Nuove frontiere dei materiali innovativi e green nel restauro e nell'edilizia

New frontiers in innovative and green materials for cultural heritage conservation and building industry

Organizzato dal Dipartimento di Scienze Biologiche, Geologiche e Ambientali dell'Università degli Studi di Catania, dal Centro Siciliano di Fisica Nucleare e Struttura della Materia e dall'Ordine Regionale dei Geologi di Sicilia in collaborazione con il Gruppo di Lavoro sui Geopolimeri della Società Ceramica Italiana (ICerS)

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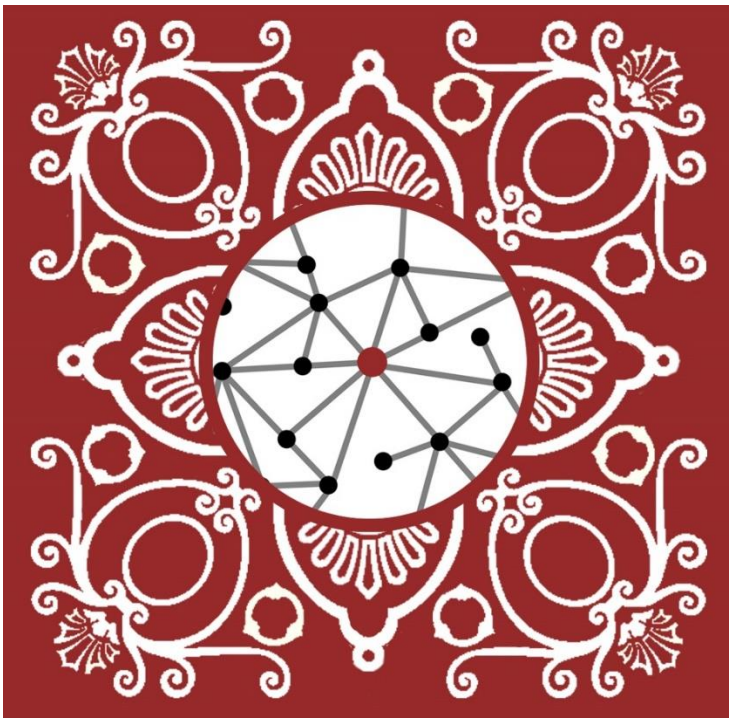

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The consolidation of carbonate stones treated with Di-ammonium phosphate

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In Cultural Heritage restoration, the consolidation is a fundamental process; over the years, different kind of materials have been studied for this procedure. Di-ammonium phosphate (DAP) is an inorganic product, thus is very compatible with stone [1]; moreover, DAP is specific for carbonate surfaces, that are widespread in the field of Cultural Heritage. DAP is extremely soluble in the water and not toxic for worker and environment. DAP reacts with carbonate of the artifacts and creates various phases of calcium phosphates, less soluble than calcium carbonate [1]. Based on previous studies, we addressed DAP application using a two-step procedure, which allowed us to reach deeper substrates. The experiments utilize lower DAP's percentages than previous interventions, respecting the rule of "minimal intervention". We experimented two different stones: Pietra di Lecce and Pietra di Finale in 5 x 5 x 2 cm size. We firstly applied a poultice of cellulose pulp on samples with 0,5% DAP in water solution and left on it for 24 hours. Then, we removed the poultice and applied a second layer in the same way but with 4% DAP in water solution. In order to have a comparative benchmark the operations were repeated with poultice without DAP in water solution on some samples. After the treatment we tested the treated samples by multiple physical and chemical investigation techniques to detect calcium phosphates and to test the effectiveness of consolidation. Thanks to the elemental mapping of P by Scanning Electron Microscope coupled with Energy Dispersive Spectrometry we detected a thin veneer impregnated by P phases at the surface of treated samples in both lithotypes. We revealed a 2.11 wt.% of P-phase in treated Pietra di Lecce and the 1.54 wt.% in the untreated. Mesoscopic surface mapping by Bruker Elio X-ray fluorescence evidenced a phosphate phase on the surface of treated samples; 28,33 % in Pietra di Lecce, 19,29% in Pietra di Finale.
Consistently, the absorption test by capillarity showed higher water absorption in untreated stone than in treated samples, while the evaporation test highlighted all absorbed water is released in both lithotypes with time. Lastly, we tested the effectiveness of DAP with the Planar Abrasion Meter and observed that after DAP treatment resistance to abrasion is increased to a depth of 1 mm, and abrasion resistance doubled. Overall, the physical tests confirmed that DAP treatment is effective even under low concentrations, although we could not detect Ca-Phosphate mineral phases, in the shallower layers of the stones (1 mm), due to instrumental detection limits.

[1] Matteini, M., Rescic, S., Fratini, F. and G. Botticelli. 2011, Ammonium phosphates as consolidating agents for carbonatic stone materials used in architecture and cultural heritage: preliminary research, Int. Journal of Architectural Heritage 5: 717–36.

Restoration applicability study of Mt. Etna volcanic ash as alkali activated mortars: the mosaics of Monreale Cathedral (Palermo, Italy)

Barone, G.[1], Belfiore, C.M.[1], Caggiani, M.C.[1], Coccato, A.[1], Finocchiaro C.[1], Fugazzotto, M.[1,2], Lanzafame, G.[1], Nucatolo, D.[3], Occhipinti, R.*[1], Starinieri, S.[3], Stroscio, A.[1], Mazzoleni, P.[1]

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The Monreale's Cathedral, located in the Metropolitan City of Palermo (Sicily), has been chosen as pilot restoration site within Advanced Green Materials for Cultural Heritage (AGM for CuHe) project (PNR 2015-2020). Since 2015 this site is part of the Arab-Norman Palermo and the Cathedral Churches of Cefalù and Monreale UNESCO Heritage, whose magnificence is given by the mosaic's extension (around 6.340 m^2), even higher than that of the Basilica of San Marco in Venice (Italy) and second in the world only to the church of Santa Sofia in Constantinople (Turkey). The internal facades are decorated by stone and glass mosaics, remaining the spirit of Byzantine culture. After a preliminary diagnostic campaign on the mosaic decorations located on the South aisle, which showed some damaged portion, a specific intervention has been designed though the application of alkali activated materials (AAMs) in the optic of the green economy and sustainable restoration. Indeed, AAMs are assumed as a "low CO_2 emission" alternative to traditional concrete and with high versatility, so they might respond to the increasing necessity of sustainability in conservation/restoration processes ensuring at the same time compatibility and durability of the interventions. Thanks to the satisfying results of previously studies on alkali activated materials (AAMs) based on volcanic ash from Mt. Etna volcano (Italy) [1-3], a small area, was selected for the tests. The restoration tests were performed in collaboration with a well-established restoration company (Piacenti S.P.A.), whose steps have foreseen: i) the application of bedding and finishing mortars for the filling of *lacunae*; ii) the reposition of detached original *tesserae*; iii) the replica of the mosaic decorations by engraving and painting on the finishing mortar. This *in situ* activity has allowed to evaluate the criticisms related to the preparation and application of these kind of materials in restoration sites.

The AGMforCuHe project is acknowledged for its financial support (PNR 2015-2020, Area di Specializzazione "Cultural Heritage" CUP E66C18000380005).

[1] Barone, G., Caggiani, M.C., Coccato, A., Finocchiaro, C., Fugazzotto, M., Lanzafame, G., Occhipinti, R., Stroscio, A., Mazzoleni, P., 2020. Geopolymer production for conservation-restoration using Sicilian raw materials: Feasibility studies, in: IOP Conference Series: Materials Science and Engineering. Institute of Physics Publishing,

[2] Barone, Germana, Finocchiaro, C., Lancellotti, I., Leonelli, C., Mazzoleni, P., Sgarlata, C., Stroscio, A., 2020. Potentiality of the Use of Pyroclastic Volcanic Residues in the Production of Alkali Activated Material. Waste and Biomass Valorization.
[3] Finocchiaro, C., Barone, G., Mazzoleni, P., Leonelli, C., Gharzouni, A., Rossignol, S., 2020. FT-IR study of early stages of alkali activated materials based on pyroclastic deposits (Mt. Etna, Sicily, Italy) using two different alkaline solutions. Constr. Build. Mater. 262.

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AGM for CuHe project

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AGM for CuHe project, started on September 2018 (PNR 2015-2020) has foreseen the development of smart and high-tech products for the conservation and restoration of Cultural Heritage, in a view of circular economy, sustainable recovery and reinforcing of the tourism attractiveness. The achievement of the target objectives is supported by the high qualified expertise and the presence of well-equipped laboratories within a multidisciplinary approach in geology, biology, chemistry, engineering, physics, material science, economic and juridical disciplines. Moreover, the synergy with the companies, involved in the scale-up in each pilot sites selected, is the connection key between two worlds: research and enterprise.
In detail, alkali activated materials based on volcanic ash and ghiara from Mt. Etna volcano, pumice of Lipari Island and ceramic wastes were synthesized. Some of them were applied in restoration pilot sites spread out around Sicily (Italy) such as for example: Monreale Cathedral in Palermo, the Odèon, the "Palazzo Centrale dell' Università", Zingali Tetto Villa in Catania. Several divulgation activities were performed with the aim to promote the tasks of the project and the fruition of Cultural Heritages. In this scenario, tourists have the possibility to follow all the experimental steps and applicative phases of the project thanks to panels and videos with the aim to increase the sense of fruition of BB.CC.
The project has favoured the employment rate in academic and company sectors, as well as the research in agreement with the European guidelines, whose actions focused on improving the impact of Cultural Heritages fruition in economy, tourism market, social challenges and employment rate are widely encouraged.
The AGMforCuHe project is acknowledged for its financial support (PNR 2015-2020, Area di Specializzazione “Cultural Heritage” CUP E66C18000380005).

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Properties and applications of highly porous geopolymers as replicas of lightweight decorative elements

Bertino, A.*[1], Occhipinti, R.[1], Finocchiaro, C.[1], Fugazzotto, M.[1,3], Motta, A.[1], Nucatolo, G. [2], Portale, S. [1,3], Starinieri, S.[2]
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With a view to a modern and innovative restoration, attention has recently been focused on the realization of high-performance materials with a low environmental impact. It is the case of porous geopolymers, materials that have given the opportunity to make decisive progresses in the field of conservation of Cultural Heritage. Geopolymers are inorganic polymeric materials obtained by mixing a solid precursor, usually an aluminosilicate one, with an alkaline activating solution [1] through a low temperature synthesis.

Fig.1 *Odeon of Catania*

As part of the project *"Advanced Green Materials for Cultural Heritage" (AGM for CuHe),* carried out by the University of Catania, with the collaboration of Restoration Centre Piacenti S.p.a., it was decided to use a porous geopolymeric paste for the realization of a decorative element reproducing a Roman capitello in Etnean basalt. The capitello was selected among the artifacts preserved inside the "*Odeon of Catania*" (Fig.1), a building dating back to the II century A.D. located in the historical centre of the city.
For the realization of the porous geopolymeric paste, the volcanic ash deriving from the numerous recent eruptive events of Mount Etna were used as precursors. These low-cost materials, easy to find in the city, give the possibility to create a geopolymer which simulates the original rock in terms of structure and colour. In this way, a material previously considered a waste of difficult and expensive disposal acquires a role of primary importance in the field of restoration.

The AGMforCuHe project is acknowledged for its financial support (PNR 2015-2020, Area di Specializzazione “Cultural Heritage” CUP E66C18000380005).

[1] Occhipinti, R., Stroscio, A., Finocchiaro, C., Fugazzotto, M., Leonelli, C., Lo Faro, M.J., Megna, B., Barone, G., Mazzoleni, P. 2020, “Alkali activated materials using pumice from the Aeolian Islands (Sicily, Italy) and their potentiality for cultural heritage applications: Preliminary study”. Construction and building materials, 120391

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Morphological, structural and chemical characterizations of geopolymers for green building and restoration sectors.

