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PRELIMINARY STUDY ON VALORISATION OF SCRAPS FROM THE EXTRACTION OF VOLCANIC MINERALS

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Abstract

Powders <3mm of pumice and lapillus (quarry scraps of national volcanic minerals) were employed in the tailoring and characterization (from the physical, chemical and mechanical point of view) of geo-polymers and lightweight aggregates.

Geo-polymers were obtained at room temperature by substituting 70 - 80 wt% of metakaolin by volcanic scraps and employing an alkaline solution with a $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio from 0.8 to 1 for pumice and lapillus series, respectively. Within 24 h and in water, bulk specimens resulted with good integrity, with pH values around 9-11 and conductivity increasing over time, but less for the lapillus-containing sample richest in metakaolin indicating more compactness. The porosity, ranging around 32-33% for all the samples, increased up to 45% for the formulation based on 80% of lapillus. The best mechanical performance was achieved by lapillus samples: compressive strength in the range 35-38 MPa against 6-8 MPa of pumice ones.

Lightweight aggregates were created by powder sintering at 1000 °C for 1 hour of 85 wt% of volcanic scraps and 15 wt% of spent coffee grounds used as pouring agent. Additional formulations were realized adding 50 wt% of nourishing mixture P and K-containing in the form of animal bone meal and vegetable biomass ashes. The specimens resulted porous and light (porosity around 60%), with good capacity of water retains, and, except in two cases, with neutral pH and conductivity values below 2 mS/cm, indicating a possible use for substrate (growing layer) in roof gardens, green roofs, house gardens, etc..

Key words: geo-polymers, lightweight aggregates, quarry scraps, recycling

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1. Introduction

The recycling of waste materials and residues is an important objective recognized at the regulatory level in the circular economy. As written by Stephen Hinton “The aim of the circular economy is to retain and recycle technical nutrients in the economy, to cycle biological nutrients from the economy to the biosphere and back, and to utilize money to facilitate transactions and trade”. In particular, while plant and animal material coming from the ecosystem return to it after being degraded (returning nutrients to the

environment), metal, plastic glass components and any other kind of residue represent parts of material or new raw material for other refurbished or created products (acquiring a new value) (EMF, 2017). This last aspect, important for those countries, such as Italy, poor in raw materials, has positive economic and job repercussions, but always with a view to environmental protection.

Construction sector, ceramics and cement factories are large users of primary raw materials from natural resources (clay, quartz, kaolin, feldspar, limestone, etc.) with a consequent negative

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environmental impact (impoverishment of the territory, climate change, transport cost, etc.) so they have increased their effort to implement secondary raw materials use. It is known that the conventional building construction consumes not renewable resources, generates waste and emitters greenhouse gases (Górecki et al., 2019). Thus, was born the context of sustainable construction with the aim of limiting the impact of this commercial sector on the environment. This new context brings new challenges about sustainable construction methods, but also great benefits too. These include lower operating costs, so it appears that the use of the latest sustainable technologies in construction processes could potentially provide significant savings of € 410 billion per year on global energy spending (BAB, 2019). Direct savings are also available to construction companies: by reducing waste, for example, would reduce the fees charged by company waste management, adopting more efficient vehicles, will save on fuel costs. Another benefit is represented by the fact that sustainable construction can help the company's reputation by demonstrating a sense of corporate social responsibility. Precisely this can also be associated with the use of recycled raw materials to realize products that, in their turn, contribute to environmental certifications such as LEED (Leadership in Energy and Environmental Design) and BREEAM (British Research Environmental Assessment Method) certifications. The tools to limit the impact of this production sector on the environment include a greater exploitation of renewable and recyclable sources, a saving in energy consumption, always taking care to create healthy and environmentally friendly environments. Moreover, the attention to new materials development with specific performances, also covering niche or expanding sectors, is of great interest for the productive compartment. Among the materials with very interesting potentialities and which can good tolerate the presence of recycling fractions we find geo-polymers and lightweight aggregates.

Geo-polymers are a class of materials that can be defined as hydraulic binders produced starting from powders, mainly aluminosilicate, which are dissolved in a highly alkaline environment. These materials can be considered "ceramics consolidated by alkaline reaction", meaning that they can be produced using a chemical reaction and not a thermal sintering, ultimately leading to the same chemical-physical and mechanical properties typical of ceramics (Leonelli et al., 2013). The prefix geo- indicates that we are talking about a product of geo-synthetic, that is, a product that mimics materials already present in nature; the suffix -polymer instead refers to the production process (geopolymerization), that is a polymerization by polycondensation. In 1978 the French chemist Joseph Davidovits used for the first time the definition of "geo-polymer" to indicate in general materials based on alkaline aluminosilicates, which are obtained by

condensation and subsequent polymerization. More generally as a subset of the family of alkali activated materials, inorganic binders derived from the reaction of an alkali metal salt with a silicate powder. More specifically as a subset of inorganic polymers, characterized by the highest content of aluminum and sodium and by the amorphous or semi-crystalline microstructure and greater cross-linking of the silicate chains. Geo-polymers, whether used pure or with fillers or reinforced, already find applications in many fields of industry from metallurgical, polymers and civil to waste treatment, restoration, biomaterials (Medri, 2009).

Lightweight aggregates (LWAs) are granular materials, manufactured with both natural materials, and by-products or recycled source materials, having particle densities not exceeding 2000 kg/m³ or loose bulk densities not exceeding 1200 kg/m³ for use in concrete and mortar according to UNI EN 13055: 2016. Other applications cover civil engineering, geotechnics or agriculture. LWAs can be divided into natural and artificial. Among the former, pumice is widely used (with very modest mechanical resistance to compression), while among the latter are very common: expanded clays, expanded clayey schists, vermiculite and perlite. The principle on which the preparation of these artificial aggregates is based basically consists in bringing the raw product to a sufficiently high temperature (1000-1300°C), such as to cause the elimination of gaseous substances, while the simultaneous formation of an appropriate quantity of liquid phase promotes sintering of the grains while maintaining a good number of cavities in the material. Expanded clay usually comes in the form of porous, light and very resistant balls, produced by firing various types of clay at high temperatures. Inside there is a porous core that gives lightness and allows liquids to be absorbed and drained, to maintain the right humidity in the environment in which it is inserted, as well as acting as a thermal and acoustic insulator. It also has a high mechanical resistance to compression, is a natural product and does not release toxic substances or particles and fibers. Anyway, a certain amount of thermal energy is requested during the expansion process.

