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Suitability of ceramic industrial waste recycling by alkaline activation for use as construction and restoration materials



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ABSTRACT

Ceramic is one of the prominent sources of waste in Europe. Its aluminosilicate composition, together with the relatively high amount of amorphous phase, makes it suitable as a potential precursor for alkali activated products. The technical characteristics of these kinds of materials, as well as the aesthetic appearance, determine a good applicability in the field of construction and for restoration purposes. This research aimed to investigate the suitability of ceramic industrial tiles waste through the alkaline activation process for the production of novel and eco-friendly materials. The applicative goal was the implementation of binder formulations to be used for the production of eco-sustainable bricks, tiles, mortars and decorative elements. The results showed that pure ceramic based geopolymers and binary mixtures obtained by adding few percentages of metakaolin can be produced at room temperature by only using sodium hydroxide and waterglass, reaching efficient technical characteristics for their employment in restoration. This work represents a starting point for future development of ceramic based geopolymeric products to be employed in construction and restoration field.

1. Introduction

Solid waste produced from construction and demolition (C&D) activities amounts to several million tons globally [1]. Ceramic is one of the most prominent waste, with bricks representing about the 45% of the total amount [1,2]. A same kind of waste is also produced by manufacturing activities such as bricks and tiles industries as residue of working [3]. Its recycling becomes therefore of strategic importance since its re-use represents an opportunity to face the current limits in the clay provision. Waste generated by C&D processes or by ceramic industries is classified as non-hazardous because it does not contain asbestos [4] and can be therefore re-used without any pre-treatment as raw material. Working with demolition waste could be challenging because of its high heterogeneity and the uncertainty of its composition. Furthermore, pre-treatment such as the extraction of possible contaminants (wood, paper, plaster, glass, plastic and rubber) is not always easily viable [4-6]. Working with construction or industrial waste is thus preferable in order to avoid these limitations and to make the experimental studies reproducible by reducing the compositional variability of the raw materials [4].

In recent years, an increasing number of researches focused on the

production of eco-friendly materials by using recycling brick waste as aggregates or as partial replacement of raw material in cement-based concrete and mortars. However, little literature is available on investigating the potentiality of the alkaline-activation of powdered ceramic waste, in particular using red brick waste [1 and reference therein].

The Alkaline Activated Materials (AAMs) are promising alternative to the classic cement and ceramic materials whose production is responsible of a huge CO_2 emission in the atmosphere [7]. Among the AAMs an interesting subgroup is represented by the so called geopolymers, which contains the highest content of Al and the lowest content of Ca [8]. AAMs are obtained by mixing an aluminosilicate precursor with high amount of amorphous phase with a liquid alkaline component usually at room temperature or below 200 °C [9]. The chemical process (geopolymerization) and the structure of the final material depend on many parameters among which the most important is the chemical composition of the precursors. The structure could be described as polycondensed due to chains and rings of alumina and silica tetrahedra linked together by oxygen atoms and with alkaline ions entrapped to balance the negative charge due to the substitution of Al in the Si chains [9–11].

Solid [12] and hollow [13] bricks, as well as tiles [12], have been

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Received 19 July 2022; Received in revised form 25 October 2022; Accepted 8 November 2022 Available online 12 November 2022 0272-8842/© 2022 Elsevier Ltd and Techna Group S.r.l. All rights reserved. previously used to obtain ceramic-based geopolymers with suitable characteristics for applications on architectural heritage. The compressive strength has been commonly used as a first indicator of the quality of the experimented geopolymeric product [1]. Geopolymers obtained by bricks or tiles precursors reached compressive strength ranging between 7 and 71 MPa after 28 days of curing [6,14] and values higher than 40 MPa after only 7 days of curing [12]. The best used alkaline solutions consist of a combination of sodium hydroxide and waterglass in different proportions and concentration, according to the chemistry of the used raw materials [2,3,6,7,15–18]. Furthermore, the curing temperature suggested is a moderate heating, between 60 and 90 °C in order to prevent any cracking at the surface [12].

The observed low reactivity of ceramic materials with respect to the most common aluminosilicate precursors [19], suggested the experimentation of binary mixtures involving more reactive components. Metakaolin (MK) is one of the most frequent reactive additives used in combination with ceramic powdered waste [7,13]. It is indeed characterized by a very high percentage of amorphous, thus reactive, silica and alumina and represents one of the first materials used for the geopolymerization process.

The mineralogical and chemical analogy of the AAMs, and particularly of the geopolymers, with natural and artificial stone substrates, together with the possibility to customize color and physic-mechanical characteristics as porosity and compressive resistance, make them attractive in conservation and restoration field. Analogously, the use of ceramic-based geopolymeric products for the restoration of ceramic substrates is absolutely desired. Nevertheless, the research devoted to bricks or tiles waste as precursors for alkali activated materials production is still in early stage [1], rising the need for further investigation to assess their feasibility [1].

