Case Studies in Construction Materials 18 (2023) e02194

Contents lists available at ScienceDirect

Case Studies in Construction Materials

journal homepage: www.elsevier.com/locate/cscm

Testing the volcanic material burying Pompeii as pozzolanic component for compatible conservation mortars

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ARTICLE INFO

Keywords:
Pozzolanic mortars
Volcanic material
Pompeii
Conservation mortars

ABSTRACT

The aim of this work is to evaluate the potential use of ashes and lapilli that buried Pompeii as pozzolanic material for the formulation of conservation mortars. XRD analyses proved that the mineralogical composition of these volcanic products is consistent with the original pozzolanic mortars preserved at the archaeological site. A first set of pozzolanic mortars were prepared by using silica sand as aggregate. After curing the lapilli-based mortars, the measured compressive and flexural strengths proved to be higher than those of the control samples made of commercial pozzolan. A second set of samples, prepared by replacing silica sand with similar size coarse ash and lapilli, proved that volcanic aggregates further enhanced the mechanical properties by the formation of interfacial transition zones. The result of this research demonstrates that the volcanic material burying the archaeological site of Pompeii could be used as raw material in the formulation of compatible conservation mortars. As volcanic pozzolan is increasingly investigated as potential Supplementary Cementitious Material (SCM) for the production of sustainable concretes, preliminary considerations about the impact of the present work to this field of research are also provided.

1. Introduction

Trying to extend the life cycle of concrete infrastructures and increase their environmental sustainability, the development of novel building materials is finding inspiration in the ancient Roman concrete [1–3]. Based on the use of natural pozzolanic materials, the so-called *opus caementicium* ensures a much lower carbon footprint than that of modern Portland cement based concrete [4], whose production is responsible for up to 5–7 % of global CO_2 emissions [5,6]. Therefore, this product provides a model for producing more environmental friendly building materials that could favour the transition towards more eco-compatible production strategies, thus mitigating the environmental impact generated by the construction industry [1,3]. Besides environmental sustainability, *opus*

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https://doi.org/10.1016/j.cscm.2023.e02194
Received 17 February 2023; Received in revised form 25 May 2023; Accepted 5 June 2023
Available online 7 June 2023
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caementicium has received comprehensive attention in the past years due to its improved durability over modern concrete [7–9].

Many analytical works recently tried the investigate complex physical and chemical transformations occurring during the hardening of *opus caementicium* [4,10–15]. Some of these studies have been carried out in the framework of international research projects aimed at unveiling the secrets of this ancient technology and at assessing the potential repercussion it could have in the development of modern, eco-compatible building materials (e.g. Romacons [16]). As a result, recent works suggested the long lifetime of ancient Roman mortars is also related to the formation of phillipsite and Al-tobermorite during the pozzolanic reaction [17,18], as those compounds act as high-resistant cementitious binders [19].

Besides benefiting from the reaction with seawater, recent literature shows the durability and mechanical properties of *opus caementicium* can be enhanced by a careful selection of raw materials. In this sense, it is well know that, whenever available, Romans made extended use of volcanic ashes as pozzolanic component [20,21]. For instance, it has been widely demonstrated that ancient Roman concrete at the Archaeological Park of Pompeii (Naples, Italy) was made using volcanic ashes from the Somma-Vesuvius volcanic complex [15,21,22]. Even though the use as aggregates of quartz-rich sand, ceramic fragments and crushed bricks has been reported [23,24], most Pompeian concretes display the predominant use of volcanic rocks from Somma-Vesuvius [15,21,22,25]. As a representative case of study, the petrographic analysis of concrete fragments sampled from the Sarno Bath complex (Pompeii) proved that these volcanic aggregates partially reacted with lime during hardening [26], thus, leading to the formation of interfacial transition zones that improve the mechanical features of the final product [27].

As the use of volcanic materials from the Somma-Vesuvius complex has been also reported at Roman archaeological sites nearby Pompeii, (including Herculaneum [28,29] and Stabiae [30]), the pozzolanic activity of this material has been pointed out as an additional factor contributing to the remarkable preservation state of the Roman structures found in the region. Further confirming the remarkable quality of this pozzolanic material, recent geochemical investigations proved that ashes and lapilli from Somma-Vesuvius were used to build the Forum of Caesar and the Forum Trajan [31], thus, identifying a trade route from Pompeii to Rome [32]. On the long-term, a better comprehension of the mineralogical transformations occurring during the hardening of *opus caementicium* will help improving the durability and sustainability of novel building materials. In addition to that, the improvement on the current knowledge about *opus caementicium* has important implications in the short-term, as it will help optimizing the selection of raw building materials to be used for the preservation of ancient Roman structures [33].

In this regard, the restoration of pozzolanic mortars preserved at the Archaeological Park of Pompeii, is generally based on the use of volcanic materials commercialized as conservation products for Cultural Heritage. However, these materials often provide unsatisfactory results, with cracks and lacunae appearing just a few years after the conservation material is applied. Trying to find a tailored solution to this critical problem, the Archaeological Park of Pompeii signed a scientific collaboration agreement with the University of the Basque Country UPV/EHU (Spain), to explore the potential exploitability of the volcanic material burying Pompeii in the production of a pozzolanic concrete to use in conservation works.

In the framework of this research project, a deep characterization of ash and pumice samples that buried Pompeii in 79 CE was carried out. After comparing their properties with those of commercial natural pozzolans conventionally used in conservation works, samples of *opus caementicium* were prepared and monitored. In the short term, this work aims to evaluate the potential exploitability of "Pompeian Pumice" eruption materials for the conservation of Roman structures from Pompeii and the archaeological sites located nearby. On the long run, the detailed long-term monitorization of the physical and chemical transformations occurring during its pozzolanic hardening will provide data of crucial importance for the development of novel sustainable concretes.

2. Materials and methods

2.1. Raw materials

To assess the potential use of volcanic materials from Somma-Vesuvius as pozzolanic components for conservation mortars, ashes and lapilli dating back to the eruption of 79 CE were sampled and studied. By taking advantage of the new conservation works carried out in the framework of the Great Pompeii Project, recently excavated volcanic materials were collected from the archaeological site in October 2017. In detail, 3 kg of ashes and 3 kg of lapilli were collected from below the "tuono", which is the cemented volcanic layer that sheltered the archaeological site from rainwater infiltrations and further external environmental stressors, thus, contributing to the preservation of the ancient city. As such, as can be inferred the sampled materials presented low alterations features.

Composition of Somma-Vesuvius materials was compared to commercial pozzolans. For this purpose, grey and pink micronized pozzolanic materials were purchased from C.T.S. España S.L. (Madrid, Spain), a company specialized in the production and commercialization of products for the conservation of Cultural Heritage. Both products come from inactive volcanoes located in the surrounding of Rome (Italy), they are primarily composed of silicates (SiO_2) and aluminates (Al_2O_3) and their reactive silica content is > 30 % (minimum requirement regulation EN 197-1 > 25 %).

