

ALKALI ACTIVATED MATERIALS AS ALTERNATIVE BINDERS FOR THE BUILT HERITAGE: STUDY OF THEIR INTERACTION WITH ORNAMENTAL STONES IN MORTARS, COMPOSITES AND CEMENTS

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INTRODUCTION

The alkaline activation is a chemical process through which precursors sufficiently rich in reactive silica and alumina, mainly available as amorphous or vitreous phases, interact with a strongly alkaline medium to give rise, under mild processing conditions, to materials with good binding and cementing properties (Van Deventer *et al.*, 2012). Nowadays, these materials are largely known as Alkali Activated Materials (AAMs), although over time, different terms have been coined, including the widespread trade name geopolymers (Davidovits, 1991; Barbosa *et al.*, 2000; Fernández-Jiménez *et al.*, 2008; Provis & Bernal, 2014).

AAMs have emerged as alternative to traditional construction materials, such as mortars or Ordinary Portland Cement (OPC), with the aim to become primary components in the development of environmentally sustainable building products, above all considering the growing interest of the scientific community for the themes of sustainability and CO₂ footprint reduction (Duxson *et al.*, 2007b; Pacheco-Torgal *et al.*, 2008; Flatt *et al.*, 2012). Many studies have been carried out employing calcined clays and industrial wastes, like ground blast furnace slags and fly ashes, or wastes deriving by various human activities, until now under-utilized or simply dismissed (Shi *et al.*, 2011; Payá *et al.*, 2014; Bernal *et al.*, 2016). It has been assessed that, depending on the raw material selection and processing conditions, AAMs can exhibit a wide variety of properties, such as high level of resistance to a range of different acids and salt solutions, fire resistance, low shrinkage and low thermal conductivity. Furthermore, they may be suitable to be used in extreme environmental conditions (Palomo *et al.*, 1999; Bakharev, 2005; Fernandez-Jimenez *et al.*, 2007). All these properties may be of high relevance when dealing with conservation of the built heritage, where their potential applicability has been little explored so far.

Materials for conservation should guarantee functional and aesthetic compatibilities with the substrate and the whole construction. The knowledge of basic properties of the new material allows to formulate suitable products depending on the different destinations of use.

This work is designed with the aim of exploring the potentiality and suitability of alkali-activated pastes, mortars and composites to be used for conserving and restoring ancient and contemporary art and architecture as well as natural and artificial stone objects. Their structural, microstructural and physical-mechanical properties have been studied in order to investigate their compatibility with existing materials belonging to Cultural Heritage. Furthermore, this research aims at addressing the issue of reuse by evaluating the use of industrial waste as precursor materials. The versatility of AAMs has led to evaluate their synergic use and interaction with stones used for ornamental purposes, in order to increase/improve the compatibility with the materials to be repaired, fundamental issue when dealing with conservation.

STARTING MATERIALS

An industrial kaolin labelled SI-K, deriving from the Seilitz kaolin deposits (Germany) and provided by Sibelco Italia S.p.A, was used. SI-K is composed of 73 wt.% kaolinite and 27 wt.% quartz and its chemical composition, determined by X-ray fluorescence (XRF), is: SiO₂ = 67.0 wt.%, Al₂O₃ = 31.5 wt.%, Fe₂O₃ = 0.32 wt.%, TiO₂ = 0.24 wt.%, CaO = 0.12 wt.%, MgO = 0.23 wt.%, K₂O = 0.35 wt.%, and its measured ignition loss is 10.02 wt.% (the theoretical value for pure kaolinite is 13.96 wt.%). The kaolin powder was submitted to thermal treatment at 800 °C for 2 hours to obtain the reactive metakaolin, hereafter labelled SI-MK. More

information about its characterization are reported in (Gasparini *et al.*, 2013; Clausi *et al.*, 2016). In the experimentations the metakaolin has been used as main precursor, both because widely studied in literature (Palomo *et al.*, 1999; Duxson *et al.*, 2007a; Lee & van Deventer, 2007), and because a pure starting material better helps to understand the final reaction products.

A sodium silicate solution supplied by Ingessil s.r.l. ($\text{Na}_2\text{O} = 14.37$ wt.%, $\text{SiO}_2 = 29.54$ wt.%, $\text{H}_2\text{O} = 56.09$ wt.%) and NaOH pellets (Sigma-Aldrich, purity $\geq 98\%$) were used as alkaline activators.

