



Pumice and lapillus scraps: New national environmental-friendly chance for the production of ceramic tiles

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ABSTRACT

Italian pumice and volcanic lapillus scraps have been used in different percentages as alternative raw materials to foreign feldspars in porcelain stoneware mixtures. The aim of this work was to create naturally colored support to limit the use of artificial dyes while maintaining the technical properties of the reference product. For this purpose, the significant presence of chromophores (Fe and Ti in particular) in by-products from extraction of Italian volcanic pumice and lapillus was exploited. The work was carried out in collaboration with a company: the products were made on a laboratory scale and then they were glazed and fired within the industrial production cycle (48 min, 1210 °C).

The resulting slip and the fired samples were characterized by measuring the efflux time, density, linear shrinkage, water absorption and tensile strength to evaluate the technological performance. In addition, thermogravimetric analysis (TG), differential thermal analysis (DTA), and optical and mechanical dilatometry were performed to study the thermal behavior of the formulations.

The obtained products could be classified as porcelain stoneware and belong to the BIa group (WA 0.5%, B.S. >35 MPa) in accordance with UNI EN 14411 ISO 13006.

1. Introduction

Italy ranks among the top seven ceramic tile producers in the world [1], and the Italian ceramic tile production in 2022 (preliminary) was found to be about 448 million m² [2] keeping production stable compared to the previous year. The World of ceramic tile production in 2021 was found to be about 18 billion m² with an increase of about 7% compared to 2020 [3].

In recent years, the ceramic industry has been challenged by first the pandemic, which caused a forced stop in production for a period, and later due to the political situation, which created problems in the supply chain of raw materials as well as an uncontrolled increase in natural gas and electricity prices. The ceramics industry is a highly energy consume industry and has also been faced with major challenges such as achieving the sustainable development goals imposed by the 2030 Agenda [4]. It must be considered that the production cycle of Italian ceramics already appears to be designed following the circular economy issues, indeed almost all production and purification waste is fed back

into the production cycle, about a quarter of raw materials travel by train, 97% of factories reuse process water, and about half of the energy used in production comes from cogeneration or renewable sources [5]. The increase in tile production, however, has led to the need to source an ever-increasing number of raw materials, and it must be considered that these turn out to be nonrenewable assets in the short term, therefore, may soon deplete. On the basis of the above considerations, rather than looking for new virgin raw materials, it is better to i) make the process more virtuous by trying to use scraps, waste or by-products from other production processes, and, in addition, ii) limit the environmental impacts caused by long-distance transportation by preferring local rather than foreign raw materials. The literature related to studies on ceramic substrates is numerous, and there are several researches based on the addition or replacement of several types of waste or refuse within ceramic mixtures for the production of porcelain stoneware. Conte et al. studied the technological behavior resulting from high percentages of flux replacement with different types of glass scraps [6] while Gualtieri et al. evaluated the inclusion of high percentages of borosilicate glass

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scraps in stoneware tiles fired at low temperature [7]. Some authors have evaluated the embedding of sodium-calcium glass scrap within the ceramic slurry [8,9] while the authors in the past have focused their attention on the reuse of glass from the disposal of cathode ray tubes [10]. The inclusion of glass scrap is a suitable option but only in small percentages because the densification process starts at lower temperatures than the reference temperatures and at high replacement rates leads to lower sintering efficiency with swelling effects [11]. The addition of these types of wastes in ceramic slurries could lead not only to a substitution of virgin raw materials but also to a reduction in firing temperature [7,8].

There are also feasibility studies in the literature related to replacing fluxes with quarry dust from zeolitic rocks, used for their fusibility, modest hardness and low cost [12] and blast furnace slag [13]. Other studies use scraps or wastes such as incinerator bottom ash and fly ash [14–16], foundry sand [17,18], eggshells to replace limestone [19], and composite materials from industrial plastic waste and recycled nylon fibers to improve the performance of floor tiles [20].

The objective of the present work was to replace foreign feldspars, mainly Turkish, within a porcelain stoneware production mixture with scraps that derive from the mining and processing operations of Italian volcanic rocks and that have limited commercialization because they are very fine: pumice and lapillus. Pumice and volcanic lapillus are aluminosilicate materials rich in alkaline earth metals that contribute to the fusibility of the system and rich in iron and titanium (3.94% and 0.54% in pumice and 9.15% and 1.08% in lapillus, respectively). Iron and titanium are chromophores, normally it is preferred that their sum is very low to obtain a white porcelain stoneware support (<1.5%). In our case, the percentage of these metals turned out to be very high, so we opted for obtaining a naturally colored support in brown tones in the case of the pumice-based mixture, and in grey/black tones in the mixture lapillus-based. Such a choice allowed the use of local by-products and permitted the reduction of the quantities of artificial pigments used for mass coloring of white supports. There are studies in the literature on the use of pumice rock as, for example, an alternative fluxing agent in the composition of transparent glazes for roof tiles [21], as a pegmatite substitute for the production of wall tiles [22] and as a micronized raw material for obtaining sanitary glazes [23].

2. Materials and methods

2.1. Raw materials and samples preparation

Italian pumice and volcanic lapillus scraps, having a size smaller than 3 mm and from their mining and processing operations in quarries located in the Vulsini Volcanic District (around Lake Bolsena, Lazio, Italy), were supplied by Europomice srl. The scraps have the role of substituting the foreign feldspars within a porcelain stoneware body taken as a reference. Changes in the properties of these rocks as a function of temperature allowed them to be considered as fluxes [24]. In addition to volcanic rock scraps, sodium-potassium feldspar scraps from the mining and processing operations of rocks located in quarries present in northern Italy were used.

The clay component, useful for providing plasticity to the ceramic piece, is provided by clays, sourced from central-western Germany and northern Italy, and kaolin, sourced from central Italy.

Sands from Emilia-Romagna (Italy), sands from Sardinia (Italy) and raw and fired scraps from the production process were also included in the mixture.

Raw materials were included within the formulations in varying percentages, and the various mixtures were tailored by comparing the resulting chemical and mineralogical analysis with those of the mixture currently in production in the industrial plant. Chemical analyses were performed with an ARL PERFORM'X model sequential X-ray fluorescence (XRF) spectrometer. Mineralogical analyses were performed with an X-ray diffractometer, model X'PERT 3 POWDER PANALYTICAL using

the Rietveld method. The quantitative analysis of the crystalline phases was obtained by Rietveld refinements, using GSAS software, and were recalculated based on the absolute mass of the corundum originally added to the mixtures as an internal standard.

All raw materials were dried in an oven at $150\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ for 4–5 h to remove moisture. To obtain the samples, the raw materials were mixed with water at a ratio of 1:0.8 or 1:0.45, depending on the density sought, and a fluidizer to increase the workability of the mixture has been used. The obtained slip was then dried, ground, and humidified to 6%. After the powders were compacted with a hydraulic press at a pressure of 70–75 MPa to obtain specimens with a diameter of 50 mm for firing (industrial cycle: 48 min at $1210\text{ }^{\circ}\text{C}$) and specimens having dimensions of $50\text{ mm} \times 100\text{ mm}$ were used for calculating flexural strength. The pressures applied are very high and do not correspond to those applied during production. These pressure values allow for water absorption values comparable to those that would be obtained by direct firing on industrial kiln rollers and not on a refractory plate (the firing mode used for the samples). The prepared formulations can be seen in Table 1; the abbreviations L and P indicate lapillus-based and pumice-based ceramic bodies, respectively. Concerning the reference sample, it contains a mix of two German clays, a mix of five Italian feldspars, and a mix of six Turkish feldspars (sodium and potash sodium) and other Italian components. The reference consists of 18 raw materials, both Italian and foreign, while the studied formulations are made with 8–10 raw materials of which only one is foreign (German clay).

2.2. Slip characterization: viscosity, density and residual fraction

The slip was placed inside a Ford cup with a 4-mm-diameter nozzle, and the time required to empty the cup was measured.

The density value was obtained according to Eq. (1), once the weight of the suspension contained in the pycnometer and that of the pycnometer itself were known:

$$d \text{ (Kg / cm}^3\text{)} = (tw - pw) / 1000 \quad (1)$$

where: d density, tw total weight (g) and pw is the pycnometer weight (g).

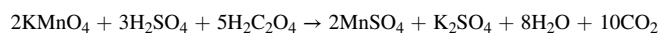
The residual fraction was obtained by passing the slip through a sieve having a mesh diameter of $63\text{ }\mu\text{m}$ and weighing the remaining solid mass on the sieve.

