

Synthesis of geopolymers as sustainable materials for applications in Cultural Heritage

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Abstract – Recently, the studies on the possible applications of geopolymers as a sustainable alternative to the traditional concretes and consolidants increased considerably in many fields such as Cultural Heritage. The potentialities linked to their production concern the lower CO₂ emissions, the possibility to reuse processing waste and the encouraging results in durability, chemical stability, and mechanical resistance. In this work, an industrial silt, a waste product of quarry rocks washing, was recycled in the synthesis of a series of Na-polysialate (siloxo) geopolymer concretes. The mechanisms of synthesis of metakaolin-based geopolymers were investigated, along with the influence of water content, described by the molar ratio H₂O/Na₂O, on the final product. The results obtained suggest that all the activating solutions effectively produced a reaction between the precursor and the activators, developing different geopolymers, but only the compositions with a low water content achieved the expected high compressive resistance qualities.

I. INTRODUCTION

In recent decades, an apparent acceleration in the rate of stone decay related mainly to the air pollution and the growing worldwide interest in preserving historic structures are promoting a significant increase in the number of studies addressed to conservation and restoration [1].

Moreover, considering the spreading of attention towards the new approaches based on the sustainability of the interventions and the growing environmental consciousness, the research is focused on the formulation of smart and innovative products able to provide high performances, being multi-tasking, eco-compatible and safe for the people's health.

Over the years various materials have been tested evaluating their efficiency and suitability for Cultural Heritage such as nanoparticles mixed with different compounds to produce self-cleaning, protecting, consolidating or antimicrobial effects [2-4]. In addition, a highly promising class of inorganic materials alternative to traditional binders are geopolymers, which are amorphous materials obtained from the alkaline activation of an aluminosilicate source in a silicate solution [5]. This source can be from natural or waste materials with a high content of aluminium or silicon, such as slag from blast furnaces from steel mills, clays, flying and volcanic ashes [6].

The advantages of geopolymers consist of a “low carbon” footprint in their production, an improvement in mechanical properties and resistance to decay processes, the absence, or just small quantities of water in the formulation for specific products [7] (important in the restoration field), the possibility to combine geopolymers in the manufacturing processes of mortars aimed at restoration practices [8].

In this paper, a waste industrial silt, a product of quarry rocks washing, was used in the synthesis of four series of Na-polysialate(siloxo) geopolymer concretes, in order to evaluate the enhancements in mechanical properties and the rate of efficiency of the polymerization process. The geopolymer binders were produced according to the molar ratios and procedures described in the work of [9].

II. MATERIALS AND METHODS

The materials used in the geopolymerization synthesis consist of metakaolin (as precursor), silt (as additive), combined with an alkali activating solution of sodium hydroxide and sodium disilicate.

Metakaolin is the commercial product Metamax (BASF SE Ludwigshafen, Germany), a very reactive metakaolin

as recently shown by [10], which was obtained through calcination of pure kaolinite at 850°C for 5 hours. It shows an intense white colour and a very fine granulometry. The composition expressed in weight percent is reported in Tab. 1.

Table 1. Composition of the commercial metakaolin Metamax.

Oxides	Wt. %
SiO ₂	52
Al ₂ O ₃	45
Na ₂ O+K ₂ O	0.37
TiO ₂	1.60
Fe ₂ O ₃	0.42
CaO+MgO	0.08
LOI	0.79

The silt is a waste obtained from a washing process during the production of aggregate materials. The washed substances are pumped out of the plant and stored in a sedimentation lake. For the current study, the silt was previously excavated from S.A.P.A.B.A. s.r.l. sedimentation lakes (Bologna, Italy) and characterized by X-ray diffraction (XRD). The composition is reported in [11]. Overall, quartz, calcite, are present such as main phases, followed by phyllosilicates such as chlorite, kaolinite/serpentine, illite/mica, and finally albitic feldspar, K-feldspar, and rare dolomite.

Sodium hydroxide (NaOH) (commonly called caustic soda) has been used in pellets with a 98% purity and negligible traces of potassium (K <0.02%), distributed by Honeywell Fluka®.

Liquid Sodium Disilicate is another alkaline activator, used to prepare geopolymers by mixing it with NaOH and water. The solution used has been produced and distributed by Ingessil SRL, with a concentration equal to 48%: this concentration, and hence the amount of water, is important for the consequent stoichiometric evaluation of the geopolymers synthesis in this work.

