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Sustainable glazes for ceramic tiles: Exploiting inertized man-made vitreous fibres waste as a resource

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ABSTRACT

Traditional ceramic tiles, and especially porcelain stoneware, are still one of the top building materials in the world. In view to fulfil the current need to produce ceramic tiles in a less impactful way for the environment along with the increasing difficulty in providing natural raw materials, the attention of the ceramic sector has been focusing on optimizing resources.

The solution can be found in a circular economy model, in which the virgin raw materials exploitation is minimized through the recycling of materials that otherwise would be disposed as waste in landfills. The ceramic industries are able to internally reuse most of their residues created during the production steps, in fact, most of the discarded materials are reinserted into the ceramic production cycle. The next step for the sector must be to adopt a circular economy model that use "extramuros waste" corresponding to waste derived from other production chains. We have developed a ceramic glaze by utilizing the thermal inertization product of Man-Made Vitreous Fibers (MMVF) as a secondary raw material. This waste material, characterized by being completely amorphous, serves as an ideal melting component in ceramic products. We have experimented with various formulations of ceramic glazes, incorporating between 40 % and 50 wt% of this glassy material. The most promising formulation involves 44 wt% of waste, resulting in a shiny, dark ceramic glaze. This outcome underscores the suitability of this waste material as a valuable secondary raw material for the manufacture of traditional ceramic glazes.

1. Introduction

In recent years, in response to the crisis of the traditional economic linear model (often termed "take-make-waste"), driven by the need of economic actors and to address growing resource scarcity, the concept of the so-called "Circular Economy" has begun to emerge. The outdated linear economy model, previously adopted and still prevalent in many production sectors today, is no longer sustainable, nor compatible with the current ecological vision. Under the linear model products, once reaching their "end of life", are treated as non-recyclable waste, either dismissed in landfills or incinerated [1].

Continued application of this economic model, heavily dependent on extracting finite natural resources is not sustainable on the long term.

In recent years, there has been a shift towards a "waste-to-value" system, where waste is exploited as secondary raw material within various production processes, thereby increasing the value of waste.

However, implementing a circular economy faces significant barriers today. There is partial awareness and knowledge of opportunities for resource saving, reuse, recovery, and recycling, coupled with challenges in identifying partners to support companies in completing reuse cycles [2]. In 2022, the total waste generated in the EU by all economic activities and households amounted to 2.233 million tonnes, of which approximately 38 % derive from construction and demolition (CDW), 23 % from mining and quarrying while 10 % from manufacture [3]. From this data is clear how crucial it would be to minimize waste and capitalize on process and product-generated waste, creating additional value through increasingly efficient recovery techniques and technologies.

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Waste recycling within the ceramic tiles industry can be traced back to the 1970s (see for example [4–7]). On the industrial front, prior to the current momentum towards a circular economy, waste recycling was primarily motivated by marketing considerations, supported by green certifications [8,9] such as LEED credits (Leadership in Energy and Environmental Design; World Green Building Council 2020. https://www.worldgbc.org/), and the forthcoming standard on ceramic tile sustainability (ISO/DIS 17889, 2019).

Most notably, the circular model is now significantly influenced by another critical factor: the depletion of raw materials and the unstable geopolitical landscape. For example, the raw materials essential for porcelain stoneware bodies, like Ukrainian ball clays or Turkish feldspar, are no longer available in sufficient quantities to meet the ceramic sector's high demand, or they originate from politically unstable regions [10,11].

Consequently, the exploration of "extramural" waste—waste from external production chains that can be integrated into manufacturing processes—has become increasingly pivotal. Incorporating such waste would offer numerous advantages, including diversifying material supply sources, maximizing the value of consumer products, reducing the extraction and transportation of thousands of tons of materials, and ultimately decreasing overall waste generation.

Recently the effect of waste recycling on technological behaviour and technical performance of ceramic tiles, has been reviewed by Zanelli and co-workers [12]. The authors considered all the data available for a large plethora of wastes tested as secondary raw materials in ceramic production at the different Technology Readiness Level (TRL), the main outcome is an outlook about feasibility and recommended recyclable amount. The authors observed that, among the wasted tested, those able to reach higher TRL are those with composition and technological behaviour close to those of ceramic raw materials, such as quarry dumps, glass cullet from sorting of municipal and fired and unfired ceramic residues. Moreover, there are some wastes that can be suitable for recycling but cannot entered into production due to difficulties in batch design due to the composition (e.g., high Ba and Sr of screen glass), release of hazardous substances during firing. or need of preventive treatments [12].

A recent paper published by Marin -Cortes and co-workers ([13] introduced a novel and effective methodology for the valorisation of Construction and Demolition Waste (CDW) – the most represented waste - as secondary raw materials in ceramics production. The valorisation of inorganic CDW was successfully approached through a homogenization process and the identification of constituent materials exploiting Infrared and Raman spectroscopy.

Recently our group recently explored the possibility of exploiting the product of inertization of man-made fibres (mineral wool) in the production of porcelain stoneware tiles [14].

Mineral wool can be regarded as a CDW, in fact, is used in a wide range of consumer such as home furniture, thermal and acoustic insulation for buildings. After the ban of asbestos this material became one of the most represented substitutes, in construction sector and even in the reinforcement for composite materials. The annual volume of mineral wool waste produced is estimated to reach more than 2.5 million tons and could increase by as much as 10 % by the end of 2030 [15,16]. This perspective will even increase quantity of fibrous waste, that will become a major problem for the environment [17,18].

Mineral wool may contain a notable proportion of tiny respirable fibres (with a diameter <3 μm, length >5 μm, and an aspect ratio (length/width) > 3 [19]), and these fibres can persist in the lungs if the material is high in silica and low in alkalis. Because of these characteristics, mineral wool has been flagged as a potential health risk to humans. Presently, mineral wool containing more than 18 wt% of alkaline oxides and alkali earth oxides falls under the classification of "suspected human carcinogens" according to the standards for carcinogenicity outlined in Regulation (EC) No 1272/2008 of the European Parliament and Council [20] and for this reason is classified as hazardous waste and need to be disposed in dedicated landfills. For the abovementioned reasons the material should be removed and handled following specific guidelines in order to preserve the surrounding environment and the health of the workers. The material, once removed, is safely closed in big bags certified for the transport of hazardous material, then is stored in dedicated warehouses waiting for final disposal in landfills.