Three varieties of stones, widely used for decorative purpose, and representative of the historic architecture of northern, central and southern parts of Italy, were selected for the synthesis of geopolymer-based mortars and/or composites. In addition to those, some common construction materials were also selected. Pietra Serena is a sandstone, provided by Pietra Serena Group of Firenzuola (Italy), 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 analysis in thin section. Pietra di Angera is a dolostone (yellow variety), composed by dolomite and subordinates contents of clay minerals ($< 5\%$). The samples used in the work come from the collection of the Department of Earth and Environment Sciences of University of Pavia and also included a historic and decorative stone artifact. Blocks of Pietra di Noto, a yellowish organogenic limestone, constituted by bioclasts (40%) with a micritic matrix (60%) and characterized by high porosity, and a historical mortar sample were made available by the Department of Civil and Environmental Engineering of Polytechnique University of Milan. Concrete samples were obtained using starting materials provided by Holcim Ltd. Brick blocks also come from the collection of the Department of Earth and Environment Sciences of University of Pavia. Chemical compositions of all materials, as determined by FESEM-EDAX energy dispersive spectrometry (EDS), were reported as oxides wt.% in Table 1.

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)

Standard deviations are in parentheses.

Sewage sludge of Pietra Serena (hereafter labelled only SPS) were provided by Pietra Serena Group S.r.l. of Firenzuola (Italy) and used after drying at 100 °C for 24 hours in oven. Their chemical composition, determined by X-ray fluorescence (XRF), is: $\text{SiO}_2 = 43.5$ wt.%, $\text{Al}_2\text{O}_3 = 8.28$ wt.%, $\text{Fe}_2\text{O}_3 = 2.44$ wt.%, $\text{TiO}_2 = 0.42$ wt.%, $\text{CaO} = 19.53$ wt.%, $\text{MgO} = 4.19$ wt.%, $\text{K}_2\text{O} = 1.74$ wt.%, $\text{Na}_2\text{O} = 1.46$ wt.%, others = 0.46 wt.%. Its measured ignition loss is 18%.

Fly ash (FA) from a thermo-electric power plant located in Andorra (Teruel-Spain) and classified as Class F in the ASTM C 618 normative was used after milling in a ball miller for 1 hour at 1200 rpm. Its chemical composition, is: $\text{SiO}_2 = 39.03$ wt.%, $\text{Al}_2\text{O}_3 = 27.06$ wt.%, $\text{Fe}_2\text{O}_3 = 19.5$ wt.%, $\text{TiO}_2 = 0.95$ wt.%, $\text{CaO} = 6.40$ wt.%, $\text{MgO} = 1.04$ wt.%, $\text{K}_2\text{O} = 1.41$ wt.%, $\text{Na}_2\text{O} = 0.16$ wt.%, $\text{SO}_3 = 1.76$ wt.%, others = 0.84 wt.%. Its measured loss on ignition is 1.8 wt.%.

EXPERIMENTAL

For the synthesis of geopolymer binders, four different sodium silicate solutions were prepared with H_2O/Na_2O ratio ranging between 10 and 20. Samples with molar ratios $SiO_2/Al_2O_3 = 3.7$ and $Al_2O_3/Na_2O = 1.04$ were obtained by mixing SI-MK with each of these solutions. In literature is reported that a SiO_2/Al_2O_3 ratio of around 4 provides the metakaolin-based geopolymers with the highest strength and without formation of crystalline zeolite-type phases (Duxson *et al.*, 2005; Fletcher *et al.*, 2005; Komnitsas & Zaharaki, 2007). Different H_2O/Na_2O molar ratios were used with the aim of improving the slurry workability and obtaining water/solid weight ratios between 0.33 and 0.66. The slurries were mixed for 10 minutes according to the European technical standard (UNI-EN 196-1:2005), under controlled conditions of temperature and relative humidity (20 °C and 65% R.H., respectively), before to be poured into prismatic steel moulds ($4 \times 4 \times 16 \text{ cm}^3$) and compacted by mechanical vibration for 60s to remove entrained air. Specimens were cured in climatic room for 28 days at 20 °C and 65% R.H. before testing.

