Geopolymers as a potential material for preservation and restoration of Urban Build Heritage: an overview

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Abstract. Since the introduction of the term ‘geopolymer’ by Davidovits in 1978, many works have been published, sometimes providing clear and concise indications, and other times creating confusion about what are a geopolymer. What seems interesting beyond the terminology discourse is the advantage of low CO₂ emissions, the use of waste industrial by-products in their implementation and the resistance to air pollution and aggressive agents. Playing on the combination of the different precursors and alkaline activators, geopolymers can reach competitive mechanical properties and significant environmental benefits. The materials, with specially designed formulations, can be fireproof, breathable, resistant to rising salts and acid rain, as well as products with low emission of carbon dioxide. Furthermore, a further advantage is the ability to imitate natural, artificial and stone materials. There are hundreds of papers about characteristics, properties both of precursors and final product, but only a few of them about the Cultural Heritage Application. Despite this, the data shown by the few publications present to date give hope for a use of these materials for the consolidation, conservation and restoration of the heritage built within the historical centres, where the low CO₂ emissions and the characteristics shown by the geopolymers could bring a huge benefit to the environment and the protection of the structures themselves. In this work, we briefly review the bibliography available on the applications of these materials to Cultural Heritage, hypothesising future uses aimed at specific urban contexts, where the application could play a key role in the future projects to restore the built heritage.

1. Introduction
The increase in the world population, the expansion of newly urbanized centres requires the production of a huge amount of cement, obtained by firing suitable raw materials at high temperatures, with a significant negative impact on the availability of natural resources and on the production of global CO₂ emissions [1]. The introduction of innovative geopolymer materials based on waste materials as solid precursors (like fly ash (FA), Ground Granulated Blast Furnace Slags (GGBFS), rice husks ash and other materials that contains, naturally or artificially enriched, aluminosilicates [2], characterized by low CO₂ emissions, could partially solve the problems by replacing partially or totally the traditional cement. In the field of Cultural Heritage, the attention to the environmental impact of the products used in terms of consolidation and reintegration has always been secondary, while in this case the compatibility with the original materials, the scarce use of water and the aesthetic imitation capacity of the geopolymers are of great interest.
Since Davidovits in 1978 used for the first time the term ‘geopolymer’, indicating an inorganic polymer obtained by a polycondensation reaction of aluminosilicate with alkalis [3–6], a lot of works has been produced about the argument [7–9], and some processes result almost clear [10–16]: from the micro-structural point of view, geopolymers result in amorphous to semi-crystalline aluminosilicate tetrahedral (\([\text{SiO}_4]_4^–\) and \([\text{AlO}_4]_5^–\)) structures with neutral charge due to the substitution of aluminum in place of silicon in tetrahedral packets and the presence of alkaline ions such as the \(\text{Na}^+\) (Figure 1).

![Figure 1. The bond between a Si and an Al tetrahedron is possible thanks to the sharing of a valence electron by an alkaline metal. The dots indicate the valence electrons: red=Si; green=O; yellow=Al and blue Na](image)

To understand the process of geopolymerization, the complete understanding of the nature of the solid precursor and alkali activator and their interaction is mandatory. The sequence of events leading to geo-polymerization starts from the dissolution of the aluminosilicate precursor into an alkaline solution, with the formation of aluminum and silicon monomers that aggregate in oligomers and finally polymers, following a pattern of dissolution, reorganization, polycondensation and polymerization. Related to the type of precursors and alkali activators there is the formation of different type of oligomers that leads to the formation of the final product with the release of water when two \(\text{OH}^-\) group sharing an oxygen atom.

From the point of view of both production and implementation of this class of materials, despite the enormous availability of raw materials, large-scale production of “green concrete” is still problematic [17]. The technology has the potential to be addressed to a specific application in Cultural Heritage, varying the raw material solid precursor and alkali activator sources, moreover the possibility to add pigments and aggregate to the formulates [18] can create different products for application that require material imitation ad specific physical and mechanical properties.