Na-polysialate(siloxo) geopolymer concretes were produced according to the molar ratios H₂O/Na₂O and procedures described in the work of [9].

A. Preparation of the concretes

The molar ratios of the different components have been selected considering [9] and reported in Table 2. Then,

four series of binders were synthesized (Table 3). Every series consist of six samples where the H₂O/Na₂O molar ratio has been gradually increased.

Table 2. Molar ratios applied in the synthesis of geopolymers concretes compared with the main ranges of [9].

Molar Ratios	Literature Values [9]	This Work
SiO ₂ /Al ₂ O ₃	3.5 – 4.5	3
H ₂ O/Na ₂ O	15.0 – 17.5	17
Na ₂ O/Al ₂ O ₃	0.8 – 1.20	1.05
Na ₂ O/SiO ₂	0.20 – 0.28	0.25

Table 3. The four series distinguished based on the UCT test and the presence of silt.

Serie	UCT	Silt
G1_7d	UCT after 7 days	no
G2_28d	UCT after 28 days	no
G3_10s	UCT after 28 days	10%
G4_20s	UCT after 28 days	20%

The final geopolymer concrete mixtures have been put into suitable moulds 5x5x5 cm sized and left to harden. (Fig.1).



Fig. 1. Example of samples obtained after the geopolymerization process.

In the first phase of the experimentation, uniaxial compressional test (UCT) was carried out to evaluate the mechanical resistance of the samples and to comply with concretes industry standards after seven and twenty-eight days of aging.

In details, in the first two geopolymers series (G1_7d and G2_28d), six different sets were synthesized, by gradually increasing their H_2O/Na_2O molar ratio (from 16 to 17.5, with a gradual increase of 0.3 per set).

In the G1_7d series, the mechanical properties were determined with the uniaxial compressional test (UCT) after 7 days of rest. In the second batch (G2_28d), the same geopolymer compositions were synthesized and tested on the UCT after 28 days of rest, to comply with concretes industry standards. The G3_10s and G4_20s series were geopolymer concretes with 10 wt.% and 20 wt.% of silt included in the mixture as an additive, respectively (Table 3). These fractions are calculated from the total metakaolin used to synthesize the geopolymer binder. Both batches were mechanically tested with UCT after 28 days of ageing to comply with concrete standards.

In the second step of the experimentation further analysis allowed for evaluating the performance achieved by the samples: X-ray diffraction (XRD) analysis was conducted on selected samples to identify the amorphous/crystalline species that compose them. Scanning Electron microscopy (SEM) imaging with energy dispersive X-ray spectroscopy (EDS) was carried out to study the morphology of the samples and the local chemistry, cross correlating the results with the other analyses performed.

III. RESULTS AND DISCUSSION

A. UCT test

It was overall recognized that, in the 7-days series, a water content increase seems to not have a relevant impact on the compressive resistance of the samples. The 28-days series samples are instead marked by a strong compressive resistance reduction for those with the highest H_2O/Na_2O molar ratio (17.2 and 17.5).

Furthermore, it was noted the importance of the 28-days maturation, where the compressive resistance of different specimens has been almost doubled if compared with those with only 7-days maturation, marking a similar behaviour between this innovative material and Portland concrete.

In the silt-added series the UCT carried out after 28 days of ageing, suggested how the aggregate seems to have disruptive effects on the geopolymers' compressive resistance (Fig. 2). Overall, the 20wt.% silt addition samples performed better in terms of final compressive resistance, if compared with the results of the 10wt.% series.

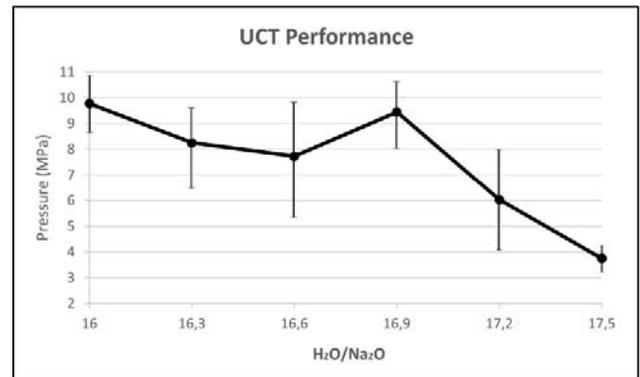


Fig. 2. UCT results for sample with 10wt.% silt after 28 days of aging, with standard deviations. The bold line highlights the trend of the resistance.