Geopolymer-based mortars were obtained by mixing the geopolymer pastes with a H_2O/Na_2O molar ratio of 20 with powders obtained by grinding Pietra Serena and Pietra di Angera stones. The granulometric fraction smaller than 0.5 mm was used as aggregate in the preparation of mortars. Clayey fractions were also included to make the colour tone of the mortars similar to that of their respective stone. Mortars were prepared in compliance with the requirements of UNI-EN 196-1:2005, choosing a binder/sand ratios of 1:1 (weight/weight), thus giving mortars with water/solid weight ratio of 0.39. The same synthesis procedure applied for the geopolymer binders was used. Samples were matured in climatic room for 14 days at 20 °C and 90% R.H., then were de-moulded and cured at the same conditions for other 14 days.

Composites were obtained by pouring geopolymer pastes, with a water/solid ratio of 0.46 and 0.66, on stones and construction materials surfaces. Samples were cured in climatic room for 28 days at 20 °C and 65% R.H. before to be demolded and cut in sections.

For the synthesis of alkali activated cements the powders of the untreated and thermal treated SPS, FA and SI-MK were mixed in different weight proportions and added to sodium hydroxide solutions (NaOH 8M and 12M) obtained by dissolving pellets of sodium hydroxide in deionised water. The slurries were mixed for 3 minutes by using a mechanical mixer before being poured in $1 \times 1 \times 6 \text{ cm}^3$ prismatic steel moulds and compacted by mechanical vibrations. Specimens were cured at 85 °C for 5 or 20 hours in sealed vessels to ensure 100% R.H. conditions and tested after one day.

Raw materials and alkali activated samples were characterized by X-ray Fluorescence (XRF), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy in attenuated total reflectance (FTIR-ATR), Thermogravimetric analysis and Differential thermal analysis (TG-DTA), Field Emission Scanning Electron Microscopy (FESEM), mercury intrusion porosimetry (MIP) and gas pycnometry, granulometry, mechanical tests and colorimetric analyses.

GEPOLYMER BASED MORTARS WITH ORNAMENTAL STONE AGGREGATES

A detailed study of geopolymer binders, characterized by a growing water/solid weight ratios (between 0.33 and 0.66), were carried out prior to synthesize mortars, with the aim of evaluating the role of water in the reaction development and to obtain workable materials without the use of additives or plasticizers. In literature is reported that water results to have great effects on the development of geopolymer gels and on the properties of the final products. In terms of strength, the minimization of water/solid ratio corresponds to an increase of compressive strength and to a reduction of permeability (Rashad, 2013; Van Deventer *et al.*, 2012; Zhang *et al.*, 2010). However, in this study, geopolymer binders characterized by high values of compressive and flexural strength (up to 72(3) MPa and 6.1(8) MPa, respectively) were obtained for all the samples. SEM analysis showed binders largely composed by amorphous binding material (Fig. 1) with a growing porosity (from 21% to 32%) and median pore radius. Infrared spectroscopy allowed to correlate the degree of amorphous gel

development with the water content increase. In all samples a broad band centered at about 990 cm^{-1} , related to asymmetric stretching of the Si-O-T bonds, where T is Al or Si in tetrahedral coordination, represented the fingerprint of the aluminosilicate geopolymer phase and demonstrated the formation of the geopolymer network, as reported in many studies (Irfan Khan *et al.*, 2015; Lee & van Deventer, 2003, 2004). This band was fitted by using three Lorentian components (one for the aluminosilicate gel, one for metakaolinite and one for quartz). It was observed that the relative area of peak from gel represented the largest part of the main peak area and it decreased slightly with increasing the water content in the geopolymer formulation. This may be interpreted as a reduction in the amount of gel, and hence of reactivity, at high water/solid ratio. However, geopolymer relative peak area was large at water/solid ratio of 0.66, thus implying that the metakaolinite conversion was high, and likewise the gel binder amount. These results led to hypothesize that the decrease of mechanical strengths have to be ascribed to the porosity increase rather than to the reduction of metakaolin conversion into geopolymer.

