

INTERACTION OF METAKAOLIN-BASED GEOPOLYMERS WITH NATURAL AND ARTIFICIAL STONES AND IMPLICATIONS ON THEIR USE IN CULTURAL HERITAGE

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Abstract

Alkali activated materials, and geopolymers in particular, have proven to be a valid alternative to traditional binders, due to their significant mechanical performances, durability and environmental advantages. The present paper describes the results of a research project, initiated in order to explore the potentiality and suitability of metakaolin-based geopolymers within the domain of cultural heritage. SEM-EDS analyses were utilized in order to evaluate the interaction of geopolymers with natural and artificial stones by assessing the variations at the boundaries due to differences in the mineral-petrographic and chemical compositions of natural and artificial stones. Three ornamental stones widely used in the historic Italian architecture were selected: Pietra Serena (sandstone), Pietra di Angera (dolostone) and Pietra di Noto (limestone). Widespread construction materials, such as concrete and brick were also included in the study. Furthermore, the interaction between geopolymers and historic elements, such as decorative stones and/or mortars, were also studied, in order to evaluate a possible application of these materials within the realm of restoration, as well as for the conservation of historic manufactures. The results revealed that adhesion appears to be satisfactory in the case of all analyzed materials. Silicoaluminate phases partially dissolve and increase the availability of Si and Al within the interface, resulting in a strongly interlinked whole, whereas carbonate phases and rocks supply Ca, which changes the local composition of the binder.

Keywords: Geopolymers; Metakaolin; Cultural heritage; Ornamental stones;

Introduction

In the last decades, a range of promising new material varieties, such as the commonly designated alkali-activated materials (AAMs) [1-3] have attracted the attention of the scientific community, particularly within the field of civil engineering, due to their low carbon footprint [4], excellent mechanical properties and high resistance to heat and acids [5-9]. AAMs derived by low-in-calcium precursors are known as geopolymers (hereafter labeled GPs) [10]. Their potential applicability in the field of cultural heritage conservation has been subject to limited exploration, up until the present day. Some studies have been conducted specifically for the consolidation of terracotta structures [11], earthen architectures [12, 13] and stone conservation [14]. However, it is worth exploring whether these materials may find application for the

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conservation and treatment of both ancient and contemporary art and architecture, as well as natural and artificial stone objects. Several different applications could be suggested: alkali-activated materials could, for example, be used to patch exposed renders, fill in gaps or repoint masonry joints, but also as adhesives or sealants.

For a proper assessment of the suitability of the material subject to utilisation in the domain of cultural monument protection, it is necessary to define the elementary criteria, which must be evaluated. Naturally, the knowledge of the basic properties of the new material is the first step to be taken, and there is a substantial body of relatively recent literature, describing AAMs, of which metakaolin-based (hereafter MK) geopolymers [15-19] are most frequently described.

The materials utilized for conservation should guarantee a functional and aesthetic compatibility with the remaining materials, in addition to the construction as a whole. This compatibility depends upon the support features, hence why the mechanical compatibility should be tuned to each particular case, and material formulation must also be studied, with particular consideration placed upon how and where it is destined to be utilized. Due to the large variability and different typologies of masonry structures included in our cultural heritage, a specific knowledge of materials, both those utilized for reparations, and those which may be used for restoration purposes, is required. Different methodologies aimed at evaluating coating performances have been carried out, in order to study the interface- both on natural and artificial stones [20, 21]. The study of the interaction between new and historical materials, which include chemical, compositional and textural analyses of the boundary between the original and new material, is a fundamental prerequisite in order to assess the suitability and applicability of new restoration materials. Therefore, within the present paper, the interaction between MK-based geopolymers and different substrates has been evaluated. Three ornamental stones widely used in the historic Italian architecture have been selected: Pietra Serena (sandstone), Pietra of Angera (dolostone) and Pietra of Noto (limestone). Widespread construction materials, namely commercial cement, a variety of historical lime mortar and handcrafted red brick have also been included within the study.

Materials and methods

Materials

Three varieties of stones, widely used for decorative purposes, and representative of the historical architecture of northern, central and southern parts of Italy were utilized for this study. In addition, some common construction materials were also selected.

Pietra Serena was provided by The Casone Group of Firenzuola, Italy. It is a type of sandstone, composed of quartz (40%), feldspars (20%), calcite (10%), micas and fragments of sedimentary (mainly carbonatic), volcanic and metamorphic rocks in terrigenous matrix (30%), as observed by modal transversal section analysis. Pietra di Angera is a dolostone (of a yellow variety), composed of dolomite and subordinate clay mineral content (< 5 %). The samples used in this work come from the collection of the Department of Earth and Environment Sciences, University of Pavia. These also include a historical and decorative stone artifact, originating from the balustrade of the central courtyard of University of Pavia building, which were provided after restoration works. Blocks of Pietra di Noto, a yellowish organogenic limestone, made up of bioclasts (40%) with a micritic matrix (60%) and characterized by a high level of porosity, were made available by the Department of Civil and Environmental Engineering of the Polytechnic University of Milan. The same Department also provided a historical mortar sample. Concrete samples were obtained using starting materials provided by Holcim Ltd. Certain blocks of brick analysed within the present paper also originate from the collection of the Department of Earth and Environmental Sciences, within the University of Pavia.

The chemical compositions of all materials, as determined by FESEM-EDAX energy dispersive spectrometry (EDS), are represented in Table 1. Mineralogical descriptions of the natural stones are given in [22-30].

Table 1. Chemical compositions (wt%) of Pietra Serena, Pietra di Angera, Pietra di Noto, red brick and concrete.

Oxides	Pietra Serena	Pietra di Angera	Pietra di Angera (historic)	Pietra di Noto	Brick	Concrete
MgO	6.3(6)	33(2)	37(7)	2.1(2)	4(2)	4(3)
CaO	5(1)	64(2)	53(7)	96(1)	14(6)	46(19)
SiO ₂	59(1)	0.8(2)	1(1)	2(1)	49(5)	26(16)
FeO	6.2(5)	2.2(1)	0.5(1)	-	7(2)	8(7)
Al ₂ O ₃	16(1)	-	0.3(2)	-	21(2)	11(8)
Na ₂ O	2.9(7)	-	5(3)	-	4(2)	2(1)
SO ₃	0.5(2)	-	4(3)	-	0.5(2)	1.5(1)
K ₂ O	2.7(7)	-	0.2(1)	-	1.5(5)	0.4(2)
TiO ₂	1.4(4)	-	-	-	-	-
Total	100(1)	100(1)	100(2)	100(1)	100(2)	100(7)

Note: standard deviations are in parentheses.