Porous minerals useful for making lightened products are pumice and lapillus. These are naturally expanded volcanic minerals. Their natural expansion is caused by the acid gases dissolved in the lavas which, released suddenly, cause the material to swell. During the rapid cooling phase, the resulting solid which is not totally crystallized has alveolar cavities produced by the imprisonment of the aforementioned gases inside the rock. The chemical composition of the pumice's magma with an average amount of SiO₂ of 56 wt% causes a high viscosity of itself and the rapid cooling hinders the gases escape, originating a rock structure with several little pores intercommunicating with each other and also externally (Fig. 1a). Instead, the magma that generated volcanic lapillus has a lower SiO₂ content, around 49 wt%, which lowers the viscosity of the lava. This associated to a slower

cooling, facilitate the escape of a certain amount of gases present within the magma. In the end, the lapillus obtained will have a lower percentage of pores than the pumice, but with larger sizes (Fig. 1b). Finally, the color difference between the two minerals, white and red for pumice and lapillus respectively, are imputable to a higher amount of Fe₂O₃ present in the second (on average 9 wt% against 4 wt%). Although these inert volcanic minerals find applications in sectors such as nursery gardening (cultivation substrates and moulds, cultivation outside of the ground, full field), green areas (sports fields, green car parking areas, hanging gardens, ornamental meadows), green roofs, building industry (lightened concretes, plasters, thermal insulation, acoustic insulation, construction of light items, fume outlets, light fillings, biological building industry), dentistry (dried pumice for polishing and whitening of natural teeth), their mining activity produces residues. The fine fraction (<3mm) of the pumice and lapillus quarrying activity extracted in Italy and which is stored in the same quarry area, do not find an adequate marketing and involves additional costs and charges. Indeed, if used as quarry restoration, the scraps have the additional cost of transport from the plant to the quarry (on average 0.6 € / m³), if piled up in areas of competence of the quarry (authorized as internal landfill) and then resold, are subjected to a regional tax of 0.30 € / m³ (Lazio). Bibliography exist on the recovery of waste from mining operations and other raw materials as result from a recent report showing that such waste is usually reprocessed with comminution and enrichment techniques that allow to obtain: valuable raw materials (metals in particular), minerals of industrial utility (quartz, kaolin for example) and residues useful for the rehabilitation of the site are (Salmine et al., 2019). Similar information does not seem to exist for scraps from the extraction of volcanic minerals. With these premises and with the aim to define new marketing sectors, this work deals with the engineering and preliminary characterization of

prototypes of geopolymers and lightweight aggregates based on the fine fractions of the volcanic inerts above described.

Briefly:

1) geopolymers, alkaline activated materials or cold-consolidated aluminosilicate materials by alkaline activation (substitution of metakaolin up to 90%) in which the presence of volcanic minerals allows to obtain promising porous and lightened geopolymers in the field of internal and / or external panels with possible applications in acoustic and thermal insulation. Volcanic minerals are suitable for alkali activation due to their high amorphous fraction formed as a result of rapid cooling during volcanic activity.

2) lightweight aggregates, i.e. materials with inert mineral matrix, with low specific weight, in which the clay components have been completely replaced with these scraps, exploiting their high content of silica (49-57%) and alumina (18-19%), and obtained by fast heat treatment (1000 °C, 1 hour). The addition in the formulation of a post-consumer product with an organic matrix (spent coffee grounds) which develops gas at the consolidation temperature, has allowed the creation of porosity. The material was then functionalized with a view to "fertilizer material" bringing two of the three main fertilizer's nutrients: P as animal bone meal ash and K as vegetable biomass ash.

From the results obtained seem that lightweight aggregates have good perspective to lighten and fertilize the soil, in particular for the pH, conductivity and porosity point of view. This is a good starting point, to be deepened, for outdoor applications as green roof or vertical forest (with a view to modern and "sustainable" architecture) and indoor cultivations (a niche sector which is however expanding). Geopolymers represent another interesting perspective: the presence of volcanic minerals leads to particularly porous and lightened matrices compared to those based on metakaolin with other interesting properties, therefore perspectives in the construction sector (ARPAV, 2007)..



(a)



(b)

Fig. 1. Pumice (a) (<http://www.europomice.com/products/pumice/>) and Lapillus (b) (<http://www.europomice.com/product/lapillus/>)

2. Materials and methods

2.1. Raw materials choice and characterization

The volcanic raw materials such as pumice and lapillus were supplied by Europomice Srl that took care natural volcanic minerals currently extracted from four quarries located near Grosseto and Viterbo (area of Lake Bolsena). The excavation of this type of minerals provided a commercial grain size material and another amount characterized by grain size below 3-4 mm which remains mainly unexploited.

Volcanic raw materials were dried at 100 °C in an oven for 24 hours in order to remove the moisture. Subsequently, they were ground and sieved under 75 µm to bring the granulometry closer to that of the main component of geo-polymers, i.e. metakaolin (MK) Argical 100 (supplied by BAL-Co and with a grain size < 80 µm).

Spent coffee grounds (SCGs), a post-consumer product, were dried in the same way of volcanic scraps. The inorganic fraction is negligible, while the organic one prevails, as can be seen from the weight loss around 98% and with a carbon contribution of 50% by weight.

Precisely for this reason it was decided to use this residue as a pore forming agent during the firing of the aggregates. Potassium which is a nutrient element was supplied by a vegetable biomass ash, while phosphorous by animal bone meal ash resulting from the calcination (900 °C) of the flour. Flour is already used as a fertilizer in organic agriculture but also as a natural supplement for feeding livestock thanks to the phosphorus content present in the composition.

