatibility is a fundamental requirement (Geraldes et al., 2016). Numerous pilot projects and experimental studies have already demonstrated the effectiveness of these solutions for the production of innovative mortars and plasters, suitable for both preventive conservation and structural restoration of historic buildings and monuments (Liguori et al., 2017); (Capasso, D'Angelo, Verniero, et al., 2023); (Capasso, D'Angelo, Fumo, et al., 2023).

Considering this evidence, geopolymers are increasingly regarded as one of the most promising technologies for reconciling Cultural Heritage protection with environmental sustainability, fostering an intervention model that respects the historical and territorial specificities of built heritage.

2. OBJECTIVES

Taking into account the current environmental, regulatory, and conservation-related challenges affecting both the construction sector and the field of Cultural Heritage preservation, the present research project aims to develop innovative geopolymer-based mortars suitable for the restoration of historic surfaces, with particular focus on the UNESCO World Heritage Site of the historic center of Naples.

The primary objective is to design materials that are behaviorally compatible with historical substrates and aligned with the principles of environmental sustainability promoted by recent European strategies, such as the Green Deal and the Renovation Wave. To this end, the research explores the potential of geopolymers formulated from natural precursors (metakaolin) and locally sourced recycled aggregates (two distinct types of volcanic tuff and brick waste), with the goal of reducing environmental impact.

In parallel, the project seeks to bridge the gap between laboratory-scale experimental formulations and practical on-site applications, through validation in real-world contexts in collaboration with the Naples Heritage Authority.

This approach is part of a broader strategy for innovation in the conservation of architectural heritage, aimed at introducing high-performance, eco-compatible materials that meet key requirements of durability, compatibility, and reversibility.

3. METHODOLOGY

The adopted methodology is based on an interdisciplinary approach that integrates expertise from the fields of materials engineering, architecture, and conservation science. In the initial phase of the research, novel geopolymeric mortars were formulated using metakaolin as the alkali-activated precursor, combined with natural aggregates and waste materials. This choice aligns with recent studies focused on the valorization of locally sourced materials to reduce CO_2 emissions and improve environmental compatibility (Liguori et al., 2017).

The resulting samples were subjected to water absorption and open porosity tests to assess their performance with respect to established standards for restoration mortars (Fernandez-Jimenez et al., 2007), and to mechanical characterization, including compressive strength, flexural strength, and Shore-D surface hardness.

The experimental activities were carried out as part of an international research collaboration, involving the ACLabs group (University of Naples Federico II) and the TEMA group (Polytechnic University of Madrid), promoting methodological exchange and the harmonization of testing protocols in accordance with European best practices in heritage conservation.

3.1 Raw materials and preparation of the geocomposites

This section provides detailed information on the raw materials used, including geopolymer precursors, alkaline activating solutions, and the preparation procedures adopted for the formulation of the geocomposites.

To formulate the geopolymeric mortars, various raw materials were examined, including both locally available geological resources and recycled waste products, with the aim of evaluating their potential effectiveness as natural substitutes for conventional aggregates. Specifically, the following types of aggregates were used:

- Chabazite-rich tuff (CH);
- Clinoptilolite-rich tuff (CL);
- Crushed brick waste (*Cocciopesto*, CP).

Both tuffs were mechanically crushed and subsequently sieved to obtain a particle size fraction of less than 0.5 mm, suitable for mortar applications.

As a reference geopolymeric mortar, a formulation labelled Geo_MK + SAND was produced using natural silica sand commonly used in construction (VG14, VAGA S.r.L, Costa De' Nobili, PV) as fine aggregate.

The metakaolin (MK) used as the reactive geopolymeric precursor was supplied by Neuvendis (Al_2O_3 41.90 wt%; SiO_2 52.90 wt%; K_2O 0.77 wt%; Fe_2O_3 1.60 wt%; TiO_2 1.80 wt%; MgO 0.19 wt%; CaO 0.17 wt%).

The alkaline activating solution was prepared by dissolving NaOH pellets (Titolchimica S.p.A., Villamarzana, RO) in a sodium silicate (SS) solution (Na_2O 8,15%, SiO_2 27,40%) supplied by Prochin Italia S.r.L. (Caserta, Italy).

These aggregates were subsequently incorporated into metakaolin-based geopolymeric matrices, aiming to optimize both chemical compatibility and physical and chemical performance.

(a) (b)

Figure 1. (a) Prismatic samples produced based on natural siliceous sand (SABBIA), crushed brick waste (CP), chabazite-rich tuff (CH), and clinoptilolite-rich tuff (CL).
(b) Cubic samples produced based on natural siliceous sand and crushed brick waste.