The thermal inertization of this waste represent a viable alternative to landfilling. Patented in 2021 [21], this procedure foresees a melting process able to destroys the fibrous shape of the wool and produces an inert non-hazardous massive glass that no longer needs to be landfilled, but can be reused as secondary raw material. In Ref. [14] it has been demonstrated that the thermally treated materials result (the so called "Re.Wo") is basically an amorphous frit that can be successfully employed as a substitute of feldspar in the production of ceramic tiles. The results of the laboratory-scale simulation of the industrial process reported in Ref. [14], demonstrated that the addition of Re.Wo in substitution to feldspars, did not induce variation in the tile-making process: the technological properties were not altered and in some cases, such as for the mechanical strength, an improvement was observed. As regards the firing behaviour, the introduction Re.Wo. allowed to lower the gresification temperature: of 20–40 °C on the basis of the amount added. Despite the decrease of the firing maximum temperature, the specimens containing the waste maintain excellent densification levels, with bulk density around 2.35 g/cm^3. However, it has been noted a tendency of the batches containing the waste to show a low stability at high temperatures, thus carefully calibrate the oven temperature resulted to be of paramount importance, in order to avoid phenomena related to the over-firing, such as bloating due to the closed pores expansion. The sole issue evidenced in the paper is that, due to a slightly elevated iron content in Re.Wo, the final colour of the tile bodies turned darker.

Even if the outcome is the production of more than 2.5M t of exhaust mineral wool waste every year [14], at the moment, the capacity of the current operating plant for the inertization of mineral wool is about 5 t/y. The commissioning of a new plant to scale the production is now underway and the plans are to reach the inertization of 6/7 Kt per year.

It is evident that currently, the available feedstock is insufficient to entirely replace the necessary amount of feldspar required for producing stoneware bodies, except perhaps in a very small proportion. Therefore, we have chosen to explore in this paper the potential use of the aforementioned inertized frits for manufacturing ceramic glazes, which require less material. In fact, considering a glaze density of 1450–1500 g/L, 350 g of the glaze per m^2 are usually used for the glazing phase. In the case of products to be smoothed, the glaze amount can reach up to 680 g per m^2 [22]. Taking an average, approximately 515 g of glaze are used to produce 1 m^2 of glazed tile vs 40 kg of raw materials employed for the bodies.

The material being investigated possesses all the necessary characteristics to be used as a substitute for conventional frits in glaze production.

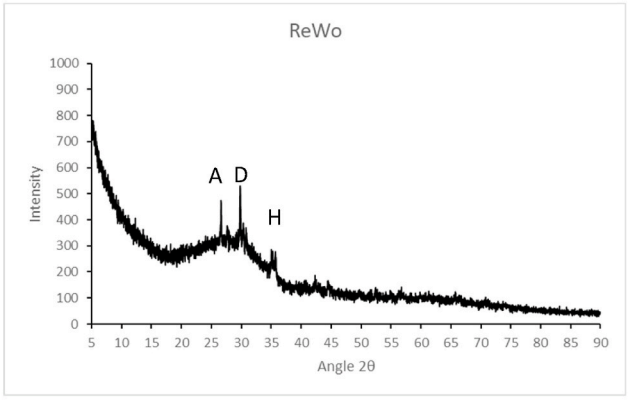
In this paper we present an optimization study aimed at the realization of glazes produced exploiting the product of inertization of mineral wool. What we want to obtain is a glaze realized with recycled material, but responding to technical, aesthetic and durability parameters required for the production of high-quality porcelain stoneware glazed tiles.

2. Experimental

2.1. Materials

For the realization of the glaze the Re.Wo employed in Ref. [14] was used. It consists in a massive and mostly glassy frit resembling obsidian (Fig. 1a). The X-Ray Powder Diffraction (XRPD) pattern indicate the presence of traces of pyroxene phases augite ((Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)$_2$O$_6$) and diopside ($CaMgSi_2O_6$) (Fig. 1b). After the inertization

(a)



(b)

Fig. 1. a Representative image of Re.Wo: the frit deriving from the inertization of mineral wool exploiting the process patented in Ref. [21]. **b** Results of XRPD analysis performed on the Re.Wo. Markers are A: Augite; D: Diopside; H: Hematite.

process, the fibrous morphology of the mineral wool is completely lost.

The chemistry of the material, taken from Ref. [14] is reported in Table 1. The data of leaching tests carried out according the procedure UNI 12457-2 [23] are not reported, but are available in the cited paper.

Different formulations were realized according to Table 2 [24,25]. In preliminary formulations Re.Wo was mixed with ventilated boric-glass (a "Pre-consumer" 100 % recycled material as defined on section 7.8.1.1 c, UNI EN ISO 14021) and K-feldspar (fluxing component). Kaolin was added with the aim to keep the solid particles in suspension within the solution and to avoid their settling after the grinding phase. The presence of kaolin allows a more homogeneous application of the glaze. Rutile (TiO_2) and cassiterite (SnO_2) were also added as 99 % pure phases. These latter materials were added with the aim to adjust the chromaticity of the glaze and to determine its final colour at the end of the firing phase.

In formulations nr. 5 to nr. 8, hematite (Fe_2O_3) was added with the aim to make the colour of the glaze darker in an attempt to obtain an iridescent metallic effect. For formulation nr. 7 and nr. 8 the albite ($NaAlSi_3O_8$) was added to replace the K-feldspar with the aim to increase the fusibility property of the glazes. In fact, it is well known from literature [26] that albite has a melting temperature lower than K-feldspar.

Table 1
Chemical composition of Re.Wo frits (after the inertization of mineral wool) taken from Ref. [14].

Oxides	Re.Wo. (wt%)	Elements	Re.Wo. (ppm)
Na_2O	3.55(2.4)	Ni	274(210)
MgO	10.2(2.3)	Co	37(119)
Al_2O_3	12.9(3.6)	Cr	969(855)
SiO_2	45.2(6.2)	V	160(30)
P_2O_5	0.17(0.1)	Ce	79(17)
K_2O	0.73(0.1)	Nd	29(9)
CaO	16.1(3.0)	Ba	333(100)
TiO_2	1.24(0.3)	La	32(6)
MnO	0.23(0.1)	Zr	777(319)
Fe_2O_3	9.67(2.1)	Y	26(7)
LOI	nd	Sr	431(119)
		Rb	11(4)
		Pb	26(22)
		As	Bdl
		Zn	807(496)
		Cu	68(31)
		Cd	5
		S	146(80)
		Cl	92(36)

Standard deviations are reported in brackets; n.d. not detected; LOI: loss on ignition.

2.2. Preparation of the ceramic glaze

The glazes were realized reproducing an industrial process at a laboratory scale. The Re.Wo was first milled for 60 s using a FRITSCH vibrating cup mill PULVERISETTE equipped with and agate grinding set. Then all the raw materials were dosed (on the basis of the recipe reported in Table 2) to obtain 100 g of dry mix. Subsequently, the obtained batches were ball milled in a porcelain jar using 120 g of dense alumina grinding balls with diameters between 5 and 18 mm and 50 wt% of water (by weight of the dry mix), for 30 min. To evaluate the sample aesthetic and technological properties of the glaze realized in the first steps of the formulations design, bulk test specimens were realized by pouring the glazes into a rectangular mould with dimensions of 6 × 1.5 cm. The glazes were then oven dried at a temperature of 105 °C for 24 h. Subsequently, the dried samples were placed on a bed of powdered alumina, realized over a refractory support, and then they were fired using a CVK-S Nannetti oven. The firing process followed the standard industrial cycle for producing porcelain stoneware. However, the maximum temperature and firing time were adjusted based on the composition, using a trial-and-error method for each subsequent formulation. The maximum temperature of firing and the firing time are reported in Table 3.

