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Raman spectroscopy potentiality in the study of geopolymers reaction degree

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Abstract

Alkali-activated materials (AAMs) and "geopolymers" are inorganic polymeric materials obtained by mixing of solid aluminosilicate precursors with an alkaline solution (generally, KOH or NaOH and Na_2SiO_3 mixed in various ratios). This class of aluminosilicate materials has emerged as a greener alternative to traditional concrete, for large-scale as well as for niche applications such as conservation and restoration of built heritage. In this work we apply Raman spectroscopy both to aluminosilicate precursors (metakaolin, pumice, volcanic ash, volcanic soils, clayey sediments, ceramic waste) and to the respective AAMs. In the field of vibrational spectroscopy, Raman is much less employed in the literature with respect to Fourier transform infrared (FTIR) to have insights into the alkali activation process from a molecular point of view. The aim of this paper is to investigate the potentiality of a Raman approach to the comparison of the employed raw materials with the respective AAMs. Raman analyses during the first hours of geopolymerization were also carried out on the clayey sediments and ceramic waste-based products. The results, differentiated according to the employed precursors, exhibit spectra relative to crystalline and amorphous phases that can give an indication about the newly formed aluminosilicate gel.

KEYWORDS
alkali-activated materials, aluminosilicates, amorphous phases, geopolymerization

1 | INTRODUCTION

Alkali-activated materials (AAMs), including those classified as geopolymers,[1] have been intensively studied and promoted in the last decades as low-carbon binder alternatives to Portland-based cements, in response to growing global concerns over CO_2 emissions from the construction sector.[2–9] AAMs can be generated from a variety of industrial minerals such as kaolinite and feldspars and from industrial solid residues or wastes such as fly ashes, metallurgical slags, and mine wastes.[2,6,10] Thus, their versatility and local adaptability make them a

powerful tool in the development of worldwide sustainable construction industry. In the framework of the Italian National Research Program "Advanced Green Materials for Cultural Heritage," local Sicilian raw materials and industrial wastes are being used as precursors for geopolymers production with the aim to contribute at reducing the carbon footprint and the environmental impact of building materials industrial production.

AAMs are produced from a mixture of several aluminosilicate materials (with high contents of Si and Al) along with an alkaline-activating solution of hydroxides (Na^+, K^+, or Ca^+) and silicates (Na^+ and K^+) and even carbonates or sulfates.[2] The result is a hardened binder based on a combination of hydrous alkali-aluminosilicate and/or alkali-alkali earth-aluminosilicate phases. Based on the nature of their cementitious components, alkaline materials may be classified as high-calcium and low-calcium cements. In the first model, Ca- and Si-rich materials are the main components, and the reaction product is a calcium aluminosilicate hydrate (C-A-S-H) gel, which takes Al in its structure, similar to the gel obtained during Portland cement hydration.[11] In the second system, the materials activated comprise primarily Al and Si. The main reaction product is a 3D inorganic alkaline polymer, a sodium aluminosilicate hydrate (N-A-S-H) gel with a highly cross-linked, disordered pseudo-zeolitic structure.[8,9,12,13] This gel is also called geopolymer or inorganic polymer. The negative charge related to the substitution of Si^{4+} by Al^{3+} is balanced by alkali-metal cations in the gel framework. In the present study, we focused on the latter system.

Several parameters must be analyzed selecting the raw materials to produce geopolymers, such as the reactive (amorphous) silica content and particle size.[14]

The reactivity of raw materials depends on their Al_2O_3 and SiO_2 content. Moreover, the alteration of Si/Al molar ratio allows the synthesis of materials with different structures as the aluminum atoms cross-link chains of SiO_4 and $MAlO_4$ tetrahedra (where M is a monovalent cation, typically Na^+ or K^+). The polymer formation rate is also influenced by the type of the alkaline metal and by the concentration of the activating solution on the development of the microstructure of the gel framework.

At the end of the reaction process, several phases are present in the system. These include unreacted particles, partially reacted particles, newly formed (alumino)-silicate gel, smaller (alumino)-silicate species liberated from the network, dissolved alkali-metal hydroxides, and water.[15,16]

The spectroscopic techniques generally used to evaluate the structure of the AAMs at short-range length scale include Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy, which have proven to be very helpful for developing models to ascertain and describe the structure of the various gels formed.[17]

For the first time, this work aims to investigate the reasons why Raman spectroscopy is much more rarely employed with respect to the other above-mentioned techniques, especially if geopolymers are considered.[18–31] This is reported to be due to high levels of fluorescence when shorter excitation wavelengths are used and to the appearance of photoluminescence bands when longer ones are preferred.[18] On the other hand, it must be considered that the silicate tetrahedron highly covalent character would make Raman spectroscopy theoretically one of the ideal techniques for these materials investigation.[18,19]