Mortars, prepared by mixing the binder with a water/solid ratio of 0.66 with crashed ornamental stones of

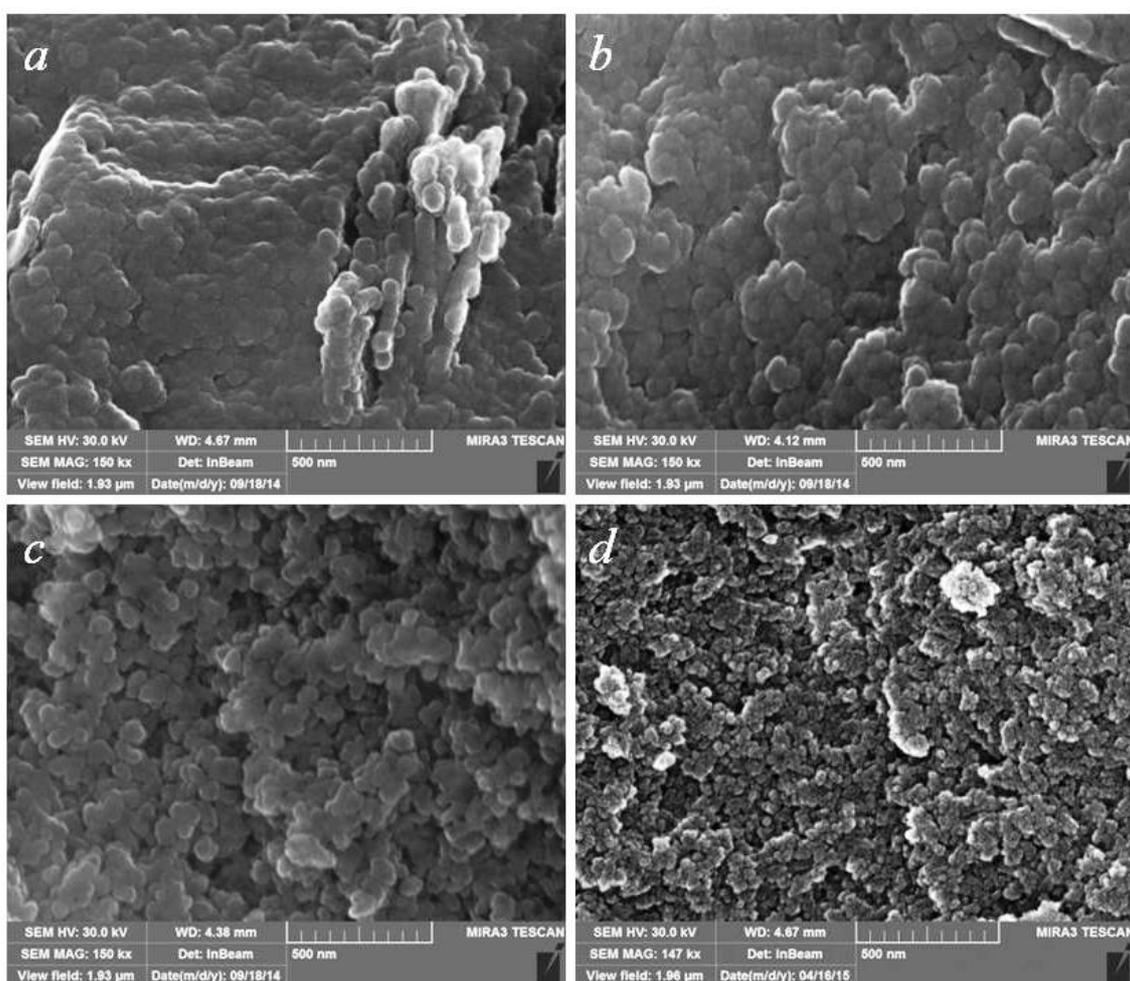


Fig. 1 - FESEM micrographs of geopolymer binders with different water/solid ratios: a = 0.33; b = 0.46; c = 0.53; d = 0.66. Scale bar and magnification are showed in each image.

Pietra Serena and Pietra di Angera, have been studied in order to evaluate a possible use of geopolymers as restoration materials in conservation of historic manufactures.