2.3. Glazing tests

For the glazing tests, two kinds of ceramic support were used: i) bodies of industrial production of "standard" porcelain stoneware tiles measuring 15 × 15 cm and supplied by a ceramic company and ii) test ceramic tiles measuring 5 × 10 cm realized with the method reported in Ref. [14] containing 3 wt% of Re.Wo as fluxing component in substitution to feldspar (sample V3 in paper [14]). These latter were used to test tiles containing Re.Wo in both the body and the glaze. The percentage of 3 wt % was chosen since the dilatometric parameters of the samples (expansion coefficient) realized with this percentage resulted in those with the highest agreement to the glazes (see following section 3.4). The glaze application was carried out in two ways, depending on the support size.

For the larger tiles, a "laboratory glazer" (doctor blade a laboratory-scale method that reproduces the waterfall application technique), suitable for applying a uniform layer of glaze of the desired thickness has been used (Fig. S1a -supplementary material). This manual instrument allows to apply different thickness of glaze, normally 0.4, 0.6 or 1.0 mm. For the smaller tiles, the glaze has been applied by direct immersion of the support (Fig. S1b). Once glazed, the samples were oven dried at a temperature of 105 °C for 24 h and then fired.

2.4. Analytical methods

Chemical characterisation of the glazes was carried out by wavelength-dispersive X-ray fluorescence spectrometry (WDXRF).

Table 2
Formulation of the glazes tested in this study.

	Re.Wo (wt %)	Boric glass (wt %)	K-feldspar (wt %)	Albite (wt %)	Kaolin (wt %)	Rutile (wt %)	Cassiterite (wt %)	Hematite (wt %)
F1	50	25	15	–	5	3	2	–
F2	50	18	22	–	5	3	2	–
F3	50	15	28	–	3	3	1	–
F4	45	15	28	–	3	3	1	5
F5	44	15	28	–	3	–	–	10
F6	39	15	28	–	3	–	–	15
F7	44	15	–	28	3	–	–	10
F8	44	10	–	33	3	–	–	10

Table 3
Maximum temperature and time used for the firing of the glazes.

Temperature - time	1225 °C - 48 min	1200 °C - 62 min	1200 °C - 68 min
F1	X		
F2		X	
F3			X
F4			X
F5			X
F6			X
F7			X
F8			X

Measurements were performed using a PANalytical Zetium spectrometer equipped with a Rh tube anode and 4 kV X-ray generator and a WDS Zetium detector. Both major and minor elements were evaluated. Aluminium supported pads were realized mixing 2.7 g of grinded material and 0.27 g of wax on a boric acid bed. The powders were then compressed under 15 N to obtain a compact tablet.

Qualitative and quantitative l phases analyses of the glazes were performed using a θ–θ Bragg-Brentano X'Pert PRO diffractometer equipped with a real time multiple strip (RTMS) detector exploiting a with CuKα (Ni filtered) radiation produced at 40 kV, 40 mA. Samples were milled using an agate mortar and the powder was mixed with 10 wt % of corundum (Al_2O_3) as an internal standard. To avoid preferred orientation side loading of the sample powder was chosen. Data were collected in the 3–90 °2θ range using step scan of 0.0167 °2θ and a counting rate of 12 s/step. A 10 mm beam mask and 0.04° Soller slits were used. A ½° divergence slits and anti-scatter slit were used. Quantitative phase analyses (QPA) of all the considered glazes compositions were obtained after Rietveld – RIR refinement [27,28] performed using GSAS software [29] with EXPGUI interface.

The microstructure of the samples was examined by scanning electron microscopy (SEM) using a JSM-6010PLUS/LA SEM microscope equipped with an Energy Dispersive X-ray (EDX) spectrometer (Oxford INCA-350). The samples were fixed on Al stubs and coated with a thin film of carbon (ca. 10 nm thick) using a Carbon Coater-Balzers CED-010.

The mechanical dilatometric analyses on the produced glazes and the supports to which they are intended to be applied were performed using a Dil 402 EP NETZSCH dilatometer, in order to check the consistency of their thermal expansion. Lapped rods with dimensions 4.5 x 0.5 × 0.5 cm were obtained from fired glazes and support. Thermal-dilatometric analysis was performed heating the rods with a gradient of 5 °C/min, from 25 °C to 700 °C. The Expansion coefficient was calculated in the range where the curve is linear (200–400 °C).

Colorimetric parameters L*, a* and b* of the glazes were determined using a spectrophotometer mod. ER CM-2600d, Konika Minolta. The colorimetric parameters L*, a* and b* were determined at 3 points for each glazed support. Six measurements were taken for each sample, except for samples F5 and F8 where there were 20 measurements (as more measurable area was available). L*, a* and b* values are the average of the values measured for each glaze formulation.

Gloss measurements on the glazed samples were performed by a digital multi-angle gloss meter (mod.SA0883, Sassuolo Lab). The angle of measurement refers to the angle between the incident and reflected light. These instruments allow the measurement of the gloss at three angles: 20, 60 and 85° and permit a measurement range of 0–199 GU (gloss unit).

Gloss is determined by a gloss meter projecting a beam of light at a fixed intensity and angle onto a surface and measuring the amount of reflected light at an equal but opposite angle. The intensity of the beam is then measured with a photodetector. Regarding gloss measures to define degrees of brilliance (G.U), a black glass standard with a given refractive index is employed and assigned a value of 100 G U, which is then used as the upper calibration point, while a perfectly opaque body is used as the 0 G U value. This type of scale is usually employed for all non-metallic materials, as their degrees of brilliance typically fall within this measurement range.

2.5. Chemical resistance and leaching tests

The chemical resistance test was carried out according to the UNI EN ISO 10545–13:2016 standard. This test was performed on glazed supports with dimensions of 5 × 10 cm. Before the test, each sample was oven dried at a temperature of 105 °C for at least 2 h and subsequently cooled to room temperature. The chemical resistance test was performed as follows [1]: the glazes were put in contact with aqueous solutions, simulating household chemicals (ammonium chloride), swimming pool salts (sodium hypochlorite) and low and high concentration acids and alkalis, for a determined period of time [2]; the samples were washed under running water for 10 min [3]; the samples were oven dried at a temperature of 105 °C and subsequently cooled to room temperature [4]; the effects of the chemical attacks were visually determined by examining the tested surface from a standard distance of 25 cm and under an artificial lighting with the aim to verify differences compared to an untreated surface. The following solutions were used for the chemical resistance test.