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Due to its excellent properties, geopolymer materials have attracted great attention as a promising material for building and restoration sectors since its discovery. For this purpose, morphological, structural and chemical properties of geopolymer materials and their raw materials, requirement for their synthesis, were analysed in detail by means of analysis like: Scanning Electron Microscopy (SEM), Rutherford Backscattering Spectroscopy (RBS), Raman spectroscopy and Energy-dispersive X-ray spectroscopy (EDX).
The goal was to identify the presence of the geopolymeric gel with its morphological and chemical characterization, to document any details, such as salts, relict minerals, the presence of fractures, voids, and to measure the region of contact between gel-relict minerals. The morphological and compositional analysis referred to the sample allow to identify the elemental composition and their variation within the matrix. This information allows us to determine if the geopolymerization process has taken place and to correlate the morphological, structural and compositional characteristics of the geopolymers to the properties of the materials used for their production and to the synthesis parameters. The study of the geopolymer matrix is certainly essential in order to obtain information about the compositional homogeneity at the micrometric level (of the product) and to optimize the geopolymer synthesis protocol.

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Evaluation of the cytotoxic and genotoxic effects of halloysite clay nanotubes from different deposits

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Nanomaterials have been considered one of the most important avant-garde materials in recent decades and reported as "21st century materials". Among these, the halloysite clay nanotubes has showed excellent performance for applications in different fields, from the biomedical, industrial use up to environmental sector. Therefore, it is of great relevance to evaluate the effects on biological systems and so human health, environment, and ecosystems.
Here, we analyzed the *in vitro* cytotoxicity and genotoxicity of four classes of halloysite clay nanotubes (HNTs) from different geological repositories, called HNT-U, HNT-P, HNT-S, HNT-N, carrying out experiments at different exposure-times and HNTs concentrations. To evaluate the cytotoxic effects, MTT assay was performed on human epithelial cell line Hela and human liver cell line HepG2 seeded in multi-wells and treated with HNTs at different concentrations and for 6, 24, 48 and 72 hours. Our MTT results, in both Hela and HepG2 cells, showed a low variability in cell viability, not directly related to the exposure time, and for HNT-U a little variability was revealed only at the highest concentration.
To evaluate the potential genotoxicity of HNTs, we used CBMN (Cytokinesis-block micronucleus) assay on Chinese Hamster Ovary (CHO) cell line, with an experimental plan which provided the exposure time of 24 hours at two different concentrations, 1 and 100 mg/L, then MNs (micronuclei) frequencies in binucleated cells was analyzed. To date, our results demonstrated the inability of all NMs (HNT-U, HNT-P, HNT-S, HNT-N) to induce a significant increase in the frequency of MNs *in vitro,* although a slight increase ($P< 0.05$) was found for the HNT-S at the highest concentration used. Given the general limited knowledge on the potential genotoxicity of the several nanoparticles under development for most different uses, it is of the great relevance to produce a robust set of genotoxic data, so duplication of all the CBMN assay is in progress.
The obtained results indicate, for all the Halloysite Nanotubes analyzed, a good biocompatibility and low cytotoxicity and genotoxicity to cells, which make them promising in several applications in the biomedical or environmental fields.
The AGMforCuHe project is acknowledged for its financial support (PNR 2015-2020, Area di Specializzazione “Cultural Heritage”).

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New hybrid halloysite based geopolymers with beeswax and microwax particles

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In recent years, interest in producing eco-friendly and low-cost materials from natural resources or industrial by-products is increasing. For these reasons, research is now focused on geopolymeric materials that offer new perspectives in environmental remediation technologies.
Geopolymers are inorganic polymeric materials that possess an amorphous network of aluminosilicates; they are formed as a result of a geopolymerization process with an alkaline activating solution, leading to the formation of three-dimensional structures with Si-O-Al bonds. Nowadays nanomaterials are widely employed also in combination with a lot of traditional materials in order to modify and improve specific properties, developing modern multifunctional products. For instance, nanoclays possess peculiar characteristics in terms of physical chemistry, morphology and charge which make them commonly used in cement concrete as performance enhancers. Among them, halloysite (HNT) is an emerging natural aluminosilicate with a singular hollow tubular structure, eco-compatibility, non-toxicity and low cost. This clay can be used as aluminosilicate precursors in geopolymer synthesis.
The main focus of this work is the preparation and characterization of new hybrid halloysite-based geopolymers with beeswax and microwax particles obtained from dried Pickering emulsion powders. Halloysite-based geopolymers usually show a hydrophilic surface but the incorporation of beeswax into the network causes a relevant change of water contact angles reaching hydrophobic values. The effect of wax on the structure of these materials and their thermal stability was investigated with TGA, FTIR and XRD. Furthermore, DSC analysis provided the enthalpy (ΔH_m) of the melting process giving information on the variation of crystallinity of wax in the geopolymeric network.
Successively, beeswax was used as sacrificial material and it was removed from the geopolymeric matrix modifying the porosity of pristine materials. Water vapor permeability tests were carried out and showed an increase in permeability in these samples.
The AGMforCuHe project is acknowledged for its financial support (PNR 2015-2020, Area di Specializzazione “Cultural Heritage”).

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Innovative approaches for modelling masonry structures and geopolymer based strengthening techniques

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The mechanical strengthening of existing structures is achieved by adding a second material to the original one, aiming at obtaining increased performance properties. The research in the field of innovative materials pursues both the improvement of the mechanical properties and the cost reduction for manufacturing, considering recyclable and easily available materials for the reinforcement with the final goal of implementing a fully circular economy. Coupling different materials in structures needs the adoption of advanced modelling strategies to simulate the static and seismic behaviour of the strengthened structures, able to account for nonlinear constitutive models and to grasp the interaction between the two materials. Within the research project “Advanced Green Materials for Cultural Heritage” (AGM for CuHe), new geopolymer based materials were proposed for civil applications; precisely, innovative composite strengthening, based on Fiber Reinforced Geopolymer Matrix (FRGM) techniques were conceived, considering a matrix made of geopolymer mortar combined with composite textiles. In this study, the Discrete Macro-Element Method (DMEM) [1], which is a modelling approach consisting in elements endowed with a simple mechanical scheme and interacting by means of discrete interfaces, is adopted for the simulation of the nonlinear behaviour of existing masonry structures. The original element, conceived for the planar behaviour of masonry walls, was subsequently extended aiming at a general modelling environment [2], accounting for the three-dimensional behaviour also in presence of curved geometry, and for the presence of strengthening based on Fiber Reinforced Composites [3]. The simulation of masonry structures strengthened with FRGM is performed at two levels. Namely, simulations of experimental tests are conducted by properly modifying the mechanical properties of the elements to which the reinforcement is applied, or by considering additional elements for the FRGM reinforcement, interacting with contiguous FRGM elements and with the masonry support by means of interfaces conveniently calibrated. The validation of the proposed approach is performed by comparing the obtained results with meaningful reference experimental tests. The proposed approach and the validations here presented can be seen as the base for full scale applications and for a reliable design of the FRGM retrofitting of existing masonry structures.
The AGMforCuHe project is acknowledged for its financial support (PNR 2015-2020, Area di Specializzazione “Cultural Heritage” CUP E66C18000380005).

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Wax/HNT Pickering Emulsion as a Coating for Cultural Heritage

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A protective coating, based on hydroxypropyl cellulose (HCP), was prepared for the treatment of artwork surfaces to prevent their ageing process. Pickering Emulsions were designed with wax/halloysite nanotubes hybrid microspheres dispersed in HPC matrix.

The system was characterized by microscopy and thermogravimetric analysis and biofilms were carried out by the solvent casting method. Contact angle and sliding angle were measured to investigate the improvement of biofilms hydrophobic behavior due to wax/halloysite microparticles, acting as a barrier, which was confirmed by the decrease of the vapor permeability of the nanocomposites. The optical properties, transparency, and colorimetric features were investigated together with the thermal properties of the films and demonstrated that the nanocomposite systems represent promising tools for surface modification has good energy storage and heat reservoir materials.

As of matter of fact, a hydraulic mortar was chosen as a sample to investigate the application, brushing, or spraying, of the wax/HNT in the HPC matrix system and their physicochemical properties as a coating layer. The electron and optical microscopies have been shown microstructures on stones prototypes, and their wettability was investigated by contact angle analysis. Colorimetric analysis has been carried out to evidence the applicability in terms of color alteration after the treatment.
The AGMforCuHe project is acknowledged for its financial support (PNR 2015-2020, Area di Specializzazione “Cultural Heritage”).

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Cultural heritage restoration and visitors' experience evaluation. Evidence from an Italian UNESCO site

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For a long time, cultural sites restoration and maintenance have been viewed as pure technical activities, necessary to the function of conservation of cultural heritage, and totally separated from visits, being often hidden to visitors. In the very last years, restoration sites have been increasingly made visible in different contexts, ranging from archaeological sites to historical buildings and churches, and the respective information has been provided to visitors to increase their awareness. While there is a very extensive literature on visitors' valuation of heritage sites (Wright & Eppink, 2016), no much attention has been paid to study how visitors value such a specific experience. This work aims at filling this gap and investigating whether and to what extent visitors experience can be enhanced by allowing people to observe restoration sites, and to receive information on restoration activities. We use novel survey data collected in the UNESCO site of Monreale (Italy), in two different scenarios. In the first one, the visitors observe the restoration in progress in an open worksite. In the second one, they receive information, through digital information panels, on recently completed restoration activities, carried on within the AGM for CuHe project with new geopolymeric materials. Results show that visitors overall appreciate to get in contact with restoration activities: however, they give more weight to information than to direct observation and that are willing to contribute more when they are provided with pertinent cultural and historical information. Moreover, they give importance to the use of eco-sustainable materials.
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Analytical methodologies for the chemical and physico-mechanical characterization of experimental geopolymers for the restoration and conservation of Cultural Heritage

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In recent years, much research was carried out on alkali-activated materials, in particular geopolymers, applied for the conservation and restoration of Built Cultural Heritage [1-3]. The growing interest in geopolymers derives from their environmental sustainability, compatibility with stone materials, durability, and mechanical performances. The present work is supported by the Industrial Research and Experimental Development project AGM for CuHe – Advanced Green Materials for Cultural Heritage. Throughout this project, geopolymers were produced using local (Sicilian) raw materials and industrial waste, to create compatible products for cultural heritage conservation. Physical, mechanical, and chemical characterization was performed on raw materials and geopolymers. The Earth Sciences and Chemistry Departments of the University of Florence contributed to the analyses on raw materials, the analyses of the technical properties of geopolymers, and the accelerated ageing tests. First, leaching test and ICP-OES analyses were performed on raw materials in order to evaluate their chemical reactivity in alkaline environment and the possible presence of trace elements harmful to health or environment. Then, the most suitable raw materials to produce the experimental geopolymers were selected. Once obtained the experimental geopolymers, physico-mechanical tests were carried out, such as: determination of physical characteristics (porosity, density, imbibition coefficient), uniaxial compressive strength test and flexural strength under concentrated load test. Finally, accelerated ageing tests including saline crystallization and acid attack were performed on a selection of geopolymers. Such multi-analytical approach aimed at providing an important contribution to the knowledge of eco-friendly materials and their application for conservation and restoration purposes.
The AGMforCuHe project is acknowledged for its financial support (PNR 2015-2020, Area di Specializzazione “Cultural Heritage”)

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Alkali-activation of carbonates-rich illitic clays