To the authors' knowledge, only two papers systematically take into account the Raman contribution to the geopolymers study.[19,20] Their Raman spectra are considered by Kosor et al.[19,20] in the same way as those of silicate glass, evaluating the silicate tetrahedra polymerization degrees present in the spectra. The Geopolymerization Index (GI), ranging between 0 and 1, is defined for fly ash geopolymers as the ratio between the integral of the normalized Raman spectrum of α-quartz and that of the investigated sample in the spectral region between 300 and 1200 cm^{-1}.[19] The Geopolymer Depolymerization Index (GDI) is instead proposed[20] as a measure of the depolymerized tetrahedra content and is defined as the ratio between the integrals of the 800–1200 and the 300–500 cm^{-1} regions, based on the same concept as the glass polymerization index.[32] In fly ash activated with sodium silicate solutions[19,21] and in fly ash pastes modified with graphene oxide,[21] the appearance of broad signals centered around 835, 940, 990, 1060, and 1160 cm^{-1} is reported and attributed, respectively, to Q^0, Q^1, Q^2, Q^3, and Q^4 silicate tetrahedron units positions. In the Q^n notation,[33] Q stands for the Si atom and n (0–4) indicates the number of bridging oxygen atoms.[34] The appearance of a peak at 1064 cm^{-1} is confirmed also for metakaolin-based AAMs[22]: in this case, the signal is sharp; nevertheless, the authors assign it to Si–O^- vibration where O^- denotes a nonbridging oxygen within a Q^3 or Q^2 unit, ruling out a possible assignment of the peak to carbonate species, because it was found also on products activated with KOH and NaOH only. On the other hand, when waterglass is employed as activator, the possibility of a carbonate contaminant generating this band must be taken into account[35] together with the eventual crystallization of efflorescences on mature products.[36,37]

A misunderstanding that apparently leads to results concerning the metakaolin-based AAMs aluminosilicate structure is that concerning the band at 143 cm^{-1} and

those at 400, 514–520, and 635–640 cm^{-1}: the former has been attributed to intratetrahedral vibrations of polymerized silicate tetrahedra,[23] and the two latter to T-O-T (T: Si or Al) bending and T-O symmetric stretching modes.[23,24] Nevertheless, these four signals must be most probably assigned to anatase present in the raw materials.[38]

Another specific application of Raman[25] or FT-Raman[18,26] spectroscopy to geopolymers study is that of investigating the material hydration detecting the hydroxyl bonds vibrations in the high wavenumber region of the spectra, also with the aid of mapping.[25]

Other employs of Raman spectroscopy in this field are rather occasional, restricted to graphite[27] or graphene[28,29] analysis, or limited to answer specific questions such as detecting calcium activity in geopolymer paste[30] or testing the efficiency of photoactive TiO_2 incorporation.[31]

The present work origins from the contradiction between the theoretical potential of Raman spectroscopy in the investigation of geopolymers and its limited use, often with debatable results. Therefore, filling a gap in the literature, it aims to systematically reconsider its suitability in the application to AAMs study, starting from new data about geopolymers made with metakaolin, volcanic materials, clay sediments, and ceramic wastes precursors. This is done comparing the results obtained on the precursors and on the respective AAMs, both the mature ones (more than 28 days after synthesis) and the fresh ones immediately after synthesis, followed during the first 8 h of the geopolymerization process.

2 | MATERIALS AND METHODS

2.1 | Materials

2.1.1 | Raw materials

In the present study, different aluminosilicate raw materials have been selected for the preparation of AAM products (Figure 1):

- Commercial metakaolin (ARGICAL™ M-1000 supplied by IMERYS, France) used either alone or in combination with the other aluminosilicate precursors. Metakaolin (hereafter labeled MK) was used without any treatment.
- Three Sicilian volcanic deposits: (i) Aeolian pumice, sampled in the dismissed quarry of Porticello (Aeolian Islands, Sicily, Italy); (ii) volcanic ashes from 2013 Mt. Etna paroxystic events, collected in the local landfill on the south-east slope of the volcano (Santa Venerina, Sicily, Italy); (iii) volcanic paleo-soils, locally known as "ghiara", having composition similar to Etnean ashes and a characteristic reddish color,[39] sampled by hand shovel in a volcanic tunnel in the south slope of Mt. Etna (Sicily, Italy).
- All these raw materials were water-washed and dried before dry milling (<75 μm).
- Sicilian clay sediments sampled in Poggio Safarello (central southern Sicily, Italy) where mainly Plio-Quaternary sediments are exposed. Once sampled, clay raw materials were calcined at 800°C for 3 h in order to improve their reactivity toward geopolymerization reaction.[40] Finally, they were dry milled to select only grain size <15 μm.
- Tiles waste provided by "La Bottega Calatina" (LBC), a Sicilian industry of painted tiles. The broken tiles or those showing imperfections are usually disposed as nontoxic material and have been selected for the purpose of this study as industrial by-products. The fragments have been retrieved, the glaze removed, and then finely ground (approximately 10 μm).