Chemical analyses of volcanic raw materials and metakaolin were performed by X-Ray fluorescence and provided by the themselves raw materials supplier companies, while those of spent coffee grounds, biomass ash and bone meal ash were performed by the same technique using XRF Thermo Scientific Model ARL PERFORM'X, software OXSAS. In order to investigate the crystalline phases into the raw materials, mineralogical analysis was carried out using an automatic diffractometer X-Pert PRO, Panalytical, with Ni-filtered Cu K α radiation; the patterns were collected on the powdered samples, characterized by a size less to 38µm, in the 5-70° 2 θ range (step size 0.02° and 1s counting time for each step). Moreover, quantitative mineralogical analysis of volcanic materials was given by Europomice Srl.

The alkaline attack test, used to determine the reactive fraction, allowed to verify the reactivity of the two volcanic minerals to obtain geo-polymers (Ruiz-Santaquiteria et al., 2011).

One gram of volcanic materials was immersed in 100 mL of 8 M NaOH solution (solid/liquid ratio of 1/100) in stirring condition for 5 hours at 80 ± 2 °C (Ruiz-Santaquiteria et al., 2011). The final solution

was filtered in order to separate the liquid and solid fraction.

The liquid fraction was acidified by HNO₃ to pH=2 in order to perform ICP/OES (VARIAN LIBERTY AX) to quantify the amount of Si and Al in the leachate (Lancellotti et al., 2013).

2.2. Geopolymers preparation

Pumice, lapillus and metakaolin were used as aluminosilicate-based materials. Na₂SiO₃ (SiO₂/Na₂O=3) solution and NaOH 8M solution were used as alkali activator by mixing in a ratio of 1:1.25 or 1:1 for pumice or lapillus-containing formulations, respectively.

In details the steps of preparation:

- volcanic ash powders and metakaolin were mixed;
- a mixture of alkaline solutions sodium hydroxide-sodium silicate was used to obtain a viscous paste;
- the paste was manually mixed for 5 min;
- the paste was poured into a plastic mold.

Curing conditions: the samples were closed inside a plastic bag for all curing time at in order to avoid air exposure and maintain a constant moisture level.

Curing time: 28 days

Curing temperature: room temperature (25 +/- 3 °C)

The protection of the sample from the air was necessary to avoid the formation of a layer of sodium carbonate on its surface. This phenomenon was due to the low reaction rate of pumice and lapillus with alkaline solution during the reticulation phase of the geo-polymers.

The characterizations of the specimens took place at a curing time of 28 days.

In this research two different series of samples were prepared; the first based on pumice instead the second based on lapillus. Both of them were characterized by the addition of metakaolin in order to optimize the aluminum content, because volcanic materials are poor of Al.

- **FIRST SERIES:** Alkali Activated Materials (AAMs) based on 70-80 wt% of pumice and 20-30 wt% of metakaolin (MK) (Fig. 2a and Table 1);

- **SECOND SERIES:** Alkali Activated Materials (AAMs) based on 70-80 wt% of lapillus and 20-30 wt% of metakaolin (MK) (Fig. 2b and Table 1).

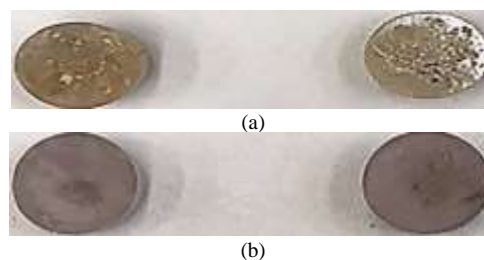


Fig. 2. Pumice AAMs at 28 curing days (a) and lapillus AAMs at 28 curing days (b)

Table 1. Formulations of Series 1 and Series 2 samples (MK: Metakaolin; P: Pumice; L: Lapillus)

Sample	MK (g)	Pumice (g)	Lapillus (g)	NaOH (mL)	Na ₂ SiO ₃ (mL)	Alkali ratio Na ₂ SiO ₃ /NaOH	H ₂ O (g)
P70	30	70	\	20	16	0.8	4
P80	20	80	\	20	16	0.8	4
L70	30	\	70	20	20	1.0	\
L80	20	\	80	20	20	1.0	\

2.3. Lightweight aggregate preparation

Four compositions were tailored based on volcanic raw materials and spent coffee grounds only or added of 50 wt% with a nourishing mixture (41% pumice + 25% vegetable biomass ash + 34% animal bone meal ash) prepared by dry-mixing in a slow ball mill for 30 min in order to give fertilizer properties, as reported in Table 2.

Table 2. Lightweight aggregates batch compositions

Sample / Raw material (wt%)	P	P/L	P I	P/L I
Pumice	85	42.5	85	42.5
Lapillus	-	42.5	-	42.5
Spent coffee grounds	15	15	15	15
Nourishing mixture	-	-	50	50

Spherical samples of aggregates about 1.5-2 g in weight were made by manual palletization using the prepared mixtures. To obtain a good plasticity needed for shaping, the powdered mixtures were moistened with an adequate water content (20-30% wt%) in order to avoid the formation of cracks. After drying in an oven at 105 ± 5 °C for at least 24 hours, in order to remove free water in the mixture to avoid possible cracking of the aggregates during firing due to sudden evaporation, the samples were inserted in an electric oven at 1000 °C for one hour. When inserted, the kiln was already hot and this is done in order to simulate the thermal shock that the aggregates undergo during industrial processes which, however, generally occur at higher temperatures (from 1200 to 1400 °C).

2.4. Geo-polymers characterization

Geo-polymers characterization was performed from chemical, physical and mechanical point of view. The samples at 28 days of curing were immersed in distilled water with solid/liquid ratio of 1/100 at room temperature for 24 hours in order to investigate the chemical stability and the compactness of their structure. This integrity test provided a qualitative evaluation on the stability of the matrix after 24 hours (Kiventera et al., 2018).

Further, the material's chemical stability in aqueous environment was monitored by pH and ionic conductivity measurements. A bulk sample was placed in distilled water (solid/liquid ratio wt% was 1/10) and stirred for 24 hours at room temperature. pH

(Laboratory PH sensor Hamilton type Liq-glass SL, OAKTON Eutech Instruments pH 5/6 and Ion 6) and conductivity (OAKTON Eutech Instruments CON 6/TDS 6) were measured at different times, such as 0, 15, 30, 60, 120, 240, 360, 1440 min in order to analyze the release of the ions in the solution during the 24 hours (Finocchiaro et al., 2020; Lancellotti et al., 2013, Lancellotti et al 2015).