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The present contribution illustrates results of a comprehensive study exploring the production of alkaline activated binders (AABs) using carbonate-rich illitic clay, largely occurring in southern Italy (Apulia and Basilicata regions). Selected clays were subjected to thermal and mechanical activation, as well as to a combination of such treatments, in order to increase their reactivity; mineralogical and textural changes of clays after activations treatments were investigated through X-ray powder diffraction, Fourier transform infrared spectroscopy and thermal techniques, while leaching tests in a 3 M NaOH solution were performed in order to select the most efficient treatment for increasing clay reactivity and thus their suitability as precursor for AABs.
Several pastes were prepared from the selected pre-treated clay in order to optimize the mix design and synthesis parameters; the obtained binders were mechanically tested, while reaction products were characterised by X-ray Powder Diffraction analysis (XRPD), Fourier-transform infrared spectroscopy (FTIR) and Scanning Electron Microscopy - Energy Dispersive X-ray spectroscopy (SEM/EDX). AABs were thus prepared using the selected pre-treated clay and NaOH activating solution in different concentrations (4, 6 and 8 M) in order to explore the effect of alkali concentration on the activation of carbonate-rich illitic clay. Furthermore, alkaline binders were prepared from binary mixtures of the clay with type F fly ashes and ground granulated blast furnace slags, and using NaOH solution (4M and 8M) as activator, in order to explore the effect of the CaO content in the precursor.
Results show that for all samples the main reaction product is a gel or mixture of C-A-S-H/(N, C)-A-S-H type gel depending to the Ca content in the precursors. In pastes prepared using the clay precursor alone, higher (6 or 8 M) activator concentrations give a more compact matrix than those prepared with 4 M NaOH. The use of a 6 M NaOH solution yields a binder with two days compressive strength >20 MPa and 28 days strength of over 30 MPa. The paste composed by 1:1 weight proportion of pre-treated clay and blast furnace slags show the most compact matrix, achieving the remarkable mechanical strength value of 45 MPa after 28 days. This study affords the opportunity for in-depth research into the role of calcium and the degree of alkalinity on alkaline activation. The obtained findings can be extrapolated to other carbonate-bearing clays as well as to other possible precursors with a similar composition.

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Valorisation of water potabilization sludges: preliminary results about their reuse as precursors for alkali-activated binders

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One of the advantages of alkali activation technology is the possibility to safeguard the exploitation of non-renewable resources by valorising waste-deriving raw materials as novel precursors in binders manufacture. The Al-rich nature of water potabilzation sludges (WPS) has made these wastes attractive as potential precursors. In this research, sludges coming from two water potabilization treatment plants, serving the Apulian territory (Italy), were investigated. Sludges were first characterized by X-ray fluorescence (XRF), X-ray Powder Diffraction analysis (XRPD), Fourier-transform Infrared spectroscopy (FT-IR), Scanning Electron Microscopy Energy Dispersive X-ray spectroscopy (SEM-EDX) and then subjected to different mechanical and thermal pre-treatment methods, in order to improve their reactivity. Alkali activated binders were finally produced by using NaOH solutions in different concentrations. The obtained products were characterized by mechanical tests and XRPD, FTIR, SEM-EDX analysis, demonstrating that the alkaline reaction occurred in all samples. The amount of gel developed varied according to the pre-treating method and the SiO_2 amount in the precursors.

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Volcanic raw materials for the low environmental impact production of pozzolanic mortars

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The aim of this study was to select a series of glassy volcanic rocks for the production of pozzolanic mortars with a low environmental impact to be used in the field of Cultural Heritage restoration and, more in general, in the construction field. To achieve this objective, we selected a series of natural pozzolans (i.e., pyroclastic rocks) from the Sardinia territory (from the Monte Arci and Fordongianus areas) as raw materials, which share a high reactivity with lime due to the pronounced fraction of the amorphous phase (up to 90% in volume). Furthermore, a silica-rich sand as aggregate ("inert") and two types of binder were used: a slaked lime for plaster, along with a natural hydraulic lime-based (deriving from the use of a marly limestone) for bedding mortars. In order to experimentally evaluate the performance of the mortars, and to define the best mix between the raw materials, several mortar specimens have been tested from a physical-mechanical point of view (by means of He-porosimetry, real and apparent density, vapour permeability, PLT test) at set times of 1 week (only in the case of hydraulic lime), 1 and then 2 months. At the same times, the various samples were analysed by means of optical and electron microscopy (SEM), in order to describe: the microstructural and textural aspects of the mortars during the setting and hardening stages, the chemical reactivity between the pozzolans and the binder, the carbonation reaction of the hydrated lime and the formation of the hydraulic phases (CSH, CAH), responsible in both cases for the mechanical resistance. The results indicate that bulk density and porosity, in response to the hydration process of calcium silicates and aluminates (with formation of CSH and CAH), experience respectively an increase and decrease of their values, leading to a consequent improvement of the mechanical properties. On the basis of the physical-mechanical and compositional features measured after 2 months, the mortars made by pozzolan+slaked lime and pozzolan+hydraulic lime proved to be suitable in the field of Cultural Heritage restoration and, in general, in construction field.

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Development of a geopolymeric grout based on recycled bricks for consolidation and conservation of terracotta works

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For the restoration of a glazed terracotta statue (Fig. 1), a geopolymeric grout was devised to consolidate glaze detachments and microfractures. One of the most important characteristicsfor this application is the fluidity, because the grout is injected and absorbed by capillarity intothe porosity. Another important point, is the compatibility between the geopolymeric material and the substrate of the terracotta work. Hence, a binder based on calcined clay was chosen.The efflorescence potential was minimized by proper formulation and choice of the activators.

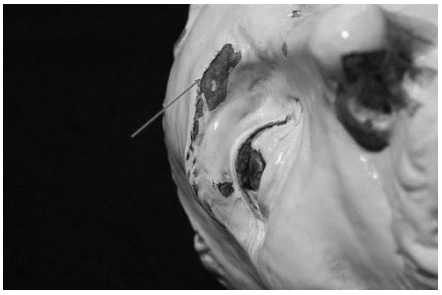

Fig. 1 Photograph of a part of a terracotta statue, where the arrow shows the detachment of the glaze in a fracture.

The binder precursor is constituted by waste production bricks, composed by feldspar, quartz,calcite, wollastonite and an amorphous fraction. Calcination of the starting clay, between 850°C and 900°C, caused the total decomposition of chlorite and the partial one of mica.
The brick powder was activated with an alkaline activator, constituted by a sodium silicate witha low silicate modulus of 0.85. The sodium silicate amount contributes to 7.3% Na_2O with respect to the solid weight. This formulation was selected among several others, because it was possible to reduce significantly the efflorescence potential yet maintaining the reactivity with a fairly short setting time (about one hour). This time span is optimal to ensure the open window for the injection of the grout.
To further reduce efflorescence, accelerate the setting time and improve the dispersant efficiency, the brick powder was mixed with a low amount (5%) of calcium carbonate. The dispersant used for this work is a poly-naphthalene sulphonate, FLUBE CR 100 from Bozzetto
S.p.A. at the dosage of 1% by the total solid weight. Calcium carbonate contributes to the earlyC-S-H formation and to the dispersability of the grout caused by polymer adsorption onto it. Metakaolin was added, both as fine filler and to increase aluminate concentration in solution,further reducing the efflorescence potential.

Finally, a redispersible latex powder was added to improve adhesion and elasticity of theinjectable grout, a very useful property to seal the capillary fractures.

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Non-Traditional Binders: Alkaline Activated Pyroclasts as an innovative and eco-friendly binder for applications in Geotechnical Engineering

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Development and validation of new methods for soil improvement in earthworks, allowing the reuse of excavated soils, are fundamental challenges in the framework of a sustainable Geotechnical Engineering design. Non-traditional binders are experiencing a growing interest in the last decades with a wide variety of materials and manufacturing processes. Alkali Activated Materials represent a group of cement-like materials formed by reacting silica- and alumina-rich solids with a solution of alkaline salts eventually hardening into a new resistant matrix [1]. The use of these efficient binders for improving the engineering performances of natural soils in soil improvement has been widely accepted in literature [2, 3]. Several studies show the effectiveness of the alkali-activation of artificial pozzolanic materials (fly ash, ground granulated blast furnace slag, etc.) as precursors of alkali-activated binders, while fewer attempts have been devoted to the alkaline activation volcanic ash and pyroclastic materials in general. A systematic study on pyroclastic materials and ashes has been started at the Department of Earth Sciences, Environment and Resources of the University of Naples Federico II with a multidisciplinary and multiscale approach, in order to develop sustainable green binders for soil improvement. In the first stage of the research, the experimental activity is being focused on the mineralogical, petrographic and physical characterization of pyroclastic materials belonging to different volcanic areas. The second stage of the experimental study will be devoted to the alkaline activation of the selected precursors. The innovative alkali activated binders will finally implemented in the treatment of natural fine-grained soils. A specific physical and mechanical experimental program on AAB-treated soils will demonstrate the efficacy and efficiency of the innovative binders with excellent cementitious properties and low environmental impact for geotechnical applications.

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A systematic study of the effects of composition and synthesis protocol on the Specific Surface Area of metakaolin geopolymers

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The mesoporous nature of geopolymers, together with their low cost and facile synthesis route, make them attractive for applications in adsorption processes. Several studies have been conducted to assess the feasibility of using geopolymer-based adsorbents for water purification [1, 2] and gas separation [3]. Owing to their moderate Specific Surface Area (SSA), thermal and chemical stability they can also be employed as catalyst supports, where appropriate noble or transition metal species can be easily introduced through ion exchange.[4] Despite the potential, little research has been conducted on the textural properties of geopolymers for functional applications. Here the authors present a systematic study of the SSA of metakaolin geopolymers, where the effects of slurry composition and synthesis parameters are evaluated. Of all variables, the choice of alkali cation had the strongest influence on the textural properties with K-geopolymers consistently achieving significantly higher SSA than their Na-based analogues, displaying increments of up to an order of magnitude depending on the composition. Increasing the SiO2/Al2O3 molar ratio on the other hand resulted in a markedly negative effect, while the H2O/Al2O3 ratio displayed an optimum around 18-20; such trend could be an indication of a possible phase separation at higher values leading to the formation of large macropores with little contribution to the SSA. Increasing the curing temperature up to 90°C led to a decrease of SSA, with samples cured at room temperature displaying the highest values. On the other hand, the duration of the curing treatment has little effect on the textural properties of the condensed geopolymer, with the SSA approaching a stable plateau value. It was noted, however, that a minimum, temperaturedependent curing period is required to stabilise the structure, below which the samples displayed rapid degradation of the SSA.

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Synthesis and characterization of pure sol-gel $Al_2O_3{\cdot}2SiO_2$ as raw material in geopolymer preparation

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Geopolymers are inorganic polymers obtained from the alkalination of aluminosilicate powders [1]. The mineralogy, the chemical composition, and the reactivity of the precursor powders (metakaolins, fly ashes, sands, etc.) influence the properties of the final product. The sol-gel method [2] is used to synthesize the amorphous $Al_2O_3{\cdot}2SiO_2$. After the calcination at 750°C in the muffle, $Al_2O_3{\cdot}2SiO_2$ is utilized for the geopolymer production. Four EtOH:H_2O ratios (1:9, 1:13, 1:17 and 1:24, respectively) were used to synthesize the aluminosilicate precursors. The Figure 1 reports the flow-chart procedure for the geopolymer synthesis. XRD analyses assessed the amorphous phase of the synthesized precursors, while FT-IR and NMR were used to follow the geopolymerization occurrence and the features of the MK and pure aluminosilicate-based geopolymers [3]. Leaching tests and different NaOH solutions were also used to understand the reactivity of the synthesized precursors evaluating the Si and Al release [4].

