# Development of reinforced alkali activated materials for cultural heritage restoration

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## INTRODUCTION

The growing need to mitigate $CO_2$ emissions coming from the construction and restoration fields has improved the development of sustainable alternatives to Ordinary Portland Cement (OPC) (Colglazier, 2015). Alkali Activated Materials (AAMs) and geopolymers represent a viable solution, offering a significantly lower carbon footprint and high physical-mechanical and chemical resistance (Provis, 2018). AAMs are a sustainable class of inorganic polymers which comes from the reaction between an aluminosilicate precursor and an alkaline solution (Davidovits, 1991). Taking into account the circular economy principles, this research focuses on the valorisation of industrial waste materials coming from the rock processing sector. Specifically, Granophyre Sawing Waste (GSW) and Basalt Sawing Waste (BSW) were selected as aluminosilicate precursors. These sludges, traditionally treated as waste and disposed of in landfills, are valorised through alkaline activation to generate high-performance binders. Despite their environmental advantages, alkali activated binders often exhibit a brittle failure behaviour, which may limit their application in strengthening interventions where tensile stresses and crack control are critical (Nawaz et al., 2020). To overcome these limitations, this study explores the reinforcement of the materials using both local natural and synthetic fibres, ensuring chemical stability and compatibility with historical substrates. The addition of fibres is proven to reduce crack propagation (*i.e.*, limiting the widths and expansion of cracks), resulting in enhanced physical and mechanical properties (Korniejenko et al., 2016). The incorporation of these fibres aims to improve the overall performance for structural restoration and conservation of cultural heritage in seismic-prone areas.

The first part of this study is mainly devoted to the analysis of the raw precursors and on the characterization of reinforced and un-reinforced materials from the mineralogical, chemical, thermal, rheological and physical-mechanical point of view. Finally, three case studies are represented in order to assess the practical application of the studied materials across three different advanced application scenarios: statistical formulation optimization by using Design of Experiments (DoE), the development of binary potassium-based binders incorporating volcanic ash and waste glass, and the rheological investigation of the slurry pastes for automated layer-by-layer extrusion (3D printing). This study aims to lay the foundation for the valorisation of industrial waste through advanced materials engineering and proposes a comprehensive framework for low-carbon structural strengthening and cultural heritage preservation in seismic-prone areas.

## METHODS

A multi-analytical approach was used in order to systematically link the chemical and mineralogical aspects of the raw precursors with the physical-mechanical performances of the consolidated binders. Raw material and binder characterizations were carried out by using X-ray Fluorescence (XRF) for bulk chemistry. X-ray Powder Diffraction (XRD) combined with an internal ZnO standard enabled the phase quantification and monitoring of the amorphous and crystalline phase evolution. Fourier-Transform Infrared Spectroscopy (FT-IR) identified shifts in Si–O–Si and Si–O–Al asymmetric stretching vibrations, which are indicative of polycondensation degree. Microstructural morphology and fibre-matrix interfacial adhesion were evaluated via Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS). Moreover, the rheological properties of fresh pastes were evaluated using a Haake Mars III rotational rheometer, to establish yield stress, structural build-up, and viscosity recovery curves. Finally, the hardened properties of the consolidated specimens were investigated by compressive and flexural strength testing after 28 curing days, porosity measurements, and accelerated freeze-thaw durability cycles in climatic chamber.

## RESULTS

The experimental investigation demonstrated that both granophyre sawing waste (GSW) and basalt sawing waste (BSW) can be successfully valorised as precursors for the production of alkali activated materials suitable

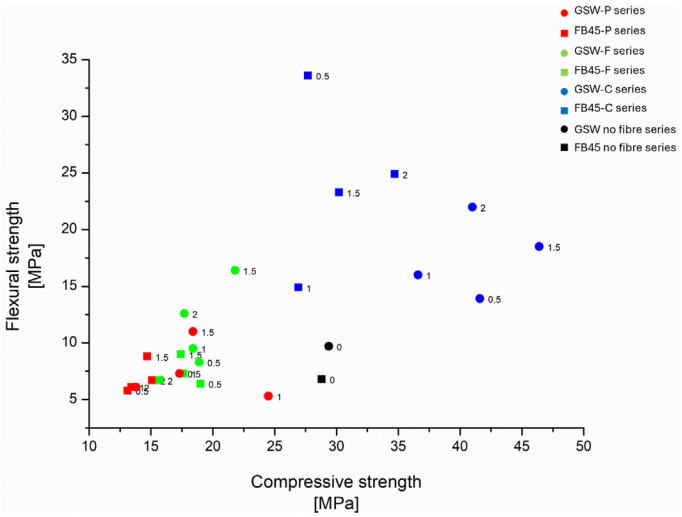


***Figure 1*** *Flexural vs compressive strengths of specimens based on granite (GSW) and basalt (FB45) sawing wastes unreinforced and reinforced (F – prickly pear fibres, P – palm fibres, C – Carbon fibres).*