The production of geopolymeric mortars (Geo_MK+SABBIA, Geo_MK+CP, Geo_MK+CH, Geo_MK+CL) involved the addition of the alkaline solution to the dry metakaolin powder (MK), and the resulting paste was mechanically mixed for about two minutes. While maintaining continuous mixing, the aggregates were gradually introduced. To improve the workability of the homogeneous paste, an additional amount of water was added, reaching a total mixing time of about eight minutes. The mortars were formulated with a binder-to-aggregate ratio of 1 and a water-to-solid (w/s) ratio of 0.42.

Fresh mortars were cast into polyethylene moulds and cured under controlled conditions for 14 days at a constant temperature of 25 °C and 90% relative humidity, with sealed containers to prevent the loss of moisture. Specimens of different geometries were produced in accordance with the standards relevant to the experimental tests to be conducted: prismatic (40×40×160 mm^3) (Fig. 1a) and cubic (50×50×50 mm^3) (Fig. 1b). Upon completion of the curing period, all samples were demoulded and stored at room temperature until characterization (Verniero et al., 2024).

3.2 Testing methods

3.2.1 *Physical characterization of the Geopolymeric Mortars*

Water absorption under vacuum and open porosity of the geocomposites were determined in accordance with the UNI 11060: 2003 (UNI 11060:2003, 2003) standard.

The specimens were first oven-dried at 60 °C until reaching a constant mass (M_1, in grams). Subsequently, each sample was immersed in water at room temperature within a vacuum chamber, where the pressure was lowered to approximately 20 mmHg and maintained constant for two hours. At the end of this phase, the pressure was gradually returned to atmospheric conditions. The samples were then weighed under water to determine their hydrostatic mass (M_2, in grams), and subsequently surface-dried with a damp cloth before being weighed again in saturated condition (M_3, in grams). Each test was performed in triplicate, and the reported results represent the average values obtained.

Water absorption (WA, %) and open porosity (OP, %) were calculated as follows:

$$WA = \frac{M_3 - M_1}{M_1} * 100 \qquad (1)$$

$$OP = \frac{M_3 - M_1}{M_3 - M_2} * 100 \qquad (2)$$

Capillarity tests were also conducted in accordance with the European standard UNI EN 15801 (UNI EN 15801:2010, 2010), with the aim of evaluating the amount of water absorbed (Q) per unit surface area as a function of time.

Considering that, over short time intervals, the relationship between absorbed water and the square root of time exhibits a linear trend, the capillary absorption coefficient (CA) was determined as the slope of the best-fit line interpolating the data collected during the first 30 minutes of testing.

3.2.2 *Mechanical characterization of the Geopolymeric Mortars*

Flexural strength (Fig. 2a) was determined in accordance with UNI EN 196-1:2016 (UNI EN 196-1:2016, 2016), using prismatic specimens with dimensions of 40×40×160 mm³. The tests were conducted using an Ibertest testing machine, applying a load at a constant rate.

Each specimen was supported on two steel rollers, with lengths between 45 and 50 mm and a diameter of 10 mm ± 5 mm, spaced 100 mm ± 0.5 mm apart. A third roller, positioned at the midpoint of the span, applied the load vertically. The flexural strength $(f, \mathrm{N/mm^2})$ was calculated using the following equation:

$$f = \frac{1{,}5 * Fl}{b * d^2} \qquad (3)$$

where: *F* is the maximum load applied at failure (N); *l* is the span between the supports (mm); *b* and *d* are the width and depth of the specimen (mm).

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

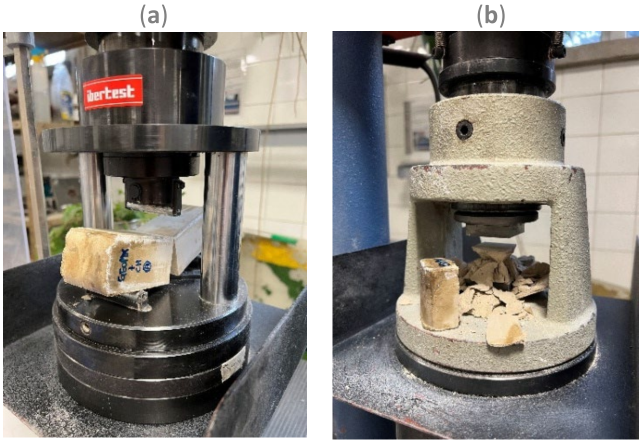

Figure 2. Flexural (**a**) and Compressive (**b**) strength test.