Pozzolanic material was mixed with two different kinds of aggregates. On one hand, mortar samples described in Section 3.2 (see below) were formulated by using standard sand purchased from the Eduardo Torroja institute (Madrid, Spain). In accordance with the norm UNE 196-1, the sand has a granulometry between 2.00 and 0.08 mm and is composed of 98 % quartz. On the other hand, the samples described in Section 3.3 were formulated by replacing sand with coarse volcanic particles (diameter > 5 mm) from Pompeian ash and lapilli, thus, replicating the formulation of original mortars analysed at the Archaeological Parks of Pompeii and Herculaneum [26].

Slaked lime ($Ca(OH_2)$) was purchased from C.T.S. España S.L. This product was chosen over the natural hydraulic lime (NHL), as the latter contains clay minerals (up to 30 wt%) that increase the hydraulic properties. Finally, ultrapure water (MilliQ, Millipore) was used to prepare pozzolan concrete samples and to perform chromatographic analysis.

2.2. Preparation of mortar samples

Prior to use, all pozzolanic materials were heated at 50 °C for a week to eliminate all residual humidity. This temperature was chosen both because it is not high enough to generate gas bubbles that could damage the sample, and for adequately removing the moisture from the sample, without removing the water of hydration from the molecules, which would generate a phase change to another mineral. In the case of Pompeian lapilli, a ball mill was used to reduce its granulometry. As the granulometry of pozzolanic materials strongly affects their reactivity, mortar samples were prepared by using raw materials of comparable grain size. In detail, knowing that 90 % of both commercial pozzolans have a granulometry below 125 µm (technical data sheet available online), Pompeian lapilli and ashes were sieved so that the smaller fraction (< 125 µm) was used as pozzolanic material while the fraction above 5 mm was used as aggregate (see Section 3.3).

Taking into account ancient technology records about Roman mortar production [34], as well as the information provided in previous works, 337.5 g of fine pozzolanic material was mixed with 112.5 g of slaked lime, 1350 g of aggregate and 225 g of water (3 pozzolanic material: 1 lime: 12 aggregate: 2 water). The mixture was homogenized using a HOBART mixer (USA) and 40 × 40 × 160 mm moulds were used to create mortar samples (3 for each formulation). Compactation was carried out using a horizontal compactor model 65-L0012/E under the norm UNE-EN 196:1 2005. Afterwards, mortar samples were covered to minimize water evaporation and demoulded after 7 days. Their mechanical properties were measured after 28 days of curing at room temperature. Afterwards, the compressive strength was evaluated on the two resulting halves of each specimen from the flexural test (halves were cut to obtain 40 × 40 × 40 mm cubic specimens).

2.3. Analytical instruments

The mineralogical composition of raw materials and mortar samples was determined by the Analytical Xpert PRO X-ray diffractometer (XRD, PANalytical, Netherlands). The XRD system is equipped with a copper tube, a vertical goniometer (Bragg-Brentano geometry), a programmable divergence slit, a secondary graphite monochromator and a Pixcel detector. The measurement conditions were set at 40 KV, 40 mA and a scan ranging between 5 and 70 2-theta. Diffractograms were acquired with a step increment in 2theta of 0.01 and a count time of 0.3 s per step. The interpretation of diffractograms was performed using WinPLOTR software, by comparison with the PDF-4 standards database [35].

Complementary molecular analyses were carried out by Fourier-transform infrared spectroscopy (FTIR). For this purpose, the JASCO 6300 system (JASCO) operating in transmittance mode was used. The instrument is equipped with a Ge on KBr beamsplitter, a Michelson interferometer and a DLaTGS detector with Peltier temperature control. Analyses were performed in the middle infrared region (from 4000 to 400 cm^{-1}) by setting 64 scans with a spectral resolution of 4 cm^{-1}. To collect transmittance spectra, KBr-matrix pellets were prepared by mixing 0.5 mg of sample with 170 mg of dry KBr (> 99 % FTIR grade, Sigma-Aldrich). After milling the mixture in an agate mortar, the resulting powder was pressed under 10 tons (CrushIR, PIKE technologies) for 8 min. FTIR spectra characterization was carried out using the Opus 7.2 software (Bruker Optics, Germany).

Concerning the elemental composition of pozzolanic materials, quantitative analyses were carried out by means of inductively coupled plasma mass spectrometry (ICP-MS). Prior to analysis, pozzolan samples were totally dissolved by following the fusion-dissolution method described elsewhere [36]. In brief, 250 mg of fine powdered sample was mixed with 500 mg of flux and put into a crucible with three drops of LiBr solution. The mixture was then fused at high temperatures using the Claiss M4 instrument (Malvern Panalytical) and following the melting program #9 [36]. The resulting melted glass was mixed with 100 mL of HNO_3 and a few drops of HF. The acid solution was then stirred until reaching the total dissolution of the solid phase. Before analysis, acid solutions were diluted (Milli-Q water), while a standard solution of HNO_3 (tracepur grade, supplied by Merck, Germany) was used to reach the optimal acidity value. ICP-MS analyses were then carried out by means of the NexION 300 system (Perkin Elmer, USA). Isotopic quantification was performed under the following experimental conditions: nebulizer flow of 0.9–1.0 mL min^{-1}, plasma flow of 18 mL min^{-1} and radio frequency power of 1400 W. Argon with a purity of 99.995 % was provided by Praxiar (Spain). Analyses were carried out inside a clean room (class 100) and quantitative data were obtained by means of external calibration curves, using calibration standards prepared form stock solutions of 1000 mg L^{-1} (Specpure, Plasma standard solution, Germany). Data acquisition and interpretation was performed using the NexION 1.5 software (Perkin Elmer, USA).

Knowing that high contents of nitrate, sulfate and chloride could compromise the mechanical features of mortars and concretes, the soluble salts content of both Somma-Vesuvius and commercial pozzolan materials was analysed by ionic chromatography (IC). Soluble salts were extracted by an ultrasound-assisted procedure with water. In brief, 1 g of powdered sample (homogenized and dried) was added to 100 mL of MIlli-Q water and sonicated in an ultrasound bath Ultrasons-H (P-Selecta, Spain), with a working frequency of 40 kHz (1000 W). After 2 h, the solution was filtered with 0.45 µm filters (PVDF, OlimPeak) and measured by IC. This pre-treatment was replicated three times for each analysed sample. The equipment used for the characterization of soluble salts was a Metrohm (Herisau, Switzerland) modular instrument, adapted to achieve a simultaneous analysis of dissolved cations and anions [36]. The instrument consists of two 930 Compact IC Flex configured as a dual channel ion chromatograph and an 815 Robotic USB Sample Processor XL for high-throughput automation, fully automated by the Metrohm standard software MagIC 3.2. Each IC is connected to a dedicated conductivity detector. For the separation and quantification of anions, a Metrosep A Supp 7-250/4.0 column was employed, using 3.6 mM Na_2CO_3 as mobile phase (flow rate of 0.8 mL·min^{-1}). For the analysis of cations, a Metrosep C 6-150/4.0 column was employed, using a mixture of 1.7 mM HNO_3 and 1.7 mM H_2SO_4 as mobile phase (flow rate of 1 mL min^{-1}).