for cultural heritage restoration applications. Due to the crystalline nature of the precursors, the incorporation of metakaolin was necessary to significantly enhanced the reactivity of the systems and balance the $SiO_2/Al_2O_3$ and $Na_2O/Al_2O_3$ molar ratios, which are crucial for the kinetics of the polymerization reaction (Elimbi et al., 2011). The incorporation of metakaolin promotes the formation of a stable amorphous aluminosilicate gel network, resulting in consolidated materials with satisfactory mechanical performance and durability. Quantitative phase analysis with Rietveld method, calibrated with a 5 wt.% ZnO internal standard (Tassew et al., 2014), demonstrated that exposing these blended precursors to highly alkaline sodium hydroxide and sodium silicate solutions induces dissolution of the silicates, followed by the nucleation of a disordered sodium aluminosilicate hydrate (N–A–S–H) gel network. Among the investigated formulations, the mixture containing 60 wt.% metakaolin and 40 wt.% granophyre sludge showed the best overall balance between chemical stability and amorphous phase development and compressive strength (*i.e.*, ~ 30 MPa), while basalt-based binders exhibited comparable mechanical behaviour (*i.e.*, ~ 29 MPa) together with a more homogeneous microstructure. Both systems displayed typical thixotropic and shear-thinning rheological behaviour, while maintained good resistance to freeze–thaw cycles (*i.e.*, average mass loss of 10 wt.%). To address the brittle failure mechanisms, the research extensively investigated the mechanical effects of the addition of different percentages (*i.e.*, from 0.5 to 2 wt.%) of local natural (palm and prickly pear tree) and synthetic carbon fibres into the matrix. The fibre-reinforcement proved its effectiveness in incorporating carbon fibres to improve both compressive and flexural strength, whereas natural fibres derived from palm tree and prickly pear plants produced more variable results due to the increase in porosity associated with their morphology (Fig. 1).

SEM-EDS analysis provided microstructural evidence that this macroscopic behaviour is governed by an interfacial transition zone between the binder matrix and the fibres. The fibres effectively act as crack-bridging elements, deflecting micro-cracks and absorbing tensile stresses by controlled debonding and fibre pull-out phenomena (He et al., 2018) (Fig. 2).

The first case study implemented the Design of Experiments (DoE) statistical model using response surface methodology to mathematically model the formulation behaviour. The DoE approach allowed