- NH_4Cl (ammonium chloride) 100 g/L;
- NaClO (sodium hypochlorite) 20 mg/L;
- HCl (hydrochloric acid) 3 % and KOH (potassium hydroxide) 30 g/L (low concentration);
- HCl (hydrochloric acid) 18 % and KOH (potassium hydroxide) 100 g/L (high concentration);

The chemical resistance to ammonium chloride and sodium hypochlorite was determined by keeping the solutions and the samples in contact for 24 h. The chemical resistance to hydrochloric acid and potassium hydroxide at low concentration was determined by keeping the solutions and the samples in contact for 96 h and replacing the first solutions after 48 h. The chemical resistance to hydrochloric acid and potassium hydroxide at high concentration was determined by keeping the samples immersed 25 mm in the solutions for 96 h (Fig. S2).

Stain resistance tests have been performed in the glazes according to UNI EN ISO 10545.14. For the staining resistance test, a green staining agent (paste prepared with 40 wt% Cr_2O_3 in light oil), olive oil and an Iodine in ethanol solution (13 g/l) were used as stain agents. The classification was made by visual inspection after the cleaning procedure.

The leaching test was exploited to verify the possible release of heavy metals or hazardous pollutants from the glaze. Nowadays, there is no suitable test to verify the leaching onto "ceramic tiles" made using alternative raw materials (in this case: man-made). For this reason, it was chosen to consider the most unfavourable case for which the analysis of the eluates was performed following the regulations UNI EN ISO 11885:2009 and UNI EN ISO 10304–1:2009 and the guidelines APAT CNR IRSA 3200 A1Man 29 2003 and ISPRA man 117 2014 for landfilling residues. The leaching test was conducted as follows [1]: fired glaze samples were crushed and sieved (size <4 mm) and subsequently they were left in deionized water (solid/liquid ratio of 1:10 kg/L), under stirring, for 24h [2]; after 24 h, filtration was carried out and the eluate was analysed exploiting the analytical technique of ICP (Inductively Coupled Plasma) Spectroscopy. The analysis was conducted to evaluate the release of heavy metals, chlorides, fluorides, sulphates and nitrates. The measured concentrations of these elements were compared with the limit concentration values established by the legislative decree of September 3, 2020, n.121(analyses performed at an accredited laboratory).

3. Results

3.1. Evaluation of the aesthetical properties of the fired glaze

The aesthetic properties of the realized glazes - in terms of homogeneity, absence of bubbles and smoothness of the surface - was evaluated on the bulk specimen samples in the first step of the design study. In these steps, in fact, it has been crucial to evaluate the bulk composition of the glazes and the firing conditions. After this first step on the bulk samples, all the features were evaluated after the glazing tests.

Formulation 1, 2 and 3 were fundamental to tune the fluxing mixture of the glaze and to obtain a homogenous and an aesthetic appeal.

Before the firing phase, the glaze produced with formulation 1 was characterized by light grey colour and high fluidity. This glaze was fired using a firing cycle characterized by a maximum temperature of 1225 °C and by a firing time of 48 min. After firing, the glaze presented brown colour with light veins and several bubbles on the surface (Fig. 2a). In the second formulation, to obtain higher temperatures stability and to prevent the occurrence of bubbles, an increase in the amount of K-feldspar was used (Table 2), the maximum T was decreased (1200 °C vs 1225 °C) while the firing time slightly increased (62 min vs 48 min) (Table 3). The fired sample appeared darker, bubbles and veins, even if in small amounts were still present (Fig. 2b).

Based on the improvements obtained in the formulation 3, the feldspar was further increased (up to 28 % of K-feldspar), while kaolin and cassiterite were decreased to 3 and 1 wt %, respectively (Table 2). The maximum firing temperature was not changed, while the firing time slightly increased (68 min) to allow a more homogenous final appearance (Table 3). The resulting glaze was characterized by darker brown colour, the veins disappeared and the bubbles were almost absent (Fig. 2c). The final appearance of the glaze made with formulation 3 is pleasing; therefore, the first glazing test was carried out with this sample. The glaze has been applied using the glazer doctor blade with thickness of 0.4 and 0.6 mm. After the firing, the colour of the glaze was lighter and the bubbles were completely absent, probably as a consequence of the reduced thickness. (Fig. 3).

Once the desired homogeneity (no veins) and surface texture of the glaze (absence of bubbles) were obtained, we decided to work on the colours and final appearance, to this aim formulation from 4 to 8 were evaluated only on the basis of the glazing tests, the firing conditions were therefore kept fixed (1200 °C of T max and 68 min of firing cycle).

To obtain a darker colour, and possibly to induce a metallic iridescent effect, hematite was added to the formulations 4, 5 and 6 in proportion of 5, 10 and 15 wt %, respectively. Before the firing phase, all the glazes showed by reddish colour. After the firing, the colour of the glaze was reddish-brown for formulation 4 and deep dark brown for formulation 5 and 6 (Fig. 4). The difference in colour was probably dictated even from the absence of rutile and cassiterite, removed from formulation 5 and 6. The iridescent metallic effect was not obtained for any of the samples, however the glaze surface realized by glazing formulation 5 was extremely shining and brilliant, with high reflectance. The higher amount of Fe_2O_3 in formulation 6 has, on the contrary, a detrimental effect leading to a reduction of shine and the rise of bubbles, probably due to Fe ions reduction, which compromise the aesthetics and make the surface rougher to the touch.

The formulation 5 resulted to be the most promising and was taken as a starting point. A further test was performed to improve the aesthetic appeal of the glaze: in formulation 7 the K-feldspar was substituted by Na-feldspar (albite), in order to evaluate the effect of a more fusible feldspar. After the firing, the glaze was characterized by dark purple colour, excellent reflectance and no surface defects (Fig. 5a). These results confirm that the higher fusibility of the albite compared to K-feldspar further improve the aesthetic of the glazed surface. On the basis of this result we decide, as a last test, to further increase the albite contents in the expense of the boric frit (more expensive), leading to the composition reported in Table 2 for formulation 8. The tests resulted in a glaze characterized by a dark colour and by a smooth and very shiny

Fig. 3. Tile glazed with glaze formulation 3 after firing.

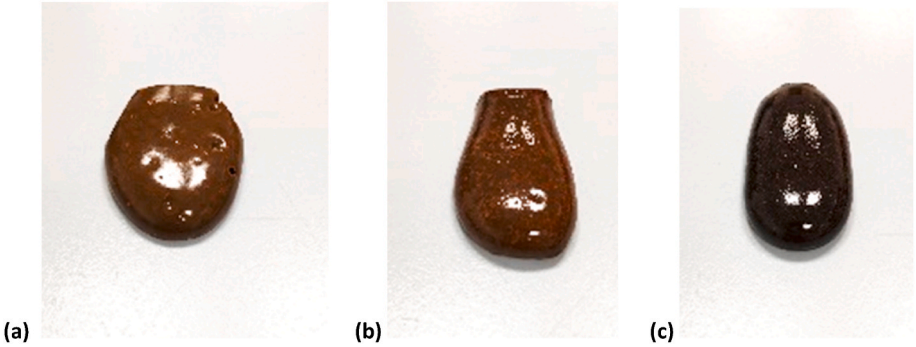


Fig. 2. a Glaze produced with formulation 1 (a), 2 (b) and 3 (c) after firing.