2.3. Unfired sample characterization

2.3.1. Permanganate oxidability

The presence of oxidizable substances within the mixture was evaluated through Kubel's method, an indirect titration method by which the ability of potassium permanganate to oxidize organic matter to CO_2 and H_2O in an acidic environment is analyzed when hot. This analysis makes it possible to assess the possible defects that could be encountered during cooking, such as, for example, the formation of black heart and subsequent swelling due to the presence of numerous oxidizable substances that would need more oxygenation to be flushed out [25].

The reaction that commands this phenomenon is as follows:



Potassium permanganate in the presence of sulfuric acid is reduced to manganous sulfate thus providing elemental oxygen for the oxidation of organic matter.

Inside a beaker containing 100 ml of double-distilled water were placed 1 g of ground sample, 5 ml of $1:3\text{H}_2\text{SO}_4$ solution and 10 ml of 0.01 M KMnO_4 , and the whole is then brought to a boil for about 10 min. After boiling, 10 ml of $\text{H}_2\text{C}_2\text{O}_4$ 0.01 M is placed inside the beaker and potassium permanganate is added until the color of the solution changes.

The result is expressed in mg/l of oxygen consumed, which is derived

Table 1

Batch prepared using P and L compared with the reference (only for the reference: a = mix of two German clays, b = mix of five Italian feldspars, c = mix of six Turkish feldspars).

	REFERENCE	L1	L2	L3	L4	P1	P2	P3	P4
German clay	35.4% ^a	34%	35%	35%	35%	33%	34%	35%	35%
Italian clay	3.8%	4%	3%	2%	2%	4%	3%	2%	2%
Italian kaolin	9.0%	8%	9%	8%	8%	6%	6%	8%	8%
Lapillus	–	13%	12%	12%	15%	–	–	–	–
Pumice	–	–	–	–	–	13%	15%	15%	16%
Italian feldspar	18.3% ^b	13%	23%	22%	19%	13%	15%	19%	17%
Turkish feldspars mix	24.1% ^c	–	–	–	–	–	–	–	–
Italian sand (Emilia-Romagna)	2.3%	–	–	3%	3%	6%	–	3%	5%
Italian sand (Sardinia)	2.3%	–	–	3%	–	–	–	–	–
Mix scraps	4.9%	15%	–	–	–	12%	12%	–	–
Chamotte	–	13%	18%	15%	18%	13%	15%	18%	17%

by multiplying the milliequivalents of permanganate consumed at the endpoint by the milliequivalent weight of oxygen and then dividing this product by the volume of sample used (0.1 L) [26].

2.3.2. Flexural strength

The flexural strength is a parameter used to evaluate the ability of the tile to resist static and dynamic loads when placed in service. The standard considers the tile as a beam, placed on two rollers spaced apart, while a force is applied in the center by a third roller. The breaking load is the weight that is borne before the specimen breaks. Measurement of this parameter on unfired ceramic specimens having dimensions 50 mm × 100 mm was carried out with a Gabbrielli Technology mini-CRC 2 Chrometer according to DIN 51030, UNI EN ISO 10545-4. Each measurement was performed on a minimum of 4 samples, and the value reported below is the average of the values of the individual samples. The instrument consists of a working base, which rests on the sensing element i.e., the electronic load cell, and houses the associated lower supports. The upper part is motorized and applies and controls the load during the working stroke (constant increment 1 N/mm²s). The breaking stress (S) is obtained by multiplying the breaking load F , i.e., the force applied at the centerline of the working surface, by the ratio L/b (roller distance/tile width). Once F is known, the breaking modulus (σ) can also be calculated according to Eq. (2):

$$S(N) = F \bullet L / b \quad (2a)$$

$$\sigma = 3FL / 2bh^2 \quad (2b)$$

The standard applies to all types of tiles and porcelain stoneware [27].

2.4. Fired sample characterization

2.4.1. Loss of ignition

Loss of ignition (LOI) was calculated according to Equation (3):

$$LOI(\%) = (w_i - w_f) / w_i \bullet 100 \quad (3)$$

where: w_i is the initial weight of the sample, w_f is the weight of the sample after firing.

2.4.2. Linear shrinkage

Linear shrinkage was calculated on fired specimens by measuring with a caliper the dimensional changes of the specimens in five different points to obtain an average value. The equation by which the parameter was calculated is as follows:

$$LS(\%) = (d_i - d_f) / d_i \bullet 100 \quad (4)$$

where: d_i is the initial diameter (50 mm) and d_f is the diameter of the sample after firing.

2.4.3. Vacuum water absorption

The fired samples were placed in a laboratory instrument (ISO-VACUUM 650, Gabbrielli Technology) to determine vacuum water absorption in ceramic tiles with fully automatic cycles. The vacuum test is carried out as follows: the tiles are placed in a special grid and fed into the tank (made of AISI - 304 stainless steel); then the cycle is started with the vacuum pump. When the required vacuum is reached and maintained, the pump stops. The tank, at this point, fills with demineralized water up to 50 mm above the maximum height of the tiles (adjustable level due to the presence of an electronic sensor). The vacuum regime is discharged, and the tiles remain immersed in the water for the time prescribed by the standard. In this way, apparent porosity, apparent relative density and water absorption can be determined. The instrument has been tested and set to perform ASTM C 373, ISO 10545-3, ISO 10545-12 4.2.6 standards. Once removed from the instrument, the samples were properly dried to remove excess surface water and weighed. The per cent water absorption (WA%) was calculated according to Eq. (5):

$$WA(\%) = (w_f - w_{pf}) / w_f \bullet 100 \quad (5)$$

where: w_f is the final weight, w_{pf} is the post-firing weight.

2.4.4. Thermal and thermomechanical characterization

A number of samples were subjected to thermal analysis and compared with the reference. The thermal characterization techniques used were thermogravimetric analysis (TG), differential thermal analysis (DTA), optical and mechanical dilatometry.

Differential thermal analysis allows evaluation of the behavior of powders as temperature increases, while thermogravimetric analysis allows the determination of the change in sample mass as a function of temperature again. This analysis was conducted on the mixtures to evaluate the firing behavior of the mixtures and to understand whether the firing temperatures could be lowered. TGA/DTA analyses were performed with a simultaneous thermal analyzer NETZSCH STA 429 (CD). The samples were ground to an impalpable powder (average particle diameter less than 20 μ m), and the analysis was carried out at a heating rate of 10 °C/min.

The optical dilatometer is an instrument used to study the sintering of ceramic bodies and their thermal stability range while avoiding the risk of swelling by providing sample expansion (%) as a function of temperature as a result. Using optical technology, the best firing cycle can be determined without risking damage to the material. The measurement was performed with the Expert system ODHT-HSM solution mod. M3MD 1600/80, at a maximum temperature of 1280 °C and a heating rate of 10 °C/min, on solid samples prepared with a height of 15 mm, and with 5 × 5 mm edges. All samples were dried in an oven at 105 ± 5 °C overnight and stored in a desiccator before use. The samples tested were not fired.

The mechanical dilatometer was used to measure the thermal expansion of the specimens to obtain the Linear Thermal Expansion

Coefficient (α). The fired sample, having a length of 38–50 mm, was subjected to a constant negligible mechanical load and simultaneously to a controlled temperature/time program. Measurements were made with a MECHANICAL DILATOMETER, Netzsch Dilatometer 402 EP, with a heating rate of 5 °C/min setting a maximum temperature of 600 °C.

2.4.5. Colorimetry

In order to determine the effect of the addition of pumice or lapillus on aesthetic properties, fired samples were analyzed using a UV–vis spectrophotometer (SPECTROPHOTOMETER CM-2600d, KONIKA MINOLTA), which operates in the CIE L*a*b* color space, allowing the set of colors perceived by the human eye to be described.

This analysis was performed by comparison between the best fired samples and the reference. For each sample, five measurements were taken at different points of the surface to analyze any color variations, given by the ΔE parameter:

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2} \quad (6)$$

If $\Delta E < 1$ two colors are no discriminable by convention.

3. Results and discussion

3.1. Characterization of mixtures

Chemical and mineralogical analyses were performed on the raw materials, not the mixtures, and were provided by the partner companies. The analyses on the mixtures reported below were not performed by spectroscopic analysis, but by calculating the percentages of the elements and crystalline phases based on the percentage of raw material in the mixture.

The formulations were selected on the basis of chemical and mineralogical similarity of the slurry samples to those of the reference. The comparison of the chemical and mineralogical analyses can be seen in Table 2 and Table 3, respectively.