Additionally, the content of carbonate/bicarbonate in the pozzolans was evaluated by titration. In brief, 1 g of powdered sample (homogenized and dried) was dispersed in 100 mL of Milli-Q water and sonicated for 2 h in an ultrasound bath Ultrasons-H (P-Selecta, Spain), with a working frequency of 40 kHz (1000 W). Then, the solution was filtered with 0.45 μm filters (PVDF, OlimPeak). The quantification of carbonate and bicarbonate ions was performed by a Metrohm 785 DMP automatic titrator (Herisau, Switzerland) equipped with an 801 magnetic stirrer, a 20 mL exchange unit and combined with a "Ecotrode Plus" pH glass electrode. To titrate 20 mL of sample, a 2 mL min^{-1} flow rate was chosen and an average of 3 mL of 0.01 M HCl was used for each titration.

In order to study the pozzolanic activity of the volcanic materials, the method proposed by Sanchez de Rojas et al. [37] was used by measuring the evolution of the material-lime reaction as a function of time. In brief, the four pozzolanic materials were put in contact with a saturated lime solution at 40 ± 1 °C for 3, 7, 28 and 90 days. At the end of each given period, the lime (mM/L) fixed by each pozzolan was calculated by the difference between the concentration in the saturated lime solution and the CaO found in the solution in contact with the sample.

To analyze the compressive and flexural strengths of the mortar samples, laboratory tests were carried out using the Ibertest instrument model C18-200-MDA. In detail, the flexural strength was evaluated from three-point bending tests of 40 × 40 × 160 mm specimens in displacement control at a test speed of 0.5 kN/s, while the compressive strength was evaluated on 40 x 40 x 40 mm specimens at a test speed of 2.4 kN/s.

3. Results

3.1. Comparative analysis of raw pozzolanic materials

3.1.1. Mineralogical composition

XRD analyses were conducted to determine the mineralogical composition of pozzolanic materials. Starting from the interpretation of Pompeian lapilli, zeolite (main peaks at 16.47°, 21.66°, 27.25°, 28.05° and 28.17°, fitting phillipsite-Na pattern 01-073-1419) phyllosilicate (8.80°, 29.93°, 34.87° and 45.33°, fitting micas patterns 00-046-1311), pyroxene (peaks at 29.86°, 30.31°, 30.60°, 35.06° and 35.61°, fitting the augite pattern 01-088-2376) minerals were detected as major phases, together with minor amounts of feldspar (27.32 and 29.93 degrees, fitting the sanidine pattern 01-086-0101) and feldspathoids (peaks at 16.52°, 25.96°, 27.32°, 30.61°, 31.49°, 31.85° and 38.00°, fitting the leucite pattern 01-085-1626). Furthermore, a remarkable amount of XRD amorphous components (this being a characteristic product in rapidly cooled volcanic materials) was also confirmed by the increase of the diffractogram's background between 15° and 40° (see Fig. 1a).

Similarly, XRD analysis of Pompeian ashes identified a high content of zeolites, plagioclase (peaks at 20.96°, 23.67°, 27.35°, 27.75°

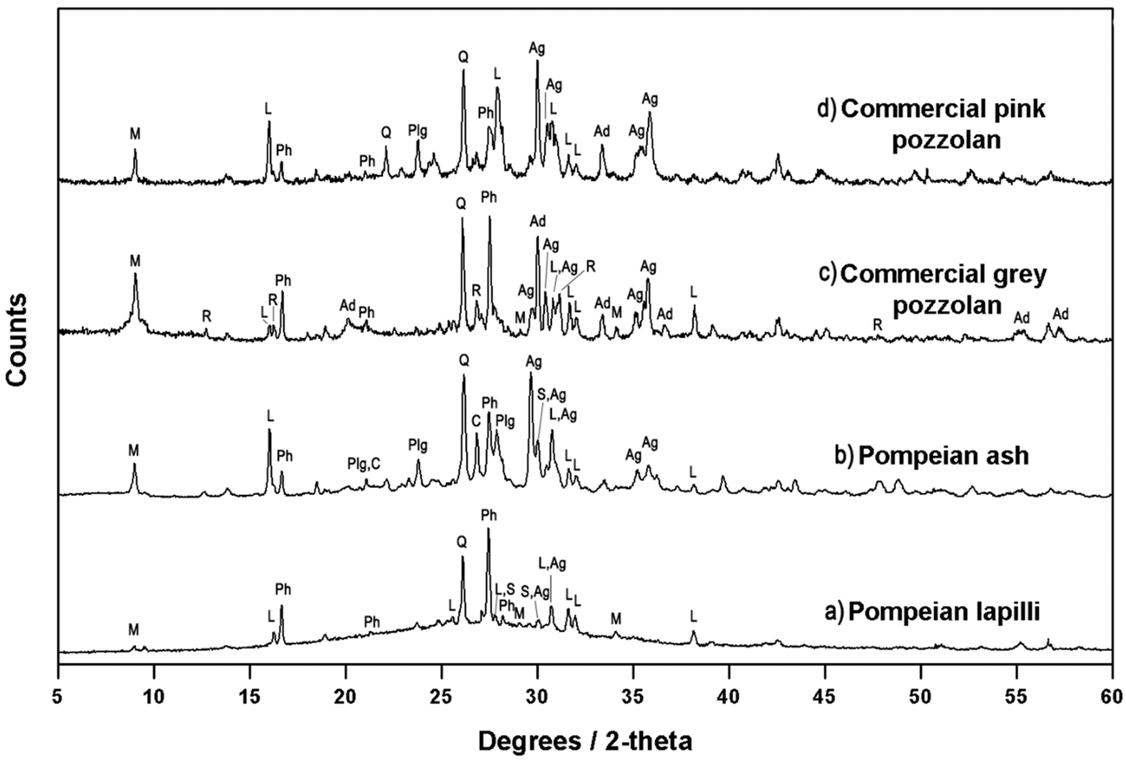

Fig. 1. XRD diffractograms of the raw materials used for the formulation of pozzolanic mortars. The main detected phases are: M – Micas; L – Leucite; S – Sanidine; Ag – Augite; Q – Quartz; Plg – Plagioclase; Ph – Phillipsite; C – Calcium carbonate; R – Rasvumite; Ad – Andradite.

and 28.07°, fitting the anorthite pattern 01-089-1460) and micas. In addition to those, calcite (peaks at 29.53°, 47.68° and 48.69°, fitting the calcium carbonate pattern 01-085-1108), and quartz (peaks at 20.96° and 26.72°, fitting the pattern 01-086-1628) were also detected (see Fig. 1b) as minor materials. Although the presence of amorphous material was also confirmed, the characteristic increase of background was found to be less intense than in the lapilli sample.

Considering that the geochemical and mineralogical composition of Pompeian ashes and lapilli has strong similarities with the volcanic materials employed by Romans (attributable to the "Pomici di Base", "Pomici di Mercato" and "Avellino Pumice" eruptions occurred between 18,000 and 3400 years BP [38]) their use as construction materials is expected to be fully compatible with the Roman structures preserved at the Archaeological Park of Pompeii [39–41].

Regarding commercial products, the grey pozzolan is mainly composed of micas, quartz, pyroxene, sulfide (peaks at 12.60°, 15.90°, 25.98°, 30.29° and 47.77°, fitting the rasvumite pattern 01-083-1322) and nesosilicate (peaks at 20.91°, 29.53°, 33.25°, 36.53°, 55.22° and 57.06°, fitting the andradite pattern 01-084-1935) minerals. The increase of the background between 15° and 30°, characteristic of amorphous materials was found to have a similar intensity to the one observed on Pompeian ashes (see Fig. 1c).