Geopolymer starting materials and synthesis

Geopolymers were synthesized starting from high-quality kaolin, used as an aluminosilicate source, and a sodium silicate solution as alkaline activator. The kaolin, labeled SI-K, was supplied by Sibelco Italia S.p.A. and derives from the Seilitz kaolin deposits in Germany. It is composed of 73 wt% kaolinite and 23 wt% quartz. More information pertaining to its characterization can be found in Gasparini et al. (2015) [31]. In order to obtain the reactive metakaolin (SI-MK), the kaolin powder was heated at 800°C for 2 hours [32]. The sodium silicate solution (containing Na₂O 14.37 wt%, SiO₂ 29.54 wt%, H₂O 56.09 wt%) was provided by Ingegssil s.r.l. It was altered by adding distilled water and dissolving solid sodium hydroxide (NaOH, purity 98%), in order to obtain GP binders characterized by the following molar ratios: SiO₂/Al₂O₃ = 3.7, Al₂O₃/Na₂O = 1.04 and H₂O/Na₂O = 1. One GP binder, characterized by an H₂O/Na₂O molar ratio of 20 (hereafter labeled GP20) was prepared and used for tests, in association with the historic element made of Pietra di Angera. The SI-MK powder was then added to the alkaline solution and stirred for 10 minutes by using a mechanical mixer, in order to form a homogenous slurry. Mixing operations were performed under controlled conditions of temperature and relative humidity (20°C and 65% R.H., respectively).

Sample preparation and characterization

GP slurries were poured on material surfaces and cured in a climatic room for 28 days at 20°C and 65% R.H. before being demolded. Samples were cut and sections analyzed by using optical and electron-scanning microscopes. Microtextural investigations were performed using an Olympus SZ61 stereomicroscope. A Field Emission Scanning Electron Microscope TESCAN Mira 3 XMU-series, equipped with an EDAX energy dispersive spectrometer, was used to determine microstructural features and the gradient concentration of elements across the interfaces between materials and GP. Samples were covered by 5nm carbon coating before being investigated to prevent charge built-up on an electrically insulating sample surface. Images were collected using backscattered electrons (BSE), at a working distance of 15.8mm with an acceleration voltage of 20kV. EDS spot analyses were performed with an accelerating voltage of 20kV, working distance of 15.8mm, beam current of 20μA and spot diameter of approximately 5μm, acquiring for an analysis of 100s per spot. Chemical compositions were recalculated in order to yield 100 wt% oxide content, without taking into account H₂O and CO₂.

Results and Discussions

Stereomicroscope observations

Macroscopic structural features common to all samples can be observed from the stereomicroscope photos (Figs. 1 and 2 for natural stones and artificial building materials, respectively): the contact regions are evident and allow for a global evaluation of the interaction between the materials. In all samples, a reaction layer (labeled as “rim” in the images) is visible between the GP binder and each material. Even at such low enlargement factors, it is possible to appreciate that the binder entered the superficial porosity of the materials ensuring good adhesion between the two. In the GP matrix, it is possible to observe the unreacted metakaolin, which appears in the form of particles with a darker tone than the matrix.

At the boundary between Pietra Serena and the GP, evidence of the reaction of the stone with alkalis in the slurry is recognizable: all the superficial mineral grains have rounded, indefinite borders, thus indicating a partial dissolution during geopolymerization processes (Fig. 1a). The same border alteration is less evident in Pietra di Angera and Pietra di Noto (Figs. 1b and 1c) at this scale of observation.

Concerning the artificial building materials, a reaction layer is evident in all samples (Figs. 2a-c), and it is particularly thick between the geopolymer and lime-based mortar (Fig. 2b).



Fig. 1. Stereomicroscope images of samples prepared with natural ornamental stones: a) Pietra Serena; b) Pietra di Angera; c) Pietra di Noto. The rims are indicated by arrows.

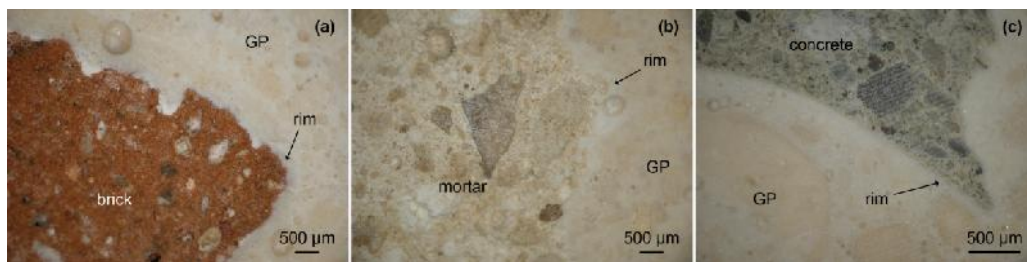


Fig. 2. Stereomicroscope images of samples prepared with artificial building materials: a) red brick; b) historic mortar; c) concrete. The rims are indicated by arrows.

SEM-EDS investigations

The microstructural features of GP binder at the interface with the different substrates have been analyzed by FE-SEM at different magnifications. The developed texture is a direct result of the chemical reaction processes responsible for geopolymer formation, in addition to the interaction with the natural and artificial substrates. Texture analysis can then be used, in order to develop a better understanding of the aforementioned reaction mechanisms, as well as providing key insights regarding the textural features of mechanical performances.

Natural stones – Pietra Serena

The interface between Pietra Serena and GP is displayed in Fig. 3a. Materials seem well bonded together. The GP binder follows the stone profile and no cracks are evident at the interface. Fractures orthogonal to interface, observed within the GP matrix, may be caused by the cutting of the specimens for metallographic preparation. The GP matrix in question possesses a quite compact microstructure, with pores of cca. 50µm in diameter. Lighter areas within the matrix are attributed to partially unreacted metakaolin.