The physical and mechanical characterization evidenced: *i*) mechanical strength values that fell within the M20 class (UNI-EN 998-2: 2010); *ii*) density values comparable to those of ornamental stones reference; *iii*) porosity values between 14 and 17%. In the mortar synthesized by using Pietra Serena the fine fraction seemed

to contribute to geopolymeric reaction, providing soluble silica and alumina. Colorimetric measurements were also carried out on samples in order to evaluate the aesthetic compatibility of the mortars with ornamental stone references. The use of rock fines with metakaolin-based binders allowed to obtain materials that mimic the stone, thus reaching good aesthetic compatibility. In restoration practice, this would allow to obtain materials that are recognizable, albeit similar, to the original substrate. In the quest of designing new, high-performance materials that meet the requirements of sustainability and compatibility with the artifacts, this study has shown good potentialities of metakaolin-based geopolymers for uses in Cultural Heritage.

COMPOSITE OF ALKALI ACTIVATED MATERIALS AND NATURAL AND ARTIFICIAL STONES

The interaction at the interface between geopolymer binders and natural (ornamental stones) and artificial (brick, mortar and concrete) stone materials, was evaluated by performing stereomicroscope and SEM analysis.

Stereomicroscope observations revealed macroscopic structural features common to all samples: the binder entered the superficial porosity of the stones ensuring good adhesion between the two materials; the contact regions showed a reaction layer visible between the binder and each material.

SEM investigations allowed to evaluate the adhesive processes involved at the contact zones at short length scale. Large differences at the boundary were observed and related to the composition of the materials.

An alumino-silicate matrix, like those of Pietra Serena and brick, seemed to have a greater physical affinity with the geopolymer binder. In these samples silicoaluminate phases partially dissolved and increased the Si and Al availability at the interface, that resulted strongly interlinked. In the composite obtained by using Pietra Serena in fact, the interaction between siliceous aggregates and the highly alkaline solution resulted in a partial dissolution of quartz and mica grains, which showed rounded and unraveled shapes (Fig. 2).

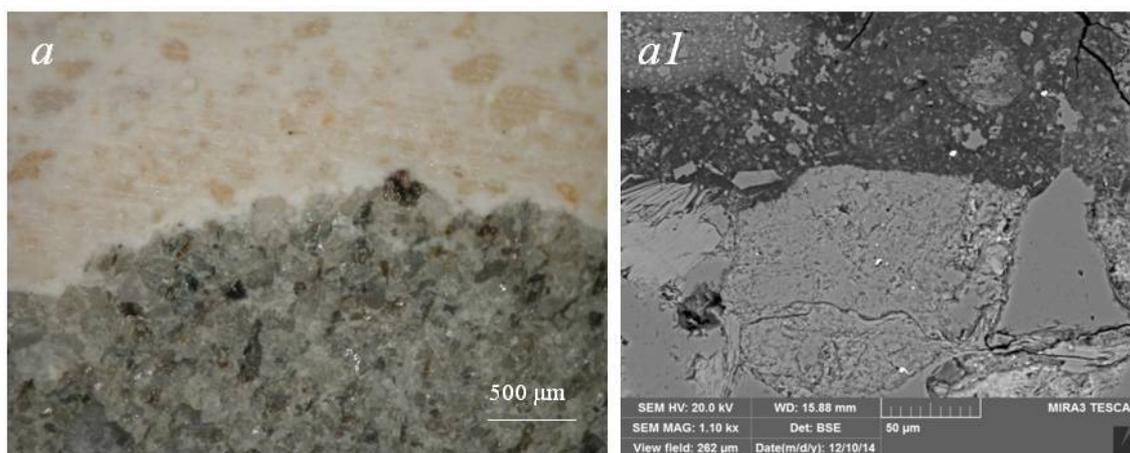


Fig. 2 - Stereomicroscope image (a) and FESEM micrograph (b) of composite prepared with Pietra Serena. Scale bar and magnification are showed in the image.

In the carbonate matrices a partial dissolution of calcite, related to crystallinity of calcite itself, and calcium diffusion into geopolymer matrix changed the local composition of the binder, giving rise to precipitation phases. However a calcium carbonate layer was observed only in the historic mortar (Fig. 3, part b), whereas in the composites obtained by using concrete and Pietra di Angera, rounded precipitation particles were observed (Fig. 3, part a). Difference in crystallinity influenced calcite precipitation: in the mortar, the reaction layer was more developed for the presence of microcrystalline calcite grains, which are more soluble than those of the carbonatic stones used in this work. Furthermore, the different solubility in highly alkaline solutions of dolomite and calcite influenced the behavior of the Pietra di Angera and Pietra di Noto at the interfaces.