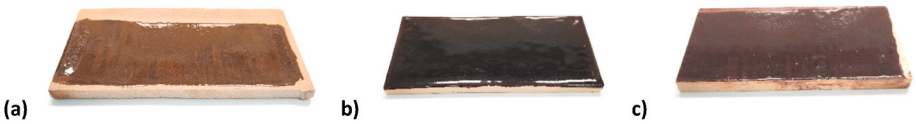


Fig. 4. Tile glazed with glaze formulation 4 (a), 5 (b), 6 (c) after firing.

Fig. 5. Tile glazed with glaze formulation 7 (a) and 8 (b) after firing.

surface (Fig. 5b). From the aesthetic point of view, this formulation represents the best result obtained.

3.2. Colorimetric analysis and gloss measures

The CIELab space is three-dimensional and covers the entire range of human colour perception. It is based on the opponent model of human vision, where red and green form an opponent pair and blue and yellow form an opponent pair. The lightness value, L^* parameter defines black at 0 and white at 100. The a^* axis is relative to the green–red opponent colours, with negative values toward green and positive values toward red. The b^* axis represents the blue–yellow opponents, with negative numbers toward blue and positive toward yellow [30]. Colorimetric analysis was performed on all the realized tiles, and the results are reported in Table S1 and in Fig. 6a and b.

It is possible to observe that the L* values for all the formulations are lower than 50, which is consistent with the dark colour of the glazed samples. Samples F1 to F4 have the highest values, appearing lighter once applied to the tiles and fired. On the contrary, samples F5 and F8 show the lowest values, although, considering the standard deviations. The a* values are all positive indicating a reddish tint in the glazes. Regarding b* parameter samples F2 to F4 shows positive values indicating shades shifted towards yellow on the contrary the F5 to F8 formulations report negative b* values therefore shades are more shifted towards blue tones.

Gloss is determined by a gloss meter projecting a beam of light at a fixed intensity and angle onto a surface and measuring the amount of reflected light at an equal but opposite angle. The intensity of the beam is then measured with a photodetector. Regarding gloss measures to define degrees of brilliance (G.U), a black glass standard with a given refractive index is employed and assigned a value of 100 G U, which is

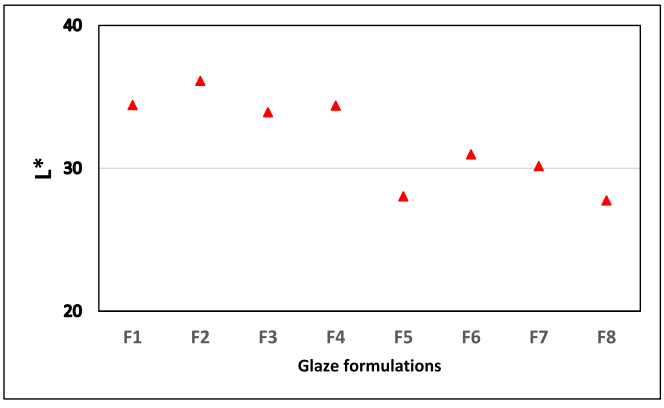


Fig. 6a. CIE-Lab parameters L* (lightness values) for the different glaze formulations.

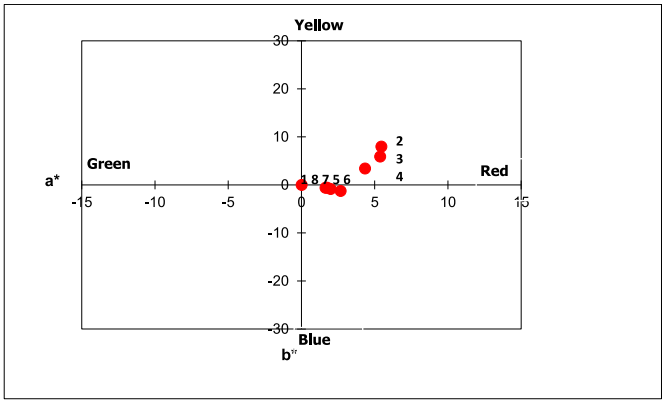


Fig. 6b. CIE-Lab parameters a* and b* for the different glaze formulations.

then used as the upper calibration point, while a perfectly opaque body is used as the 0 G U value. All glazed samples measured have values higher than 70 GU with respect to angle 60° for this reason is more reliable the data obtained by 20°angle as reported in Table 4. High gloss surfaces are recommended to be measured with 20° settings. Glossiness is related to the amount of light reflected in the specular direction and it is influenced of the surface roughness, the refractive index and the angle of incident light. As reported in other studies [31] to obtain high gloss values it is necessary a smooth surface, the glaze must be free from phase separation, low refractive index crystals, and from gaseous defects. In our case the sample 8 show the highest value at 20°.

3.3. Chemical and stain resistance

Chemical and resistance to stain tests were performed only on the glaze formulations 5 and 8. This choice was due to the fact that they were considered the best formulations containing K-feldspar and albite respectively. The results of the chemical and staining resistance tests are reported in Table 5.

Table 4
Gloss parameters at 20°and 60° of incidence of the glazed tile.

Gloss	20°	60°
Glaze 1	33	80
Glaze 2	25	80
Glaze 3	25	75
Glaze 4	68	97
Glaze 5	50	94
Glaze 6	45	86
Glaze 7	61	100
Glaze 8	69	105

Table 5
Classification of the glazes 5 and 8 based on results of the chemical resistance test. (V indicate: visual inspection).

Chemical resistance test	Glaze 5	Glaze 8
NH_4Cl - NaClO	Class A(V)	Class A(V)
HCl - KOH low concentration	Class LA(V)	Class LA(V)
HCl - KOH high concentration	Class HA(V)	Class HA(V)
Stain resistance test	**Glaze 5**	**Glaze 8**
Green staining agent	5	5
Olive oil	5	5
Iodium solution in ethanol	5	5

Class A, Class LA and Class HA refer to the resistance at chemical attacks by NH_4Cl – NaClO, HCl – KOH at low concentration and HCl -KOH at high concentration, respectively. They all corresponds to the description: no visible effect. Indeed, once the tiles were dried and cooled to room temperature after the contact with the solutions of interest, no differences were found respect to the untreated surface.

These results certify marketability of these glazes from the point of view of chemical resistance.

Regarding the staining resistance tests, all the results reported in Table 5 show that the two formulations show good resistance to all stain agents used. The cleaning degree of glaze surfaces, consisting of different crystalline phases embedded in a glassy phase, depends rather on surface micro-and macro-roughness than on chemical composition of the phases in the surface. The rule classified the glazed surfaces in different five classes 5 = stain cleaned with water; 4 = stain cleaned with blear agent; 3 = stain cleaned with strong agent; 2 = stain eliminated after acetone immersion; 1 = stain not eliminated.