To obtain quantitative information on the microstructure of alkali-activated materials and their lightness characteristics, the total porosity percentage (TP (%)) was obtained by processing absolute (Mycrometrics Accupyc 1340), and apparent (Enveloped Density Micrometrics Geopyc 1360) density data, indicated as ρ_{abs} and ρ_{app}, using Eq. (1):

$$TP(\%) = \frac{\rho_{abs} - \rho_{app}}{\rho_{abs}} \cdot 100 \quad (1)$$

Finally, mechanical compressive test was performed on the specimens after 28 curing days at room temperature. Four samples of each composition in cubic form with a side of 2 cm were subjected to compressive test according to the standard UNI EN 826 (Barone et al., 2020) employing an Instron 5567 Universal Testing Machine with 30 kN load limits and displacement of 3 mm/min.

2.5. Lightweight aggregates characterization

To analyze the weight variation of the aggregates during firing (water, organic matter, carbonates, etc.) a weight loss test was performed. This procedure was a preliminary test to check the stability and the preliminary resistance of the matrix (Andreola et al., 2019). Firstly, the specimen was dried and weighed (W_i), then this one was weighted after the firing (W_f); so, the weight loss percentage (WL (%)) was determined by Eq. (2):

$$WL(\%) = \frac{W_i - W_f}{W_i} \cdot 100 \quad (2)$$

In order to investigate the capacity of water retain, very important characteristic in gardening applications, the water absorption was determined. This parameter is related to the open porosity. The measure was conducted according to the standard EN ISO 772-21:2011. The specimen was immersed in distilled water in static condition for 24 hours at room temperature. The sample, after drying, was weighted

before (W_i : initial weight) and after (W_f : final weight) the immersion in water. Water absorption percentage (WA (%)) was quantified using Eq. (3):

$$WA(\%) = \frac{W_f - W_i}{W_i} \cdot 100 \quad (3)$$

The total porosity was calculated by Equation 1 from the absolute and apparent densities measured with the same procedure described in 2.4 paragraph.

pH and electrical conductivity measurements were carried out as reported in UNI EN 13037:2012 (pH rule standard) and UNI EN 13038:2012 (conductivity rule standard). The content of the soluble salts in the soil should be controlled because of their excess could lead to a serious plant imbalance as well as a pH different from neutrality could cause serious problems. Bulk specimens (10 g) were placed in distilled water with solid/liquid ratio as 1:5 in stirring condition (360 rpm) for 1 hour at room temperature. The liquid was filtered in order to obtain a transparent liquid fraction; on this eluate pH and electric conductivity were measured.

3. Results and discussion

3.1. Raw materials characterization

Chemical data of raw materials as pumice, lapillus, metakaolin, spent coffee grounds, biomass and bone meal ashes are shown in Table 3. Volcanic mineral scraps were suitable to form a silico-aluminate matrix both for geo-polymers and lightweight aggregates.

The high Loss of Ignition of SCGs underlined the presence of organic compounds (fatty acids, amino acids, polyphenols and polysaccharides as referred in Andreola et al 2019) and confirmed by the elemental

analysis (%): 2.39 N, 50.28 C, 6.99 H, 0.08 S and 38.54 O suitable to induce porosity during aggregates firing. Finally, vegetable biomass and animal bone meal ashes were considered as nutrient supplier mainly of potassium and phosphorous, respectively. For geo-polymers the content of $\text{SiO}_2 + \text{Al}_2\text{O}_3$ is important together with the amorphous fraction in order to have optimized alkali activation. The $\text{SiO}_2 + \text{Al}_2\text{O}_3$ of pumice was equal to 75.2% while for lapillus was 67.4%. These two parameters allow to hypothesize that pumice could be a more suitable material for alkali activation. Furthermore, Table 3 shows the presence of small percentage of Ba, Sr, Zr and Mn in volcanic materials.

The quantitative information about the mineralogical composition of pumice and lapillus is reported in Table 4. Since pumice contains 79.7% of amorphous phase while lapillus 11%, the former was considered a more suitable material to make AAMs as discussed above. Both raw materials contained Sanidine $(\text{K,Na})(\text{Si,Al})_4\text{O}_8$, Anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$, Analcime $\text{NaAlSi}_2\text{O}_6(\text{H}_2\text{O})$, Hematite Fe_2O_3 and other crystalline phases in smaller percentage as reported in Table 4.

The engineering of geo-polymeric materials went from a pre-screening to determine the reactive fraction in terms of Si and Al ions released in alkaline environment being known that a Si/Al mass ratio between 2 and 3 is associated to materials with a 3D rigid network, suitable for a cement, concrete (Lancellotti et al.2013). Table 5 shows Si/Al mass ratios very similar for both volcanic materials, compared with the ratio of metakaolin.

Pumice shows higher release values for both Si and Al, in agreement with the higher amorphous fraction detected by XRD. Both ratios for volcanic materials are higher with respect to metakaolin, probably due to the less amount and solubility of Al in these materials.

Table 3. Chemical composition (wt%) of raw materials used

Oxide	Pumice	Lapillus	Metakaolin	Spent coffee grounds	Vegetable biomass ash	Animal bone meal ash
SiO ₂	56.6	49.1	58.97	0.01	1.57	0.43
Al ₂ O ₃	18.6	18.3	34.70	\	0.37	0.02
Fe ₂ O ₃	3.94	9.15	1.40	0.02	1.13	0.01
TiO ₂	0.54	1.08	1.30	\	\	\
CaO	3.06	9.27	0.10	0.24	5.78	53.89
MgO	1.17	4.25	0.10	0.09	0.54	1.11
Na ₂ O	1.98	2.35	0.10	0.06	0.56	1.40
K ₂ O	8.55	3.66	0.70	0.89	59.81	0.04
P ₂ O ₅	0.13	0.45	\	0.16	1.46	41.24
Mn ₃ O ₄	0.13	0.14	\	\	\	\
BaO	\	0.09	\	\	\	\
SrO	\	0.11	\	\	\	\
ZrO ₂	0.07	1	\	\	\	\
SO ₃	0.13	\	\	0.06	4.99	\
Cl	\	\	\	0.01	6.77	\
LOI	4.84	1.44	2.63	98.11	16.60	1.00