As displayed in Fig. 1d, the commercial pink pozzolan is composed of pyroxene, plagioclase, zeolite (fitting the leucite pattern 01-085-1421) and micas. This is a difference compared to the grey pozzolana. Compared to previous samples, the background of this diffractogram was found to be almost completely flat, this suggesting a lower content of amorphous phases than Pompeian materials and grey commercial pozzolan.

3.1.2. Molecular composition

FTIR spectra of raw pozzolanic materials are displayed in Fig. 2. The presence of silicious mineral phases is confirmed by the detection of an intense band around 1025 cm^{-1} (Si-O-Al stretching vibration) [42] together with a secondary signal between 436 and 450 cm^{-1} (in-plane Si–O bending vibrations in SiO_4 tetrahedra) [43] and a weak shoulder around 1220 cm^{-1} (Si–O–Si asymmetric stretching in internal tetrahedra of the SiO_4) [42,44]. Depending on the sample, the position of the main band shifts from 1018 (Pompeian lapilli) to 1031 cm^{-1} (commercial grey pozzolan) as a consequence of the different Si/Al ratio [45] ranging from Si/Al 3.04 in Pompeian lapilli to Si/Al 3.64 in commercial grey pozzolan.

The vibrational spectra obtained from the Pompeian ash show clear peaks at 711, 873 and 1427 cm^{-1} that are consistent with the presence of a relevant amount of calcium carbonate [46]. The same peaks are visible in the other three spectra, although their intensity

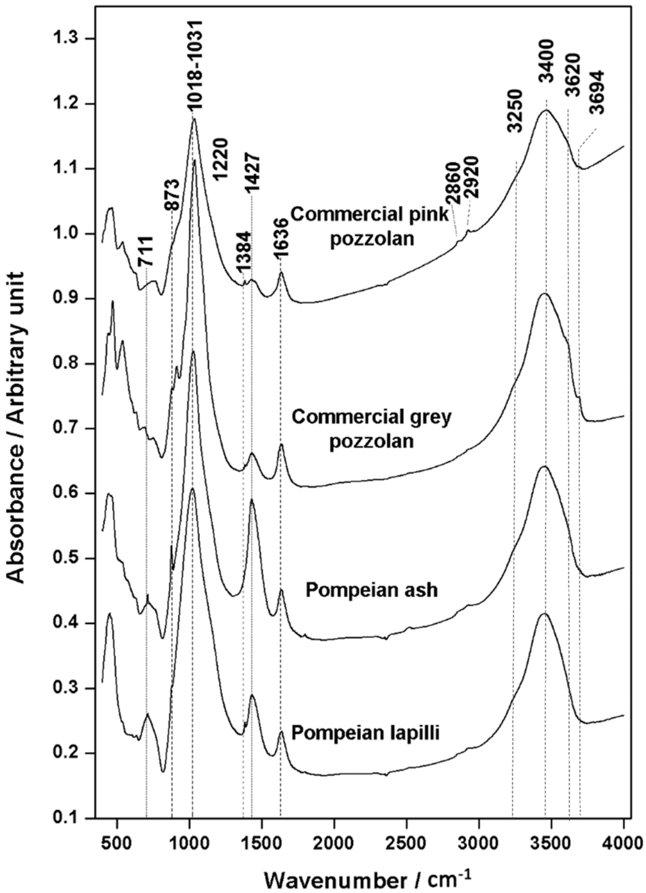

Fig. 2. : FTIR spectra of the raw pozzolanic materials used in this work to produce mortar samples.

Table 1
Elemental composition of pozzolanic materials as inferred from ICP quantitative analyses.

Sample	Mayor elements (> 1 wt%)							Minor elements (0.1–1 wt%)							
	Si	*Al*	*Ca*	*Fe*	*K*	*Mg*	*Na*	*Ti*	*Be*	*P*	*Sc*	*Mn*	*Ba*	*Bi*	*Sr*
Commercial pink pozzolan	49 ± 3	17 ± 2	10 ± 2	9.5 ± 0.5	4 ± 1	4.0 ± 0.2	2.5 ± 0.2	1.0 ± 0.1	0.7 ± 0.2	0.5 ± 0.3	0.4 ± 0.1	0.14 ± 0.03	0.11 ± 0.04	0.18 ± 0.05	0.11 ± 0.01
Commercial grey pozzolan	51 ± 8	18 ± 2	10 ± 2	8.0 ± 0.8	5.4 ± 0.5	2.9 ± 0.1	0.9 ± 0.2	0.8 ± 0.1	0.7 ± 0.1	0.4 ± 0.1	0.4 ± 0.1	0.19 ± 0.09	0.33 ± 0.05	0.21 ± 0.09	0.17 ± 0.04
Pompeyan ash	52 ± 5	18 ± 2	10 ± 2	5.1 ± 0.3	6 ± 1	2.8 ± 0.3	3.1 ± 0.5	0.6 ± 0.2	0.9 ± 0.2	0.4 ± 0.2	0.5 ± 0.2	0.12 ± 0.07	0.12 ± 0.01	0.2 ± 0.1	0.08 ± 0.02
Pompeyan lapilli	56 ± 5	20 ± 3	5 ± 2	3.4 ± 0.3	8.1 ± 0.4	0.8 ± 0.1	3.9 ± 0.4	0.4 ± 0.1	0.8 ± 0.1	0.24 ± 0.05	0.25 ± 0.05	0.12 ± 0.04	0.07 ± 0.03	0.24 ± 0.05	0.06 ± 0.02

suggests lower carbonate content [42].

In all materials the bands due to –OH vibrations are present. According to literature, the band at 1636 cm^{-1} would be due to –OH bending vibration of H_2O adsorbed in the zeolite (hydrogen-bonded water) [47,48]. In contrast, the literature is not clear regarding the bands located at 3250, 3400, 3620 and 3694 cm^{-1}. Apparently, there are several band overlappings involving vibrations due to Si-OH, Al-OH and H_2O. For example, the band at 3250 cm^{-1} would be due to Si-OH group interacting with adsorbed H_2O in the zeolite [48]. The bands at 3400, 3620 and 3694 cm^{-1} would be due to Si-OH, Si-OH-Al and Si-OH vibrations respectively [49], even though contribution of adsorbed H_2O vibration modes is also possible.

A weak peak at 1384 cm^{-1} was found in all samples (except Pompeian ash), thus proving the additional presence of nitrates. Furthermore, it must be underlined the detection of two minor peaks around 2920 and 2860 cm^{-1} in all samples (especially in the commercial pink pozzolan) which can be related to the presence of organic material (C-H stretching).