Table 2. EDS analyses performed on samples prepared with natural stones expressed as wt%.

Point analyses	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	FeO
PS1	4.29	0.56	28.33	63.04	0.34	0.51	2.34	0.59
PS2	4.72	0.62	27.00	63.64	0.35	0.58	2.60	0.48
PS3	4.52	0.51	28.56	62.79	0.30	0.60	2.14	0.59
PS4	6.69	0.36	22.64	67.63	0.28	0.57	1.08	0.76
PA1	7.65	3.29	13.62	41.94	-	0.42	33.07	-
PA2	6.29	3.85	9.96	50.95	-	0.28	28.66	-
PA3	8.18	1.90	18.95	46.79	-	0.41	23.76	-
PA4	9.13	3.58	20.62	59.00	-	0.66	7.02	-
PA5	7.50	2.77	10.19	26.14	-	0.33	53.07	-
PA6	7.63	3.28	13.35	48.04	0.37	0.49	26.56	0.29
PA7	9.08	2.58	16.41	59.93	0.33	0.64	10.65	0.38
PA8	5.45	5.84	9.45	34.01	0.14	0.33	44.29	0.49
PAh1	14.99	1.40	16.85	59.05	3.30	0.92	3.17	0.32
PAh2	10.13	1.10	18.01	64.00	1.67	1.23	3.30	0.55
PAh3	13.01	1.09	22.64	52.50	6.79	0.85	2.49	0.62
PAh4	10.97	0.84	18.91	62.30	2.63	0.97	2.88	0.50
PAh6	10.04	0.93	11.88	69.26	3.31	0.79	3.28	0.51
PAh7	12.12	1.03	19.73	59.99	2.23	1.00	3.40	0.51
PN1	12.44	1.02	17.53	64.18	-	-	4.83	-
PN2	12.41	0.55	20.79	63.47	-	-	2.78	-
PN3	13.76	0.74	18.18	62.62	-	-	4.71	-
PN4	13.46	0.40	19.20	64.26	-	-	2.67	-
PN5	16.64	0.36	22.56	59.08	-	-	1.36	-
PN6	15.63	0.47	21.80	59.52	-	-	2.58	-
PN7	14.52	0.38	18.23	64.58	-	-	2.29	-
PN8	14.86	0.39	20.10	62.21	-	-	2.44	-
PN9	16.85	0.44	19.50	60.53	-	-	2.68	-
PN10	11.17	0.41	27.73	59.22	-	-	1.48	-

Note: labels indicate spot analyses, as displayed in Fig. 3d (PS); Figs. 4c and 4d (PA); Fig. 5b (PAh) and Fig. 6b (PN). In the case of PAh and PN, analyses are performed along the transects indicated by the red lines in the figures and go from the stone to the binder.

At a higher magnification (Figs. 3b and 3c), the interaction between siliceous aggregates and the highly alkaline solution results in a partial dissolution of quartz and mica grains, which revealed rounded and unraveled shapes, respectively. Despite this fact, no crystalline interfacial products are present, owing to the presence of an intermediate zone, which possesses a darker color in BSE images, thus suggesting a difference in terms of composition, which can be clearly seen along the contact area and for 500µm in depth into the GP matrix. This may be due to the dissolution of siliceous aggregates, which in turn modifies the SiO₂/Al₂O₃ ratio locally, whilst simultaneously promoting geopolymerization on the stone surface. Further evidence of the partial dissolution of Pietra Serena can be found in the presence of stone relicts inside the GP matrix, as displayed in Fig. 3d.

Furthermore, the EDX analyses of this area (Table 2; labels as reported in Fig. 3d) verify the presence of calcium deriving from Pietra Serena, within the GP binder. The presence of calcium may be caused by the water flow existent during the first steps of geopolymerization.

However, an average concentration of CaO wt% of less than 2.0(7) wt% is too low to favor the formation of C-S-H phases, as already indicated by Yip et al. [33], but enough to improve adhesive mechanical strength.

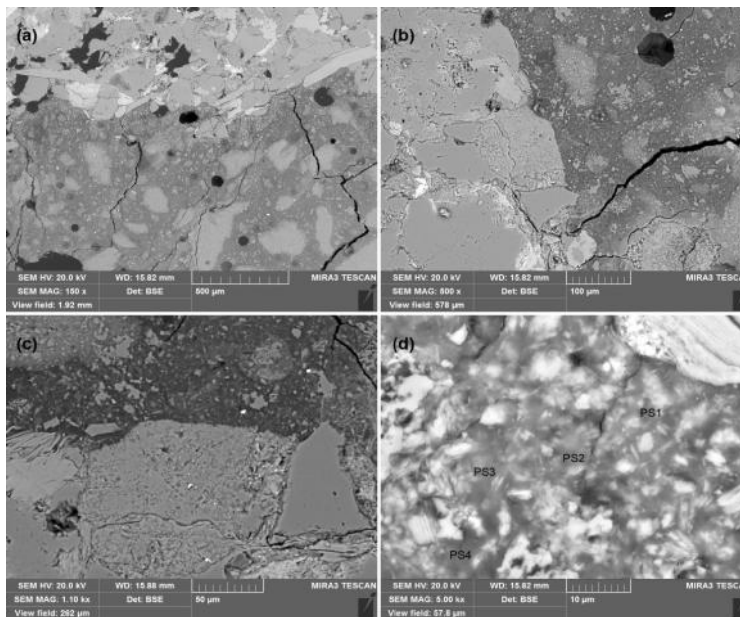


Fig. 3. FESEM micrographs of sample prepared with Pietra Serena at different magnifications: (a) 150X; (b) 500X; (c) 1100X; (d) 5000x. Labels PS1 to PS4 in Fig. 3d refer to spot analyses reported in Table 2.