By considering the comparison of chemical analyses, the slurries containing lapillus have similar percentages of silica and alumina to the reference with the exception of sample L2. The percentage of titanium oxide is comparable to the reference while iron oxide is almost two times that of the reference with the exception of sample L4 which has a higher percentage value, but in this case, it turns out to be an added value as it provides a darker coloration than the reference. CaO, MgO and K₂O are present in larger amounts than the reference while Na₂O is present in smaller amounts. As for the slurries pumice-based, the amounts of silica and alumina are found to be remarkably similar to those of the reference in all the formulations studied. The titanium oxide content is practically the same as the reference; therefore, it does not affect the coloration of the ceramic piece, while iron oxide has intermediate percentages between the reference and the lapillus-based slurry; in fact, it takes on an intermediate coloration visible in Fig. 1. Again CaO and K₂O are present in larger amounts while MgO and Na₂O vary and are present in smaller percentages.

An interesting ratio is that of silica/alumina, which turns out to be

identical to the reference in sample L4 and P2 and very similar in the other samples except L3.

Fig. 2 displays the different percentages of the oxides. It is possible to see a decrease in alkaline oxides and increase in alkaline-earth oxides. The ratio between alkali and alkaline-earth oxides drops significantly especially in P4. Alkaline-earth oxides help sintering by reducing temperature, so increasing their percentages improves the sintering process by affecting properties such as: shrinkage, water absorption and flexural strength.

Mineralogical analysis shows that samples L4, P3 and P4 have about the same quartz content compared to the reference, the percentage of kaolinite is found to be a bit lower for all samples except L1 where it increases slightly. The illite/mica content decreases in all samples and no sample except L3 has montmorillonite content. In general, the percentage of clay component decreases. The percentages of albite and plagioclase are found to be significantly lower than in the reference while the percentages of orthoclase increase in all samples.

The mineralogical analysis, unlike the chemical analysis, shows very different crystalline phases, and it can be seen that there are extremely high percentages of unreported phases in all the mixtures studied unlike the mixture taken as the reference.

The very high percentages in the samples containing pumice are mainly due to the percentage of amorphous fraction detected in the pumice (about 80%), while in the samples containing lapillus it is due not only to the amorphous fraction but also to the presence of hematite, which were not considered in the comparison with the reference.

3.2. Characterization of unfired samples

Fig. 3 and Table 4 show the values of the parameters analyzed on the slips and unfired sample.

The results of the measurements show quite similar values of efflux time working at low densities (1.4–1.5 kg/cm³) in the case of both lapillus-based and pumice-based samples. As the density increases, moving closer to the value of the reference, there is an increase in the efflux time, and this is due to higher viscosity of the slip as there is more solid loading and less water. If the efflux time value of the reference is compared with samples L4, P3 and P4, which have similar densities to the standard, it can be seen that its value is much lower in the sample containing lapillus than in the one containing pumice. The latter has efflux time values comparable to those of the standard while the lapillus-containing sample has lower values; this could allow, for the same fluidizer, a decrease in the amount of water required for slip preparation in favor of solid loading or use a lower amount of deflocculating agent.

The residual fraction was measured because it represents an important process parameter, as it allows an assessment of whether the grinding time of the mixture is adequate. The results reported for L4, P3 and P4 are very similar to those of the reference while the other samples presented much lower values. The difference can be attributed to the fact that the above samples were ground for 7 min while the remaining samples were ground for 9 min. It can be assumed that a grinding time of 9 min appears to be too long.

Regarding the presence of oxidizable substances in all samples, the

Table 2
Chemical analysis.

	Reference	L1	L2	L3	L4	P1	P2	P3	P4
SiO ₂	69.7	68.2	58.7	69.6	68.4	69.6	68.8	69.5	69.4
Al ₂ O ₃	17.8	17.8	14.5	16.7	17.5	17.4	17.9	17.5	17.4
Fe ₂ O ₃	1.2	2.3	2.1	2.2	2.4	1.6	1.7	1.7	1.7
TiO ₂	0.7	0.8	0.7	0.7	0.8	0.7	0.7	0.7	0.7
CaO	0.6	1.9	1.4	1.7	2.0	1.1	1.1	1.0	1.1
MgO	0.7	0.9	0.7	0.8	1.0	0.5	0.5	0.5	0.5
K ₂ O	2.2	2.6	2.5	2.9	2.8	3.3	3.4	3.5	3.6
Na ₂ O	3.4	1.7	0.9	1.5	1.5	1.7	1.7	1.5	1.5
Others	3.7	3.8	18.5	3.8	3.8	4.1	4.1	4.2	4.3

Table 3
Mineralogical analysis.

	Reference	L1	L2	L3	L4	P1	P2	P3	P4
Quartz	30.7	29.8	31.7	32.8	30.4	30.6	28.3	30.5	30.5
Kaolinite	15.6	16.1	15.0	14.6	14.6	15.0	14.9	14.6	14.6
Illite/Mica	11.8	10.5	8.4	8.4	8.4	10.1	10.3	8.7	8.8
Montmorillonite	0.3	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0
Albite	23.3	5.9	5.1	5.4	4.8	6.4	5.7	4.8	4.7
Orthoclase	5.6	8.0	9.3	10.1	9.1	7.3	7.4	7.8	7.5
Plagioclase	8.1	3.4	1.6	1.6	1.6	2.8	2.5	1.2	1.2
Other or not reported	4.7	26.4	28.9	27.0	31.3	27.7	30.8	32.5	32.7

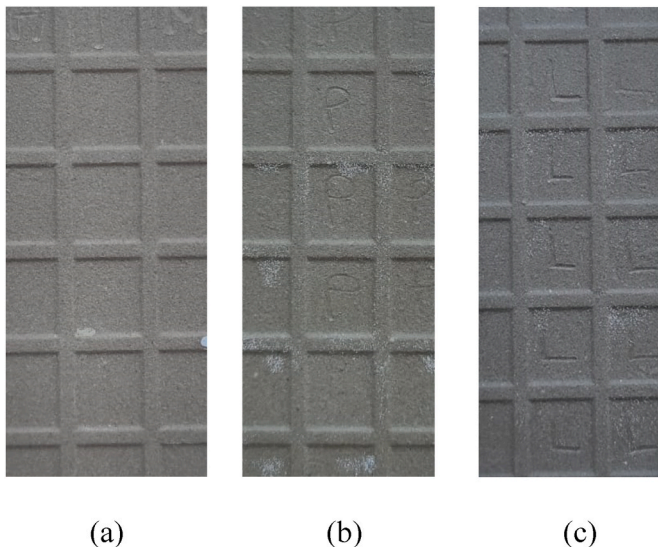


Fig. 1. Color variation in different mixtures: (a) is the reference, (b) is a pumice sample, and (c) is a lapillus sample.

values obtained were adequate and lower than the maximum limit imposed on the reference. Excessive presence of oxidizable substances could lead to the swelling of the ceramic piece due to the incomplete degassing of the organic products that burn turning into gas.

Flexural strength is measured because the tiles during transportation and processing are subjected to stresses, and the minimum reference value required is 35 MPa. The lowest strengths were recorded in samples L4, P2 and P3. L4 and P2 still presented acceptable values while P3 presented a value below the minimum required. One consideration that can be made is that, in general, the modulus of rupture tends to increase as the porosity decreases so the lower the water absorption, the lower the porosity and the higher the flexural strength of the tile. It should be considered that flexural strength, porosity, water absorption, and shrinkage during firing are parameters that could also depend on the number of alkaline-earth oxides as shown in some works in the literature, from which it was found that the extent of these properties depended precisely on the amount of CaO and MgO [28,29]. P3 presented a higher absorption value and consequently its flexural strength decreased. In the other samples, the value obtained is higher than the require minimum. The results obtained are consistent with the percentages of alkali-earth oxides in the various formulations, as shown in Fig. 2.

The optimized mixtures result to be L4 and P4, therefore the thermal characterization was performed on these formulation only. Figs. 3 and 4 describe the TG (red curve) and DTA (blue curve) with thermograms showing peaks, endothermic or exothermic, and weight change of the material under test.

Fig. 4 describes the behavior of the standard as temperature increases. The TG shows a not very high mass loss (4.06%), and the greatest loss occurs between 400 °C and 700 °C. From the DTA it can be

seen that:

- Up to about 150 °C, there is a loss of adsorbed water and crystallization;
- Between 370 °C and 479 °C, dihydroxylation of the clay component occurs;
- At about 570 °C the endothermic peak could be associated with the transformation of kaolinite to metakaolin;
- At 980 °C, on the other hand, an exothermic peak probably related to the crystallization of mullite, or alumina occurs;

around 1200 °C, an endothermic peak occurs due to the melting of the crystal lattice that makes up the material.