3.1.3. Elemental composition

ICP analyses were performed to determine the elemental composition of the raw materials. As represented in Table 1, the four samples are dominated by Si (between 49.2 and 55.8 wt%) and Al (from 16.8 to 20.1 wt%), while other major elements are Ca, Fe, K, Mg and Na (concentration from 0.8 to 9.7 wt%). In addition to those, several minor elements (concentration between 1.0 and 0.1 wt%) were detected including Ti, Be, P, Sc, Mn, Ba, Bi and Sr. Sample comparison indicates that Vesuvius ashes and lapilli mainly differ from commercial pozzolans by a higher concentration of Si and a lower content of Fe. Furthermore, it can be noted the higher concentration of Al and K in Pompeian lapilli is compensated by a lower content of Ca, Fe and Mg. Noteworthy is the low Na concentration in commercial grey pozzolan compared to the other materials.

3.1.4. Pozzolanic activity

As described in Section 2.3, the pozzolanic activity of the four pozzolanic materials was investigated by following the method of Sanchez de Rojas et al. [37]. The amount of calcium hydroxide fixed by the pozzolanic materials was measured after 3, 7, 28 and 90 days and the results are represented in Fig. 3. After 3 days, the amount of lime fixed by Pompeian lapilli (9.7 mM/L) was slightly higher than commercial grey pozzolan (9.07 mM/L) and Pompeian ash (7.57 mM/L), while the commercial pink pozzolan provided the lower results (5.18 mM/L). The four pozzolanic material displayed a constant increase of lime fixation with time. By the end of the monitorization (90 days) the amount of lime fixed by Pompeian lapilli, Pompeian ash, grey pozzolan and pink pozzolan was 15.40 (+ 59 %), 14.04 (+ 84 %), 14.84 (+ 63 %) and 12.27 mM/L (+ 137 %), respectively. In a general perspective, these results confirm that, unlike Portland-based mortars (for which consolidation is considered to be completed after 28 days of curing), the fixation of lime by pozzolanic materials occurs over a longer period of time.

More in detail, the different lime-fixation capability displayed by the analysed materials can be directly related to their content of amorphous materials. Indeed, knowing amorphous material easily reacts with lime during the pozzolanic reaction, the higher content detected by XRD in the Pompeian lapilli facilitated a higher fixation of lime in the early stage of the monitorization. Similarly, the reasons for the poor mechanical properties of the mortars prepared with commercial pink pozzolan can be found in the low content of amorphous phases of this volcanic material. Although the remarkable differences measured after 3 days have been partially compensated over time, it is important to underline the amount of lime fixed by Vesuvius materials by the end of the monitorization was in line with that of the commercial grey pozzolan and markedly higher than the pink commercial one. These results suggest the

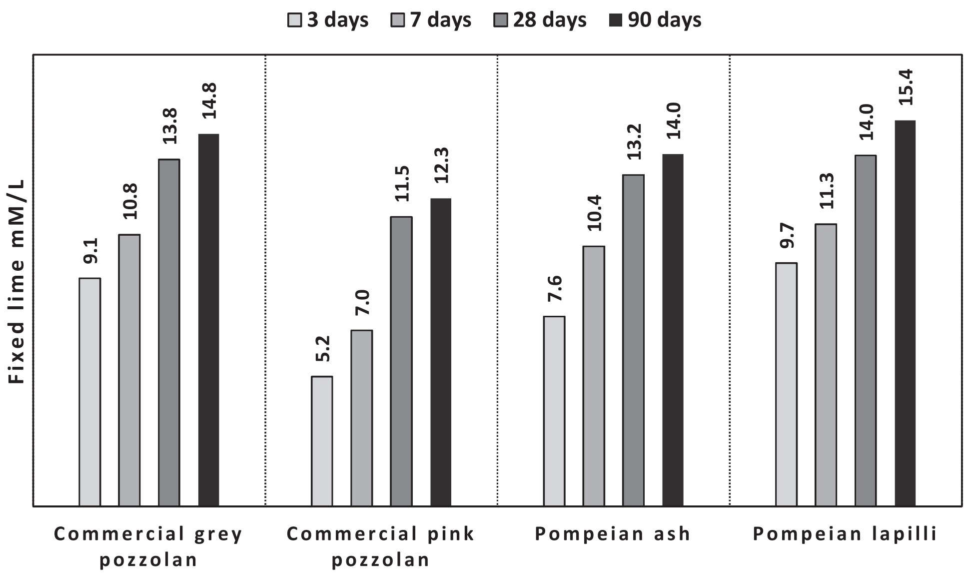

Fig. 3. Monitorization of lime fixed over time by the pozzolanic materials, as inferred from the test presented by Sanchez de Rojas et al. [37].

volcanic materials burying Pompeii (especially lapilli) could be used as pozzolan.

3.1.5. Soluble salts content

As summarized in Table 2, Na^+, K^+, Ca^{2+} and Mg^{2+} are the main cations detected by the IC analysis of the four pozzolans. Among them, Pompeian lapilli and commercial grey pozzolan have a higher content of Ca^{2+} (851 ± 17 and 755 ± 20 μg/g, respectively), while commercial pink pozzolan show lower amounts of Na^+ (80.3 ± 0.8 μg/g), K^+ (208 ± 26 μg/g) and Mg^{2+} (25.6 ± 3.0 μg/g). Concerning the detection of anions, Pompeian lapilli display a notable amount of NO_3^- (353 ± 81 μg/g (in accordance with the detection of nitrates by FTIR) followed by Cl^- (198 ± 44 μg/g), SO_4^{2-} (146 ± 26 μg/g) and F^- (689 ± 12 μg/g). Compared to this, commercial grey pozzolan mainly differs by the higher content of SO_4^{2-} (300.6 ± 6.5 μg/g) and F^- (167.5 ± 8.5 μg/g), which is partially compensated by a lower concentration of NO_3^- (7.7 ± 0.7 μg/g). The comparison also proves that the anion content of Pompeian ash and commercial pink pozzolan are remarkably lower than in other two samples, being the concentration values below 56 μg/g in all cases. Regarding titration results, Table 2 proves that bicarbonate is the main anion in all pozzolanic materials, as its measured concentration ranges between 1507 ± 13 and 3020 ± 23 μg/g). Unlike commercial materials, Pompeian ashes and lapilli display the additional presence of CO_3^{2-} (579.8 ± 8.3 and 523.2 ± 8.2 μg/g, respectively).

Considering the detected anions, it is important to underline that sulfate, chloride and nitrate affect the usability of pozzolans as conservation materials. Indeed, as is well known these soluble salts can lead to the crystallization of crypto and superficial efflorescence, thus triggering chemical and physical damages of the mortar. As represented in Table 3, conservation risk of a mortar can be directly inferred from its level of contamination, which considers the concentration by weight (wt%) of Cl^- SO_4^{2-} and NO_3^- ions [50].

Converting the values listed in Table 2 from μg/g to wt%, the concentration of chlorides, sulfates and nitrates in the four pozzolanic materials is always below 0.02, 0.01 and 0.04 wt%, respectively. Although a low contamination in commercial pozzolans was expected, this result proves the soluble salt content of Pompeian ash and lapilli is so low that they can be used in the formulation of mortars without the need of previous desalinization treatments.

3.2. Mortar samples made by using standard sand as aggregate

A first set of mortar samples was created by following the formulation described by Pliny the Elder [34]. As such, specimens were made by using silicic sand as aggregate and by fixing its concentration ratio with the binder (lime + pozzolanic material) to 3/1.