This research aimed to explore the suitability of ceramic industrial waste in alkaline activation process and, consequently, to investigate properties and microstructure of the obtained products, by understanding the influence of the parameters involved in the geopolymerization process. For this purpose, the type of alkaline activator, raw material and temperatures of synthesis and curing were kept fixed, varying the MK/ceramic and sodium hydroxide/waterglass ratios to create 9 different formulations.

2. Materials and methods

2.1. Raw materials

The employed raw materials were industrial tiles (LBCa), provided by La Bottega Calatina - Caltagirone (Sicily, Italy), characterized by a fine and homogeneous structure and obtained by the use of commercial clay. According to the manufacturer, the tiles were fired at around 1100 °C after natural drying. Industrial MK ARGICALTM M – 1000 supplied by IMERYS (France) was added (10 or 20 wt% of the total solid precursor) in order to prompt the reactivity of the aluminosilicate precursor during the alkaline activation process. The chemical composition of the raw materials is shown in Table 1.

The precursors were grounded by porcelain jars in order to reach the desired granulometry of about 10 μ m. According to preliminary tests this grainsize should be preferred to that of 75 μ m suggested by Lancellotti et al. [21]. Smaller granulometry indeed has a higher specific surface that eases the contact with the activating solution, promoting the reaction [1,19]. Furthermore, this granulometry, similar to those of the

industrial MK, allows to work with precursors of comparable granules dimension, facilitating the mixing.

The L/S ratio (where L = liquid and S = solid) was chosen according to previous preliminary tests and desired workability.

The mineralogical composition of the LBCa precursor is given by quartz, diopside, gehlenite, hematite, feldspars (K-feldspar and Caplagioclase) and wollastonite and by an amorphous content of \sim 33%. MK is characterized by anatase, illite and quartz, with \sim 77% of amorphous component [22].

2.2. Alkaline solution

According to literature [2,3,6,12,13,15,17,23-25] and after some preliminary tests, sodium hydroxide (NaOH) mixed in different proportions with sodium silicate (Na₂SiO₃) was selected as alkaline activating solution.

8 M NaOH was chosen in order to have enough alkaline medium, not excessively aggressive towards the environment, and to prevent an excessive formation of efflorescence. The desired molarity was obtained by diluting a commercial 10 M NaOH solution supplied by Carlo Erba company.

The used sodium silicate, provided by Ingessil srl, is characterized by a molar ratio $SiO_2/Na_2O = 3.3$ and pH = 11.5. In order to avoid the heat development during the mixing procedure, the liquid solution was used after 30 min.

2.3. Geopolymers preparation

The synthesis process was carried out prior preparation of the solid and liquid raw materials, following the procedures indicated in the previous paragraphs.

In addition to pure ceramic slurries, binary mixtures were also prepared and analysed by the addition of different proportions of MK. MK was dried in the oven and sieved before adding it to the ceramic, in order to avoid the formation of MK granules. The powdered components were carefully homogenized in a porcelain jar before the addition of the activating solution. The liquid was then poured on the powders and immediately subjected to mechanical mixing for 5 min. The obtained slurries were then poured into molds and manually stirred for 1 min in order to facilitate the escape of air bubbles from the mixture [6,12,26, 27]. After 24 h at room temperature (~25 °C), the samples were demolded and wrapped with polyethylene film for the remaining curing time (fixed at 28 days). Maturation was carried out at room temperature.

Three geopolymeric series based on different sodium hydroxide/ waterglass ratio (7/3, 1/1, 3/7) were experimented. Each series consists in three formulations based on the MK wt% (0%, 10% and 20%). The experimented binders were labelled to describe the formulations, e.g. LBCa 3/7 + 10MK indicates a sample obtained by using LBCa as raw material, a ratio of sodium hydroxide/waterglass equal to 3/7 and 10 wt % of MK as reactive additive.

2.4. Test methods

The mineralogical study of the obtained samples was performed by means of a PANalytical X'Pert PRO X-Ray Diffractometer, with Cu K α radiation and operating at 45 kV and 40 mA. The following operative conditions were used: time 20 s, step 0.04 in a range of 3–70 20. High Score Plus software v.4.8 was used for the qualitative investigation. The

Table 1

XRF results on the ceramic waste LBCa selected as precursor and on the MK used as additive. LOI = Loss of Ignition; Not Det. = Not	Determined	d.
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Major Oxides (%)	SiO_2	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P_2O_5	LOI	Tot.
LBCa	60.67	16.30	5.69	0.08	2.31	8.73	1.35	3.27	0.69	0.14	0.47	99.70
MK ^a	58.56	34.03	2.57	Not det.	Not det.	2.08	Not det.	0.69	1.88	0,20	Not det.	

^a [20].

quantification of the amorphous phases was done by Rietveld Refinement [28], using 5% by weight of corundum as internal standard and by using Profex software for the phase interpretation [29].

FTIR-ATR spectroscopy both performed on the synthetized samples and on the precursors allowed to study the occurrence of the geopolymerization process. The analyses were conducted by means of a Thermo Fisher Scientific Nicolet 380 FT-IR spectrometer with a Smart Orbit diamond attenuated total reflectance (ATR) cell. The spectra were collected at room temperature in the 400-4000 cm⁻¹ range, with 4 cm⁻¹ resolution and averaging 64 scans. For each sample three measurements were acquired and the spectra averaged in order to have representative results.