All the precursors mentioned above have aluminosilicatic composition and amorphous fraction, both necessary for the production of geopolymers. These raw materials were analyzed before their use as precursors in alkaline activation; their chemical and mineralogical results are reported in previous works[36,37,41,42]; the latter are summarized in Table S1, whereas SiO_2/Al_2O_3 ratios are reported in Table S2.
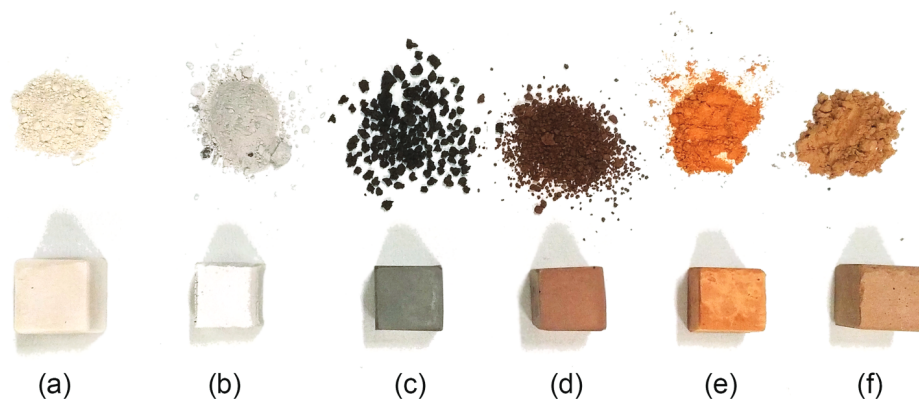

FIGURE 1 (a) Metakaolin, (b) pumice, (c) volcanic ash, (d) ghiara, (e) clay, and (f) LBC ceramic waste precursors (top) and respective representative AAMs (bottom) [Colour figure can be viewed at wileyonlinelibrary.com]

(a)   (b)   (c)   (d)   (e)   (f)

- Laboratory grade sodium hydroxide (8M), potassium silicate (molar ratio 0.65 Si/K), commercially known as Geosil 14515 (provided by Wollner), and sodium silicate (molar ratio $SiO_2/Na_2O = 3$) (provided by Ingessil s.r.l., Italy) solutions alone or in mixture have been used as alkali activators.

2.1.2 | Alkali-activated materials

In this paragraph, the alkali activation procedures are briefly exposed; details concerning each studied formulation are reported in Table 1.

A formulation made only of metakaolin has been prepared, and the activated product has been analyzed. This MK-based binder has a much simpler composition compared with the other AAMs produced from multiphase raw materials (Table S1) and is necessary as reference and comparison.

All aluminosilicate precursors have been used either alone or in binary mixtures with small additions of MK (10–20 wt%).

Solid mixtures were then activated with Na_2SiO_3 and NaOH or K_2SiO_3 solutions, choosing among the best formulation.[36,37,41,43]

The slurries were mechanically mixed for 5 min, poured into molds, and then cured at room temperature ($22 \pm 3°C$) for 28 days, covered by a thin polymer film to maintain a constant level of moisture. This condition could not be maintained for the products analyzed soon after synthesis, which were exposed to air during the Raman analyses.

2.2 | Methods

Preliminary tentative investigations with a portable instrumentation with handheld measuring head

TABLE 1 Details of alkali-activated materials formulations

Precursor	AAMs label	Precursor/MK ratio (wt%)	NaOH/Na₂SiO₃ (wt%)	Liquid/solid ratio[a]
Metakaolin	MK-GP	0/100	50/50	0.68
Pumice	POM 1-30	70/30	50/50	0.72
Volcanic ash	Na-VM10	90/10	37.5/62.5	0.32
	Na-VM20	80/20	37.5/62.5	0.32
	VM1-10	90/10	23/77	0.52
	VM1-20	80/20	23/77	0.52
	K-VM10	90/10	0/100	0.31
	K-VM20	80/20	0/100	0.31
Ghiara	Na-GM10	90/10	37.5/62.5	0.32
	Na-GM20	80/20	37.5/62.5	0.32
	GM1-10	90/10	27/73	0.44
	GM1-20	80/20	27/74	0.44
	K-GM10	90/10	0/100	0.31
	K-GM20	80/20	0/100	0.31
Clay	PS3	0	23/77	0.52
LBC ceramic waste	LBCa30-70	100	30/70	0.45
	LBCa30-70+10	90/10	30/70	0.45
	LBCa30-70+20	80/20	30/70	0.47
	LBCa50-50	100	50/50	0.44
	LBCa50-50+10	90/10	50/50	0.43
	LBCa50-50+20	80/20	50/50	0.45
	LBCa70-30	100	70/30	0.43
	LBCa70-30+10	90/10	70/30	0.44
	LBCa70-30+20	80/20	70/30	0.44