It is observed that the two formulations tested show the maximum class 5 where the stain was eliminated using tap warm water. This result confirms the chemical resistance data (class A), where the glaze surface does not present any change in the visible aspect, the metals and anions leaching has been evaluated.

3.4. Leaching tests

Metals and anions leaching has been evaluated to unravel the possible hazard in using waste in a new process or in a new product. The man-made vitreous fibres (used as frit component in the glazes) contains small amounts of heavy metals as Pb, Cu, Cr, Zn, Ba, etc. To evaluate if, after thermal treatment, the materials obtained are inert and suitable for use, an investigation of hazardous substance mobility was performed on the glazed samples and on the ceramic supports to understand the specific influence.

Table 6 are reported the results obtained from the analysis of the eluates compared to the concentration limit values for acceptability in landfills for inert waste according to Legislative Decree 121/2020.

The leaching tests were conducted on glazed porcelain stoneware tiles with 5 and 8 glazes formulations and on a porcelain stoneware unglazed tile to verify the effective contribute to the leaching of metals. The results ~~of the leaching tests,~~ indicate that the levels of hazardous elements released by the glazed tiles are below limit set by the law so, these products could be marketed. Be, Co, V and nitrates were present but these elements are not subjected to regulation.

3.5. Mechanical dilatometric analysis

Mechanical dilatometric analyses were performed to test the thermal expansion of the realized glazes and of some supports on which the glaze should be deposited. These tests allow to evaluate the dilatometric agreement of the glazes formulations studied with the ceramic supports where they are applied. This is of paramount importance to understand whether, after glazing, a different dilatometric behaviour among glaze and body could generate tensions or tile deformations after firing. Sample V3, V6 and V9 correspond to porcelain stoneware bodies realized by adding 3, 6 and 9 % of Re.Wo to the batch in place of feldspar (the procedure employed for their production is described in Ref. [10], while sample V0 represent a standard porcelain stoneware body. The α values were calculated in the temperature ranges 200–400 °C and are reported in Table 7 and Fig. 7.

Table 6
Leaching test for glazed porcelain stoneware tiles with 5 and 8 glazes formulations and unglazed porcelain tile compared to the Italian regulation limits.

Elements	Concentration limit (mg/L)	Glaze 5	Glaze 8	Ceramic support (V3)
As	0.05	<0.002	<0.002	<0.002
Ba	2	<0.1	<0.1	<0.1
Be	n.d.	<0.001	<0.001	<0.001
Cd	0.004	<0.001	<0.001	<0.001
Co	n.d.	<0.005	<0.005	<0.005
Cr	0.05	<0.005	<0.005	<0.005
Cu	0.2	<0.005	0.0107	0.0181
Hg	0.001	<0.0005	<0.0005	<0.0005
Mo	0.05	<0.005	<0.005	0.0077
Ni	0.04	<0.002	0.0027	0.0119
Pb	0.05	<0.01	<0.01	<0.01
Sb	0.006	<0.002	<0.002	<0.002
Se	0.01	0.0022	<0.002	<0.002
V	n.d.	<0.02	<0.02	<0.02
Zn	0.4	0.0647	0.0533	<0.05
Cl	80	<5	<5	<5
F	1	<0.1	<0.1	<0.1
SO_4	1000	<10	<10	<10
NO_3	n.d.	2	3	2
C	50	<10	<10	<10

Glazes and bodies containing clays expand during firing. As they cool, they shrink. The best situation is for the support to shrink a little more than the glaze; this keeps the glaze in slight compression (α support values> α glaze values). If the glaze shrinks more than the body, it will crack, creating small crack lines ("crazing" defect) [32].

The α values for the formulation 6 was not determined since it was characterized by large bubbles that prevented sample preparation for this analysis (the material was extremely brittle and the specimen realized broke during cutting). The α values of support body decrease with the amount of Re.Wo increase, due to the positive effect on the sintering. From the data reported V0 and V3 samples have a good dilatometric match with the formulations tailored showing α values slightly higher than the glazes. In particular, for F8 formulation despite the support coefficient is slightly lower the sample did not present any defects (crazing). It is possible to indicate that the difference between the two α values is within the tolerance.

3.6. Quantitative phase analysis (QPA)

Quantitative phase analysis (QPA) was performed on all the fired glaze realized. The results of the QPA are reported in Table 8 and Fig. 8.

Table 7
α values calculated in the temperature range 200–400 °C for the bodies V0, V3, V6, V9 and for all the glazes created; n.a. not available.

	Samples	200–400 °C
Bodies	**V0 (standard batch)**	7.71×10^{-6}
	V3 (3 wt % Re.Wo)	7.44×10^{-6}
	V6 (6 wt % Re.Wo)	7.32×10^{-6}
	V9 (9 wt % Re.Wo)	7.28×10^{-6}
Glazes	**F1**	7.59×10^{-6}
	F2	7.47×10^{-6}
	F3	7.61×10^{-6}
	F4	7.37×10^{-6}
	F5	7.44×10^{-6}
	F6	na
	F7	8.11×10^{-6}
	F8	8.19×10^{-6}

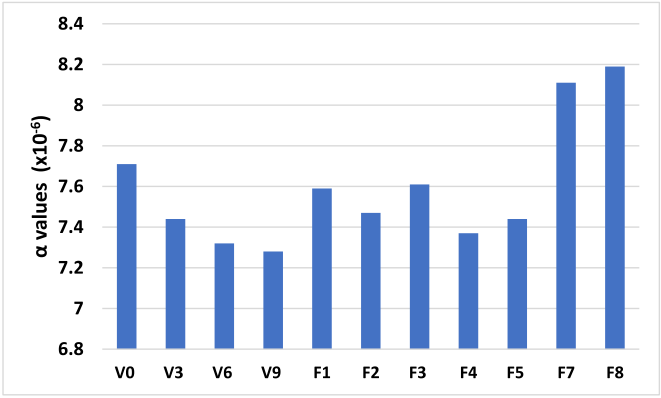


Fig. 7. Graphic reporting α values ($x10^{-6}$) calculated in the temperature range 200–400 °C.

The results of the QPA analysis show the mineralogical compositions of glazes after the firing phase. Comparing these data and the starting batches (Table 3, Fig. 8), it is possible to understand how the glazes evolved during the firing phase. In the formulation 2, quartz probably was already present in the feldspar sand or in the kaolin used for the glaze preparation, whereas hematite, not present as crystalline phase in the starting batch, could derive from the crystallization of part of the Fe present in high levels in Re.Wo (Table 1). Furthermore, it is possible to observe how only half of the cassiterite was melted in this sample. This was probably the reason for the light veins observed on the fired glazes 1 and 2. In fact, on the basis of this results, only 1 % cassiterite was included in formulation 3 and 4. Quartz was the only mineralogical phase present after the firing in the formulation 3. The absence of residual cassiterite could also be linked to the disappearance of the light veins present on the surface of the glaze in previous formulations.