The micro- and nano-structural investigation and the chemical study of the appearing gel were performed using Scanning (SEM) and Transmission (TEM) Electron Microscopies, coupled with Energy Dispersive X-Ray Probe (EDS). Three different SEM equipment were used, according to the availability and the magnification required. The employed SEMs were 1) Tescan Vega LMU Scanning Electron Microscope equipped with energy dispersive X-ray spectroscopy (EDS) microanalysis. Data were collected by focusing the e-beam on the sample at an energy of 25 kV and current of 0.2 nA; 2) Zeiss FEG-SEM Supra 25 Field Emission Scanning Electron Microscope equipped with InLens detector coupled with an energy dispersive X-ray spectroscopy (EDS) microanalysis where data were collected by focusing the e-beam on the sample at an energy of 25 kV and current of 0.2 nA; 3) Carl Zeiss SMT Field Emission Scanning Electron Microscope (AURIGA Series) equipped with InLens detector and an energy dispersive X-ray spectroscopy (EDS) microanalysis with energy of 20 kV and current of 0.2 nA. The measurements were performed on carbon coated samples.

TEM investigations were done by a Thermo Fisher Scientific TALOS F200X Transmission Electron Microscopy equipped with energy dispersive X-ray spectroscopy (EDS) operating at 200 kV and with an EDAX solid-state energy-dispersive X-ray detector. Powder samples were deposited on carbon-coated Cu grids. Quantitative chemical analyses were obtained in STEM mode using a scan window of 20×100 nm.

The physical-mechanical properties of the geopolymers were tested by using a Mercury Intrusion Porosimetry (MIP) and a Uniaxial Compressive test on cubic samples. A Thermoquest Pascal 240 porosimeter was used in order to explore the pore size distribution with radii comprised between 0.0074 μm and 15 μm , and a Thermoquest Pascal 140 porosimeter to investigate the pore radii range 3.8 $\mu m-116$ μm . Before the analysis, the fragments of about 1 cm³ size were dried in an oven for 24 h at 100 °C. Six replicates of 2 \times 2 \times 2 cm for each formulation were subjected to compressive tests using a 70-T1182 Uniframe (Controls) mechanical press with the following operative conditions: 2000 kN of maximum peak, 0.1 cell load and a velocity of 2400 N/s.

All the measurements were conducted on mature samples, after 28 days of curing, and compared with data acquired on the precursors. For the comparison of the ATR spectra of binary geopolymers, dry mixtures of the raw materials (10 wt% and 20 wt% of MK added to powdered ceramic waste) were considered.

3. Results

3.1. Mineralogical characterization by XRD

XRD patterns of the studied binders are reported in Fig. 1 (binders from ceramic waste) and Fig. 2 (binary mixtures), where patterns acquired on raw ceramic and MK are reported for comparison. All diffraction patterns display peaks due to crystalline phases deriving from the precursors, namely quartz, diopside, gehlenite, hematite, feldspars (K-feldspar and Ca-plagioclase) and wollastonite, with the addition of illite in the binary samples. New phases related to efflorescences (mainly thermonatrite) are identified. No significant differences are enhanced between geopolymer series with different alkaline solution ratios.

The Rietveld elaboration allowed to study the amorphous content increment from the precursors to the related geopolymers. It is summarised in Fig. 3, along with the content of efflorescences. These are indeed two important parameters to be considered in order to establish the quality of the geopolymer for further improvements.

The amorphous content behaviour is not linear with the increase of sodium hydroxide and MK in the paste, as instead it could be assumed. It is higher in the 1/1 set and only in the sample with 20 wt% of MK of the 3/7 set, whereas it decreases drastically in the set richer in soda, i.e. the 7/3 set (excepted the sample without MK). According to the amount of



Fig. 1. XRD diffraction patterns of LBCa 3/7, LBCa 1/1, LBCa 7/3 and LBCa raw; qz = quartz; di = diopside; gh = gehlenite; hem = hematite; kfs = K-feldspar; an = anorthite; wo = wollastonite; tnat = thermonatrite [30]; * indicates the corundum, added as internal standard. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 2. XRD diffraction patterns of 10 wt% MK and 20 wt% MK samples and the relative raw materials LBCa and MK; qz = quartz; di = diopside; gh = gehlenite; hem = hematite; kfs = K-feldspar; an = anorthite; wo = wollastonite; ilt = illite [30]; * indicates the corundum, added as internal standard. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 3. Histograms of the geopolymer series showing the amorphous content increase (a) and efflorescence amounts (b). The amorphous content has been calculated after the normalization of the data without efflorescence amounts.

MK it is evident that the samples with 10 wt% of MK show lower increase with respect to the corresponding samples with 20 wt% of MK or without MK. As for the efflorescences, the samples characterized by a higher amount of salts are those with higher sodium hydroxide/water-glass ratio; the salts content furthermore decreases with the increase of MK in the slurry.