2. The term in literature

From 1978 up today a lot of paper has been written giving different point of view about the meaning of the terms ‘geopolymer’ and ‘alkali activated material’: different terms have been used in the literature to define materials that starting from an alkaline activated aluminosilicate solid precursor lead to the obtainment of a geomaterial consisting of crystalline amorphous polymer chains (Table 1). Rahier et al. [12,13] came to the conclusion that, because of the complete dissolution of metakaolin in the alkali solution, the final product is a “low-temperature aluminosilicate glass”. Further studies that involve the follow up of the geopolymerization process involving the thermal analysis and X-ray diffraction [19–21] have demonstrated that metakaolin precursor only partially dissolved in the alkali solution.
Taking into consideration the literature, beyond the different terms that have been and are used, we can say that geopolymers are a generic range of materials consisting of an aluminosilicate source in an alkali silicate solution, where alkali silicate acts like an activator for poorly crystalline or amorphous inorganic polymers in the form of hard solid dispersion or ceramic-like material.

### Table 1. Terms used in literature and relative references

| Term                              | references              |
|-----------------------------------|-------------------------|
| Geocement                         | Krivenko [22]           |
| Low-temperature aluminosilicate glass | Rahier et al. [12], Rahier et al. [13] |
| Alkali-activated cement           | Palomo et al. [23]      |
| Hydroceramic                      | Bao et al. [24]         |
| Inorganic polymer concrete (IPC)  | Sofi et al. [25]        |
| Alkali-bonded ceramic             | Mallicoat et al. [26]   |

3. **Geopolymer and alkali-activated materials in Cultural Heritage**

As reported previously in the literature we can find different terms for geopolymer and alkali activated material: all of them refer to an inorganic polymer made by an aluminosilicate solid and an alkaline solution. The process of geopolymerization starts with the dissolution of solid precursor (alumino-silicate species) thanks to the reaction with an alkaline solution and continues with a polycondensation reaction. Among the different available materials, the most used precursor in geopolymer for Cultural Heritage is metakaolin obtained starting from thermal treatment of kaolinite. The metakaolin result in high reactivity due to its disordered layer. Adding an alkaline activator, such as sodium/potassium silicate, the metakaolin dissolves its amorphous phases. After the dissolution, the reaction proceeds with the formation of monomers, oligomers and, thanks to a polycondensation, the final products are polymers.

4. **Application in Cultural Heritage**

Geopolymer materials have the potential to be widely used in the restoration of cultural heritage given their eco-compatibility and the possibility, offered by them, to create specific products that do not use water in their formulation or very small quantities. Different commercial and non-commercial products were used for different purposes (Table 2).

Recently Barone et al. [27] with the project Advanced Green Material for Cultural Heritage (AGM for CuHe) carried at University of Catania (Italy) propose and explore the use of local resources and waste materials in order to create geopolymer formulations suitable for application in Cultural Heritage. This is a good example of integration between new technology research, local resources and waste management, and green application in the heritage field.

The possibility to use geopolymeric formulation for stone consolidation or producing mortars for restoration was explored by Rescic et al. [28]: they modify starting materials mechanically (grinding at different grain-sizes) and chemically (different alkaline solution at different pH values) in order to reach specific mechanical properties.