Comparing the QPA results of the formulations 4, 5 and 6 and considering their initial amounts of hematite (5,10 and 15 % hematite respectively), it is clear that only 5 % of this mineralogical phase was consumed during the firing phase. Furthermore, pseudo-brookite (Fe^{3+}, Fe^{2+})$_2$(Ti, Fe^{3+})O_5 has been detected only in the glaze 4, since it was the only Fe and Ti bearing formulation.

Formulation 5 was considered the best one among those containing K-feldspar while formulation 8 was considered the best one among those containing albite. Comparing their QPA results, it was clear that the replacement of K-feldspar with albite led to an increase of the glaze fusibility. In fact, formulation 8 was characterized by only 0.1 % of residual quartz while formulation 5 preserve 3.0 % of this mineralogical phase.

The hematite content decreases for all the glazes considered, but in different percentages. For formulations F4-F6-F6 the overall composition is the same, the only differences are related to the amount of hematite in the starting batch (5,10,15 % respectively). After the firing the amount of hematite left in the glaze is proportional to that present in the starting batch: for samples F4 we observe a decrease of 85 % (0.74 wt %)), for F5 of 45 % (5.34 wt%) and for F6 of 33 % (10.00 wt %). The situation is different for samples 7 and 8: notwithstanding the addition of the same percentage of hematite in the starting batch, after firing F8 shows a higher amount with respect to F7 (6.83 vs 4.86). In a recent paper aimed at the understanding of the iron behaviour in High-Fe porcelain stoneware bodies [33], the authors demonstrate that the behaviour of the Fe ions and, specifically of the persistence of hematite is strongly influenced by the chemistry of the vitreous phase. We cannot directly compare our system with that of [33], since the chemistry is completely different, anyway we can suppose that F8, containing less boric frit, could represent a less fusible system, thus can lead to a higher hematite persistence.

3.7. SEM

SEM was used to examine the microstructure of selected glaze (formulations 4, 5, 6 and 8). EDX spectrometer was used to unravel the major elements present within the various components of the glazes. The samples were analysed both on the cross section and on the surface, nevertheless the cross-section observations proved to be the most promising. As expected, all the glazes analysed were characterized by a glassy matrix within which residual quartz crystals and high atomic number dendritic micro crystals were immersed (Fig. 9). The major elements present within the glassy matrix were: Si, Al, Na, Mg, Ca, K and Fe. The high contrast phase contains basically Fe and Ti (Figs. S3 and S4).

4. Discussion

4.1. The recycling of wastes in the production of pigments and glazes

The ceramic industry is increasingly seeking to source waste materials from other sectors to use as secondary raw materials. Alongside ongoing efforts to find alternative raw materials to replace natural ones in the formulation of ceramic bodies [12,14,34–37], recent research is also focused on enhancing the sustainability of the glaze production supply chain.

A recent study by Carneiro et al. [38] explored the use of waste from various industrial sectors, such as sludge from galvanic processes and marble and granite processing, for the production of inorganic pigments. These pigments were then added to transparent and glossy glazes to

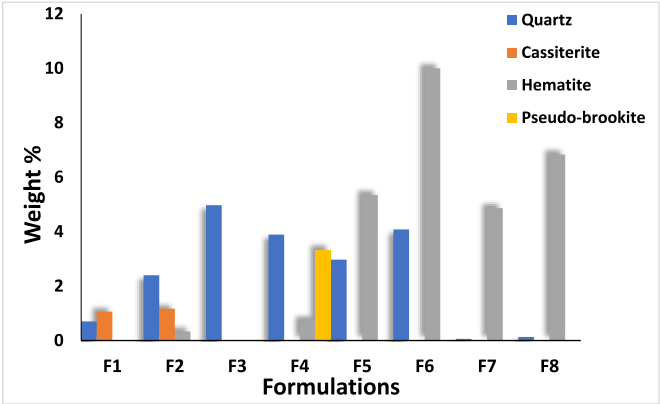


Fig. 8. Histogram reporting the crystalline phases concentration for each formulation.

Table 8
Mineralogical compositions of the glazes after the firing phase.

wt%	F1	F2	F3	F4	F5	F6	F7	F8
Quartz	0.7(5)	2.4(1)	4.97(7)	3.89(6)	2.97(6)	4.08(8)	0.06(5)	0.13(4)
Cassiterite	1.06(1)	1.17(3)	–	–	–	–	–	–
Hematite	–	0.33(4)	–	0.74(4)	5.34(4)	10.00(7)	4.86(5)	6.83(4)
Pseudo-brookite	–	–	–	3.34(8)	–	–	–	–
Amorphous	98.3(5)	96.1(1)	95.03(7)	92.0(1)	91.69(7)	85.9(1)	95.14(5)	93.04(6)

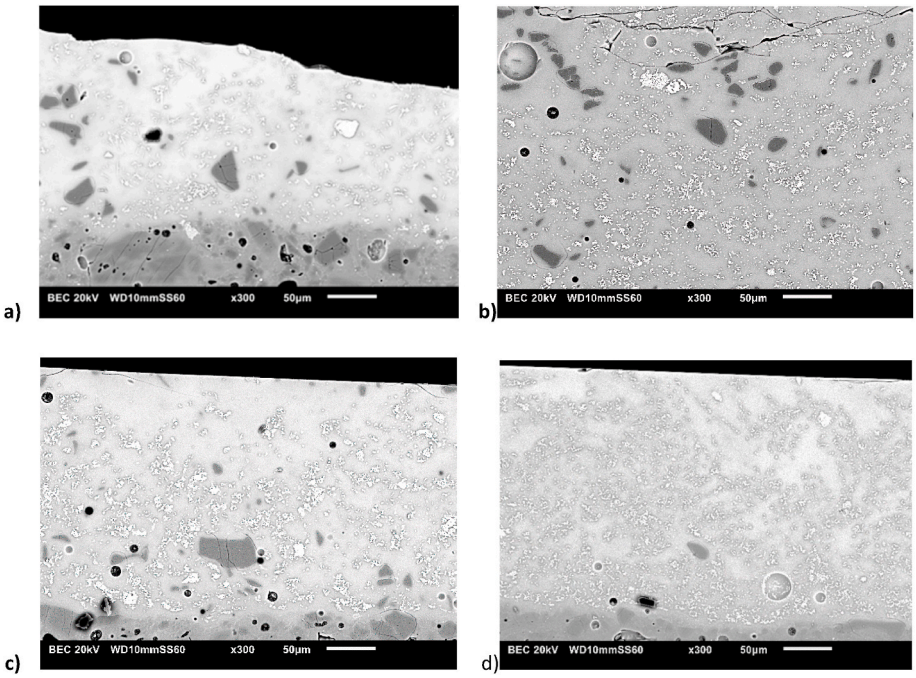


Fig. 9. BSE image of the microstructure of the firing glaze deriving formulations 4 (a), 5 (b), 6 (c), 8 (d), all presenting a glassy matrix within which residual quartz crystals (dark grey) and high contrast crystals.

evaluate their tone and colouring power. The results were promising, showing a trend toward darker tones with increasing temperature—a common colour transition observed in ceramic materials.