Considering the decrease of the single phases, the higher contribution in the dissolution for the geopolymerization process is related to gehlenite (c.a. decrease of 70%), K-feldspar and hematite (c.a. 60% each) and Ca-plagioclase (c.a. 30%).

3.2. Gel investigation by FTIR-ATR

As expected, all the ATR spectra (Fig. 4) are characterized by a main, wide and intense band, appearing between 1240 and 815 cm⁻¹, the aluminosilicates absorption band. The interpretation of this region may be quite difficult because of the overlap of the vibrational signals of different compounds, thus determining a highly complex spectrum [15].

Overall, Fig. 4 highlights a change in the shape of the main band, which is characterized in the raw materials by a broad profile, organized

in different components: the position related to the maximum intensity (marked with a black dotted line in the figure), indicating the Si-O-T (T = Al, Si) stretching vibration [3,13,31], is centred at 1012 cm⁻¹. A shoulder band at 965 cm⁻¹ is also highlighted. In the geopolymer spectra, the maximum peak undergoes a shift towards lower wavenumbers. While the samples without MK, maintaining more or less the same shape of the raw material, show the shoulder band at 965 cm^{-1} as the new maximum of the main band (Fig. 5a), the binary samples show a narrower band with the maximum between 990 and 963 cm^{-1} (Fig. 5b). In order to obtain more accurate interpretations related to the shift of the maximum of the aluminosilicate band, the region of the main band has been extracted from each spectrum and compared with those of the precursor dry mixtures. Hence, the dry mixture with 20 wt% MK shows the maximum at 1017 cm⁻¹, conveying the influence of the main absorption band of MK, attested at 1040 cm⁻¹, whereas the related geopolymer samples LBCa 3/7 + 20MK, LBCa 1/1 + 20MK and LBCa 7/3 + 20MK 20MK show maximum peaks at 984, 978 and 963 cm⁻¹, respectively. The dry mixture with 10 wt% MK shows the maximum at 1012 cm^{-1} and its related geopolymers LBCa 3/7 + 10MK, LBCa 1/1 + 10MK and LBCa 7/3 + 10 MK display maximum peaks at 990, 978 and 975 cm⁻¹



Fig. 4. ATR spectra of the LBCa 3/7, LBCa 1/1 and LBCa 7/3 series, together with the raw materials LBCa, MK and the dry mixtures LBCa+10MK and LBCa+20MK. The spectra have been normalized in order to allow direct comparisons and stacked for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 5. (a) Zoom of the main band observed in LBCa geopolymer samples without MK, compared with the ceramic raw material LBCa; (b) zoom of the main band observed in the LBCa geopolymer samples with 10 wt% and 20 wt% MK, respectively compared with the dry mixtures of the raw materials LBCa with 10 wt % and 20 wt% MK. The spectra have been normalized in order to allow direct comparisons and stacked for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

respectively. The shift appears greater for the geopolymers without MK, while for those with MK it increases with the amount of both sodium hydroxide in the slurry and MK.

This shift occurs due to the formation of aluminosilicate gel [6,31, 32], as the asymmetric stretching vibrations of the newly formed Si–O-T bonds promotes the appearance of a new band around 950 cm⁻¹ [33, 34].

This interpretation finds confirm on what already seen by applying DRIFT on this kind of samples in previous investigations [35], where in the extracted region of 1300-900 cm⁻¹ - linked to aluminosilicates signals - a shift towards lower wavenumber of the principal band (1064-1077 cm⁻¹) is observed with respect to MK main position (1079 cm⁻¹) and to raw ceramic precursor (1071 cm⁻¹). This suggests the occurrence of the geopolymerization process according to Mladenović

et al. [36].

Apart from the main band signal, other significant ones appear in the geopolymer spectra. The broad band at 3440 cm⁻¹ together with the signal at 1650 cm⁻¹ represent the stretching and bending vibration of the OH bonds and of the absorbed water molecules in the geopolymer mixtures [3,7,13,31], which is more evident in the samples with MK. The signals at 1440 and 865 cm⁻¹, mostly visible in the samples without MK, represent the O–C–O asymmetric stretching linked to the formation of carbonate phases [6,7,12,13,37]. The band at around 450 cm⁻¹ decreases in intensity comparing the geopolymers with the raw materials; this could be attributed to the dissolution of Al–O and Si–O species with subsequent formation of Si–O–Al bonds [7].

Furthermore, looking at the doublet 798 and 779 cm^{-1} , distinctive of quartz, it is possible to notice a consistent intensity reduction in the

geopolymer spectra in comparison with the raw material, indicating quartz partial reaction [15].

3.3. Investigation of the microstructure by SEM-EDS

To point out the differences in the microstructure and chemical composition of the developed geopolymers, SEM-EDS analyses at different length scales were carried out.