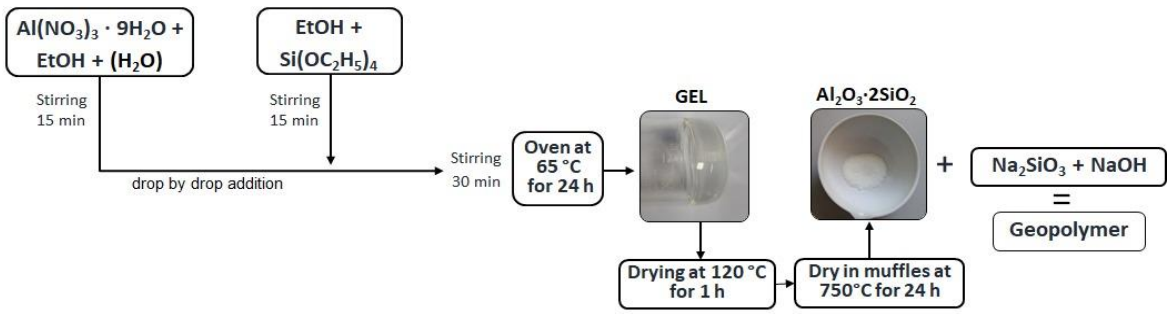

Figure 1. Flow-chart procedure of the geopolymers from pure $Al_2O_3{\cdot}2SiO_2$.

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3D Surveys and GIS application for Cultural Heritage conservation management: a case study from Catania's historical buildings

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Nowadays the advanced instruments and techniques, such as Laser Scanner (LS), Umanned Aericole Vehicole (UAV) and Structure for Motion (SfM), are large used in the monitoring of the state of conversation of the historical building.
For this purpose, in the framework of the Italian National Research Program "Advanced Green Materials for Cultural Heritage", the GeoDynamic & GeoMatic research group start to monitor eight historical buildings located in the Catania city center (Sicily).This approach would be a contribution for monitoring the knowledge of stone deterioration and facilitating the information collected in the most appropriate sustainable way. The 3D data obtained by LS and SfM were analyzed using the software CloudCompare in order to obtain the surfaces and volumes of the degraded parts of these buildings. After they were added into the geodatabase named the AGM (Advanced Green Materials), created in the Geographic Information System software (Arcmap 10.7.1). The final pilot system allows to: i) to import and export different graphical and alphanumerical data in varius coordinate systems (cadastral data); ii) to generate new thematic maps by querying the database (map of alteration processes in relation to the type and exposure of the elevation); iii) to relate to each other different physical or logical data (processes of natural and anthropogenic environmental pollution); iv) to define, in a parametrical manner, queries and entities properties directly from the user interface (extract mathematical and analytical models of the interrogated processes). SfM (Structure from Motion) techniques, automatic digital photogrammetry systems and Laser Scanner survey have been used to measure the geometries of the architectural elements.
The result was the development of powerful tool for managing all the historical buildings information.

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Microfluidic-based synthesis of $Ca(OH)_2$ nanoparticles for cultural heritage conservation

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Conventional methods for the synthesis of nanomaterials suffer from inaccuracies in reagents mixing, nucleation, growth of the nanostructured material and from lack of reproducibility of the chemical-physical properties of the reaction environment. The synthesis of nanomaterials carried out in microfluidic devices takes advantage of the confinement of reagents into the microfluidic environment while permitting a robust control of all the reaction parameters. The microfluidic-based flow chemistry approach may integrate all reaction steps in a single device and represents an intrinsically scalable synthetic route for nanomaterials [1]. Lime-based nanomaterials have been used to consolidate degraded limestone matrices [2]. In particular, $Ca(OH)_2$ nanoparticles are well suited for this purpose. The synthesis of $Ca(OH)_2$ nanoparticles by conventional synthetic route [3-5] is strongly hindered by carbonation and low solubility in water of the particles. We present the synthesis of $Ca(OH)_2$ nanoparticles in water/oil microemulsion. We used specifically designed microfluidic devices for water in oil droplet generation and $Ca(OH)_2$ nanoparticles confinement. Nonionic surfactant in the oil carrier medium stabilized drops, thus inhibiting carbonation phenomena. We used Raman spectroscopy to characterize $Ca(OH)_2$ nanoparticles and monitor the progress of the carbonation reaction after 24 hours of exposure to air. The transfer of the obtained nanoparticles from the water/oil microemulsion to an organic solvent allowed the dimensional characterization of the nanoparticles by dynamic light scattering. Hydrodynamic diameter in the range of a few hundred nanometers was measured with a low polydispersity index. Nanoparticles dimensional properties were maintained for at least 20 days.
The AGMforCuHe project is acknowledged for its financial support (PNR 2015-2020, Area di Specializzazione "Cultural Heritage" CUP E66C18000380005).

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Non-destructive SWIR monitoring of white marble surfaces from the Santa Maria del Fiore cathedral (Florence, Italy)

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Non-destructive monitoring of outdoor rock surfaces, exposed to numerous decay processes, is fundamental in planning conservation and restoration activities. Namely, this procedure could in principle allow monitoring the progress of the manufact restoration (Vettori et al. 2021). In this study, we undertook the validation of the fully non-destructive procedure, established using VIS and SWIR radiation ranges, on white marble surfaces affected by chemical decay (sulfation process). The sampling and analytical protocol was established by Suzuki et al. (2018). The case study is provided by the outdoor surfaces of the walls of the Santa Maria del Fiore Cathedral in Florence. This study compares two datasets obtained in two sampling campaigns on the same experimental sites, carried out in 2012 and 2021. Spectrometric investigations (VIS colorimetry and SWIR spectroscopy) were operated on stones at eye level. The obtained results clearly support the proposed monitoring approach as a facile, fast and semi-quantitative tool to trace evolution of the sulfation status of the considered rocks. Besides, further considerations, after integration with information about conservation/restoration interventions occurred in the time interval of this study, will be fruitful to assess the changes of the status of the stone walls with respect to the microclimate of the square around the church. The authors propose the present experimental approach as a tool for also other rock lithotypes, with consequences for functional assessment of the rocks and for conservation issues, including restoration with innovative materials.

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Physical-mechanical characterization of alkali activated binders and mortars produced by using volcanic ashes from Mt. Etna volcano

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Alkali activated materials (AAMs) can be regarded as synthetic materials due to the production process itself which foresees the mixing of solid aluminosilicate precursors with alkaline activators. Moreover, they are assumed as a “green” alternative to traditional concrete with high potentiality of use in different application fields (e.g., restoration of built heritage) [1-2] . According to this foreword and the satisfying results of previous studies on AAMs based on volcanic ash from Mt. Etna volcano [2-4], in this work we propose a comparison, at laboratory scale, between AA-binders and AA-mortars. In particular, four different set of samples were prepared, two of which (binders) through the addition of specific quantities (10 and 20 wt.%, respectively) of metakaolin (MK) as solid additive to the total amount of the volcanic source. The mortars were manufactured by adding to the previous binders 30 wt.% of pyroclastic aggregate (< 2 mm) and mixing with 2 wt.% of tap water to achieve a satisfying workability. All samples have been shaped with a small cubic size (2x2x2 cm). Afterwards, the four AAMs series have been cured for 28 days before being analysed to ensure the total hardening. The following analytical techniques have been then applied to assess the physical behaviour of the tested materials: i) infrared thermography to evaluate the heat release during the natural cooling of samples; ii) capillary water absorption test to assess their hydric behaviour as a function of textural features and pore structure. In addition, tests of uniaxial compressive and drilling strength were also carried out to estimate the mechanical performance of the sample set.
The AGMforCuHe project is acknowledged for its financial support (PNR 2015-2020, Area di Specializzazione “Cultural Heritage” CUP E66C18000380005).

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Ceramic industrial waste recycling for alkaline activated restoration materials

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Ceramic waste is one of the prominent source of waste in Europe, representing an ordinary problem for tiles and brick industries as well as a critical environmental issue [1]. Thus, converting it in new resources is today a challenge.
In addition, in the current climatic scenario the outdoor exposed cultural patrimony, which for the archaeological contexts is mainly made by ceramic materials, suffers of many intense decays not solved by the traditional restoration products [2].
The simultaneous need to face the disposal problem and to research new efficient restoration materials for ceramic, finds a unique solution in the development of alkali activated materials (AAMs) based on the recycling of ceramic industrial waste.
Their recognized chemical and mineralogical affinity with traditional ceramics make them attractive for the ceramic conservation and restoration field [3] and their low environmental impact encourages their applications.
This research aims to investigate the feasibility of reusing industrial tiles waste as precursor in the alkali activation process, in order to produce suitable materials for brick masonries' restoration: a topic still not exhaustively explored.
Many formulations have been studied by mixing at room temperature the ceramic precursor with low amount of metakaolin and a sodium alkaline solution, made by NaOH and waterglass. Considering the results in terms of workability, efflorescence and further technical parameters (e.g. mechanical strength and porosity), among all the formulation studied three binders where selected for the improvement of restoration mortars and pre-casted elements (e.g. bricks) for substitutional interventions.
The micro-structural investigation, together with the study of the mechanical, adhesion and aesthetical properties, and the comparison with those of archaeological samples, allowed to confirm the good potentiality of reusing industrial tiles waste for creating materials for efficient, compatible and eco-sustainable ceramic restoration interventions.

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Italy's mining framework and extractive waste management

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Italy has a peculiar mining legislation that still dates back to Royal Decree No. 1443/1927, which distinguishes extractive industries of strategic minerals (first category, named "mines") from those with less economic impact (second category, named "quarries").

Nowadays, the control over the extraction of non-energy minerals, previously managed at national level, has been transferred to the Regions. In this fragmented framework, the Geological Survey of Italy (SGI) of ISPRA is developing an INSPIRE compliant geodatabase aiming at collecting all relevant information from national, regional and local available sources. So far, all of the active quarries and mines within the national territory have been identified and georeferenced. More than 90% of the 3016 mines opened since 1870 have also been located.

The main purpose of this database is to define the national situation of mineral resources from mines and quarries including geological, environmental and economic aspects, with particular attention to environmental impact of mining practices and potential exploitation of decommissioned mining assets and extracted waste piled up over time.

Italy has a long mining history, dating back to pre-roman times. The exploitation of metal ores was most prevalent in the Alpine Arc, Tuscany, Calabria and Sardinia. Sicily has been the world leader of sulphur production for a long time. Currently in Italy there are only 76 operating mines, extracting cement marls, rock salt, feldspar, kaolin, bentonite and other industrial minerals. The extraction of metal ores is limited to the recent reopening of a mine in Sardinia. Because of how geologically complex Italy is, the exploitation of aggregates and dimension stones from quarries regards a wide range of rocks. Sand and gravel quarries are widespread along valleys and plains. Limestone crops out in Apulia, central Apennine, western Sicily and north-eastern Alps. Sandstone extraction mainly affects the Northern Apennine. The exploitation of effusive igneous rocks is developed in Sicily's and Campania's active volcanic areas, in the Pleistocene Tyrrhenian volcanoes and in the Permian volcanic rocks of Trentino-Alto Adige. Intrusive igneous rocks mainly characterize quarrying in Sardinia (granite). The metamorphic rocks are intensively exploited in the Alpine Arc, especially in Piedmont (gneiss), in the Apuan Alps (Carrara Marbles) and in Liguria (slate).

Former extractive industries have generated huge quantities of extractive waste, which originated from mineral excavation (e.g. overburden or waste-rock), mineral processing/treatment (e.g. tailings, waste gravel, sand and clays) and drilling mud and other drilling waste (e.g. discarded drill cuttings). Such waste may still contain a fraction of useful and potentially recoverable ore. The abovementioned waste may represent potential "new deposit" of primary, critical and non-critical resources, which could be reused in a circular economy perspective.