Fig. 5 describes the behavior of the sample containing lapillus. TG shows greater mass loss than the standard (6.14%), and the greatest loss occurs up to 600 °C. DTA shows that:

- Up to about 120 °C there is loss of adsorbed water and crystallization;
- Between 390 °C and 507.5 °C dihydroxylation of the clay component occurs;
- At around 571 °C the endothermic peak could be associated with the transformation of kaolinite to metakaolin;
- around 1150 °C an endothermic peak occurs due to the melting of the crystal lattice that makes up the material.

Comparing the lapillus-containing sample with the reference one, it can be stated that: the dihydroxylation of the clay component in the lapillus-based sample begins at higher temperatures; the peak at around 570 °C occurs at about the same temperature; the melting of the crystal lattice in L4 sample occurs at lower temperatures than in the reference.

Fig. 6 shows the thermal behavior of the mix containing pumice. TG shows a higher mass loss (6.78%) than the other two samples, and the highest loss occurs between 200 °C and 500 °C. DTA allows us to say that:

- Up to about 100 °C, there is a loss of adsorbed water and crystallization;
- Between 380 °C and 500 °C, dihydroxylation of the clay component occurs;
- At around 570 °C, the endothermic peak could be associated with the transformation of kaolinite to metakaolin;
- around 1150 °C, an endothermic peak occurs due to the melting of the crystal lattice that makes up the material.

When comparing the pumice-based mixture with the other two, it is possible to say that the sample has intermediate thermal characteristics between them. The dihydroxylation of the clay component in the pumice-containing sample begins at temperatures higher than the reference but lower than in the lapillus-based sample; the endothermic peak at about 570 °C occurs at about the same temperature for all samples while the melting of the crystal lattice in the L4 and P4 samples occurs at about similar temperatures but lower than the reference.

Optical dilatometry was performed on the standard and on L4 and P4 samples, and the results can be seen in Figs. 7–9, respectively. This

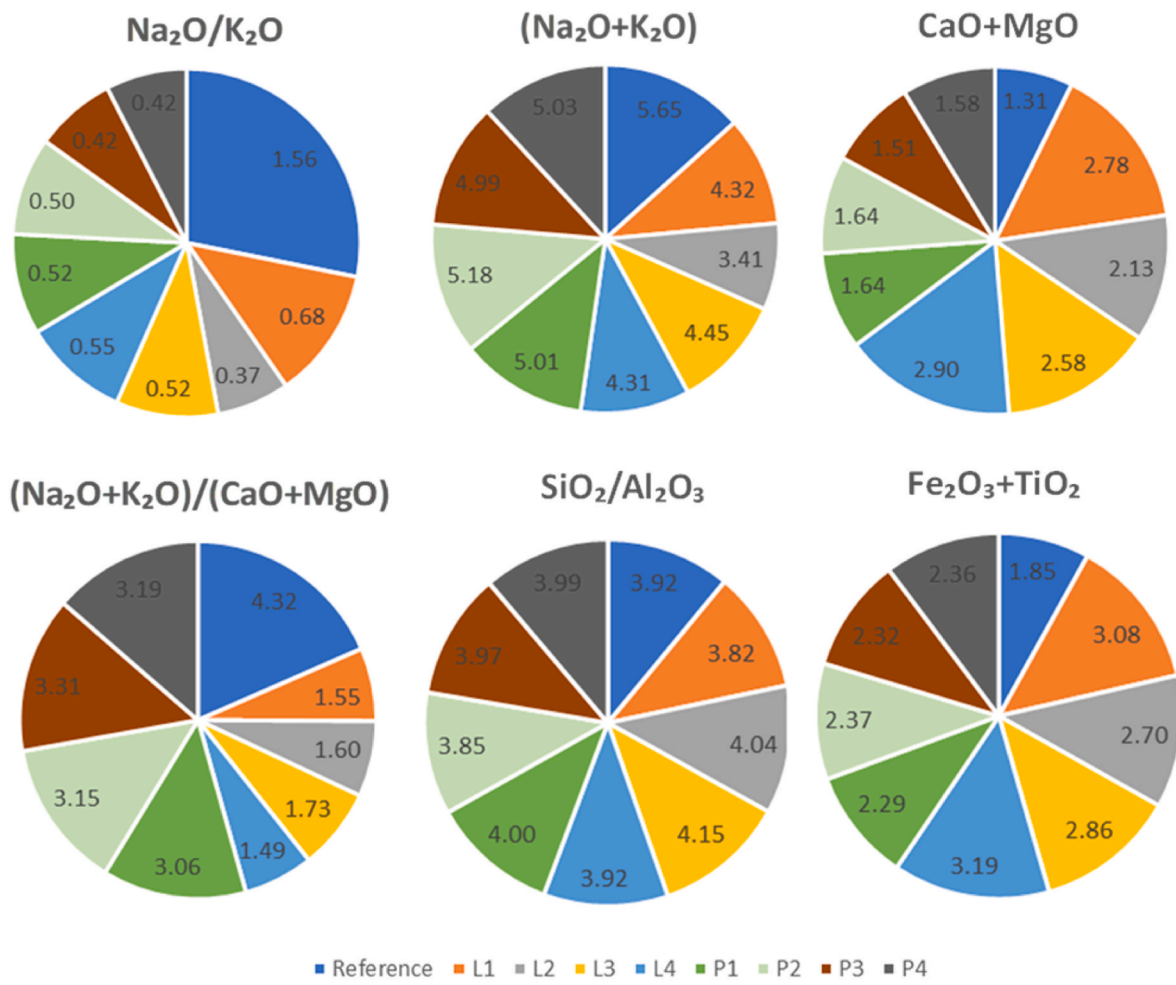


Fig. 2. Different percentages of oxides in the reference and formulations studied.

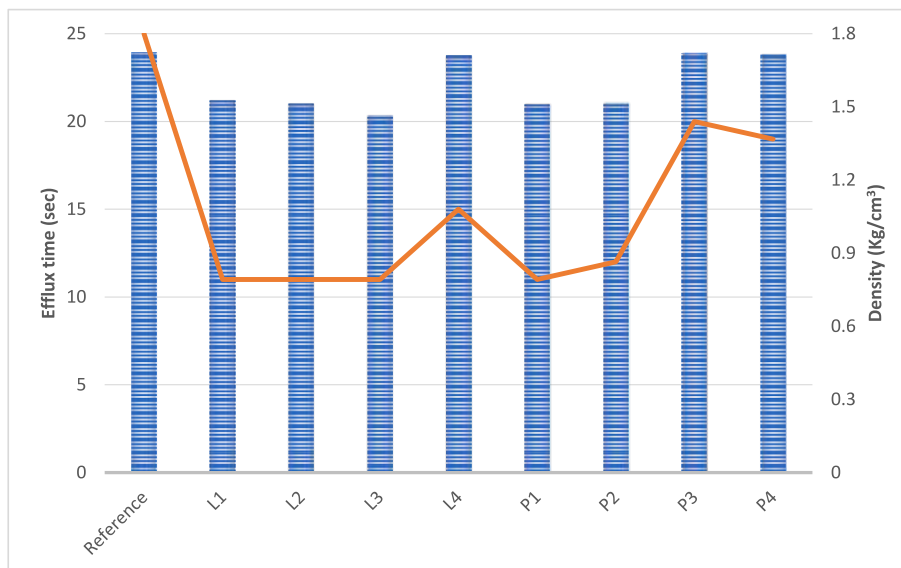


Fig. 3. Effect of efflux time variation as a function of density.

technique allows to estimate the temperatures corresponding to the beginning of sintering and the maximum sintering rate. There are two curves in each Figure: a blue curve that represents the sintering curve

and describes the behavior of the sample (expansion/shrinkage) as temperature increases and a dark pink curve that is derivative of the previous curve and allows the maximum sintering speed to be identified.

Table 4
Residual fraction, oxidizable substances and flexural strength.