Table 4. Quantitative mineralogical analyses (wt%) of Pumice and Lapillus

<i>Mineralogical phase</i>	<i>Pumice</i>	<i>Lapillus</i>
Amorphous	79.7	11.0
Quartz SiO₂	1.1	\
Sandino (K,Na)(Si,Al)₄O₈	11.2	19.8
Anorthite CaAl₂Si₂O₈	3.0	26.1
Analcime NaAlSi₂O₆(H₂O)	7.2	13.2
Diopside CaMgSi₂O₆	0.3	2.1
Muscovite KAl₂(Si₃Al)O₁₀(OH,F)₂	1.5	1.2
Hematite Fe₂O₃	8.8	4.5
Plagioclasio (Na,Ca)(Si,Al)₄O₈	3.1	6.9

Table 5. Si and Al release in NaOH 8M at 80 °C detected by ICP-OES

<i>Element (mg/L)</i>	<i>Pumice (mg/L)</i>	<i>Lapillus (mg/L)</i>	<i>Metakaolin</i>
Al	491	134	316
Si	1063	309	594
Si/Al	2.16	2.31	1.89

The error associated to the measurement is to20%

3.2. Geopolymers characterization

All the compositions, submitted to integrity test in water for 24 h, resulted unchanged confirming the efficacy of the geo-polymerization process and the compactness of the matrix.

Monitoring of pH and conductivity in aqueous environment and at established times and temperature allowed to evaluate the crosslinking of the sample network and the geo-polymerization reaction.

The first series of samples (Fig.3a), characterized by the presence of pumice, showed a value of pH that increases during 24 h for P80 (from 8.70 to 10.23), instead for P70 samples the pH values follow a constant trend from 9.60 to 10.02 in 24 h. For both formulations P80 and P70 the conductivity measurements increased during 24 h from 12.4 to 280 mS/m due to the ions release in the solution but Fig. 3a show no significance variation between the two formulations. This means that a higher amount of metakaolin into the matrix (from 20 to 30%) didn't involve reinforcement of the matrix and better chemical stability. The pH of the second series, containing lapillus, showed a constant trend for both formulations L80 and L70 during 24 h (from 10.2 to 10.01). This mean that a higher amount of metakaolin produced a more compact and stable sample in aqueous environment confirmed by reduction of released ions within the solution. The pH and conductivity measurements are characterized respectively by an error of 2% and 8%.

The total porosity (TP %), calculated by elaborating the experimental density values according to Eq. (1), was studied to confirm the light weighting nature of pumice and lapillus.

Looking at Fig. 4, it appears evident that the amount of volcanic mineral (80 or 70%) and the consequent amount of metakaolin (20 and 30%) is irrelevant within pumice-containing geo-polymers, and almost the same value of TP% was calculated for 70% of lapillus-containing sample. A material more porous and lightweight was obtained with 80% of lapillus and 20% of metakaolin, reaching a TP% around 45% instead of a mean of 32% for the other specimens.

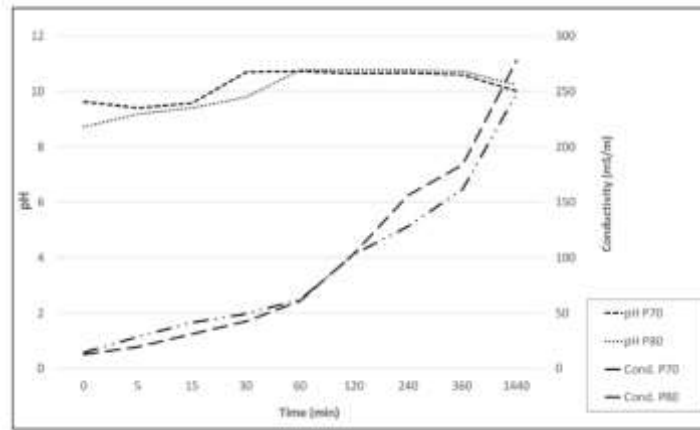
In order to investigate the mechanical properties of the pumice and lapillus specimens and the comparison between the two series, the compressive analysis was carried out. Fig. 5 shows that lapillus samples were characterized by the best results in terms of compressive strength (38MPa) with respect to pumice ones (6MPa) and these values are really similar to metakaolin geopolymer reported as standard. The amount of metakaolin inside the compositions does not show appreciable effect, for both the series. The results show the higher performance of lapillus sample with respect of pumice one due to the increase of geo-polymerization reaction and the dissolution of lapillus particles under the effect of alkali activators.

Data obtained are supported by bibliography. Values from 32 to 38 MPa were obtained by Barone et al. 2020 on geo-polymeric specimens 75 wt% volcanic ash and 25 wt% metakaolin-containing and with 28 curing days. Dener et al. 2021 working on alkali activated blast furnace slag/Portland cement composite using 80, 70 and 60% lightweight pumice aggregate by volume of total aggregate obtained the highest values ranging from about 18 to 22 MPa and 8 to 13 MPa for specimens 60 and 80 wt% of pumice

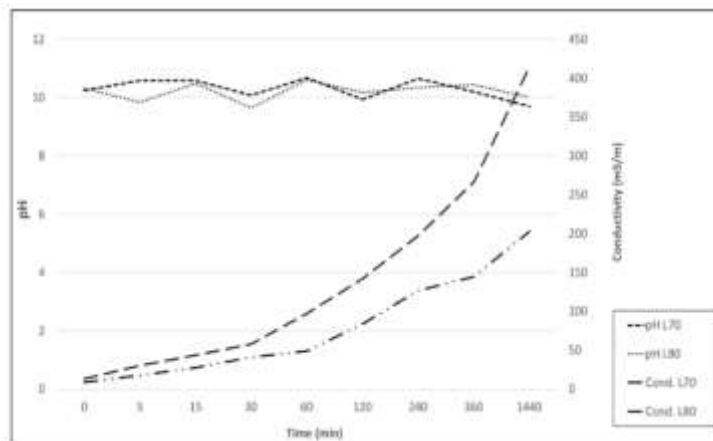
content, respectively.