Natural stones – Pietra di Angera

In Fig. 4a, one can observe how well the GP binder entered the superficial porosity of the stone, thus enhancing the contact existent between the two materials, and therefore implying a good level of adhesion between the two materials. A dark layer of approximately 50 μm developed inside the GP, once having been put into contact with Pietra di Angera, thus suggesting that the two materials reacted once they were put together. In addition, it was noted that calcium can take part in the geopolymerization process, its presence therefore affecting the final products. It is important to evaluate its concentration along the borders and especially within the reaction layer. Different features, caused by the interaction of Pietra di Angera and the GP binder can be observed in Fig. 4c. EDX semi-quantitative analyses were performed in different spots on the area in Fig. 4c and the corresponding results are reported in Table 2.

Point analyses PA1, PA2 and PA3 correspond to the reaction products. PA1 and PA2 are located on the alteration rim of a dolomite grain, whereas in the spot corresponding to PA3 the dolomite relict is no longer present, with a new round phase having taken its place. The calcium diffusion is also evident upon observing Fig. 4c, wherein calcium-rich vein is present within the geopolymer matrix. The composition of the reaction layer must be evaluated, so as to gain a better understanding of the development of new phases. In Fig. 4d, it is possible to observe the existence of a reacted dolomite grain from Pietra di Angera, which offers new reaction by-products towards the experiment. Microchemical analyses were performed on both the new phases and the area surrounding them, in order to observe how the elements' concentration varied in different areas. Results are reported in Table 2. It is therefore possible to state that dolomite, which is the main mineral phase in Pietra di Angera, reacts with the geopolymer slurry, which results in an intermediate product richer in CaO than the geopolymer surrounding the dolomite relict. A coronitic structure is also evident.

Natural stones – Historical Pietra di Angera

The interaction between a historical decorative stone element, originating from Pietra di Angera and a fluid GP binder was also evaluated. The sample was originally exposed to an outdoor environment. Chemical analyses carried out on the stone by FESEM-EDAX (Table 1) unearthed the presence of SO₃, concentrated within certain areas, a fact which may possibly refer to the chemical decay of the stone, caused by the atmospheric pollutants. Thus, polluted environments influence the conservation of carbonatic stones, therefore increasing the susceptibility to decay in outdoor conditions [34, 35]. Among pollutants, sulfurous oxides produce the sulfation of substrates, especially in the case of poor durable stones, such as Pietra di Angera [36].

The interface zone (Fig. 5a) clearly shows that the GP binder is less bonded to the stone, with regard to the sample in which the quarry element of Pietra di Angera was utilized. Furthermore, the GP matrix is widely fractured, with cracks (ranging in size from a few μm to 1-2 mm long), a fact which may be due both to the water loss during the curing, as well as the sample preparation procedures. In Fig. 5b, a transect of approximately 200 μm in length and perpendicular to the contact zone indicates the points (labeled PAh1 to PAh7 in Table 3) where microchemical analyses of the GP matrix were performed. The results therefore demonstrate the presence within the matrix of SO₃ and CaO, with values reaching an average of 3(2) wt% and 3(1) wt%, respectively. The diffusion of these elements in the matrix is attributed to the water contained in the alkaline solution, which flows through the stone pores during the first phases of geopolymerization. However, no new phases, such as thenardite or ettringite, could be observed within the binder. Therefore, sulfur may remain trapped within the amorphous network of GP gel, without giving rise to potentially harmful by-products [37]. Consequently, the trapping function of GP can be positively considered in conservation practices.

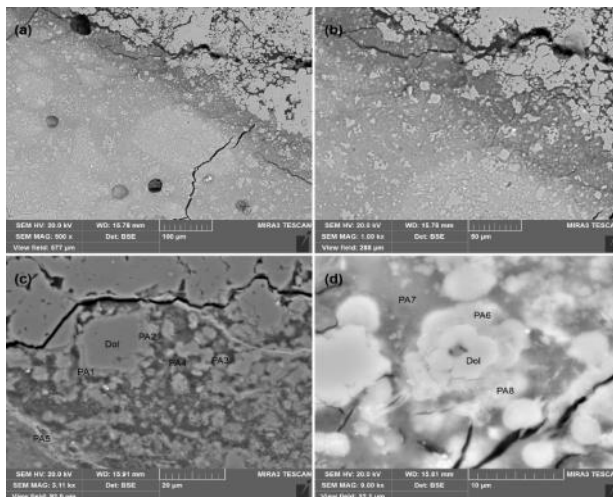


Fig 4. FESEM micrographs of sample prepared with Pietra di Angera at different magnifications: (a) 500X; (b) 1000X; (c) 3.1100X; (d) 9000X. Labels PA1 to PA8 in Figs. 4c and 4d refer to spot analyses reported in Table 2; Dol - dolomite.

Natural stones – Pietra di Noto

The interface between Pietra di Noto and GP is displayed in Fig. 6a. A good adhesion between the two materials can be observed, with the high porosity and rough profile of the stone being cited as possible causes. This therefore allows the GP binder to better permeate the stone up to a distance of 500μm from the interface, thus assuring a physical interlock and improving the adhesion between the two. Different authors relate the adhesion property to the roughness degree of the substrate [38], the porosity of the binder [39] and also the presence of

the aggregates and their morphology [40-42]. Within the realm of conservation practices, a good adhesion between substrate and binder could reduce the possibility of decay caused by water infiltration. In the present work, the high degree of porosity possessed by Pietra di Noto could increase the cohesive strength, therefore positively influencing the performance of adhesion. However, the porosity of the stone also facilitates the migration of water contained within the slurry towards the stone, therefore creating a region rich in cracks (of approximately 1mm in width) from the interface zone within the GP matrix.

The microchemical analyses of the GP matrix were performed along a 1mm long transect perpendicular to the contact zone, as shown in Fig. 6b. Analyses are reported in Table 2 and named PN1 to PN10. No reaction layers can be appreciated. A decrease in CaO wt% values from 4.8 to 1.3wt% suggests the diffusion of calcium into the matrix with the same methods as those described in the case of distinct stone varieties.

In all natural samples described above, GP contains a certain amount of calcium, despite its being synthesized from a Ca-free precursor, such as metakaolin. It was therefore established that the presence of this element within the geopolymer must have been caused by the interaction between the different carbonates contained within all the aforementioned stones and the geopolymer itself. The water contained within the geopolymer slurry allows for the migration of calcium cations from the rock towards the geopolymer. This in turn may likely affect its formation reaction and resulting mechanical and physical properties.