Overall, the samples show a homogeneous and well reacted structure, bonding the particles at micrometric scale (Fig. 6a and b), similar to those observed in the literature related to ceramic-based geopolyemers [6,7,14,15]. All matrices appear compact with a dense, and in some areas vitreous-like, texture. Comparing the samples, the structure seems to become denser with decreasing sodium hydroxide/waterglass ratio, as expected [9]. Morphologically, the matrix is characterized by "sintered" granules, arising both as surface and internal features, which is possible to associate to the geopolymeric gel morphology [38], mainly N-A-S-H or (N,C)-A-S-H [39]. These observations confirm the development of an amorphous phase.

The EDS analysis acquired in different points of the matrices is compatible with a multi-component system of (N,C)-A-S-H (e.g. Fig. 6c and d), with the granular matrix and massive areas sharing more or less the same composition.

A distinctive feature characterizes the samples with 10 wt% MK, where, beside the granular morphology, smooth prisms apparently hollow and of heterogeneous composition are also visible (Fig. 7a). Similar structures are interpreted by Wan et al. [40] as a geopolymeric gel, but as far as we know there are no further explanation in the current literature.

Furthermore, LBCa 7/3 + 20MK stands out from the other samples because it shows a unique morphology characterized by mammillary-botryoidal aspect, distinguishable at high magnification (Fig. 7b). Nevertheless, the chemical composition of the botryoidal features characterizing sample LBCa 7/3 + 20MK does not deviate from the averaged chemical composition of the gels detected in the other samples.

No new further minerals are detected, while some relict minerals not

completely dissolved (Fig. 7c) are visible as residual particles of the aluminosilicate precursors. Among the phases detected, quartz, K-feld-spar and MK lamellae were identified.

The geopolymers are also characterized by a variable porosity heterogeneously distributed. As visible in Fig. 7d, spherical voids of $20-50 \mu$ m in size characterize the pore structure at low magnification, probably due to air bubbles trapped in the matrix during the synthesis [6,12,26, 27].

Different secondary products are distinguishable:

- soft-looking tufts of about 3 μm wide are spread all over the surface in samples LBCa 3/7 (Fig. 8a) and LBCa 7/3 (Fig. 8c). Increasing the magnification, these products show different morphologies and patterns: while the tufts appearing in sample LBCa 3/7 seem to be of secondary precipitation growing in the empty spaces, the tufts characterizing sample LBCa 7/3 appear as aggressive particles attached to the massive substrate;
- acicular/star-like crystals embedded in the amorphous matrix, thus interrupting its continuity, are visible in sample LBCa 7/3 (Fig. 8e);
- few superficial filaments are visible as secondary products on the surface of the sample LBCa 1/1 (Fig. 6b);
- long whiskers growing inside cavities and interstices, which could be interpreted as sodium carbonate [15], are observed at high magnification in the sample LBCa 1/1 + 20MK (Fig. 8e).

The EDS analyses performed on the tufts present in samples LBCa 3/7 (Fig. 8b) and LBCa 7/3 (Fig. 8d) confirm their different nature: the tufts of sample LBCa 7/3 are almost completely composed of Ca and Si, while Na and Al are also relevant in the tufts precipitating in sample LBCa 3/7.

EDS analyses performed on the other secondary products were unable to identify their composition because of their small dimensions.

From semi-quantitative EDS analyses of more than 150 points, the type of gel was better identified (Figs. 9 and 10).

The Al_2O_3/SiO_2 and CaO/SiO₂ ratios were plotted in Fig. 9; the compositional ranges which characterize the main types of gels, (C–S–H, C-(A)-S- H, C-A-S-H, N-A-S-H and (N,C)-A-S-H), are also marked in the figures according to literature [41,42]. Overall, the points analyses



Fig. 6. SEM images at different magnification of LBCa 1/1, as representative sample. The images show the dense matrix morphology (a and b) and the related EDS spectra (c and d). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 7. SEM images showing details of prismatic morfologies found in the samples with 10 wt% MK (a), the botryoidal structure of the sample LBCa 7/3 + 20MK (b), an example of relict mineral (c) and the visible porosity d). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

acquired on the different samples show a chemical composition with a prevalent attribution to (N,C)-A-S-H and only partially to N-A-S-H (mainly for samples with 20 wt% MK) or C-A-S-H (mainly for samples with 10 wt% MK). Regarding the samples with 10 wt% MK, plotting both the data acquired on the granular morphology and those acquired on the prisms, two clusters could be drawn, with partial overlap. Indeed, while the majority of the points related to the first morphology falls in the (N, C)-A-S-H and N-A-S-H region, with only some point toward the C-A-S-H region, the composition of the prisms is distributed between (N,C)-A-S-H and C-A-S-H, always with a moderate alumina/silica ratio. These interpretations are confirmed by the visualization of data in the SiO₂. –Al₂O₃–CaO ternary diagram for the gel reported in Fig. 10 and compared with the literature data [9]. The chart exposed in Fig. 11 summarizes the SEM-EDS observations.