The metakaolin-based geopolymers seem to be very promising in terms of durability, mechanical performances and environmental advantages. Clausi et al. [29] explore the possibility to use metakaolin-based formulations with artificial and natural stones: different ornamental stones used in historical Italian architectures and construction materials, such as mortars and bricks, were tested by mean of SEM-EDS in order to evaluate the interaction of geopolymer formulations with the natural and artificial stones. The interest in these new materials by the world of restoration seems to be aimed at the replacement of materials (limes and polymer resins) in favour of new materials with a greater adhesion, breathability and eco-compatibility properties. Clausi et al. [30] explore the addition of
ornamental stones as aggregate in the formulation of metakaolin-based geopolymer for restoration purposes. The materials created show good mechanical properties in the case of using a little amount of water and mimic perfectly the ornamental stones considered. Moreover, they suggest the use of metakaolin-based geopolymer (MGP) for structural element and in substitution of Portland cement. The use in Cultural Heritage is advocated for the possibility, through appropriate mix design, of obtaining products that almost perfectly imitate natural ones. Moutinho et al. [31] published a work about the utilization of geopolymer formulates in substitution of classical methods that involve the use of lime mortar and organic resins for filling gaps in tiles. The work aims to evaluate a specific application testing the compatibility between tile and geopolymer formulates in the restoration of historical building tiles. They use different commercial formulates in order to compare their characteristic once in use. Speaking about the use of geopolymer formulates in tiles restoration Geraldes et al. [32, 33] also propose the use of geopolymer materials for filling the lacunae gaps in tiles (Azulejos). They find a great advantage in using ceramic-like materials as geopolymers in terms of compatibility with Portuguese faiência and find that limiting of water evaporation during geopolimerization process is an important factor to avoid the cracking in the final product.

In the historical building, there is also a typology of structures, very delicate by their nature, which is subject to rapid degradation, especially if exposed to particularly aggressive environments. In this field, the use of the new geopolymer formulas would allow to consolidate and protect these types of structures by offering greater eco-compatibility, adhesion and resistance to degradation factors. Elert et al. [34] propose the use of alkaline activated materials to consolidate the earthen architectures typical of some sites of Spain (Alhambra, Huelva, Aragon and Castilla-León). The paper results show that the use of a KOH solution instead of typical ethyl silicate treatment has a superior penetration and duration due a partial dissolution of soil minerals and formation of an amorphous cementitious phase, which does not generate dangerous salts avoiding loss of colour to the consolidated material. In terms of consolidation, Hanzlíček et al. [35] propose to use geopolymer composites for fixing and joining elements in terracotta sculptures. The work shows that in the cross-section of the geopolymer the colour does not match the original ones of the terracotta, while on the outer surface the colour is very similar thanks to the iron-oxide presence due to the water evaporation. This unprecedented case study shows the great potential of the use of geopolymer technology in the field of restoration of Cultural Heritage.

Allali et al. [15] propose a partial substitution of metakaolin with calcium hydroxide and calcium carbonate for the restoration of mortars using more compatible materials. Using the CaCO₃, the reaction dissolves only a little amount in alkaline solution both with Na and K silicate activator while using Ca(OH)₂, the reaction is dominated by a fast hydration process that limits the polycondensation. Even if there is no real case application in the paper, the data obtained from the mechanical properties show good values in the case of partial substitution of CaCO₃ in SiK environment, Ca(OH)₂ both in SiNa and SiK environment, while for the case of CaCO₃ in the SiNa environment show quite poor mechanical properties due to a partial or no dissolution of CaCO₃.

Ricciotti et al. [18] explore the possibility to use geopolymer formulates based on metakaolin precursor for preserving, consolidating and restoring materials in Cultural Heritage. They conducted application tests on tuff and cement in the transition zone in order to study the interaction between geopolymer formulates and original materials. They reach the conclusion that geopolymer binders are good for adhesion properties and, moreover, they can be easily coloured by adding pigments to original formulates based on metakaolin.
Table 2. Commercial and non-commercial products used in Cultural Heritage application