Furthermore, stereomicroscopic observations and elemental chemical analyses do not reveal the presence of efflorescence, either in the case of the geopolymer matrix, or in that of the stones subject to the present analysis. The use of an alkali-rich solution as an activator for geopolymerization could affect the potential applicability of GP in restoration. However, the presence of calcium within the GP gel can be of significant aid, in terms of reducing the formation of carbonates, as already noted by Najafi Kani et al. [41].

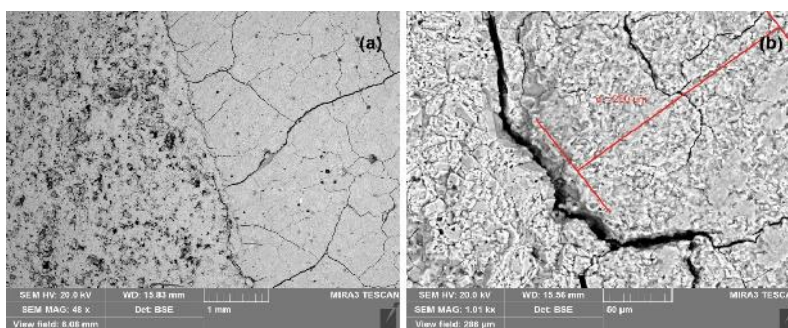


Fig. 5. FESEM micrographs of the sample prepared with the decorative element of Pietra di Angera at different magnifications: (a) 48X; (b) 1000X.

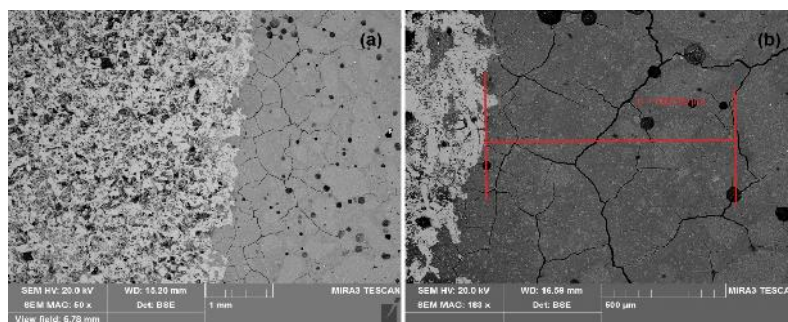


Fig. 6. FESEM micrographs of sample prepared with Pietra di Noto at different magnifications. (a) 50X; (b) 183X.

Chemical analyses along the transect shown by the red line in Figs. 5 and 6 are reported in Table 2.

Artificial construction materials – Red brick

A thin and discontinuous dark layer characterizes the interaction zone between red brick and GP binder, as shown in Fig. 7a. Fractures orthogonal and parallel to the interface are observed within the GP matrix. The former may be ascribed to the preparation of specimens for analysis; the latter are likely due to the shrinkage of the binder, caused by the migration of water from GP into the brick. In either case, in the proximity of the interaction zone, the GP matrix has a rather compact microstructure, and the rough profile of the brick facilitates adhesion between the two materials. At a higher magnification, (Fig. 7b) deteriorated and reacted crystals are evident within the interaction zone. This could either be due to the interaction with alkalis, or caused by the high temperatures during brick production processes.

Microchemical analyses were performed in the GP matrix, along the length of a 1 mm transect. The presence of aluminum and silicon within red bricks increases the SiO₂/Al₂O₃ ratio at a local scale, thus promoting the geopolymerization process in the vicinity of the interface. SiO₂/Al₂O₃ presence varies from 3.5(1) to 2.9(4), moving from interface (the darker layer) towards the GP matrix. Detected CaO wt% values vary from 2.7 wt% to 1.2 wt%, with an average value of 1.8(6) wt%. Calcium values found in this sample are lower than the ones found in other samples, prepared both with natural stones and artificial building materials.

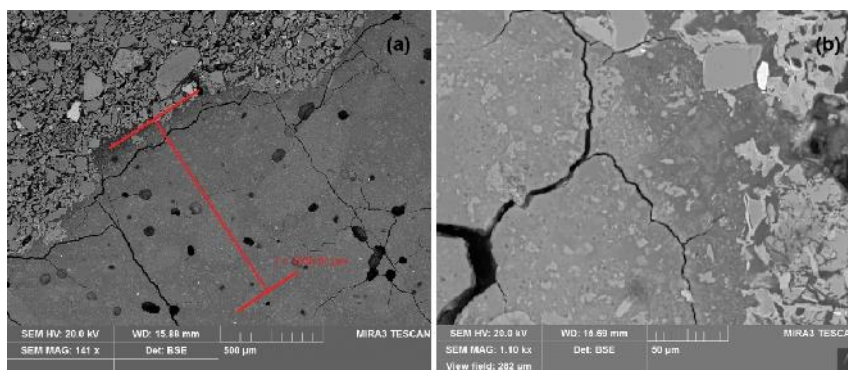


Fig. 7. FESEM micrographs of samples prepared with red brick at different magnifications: (a) 141X; (b) 1100X.

Table 3. EDS analyses performed on samples prepared with artificial building materials expressed as wt%.

Point analyses	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO
MN1	1.06	0.86	1.01	2.46	0.39	0.16	94.7
MN2	11.21	1.66	14.25	40.23	0.19	0.41	32.04
MN3	7.55	0.94	21.33	60.04	0.35	0.66	9.11
MN4	10.76	1.38	17.26	51.60	0.31	0.43	18.26
MN5	6.94	1.15	16.02	50.38	0.40	0.60	24.51
MN6	10.02	1.25	17.17	46.79	0.27	0.43	24.07
C1	9.49	3.01	19.40	58.31	0.97	0.53	8.24
C2	8.50	1.43	19.23	54.72	0.87	0.50	14.75
C3	8.08	0.98	21.80	62.62	0.94	0.54	5.03

Note: labels as in Figs. 8d (MN) and 9b (C).