[a]Liquid to solid ratio is referred to the ratio between the alkali solution and the solid precursor.

(i-Raman® Plus spectrometer [B&W Tek], equipped with a 785 nm diode laser) were carried out.

Nevertheless, the analyses were mainly conducted with a fixed micro-Raman instrumentation, a Jasco NRS3100 spectrometer equipped with a Notch filter and a Peltier-cooled ($-49°C$) 1024×128 CCD. In this work, the 532-nm excitation wavelength was employed, reaching, with the 1800 g/mm grating, a spectral resolution of ~ 3 cm^{-1}. The calibration of the system was verified using the 520.7-cm^{-1} Raman band of silicon before each experimental session.

Precursors and mature—more than 28 days—AAMs were analyzed for all the groups of considered materials. In order to achieve the wider analytical representativity possible, 10 spectra per each powdered sample were acquired on different spots employing an Olympus (Japan) $20\times$ objective (N.A. = 0.45), with a spatial resolution of about 4 μm. The laser power value was controlled through optical density filters and kept around 1 mW on the sample to avoid heating effects. Time and number of accumulations were regulated according to the sample response. Both the low wavenumber region (130–1200 cm^{-1}) and the high one (3100–3700 cm^{-1}) were investigated.

For clay and LBC ceramic waste, measurements during the geopolymerization process were also carried out. A small quantity of powders of the two precursors were alkali activated (see Section 2.1.2) and, immediately after, analyzed using an Olympus (Japan) $50\times$ LWD objective (N.A. = 0.50) in the 130–1200 cm^{-1}. The laser power was set at ~ 1.5 mW, the time at 60 s, and the accumulations at 10. At the end of each 10-min measurement, a minimal adjustment of the focus was done and a new spectrum was started, for a total of 8 h.

In general, the spectra are presented as such, with the aim of providing an accurate idea of the Raman

TABLE 2 List of the signatures found in the different materials of the present work and respective attributions

| Signals (cm^{-1}) | Attribution | Materials | | Ref. |
		Precursors	AAMs	
150, 200, 395, 518, 638	Anatase	MK, CL	MK, PM, VA, GA, CW	Murad[38]
620	Rutile		VA	Lafuente et al.[44]
327, 392, 525, 560, 666, 770, 1009	Augite/diopside	PM	VA, GA	Minčeva-Šukarova et al.[45]
461	Quartz		PM, CW	Lafuente et al.[44]
480, 505	Anorthite	VA	GA	Lafuente et al.[44]
823, 855	Olivine	VA	VA, GA	Kuebler et al.[46]
224, 244, 292, 408, 500, 606	Hematite	GA, CL, CW	GA, CL	Froment et al.[47] and dos Santos et al.[48]
730	Maghemite	GA	VA, GA	Froment et al.[47] and Tanevska et al.[49]
660–673	Magnetite	VA, GA, CL, CW	VA, GA, CL, CW	Froment et al.[47]
	Disordered hematite (Al-for-Fe substitution in hematite; hematite recrystallization)			Zoppi et al.,[50] Leon et al.,[51] and Marshall et al.[52]
680–690	Spinel-like mineral belonging to the ferrite group	VA	VA	D'Ippolito et al.[53]
960–1000, 1062–1068	Q^2, Q^3 (silicate tetrahedron)		PM, VA, GA, CL, CW	Kosor et al.[19,20] and Xu et al.[21]
488, 790	Si–O–Si Bending, Q^0 (silicate tetrahedron)	PM		Colomban[32,54]
1045, 1100	Q^3 (silicate tetrahedron)	GA		Kosor et al.[19] and Arnoult et al.[55]
3440	OH stretching vibrations		CL, CW	Szechyńska-Hebda et al.,[18] Steinerová and Schweigstillová,[25] and Mierzwiński et al.[26]
3630	Si-OH		CW	Walrafen[56]

Note: MK: metakaolin; PM: pumice; VA: volcanic ash; GA: ghiara; CL: clay; CW: LBC ceramic waste.