	Reference	L1	L2	L3	L4	P1	P2	P3	P4
Residual fraction (g)	3.5–4.5	2.29 ± 0.05	1.94 ± 0.05	0.28 ± 0.05	3.75 ± 0.05	2.22 ± 0.05	1.82 ± 0.05	3.12 ± 0.05	3.72 ± 0.05
Oxidizable substances (mg/L)	<1	0.47 ± 0.05	0.63 ± 0.05	0.63 ± 0.05	0.63 ± 0.05	0.57 ± 0.05	0.60 ± 0.05	0.63 ± 0.05	0.63 ± 0.05
Flexural strength (MPa)	35–50	55.37 ± 0.5	42.52 ± 0.5	40.48 ± 0.5	37 ± 0.5	52.23 ± 0.5	35.54 ± 0.5	32 ± 0.5	45.63 ± 0.5

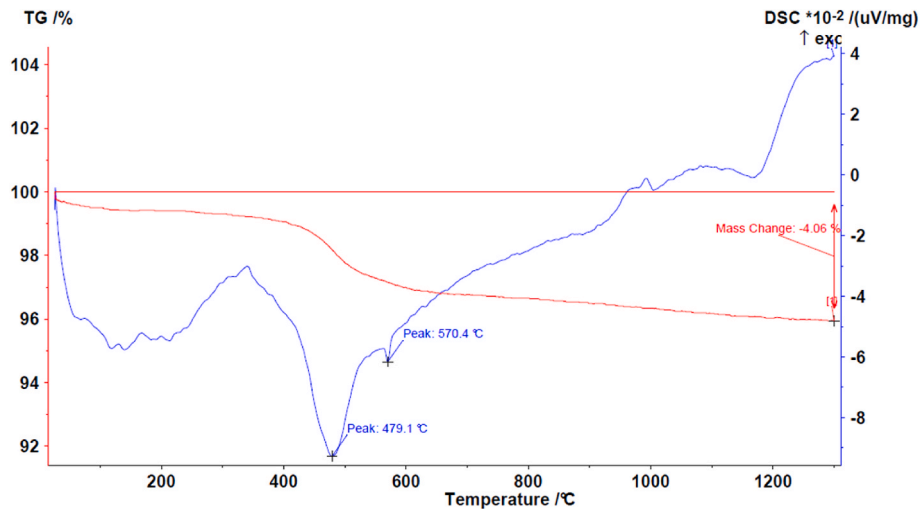


Fig. 4. TG/DSC reference body.

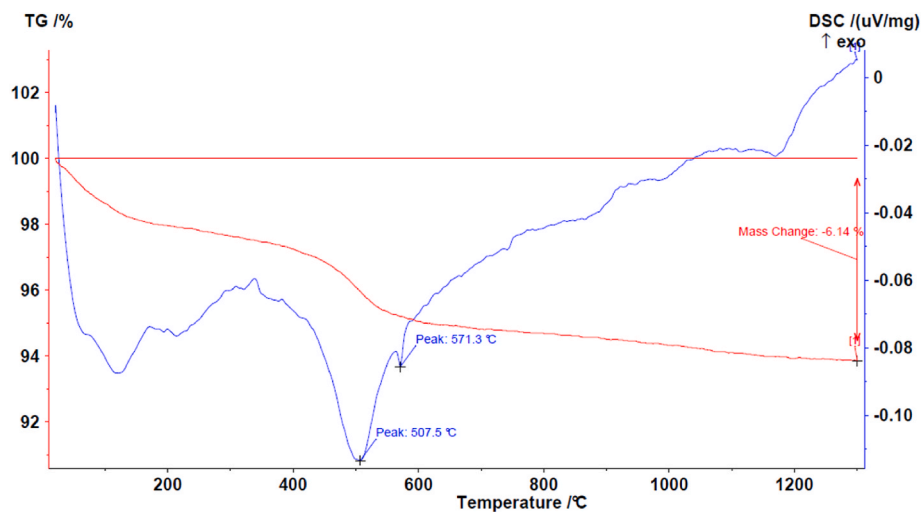


Fig. 5. TG/DSC lapillus-based sample (L4).

Dilatometric analysis of the reference shows that there is an initial phase of loss of body water, structural water and organic matter up to about 500 °C, followed by an expansion phase at which sintering begins, and finally from about 1000 °C there is the vitrification phase with shrinkage of the ceramic piece. The ideal maximum firing temperature of the mixture is 1204 °C which corresponds to a shrinkage of about 3.2%.

Dilatometric analysis of the lapillus-based sample shows that there is again an initial phase of loss of body water, structure water and organic matter up to about 500 °C, followed by an expansion phase at which sintering begins, and finally from about 900 °C there is the sintering with viscous liquid phase where shrinkage of the ceramic pieces occur. The ideal maximum firing temperature of the mixture is 1205 °C which corresponds a shrinkage of about 3.9%.

The pumice-based sample exhibited loss of body water, structure

water and organic matter up to about 500 °C, a subsequent expansion phase (sintering), and from about 900 °C the sintering with viscous liquid phase permits the shrinkage of the ceramic piece. The ideal maximum firing temperature of the body is 1201 °C to which corresponds a shrinkage of about 4.1%.

The greatest shrinkage is evident in the pumice-based mixture. The ideal temperatures at the inflexion points are very similar to each other, but the pumice-containing formulation is slightly lower, probably due to the fact that as the maximum allowable temperature increases, the linear shrinkage of the ceramic piece increases.

3.3. Characterization of fired samples

Linear shrinkage, water absorption and loss of ignition were evaluated on the fired samples, and the values obtained can be seen in Fig. 10.

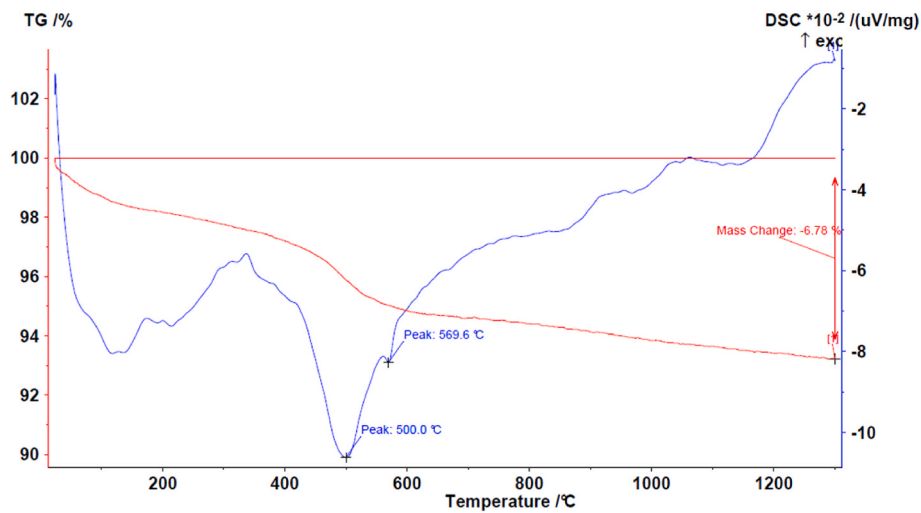


Fig. 6. TG/DSC pumice-based sample (P4).