3.4. Investigation of the nanostructure by TEM-EDS

Two samples, LBCa 1/1 and LBCa 1/1 + 20MK were selected and analysed under TEM after 28 days of curing in order to investigate the differences in the geopolymeric gel characteristics between pure ceramic samples and binary mixtures. Fig. 12 shows the formation of a different structure of the gel between the two samples. While the one without MK has a quite angular structure, where pseudo-geometric morphologies are identifiable, in that with MK these shapes disappear and the general appearance of the analysed fragment is cloudier (granular) and amorphous-like. The diffraction analyses performed in some points of the samples fragments confirm the amorphous nature of the gel, being sometimes also semi-crystalline. In order to understand the possible distribution of the type of gels (N-A-S-H and/or C-A-S-H), an elemental mapping was carried out. Hereafter it is reported an overlap of the distribution of Ca and Na elements. Fig. 13 shows a strictly intermingled Ca-Na composition in this geopolymeric gel. These results could be interpreted as a contemporary formation of both C-A-S-H and N-A-S-H as two phases strictly linked in nanometric structure. The results are consistent with those from the literature [41].

3.5. Compressive strengths by Uniaxial Compressive test

The results of Uniaxial Compressive Tests are shown in Fig. 14, while all the data analysis are in Table S1 (Supplementary).

The compressive strength increases with the increase of the percentage of MK and waterglass in the binders, as expected [6,7,13,15,22, 27,44–46]. The higher value is 28.72 MPa obtained for sample LBCa 3/7 + 20MK, followed by 20.14 MPa for the sample LBCa 1/1 + 20MK. Intermediate values are instead obtained for the formulations with 10 wt % MK, specifically 16.61 MPa for LBCa 3/7 + 10MK and 13.11 MPa for LBCa 1/1 + 10MK. The binders with the 7/3 ratio of sodium hydroxide/waterglass show the lowest values of resistance and a low brittle behaviour; in particular, samples LBCa 7/3 and LBCa 7/3 + 10MK do not reach the threshold of 5 MPa, arbitrarily chosen to consider the geopolymeric binder acceptable according to the desired applications in this research. All the samples with a lower resistance do not show the typical abrupt failure of the cement materials. The sample LBCa 1/1 also does not overcome that value. It is worth to note the peculiar behaviour of sample LBCa 3/7, which reaches resistances comparable to samples with 10 wt% MK. According to the standard deviation values, the sample with more reliable results is LBCa 1/1 + 20MK.

All the data acquired, after the exclusion of the aberrant ones, show Coefficient of Variation (CoV) values well below the threshold and can be considered of high quality with respect to the technical Italian legislation of concretes [47]. Under compression, the samples showed abrupt failure, typical of cements [22,48], with a detachment of the external walls. Only the samples with compressive strength lower than 10 MPa show a soft disintegration under compression.

3.6. Pore structure study by MIP

All the binders were analysed by Mercury Intrusion Porosimetry to investigate their porous structure and the bulk density. All the data (bulk density, accessible porosity to Hg, total pore volume, average pore diameter, modal pore diameter and incremental volume of the pores) are shown in Table 2.



Fig. 8. Detailed SEM images of secondary products. The images show details of tufts particles observed in the samples LBCa 3/7 and LBCa 7/3 (a and c) with the related chemical composition (b and d); the acicular crystals found in the sample LBCa 7/3 (e) and the whiskers of the sample LBCa 1/1 + 20MK. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Bulk density and percentage of accessible porosity, as well as the total pore volume, are similar for all the samples (accessible porosity of \sim 30%) whereas the porosimetric distribution on the different ranges varies among the samples. The more abundant pore range is represented by the fractions 1–0.1 and 0.1–0.01 μ m, with a prevalence of the coarser one, excepting for the samples LBCa 1/1 + 20MK and LBCa 3/7 + 20MK where the most prevalent is the $0.1-0.01 \ \mu m$ fraction. In order to study the influence of MK in the formulation, each series was considered separately (Figs. S2, S3, S4 - Supplementary); furthermore, the LBCa 3/ 7, LBCa 7/3, LBCa 3/7 + 20MK, LBCa 7/3 + 20MK are shown together (Fig. S5 - Supplementary) for comparison. Overall, with the increase of MK in the slurries, the pore diameter decreases. This phenomenon is well visible for the 3/7 series where the addition of 20 wt% MK determines a decrease of the average pore diameter from the range 10-1 μ m (with a peak at 2.5 μ m) to 0.1–0.01 μ m, while it is only slightly visible for the 7/3 series.

In order to study the influence of waterglass content in the slurry, the samples without MK were compared (Fig. S6 – Supplementary). Sample LBCa 7/3, the one with the lowest waterglass amount with respect to sodium hydroxide, shows a porosity characterized by a visibly smaller pore dimension, while the other two samples could be considered identical. Series 7/3 (with the exception of the first sample) is characterized by a more abundant and coarser porosity. It decreases in the

series 1/1 and 3/7, which show a similar porous structure. Noteworthy is the lower diameter of the porosity characterizing the samples with 20 wt% MK.

4. Discussion

According to the chemical (EDS), molecular (FTIR-ATR) and morphological (SEM, TEM) analyses, it was possible to assess the occurrence of the geopolymeric process, enhancing some differences between the samples, particularly regarding the polymerization network, as well as the formation of secondary salts.