3.2.1. Mechanical tests

Mortar samples were prepared as described in Section 2.2 and their mechanical properties were measured after 28 days of curing at room temperature. The results of laboratory mechanical tests are shown in Fig. 4. Compressive (from 1.24 to 2.36 MPa) and flexural (from 0.32 to 0.51 MPa) results are in line with the values obtained in previous work from the analysis of further pozzolanic conservation mortars [52,53]. It is important to underline that mortars made of Pompeian lapilli ensured the best compressive performance (2.36 ± 0.51 MPa), followed by Pompeian ash (2.05 ± 0.44 MPa) and commercial grey pozzolan (2.04 ± 0.38 MPa), being the results of the pink pozzolana the lowest (1.24 ± 0.32 MPa). This could be justified by the low pozzolanic reactivity of the raw material, as inferred from the results provided in Section 3.1.3. Flexural results followed a similar tendency, being the mortars made with Pompeian lapilli ≈ 60 % stronger than those based on the use of commercial pink pozzolana (0.51 ± 0.17 vs. 0.32 ± 0.06 MPa).

As the formulated mortars are mainly meant to be used for the conservation of ancient Roman structures preserved at Pompeii and Herculaneum (among others), their mechanical properties need to be similar to the original mortars used by Romans at the archaeological sites. In this regard, a work published by Autiero et al. [51] analysed the mechanical strength of 11 original mortars sampled from masonry structures recently excavated at the Regio V of the Archaeological Park of Pompeii, obtaining values ranging from 0.34 to 1.61 MPa. Although these values agree with the mechanical tests performed in this work, it must be underlined that original ancient mortars undergone a much longer curing period while being subjected to alteration process during burial. As such, the values measured in modern times may be very different from their former compressive strength.

In light of all the above, two main consideration can be inferred: 1) As mortars made of Pompeian ash and lapilli ensure similar (or better) mechanical properties than commercial pozzolanic products, the volcanic materials burying Pompeii proved to be a suitable product for the formulation of conservation mortars; 2) As the compressive and flexural strengths of Pompeian mortars are similar to

Table 2
Soluble salt contents of pozzolanic materials as inferred from IC and titration quantitative analyses. Ions with a concentration below 10 μg/g are not shown, as they are considered not relevant to this research.

Sample	Cations (μg/g)				Anions (μg/g)					
	Na^+	K^+	Ca^{2+}	Mg^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-
Commercial grey pozzolan	206.9 ± 2.6	512 ± 29	755 ± 20	44.6 ± 5.6	167.5 ± 8.5	35.0 ± 0.6	7.7 ± 0.7	300.6 ± 6.5	< LOD	2499.1 ± 3.9
Commercial pink pozzolan	80.3 ± 0.8	208 ± 26	438 ± 30	25.6 ± 3.0	10.6 ± 0.8	1.5 ± 1.4	3.6 ± 0.5	20.7 ± 1.5	< LOD	1507 ± 13
Pompeian lapilli	240 ± 40	693 ± 111	851 ± 17	82.4 ± 5.4	68 ± 12	198 ± 44	353 ± 81	146 ± 26	579.8 ± 8.3	3020 ± 23
Pompeian ash	228 ± 22	754 ± 24	585 ± 46	46.9 ± 9.3	33.3 ± 2.3	33.6 ± 2.5	19.5 ± 1.2	55.6 ± 3.5	523.2 ± 8.2	3117 ± 21

Table 3
Risk of degradation of mortars on the basis of individual salt anions [51].

State of contamination	Soluble salts in % by weight		Degree of risk
	Chlorides, sulfates	*Nitrates*	
Clean	< 0.10	< 0.05	No risk. Conservation
Slight	0.20–0.50	0.06–0.10	Low
Medium	0.60–1.50	0.10–1.50	Medium – Visible damage
High	1.60–3.00	1.60–3.00	High – Heavy damage
Severe	> 3.00	> 3.00	Certain -Wide destruction

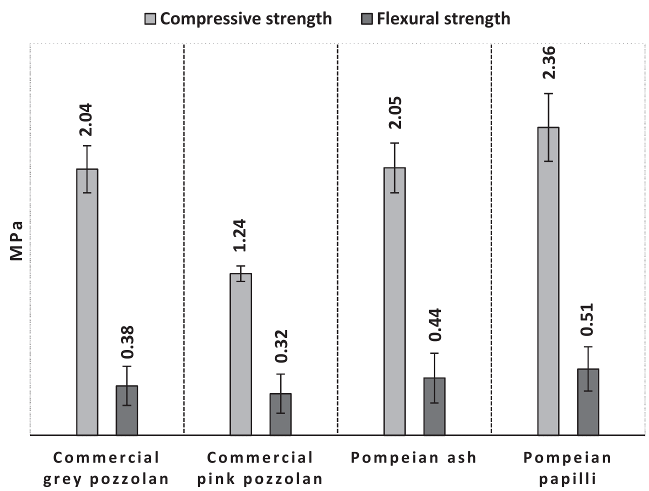

Fig. 4. Compressive and flexural strengths of mortar samples prepared by using standard sand as aggregate. Measures were performed after 28 days of curing at room temperature.

those presented in this study, pozzolanic mortars made of Pompeian ash and lapilli could be considered as mechanically compatible with the original Roman structures preserved at Pompeii and surrounding archaeological sites (Herculaneum, among others).

3.2.2. Mineralogical composition

After mechanical tests, mortars fragments were selected from the prepared samples and, after powdering, their mineralogical composition was studied by XRD analysis. The diffractograms obtained from the 4 different samples display very intense peaks at 26.66, 20.88, 50.18, 36.57 and 39.50 2-theta, among others, fitting the quartz pattern 01-086-1628. The intensity of the detected signal is due to the contribution of the standard sand used as aggregate, which is almost entirely composed of SiO_2. The intensity of the quartz peaks (which make up 65 wt% of the samples) makes it difficult to detect additional phases. In spite of that, some of the characteristic phases of the pozzolanic materials used in the formulation of the different mortars (see Section 3.1.1) were observed, including zeolite, micas, feldspar and pyroxene. In addition to these, the detected calcite ($CaCO_3$, found in all samples), can be related to the carbonation reaction of lime with CO_2.

3.3. Mortar samples made by using volcanic material as aggregate

Unlike the formulation described by Pliny the Elder [34] the mineralogical analysis of mortars from the Archaeological Parks of Pompeii and Herculaneum proves that, in this region, Romans made extensive use of volcanic material from Vesuvius as aggregate (rather than silicic sand). Having this in mind, a second set of mortars was prepared, using powdered Pompeian ash and lapilli as pozzolan (grain size < 125 μm) and as aggregate (grain size > 5 mm [22]). As volcanic aggregates partially participate to the pozzolanic reaction, thus, leading to the formation of interfacial transition zones [27], the analysis of this set of samples was meant to evaluate to which extent such reaction contributes at improving the mechanical features of the mortars.

Furthermore, considering the results presented in Section 3.1.3 proved the pozzolanic activity of the tested materials constantly increased as a function of time, this section also sought to monitor how the mechanical properties of pozzolanic mortars evolved over a period of 6 months.