Interesting results were obtained by the interaction between a historic decorative stone element made in Pietra di Angera and the most fluid geopolymer paste (water/solid ratio of 0.66). The stone sample was originally exposed to an outdoor environment and chemical analyses evidenced the presence of SO_3 (Table 1) as effect of chemical decay of the stone due to the atmospheric pollutants. Among pollutants, sulfur oxides produce sulfation of substrate especially for poor durable stones like Pietra di Angera (Gulotta *et al.*, 2013). At the interface the results showed the presence in the geopolymer matrix of SO_3 with an average value of 3(2) wt.% and 3(1) wt.%, respectively. The diffusion of these elements in the matrix was attributed to the water contained in the alkaline solution that flows through the stone pores during the first part of geopolymerization. However, no new phases such as thenardite or ettringite were observed in the binder. Sulfur may remain trapped in the amorphous network of GP gel, without giving rise to potentially harmful by-products (Rodriguez-Navarro *et al.*, 2000). Consequently, the trapping function of geopolymers can be positively considered in conservation practices.

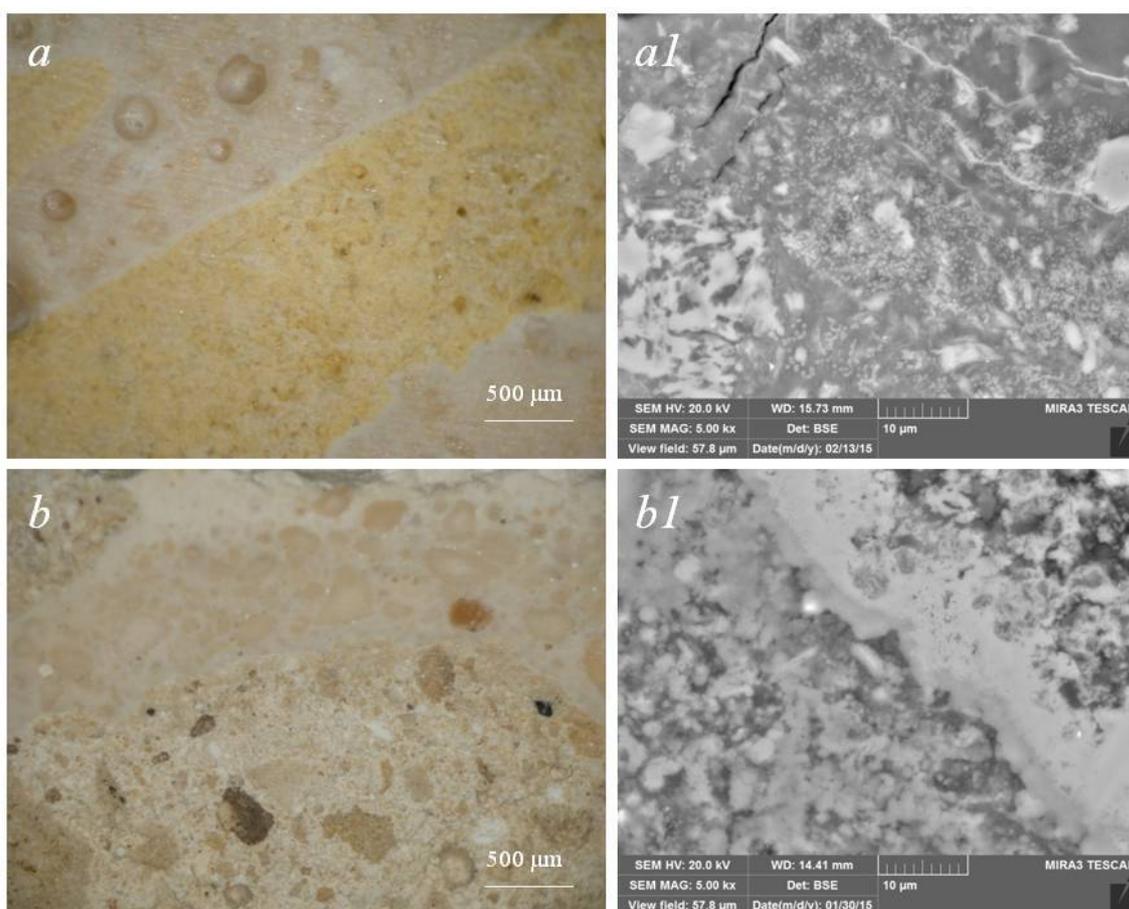


Fig. 3 - Stereomicroscope images (a; b) and FESEM micrographs (a1; b1) of composites prepared with Pietra di Angera and historic mortar respectively. Scale bar and magnification are showed in each image.

