FUNCTIONALIZED GEOPOLYMERS FOR RESTORATION: NEW MATERIALS FOR BRICK MASONRIES RECOVERY IN MEDITERRANEAN ARCHAEOLOGICAL SITES

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INTRODUCTION AND STATE OF ART

For the archaeological Cultural Heritage, the most diffused and important material is represented by ceramics; a vulnerable material when exposed outdoors, thus undergoing extensive damage, like lacunae and disintegration, often with subsequent structural consequences in case of monuments. In the current scenario of climatic emergency, the conservation policies became more and more attentive to green practices for environment safeguard, determining more complex requirements for the new restoration products, in respect to the traditional ones. Indeed, they need to be at the same time compatible with the original substrate and reversible, but also as much eco-friendly as possible. This research project aimed to develop alkali activated materials (among which geopolymers) suitable for the restoration of brick masonries in Mediterranean archaeological sites, generally exposed to aggressive environmental conditions. Alkali activated materials (AAMs) are a group of innovative eco-friendly products, with promising features in the field of construction and restoration of stone materials. This is due to their chemical, physical and mechanical characteristics (such as the breathability, the high compressive resistance or the durability), together with their high versatility. AAMs are synthesized starting from alumino-silicate powdered precursors (such as clay, ceramic, fly ash, etc.) which, after reacting with an alkaline solution, determine the formation of a durable material, consolidated at low or room temperature, reducing the CO_2 emissions (De Azevedo *et al.*, 2018). Considering the current literature, geopolymers application in the restoration field is completely new and quite unexplored (Geraldes *et al*., 2016).

RAW MATERIALS

In order to achieve a chemical-physical as well as chromatic compatibility with the bricks to restore, ceramics have been used in this project as raw material. Furthermore, the use of ceramic waste supplied by local industries promotes also a process of circular economy.

Among different kind of ceramic waste, tile waste (labelled LBCa – supplied by *La Bottega Calatina* from Caltagirone) and hollow bricks waste (labelled CWF – supplied by *Laquattro* from Rometta) have been selected for the synthesis, as more abundant and representative waste. The natural reactivity of the selected precursors has been measured thanks to a basic attach (NaOH 8Mol at room temperature), which revealed as less than 1% of the total silica and alumina measured by XRF goes in solution. Thus, in order to make more efficient the geopolymerization process, metakaolin (MK) has been used as additive, as source of reactive silica and alumina.

EXPERIMENTAL STUDY: BINDERS

Synthesis

Keeping fixed the synthesis conditions (room temperature) and the type of activators (NaOH 8Mol + Na_2SiO_3 R = 3.3 – where R = SiO_2/Na_2O), three set of geopolymeric binders for each precursor have been synthetized, by changing the sodium hydroxide/waterglass ratio (3/7; 1/1; 7/3) and the MK% (0; 10; 20). After 28 days of curing, the obtained geopolymeric samples have been tested from the chemical-mineralogical point of view, in order to investigate the presence and nature of the formed gel, and from the mechanical and aesthetical point of view, in order to verify their performance and suitability for the purposes of this work.

Geopolymeric characterization - gel investigation

The overall increase of the amorphous amount, measured by XRD in all the geopolymeric samples in respect to the precursors, suggested the occurrence of the geopolymeric gel formation. It has been confirmed by the appearance of a significant shift of the maximum of the alumino-silicate band in the ATR-FTIR spectra of the geopolymers toward lower wavenumber in respect to the precursors, interpreted as a chemical rearrangement due by a polycondensation reaction (Robayo *et al.*, 2016). SEM investigations allowed to observe a homogeneous and well reacted microstructure, similar to those observed in literature related to ceramic-based geopolyemers (De Azevedo *et al.*, 2018; Reig *et al.*, 2013; Robayo *et al.*, 2016; Sun *et al.*, 2013). The chemical composition acquired by means of EDS probe in different points of the matrices is compatible with a multi-component system of (N, C)-A-S-H, where N = Na_2O; C = CaO; A = Al_2O_3; S = SiO_2; H = H_2O. The results are consistent with the further TEM observations.

Physico-mechanical characteristics

The porosimetric structure has been investigated by means of Mercury Intrusion Porosimetry, that highlighted no significate differences in accessible porosity among the samples, whereas the porosimetric distribution on the different ranges seems to be linked to the different MK and waterglass%. MK and waterglass% furthermore clearly positively affect-the compressive strength, measured by uniaxial compressive test on six cubic samples (2 cm side).

Colorimetry

From the colorimetric point of view, the parameter which mainly influences the color appearance is the Lightness, while Chroma, and particularly Hue, remain near the threshold of not perceptibility. A large range of total color difference shows as starting from the same raw material, changing the parameters it will be possible to manage the color of the final product to obtain.

EXPERIMENTAL STUDY: MORTARS

Synthesis

Among the nineteen binders experimented, considering all the analytical data acquired, four binders have been selected for implementing the restoration products. Three kind of aggregates have been used for the implementation of the mortars: a siliceous sand, a carbonate sand and the same tile waste used as precursor, in an aggregate/binder ratio equal to 1 and following a standard granulometric curve (UNI EN 196-1:2016). The CWF selected binder for the implementation of pourable materials has been modified by adding carbonate sand and fine powdered marble, as suggested from the restorers, in two granulometric fractions.