Artificial construction materials – Historic Mortar

In this work, the use of historic mortar allowed for the study of the interaction of GP with the closest material in terms of properties and destination of use to be carried out. In Fig. 8a, an evident reaction layer can be observed, at the interface between the two materials. The reaction layer is continuous and runs along the contact interface. The geopolymer matrix appears homogeneous and no cracks can be observed at the interface. The texture of the geopolymer, however, changes, moving away from the mortar contact area, and becoming more homogeneous, with fewer metakaolin and mortar relicts being found inside the matrix (Fig. 8b). Observing the interface at higher magnifications (Figs. 8c and 8d), different reaction layers can be recognized. Point analyses performed in the area shown in Fig. 8d are reported in Table 3. Starting from the mortar (upper right), and continuing towards the GP, the first layer, 10 to 15 μm wide, is entirely composed of calcium carbonate (Ca is 94.07wt% at MN1), appears rather compact and homogeneous, and grows from the mortar. The precipitation of new phases is therefore caused by dissolution of the mortar by the alkaline geopolymer slurry. The second sample, 2 to 5 μm wide, is darker than the first one. The SiO_2 , Al_2O_3 and CaO concentrations, judging by the MN2 spot analysis, reveal the presence of C-A-S-H gel formed as a reaction by-product. A third reaction layer, of approximately 100 μm in size, may be found inside the GP matrix (point analyses MN3, MN4, MN5). It appears less homogeneous than the others, and mainly formed by new rounded phases. The presence of different, calcium-rich reaction layers could therefore improve the mechanical properties, in the case of any interfaces which may exist between the two materials.

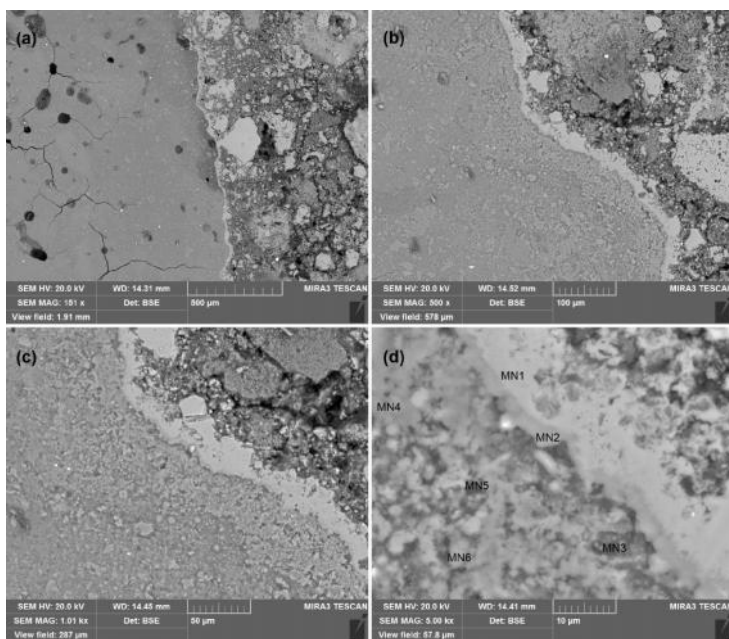


Fig. 8. FESEM micrographs of a sample prepared with a historic mortar at different magnifications: (a) 250X; (b) 644X; (c) 1100X; (d) 5000X. Labels MN1 to MN6 in Fig. 8d refer to spot analyses reported in Table 3.

Artificial construction materials – Concrete

Adhesion between geopolymer and concrete is good—as shown in Fig. 9a. There is no reaction layer between the two materials, despite the fact that the GP matrix becomes more homogeneous, once having been moved away from the concrete contact surface, therefore highlighting three distinct textural areas. However, microchemical analyses performed on three

areas of $100\ \mu\text{m}^2$ along the transect displayed in the above figure reveal no differences in terms of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. Cracks caused by the sample preparation can be noted both within the matrix and the concrete. The interaction zone was analyzed at a higher magnification (5000X) (Fig. 9b). Analyses were performed on three spots labeled C1 (close to the interface), C2 (on the brightest spot) and C3 (on the GP matrix), and reported in Table 3. According to the chemical analyses, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio remains constant, with an approximate value of 2.9(1) wt% in all points. A fairly high calcium content was observed in all analyzed points, and it affected the geopolymerization reaction in two different ways. In C1 and C2, new phases developed, characterized by rounded shapes, resembling the ones found in the third reaction layer of the sample prepared with the historic mortar. In the case of matrix (C3), calcium presence modifies the composition of the gel, which approaches that of calcium silico-aluminate hydrate (C-A-S-H) gels.

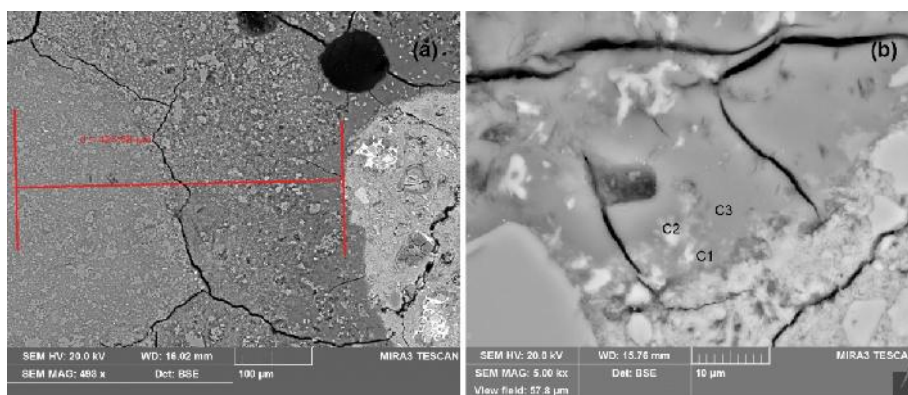


Fig. 9. FESEM micrographs of sample prepared with concrete at different magnifications: (a) 493X; (b) 5000X. Labels C1 to C8 in Fig. 9b refer to spot analyses reported in Table 3.

Conclusions

Within the present work, the interactions between metakaolin-based geopolymers and widespread materials used in cultural heritage were studied. SEM investigations allowed for the evaluation of the adhesive processes involved in the contact zones, at a short-length scale.