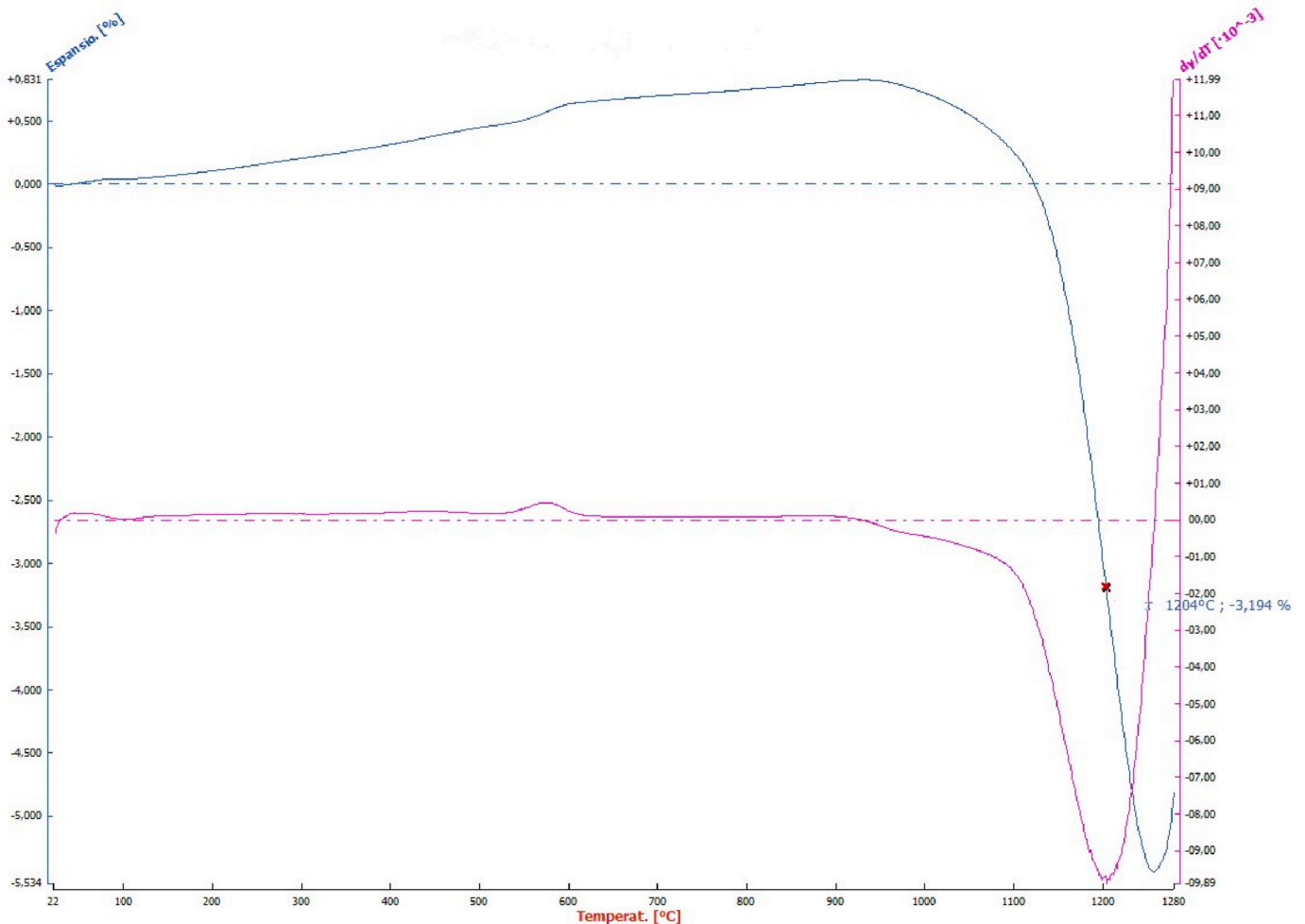


Fig. 7. Dilatometric analysis of reference.

The loss on ignition value obtained for the samples is similar to the standard one except for samples L1 (higher) and L2 (lower). The weight variation of the samples is monitored because it is necessary for the determination of the amount of organic and inorganic matter.

The standard presented a linear shrinkage value ranging from 4.6 to 4.9%. Sample L1 presented a very low shrinkage so it can be inferred

that it sintered less than the others at the same temperature. This could be attributed to the lower presence of Italian feldspar along with the presence of a mix of raw and fired ceramic scraps (chamotte) within the mixture. The other samples lapillus-containing presented values that were within or very close to the range of variation of the reference. As for the samples containing pumice in all cases, linear shrinkage took

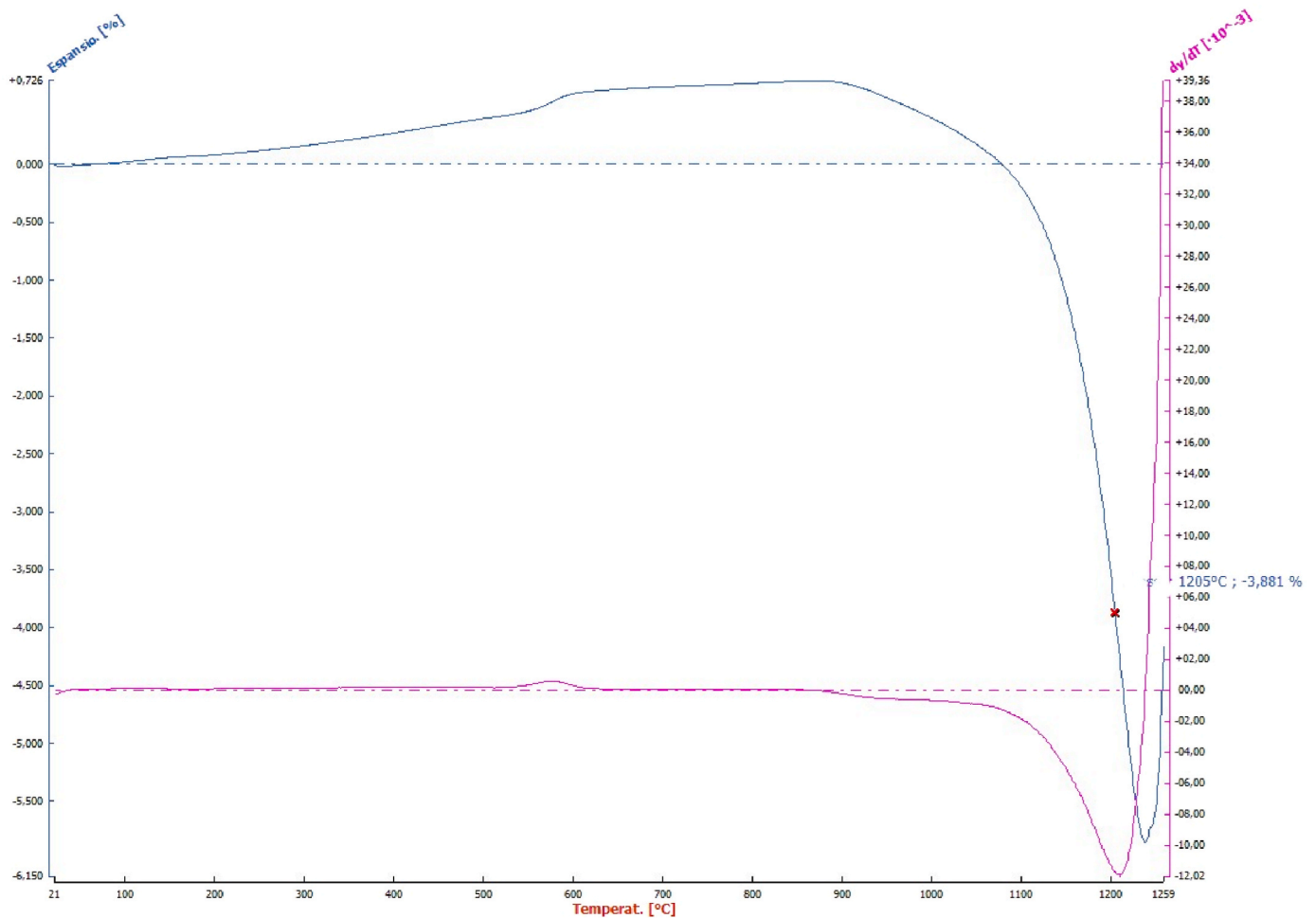


Fig. 8. Dilatometric analysis of lapillus-based sample.

higher values than the reference.

Water absorption is a normative parameter, and thanks to it, it is possible to make a classification of ceramic tiles according to their open porosity. International standards EN 14411 - ISO 13006 classify tiles according to the percentage of water absorption as follows:

- BIa: $WA (\%) \leq 0.5\%$;
- BIb-BIIa: $3\% < WA (\%) \leq 6\%$;
- BIIb: $6\% < WA (\%) \leq 10\%$;
- BIII: $WA (\%) > 10\%$

B indicates that the product was formed by pressing.

The reference is a porcelain stoneware tile that falls into class BIa (water absorption $< 0.5\%$). Based on the reported values, tiles can be obtained from all mixtures that fall in the same class as the standard except for the P3 mixture, which has a higher value. The water absorption was evaluated on unglazed samples so it can be deduced that the value could be further reduced, as the glaze could close the open porosity of the sample. It can be seen that samples L2 and L3 have a variation in the value of absorption, and this could be due to the inclusion of Italian sands in L3 leading to the decrease in the value of this parameter. Most of the samples, although unglazed, showed acceptable water absorption values, and this could be explained by the increased content of alkaline-earth oxides in the studied formulations (Fig. 2), in agreement with literature data [28,29].

Mechanical dilatometry was performed on the reference, L4 and P4 samples but also on the glaze and engobe used in the company to assess the dilatometric agreement of the mixtures studied with the latter. The

data obtained are shown in Table 5.

When glaze and mixtures containing clay are heated, they expand. As they cool, they shrink. The best situation is when the support shrinks a little more than the glaze; this keeps the glaze in slight compression. If the glaze shrinks more than the support, there is cracking creating small fracture lines (“cavillo” defect). If the glaze shrinks less than the support it is subjected to compression, which being too high causes it to peel off, especially at the edges, or the glaze clumps leaving surfaces of the support exposed [30].