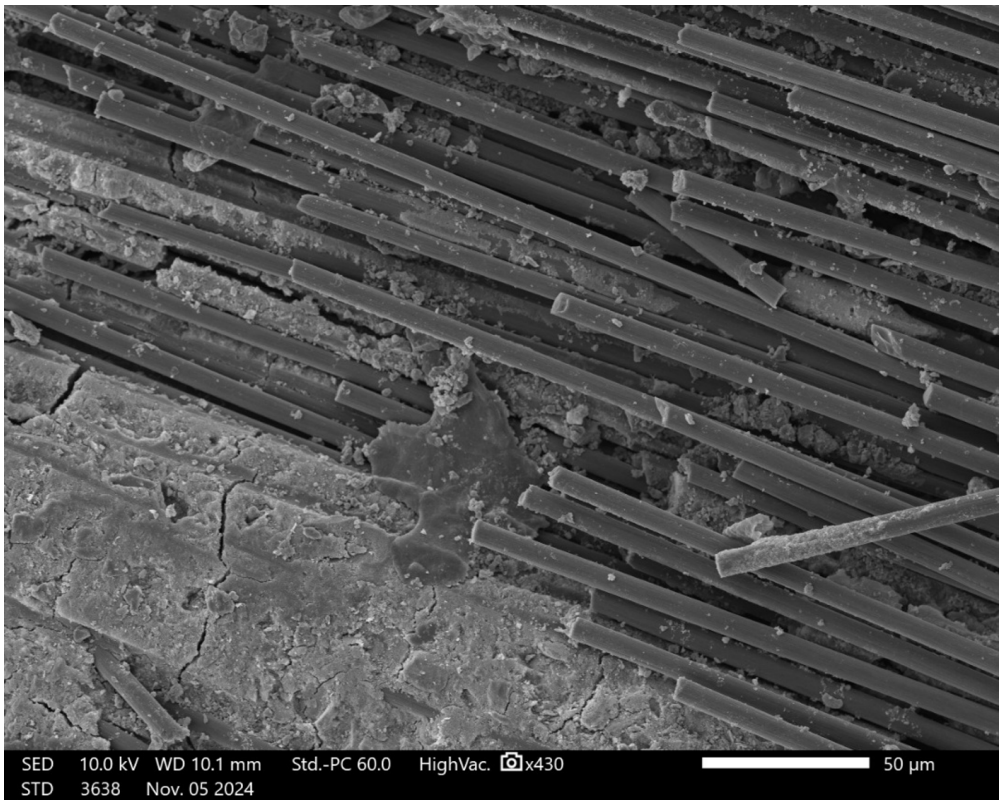


***Figure 2*** *SEM micrograph of GSW-based specimens reinforced with carbon fibres.*

*Table 1 Experimental Compressive Strength values of predicted formulations and the experimental values obtained after testing.*

| ID RUN | Predicted formulation | | | | Predicted compressive strength [MPa] | | | Experimental compressive strength [MPa] |
|---|---|---|---|---|---|---|---|---|
| | FB [%] | MK [%] | NaOH [%] | $Na_2SiO_3$ [%] | Low | Average | High | |
| PRED1 | 48 | 20 | 10 | 22 | 24.8 | 27.0 | 29.2 | 27.4 ± 1.7 |
| PRED2 | 60 | 15 | 10 | 15 | 20.2 | 23.5 | 26.8 | 19.7 ± 1.6 |
| PRED3 | 62 | 10 | 8 | 20 | 22.3 | 25.4 | 28.6 | 25.8 ± 2.9 |
| PRED4 | 58 | 15 | 10 | 17 | 20.9 | 23.7 | 26.4 | 24.4 ± 1.0 |
| PRED5 | 57 | 18 | 9 | 16 | 20.2 | 22.9 | 25.6 | 20.7 ± 2.8 |

to successfully predict the compressive strength (Table 1) and ion conductivity in water (*i.e.*, index of the chemical stability of the materials), confirming the reliability of statistical modelling for mix-design optimisation and substituting traditional empirical trial and error approaches with a mathematically validated optimization protocol.

The second case study explored potassium-based binders produced from volcanic ash from Mount Etna and waste glass. The interaction between the two powdered precursors and the potassium hydroxide solution developed dense and highly polymerised microstructures, especially when higher KOH molarity and larger glass fractions were employed, resulting in improved physical-mechanical properties (Table 2).

In fact, comparing the 7M and 9M KOH activator solutions, the quantitative mineralogical calculations and open porosity measurements revealed that the 9M-based specimens have an enhanced cross-linking compared to the 7M-based potassium aluminosilicate gel (K–A–S–H). This highly consolidated and dense microstructure exhibited a reduced porosity, which is linked to the improved mechanical strengths and enhanced durability when exposed to aggressive environments (*i.e.*, boiling test). Finally, the third case study explored the rheological properties of the slurries based on volcanic ash and waste glass for additive manufacturing 3D printing techniques. An advanced rotational rheometer was used to evaluate the critical viscoelastic properties including static and dynamic yield stress thresholds, structural build-up kinetics, and viscosity recovery parameters. The storage modulus (G') and loss modulus (G'') under oscillatory shear revealed a highly responsive thixotropic breakdown within the slurry molecules, allowing smooth extrusion through the printing

*Table 2 Physical-Mechanical properties of volcanic ash and waste glass-based consolidated materials: weight loss after boiling test (ΔM, %); open porosity (OP, %); total porosity (TP, %); pH; uniaxial compressive strength (σ, MPa).*

| Sample | ΔM [%] | OP [%] | TP [%] | pH | σ [MPa] |
|---|---|---|---|---|---|
| VG1.5(7) | 10.2 | 24 | 24.7 | 12.6 | 21 ± 1 |
| VG1.5(9) | 6.6 | 20 | 21 | 12.7 | 23 ± 2 |
| VG4(7) | 15.2 | 21.5 | 24.7 | 12.6 | 10 ± 2 |
| VG4(9) | 9.1 | 20.2 | 21.8 | 12.8 | 13 ± 2 |
| G(7) | 6.4 | 17.1 | 18 | 12.2 | 12 ± 1 |
| G(9) | 4.9 | 14.5 | 16 | 12.1 | 36 ± 3 |

nozzle, followed by an immediate structural rebuilding post-extrusion. This rapid viscosity recovery ensures that the extruded inks have sufficient static yield stress to sustain the load of the subsequently stacked layers without implying structural layer collapse (Fig. 3).