Adhesion at the interfaces appeared to be good for all natural stones and artificial building materials taken into consideration. A calcium carbonate layer was observed only in the case of the historic mortar, despite the fact that, in all samples, the binder contains calcium at the interface, deriving from the stones or artificial material that modified the initial geopolymer composition. The presence of calcium did not give rise to new crystalline phases, but once the binder came into contact with the historic mortar, concrete and Pietra di Angera, rounded precipitation particles could be observed. It should also be noted that the difference in crystallinity influences calcite precipitation as follows: in the case of the mortar, the reaction layer is more developed, due to the presence of microcrystalline calcite grains, which are more soluble than those of the carbonatic stones utilized in the present work. Furthermore, the different solubility in highly alkaline solutions of dolomite and calcite may influence the behavior of the Pietra di Angera and Pietra di Noto at interface level. The binding matrix of stone materials used in the experimentation was also noted to influence the properties of adhesion. An alumino-silicate matrix, such as that which exists within the Pietra Serena and in the brick seems to possess a greater physical affinity with the geopolymer binder. On the other

hand, the carbonate matrix produces a calcium-rich zone, which may likely positively affect the mechanical and physical properties obtained at the end of research.

In spite of the fact that AAMs are currently not utilized for conservation purposes, the results obtained within the present study are promising. In restoration practices, the versatility of AAMs would allow for binders with distinct characteristics to be obtained, thus increasing the compatibility with the substrate to be repaired. Our future aim is to continue the present research, by performing physical and mechanical analyses and carrying them out within the context of relevant experimentations.

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References

- [1] A. Palomo, P. Krivenko, I. Garcia-Lodeiro, E. Kavalerova, O. Maltseva, A. Fernández-Jiménez, *A review on alkaline activation: New analytical perspectives*, **Materials de Construcción**, **64**(315), 2014, pp. e022.
- [2] F. Pacheco-Torgal, J. Castro-Gomes, S. Jalali, *Alkali-activated binders: A review*, **Construction and Building Materials**, **22**(7), 2008, pp. 1305-1314.
- [3] J.L. Provis, A. Palomo, C. Shi, *Advances in understanding alkali-activated materials*, **Cement and Concrete Research**, **78**, 2015, pp. 110-125.
- [4] J.S.J. Van Deventer, J.L. Provis, P. Duxson, *Technical and commercial progress in the adoption of geopolymer cement*, **Minerals Engineering**, **29**, 2012, pp. 89-104.
- [5] A. Palomo, M.T. Blanco-Varela, M.L. Granizo, F. Puertas, T. Vazquez, M.W. Grutzeck, *Chemical stability of cementitious materials based on metakaolin*, **Cement and Concrete Research**, **29**(7), 1999, pp. 997-1004.
- [6] T. Bakharev, *Resistance of geopolymer materials to acid attack*, **Cement and Concrete Research**, **35**(4), 2005, pp. 658-670.
- [7] T. Bakharev, *Durability of geopolymer materials in sodium and magnesium sulfate solutions*, **Cement and Concrete Research**, **35**(6), 2005, pp. 1233-1246.
- [8] J. Temuujin, W. Rickard, M. Lee, A. van Riessen, *Preparation and thermal properties of fire resistant metakaolin-based geopolymer-type coatings*, **Journal of Non-Crystalline Solids**, **357**(5), 2011, pp. 1399-1404.
- [9] C. Shi, A.F. Jiménez, A. Palomo, *New cements for the 21st century: The pursuit of an alternative to Portland cement*, **Cement and Concrete Research**, **41**(7), 2011, pp. 750-763.
- [10] J.L. Provis, S.A. Bernal, *Geopolymers and Related Alkali-Activated Materials*, **Annual Review of Materials Research**, **44**(1), 2014, pp. 299-327.
- [11] T. Hanzlí ek, M. Steinerová, P. Straka, I. Perná, P. Siegl, T. Švarcová, *Reinforcement of the terracotta sculpture by geopolymer composite*, **Materials & Design**, **30**(8), 2009, pp. 3229-3234.
- [12] K. Elert, E.S. Pardo, C. Rodriguez-Navarro, *Alkaline activation as an alternative method for the consolidation of earthen architecture*, **Journal of Cultural Heritage**, **16**(4), 2015, pp. 461-469.