Compressive strength (Fig. 2b) was determined using an Ibertest testing machine, by applying a progressively increasing load without acceleration to two opposite faces of the prismatic specimens until failure occurred. The samples used for this test correspond to the two broken halves obtained after the flexural strength test, in accordance with UNI EN 196-1:2016. These halves were positioned between two steel plates with dimensions of 40 mm in length × 40 ± 1 mm in width and 10 mm in thickness. The compressive strength ($\sigma, \mathrm{N/mm^2}$) was calculated using the following equation:

$$\sigma = \frac{P}{S} \qquad (4)$$

where P is the maximum load applied at failure (N) and S is the cross-sectional area of the specimen (mm²).

4. RESULTS

4.1 Physical characterization of the Geopolymeric Mortars

The effects of incorporating tuff and crushed brick waste as aggregate in the formulation of metakaolin-based geopolymer mortars were investigated, with a particular focus on key physical properties relevant to conservation applications. The experimental results obtained from triplicate tests are reported in Table 1. The geopolymer samples exhibited comparable values of open porosity and capillary water absorption, indicating consistent formulation performance and suggesting homogeneous physical behavior across the different mortars analyzed.

Furthermore, to evaluate the actual suitability of the developed formulations for applications in the field of Cultural Heritage conservation, these results were compared with data available in the literature for traditional materials commonly employed in architectural restoration (Table 2).

Table 1. Main physical properties of the Geocomposites. Partial data already reported in (Verniero et al., 2024)

Sample	Open Porosity [%]	Water Absorption [%]	CA [mg/cm^2 s$^{-1/2}$]	Q_{max} [mg/cm^2]
MK+SA	40.29 ± 0.96	26.71 ± 1.07	40.10 ± 0.50	1704.439
MK+CP	40.87 ± 0.25	28.24 ± 0.10	29.17 ± 1.63	1804.045
MK+CH	43.53 ± 0.51	34.46 ± 0.49	32.06 ± 2.35	1916.40
MK+CL	42.39 ± 0.18	32.61 ± 0.27	24.80 ± 1.40	1709.88

Table 2. Physical properties of some mortars widely used for restoration purposes.

Sample	Open Porosity [%]	CA [mg/cm ^{2} s$^{-1/2}$]	Q_{max} [mg/cm^2]	Reference
OPC mortar (CEMII B/L 32.5)	18.80	3.40	2030	(Silva et al., 2015)
Natural Bioclastic Limestone	24-30	31.32	n.d.	(Maravelaki-Kalaitzaki et al., 2005)
Repair mortar NHL-Z 3.5 with crushed bricks and silica sand	26.23 *	24.16 *	n.d.	(Maravelaki-Kalaitzaki et al., 2005)
Hydraulic lime mortar NHL 5	23.50	9.40	3970	(Garijo et al., 2020); (Silva et al., 2015)

* Evaluated after 12 months. n. d.: not determined.

The geocomposites demonstrated capillary absorption and open porosity values consistent with those reported for historical construction materials and traditional plasters (Maravelaki-Kalaitzaki et al., 2005); (Garijo et al., 2020); (Silva et al., 2015).

Preliminary findings highlight the potential applicability of these innovative materials as a sustainable and functional alternative to conventional products typically employed in the conservation of Cultural Heritage assets.

4.2 Mechanical characterization of the Geopolymeric Mortars

The average values of flexural and compressive strength for each geocomposite formulation are presented in Table 3.

Among the materials tested, the GEO_MK+CP formulation —based on metakaolin and crushed brick waste (*cocciopesto*)— showed the best mechanical performance compared to formulations incorporating natural tuff (GEO_MK+CH and GEO_MK+CL).

In the context of geopolymeric materials, mechanical performance is not solely determined by the intrinsic strength of the binder matrix. Rather, it results from the synergistic interaction of three key components: the alkali-activated binder, the physical and mechanical characteristics of the aggregate, and the quality of the interface that develops between these phases during the polycondensation and curing processes (Capasso et al., 2019).

Table 3. Flexural and Compressive strengths of the Geocomposites.

Mortar type	Flexural Strength [MPa]	Compressive Strength [MPa]	Surface Hardness
MK+SA	1.8 ± 0.2	8.9 ± 0.7	67.8 ± 2.5
MK+CP	3.6 ± 0.8	14.5 ± 4.0	80.9 ± 3.6
MK+CH	1.2 ± 0.0	4.7 ± 1.2	73.2 ± 3.7
MK+CL	1.4 ± 0.1	5.9 ± 2.9	73.8 ± 3.8

In this specific case, the experimental data suggest that the tuff powders used as aggregates in GEO_MK+CH and GEO_MK+CL generated a less effective interfacial transition zone compared to that developed by the brick waste (*cocciopesto*) aggregate in the GEO_MK+CP formulation.