Adhesion tests and physico-mechanical characteristics

In order to test the adhesion properties between the geopolymeric materials and the traditional ceramics to restore, two fragmentary bricks of archaeological interest have been used. The three points flexural test applied on a section of the obtained sandwich brick/mortar/brick highlighted a good adhesion of the samples with ceramic and carbonate aggregates; while those with silicate sand failed the test. The compressive tests showed as the addition of different kind of aggregates determines a difference in the compressive strength of the final product. The obtained data are compatible with the values of the typical resistance of the historical bricks, 4-15 MPa (Curioni, 1868). Furthermore, the possibility to play with the aggregate type for creating products with different strength allows to choose the right product for the specific application case by case. Regarding the porous structure, the most important results is that the dimension of the pores in the mortars is lower than that in the brick of archaeological interest, as generally required in the restoration context in order to preserve the substrate from eventual humidity damages (Rescic & Fratini, 2013).

Colorimetry

Comparing the mortars' color with those of the binder precursors, it was possible to asses that a general Lightness increase occurs, while Chroma and Hue changes are not well perceptible.

CASE-STUDIES – STUDY OF VERSATILITY

The mortars with the best results have been applied for different case-studies. Reintegration mortars have been applied in the pillars of the *Odéon* of Catania (Fig. 1). Two areas have been chosen, one sheltered from the environmental agents; the other directly exposed. The support has been previously wetted in order to avoid the preferential absorption of the liquid component (essential for the geopolymerization process) from the substrate. The product has been put layer by layer, in order to give it the time to start setting and not collapsing. The interventions were than monitored for three months, showing excellent results, as no shrinkage, no efflorescence, no cracks and very good adhesion. The interventions did not alter the entire readability of the monument, but looking in detail it is possible to recognize them, as requested in restoration field. With the aim to test the versatility of the products and the possibility to work them at medium scale, the development of bricks and tiles have been experimented, thanks to the same company which supplied the waste tiles, thus actually realized a circular economy. The geopolymeric tiles have been realized with the dimensions of the tiles of the pavement of the historical *villa Zingali-Tetto* in Catania (Fig. 2a). Glazing tests have been performed in order to recreate the tiles used for the monumental staircase in Caltagirone (Fig. 2b). And finally, out from the initial aims of this work, the mortars have been tested for the reintegration of potsherds. The work has been conducted with the help of the restorers of the *Parco archeologico e paesaggistico* of Catania. In this case, the mortar has been modified in order to make it more plastic and to have the possibility to replicate details.

Fig. 1 - Case study: *Odéon* of Catania - steps of applications of geopolymeric mortars.

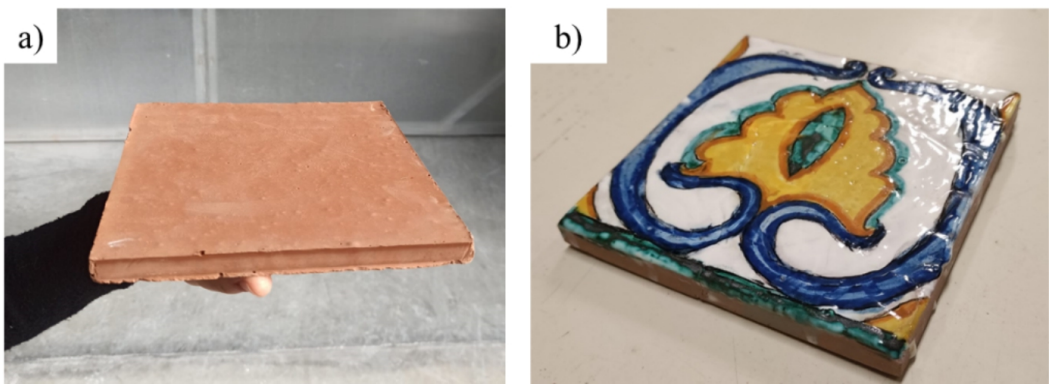

Fig. 2 - Geopolymeric tiles, a) raw and b) glazed.

CONCLUSIONS

The experimental study exposed in this work led to a series of important outputs for the scientific development in the field of green restoration of ceramic materials, with particular interest towards bricks and brick masonries of archaeological interest. Furthermore, interesting discussion points could be put forward for the improvement of the comprehension of geopolymerization mechanisms in ceramic waste alkali activation, a research topic still little investigated.

Good physical and mechanical performative materials of geopolymeric nature have been obtained by alkali activating ceramic waste supplied by local industries, without pre-treatment and with curing at environmental temperature. This is the most important outcome obtained by this study, together with the assessment of the great versatility of the products experimented, allowing to assess the suitability of these materials for on-site restoration campaigns, and for encouraging a circular economy while simultaneously reducing production costs.

Further outcomes that need to be mentioned are the assessing of the usefulness of spectroscopic techniques not usually applied for the characterization of geopolymeric materials, namely DRIFT and Raman. Results are available in Caggiani *et al.* (2022a, 2022b).

Concluding, by changing and optimizing the chemical and physical parameters of the synthesis, it has been possible to functionalize the products in order to obtain both restoration mortars, to apply *in situ*, and pre-casted bricks and decorative elements for substitutions. The comparison between original archaeological samples and the new experimented materials allowed the improvement of suitable restoration products, promoting a green restoration ad hoc, compatible, efficient and eco-friendly.

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