This characterization demonstrated that the development of alkali activated inks have suitable viscosity recovery, structural build-up and printability properties for 3D-printing applications.

## DISCUSSION

The results confirm the potential of industrial stone processing wastes as sustainable alternatives to conventional cementitious materials (*i.e.*, Ordinary Portland Cement), supporting circular economy principles while reducing dependence on virgin raw materials. Moreover, the critical role played by precursor composition in determining the performance of the developed alkali-activated binders was demonstrated. The limited intrinsic reactivity of the waste precursors was overcome through the addition of metakaolin, which promotes the dissolution of aluminosilicate species and the subsequent formation of a well-consolidated aluminosilicate network (Li et al., 2023). The progressive increase in metakaolin content not only enhanced the extent of the polymerisation reaction but also contributed to the development of a denser and more homogeneous microstructure, which was reflected in the improved mechanical performance observed for the optimised mixtures (Granizo et al., 2007).

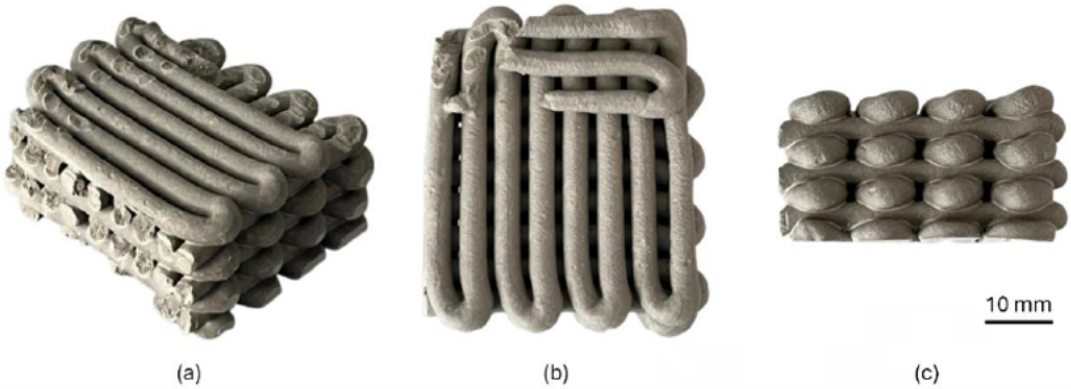


*Figure 3 3D printed specimens: whole specimen **(a)**; top view **(b)**; side view **(c)**.*

In particular, the superior behaviour of the formulation containing 60 wt.% metakaolin and 40 wt.% granophyre sludge suggested that an appropriate balance between reactive and less reactive phases is essential to maximise strength development while maintaining chemical stability. A comparison between the granophyre- and basalt-based systems revealed that, despite their different mineralogical compositions, both wastes can successfully participate in alkali activation processes and generate materials suitable for restoration applications. However, the distinct microstructural features observed in the two systems indicate that precursor chemistry strongly influences reaction kinetics and gel development. The basalt-based binders generally exhibited a more homogeneous matrix, whereas the granophyre-based formulations showed a greater sensitivity to precursor proportions and activator efficiency. These findings underline the importance of tailoring mix designs to the specific characteristics of locally available waste materials rather than applying a universal formulation. Moreover, the choice of the alkaline activator plays a crucial role in the final properties of the consolidated materials: the potassium-based solutions promote the stabilization of the aluminosilicate network by balancing the negative charges of $AlO_4^-$ tetrahedra, resulting in the formation of cross-linked aluminosilicates and a denser gel network with superior thermal stability (Christophliemk et al., 2022). The fibre reinforcement proved to be a critical parameter in tailoring material performance: carbon fibres enhanced strength and reduced the brittleness typically associated with alkali-activated systems (Kumar Gupta et al., 2022), whereas natural fibres offered a more environmentally friendly option but were better suited to non-structural applications due to their influence on porosity and mechanical response (Madueke et al., 2023). The case studies further demonstrate the versatility of alkali activated materials. The successful implementation of the DoE method indicates that predictive statistical tools can significantly reduce experimental effort while maintaining reliable performance predictions (Venkatesan et al., 2019). The study on the development of volcanic ash and waste glass-based binders showed that the careful control on the activator concentration and precursor ratios directly influences the microstructural evolution and mechanical behaviour. Finally, the rheological study highlighted the compatibility of these waste-derived binders with the emerging technologies, opening new opportunities for sustainable construction and restoration practices.