CEMENTS FROM PIETRA SERENA SEWAGE SLUDGE IN MATRICES OF FLY ASHES AND METAKAOLIN

The research was focused at addressing the issue of reuse by evaluating the use of sewage sludge derived by the cultivation of Pietra Serena as precursor material in the synthesis of alkaline cements or geopolymers.

Results revealed different usability of the Pietra Serena sewage sludge. The cement produced exclusively by using the untreated sludge did not achieve high strength, but the results seem to be promising.

SPS has been used in synergy with fly ash and metakaolin. The main reaction product was a N-A-S-H type gel, which was responsible of the good behaviour of the whole system. In particular SPS mixed with FA acted mainly as fine filler, enhancing the packing density and improving the compressive and flexural strength if compared to cement produced exclusively with SPS. These cements may be used to develop materials with strength values and colours appropriate to be used as Pietra Serena stone substitute.

The decarbonation process of the sewage sludge also provided a useful tool for the valorisation of this type of waste. In binary or ternary matrices with metakaolin and fly ash SPS acted as a pozzolanic cement in which the calcium oxide (CaO) was hydrated and reacts with the silica present in the material to generate a gel C-S-H and Ca(OH)₂. In these mixtures, the interaction between the different precursors gave rise to a mixture of (N, C)-A-S-H / C-A-S-H gels, similar to those produced in so-called mixed alkali cements or hybrid cements.

REFERENCES

- ASTM C 618: Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete.
- Bakharev, T. (2005): Resistance of geopolymer materials to acid attack. *Cem. Concr. Res.*, **35**, 658-670.
- Barbosa, V.F.F., MacKenzie, K.J.D., Thaumaturgo, C. (2000): Synthesis and characterisation of materials based on inorganic polymers of alumina and silica: Sodium polysialate polymers. *Int. J. Inorg. Mater.*, **2**, 309-317.
- Bernal, S.A., Rodríguez, E.D., Kirchheim, A.P., Provis, J.L. (2016): Management and valorisation of wastes through use in producing alkali-activated cement materials. *J. Chem. Technol. Biotechnol.*, **91**, 2365-2388.
- Clausi, M., Tarantino, S.C., Magnani, L.L., Riccardi, M.P., Tedeschi, C., Zema, M. (2016): Metakaolin as a precursor of materials for applications in Cultural Heritage: Geopolymer-based mortars with ornamental stone aggregates. *Appl. Clay Sci.*, **132-133**, 589-599.
- Davidovits, J. (1991): Geopolymers - Inorganic polymeric new materials: *J. Therm. Anal.*, **37**, 1633-1656.
- Duxson, P., Provis, J.L., Lukey, G.C., Mallicoat, S.W., Kriven, W.M., Van Deventer, J.S.J. (2005): Understanding the relationship between geopolymer composition, microstructure and mechanical properties. *Colloids Surf. A*, **269**, 47-58.
- Duxson, P., Lukey, G.C., van Deventer, J.S.J. (2007a): Physical evolution of Na-geopolymer derived from metakaolin up to 1000 °C. *J. Mat. Sci.*, **42**, 3044-3054.
- Duxson, P., Provis, J.L., Lukey, G.C., van Deventer, J.S.J. (2007b): The role of inorganic polymer technology in the development of 'green concrete'. *Cem. Concr. Res.*, **37**, 1590-1597.
- Fernandez-Jimenez, A., Garcia-Lodeiro, I., Palomo, A. (2007): Durability of alkali-activated fly ash cementitious materials. *J. Mat. Sci.*, **42**, 3055-3065.
- Fernández-Jiménez, A., Palomo, A., Pastor, J.Y., Martín, A. (2008): New Cementitious Materials Based on Alkali-Activated Fly Ash: Performance at High Temperatures. *J. Am. Ceram. Soc.*, **91**, 3308-3314.
- Flatt, R.J., Roussel, N., Cheeseman, C.R. (2012): Concrete: An eco material that needs to be improved. *J. Am. Ceram. Soc.*, **32**, 2787-2798.
- Fletcher, R.A., MacKenzie, K.J.D., Nicholson, C.L., Shimada, S. (2005): The composition range of aluminosilicate geopolymers. *J. Eur. Ceram. Soc.*, **25**, 1471-1477.
- Gasparini, E., Tarantino, S.C., Ghigna, P., Riccardi, M.P., Cedillo-González, E.I., Siligardi, C., Zema, M. (2013): Thermal dehydroxylation of kaolinite under isothermal conditions. *Appl. Clay Sci.*, **80-81**, 417-425.
- Gulotta, D., Bertoldi, M., Bortolotto, S., Fermo, P., Piazzalunga, A., Toniolo, L. (2013): The Angera stone: A challenging conservation issue in the polluted environment of Milan (Italy). *Environ. Earth Sci.*, **69**, 1085-1094.
- Irfan Khan, M., Azizli, K., Sufian, S., Man, Z. (2015): Sodium silicate-free geopolymers as coating materials: Effects of Na/Al and water/solid ratios on adhesion strength: *Ceram. Int.*, **41**, 2794-2805.
- Komnitsas, K. & Zaharaki, D. (2007): Geopolymerisation: A review and prospects for the minerals industry. *Miner. Eng.*, **20**, 1261-1277.
- Lee, W.K.W. & van Deventer, J.S.J. (2003): Use of infrared spectroscopy to study geopolymerization of heterogeneous amorphous aluminosilicates. *Langmuir*, **19**, 8726-8734.
- Lee, W.K.W. & van Deventer, J.S.J. (2004): The interface between natural siliceous aggregates and geopolymers. *Cem. Concr. Res.*, **34**, 195-206.