The reductions in compressive strength were more evident when the pumice aggregate content was increased from 70% to 80%. Values of compressive strength around 40MPa were also found by Jaya et al. (2020) for metakaolin-based geopolymers with alkali ratio 0.8-1.0 as for geopolymers prepared in this

research. Higher compressive strength (from 55 MPa for 3 days' age to 65 MPa for 90 days' age) values were found by Karatas et al. (2019) for blend produced with entirely kaolin, but in this case with a $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio of 3, higher than the ratios used in this research (0.8 and 1).



(a)



(b)

Fig. 3. pH and conductivity of pumice-containing samples vs. time (a) and of volcanic lapillus-containing samples in function of time (b)

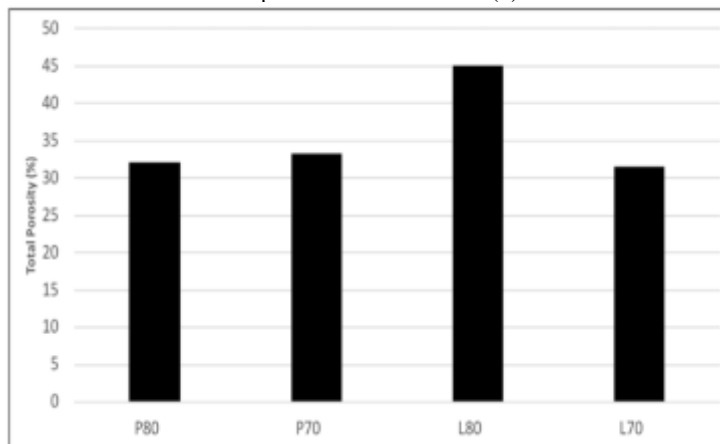


Fig. 4. Total porosity percentage of pumice and volcanic lapillus-containing samples

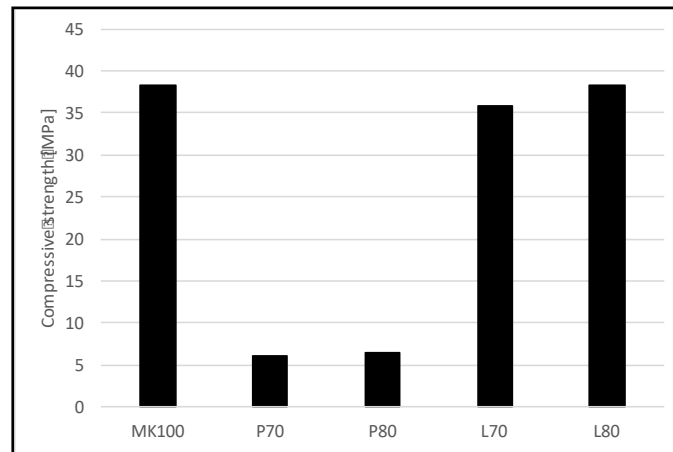


Fig. 5. Compressive strength of pumice (P70-P80), lapillus (L70-L80) samples and the reference specimen MK100 (Metakaolin 100%)

3.3. Lightweight aggregates characterization

In this study, the authors completely replaced the red clay used in the LAWs composition reported in previous paper (Barbi et al., 2020), maintaining the ratio of components mineral /porous agent 85/15. The optimization of the SCGs amount was studied in Andreola et al. (2019). All compositions characterized, were codified indicating the volcanic mineral matrix P: total pumice and P/L: matrix composed in equal amount of pumice and lapillus. For completing the mixture, the 15 wt% of SCGs as pore forming agent was added. These compositions can act as draining medium in the green roof. The compositions named P1 and P/L1 correspond to the above matrix described with the addition of 50 wt% of a nourishing mixture containing two kinds of agroashes which provide the main nutrients (P and K) for the vegetal culture. These compositions were tailored with the aim of using them as fertilizer. Physical features of the aggregates were measured in order to verify the feasibility to use the volcanic scraps as alternative raw materials. The weight loss (WL %) allows to appreciate the lightness of the specimens after firing. The values calculated are around a range from 15 to 20% for all specimens, except the P / L composition which has a high value. The WL% is associated to the loss of free water necessary for the paste preparation (~20-25%), organic compounds decomposition (from SCGs) and carbonates decomposition (from animal bone meal ash).

The UNI EN 13055:2016 rule specifies that an aggregate is considered as Lightweight Aggregate (LWA) when the particle density is lower than 2.00 g/cm³. Table 6 shows that all analyzed samples complied with the limit required for the standard. The aggregates containing only the matrix resulted lighter respect to those containing also the agroashes. The density is particularly important factor for the use of materials as a drainage component in layers of green roofs (formulations with only volcanic mineral scraps) and, again, as a light substrate, with fertilizing properties (aggregates formulations with nutrients). Regarding the absolute density values, they derived

from the components into the formulation. In fact, the P/L compositions show a greater density respect to the P ones (density of pumice = 0.5-0.6 g/cm³; density of lapillus = 1.05-1.15 g/cm³ (EuroPomice, 2018; EuroPomice, 2019). Besides, the presence of agroashes increases the absolute density values. In summary, the aggregates obtained are effectively porous and light, the calculated total porosity is around 60% for all compositions tested (Table 6).

Finally, the water absorption, strictly related to the open porosity, is an important factor to choose the aggregate's application. From the Fig. 6 it can be observed that P/L sample showed the highest WA% values, P1 and P/L1 show intermediate values and P composition resulted with the lowest value indicating a high sintering degree.