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A multidisciplinary study for the cultural heritage safeguard: seismic soil-to-structure interaction of three historical buildings of the University of Catania (Sicily, Italy)

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This study aims at evaluating the soil-to-structure interaction of three historical buildings of the University of Catania. Villa Cerami and Palazzo Boscarino host the Law Department, whereas Villa Zingali Tetto is the seat of the Casa della Città University Museum.
The results point out a multiple dynamic behaviour of Villa Cerami and Palazzo Boscarino showing different oscillation modes, which is confirmed by the variability of computed damping, linked to the different rigidity of the structures since one is built in massive stone, whereas the other is a reinforced concrete building without earthquake-resistant design. Villa Zingali Tetto, which is a reinforced concrete building without earthquake-resistant design, shows significant torsional effects, mainly linked to the irregularities of the structure. The comparison between the buildings' fundamental periods and site frequencies, did not evidence potential soil-to-structure resonance effects during a seismic event. Modelling of the local seismic response confirms experimental site frequencies, setting into evidence that there are not important amplification factors. On the other hand, from both the computed Spectral Accelerations and Peak Ground Accelerations for a M7.3 earthquake (Fig. 1), we estimated intensity values for which Villa Cerami could suffer heavy structural damage and Palazzo Boscarino and Villa Zingali Tetto very heavy non-structural damage. Reinforcement is required to the safety of the buildings considering they are also used for educational purposes.

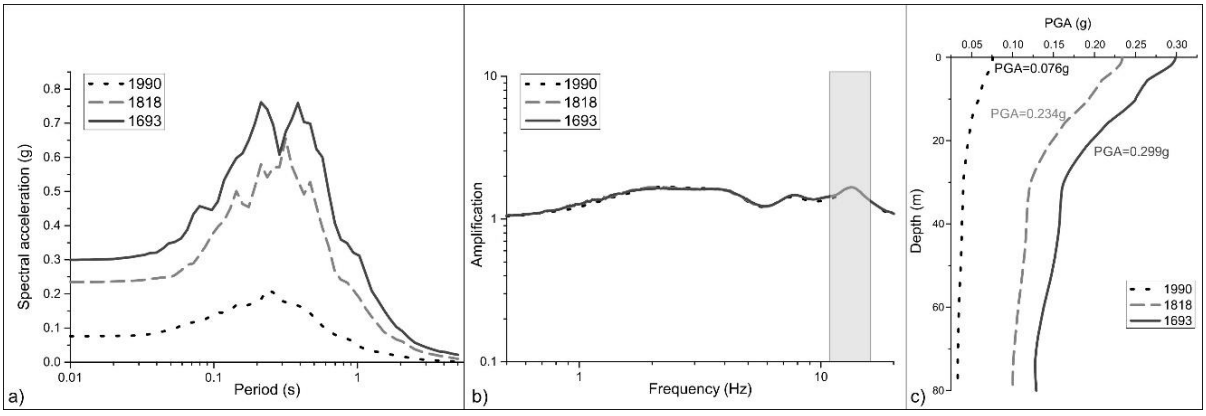

Fig. 1: a) Acceleration response spectra, **b)** mean amplification function, and **c)** peak ground acceleration profile obtained from the one-dimensional modelling performed through the code STRATA at Villa Cerami; for a M5.7 earthquake, a M6.2 earthquake and a M7.3 earthquake.

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Development of functional and eco-sustainable sol-gel based geopolymers for cultural heritage applications

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Recently, new synthetic inorganic and organic materials were developed with the aim of promoting their application as protective coatings and/or structural consolidants in construction and cultural heritage sector. In this context, the scientific community paid attention to geopolymers and their new hybrid functional derivatives to design and synthetize innovative and sustainable composites with better chemical resistance, durability and mechanical characteristics. Geopolymers are aluminosilicate-based amorphous inorganic materials obtained through a polymerization process, starting from natural or waste materials with a high content of aluminum or silicon, such as slag (from blast furnaces or from steel mills), clays, flying and volcanic ashes or other aluminosilicate sources (such laterite deriving from tropical areas) [1]. They are quite similar to ceramic bodies for their structure and mineralogical properties; nevertheless, geopolymers are featured by scarce rheological properties due to their low viscosity, which make them almost inapplicable in restoration works mostly of vertical buildings. To overcome this problem, thus increasing their chemical, physical and mechanical properties, it's possible to use other copolymers or sol-gel based cross-linkers (polysiloxane oligomers, alcoxysilane agents or epoxy resin precursors), as well as opportune and functional molecules, nanofillers or consolidants: this functionalization of the alkali-activated material improves the performance of the final product, as it allows an increase in the viscosity of the mixture, making the hybrid material more versatile in architectural and renovation of new/ ancient buildings, or in the restoration and conservation of cultural heritage [2]. The present work concerns the modification of the geopolymer at the chemical and nanostructural level, through the condensation process in alkaline conditions for the implementation of their properties, in particular by mean of the sol – gel technique, which is an eco-friendly approach to functionalize geopolymers, without high temperature treatments, in accordance with the principles of circular economy and green chemistry [2]. The chemical properties of the final functional geopolymers, together with the precursor ones, were studied by using X-ray fluorescence and diffraction investigations. Finally, corrosion resistance and hydrophobicity of these functional geopolymeric monoliths were tested by immersion and wettability tests.
The AGMforCuHe project is acknowledged for its financial support (PNR 2015-2020, Area di Specializzazione "Cultural Heritage").

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Chemical resistance in acids of alkaline activated materials from volcanic ash and paleo soil

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Etna volcano has available huge quantity of volcanic products, such as volcanic ash and paleo-soils, characterized by a high amorphous content (volcanic glass). They have been tested to be used in alkali activated materials production due to their high aluminosilicate and amorphous content [1]. To enhance mechanical properties and reduce the long setting time, different percentages of metakaolin (5-25%) to the alkali activated paste were added. This compositional optimization is important for their use in restoration sites.
The geopolymeric samples were characterized from a chemical and mechanical resistance point of view; the integrity of the sample was assessed, which provides information on the geopolymerization process. The degree of geopolymerization was analyzed by measuring pH and conductivity, and the reactivity of the geopolymers by the hydrochloric acid test. It determines the percentage of material that has been converted to "cement" and the portion that has not reacted with the alkaline solution.

The deteriorating effect of acids on cement based constructions has become a worrying problem over the world. The durability at acid attack is a desirable property for structural materials because the phenomenon of acid rains is a widespread, serious and a real problem. Samples were tested on the resistance to acid attack in terms of weight loss, appearance analysis and porosity change. The acids that have been analyzed are weak and strong; as weak acid there is Acetic acid 0,5 N that evaluates the behavior of a material to the action of meteoric waters [2]. Among strong acids there are Sulfuric acid at different concentrations, Nitric acid and Hydrochloric acid. The results obtained are compared with those resulting from the attack of geopolymers containing 100% metakaolin which are considered as reference. Samples containing volcanic materials show less weight loss with respect to metakaolin geopolymers. The high weight loss in hydrochloric acid is related to the dissolution of crystalline phases rather than to the dissolution of geopolymeric gel. The compressive strength after the acid attack shows that metakaolin geopolymers are more resistant, but after the attack these samples show high deterioration.
The AGMforCuHe project is acknowledged for its financial support (PNR 2015-2020, Area di Specializzazione “Cultural Heritage”).

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The “Ghiara” volcanic paleosoil (Mt. Etna, Italy): petrologic characters, genetic model and use for AAM production

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In this work, we investigated samples from a peculiar aggregate locally named "Ghiara" collected at Mt. Etna volcano. This material, found exclusively beneath solidified lava flows, was employed in the past centuries in construction field for its reddish hue and the high pozzolanic activity. For the same reasons it has now raised the interest of the scientific community involved in the formulation and production of eco-friendly materials alternative to the traditional ones such as geopolymers [1,2,3]. The aim of this study is to define its chemical and mineralogical characters and to provide a model for its genesis. Multidisciplinary analysis, including X-ray fluorescence (XRF), synchrotron radiation X-ray diffraction (XRD) and Raman and Fourier-transform infrared (FT-IR) methods were employed to fully characterize samples from various Etnean outcrops. Results show that the original paleosoils with chemical and mineralogical composition resembling those of the Etnean products, once covered by lava flows, underwent marked modifications that produced the unique mineral assemblage of the Ghiara, characterized by the presence of hematite responsible for the reddish appearance. The heterogeneity of the samples, however, does not allow to define a univocal genetic model. We propose a range of models for its formation that fits the characters of each sample. The genesis can be ascribed to one or to the combination of the following phenomena: i) chemical oxidation, ii) biological oxidation and iii) hydrothermal transformation by interaction of meteoric waters with volcanic volatiles from lavas. This work represents a first contribute in the knowledge of Ghiara characters and genesis, which will help to a better use in its employment for construction purposes and especially in the geopolymers production.
The AGMforCuHe project is acknowledged for its financial support (PNR 2015-2020, Area di Specializzazione “Cultural Heritage” CUP E66C18000380005).

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Preliminary Study of the Cold Sintering Process (CSP) for Geopolymer Powders

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The sintering process is an essential step in transforming particulate materials into dense ceramic materials [1]. Already starting from the Paleolithic, humans made use of this process to create ceramic manufacturers, as shown by the iconic figurine of Venus of Doli Vestonice [2]. Despite its ancient origin, sintering is still nowadays a crucial stage in the production of ceramic products [3]. However, since it needs high temperatures (between 50% and 75% of the melting temperature to theoretical density of 95% of the product), the classic sintering is not so eco-sustainable [2].
In 2016, Randall and his research team introduced and patented the so-called cold sintering process (CSP) where a ceramic powder is densified with the aid of a liquid phase under an external pressure and limited heating conditions (below 350°C). In doing so, a drastic decrease of the energy amount is obtained, reducing the environmental impact of the process. Up to date, different materials have been successfully processed through CSP with extraordinary results in terms of final properties [3].
In this presentation, preliminary results obtained from the implementation of the CSP for geopolymer powders are reported.
Briefly:
a) High geometric density, indicating low residual internal porosity;
b) Very good chemical stability, as confirmed by passing the boiling test. Indeed, materials possessing a not-fully condensed geopolymer network are sensitive to water, undergo swelling, dissolution or total destruction [4];

The evidence obtained confirms the technological excellence of CSP for the production of geopolymer bodies as an alternative to casting. Obviously, further research will be necessary to understand the diffusion and densification mechanisms that occurs during cold sintering of geopolymer powders.

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Rheological behaviour of volcanic ash fresh pastes

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Fresh paste of alkali activated volcanic ash have been formulated to match historically significant build materials in the inhabited areas around the Mt. Etna volcano in Sicily, Italy [1]. In this scenario, the formulations presented in this work aim to reproduce aesthetically the ancient mortars so that to represent useful replacement during restoration operations.

The alkaline activator has been prepared by mixing NaOH, Na silicate and tap water, after addition to the finely ground volcanic ash (average diameter around 20 μm, D_{50}=19 μm) a homogeneous paste was obtained. As soon as prepared the fresh paste was tested in a rotational control stress rheometer. For the evaluation of the rheological behaviour, the instrument was used in: i) Control Stress (CS) mode for the determination of the flow limit (yield point) and ii) Control Rate (CR) mode for the determination of the flow curve and viscosity curve [2]. To test this type of material (concentrated pastes) the most suitable sensors are serrated parallel plates 2 cm in diameter with knurling to avoid slippage as much as possible. The distance between the two plates was 1.50 mm, 5 times wider than the coarsest volcanic ash grain, i.e. 285 μm. All tests were carried out at a constant temperature (20°C ±1°C).

Rheological tests have been performed on the ash fresh pastes added with 0.25 and 0.5 wt% of plasticizer agents in in order to evaluate their influence on the yield stress point and plastic viscosity. The yield stress point is a very important parameter to set the workability of the paste during application [2]. The results indicated that the fresh pastes showed a plastic behavior. These agents modified the yield point values respect the base paste while viscosity values did not suffer a great variation. These additives affect the compressive strength and the chemical stability very slightly, meaning that the geopolymeration process generate a stable aluminosilicate network with a promising good durability.
The effect of the preparation time was studied by letting the paste rest for 15 min before measurement. The viscosity curves show an increases the viscosity at low shear for the addition of 0.25% additive on resting time before application. On the contrary, it slightly lowers the viscosity values at low shear for the addition of 0.50%.
The AGMforCuHe project is acknowledged for its financial support (PNR 2015-2020, Area di Specializzazione “Cultural Heritage”).