B. XRD analysis

After UCT analysis, the samples with the highest and the lowest compressive resistance by each series have been selected and undergone XRD analysis.

All the samples showed an amorphous hump between 15° to about $40^\circ 2\theta$; the presence of Anatase (TiO_2), found in the metakaolin precursor, suggesting its unreactive behaviour during the synthesis; the presence of Thermonatrite [$Na_2CO_3 \cdot (H_2O)$], a neoformation mineralogical species. This indicates that in all the samples an unreacted portion of NaOH was left and reacted with the atmosphere through carbonatation.

C. SEM-EDS analysis

Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometry (EDS) analysis were carried out on the G2_28d series, aged 28 days before the UCT analysis according to the standard of Ordinary Portland Concrete. Moreover, the samples with the highest compressive resistance of the series were selected. The SEM-EDS results suggested that:

- the samples with lower water content developed a homogeneous geopolymeric texture (Fig. 3), while those with higher water content showed instead a spongy-like texture, with extended cracks and vesicles (Fig. 4).
- Silt/geopolymer composites showed a complex fracture system developing across the interstitial transition zone (ITZ) between the geopolymer matrix and the aggregate particle, although the aggregate particles' shapes influence their development.
- EDS analysis was used to confirm the presence of the aggregate particles inside the geopolymers. In the sample with no silt addition, the EDS analysis confirmed the development of the homogeneous geopolymeric texture.

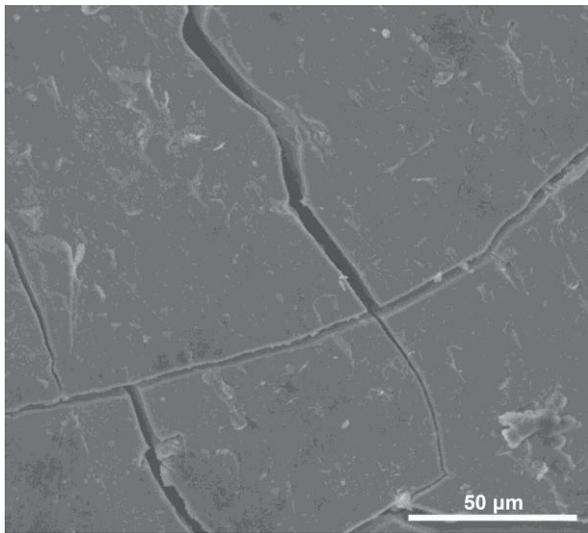


Fig. 3. Detail of the smooth and more homogeneous surface, and cracks in the G2_28d samples with low water content.

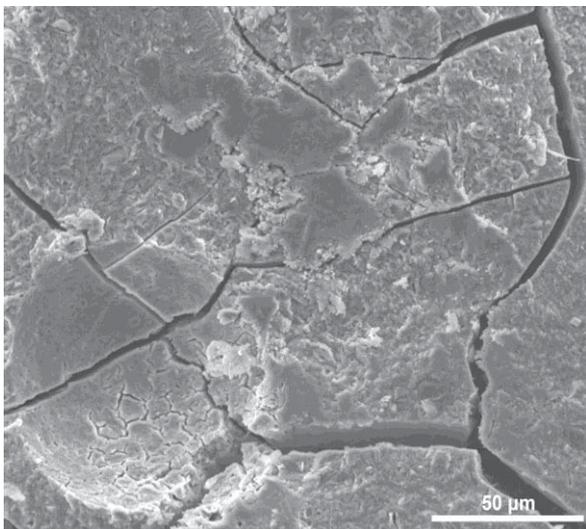


Fig. 4. Detail of the irregular surface, vesicles, and cracks in the G2_28d samples with high water content.

IV. CONCLUSIONS

The work highlighted the potentiality and the versatility of geopolymers opening to their possible use in conservation and restoration practises. In this regard, the possibility to study and to modify the geopolymerization process including also waste materials underlines the sustainability and the eco-compatibility of geopolymers based products.

The experimentation clarified the role of water in the production of Na-Polysialate(siloxo) geopolymers: there is a direct correlation between the compressive strength of the newly synthesized material and the content of water in the activating solution used to develop the geopolymerization reaction.

It must be recognized that, although with different results, all the activating solutions effectively produced a reaction between the precursor and the activators, that gave rise to different geopolymers. Among them, only low-water compositions reached the expected high compressive resistance qualities suggesting there are some problems in the polymerization reaction with high water content.

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