- [13] K. Elert, E. Sebastián, I. Valverde, C. Rodriguez-Navarro, *Alkaline treatment of clay minerals from the Alhambra Formation: Implications for the conservation of earthen architecture*, **Applied Clay Science**, **39**(3-4), 2008, pp. 122-132.
- [14] S. Rescic, P. Plescia, P. Cossari, E. Tempesta, D. Capitani, N. Proietti, F. Fratini, A.M. Mecchi, *Mechano-chemical activation: an ecological safety process in the production of materials to stone conservation*, **Procedia Engineering**, **21**, 2011, pp. 1061-1071.
- [15] A.M. Rashad, *Alkali-activated metakaolin: A short guide for civil Engineer – An overview*, **Construction and Building Materials**, **41**, 2013, pp. 751-765.
- [16] F. Pacheco-Torgal, D. Moura, Y. Ding, S. Jalali, *Composition, strength and workability of alkali-activated metakaolin based mortars*, **Construction and Building Materials**, **25**(9), 2011, pp. 3732-3745.
- [17] H. Wang, H. Li, F. Yan, *Synthesis and mechanical properties of metakaolinite-based geopolymer*, **Colloids and Surfaces A: Physicochemical and Engineering Aspects**, **268**(1-3), 2005, pp. 1-6.
- [18] P. Duxson, S. Mallicoat, G. Lukey, W. Kriven, J.S. van Deventer, *Microstructural Characterisation of Metakaolin - Based Geopolymers*, **Advances in Ceramic Matrix Composites X**, **165**, 2005, pp. 71-85.
- [19] F. Pelisser, E.L. Guerrino, M. Menger, M.D. Michel, J.A. Labrincha, *Micromechanical characterization of metakaolin-based geopolymers*, **Construction and Building Materials**, **49**, 2013, pp. 547-553.
- [20] G. Cappelletti, P. Fermo, M. Camiloni, *Smart hybrid coatings for natural stones conservation*, **Progress in Organic Coatings**, **78**, 2015, pp. 511-516.
- [21] G. Cappelletti, P. Fermo, F. Pino, E. Pargoletti, E. Pecchioni, F. Fratini, S.A. Ruffolo, M.F. La Russa, *On the role of hydrophobic Si-based protective coatings in limiting mortar deterioration*, **Environmental Science and Pollution Research**, **22**, (2015), pp. 17733-17743.
- [22] G.M. Bargossi, F. Gamberini, G. Gasparotto, G.C. Grillini, M. Marocchi, *Dimension and ornamental stones from the Tosco-Romagnolo and Bolognese Apennine*, **Periodico di Mineralogia**, **73**(Special Issue 3), 2004, pp. 171-195.
- [23] E. Cantisani, C.A. Garzonio, M. Ricci, S. Vettori, *Relationships between the petrographical, physical and mechanical properties of some Italian sandstones*, **International Journal of Rock Mechanics and Mining Sciences**, **60**, 2013, pp. 321-332.
- [24] V. Riganti, R. Rossetti, F. Soggetti, F. Veniale, U. Zezza, *Alterazione e protezione delle pietre dei monumenti storici dell'Università di Pavia*, **Atti Società Italiana Scienze Naturali**, **119**(1), 1978, pp. 85-109.
- [25] A. Fiumara, V. Riganti, F. Veniale, U. Zezza, *On the preservation treatments of the Angera stone*, **Geologia Applicata e Idrogeologia**, **14**, 1979, pp.191-214.
- [26] F. Soggetti, U. Zezza, *Possibility of exploitation and technical properties of the Angera stone, Lago Maggiore*, **Geologia Applicata e Idrogeologia** **18**, 1983, pp. 81-93.
- [27] F. Veniale, M. Setti, C. Rodriguez-Navarro, S. Lodola, *Role of clay constituents in stone decay process*, **Materiales de Construcción**, **51**, 2001, pp. 163-182.
- [28] G. Alessandini, A. Bocci, R. Bugini, D. Emmi, R. Peruzzi, M. Realini, *Stone materials of Noto (Siracusa) and their decay*, **Proceedings of the 7th International Congress on Deterioration and Conservation of Stone**, June 15–18 1992, Lisbon, Portugal, pp. 11–20.
- [29] M.F. La Russa, G. Barone, C.M. Belfiore, P. Mazzoleni, A. Pezzino, *Application of protective products to “Noto” calcarenite (south-eastern Sicily): a case study for the conservation of stone materials*, **Environmental Earth Sciences**, **62**, 2011, pp. 1263–1272.
- [30] L. Anania, A. Badalà, G. Barone, C.M. Belfiore, C. Calabrò, M.F. La Russa, P. Mazzoleni, A. Pezzino, *The stones in monumental masonry buildings of the “Val di Noto” area: New*

- data on the relationships between petrographic characters and physical–mechanical properties*, **Construction and Building Materials**, **33**, 2012, pp. 122-132.
- [31] E. Gasparini, S.C. Tarantino, M. Conti, R. Biesuz, P. Ghigna, F. Auricchio, M.P. Riccardi, M. Zema, *Geopolymers from low-T activated kaolin: Implications for the use of alunite-bearing raw materials*, **Applied Clay Science**, **114**, 2015, pp. 530-539.
- [32] E. Gasparini, S.C. Tarantino, P. Ghigna, M.P. Riccardi, E.I. Cedillo-González, C. Siligardi, M. Zema, *Thermal dehydroxylation of kaolinite under isothermal conditions*, **Applied Clay Science**, **80-81**, 2013, pp. 417-425.
- [33] C.K. Yip, J.L. Provis, G.C. Lukey, J.S.J. van Deventer, *Carbonate mineral addition to metakaolin-based geopolymers*, **Cement and Concrete Composites**, **30**, 10, 2008, pp. 979-985.
- [34] A. Török, T. Licha, K. Simon, S. Siegesmund, *Urban and rural limestone weathering; the contribution of dust to black crust formation*, **Environmental Earth Sciences**, **63**(4), 2011, pp. 675-693.
- [35] R. Bugini, L. Folli, *Stones used in Milan architecture*, **Materiales de Construcción**, **58**(289-290), 2008, pp. 33-50.
- [36] D. Gulotta, M. Bertoldi, S. Bortolotto, P. Fermo, A. Piazzalunga, L. Toniolo, *The Angera stone: A challenging conservation issue in the polluted environment of Milan (Italy)*, **Environmental Earth Sciences**, **69**(4), 2013, pp. 1085-1094.
- [37] C. Rodriguez-Navarro, E. Doehne, E. Sebastian, *How does sodium sulfate crystallize? Implications for the decay and testing of building materials*, **Cement and Concrete Research**, **30**(10), 2000, pp. 1527-1534.
- [38] A. Garbacz, L. Courard, K. Kostana, *Characterization of concrete surface roughness and its relation to adhesion in repair systems*, **Materials Characterization**, **56**(4-5 Spec. Iss.), 2006, pp. 281-289.
- [39] J.B. De Aguiar, M.D. Cruz, *A study of the adhesion between hydraulic mortars and concrete*, **Journal of Adhesion Science and Technology**, **12**(11), 1998, pp. 1243-1251.
- [40] S. Caliskan, B.L. Karihaloo, *Effect of surface roughness, type and size of model aggregates on the bond strength of aggregate/mortar interface*, **Interface Science**, **12**(4), 2004, pp. 361-374.
- [41] E. Najafi Kani, A. Allahverdi, J.L. Provis, *Efflorescence control in geopolymer binders based on natural pozzolan*, **Cement and Concrete Composites**, **34**(1), 2012, pp. 25-33.
- [42] I. Sandu, V. Cotiuga, A.V. Sandu, A.C. Ciocan, G.I. Olteanu, V. Vasilache, *New archaeometric characteristics for ancient pottery identification*, **International Journal of Conservation Science**, **1**(2), 2010, pp. 75-82.

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