3.3.1. Mechanical tests

The compressive strength of the prepared samples was measured after 28, 90 and 180 days. From the results plotted in Fig. 5, two main considerations can be inferred. On the one hand, the compressive strength ensured by Pompeian ash- and lapilli-based samples after 28 days of curing was 2.94 ± 0.32 and 3.36 ± 0.27 MPa respectively. As the obtained values are 44 % and 42 % higher than those measured from mortar sample prepared using standard sand as aggregate, this result confirms that volcanic coarse grains partially participated to the pozzolanic reaction, thus actively contributed at improving the mechanical properties of the mortars.

On the other hand, Fig. 5 clearly shows a significant increase of compressive strength with curing time. After 6 months of aging, mortars made of Pompeian ash reached a strength of 4.21 ± 0.32 MPa (+ 43 %), while the lapilli ones went up to 4.46 ± 0.42 MPa (+ 33 %). While confirming the curing of pozzolanic mortars occurs over a longer period than Portland-based ones (generally, optimal values are reached after 28 days), the projection of the observed growth suggests that an even higher compressive strength could be reached on the long term.

3.3.2. Mineralogical composition

After mechanical tests, the mineralogical composition of powdered mortars was assessed by XRD. The diffractograms obtained after 180 days of curing are represented in Fig. 6. Compared to the XRD results presented in Section 3.2.2, the detection of volcanic and pozzolanic phases was improved due to the absence of standard sand in the samples. All mineral phases identified during the analysis of the raw volcanic material (see Section 3.1.1) were detected in the XRD analysis of this set of mortars. An increased amount of calcium carbonate was also found in all samples, this being the product of lime carbonation (calcite). Moreover, the detection of calcium hydroxide (peaks at 21.11°, 25.39°, 26.57°, 27.26° and 27.62°, fitting the portlandite pattern 01-087-0673) after 180 days of curing suggests that additional pozzolanic reactions can still occur (e.g. with the remaining zeolites and amorphous material). This indirectly confirms that the mechanical strength of both mortars could further increase over time.

3.3.3. Molecular composition

FTIR spectra collected after 180 days of curing, displayed in Fig. 7, present similar absorbance profiles. Both mortars show the characteristic signals of calcium carbonate, where the sharp peaks at 711 and 873 cm^{-1} are due to the C-O bending, while the intense band centred at 1422 cm^{-1} is produced by C-O stretching vibrations. Calcite bands from the Pompeian ash mortar are more intense than the lapilli one (an additional secondary peak of calcium carbonate at 1794 cm^{-1} is also observed), thus, suggesting a higher concentration of this mineral phase in the analysed sample. Despite the presence of calcium carbonate in the raw materials, carbonation can happen due to reaction with atmospheric CO_2 in samples containing excess of calcium hydroxide that did not react with the natural zeolite [42].

Compared to raw pozzolan materials, the band found around 1000 and 1220 cm^{-1} strongly increases in intensity. This suggests that calcium-silicate-hydrate (C-Si-H) binding phases formed during the pozzolanic reaction. As presented by Yu et al. [54], the mean frequency of the C-Si-H band varies according to length of the silicate chains and the ratio between CaO and SiO_2 (C/Si ratio). As the C-Si-H peak from the lapilli mortar is found at lower wavelength than the ash one (963 vs 986 cm^{-1}), it can be inferred the pozzolanic reaction of Pompeian lapilli lead to the formation of shorter silicate chains and a higher C/Si ratio. Finally, compared to raw pozzolans, the characteristic bands related to bound water (around 3400, 3245–3249 and 1632–1636 cm^{-1}, respectively) almost completely disappeared. This change was expected since water molecules are consumed during the pozzolanic reaction.

4. Conclusions

XRD, FTIR and ICP analysis performed in this work confirmed the Pompeian materials are mineralogically and geochemically similar to commercial pozzolans. Furthermore, it was analytically proved their pozzolanic activity is similar to (and even higher than) commercial pozzolans.

After charactering the raw materials, Pompeian ash and lapilli were used to formulate a first set of pozzolanic mortars. The

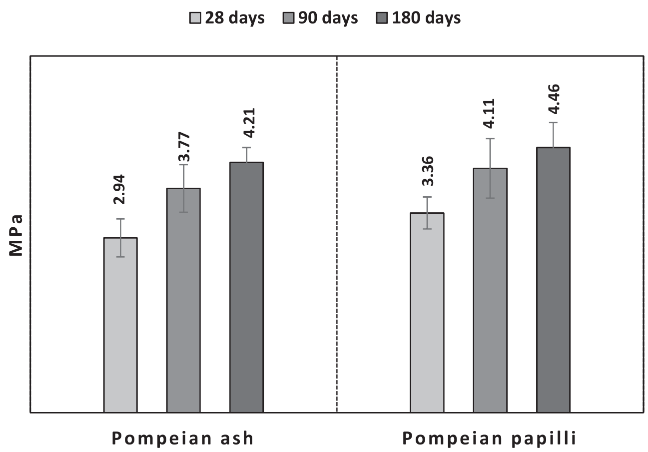

Fig. 5. Compression strength of mortar samples prepared by using coarse volcanic grains as aggregate. Measures were performed after 28, 90 and 180 days of curing at room temperature.