The coefficients obtained show that there is a dilatometric agreement between glaze, engobe and samples L4 and P4.

Sample P4 shows values very close to those of the reference, while sample L4 shows values of the coefficient lower than the standard. Thus, it can be assumed that the studied compositions could be substituted for the reference without making ad hoc glazes or engobes for the new substrates in question.

Colorimetry was performed with the CIE $L^*a^*b^*$ system, most widely used in the ceramic industry. This method allows the color of tiles to be determined by measuring the three parameters L^* (brightness) from absolute white $L = 100$ to absolute black $L = 0$, a^* (red-green), b^* (yellow-blue) processed from the visible spectra. Table 6 shows the results obtained.

A decrease in L^* , a^* , b^* parameters was seen with the presence of pumice and lapillus in the composition. Comparison between the reference and the pumice-based sample showed that the latter was greener and darker. On the other hand, comparison between the reference sample and the lapillus-based sample shows that the presence of lapillus makes the color darker and closer to the blue zone.

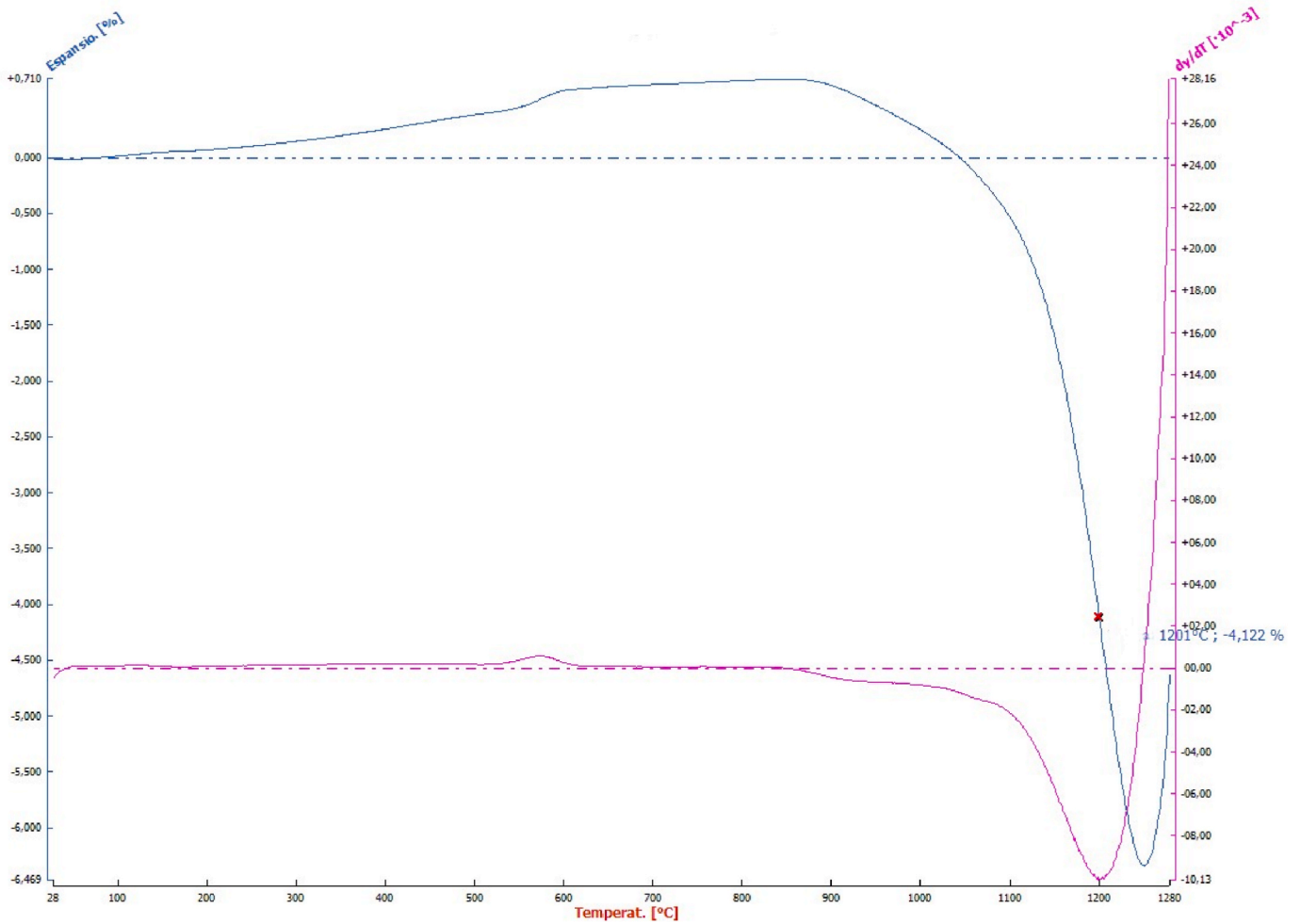


Fig. 9. Dilatometric analysis of pumice-based sample.

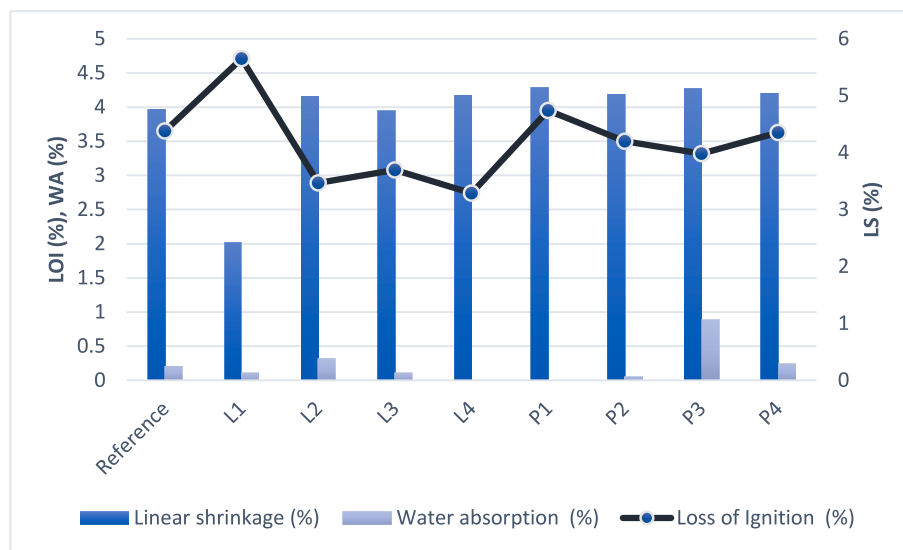


Fig. 10. Linear shrinkage (LS), water absorption (WA) and loss on ignition (LOI).

4. Conclusions

Ceramic bodies have been formulated by replacing foreign feldspars with about 40–50% waste and refuse, of which 10–16% is volcanic raw

material scraps. Pumice and lapillus have been successfully incorporated and used not only as fluxes but also as natural colorants. The mixtures studied have shown good mechanical properties, low absorption, acceptable linear shrinkage and good dilatometric concordance with

Table 5

CIELab values obtained for the best samples compared to the reference.

	L*	a*	b*	ΔE^*
Reference	59.69	4.48	10.91	0
L4	48.73	1.34	5.42	12.66
P4	52.98	2.36	10.29	7.06

Table 6Linear thermal expansion coefficient (α).

α	α (100–400 °C)	α (200–400 °C)	α (200–500 °C)	α (100–500 °C)
Reference	8.52E-06	8.79E-06	9.09E-06	8.81E-06
Glaze	7.48E-06	7.64E-06	7.64E-06	7.52E-06
Engobe	8.03E-06	8.30E-06	8.64E-06	8.36E-06
L4	8.24E-06	8.52E-06	8.88E-06	8.58E-06
P4	8.49E-06	8.75E-06	9.09E-06	8.81E-06

glazes and engobes currently in use, without changing the current industrial production cycle. Comparing the obtained mixtures with the reference, the number of raw materials has been decreased from 18 to a maximum of 10, at least 4 of which are recycled; the environmental impacts related to the extraction of raw materials and transportation of materials from foreign countries are decreased with a corresponding easier logistic; the volumes of water required for the production of slip in the case of the lapillus-based mixture are reduced; and the use of artificial dyes is significantly lowered. A product thus obtained, therefore, is a good example of circular economy and sustainability.