- Lee, W.K.W. & van Deventer, J.S.J. (2007): Chemical interactions between siliceous aggregates and low-Ca alkali-activated cements. *Cem. Concr. Res.*, **37**, 844-855.
- Pacheco-Torgal, F., Castro-Gomes, J., Jalali, S. (2008): Alkali-activated binders: A review. Part 2. About materials and binders manufacture. *Constr. Build. Mater.*, **22**, 1315-1322.
- Palomo, A., Blanco-Varela, M.T., Granizo, M.L., Puertas, F., Vazquez, T., Grutzeck, M.W. (1999): Chemical stability of cementitious materials based on metakaolin. *Cem. Concr. Res.*, **29**, 997-1004.
- Payá, J., Monzó, J., Borrachero, M.V., Tashima, M.M. (2014): Reuse of aluminosilicate industrial waste materials in the production of alkali-activated concrete binders. *Handbook of Alkali-Activated Cements, Mortars and Concretes*, 487-518, 10.1533/9781782422884.4.487.
- Provis, J.L. & Bernal, S.A. (2014): Geopolymers and Related Alkali-Activated Materials. *Ann. Rev. Mater. Res.*, **44**, 299-327.
- Rashad, A.M. (2013): Alkali-activated metakaolin: A short guide for civil Engineer - An overview. *Constr. Build. Mater.*, **41**, 751-765.
- Rodriguez-Navarro, C., Doehne, E., Sebastian, E. (2000), How does sodium sulfate crystallize? Implications for the decay and testing of building materials. *Cem. Concr. Res.*, **30**, 1527-1534.
- Shi, C., Fernández-Jiménez, A., Palomo, A. (2011): New cements for the 21st century: The pursuit of an alternative to Portland cement. *Cem. Concr. Res.*, **41**, 750-763.
- UNI-EN 196-1 (2005): Methods of testing cement. Determination of strength.
- UNI-EN 998-2 (2010): Specification for mortar for masonry - Part 2: Masonry mortar.
- Van Deventer, J.S.J., Provis, J.L., Duxson, P. (2012): Technical and commercial progress in the adoption of geopolymer cement. *Miner. Eng.*, **29**, 89-104.
- Zhang, Z., Yao, X., Zhu, H. (2010): Potential application of geopolymers as protection coatings for marine concrete I. Basic properties. *Appl. Clay Sci.*, **49**, 1-6.