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The legal regime of materials in the perspective of the green transition

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Environmental legislation has had the function of preserving the ecosystem through sectoral disciplines (pollution, waste disposal, etc.) according to a conservation logic.
Today the approach seems to change and the disciplines that correspond to the protection of the public interest in "conservation" must be reread in a dynamic perspective. The environment becomes a "resource" for the inhabitants of the earth and for future generations and becomes a principle, an immanent "value" of the law that must take on an ecological dimension for the construction of an eco-legal order.
In the ecological principle there is the synthesis of the personalist and solidarity principles (art. 2 of the Italian Constitution), starting from the person towards the other: other - community, other - future generations, other - nature, creating the new eco-juridical order where man does not dominate the territory but is in the territory. Where man is not isolated, having to take charge of others and future generations.
In this context, the disciplines (for example, the discipline on waste) must correspond to a primary need for "circularity", guaranteeing the principle of environmental sustainability that inspires and animates the new legal perspective.
One of the building blocks on which the modern circular economy is based is the use of low environmental impact materials that come from "waste". It is used in strategic sectors such as construction, agriculture, clean energy, etc. This is how the form of state qualifies as "circular".
Annex no. 2 of the Ministerial Decree of the Ministry of Economic Development of 06/11/2020 indicates that "circular economy means an economic model in which the value of products, materials and resources is maintained as long as possible, and production of waste is reduced to a minimum ".
The National Recovery and Resilience Plan (NRRP) strengthens the path and urges it by providing for an ecological transition based on sustainable agriculture, renewable energy, energy efficiency, redevelopment of buildings, etc.
The AGM for Cuhe project is placed in this context, which envisages the development of new materials for restoration starting from low-cost (environmental) materials to be waste.
Gravel, clay, diatomite, blast furnace slag, ceramic waste, sawing mud, volcanic ash, become "resources". But to be such it is necessary to adapt the relative legal regime to the dynamic perspective we have described.
However, the current legislation is a limit. For example, the volcanic ash has been classified as "special waste" (residue from street cleaning) with code CER 200303 which must be treated and sent to landfill as inert material (with high costs). And this while studies highlighted the possible reuse of volcanic ash, especially in the construction field, but not only.
The solicitations led to a legislative modification of the volcanic ash regime for a (re)use that would avoid its disposal as waste, promoting the transition towards a circular economy, towards more sustainable solutions, with an undoubted environmental advantage, for example, in terms of reduction of CO2 emissions.

Paragraph 1 of Art. 35 of the Law Decree n. 77/2021 (measures of simplification for the promotion of the circular economy) establishes: "In order to allow the correct management of waste and the best implementation of the interventions envisaged by the National Recovery and Resilience Plan, also in order to promote the activity of recovery in waste management in a circular economy vision as envisaged by the new European Action Plan for the Circular Economy, in the Legislative Decree 3 April 2006, no. 152, the following amendments are made to article 185: at paragraph 1, letter c), the following words are added at the end: "volcanic ash, if reused to replace raw materials within production cycles, by means of processes or methods that don't harm the environment or endanger human health ".
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Cognitive investigations for the safeguard of the traditional architecture of the Etna territory

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The wide built heritage that characterizes the Italian territory requires an in-depth preliminary knowledge of the architectural heritage for the purpose of their protection from risks (environmental, seismic, anthropogenic) which unfortunately are more and more recurrent. The description of the existing building heritage requires an interdisciplinary and systemic approach, mainly oriented to the preservation of the asset under protection. In this paper the research group has outlined a specific process of knowledge that takes advantage of the expertise provided by the disciplines of representation and technical architecture. The methodology of the architectural survey was applied to the historical, geometric, material and constructive considerations.The two architectures chosen as case studies are a late liberty villa (Villa Zingali Tetto) and a rural architecture (Noria). Both architectures are located in the territory of Catania (Italy). The cognitive path foresaw the adoption of the digital instrumental survey (close-range photogrammetry and laser scanning) as means to identify spatial and material characteristics. The results of this research consist in digital replicas of the artifacts that allow the consultation of the metric data and the analysis of the state of conservation of the artifacts. Moreover, these digital models are also prone to further implementations (such as H-BIM methodologies) aimed at defining appropriate conservation strategies.

Fig: 1. On the left: view of the point cloud of villa Zingali - Tetto; On the right: view of the Noria's point cloud.

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The sarcophagus of Sparano from Bari: investigation of a protective coating based on nanostructured titanium dioxide"

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The preventive conservation of stone buildings and monuments is a crucial challenge to be tackled by art conservator due to the extraordinary relevance of cultural heritage in many regions and countries. In this perspective nanotechnology can play a significant role, allowing the development of nanostructured materials suited to comply many fundamental conditions, both functional and aesthetic in nature.

This work represents an interdisciplinary study performed to design and develop the most appropriate protective nanostructured coating to be applied on the sarcophagus of Sparano from Bari, on the occasion of its restoration. This monument dates back to late 1200 and is located on the exterior, lateral façade of St. Nicola's Basilica in Bari (Italy).

TiO_2 has been selected considering its photocatalytic properties, that make it an ideal candidate for a self-cleaning and antimicrobial protective coating. In particular, the developed coating relies on an original material made by rod-shaped TiO_2 nanocrystals (TiO_2 NRs) that are obtained by means of a colloidal chemistry route and capped with oleic acid molecules that make them dispersible in organic solvents.

After petrographic and microbiological analysis, carried out in order to characterize the stone forming the sarcophagus and its preservation state, samples of the same lithotype, which was identified as a limestone (Calcare di Bari), were prepared with the aim of detecting in laboratory the most suitable application conditions and studying the coating performance.

A comprehensive set of experiments was performed by depositing the TiO_2 NRs based formulation on the limestone samples surface by brush interposing Japanese paper, in order to assess self-cleaning, hydrophobic and photocatalytic properties of the TiO_2 NRs based coating. The characteristics of the resulting coating were thoroughly elucidated by complementary techniques and its photocatalytic behavior under sunlight was assessed.

The results demonstrated the effectiveness of TiO_2 NRs as an active component in formulations for stone protection, thus prompting their application on the restored surface of the sarcophagus. The performance of the protective coating on the monument is currently under monitoring.

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Geopolymer materials: from building sector to added value materials

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The versatility of geopolymer materials is well known and starting from this assumption, the research on geopolymers at CNR-ISTEC is addressed to several application sectors (Fig. 1). Regarding the building sector several foams and composite panels, for heat and sound insulation, have been produced exploiting the addition of fillers as vermiculite, perlite and waste materials as silica fume, biomass ashes, wool. These materials underlined the possibility of obtaining innovative materials thanks to the use of a wide variety of components, including recycled ones, capable of enhancing the green and eco-sustainable aspect combined with good performance. Furthermore, transports and aeronautics can enjoy of heat resistant shields [1]. In the last years, starting from benchmark geopolymer formulations new applications with high added value have been placed under investigation. Indeed, in this perspective geopolymers have recently been addressed as alternative, cost-effective, environmentally friendly adsorbents for the removal of pollutants from gaseous or liquid streams. Different production processes were applied to easily mold geopolymers into different shapes as monoliths, granules or beads for easiness of operation and to facilitate the handling and storage. The possibility to tailor the porosity and the ionic exchange and electrostatic interaction properties were exploited, together with opportunity of functionalize the matrices with fillers in order to create more performing composite materials and broaden the spectrum of applications. Geopolymer matrices and geopolymer-composites were studied as oxygen carriers as well as adsorbents for wastewater treatment and CO_2 [2].

Fig. 1 Geopolymers at CNR-ISTEC: from building to transports and environmental application

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A sustainable design strategy for the restoration of the paving stone of the "Palazzo Centrale dell' Università", Catania, Italy

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The current headquarters of the University of Catania, known as "*Palazzo Centrale dell'Università*" dates back to the end of 1600. After being destroyed by the earthquake of 1693, it was rebuilt in Baroque style by the architects Francesco and Antonino Battaglia and Giovan Battista Vaccarini. This latter elaborated the decorative paving stones adorning the pavement which nowadays represents a symbol of the Etnean city.

The pavement is made by black gravels of volcanites, with a rounded shape, inserted in white slabs of limestone. This configuration of stones juxtapose one by one reminds a mosaic with floral and geometric motifs typical of the Sicilian Baroque. Despite the recent conservation-restoration intervention (in 2017), the paving is currently affected by biological decay. For this reason, the pavement has been selected such as a case study for testing new protective materials in the framework of the project *Advanced Green Materials for Cultural Heritage (AGM for CuHe)* which aims to develop new technological and sustainable products in the field of restoration.

In collaboration with Restoration Centre Piacenti S.p.a, three different biocide products (commercial and experimental) were selected and tested on small areas of the pavement. Their efficiency and their environmental sustainability have been evaluated. After cleaning operation protective tests have planned and they are currently underway on two restricted areas of the pavement in order to assess their efficiency at different exposition conditions.

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High Shear Wet Granulation of Geopolymer and Geopolymer-Zeolite powders for CO_2 adsorption

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Being widely used by the pharmaceutical industry, granulation of powders is a very simple method requiring, however, a strict control of processing parameters. The purpose of this research was to produce geopolymer granules from the controlled agglomeration of geopolymer and zeolite powders, to be used inside a fixed-bed column system for testing CO_2 adsorption. Granules composed of pure geopolymer and geopolymer/zeolite, were successfully produced using a high shear wet granulation technique. Granules of different dimensions were tested by compression, and their main characteristics were assessed by SEM, BET, and porosity measurements. The adsorption capacity was measured as grams of CO_2 per kilogram of sorbent. The breakthrough curves from continuous adsorption tests were obtained using different concentrations of CO_2 in air. The produced granules showed CO_2 adsorption capacity like other materials reported in the literature

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Eco-sustainable binders based on alkali activated red mud-blast furnace slag precursors

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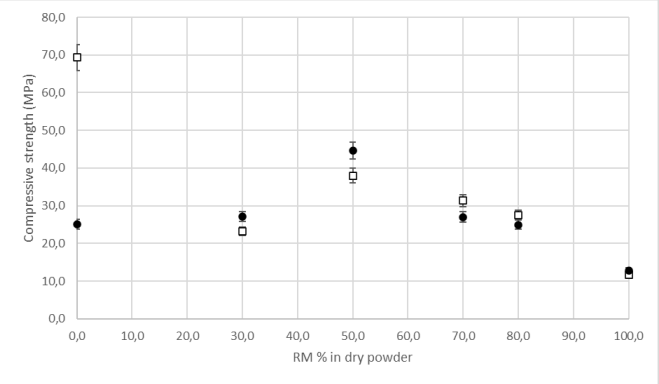
Aluminum is one of the most used materials in the world. In fact, more than 120 Gtons are produced every year [1]. The most commonly used ore for aluminum production is bauxite, but the production of 1 ton of aluminum generates 0.9–2 tons of residue, called red mud (RM), depending on the initial composition of bauxite.
In this work, the use of RM as a co-precursor in the production of alkali-activated binders, was studied. Pastes were obtained by combining RM with blast furnace slag (BFS), activated by sodium silicate solution and cured at different temperatures. Obtained samples have been characterized by chemical, structural, microstructural and mechanical points of view.
The sample prepared with 100% RM showed a strength value close to 12 MPa, but a small amount of BFS (20 wt.%) was sufficient to more than double the strength, reaching values close to 30 MPa. Samples prepared with RM co-reacted with BFS in a 1 to 1 ratio, showed very interesting strength values of about 45 MPa. The microstructure was composed of a (NASH-CS(A)H) matrix, in which particles consisting of calcium carbonate, iron, aluminum, and titanium oxides were randomly distributed. This type of structure, with the presence of unreacted particles in an amorphous phase, reduced shrinkage problems by limiting the formation of cracks and micro-cracks [2].
The mixes studied in the present work can be likely used as alternative binders in pre-cast units.
An evaluation of the environmental impact of possible industrial productions as bricks, pavement blocks or pre-cast units in the building industry is ongoing.