## CONCLUSIONS

This doctoral research has demonstrated that alkali activated materials derived from industrial waste, with particular attention to granophyre and basalt sawing sludges, can satisfy both environmental, mechanical and technological requirements. These materials can represent efficient alternatives to Ordinary Portland Cement (OPC), addressing the urgent need for ecological transition within the cultural heritage restoration and the construction fields. The results demonstrated that both wastes can be successfully incorporated into alkali activated systems when combined with metakaolin, leading to the formation of stable aluminosilicate networks and mechanically resistant binders. Among the investigated formulations, the mixtures containing higher metakaolin contents showed the most favourable balance between reactivity, microstructural development and strength, confirming the importance of precursor design in overcoming the limited intrinsic reactivity of crystalline industrial residues. The experimental comparison between granophyre and basalt-based systems further underlined the adaptability of alkali activation technologies to different locally available waste sources, suggesting that material formulations can be tailored according to resource availability. The three case studies expanded the scope of the investigation and demonstrated the versatility of alkali activated materials across different applications. The Design of Experiments (DoE) approach proved to be an effective tool for predicting performance and supporting mix optimisation, while the volcanic ash–waste glass systems confirmed the potential of alternative waste-derived precursors for the development of high-performance binders. In addition, the rheological and printability studies showed that these materials can be adapted to emerging additive manufacturing technologies, opening new possibilities for sustainable construction and restoration practices. In conclusion, the study proved that alkali activated materials derived from industrial residues represent a promising pathway towards more sustainable and resource-efficient construction materials. Future research will focus on long-term durability under real environmental conditions, compatibility with historic substrates, and the scale-up of production processes.

## REFERENCES

Christophliemk, M.P., Pikkarainen, A.T., Heponiemi, A., Tuomikoski, S., Runtti, H., Hu, T., Kantola, A.M., Lassi, U. (2022) - Preparation and characterization of porous and stable sodium- and potassium-based alkali activated material (AAM). Appl. Clay Sci., 230, 106697.

Colglazier, W. (2015) - Sustainable development agenda: 2030. Science, 349, 1048–1050.

Davidovits, J. (1991) - Geopolymers - Inorganic polymeric new materials. J. Therm. An., 37 1633–1656.

Elimbi, A., Tchakoute, H.K., Njopwouo, D. (2011) - Effects of calcination temperature of kaolinite clays on the properties of geopolymer cements. Constr. Build. Mater., 25, 2805–2812.

Granizo, M.L., Blanco-Varela, M.T., Martínez-Ramírez, S. (2007) - Alkali activation of metakaolins: Parameters affecting mechanical, structural and microstructural properties. J. Mater. Sci., 42, 2934–2943.

He, P., Jia, L., Ma, G., Wang, R., Yuan, J., Duan, X., Yang, Z., Jia, D. (2018) - Effects of fiber contents on the mechanical and microwave absorbent properties of carbon fiber felt reinforced geopolymer composites. Ceram. Int., 44, 10726–10734.

Korniejenko, K., Frączek, E., Pytlak, E., Adamski, M. (2016) - Mechanical Properties of Geopolymer Composites Reinforced with Natural Fibers. Procedia Eng., 151, 388–393.

Kumar Gupta, M., Singh Rajput, N., Singhal, V. (2022) - Applications and Challenges of Carbon-fibres reinforced Composites: A Review. Evergreen, 9, 682–693.

Li, L., Xie, J., Zhang, B., Feng, Y., Yang, J. (2023) - A state-of-the-art review on the setting behaviours of ground granulated blast furnace slag- and metakaolin-based alkali-activated materials. Constr. Build. Mater., 368, 130389.

Madueke, C.I., Mbah, O.M., Umunakwe, R. (2023) - A review on the limitations of natural fibres and natural fibre composites with emphasis on tensile strength using coir as a case study. Polym. Bull., 80, 3489–3506.

Nawaz, M., Heitor, A., Sivakumar, M. (2020) - Geopolymers in construction - recent developments. Constr. Build. Mater., 260, 120472.

Provis, J.L. (2018) - Alkali-activated materials. Cem. Concr. Res., 114 40–48.

Tassew, S.T., Lubell, A.S. (2014) - Mechanical properties of glass fiber reinforced ceramic concrete. Constr. Build. Mater., 51, 215–224.

Venkatesan, M., Zaib, Q., Shah, I.H., Park, H.S. (2019) - Optimum utilization of waste foundry sand and fly ash for geopolymer concrete synthesis using D-optimal mixture design of experiments. Resour. Conserv. Recycl., 148, 114–123.