Concerning the chemical properties, pH and electrical conductivity were measured on the filtered liquid after contact with the aggregates. The pH of the soil measures the concentration of hydrogen ions in the circulating solution, i.e. the liquid phase found in the spaces left free between the particles of the solid fraction (clay, sand and silt). Its value depends of the kind of ions present (alkali or not). This chemical parameter greatly influences the microbiological activity (responsible of the breaking down organic matter), the availability of mineral elements and the adaptability of the various plant species. The pH of the soil also influences the solubility of the various mineral elements in the solution of the soil both from the decomposition of the minerals of origin and from the fertilizers distributed, determining their accumulation in forms more or less available for the plants or their leaching towards the lower layers deep. In general, the best pH condition of the soil for the development of crops is around neutrality (pH between 6.5 and 7.5): in a neutral environment the nutrients in solubilisation phenomena are in fact reduced or absent, the supply of mineral elements is generally more balanced and microbiological activity is favoured. Soils that have a pH below 5.5 generally are characterized by low percentage of calcium, magnesium, and phosphorus and in these conditions

the solubility is high for aluminium, iron, and boron, while is low for molybdenum (USDA, 1998). Based on these considerations, lightweight aggregates should have a pH as close as possible to neutrality. The data reported in Fig. 7 show that all the samples meet the conditions of neutral pH, with a slight overshoot towards the alkalinity only of the pumice-based aggregate (7.7).

Another fundamental parameter to be monitored is electrical conductivity. The soluble salts present in the soil (coming from the soil, groundwater or irrigation water, fertilizers) are essential for plant nutrition, but their concentration must be contained within certain values. For crops, the range corresponds to values greater than 0.2 mS/cm and less than 2 mS/cm. High salt concentrations can cause nutritional imbalances, toxic effects on plants, damage to the soil structure and, in some cases, changes in pH. Apart from these extreme situations, an increase in salinity generally determines an increase in the driving force

of the circulating solution which in turn causes greater difficulty in absorbing water and mineral elements by plants: this phenomenon depends not so much on the salt content soluble, but by the osmotic pressure exerted by them.

Although electrical conductivity, E.C., provide no direct measurement of specific ions or salt compounds, it has been correlated to concentrations of ions such as nitrates, potassium, sodium, chloride, sulphate, and ammonia (USDA, 2006). As far as conductivity is concerned, it is noted that only the composition based on pumice and lapillus (P/L1) with the addition of 50% of nutrients exceeds the threshold value of 2 mS/cm, therefore it could only be suitable for more resistant crops. The conductivity values of the other compositions fall within the reference range. It is possible to observe that the compositions without nutrients show very low values (Fig. 8). These results indicate the ease of release of the ions present in the ashes at the pH of use.

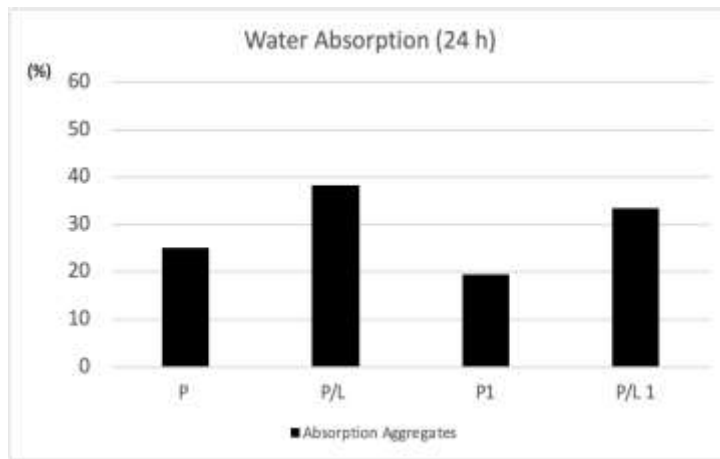


Fig. 6. 24h-immersion water absorption of the prepared aggregates

Table 6. Physical properties of the lightweight aggregates

Sample code	Absolute density (g/cm ³) (standard deviation)	Apparent density (g/cm ³) (standard deviation)	Total porosity (%)
P	2.1913±0.0016	0.9953±0.0043	59
P/L	2.5650±0.0015	0.9609±0.0018	63
P 1	2.9820±0.0010	1.1009±0.0013	59
P/L 1	3.0805±0.0016	1.1359±0.0024	59

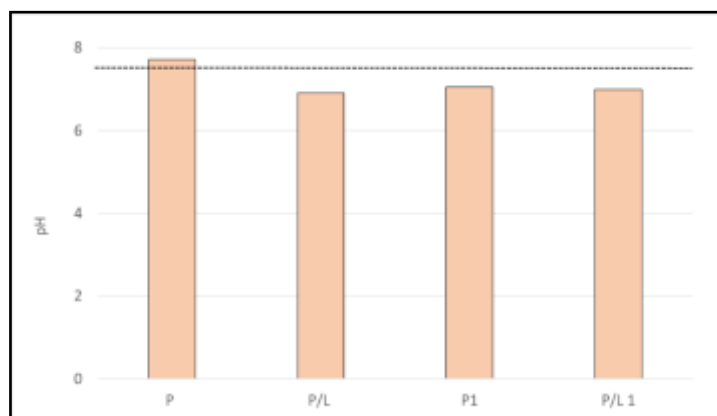


Fig. 7. pH of the prepared aggregates

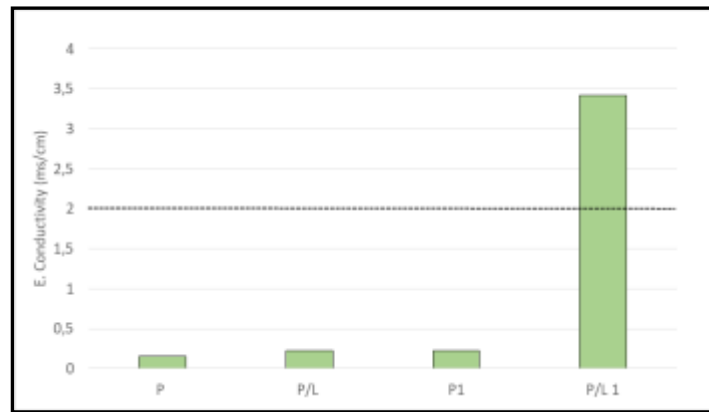


Fig. 8. Electrical conductivity of the prepared aggregates

4. Conclusions

In this preliminary study the feasibility to use the volcanic inert scraps in the manufacturing of geo-polymers and lightweight aggregates was demonstrated. The research proposed to avoid the landfill disposal of both the volcanic inert finer fraction and the spent coffee grounds used as pore-forming agent. On the basis of the findings, the following specific conclusions can be drawn.