| Product                                                                 | Application                                                                 | References |
|------------------------------------------------------------------------|-----------------------------------------------------------------------------|------------|
| - Quartz                                                               | Creation of different geopolymer materials suitable for rock consolidation and restoration mortars production. | [28]       |
| - Kaolin                                                               | Restoration mortars (Class M20) for restoration of stone-works.              | [29,30]    |
| - KOH                                                                  | Historic Tiles conservation.                                                 | [31]       |
| - NaOH                                                                 | Filling gaps in architectural tiles.                                         | [32,33]    |
| - NH₄OH                                                                | Alkaline activators for consolidation of Earthen structures.                | [34]       |
| - Si-K Kaolin (Sibelco Italia S.p.A.) + Sodium Silicate (Ingessil S.r.l.) and NaOH (Sigma-Aldrich) + Aggregates= “Pietra di Angera” and “Pietra Serena” |                                      |            |
| - GEO-MKZL= ARGICAL 1200S + ZeoBau (Zeocem, Slovakia) + Sodium Hydroxide and Sodium Silicate. |                                      |            |
| - GEO-MK1000= ARGICAL 1000 + Sodium Hydroxide and Calcium Hydroxide. |                                      |            |
| - GEO-MK1000C= ARGICAL 1000 + Fly Ash (Burning of Cork- DOF-Cork).       |                                      |            |
| - MK1000=ARGICAL 1000                                                 | Mortar restoration                                                          | [15]       |
| - MK1200= ARGICAL 1200S                                               | Restoration of Cultural Heritage materials                                  | [18]       |
| - MK-501= MetaStar 501                                                |                                                                        |            |
| - Sodium Hydroxide pellets (Carlo Erba Reagents S.A.S.)                |                                                                        |            |
| - Potassium Hydroxide pellets (E.Merk, Germany)                        |                                                                        |            |
| - Sodium Silicate solution (Sigma-Aldrich).                            |                                                                        |            |
| - Calcium Hydroxide (Codex, Carlo Erba).                               |                                                                        |            |
| - Silica Fume (Cab-o-Sil® M5, Germany).                                |                                                                        |            |
| - Estel 1000 Ethyl Silicate (C.T.S., Spain) + Alcool.                  |                                                                        |            |
| - KOH Potassium Hydroxide (E. Merck, Germany) + deionized water.      |                                                                        |            |
| - Kaolinitic Clay (High Fe³⁺)                                         |                                                                        |            |
| - High kaolinite content clay                                         |                                                                        |            |
| - Montmorillonitic clay                                               |                                                                        |            |
| - Naturally fired shale                                                |                                                                        |            |
| - China Chalk                                                          |                                                                        |            |
| - Calcareous Sand (CaCO₃) containing quartz, dolomite and muscovite.  |                                                                        |            |
| - Calcium Hydroxide (Ca(OH)₂)                                         |                                                                        |            |
| - Metakaolin M1 (Imerys, Germany).                                     |                                                                        |            |
| - Metakaolin                                                          |                                                                        |            |
| - Sodium Hydroxide                                                    |                                                                        |            |
| - Sodium silicate solution                                            |                                                                        |            |
| - Epojet®                                                              |                                                                        |            |
| - Marble powder                                                        |                                                                        |            |

5. Conclusions
Some conclusion can be derived from this short ‘state of the art’ about geopolymers in Cultural Heritage and their potential application for build heritage. Although the publications on the possible applications of these materials for the consolidation and restoration of Cultural Heritage are few, we can immediately understand from them what enormous potential is hidden in this class of materials: the possibility of studying specific formulations aimed at the consolidation and restoration of specific materials, the ability to determine the physical and mechanical properties depending on the
environment in which the materials are to be applied, safeguarding the environment, compatibility in terms of adhesion and imitation of the original materials make it a multi-tool knife. The example of the Spanish Azulejos shows us a potential real application of these materials in built heritage, as well as the application in the recovery of terracotta statues and other stone materials. In the case of the Italian territory, there are several realities, consisting of important historical centres in which there is a heterogeneity of materials used for the built heritage that would benefit most from this class of new materials. From southern Sicily to small villages perched on the Alps: heterogeneous realities that require specific geopolymer formulations that meet compatibility criteria with local materials and that resist the specific degrading agents present in such heterogeneous environments.

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