Considering the promising results achieved in this research and to encourage industrial transferability, an environmental impact assessment is underway through the LCA procedure.

Declaration of competing interest

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

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References

- Luca Baraldi, World Production and Consumption of Ceramic Tiles”, vol. 148, Ceramic World Review, 2022, pp. 36–50. <https://www.ceramicworldweb.com/en/economics-and-markets/world-production-and-consumption-ceramic-tiles-2021>. accessed 02/07/2023.
- Paola Giacomini, The Italian ceramic tile industry weathers the storm in 2022, Ceram. World Rev. 150 (2023) 40–46. <https://ceramicworldweb.com/en/news/italian-ceramic-tile-industry-weathers-storm-2022#:~:text=The%20increase%20in%20selling%20prices,sqm%20to%2016.7%20%E2%82%AC%2Fsqm>. accessed 02/07/2023.
- <https://www.ceramicworldweb.com/it/economia-e-mercati/il-made-italy-frendo-un-2022-da-record> accessed 01/07/2023.
- <https://asvis.it/l-agenda-2030-dell-onu-per-lo-sviluppo-sostenibile/> accessed 30/06/2023.
- <https://www.ceramica.info/articoli/ceramica-italiana-scelta-sostenibile-video-br-ochure/> accessed 30/06/2023.
- S. Conte, C. Zanelli, C. Molinari, G. Guarini, M. Dondi, Glassy wastes as feldspar substitutes in porcelain stoneware tiles: thermal behaviour and effect on sintering process, Mater. Chem. Phys. 256 (2020), 123613, <https://doi.org/10.1016/j.matchemphys.2020.123613>.
- M. Lassinanti Gualtieri, C. Mugoni, S. Guandalini, A. Cattini, D. Mazzini, C. Alboni, C. Siligardi, Glass recycling in the production of low-temperature stoneware tiles, J. Clean. Prod. 197 (2018) 1531–1539, <https://doi.org/10.1016/j.jclepro.2018.06.264>. Part 1.
- A. Tucci, L. Esposito, E. Rastelli, C. Palmonari, E. Rambaldi, Use of soda-lime scrap-glass as a fluxing agent in a porcelain stoneware tile mix, J. Eur. Ceram. Soc. 24 (1) (2004) 83–92, [https://doi.org/10.1016/S0955-2219\(03\)00121-3](https://doi.org/10.1016/S0955-2219(03)00121-3).
- S.S. Owwoye, T.S. Toludare, O.E. Isinkaye, U. Kingsley, Influence of waste glasses on the physico-mechanical behavior of porcelain ceramics, Bol. Soc. Esp. Ceram. V. 58 (2) (2019) 77–84, <https://doi.org/10.1016/j.bsecv.2018.07.002>.
- F. Andreola, L. Barbieri, E. Karamanova, I. Lancellotti, M. Pelino, Recycling of CRT panel glass as fluxing agent in the porcelain stoneware tile production, Ceram. Int. 34 (5) (2008) 1289–1295, <https://doi.org/10.1016/j.ceramint.2007.03.013>.
- F. Andreola, L. Barbieri, I. Lancellotti, C. Leonelli, T. Manfredini, Recycling of industrial wastes in ceramic manufacturing: state of art and glass case studies, Ceram. Int. 42 (12) (2016) 13333–13338, <https://doi.org/10.1016/j.ceramint.2016.05.205>.
- R. Gennaro, P. Cappelletti, G. Cerri, M. Gennaro, M. Dondi, G. Guarini, A. Langella, D. Naimo, Influence of zeolites on the sintering and technological properties of porcelain stoneware tiles, J. Euro.Ceram.Soc. 23 (13) (2003) 2237–2245, [https://doi.org/10.1016/S0955-2219\(03\)00086-4](https://doi.org/10.1016/S0955-2219(03)00086-4).
- E. Karamanova, G. Avdeev, A. Karamanov, Ceramics from blast furnace slag, kaolin and quartz, J. Eur. Ceram. Soc. 31 (6) (2011) 989–998, <https://doi.org/10.1016/j.jeurceramsoc.2011.01.006>.
- L.M. Schabbach, F. Andreola, L. Barbieri, I. Lancellotti, E. Karamanova, B. Ranguelov, A. Karamanov, Post-treated incinerator bottom ash as alternative raw material for ceramic manufacturing, J. Eur. Ceram. Soc. 32 (11) (2012) 2843–2852, <https://doi.org/10.1016/j.jeurceramsoc.2012.01.020>.
- A. Karamanov, E. Karamanova, L. Maccarini Schabbach, F. Andreola, R. Taurino, L. Barbieri, Sintering and phase formation of ceramics based on pre-treated municipal incinerator bottom ash, Open Ceram 5 (2021), 100044, <https://doi.org/10.1016/j.oceram.2020.100044>.
- Q. Yuan, D. Robert, A. Mohajerani, P. Tran, B. Kumar Pramanik, Utilisation of waste to-energy fly ash in ceramic tiles, Construct. Build. Mater. 347 (2022), 128475, <https://doi.org/10.1016/j.conbuildmat.2022.128475>.
- C. Sgarlata, M.C. Ariza-Tarazona, E. Paradisi, C. Siligardi, I. Lancellotti, Use of foundry sands in the production of ceramic and geopolymers for sustainable construction materials, Appl. Sci. 13 (8) (2023) 5166, <https://doi.org/10.3390/app13085166>.
- T. Bahtli, Y. Erdem, The use of foundry waste sand from investment casting in the production of porcelain tiles, Ceram. Int. 48 (19) (2022) 27967–27972, <https://doi.org/10.1016/j.ceramint.2022.06.100>. Part A.
- I.S. Vilarinho, E. Filippi, M.P. Seabra, Development of eco-ceramic wall tiles with bio-CaCO₃ from eggshells waste, Open Ceram. 9 (2022), 100220, <https://doi.org/10.1016/j.oceram.2022.100220>.
- M.M. Owen, E.O. Achukwu, A.Z. Romli, A.H. Bin Abdullah, M.H. Ramlee, S. Bin Shuib, Thermal and mechanical characterization of composite materials from industrial plastic wastes and recycled nylon fibers for floor paving tiles application, Waste Manag. 166 (2023) 25–34, <https://doi.org/10.1016/j.wasman.2023.04.038>.
- H.B. Poyraz, N. Erginel, N. Ay, The use of pumice (pumicite) in transparent roof tile glaze composition, J. Euro.Ceram.Soc. 26 (4–5) (2006) 741–746, <https://doi.org/10.1016/j.jeurceramsoc.2005.06.032>.
- Z. Bayer Ozturk, E. Eren Gültekin, Determination of tile effect of the addition of pumice on the technological properties of wall tile using the factorial design method, Adv. ceram. Sci. Eng. 3 (2014) 1–10, <https://doi.org/10.14355/acse.2014.0301.01>.
- Z. Bayer Ozturk, A. Can, The use of micronized pumice in the production of ceramic sanitaryware glazes with sustainable industrial characteristics, J. Facult. Eng. Architect. Gazi Univ. 38 (3) (2023) 1967–1977.
- L. Barbieri, F. Altimari, F. Andreola, B. Maggi, I. Lancellotti, Characterization of volcano-sedimentary rocks and related scraps for design of sustainable materials, Materials 16 (9) (2023) 3408, <https://doi.org/10.3390/ma16093408>.
- <https://www.zschimmer-schwarz-ceramco.it/zs-lab/lo-sapevi-che/16-cuore-nero-origine-del-problema-e-soluzioni-possibili> accessed 03/07/2023.
- <https://envitech.co.uk/wp-content/uploads/downloads/documents/articles/o-m18-%20Water%20monitoring%20in%20drinking%20water%20plants.pdf> accessed 03/07/2023.
- <https://www.ingegno-web.it/articoli/le-caratteristiche-tecniche-piu-importanti-de-ile-piastrelle-di-ceramica-per-ambienti-pubblici/> accessed 03/07/2023.
- Z. Bayer Ozturk, N. Ay, An investigation of the effect of alkaline oxides on porcelain tiles using factorial design, J. Ceram. Process. Res. 13 (2012) 634–640.
- Z. Bayer Ozturk, N. Ay, Investigation of porosity of ceramic tiles by means of image analysis method, J. Ceram. Proc. Res. 15 (6) (2014) 393–397.
- <https://lameridiana.fi.it/wp-content/uploads/2019/04/LA-MERIDIANA-Note-tecniche-4.pdf> accessed 03/07/2023.