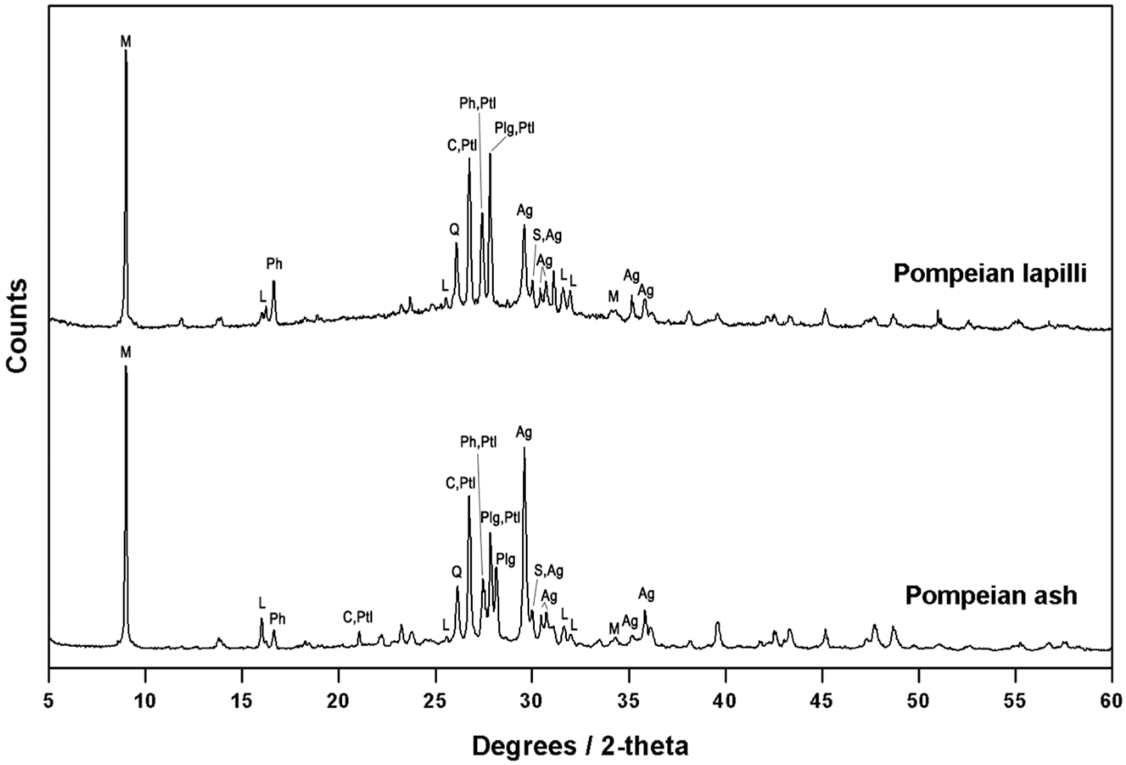

Fig. 6. XRD diffractograms of 180 day-old pozzolanic mortars formulated by using Pompeian volcanic material as aggregate. The main detected phases are: M – Micas; L – Leucite; S – Sanidine; Ag – Augite; Q – Quartz; Plg – Plagioclase; Ph – phillipsite; C – Calcium carbonate; Ptl – Portlandite.

compressive and flexural strengths measured after 28 days of curing proved to be compatible to the values obtained from: 1) commercial pozzolanic mortars prepared in this work, and 2) original Pompeian mortars tested in previous works.

A second set of samples were then prepared by replacing the silicic sand with coarse grains of Pompeian ash and lapilli, this resulting in a remarkable improvement of their compressive strength after 28 day of aging. These tests confirmed that volcanic aggregates promoted the formation of interfacial transition zones, which improved the mechanical properties of the mortars. Further mechanical tests, performed after 180 days, showed a further increase in the mechanical properties of Pompeian ash- and lapilli-based mortars, which reached a compressive strength of 4.21 and 4.46 MPa, respectively. In light of the comprehensive study summarized in this manuscript, it can be assumed that the volcanic material burying Pompeii could be converted into a valuable conservation product.

However, the real potentiality of Pompeian ash and lapilli as pozzolanic material is still far to be constrained. In this sense, further laboratory tests need to be carried out to optimize the formulation of the mortars. Furthermore, additional physical and chemical properties need to be evaluated to fully assess their potential use as conservation material, including bulk density, porosity and water absorption (among others). Considering this work is being performed in close collaboration with the Archaeological Park of Pompeii (PAP) and the Archaeological Park of Herculaneum (PAERCO), the final objective of this research is to convert the volcanic material burying Pompeii into a valuable resource for the conservation of the archaeological sites located in the Vesuvius region.

On the long term, the present research line will also provide valuable information to consider in the formulation of novel construction materials. For instance, to better constraint the mineral products generated during the pozzolanic reactions could favour the use of volcanic pozzolan as supplement cement material (SCM) in modern concretes. Such use would be particularly beneficial in coastal area, due to the higher resistance of construction materials based on volcanic pozzolan (over conventional Portland cement) to the damages produced by the exposition to salty water.

CRediT authorship contribution statement

Idoia Etxebarria: Writing – original draft, Methodology, Data curation. **Marco Veneranda:** Conceptualization, Writing – review & editing. **Ilaria Costantini:** Investigation. **Nagore Prieto-Taboada:** Data curation, Investigation. **Aitor Larrañaga:** Data curation. **Cristina Marieta:** Data curation. **Bruno De Nigris:** Resources. **Alberta Martellone:** Resources. **Valeria Amoretti:** Resources. **Gorka Arana:** Supervision, Project administration, Funding acquisition. **Juan Manuel Madariaga:** Supervision. **Kepa Castro:** Conceptualization, Writing – review & editing. All authors are in agreement with the content of the manuscript.

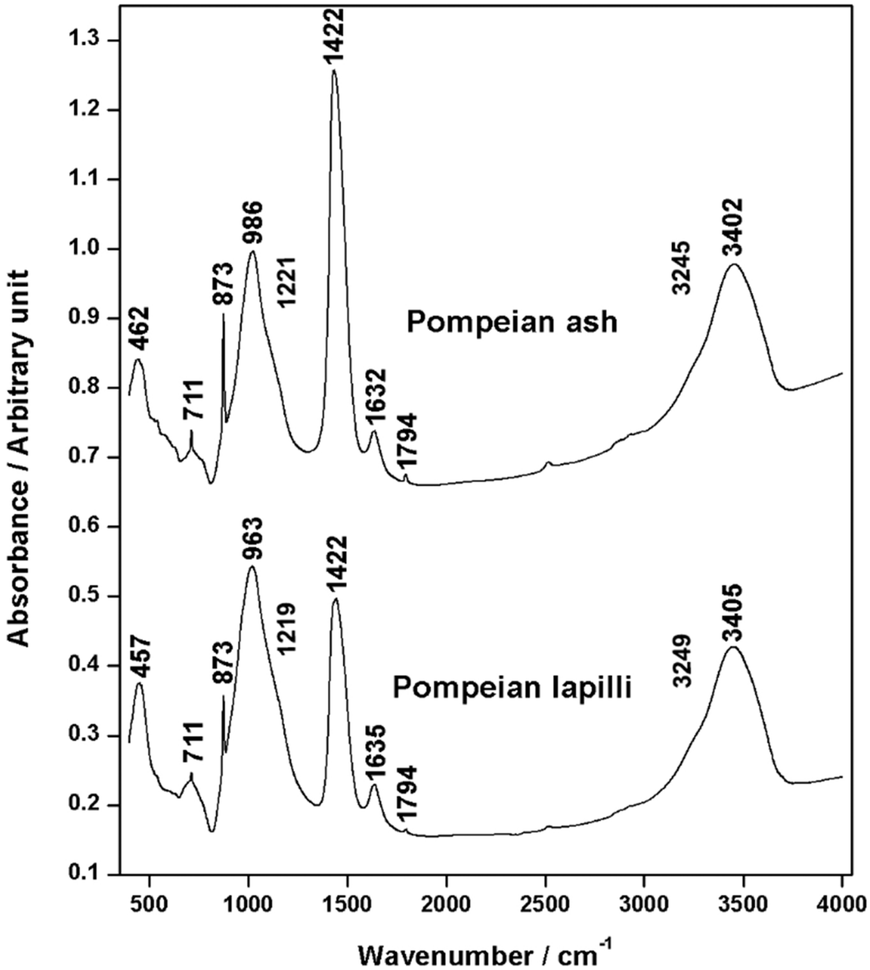

Fig. 7. FTIR absorbance spectra obtained from the analysis of pozzolanic mortars based on the use of Pompeian volcanic material as aggregate.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: G. Arana reports financial support was provided by Ministry of Science and Innovation, Spanish Government.

Data Availability

Data will be made available on request.

Acknowledgements

This work has been financially supported by the DEMORA project (Grant no. PID2020-113391GB-I00), funded by the Spanish Agency for Research (through the Spanish Ministry of Science and Innovation, MICINN, and the European Regional Development Fund, FEDER). I. Etxebarria gratefully acknowledges to the Basque Government for her pre-doctoral contract (Pre-doctoral Programme for the Training of Non-PhD Research Staff).

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