The XRD investigations confirm the general increase of the amorphous phase in all the samples mainly to the expenses of crystalline aluminosilicate phases, in accordance with what expected after a process of alkaline activation [3,13,16,22,20,49,50].

From SEM observations it is possible to deduce that while the sodium hydroxide/waterglass ratio influences the density of the structure, producing denser matrix with higher waterglass proportions [6], it does not seem to have any particular effect on the type of gel formed. This latter is instead mainly determined by the different proportions of MK to the ceramic precursor. Indeed, samples with the same MK percentage show globally the same kind of gel. From a hybrid and homogeneous (N, C)-A-S-H gel of the samples without MK, the gel changes composition



Fig. 9. Al₂O₃/SiO₂ vs. CaO/SiO₂ ratios for gels precipitating in hybrid cements (based on EDS findings); (a) LBCa binders without MK; (b) LBCa binders with 10 wt% MK; (c) LBCa binders with 20 wt% MK. The gel ranges indicated are reported from the literature [41,42]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

with the addition of MK, increasing the N-A-S-H component. Furthermore, C-A-S-H clusters are present in the intermediate samples, particularly in correspondence of the individuated prismatic structures.

This unusual behavior is not well understood, but we speculate that it could be attributable to particular stoichiometric conditions [9,51] which negatively affect the continuity of the geopolymerization process.

Being unvaried all the other synthesis parameters (as liquid components proportions or molarity, environmental conditions, etc.), the only parameter which could determine variations is the elemental proportions. It could be possible that in presence of the sole ceramic precursor, the alkaline activation starts to dissolve the Ca-species, giving a hybrid gel with a slower but homogeneous growing. With the addition of



Fig. 10. SiO₂–Al₂O₃–CaO ternary diagram for the gel detected on all the AAMs series developed: LBCa 3/7 series, LBCa 1/1 series and LBCa 7/3 series. The gel ranges indicated in the diagram proceed from the literature [9,43]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

0% MK	Compact matrix Granular appearance N,CASH Tufts precipitates (Na+Al+Ca+Si)	Compact matrix Granular appearance N,CASH Filaments	Compact matrix Granular appearance N,CASH Tufts attaching (Ca+Si)
10% MK	Compact matrix Granular appearance Prisms NASH - N,CASH CASH	Compact matrix Granular appearance Prisms NASH - N,CASH CASH	Compact matrix Granular appearance Prisms NASH - N,CASH CASH
20% MK	Compact matrix Granular appearance NASH N,CASH	Compact matrix Granular appearance NASH N,CASH Long whiskers	Compact matrix Granular appearance Botryoidal matrix NASH N,CASH
	3/7	1/1	7/3

Texture density

Fig. 11. Gel type chart of LBCa binders: schematic summary of the SEM-EDS results.

some amounts of MK, the geopolymerization process readily affects the more reactive phases (those coming from MK, as indicated by Azevedo et al. [7], Buchwald et al. [19] and Rovnaník et al., [13]), somehow inhibiting the participation of the dissolved ceramic phases to the polycondensation reaction. This could determine the re-precipitation of Ca-rich phases (e.g. calcium aluminosilicate hydrates as strätlingite, or AFm phases) already found together with C-A-S-H gel in blended systems [41,42,43] and possibly represented by the prismatic morphologies. The higher amount of alumina in the samples with 20 wt% MK could justify the absence of the prisms, because of the more cross-linked

structure which could allow the blocking of the possible Ca excess within the gel [10,52,53]. Further investigations are needed in order to confirm this hypothesis.

However, in the blended systems the type of the final product is determined, besides the reaction conditions and the system chemistry, by the reaction mechanisms which can involve the evolution of the gel and the different phase equilibria [9,39,41,43,54,55]. The compatibility of the two gels (N-A-S-H and C-A-S-H) characterizing the hybrid systems is still a key topic of the current researches on geopolymers [39].

Considering the curing time and the theoretical parameters, we



Fig. 12. TEM micrographs of a fragment of sample LBCa 1/1 (a) and of LBCa 1/1 + 20MK (b). The image shows also two diffraction patterns obtained in two representative areas, red square. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 13. TEM map overlapping the distribution of Ca (yellow) and Na (blue) on the fragment of LBCa 1/1 + 20MK. The superimposed image has been obtained after the processing of the original images by median filter. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

would expect a linear increase of those properties related to the geopolymer gel growth, as the amorphous amount and the compressive resistance, according to the amount of MK in the mixture [7,56]. Nevertheless, results of this work indicate a higher amorphous amount and better resistance to the compression for the samples without MK compared to those with only 10 wt% MK. The samples with 20 wt% MK



Fig. 14. Compressive strength average, measured on all the experimented geopolymers. The standard deviation bar is indicated. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

show, instead, the highest results as expected. When considering resistance only, this trend is valid strictly for the 3/7 series, while for 7/3 and 1/1 series the behaviour is more homogenous. This uncommon pattern could be clarified thanks to the SEM data, which illustrate a complex system.