Geo-polymers:

Volcanic minerals are suitable to obtain geo-polymeric materials; their presence does not hinder geo-polymerization process. pH remains constant with values typical for metakaolin geo-polymers. Conductivity shows different behavior depending on the presence of pumice or lapillus. Pumice maintains low values while lapillus leads to higher values of conductivity. This can be related to the chemical composition of lapillus richer in Ca, Mg and Na, but also to the more porous structure of lapillus-based geo-polymers. Further, compressive strength is particularly high for geo-polymers containing lapillus; in particular, this one confirms its stability both chemically and mechanically.

This research will help to support the choice of matter recycling as viable alternative and reduce CO₂ emissions in building manufacturing.

LWAs:

All compositions tested resulted in lightweight aggregates according to the standard UNI-EN. Furthermore, these aggregates have water absorption values and total porosity of the same order as commercial products like Arlita Leca L used in gardening, horticulture and roof insulation applications. Besides, they present adequate pH and E.C. values to be used as growth substrates in agronomic applications.

The complete replacement of natural clay minerals with inert volcanic scraps and the use of post-consumer residue (SCGs) represent an interesting alternative to manufacture lightweight aggregates for agronomic purposes (draining and fertilizer materials), using low sintering temperature with less environmental impact and economic savings.

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References

- Andreola F., Borghi A., Pedrazzi S., Allesina G., Tartarini P., Lancellotti I., Barbieri L., (2019), Spent Coffee grounds in the production of lightweight clay ceramic aggregates in view of urban and agricultural sustainable development, *Materials*, **12**, 3581.
- ARPAV, (2007), Regional Agency for Environmental Prevention and Protection of Veneto, Interpretation of soil analysis Tool for environmental sustainability, Ed. Soil and Waste Observatory Service-Provincial Department of Treviso, Italy, On line at: <https://www.arpa.veneto.it/bollettini/meteo.php>.
- BAB, (2019), British Assessment Bureau, What is sustainable construction and why is it important?, On line at: <https://www.british-assessment.co.uk/insights/what-is-sustainable-construction-and-why-is-it-important/>.
- Barbi S., Barbieri F., Andreola F., Lancellotti I., Martínez García C., Cotes Palomino T., Montorsi M., Barbieri L., (2020), Design and characterization of controlled release PK fertilizers from agro-residues, *Environmental Engineering and Management Journal*, **19**, 1669-1676.
- Barone G., Finocchiaro C., Lancellotti I., Leonelli C., Mazzoleni P., Sgarlata C., Stroschio A., (2020), Potentiality of the use of pyroclastic volcanic residues in the production of alkali activated material, *Waste and Biomass Valorization*, **12**, 1075-1094.
- Dener M., Karatas, M., Mohabbi M., (2021), High temperature resistance of self-compacting alkali activated slag/Portland cement composite using lightweight aggregate, *Construction and Building Materials*, **290**, 123250.
- EMF, (2017), Ellen MacArthur Foundation, The Circular Economy in detail, On line at: <https://www.ellenmacarthurfoundation.org/explore/the-circular-economy-in-detail>.
- EuroPomice, (2018), Technical sheet Pumice for gardening by EuroPomice srl., On line at: www.europomice.it/documentazione/schede-tecniche/.
- EuroPomice, (2019), Technical sheet Lapillus for gardening by EuroPomice srl. On line at: www.europomice.it/documentazione/schede-tecniche/.
- Finocchiaro C., Barone G., Mazzoleni P., Sgarlata C.,

- Lancellotti I., Leonelli C., Romagnoli M., (2020), Artificial neural networks test for the prediction of chemical stability of pyroclastic desposits-based AAMs and comparison with conventional mathematical approach (MLR), *Journal of Material Science*, **56**, 513-527.
- Górecki J., Núñez-Cacho P., Corpas-Iglesias F.A., Molina V., (2019), How to convince players in construction market? Strategies for effective implementation of Circular Economy in construction sector, *Cogent Engineering*, **6**, 1690760 doi: <https://doi.org/10.1080/23311916.2019.1690760>.
- Jaya N.A., Liew Yun-Ming L., Cheng-Yong H., Abdullah M.M.A.B., Hussin K., (2020), Correlation between pore structure, compressive strength and thermal conductivity of porous metakaolin geopolymer, *Construction and Building Materials*, **247**, 118641.
- Karatas M., Dener M., Mohabbi M., Benli A., (2019), A study on the compressive strength and microstructure characteristic of alkali-activated metakaolin cement, *Revista Materia*, **24**, doi: <https://doi.org/10.1590/s1517-707620190004.0832>.
- Kiventera J., Lancellotti I., Catauro M., Dal Poggetto F., Leonelli C., Illikainen M., (2018), Alkali activation as new option for gold tailings inertization, *Journal of Cleaner Production*, **187**, 76-84.
- Lancellotti I., Cannio M., Bollino F., Catauro M., Barbieri L., Leonelli C., (2015), Geopolymers: An option for the valorization of incinerator bottom ash derived “end of waste”, *Ceramics International*, **41**, 2116-2123.
- Lancellotti I., Ponzoni C., Barbieri L., Leonelli C., (2013), Alkali activation processes for incinerator residues management, *Waste Management*, **33**, 1740-1749.
- Leonelli C. and Romagnoli M., (2013), *Geopolymers: Chemically activated inorganic polymers*, Ed. Italian Ceramic Society (IcerS), Faenza, Italy.
- Medri V., (2009), Geopolymers: Ceramics for a sustainable development. National Research Council - Institute of Science and Technology for Ceramics, Faenza (Italy).
- Ruiz-Santaquiteria C., Fernández-Jiménez A., Palomo A., (2011), *Quantitative determination of reactive SiO₂ and Al₂O₃ in aluminosilicate materials*, Proc. of XIII Int. Cong. on the Chemistry of Cement, Madrid, Spain.
- USDA, (1998), United State Department of Agriculture, Soil quality indicators: pH, Soil Quality Information Sheet, On line at: https://www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/nrcs142p2_052208.pdf.
- USDA, (2006), U. S. Department of Agriculture, Soil quality indicators: Electrical conductivity, Soil Quality Information Sheet, On line at: www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/nrcs142p2_053280.pdf.