Compressive strength values. □: room temperature-cured samples; ●: samples cured at 60 °C for 24 h

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Durability of alkali activated binders and mortars from Mt. Etna volcanic precursors: preliminary tests

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Volcanic ash from Mt. Etna and an oxidated paleosoil, locally named “ghiara”, have been recently used to produce alkali activated materials to be employed in the restoration of the ancient buildings of the Etnean area [1, 2]. Aesthetic compatibility and adequate properties of these products have been demonstrated.
On the other hand, despite the good preconditions and the huge availability of these raw materials, their study is still in the early stage and a durability evaluation must be undertaken.
To simulate local environmental conditions, volcanic ash and ghiara-based geopolymer binders and mortars have been subjected to atmospheric exposure for 6 months (summer-autumn) with the aim of preliminarily testing their durability.
Consequently, the geopolymers before and after weathering were characterized with a multi-analytical approach. The possible effect of carbonation due to the leaching of sodium, the variation of composition (XRD, pXRF, FT-IR), micro-structure (SEM-EDS), mechanical properties (compressive and flexural strength), dynamic vapour sorption (DVS), and aesthetic appearance (colorimetry) were evaluated.
The results of these preliminary tests are encouraging showing a good stability to weathering in relation to the tested period. Both groups of products show good visual aspect after six months of outdoor exposure; good mechanical properties were highlighted too, with compressive strength increased after exposure for all the samples, while flexural strength increased for volcanic ash products only. On exposed materials, only natrite (Na_2CO_3) occurred as by-product. DVS measurements evidenced the fundamental role of aggregates in lowering the water uptake of materials.
Despite the need for further tests, such as compatibility with the substrates, the proposed formulations look promising from the chemical, mechanical and aesthetic points of view, as required in a good conservation practice.
The AGMforCuHe project is acknowledged for its financial support (PNR 2015-2020, Area di Specializzazione “Cultural Heritage” CUP E66C18000380005).

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Modelling of masonry buildings enhanced by structural geopolymer based strengthening techniques, application to case studies

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Among the current proposed retrofitting strategies of existing masonry buildings, some are characterized by a limited interference with the activities that take place in the structure, which is a desirable condition to avoid relocation, even temporary, and to reduce the downtime period [1]. Low-impact retrofitting strategies, although usually characterized by fast application and limited costs, lead to a significant reduction of the seismic vulnerability being conceived to act on specific collapse mechanisms by limiting their activation or increasing their resistance and ductility. Among the several strengthening solutions that can be adopted to existing masonry buildings, new geopolymer based techniques may represent an optimal solution by determining significant improvements of the global resistance and ductility, even applied on the external facing of the peripheral walls only in order to reduce the downtime period. Within the research project “Advanced Green Materials for Cultural Heritage” (AGM for CuHe), new geopolymer based materials were developed for civil applications; precisely, innovative composite strengthening, based on Fiber Reinforced Geopolymer Matrix (FRGM) techniques were conceived, considering a matrix made of geopolymer mortar combined with composite textiles. In this paper two existing masonry buildings, part of the Cultural Heritage of Catania (Italy), both in the unreinforced and FRGM reinforced configurations, have been numerically modelled by means of the Discrete Macro-Element Method (DMEM) [2]. The case studies have been, first, subjected to extensive in-situ non-destructive tests and the mechanical masonry properties have been inferred to provide the non linear DMEM model of the unreinforced configuration. Then, by means of a proper modification of the mechanical properties of the masonry elements, to which the reinforcement is applied, the numerical models of the relevant FRGM reinforced configurations have been also formulated. The adopted numerical method guarantees, on one hand, reliable estimation of the nonlinear behaviour of the masonry structures and, on the other, low computational burden in comparison to refined finite element models. The buildings have been analysed by static nonlinear analyses by considering several input directions aiming at investigating on the influence of structural irregularities on the collapse behaviour. The results demonstrate that the polymeric based strengthening solution enhances the seismic performance of both case studies even though application of the reinforcement solely on the external wall facing is chosen.
The AGMforCuHe project is acknowledged for its financial support (PNR 2015-2020, Area di Specializzazione “Cultural Heritage” CUP E66C18000380005).

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Upcycling of composite materials waste into geopolymer-based mortars for applications in the building sector

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Composite materials (e.g. commercially known as Okite or Ilexa) are commonly used in the building sector for architectural design applications for housing, like kitchen slabs, sinks or washbasins. Despite being highly versatile, durable, and aesthetically interesting, at end-oflife these materials represent a serious environmental problem. In fact, the presence of resin mixed to inorganic aggregates is deemed unsolvable, posing serious waste problem to the producers. The recycling of industrial swarfs as well as the recovery and possible recycling of end-of-life waste is, in fact, very difficult and economically not feasible for these materials. Also, the components of composites vary widely from one company to the other, with resin varying between 5 and 40 wt.% and the rest being an aggregate composed of a mineral charge of quartz or a mixture of quartz and K-feldspar. In this study, we tested the possibility to use composite swarfs as the aggregate components in geopolymer-based mortars, to produce materials for different upcycling applications, to be used in the building industry as tiles or slabs. Two different composites (A-type: 90% quartz and 10 wt.% unsaturated polyester resin, B-type: 60 quartz and 40 wt.% acrylic resin) were characterised by X-ray diffraction (XRD), optical microscopy and Scanning Electron Microscope (SEM), to elucidate their mineralogical and chemical composition, as well as determine the textural relations among components. Geopolymer-based mortars were produced with the objective to introduce 60 wt.% of composite waste in a geopolymer matrix, constituted by variable amounts of metakaolin and fly-ash, acting as precursors, and K-silicate. Preliminary results indicate that the grain-to-matrix boundary are in perfect contact and that 2D porosity, measured by image analysis along different orientations, does not exceed 4%, with only spherical unconnected pores. Density is between 1,7 and 1,8 g/cm3. Flexural and compressive tests, carried out according to EN standards for cement, indicate good mechanical properties varying in the range of 39,5 – 48,5 MPa at 28 days. The preliminary tests revealed that composite materials could be effectively recycled using geopolymers and that the new materials produced are very promising for application in the building sector, postponing therefore the end-of-life of these composites, otherwise destined to be landfilled.

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Developing raw materials into a major strength for Europe

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Minerals, metals and advanced materials are key enablers to achieve the objectives of the European Green Deal. Today, only a fraction of the most relevant raw materials is produced in Europe. This can be changed through a circular economy approach, through innovation in recycling, substitution, processing, mining, and exploration. It is the objective of EIT RawMaterials to secure a sustainable raw materials supply by driving innovation, education, and entrepreneurship across European industrial ecosystems.
EIT RawMaterials provides a collaborative environment for disruptive and breakthrough innovations by connecting business with academia, research, and investment. It also invests in future generation of innovators for the raw materials sector through initiatives ranging from education of school students to higher qualifications for industry professionals.
The company is committed to supporting Europe's transition towards a circular, green, and digital economy whilst strengthening its global competitiveness and securing employment. On this foundation, EIT RawMaterials has been mandated by the European Commission to lead and manage the European Raw Materials Alliance (ERMA).

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Thermal and morphological characterization of geopolymers based on sicilian volcanic precursors

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Geopolymers are materials produced by the activation of an aluminosilicate source with an alkaline solution. They are attracting growing interest in research and development, due to their technical properties, accessibility and cost-effectiveness of the raw materials [1]. Here we describe the thermal and morphometrical characterization of a geopolymer set made by using volcanic precursors (Etnean volcanic ash and paleo-soil, locally known as “ghiara”, and aeolian pumice) [2]. Several formulations, differing by the added weight percentages of metakaolin (from 0 to 25%), the ratio between the activators, the typology of sodium silicate used and the final liquid/solid ratio of the mixture, have been investigated by the combination of Thermogravimetric analysis (TGA) coupled to the Evolved gas Analysis (EGA) through Fourier Transform Infrared Spectroscopy (FTIR) and micro Computerized Tomography (micro-CT). All the samples showed in the thermal degradation profile a main peak loss below 150°C, attributed to the loss of the evaporable water, which remains adsorbed onto the surface or trapped in the geopolymer cavities during the geopolymerization reaction. The other peak observed (in the range of 400-600°C, mass loss around 1%) was identified in the degradation of carbonates, formed secondarily during the curing sample (i.e., efflorescence phenomena). Besides, micro-CT showed that the samples had a variable porosity (from 10 to 57 vol.%), with the main void phase constituted by millimetric pores (PVD >0.6 for the 1-10 mm^3 range), together with a high number of small voids (10^{-4} mm^3). Overall, the morphometry seemed more related to the features of raw materials than to the differences in the geopolymer preparation (e.g. choice of activator, ratio liquid/solid, % of metakaolin).

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Hydrolysis at crystal surfaces using the Nudged Elastic Band method

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One of the keys to finding greener alternatives to Portland cement is better understanding the interactions between water and crystal surfaces. Density Functional Theory has become an indispensable means of not only predicting the properties and behaviour of materials but also as a tool to study systems at disequilibrium on the atomic scale. A common DFT approach to studying surface chemistry is by ab-initio molecular dynamics simulation, capable for systems of hundreds to thousands of atoms at femtosecond time resolution. However, for rare events that are limited by slow kinetics, particularly at lower temperatures, other theoretical approaches can be advantageous. Here we examine the interaction of H_2O at the surface of various crystalline compounds using the Nudged Elastic Band (NEB) method based on Density Functional Theory. Surfaces are generated by integrating a vacuum gap to the periodic boundary conditions of the lattice resulting in a slab-like system. A dipole correction is imposed to neutralize the electric field within the narrow gap and molecular species such as H_2O can be inserted into the gap. We begin by examining a series of calculations constrained only by the water to surface distance in search of metastable hydrolised products. We then apply the NEB method to examine the contour of the potential energy surface separating these species in order to find the minimum energy path (MEP) and activation energy along each reaction coordinate according to conventional transition state theory.

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Valorization of natural waste materials: volcanic ash from the 2021 eruption at Cumbre Vieja (La Palma Island, Spain).

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In this work, we evaluate the suitability of volcanic ash from Cumbre Vieja volcano at La Palma Island (Spain) as raw material for alkali activation process. The aim of this work is valorize what commonly constitutes a natural waste material in active volcanic areas and use it for building or conservation purpose. To date, ash deposits constitute a serious problem not only because they are difficult to dispose, but also because it is not clear how to use them. During last eruption, started the 19th of September 2021, pyroclastic fallouts covered wide cultivated and residential areas within a radius of tens of kilometers from the eruptive center.

To give value back to this natural waste, we propose to employ it for the production of low energy consuming and cost-efficient geopolymers. Indeed, volcanic ash has been proved as an efficient precursor for geopolymer production as demonstrated by recent formulations using Etnean pyroclasts [1,2,3]. For this reason, ash from Cumbre Vieja 2021 eruption has been sampled from proximal to distal areas of the emission point and will be characterized by morphologic, mineralogical and chemical techniques in order to define the best mix design for the geopolymer formulation. We expect good results in terms of mechanical and physical properties of these materials with promising application in building construction and restoration field.

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Geopolymer mortars derived from ceramic wastes for applications in Art & Design

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Ceramic wares represent an important and strategic “made in Italy” product. However, unfortunately, the ceramic industry has a high environmental impact and produce a large amount of solid waste, usually sent to landfills.
In response to the challenging requests of circular economy and of the Ecological Transition Plan, an effective route should be found for the reuse and valorization of these huge amount of waste. A possible solution could be envisages in the production of alkali-activated materials and geopolymers [1, 2].