Concerning the samples without MK, the good compressive resistance of sample LBCa 3/7 could be explained by the dense and vitreous texture of the matrix, likely due to the high waterglass proportion in the slurry [9], which makes the matrix more compact despite the presence of efflorescence. The considerable increase in the amorphous content for this sample is consistent with this interpretation. On the contrary, sample LBCa 7/3 completely failed the compressive test. This could be associated to the abundance of crystalline structures which interrupt the continuity of the geopolymeric gel [57]. The relatively high amount of amorphous fraction in this sample could be associated to the presence of dissolved material which is however not fully consolidated (probably the individuated tufts).

In addition to an apparently well-reacted compact structure, prismatic structures interrupting the matrix continuity are well visible in samples with 10 wt% MK. These crystalline structures certainly contribute, together with a high amount of efflorescence (with the exception of sample LBCa 1/1 + 10MK), to lower the general quantification of the amorphous fraction and the compressive resistance of sample LBCa 3/7 + 10MK.

Concerning samples with 20 wt% MK, as observed for those without MK, the higher the silicate proportion in the mixture, the denser is the matrix [9]. This is confirmed by the compressive resistance data and by the measured amorphous amount.

Therefore, comparing all the data, the samples with the highest waterglass and MK amount show the best results. In this context, sample LBCa 7/3 + 20MK shows poor results, with medium-low resistance, low amorphous increase and simultaneous high efflorescence amount. Furthermore, its morphology observed with SEM at high magnifications appears poorly vitreous, with a particular botryoidal structure.

Another component influencing the mechanical resistance and durability of the material is the porous structure [58]. From the MIP data overview, it is possible to affirm that the parameters which mainly affect the porous structure of these geopolymers is the MK presence that is responsible for the reduction of the pore diameters without affecting the total porosity amount.

Table 2										
MIP data of the LBCa geopoly	meric slurries.									
		LBCa 7/3	LBCa $7/3 + 10MK$	LBCa $7/3 + 20$ MK	LBCa 1/1	LBCa $1/1 + 10MK$	LBCa $1/1 + 20MK$	LBCa 3/7	LBCa $3/7 + 10MK$	LBCa $3/7 + 20MK$
Bulk density (g/cm ³)		1.84	1.84	1.76	1.92	2.16	1.65	1.85	1.79	1.76
Accessible Porosity (%)		32.37	28.11	32.09	26.85	30.56	28.42	27.88	27.15	26.92
Total Pore Volume (cm^3/g)		0.18	0.15	0.18	0.14	0.14	0.17	0.15	0.15	0.15
Average Pore Diameter (µm)		0.29	0.26	0.24	0.94	0.13	0.04	0.46	0.09	0.04
Modal Pore Diameter (µm)		0.77	0.60	0.47	2.19	0.25	0.06	2.19	0.14	0.05
Incremental Volume (cm ³ /g)	100-10 µm	0.07	0.02	0.00	0.08	0.01	0.00	0.02	0.01	0.00
	10-1 µm	0.72	0.21	0.02	7.22	0.03	0.01	6.96	0.02	0.00
	1-0.1 µm	76.84	39.99	37.24	16.07	38.78	0.01	24.71	19.96	0.00
	0.1-0.01 µm	45.52	21.96	24.18	13.78	26.28	109.47	17.85	46.21	98.02
	0.01-0.001 µm	16.91	7.49	60.6	6.14	7.05	9.77	7.36	7.56	9.45

5. Conclusions

To summarize, the most important results are hereafter listed:

- An aluminosilicate amorphous gel typical of geopolymers is formed in all the samples by synthesis performed at room temperature by alkaline activation of ceramic waste.
- The density of the matrix, always homogeneous and well reacted, increases with the increase of waterglass in the formula.
- The amorphous phase amount increases in the geopolymers with respect to the original content in the precursors in a not linear way, with higher values for the samples without MK and with 20 wt% MK; this could be attributed to particular stoichiometric conditions which may determine the formation of crystalline prisms only in the samples with 10 wt% MK.
- The gel appears as a multicomponent system dominated by a (N,C)-A-S-H composition, showing also N-A-S-H (mainly for samples with 20 wt% MK) or C-A-S-H (mainly for samples with 10 wt% MK) areas.
- On the whole, the compressive strength increases with the increase of amorphous, with a maximum value measured slightly over 28 MPa and an abrupt failure mode obtained on all the samples with a compressive strength higher than 10 MPa.
- Samples with the higher ratio sodium hydroxide/waterglass are affected by the formation of efflorescence, which influences also the mechanical performances; efflorescence amount decreases with the increase of MK in the formula.
- Accessible porosity (~30%) and total pore volume is similar even when the geopolymer composition changes.

Concluding, this research confirms a good geopolymeric reaction of the waste ceramic raw material LBCa, which has a high potentiality for producing at room temperature binders with good characteristics. The compressive strengths and porosity of the synthetized products could be tailored by changing the proportions of the solid and liquid components, obtaining case by case the best characteristics for the implementation of suitable construction and restoration materials.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.

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