The results obtained from Shore-D surface hardness tests (Fig. 3), reported in Table 2, further support the mechanical behaviour trends described above. As expected, all GEO_MK+CP specimens exhibited higher hardness values than those containing tuff aggregates, corroborating the superior mechanical integrity of the CP-based geocomposite.

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

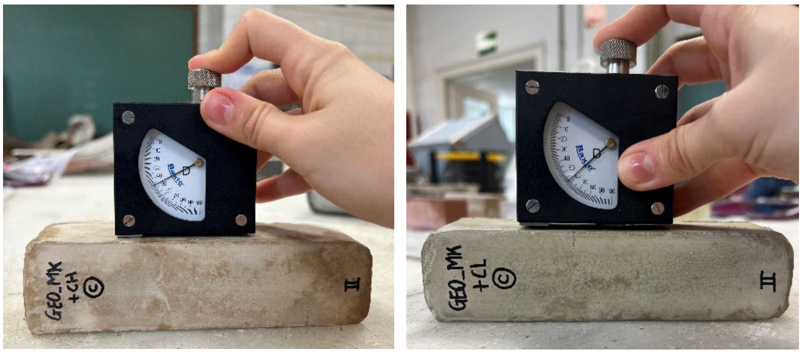

Figure 3. Shore-D surface hardness test on samples: (**a**) chabazite-rich tuff, (**b**) clinoptilolite-rich tuff

In the context of architectural heritage conservation, it is essential that the repair mortar exhibits mechanical properties compatible with those of the pre-existing materials, avoiding both excessive strength relative to the original mortar and insufficient strength compared to adjacent masonry units (Silva et al., 2014). In accordance with these principles, the geopolymer samples incorporating tuff waste (CH and CL) exhibited compressive strength values consistent with those of traditional reference mortars (Table 4), indicating a promising potential for structural integration with historical substrates.

The samples containing crushed brick waste (CP) showed higher mechanical strength values in both flexural and compressive tests (Table 3). However, these values remain within acceptable limits for application in the restoration of historic buildings, in accordance with the performance and compatibility requirements defined for conservation mortars, as shown in Table 4. (Maravelaki-Kalaitzaki et al., 2005); (Garijo et al., 2020); (Silva et al., 2015).

Table 4. Mechanical properties of some mortars widely used for restoration purposes.

Sample	Flexural Strength [MPa]	Compressive Strength [MPa]	Reference
OPC mortar (CEMII B/L 32.5)	4.70	24.80	(Silva et al., 2015)
Natural Bioclastic Limestone	n. d.	10.09	(Maravelaki-Kalaitzaki et al., 2005)
Repair mortar NHL-Z 3.5 with crushed bricks and silica sand	n. d.	3.48	(Maravelaki-Kalaitzaki et al., 2005)
Hydraulic lime mortar NHL 5	1.00	3.70	(Garijo et al., 2020); (Silva et al., 2015)

n. d.: not determined

5. CONCLUSIONS AND PERSPECTIVES

The experimental results obtained in this study highlight the significant potential of geopolymeric mortars as innovative solutions for the restoration and conservation of architectural heritage. Laboratory tests conducted on metakaolin-based formulations incorporating recycled aggregates demonstrated satisfactory performance in terms of water absorption, open porosity, capillary uptake, and mechanical resistance. The analyzed formulations exhibited mechanical and physical behaviour comparable to— and in some cases exceeding—that of conventional restoration materials, while offering the added value of a significantly lower environmental impact, in line with the principles of sustainability and circular resource management.

Based on these preliminary findings, future research developments will proceed along two main directions. First, durability tests will be carried out under controlled laboratory conditions, specifically targeting wet-dry resistance and salt crystallization behaviour, to assess the stability of the materials under severe environmental conditions simulating real exposure scenarios. Second, the research aims to translate laboratory outcomes into real-world applications by obtaining the necessary permits and authorizations for in situ testing of the developed mortars. These pilot interventions will represent a critical step toward validating the proposed formulations in operational contexts and may facilitate their adoption within established restoration practices.

In conclusion, this research seeks to make a meaningful contribution to the advancement of conservation techniques by promoting the integration of scientific innovation, environmental sustainability, and cultural heritage protection.

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