In this contribution the preparation and characterization of geopolymer mortars obtained from waste deriving from the production process and the “end of life” of porcelain stoneware products, is presented. Structural, morphological and mechanical studies carried out on different kinds of geopolymer mortars prepared by using several types of by-products (pressed burnt and extruded ceramic waste, raw pressed and gypsum resulting from exhausted molds) point out that these mortars can be easily cast also in complex shapes and show a more consistent microstructure in respect to the geopolymer paste, with a reduced amount of microcracks.
Finally, the negligible absorption of water and the excellent adhesion of these materials to common substrates such as tuff, concrete, and marble, even for elevated concentration of filler, suggest their use in the field of Art, Design and Cultural Heritage [3].

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Novel techniques for the assessment of injectability and environmental resistance of injection grouts for mosaic conservation.

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Several commercial injection grouts for restoration and stabilization of architectural surfaces have entered the market in the last two decades, and they are extensively used by conservators around the world as an alternative to custom formulations. No standard test methods have been specifically developed for this class of injection grouts to evaluate injectability and flowability during the conservation of plasters, wall paintings, and mosaics, as well as their resistance to saline attack. The present work characterized five different commercially available injection grouts by a proposed adaptation (Biçer-Simsir & Rainer 2011, Evaluation of lime-based hydraulic injection grouts for the conservation of architectural surfaces. A Manual of Laboratory and Field Test Methods. The Getty Conservation Institute) of the sand column test (EN 1771-Determination of injectability by the sand column test). The suggested protocol allows determination of the ability of grouts to fill a capillary network of different granular materials, either dry or pre-wetted, under constant pressure.
The injectability test was paralleled by the systematic rheometric characterization of the grouts currently used for the consolidation and re-adhesion of mosaics, at different water-binder ratios. The rheometric measurements were complemented by grain size distribution profiles, microscopic imaging of the filled pores, mechanical tests, and assessment of the resistance of the grouted samples to sulphate attack.
The results of the combined rheometric - complementary tests allow a thorough understanding of the flowability behaviour of the available grouts, and to suggest improved formulations of binders for mosaic conservation.

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Nano-TiO_2 coating for cultural heritage conservation: safe or toxic?

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Recently, an increasing number of studies addressed to conservation and restoration of the historic structures have been performed. It is known that decay phenomena produced by a constant exposure to natural weathering, especially water, and also urban pollution can affect cultural heritage. Once water penetrates, it carries out its deteriorating effect including chemical dissolution of the stones' component promoting microorganisms growth on the surfaces which enhances deteriorative processes [1]. For these reasons, the use of nanoparticles is growing in this field in order to preserve, if properly dispersed in coatings, the cultural heritage. Moreover, nanoproducts can promote photocatalysis-based degradation of pollutants and the inhibition of microorganisms. Among these, it has been shown that titanium oxide (TiO_2), thanks to its photocatalytic properties, produces biocidal effects potentially useful for this purpose, and when introduced in cementitious matrices, it enhances their resistance to chemical attack [2]. Nanoparticles as considered biologically inactive and inert, but data about potential toxicological effects including oxidative stress, apoptosis, alterations in embryonic development or growth inhibition of embryos, are lacking.
The potential toxic effect of TiO_2-NPs (Degussa P25, Sigma-Aldrich), characterized by SEM analyses, on *Artemia salina* and *Danio rerio* by acute toxicity assay was investigated. Our results have shown that TiO_2-NPs don't affect hatching of cysts on *A. salina* giving low percentage of immobilization of nauplii, also in *D. rerio* the embryonic development has not been disturbed (fig.1). Therefore, the immunofluorescence investigation has confirmed the ability of embryos to respond to the presence of TiO_2-NPs with the expression of Metallothioneins, specific detoxification system. Despite the nontoxicity of TiO_2-NPs, it is required define a toxicological profile of NPs in concrete and evaluate the impact of them on the environment.

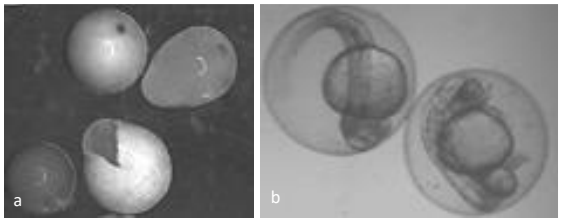

Fig.1: A. salina cysts (a) and D. rerio embryos (b) exposed to TiO_2-NPs

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Characterization of Sicilian clayey sediments as precursor for geopolymers

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In this work, we focused on the possibility to use clay sediments cropping out in Sicily as precursors in the production of geopolymers considering in the last decade the growing interest in the scientific community regarding the themes of sustainability and CO_2 footprint reduction [1]. The three different clay raw materials selected for this study as precursor are: Plio-pleistocenic clay, Numidican Clay and Variegated clay sampled in different parts of Sicily. The main advantages of the use of clay sediments are the simplicity in finding materials thus obtaining a reduction of transport distances and favoring local economies. In this study, clay raw materials selected and analysed are suitable as precursors for the alkali activation process due to their chemical and mineralogical compositions (SiO_2/Al_2O_3>70%). In this regard, different formulations have been prepared by using clays, thermally treated in order to improve their reactivity [2], activated with sodium hydroxide solutions and sodium silicate. All samples were cured at 85°C for 20h, and at room temperature (22±3°C) for 28 days keeping the humidity level >90%. At the end of the curing, specimens were demoulded, stored and analysed by XRD, FTIR-ATR and DRIFT Spectroscopy, SEM/EDS analyses and mechanical strength. Before these characterizations, an integrity test has been performed for all samples in order to check the chemical stability of geopolymers in water. New crystalline phases, as Tobermorite, Sodalite or zeolites as Faujasite, have been detected with XRD suggesting the formation of more ordered structure during the polymerization process. Microanalysis carried out by SEM/EDS has shown the presence of alumino-silicate gel. The obtained compressive strength values are promising and demonstrating like the presence of silica in the sodium silicate solution favors the polymerization process, producing a material with an increased mechanical strength as already reported in literature [3]. According to our results, this selected Sicilian clay raw materials has a good chance to be used in alkali activation process. Indeed the obtained geopolymer binders provided good chemico-physical and mechanical characteristics compared to traditional materials utilized in building construction.

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Circular economy approaches in the design of alkali-activated calcined clays

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Though alkali-activated materials have received much attention form the scientific community, they still represent a niche in terms of practical applications. One of the factors limiting the use of such materials, along with the lack of standards and regulations, is the economic and ecological cost associated with the alkaline activators. Therefore, strategies that envisage a minimisation of the activator content may likely contribute to unlocking access to the market for these materials.
In this contribution, we assess a strategy aimed at mitigating the ecological footprint and cost of alkali-activated calcined clay formulations containing secondary calcium carbonate (SCC) powder derived from marble quarrying, cutting and polishing, which constitutes a potentially hazardous waste. The rationale for this approach is concurrently reducing the amount of alkaline activator along with the fraction of silico-aluminates (here metakaolinite) replaced by SCC.
Fresh and hardened properties, as well as microstructural and compositional features of alkali-activated calcined clay soils, containing variable quantities of SCC, are studied in detail. Our findings suggest that additions of up to 30 wt.% SCC can improve the strength and other properties of alkali-activated calcined clays. The observed limited reactivity of SCC suggests that $CaCO_3$ particles mainly act as micro-aggregates, possibly enhancing particle packing.
The benefit deriving from the use of SCC from marble quarrying (and, more in general, waste slurries from the dimension stone industry) can be summarised in:
a) reduced amount of alkaline activator, leading to reduced cost and CO_2 footprint; b) lower amount of material (clay) needing thermal treatment, leading to energy savings; c) valorisation of waste streams from dimension stone quarrying and processing.

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Geopolymers-based application for the up-cycling utilization of Construction and Demolition Waste from the 2016 Central Italy earthquakes

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Construction and demolition waste (CDW) accounts for more than one third of the total amount of waste produced in the EU. In Central Italy, following the 2016 earthquakes which produced huge amounts of rubble, the lack of CDW recycling is putting at risk the process of building demolition/reconstruction, due to CDW accumulation. This area will become the largest building reconstruction site in Europe for many years, calling therefore for testing new ways of CDW recycling and production of new green materials, in view of the EU Green Deal and circular economy regulations.

CDW recycling is a complex problem, given its extreme heterogeneity, which normally precludes recycling processes other than as backfilling or as concrete aggregate. Its nature depends on many factors, such as the type, age and architectural style of the buildings, the geographical area and geology and availability of construction materials.

In this study, we tested the possibility to use CDW in geopolymer-based mortars, for upcycling applications in the building sector, like blocks and tiles. In order to elucidate the mineralogical and chemical composition, CDW samples have been preliminary characterised by X-ray diffraction (XRD) and X-ray fluorescence (XRF), respectively. CDW grainsize was selected, using a granulometric curve with clasts <2mm.

Geopolymer-based mortars have been produced with the objective to introduce a minimum of 55 wt.% CDW in a geopolymer matrix, in order to assure a good proportion of waste incorporation into new materials. Different precursors like metakaolin or fly-ash (added to K_2SiO_3 or Na_2SiO_3 solutions) will contribute to increase the possible amount of waste introduced (up to 20 wt.%). Preliminary tests show results very promising in terms of materials characteristics for possible applications. Mechanical properties were obtained according to EN standards for cement, with tests carried out at 7 and 28 days. Flexural tests and compression tests results are comparable to those of ordinary cement mortars. Microstructural observation of aggregate shape, grain-to-matrix contacts and porosity have been characterized by optical microscopy, Scanning Electron Microscopy (SEM) and image analysis. Macro-porosity is less than 4 vol.% and is characterized by spherical pores not connected with each other. Density and water absorption have been determined and compared to other geopolymer-based materials and cement mortars.

The results revealed that CDW can be recycled using geopolymers for upcycling products and that the new materials are suitable for application in the building sector.

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Fiber composite geopolymers using Mt. Etna volcanic ash as precursor

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In the last years, a particular attention has been paid to “green” materials. Among these there are geopolymers, inorganic polymeric materials obtained by mixing a solid aluminosilicate precursor with an alkaline solution [1]. They represent innovative products in terms of recycling and sustainability since their synthesis is carried at low temperature and involves the re-use of waste materials from human activity [2]. These products are largely used in the cultural heritage field due to their rapid installation, light weight, low impact on the original geometry of the substrate and the possibility of controlling their density and texture according to each specific requirement [3]. Recent innovations in geopolymer technology have led to the development of fiber reinforced composite geopolymers. The addition of different types of fibers, both organic or inorganic, is proved to increase mechanical properties such as tensile and flexural strength [4].
This study was carried out within the project “Advanced Green Materials for Cultural Heritage” (AGM for CuHe), carried by the University of Catania, which aims to use and valorise local raw materials as precursors to produce geopolymers. This study focused on analysing the structure and the mechanical properties of fibre reinforced geopolymer made using Mt. Etna volcanic ash as precursor and adding organic local prickly pear fibres. The samples obtained were analysed under scanning electron microscope (SEM/EDS) to evaluate both the amorphous gel formation and the adhesion of geopolymer matrix to the natural fibres net. Compressive and flexural strength were tested in order to compare the mechanical properties of geopolymer composites both with and without fibers. The addition of fibres is expected to enhance the brittle failure mode of geopolymer binders, reducing the shrinkage and leading up to an improvement in terms of durability of the system, which is highly demanded in the delicate question of Cultural Heritage preservation.
The AGMforCuHe project is acknowledged for its financial support (PNR 2015-2020, Area di Specializzazione “Cultural Heritage” CUP E66C18000380005).

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