Another study [39] investigated the potential of using glassy materials derived from the immobilization of hazardous waste, such as sludge and slags from industrial processes, or fly ashes containing toxic elements like Pb, Cu, Cr, Zn, Cd, and Hg. The study tested the possibility of producing frits for ceramics from these glassy matrices through a process of heating and subsequent quenching in water.

Glass ceramics obtained by sintering have attracted growing interest due to their excellent technological properties. Recent research has demonstrated the feasibility of producing glass-ceramic glazes for porcelain stoneware tiles. The production of these glazes is closely tied to the glass sintering process. Typically, a 0.3 mm thick layer is sintered onto a ceramic substrate using rapid firing cycles in roller kilns. These glazed ceramic substrates can withstand short thermal cycles (between 25 and 35 min) and peak firing temperatures between 1140 and 1200 °C. Additionally, they result in a final surface that is chemically inert, impervious to liquids and gases, easy to clean, smooth, resistant to abrasion and scratches, mechanically strong, and capable of being decorated during the process [39].

A different research [40] studied the feasibility to reformulate a commercial ceramic glaze composed by both olivine (magnesium iron silicate, $(Mg,Fe)_2SiO_4$) and commercial frits, rich in lead (about 30 wt %), by using alternative raw materials (CRT cone glass and municipal solid incinerator post-treatment bottom ashes before and after vitrification). The waste-based glazes produced were characterized and, compared to the standard glaze, showed better acid resistance, comparable aesthetic characteristics and slightly lower stain resistance. Environmental benefits were obtained by saving natural raw material (olivine), by reducing lead percentage in the proposed formulations (from around 30 to 5 wt%), by energy saving (for the avoided use of commercial frits) and by reducing lead content in the new compositions [40].)

4.2. A coloured, safe and stable ceramic glazes

Glazes 5 and 8 contain between 50 % and 60 % secondary raw materials (44 % Re.Wo and 15 % and 10 % boric glass, respectively) and are characterized by a dark colour, a smooth and highly glossy surface, and high reflectance.

In the late 20th century, dark ceramic glazes were typically produced using raw materials or semi-finished products containing hazardous heavy metals [23]. One of the primary components of traditional ceramic glazes was lead. Lead oxides, such as lead monoxide (PbO) or tri-lead tetroxide ($2PbO{\cdot}PbO_2$), were added in concentrations ranging from 58 % to 70 % to achieve dark hues. However, the use of frits or other raw materials containing lead or other heavy metals has become increasingly restricted due to their environmental impact and classification as hazardous to human health. Lead has been replaced by other metals, such as chromium and nickel [41]. It is important to note that nickel oxides (NiO) are classified as carcinogenic by the International Agency for Research on Cancer (IARC), and chromium, commonly used as chromium oxide (Cr_2O_3), can also be associated with lead in lead chromate ($PbCrO_4$). Therefore, both elements require careful handling.

In this project, the "colouring" raw material used for the glaze development was Re.Wo. As shown in Table 1, which details the chemical composition of Re.Wo frits, the concentrations of Pb, Cr, and Ni are in the order of parts per million (ppm). These findings indicate that our glazes contain negligible quantities of heavy metals and do not pose any significant health risks. Additionally, the results of the leaching test on our most promising samples (Glazes 5 and 8) are presented in Table 6, along with the concentration limit values. It is evident that the levels of hazardous elements released by these glazes are well below the legal limits.

Moreover, after undergoing chemical resistance tests, these glazes were classified as Class A(V), Class LA(V), and Class HA(V). They exhibited no visible effects when subjected to chemical attacks by NHCl – NaClO, HCl – KOH at low concentrations, and HCl – KOH at high concentrations. For all these reasons, Glazes 5 and 8 can be considered excellent examples of "green" ceramic products. They demonstrate the successful application of an efficient circular economy model, resulting in a safe and marketable product.

4.3. The effect of hematite

Many chromophore oxides are used in the ceramic industry with the aim to obtain glazes with different tonality and effects [41]. For example, important oxides, used to obtain a brown glaze after the firing, are Fe_2O_3, CuO, MnO_2, TiO_2, which are mixed together with the addition of specific additives [25]. Iron oxide is one of the most widely used chromophore elements thanks to its high colour intensity, thermal and chemical stability [42,43]. The colour of traditional ceramics is closely related to the oxidation state of the iron [42]. Since the firing environment is oxidising, glazes containing iron oxide will show colours ranging from light yellow to dark brown. Furthermore, the glazes present black tones and stains on the surface when hematite is used in alkaline conditions at high temperatures and with percentages equal or higher than 10 % [44,45]. In this project, we used rutile (TiO_2), cassiterite (SnO_2) and hematite (Fe_2O_3) as chromophore elements. The first two oxides were added in low percentages in the glaze formulations from 1 to 4 with the aim to adjust the chromaticity of the glaze and to obtain a brown colour at the end of the firing phase. The results obtained shows that the addition of rutile and cassiterite in low percentages led to the brown colour desired (Figs. 1–3 and 4a). Higher amounts of hematite were added in formulation from 5 to 8 with the aim to make the colour of the glaze darker and to obtain an iridescent metallic effect. The addition of hematite to these formulations resulted in a darker colour of the glazes and in a shiny and brilliant surface, but the iridescent metallic effect was not obtained for any of the samples (Figs. 4 and 5). Glazes 5 and 8 are considered the best results obtained, containing K-feldspar and albite respectively.

The results show that for all the glazes analysed, the hematite content decreases after firing. The amount of hematite remaining in the glaze is generally proportional to the amount present in the initial formulation, with the exception of samples 7 and 8. Although these formulations contain the same amount of hematite in the batch, they retain different percentages in the final enamel. This difference is attributed to the varying fusibility of the systems; F8 represents a less fusible system, leading to greater hematite persistence. This aligns with findings from our recent paper [33], where we demonstrated that the persistence of hematite is strongly influenced by the chemistry of the vitreous phase.

Depending on the cooling time, glazes containing metal oxides are characterized by the nucleation of crystals with various shapes. Metallic elements, which promote crystals formation, dissolve in the glaze during the first half of the firing cycle and subsequently crystallize during the cooling phase. The atoms bond to each other and begin nucleation, as soon as the melt reaches the crystallization temperature. Dendritic crystals are formed when cooling occurs homogeneously. The cooling rate affects both the crystallization rate and the size of the crystals [46]. The SEM images of the cross section of the glazes (Fig. 6 and S3 and S4) allowed us to observe the presence of high atomic number dendritic micro crystals immersed within the glassy matrix. The EDX spectrometer revealed that the micro crystals are basically formed by Fe and Ti. Looking at the initial formulations of the glazes (Table 2), these elements could derive from the additions of hematite and rutile but also from their presence within the Re.Wo (Table 1). Quantitative phase analysis confirmed the presence of these crystals in the form of residual hematite and pseudo-brookite (Table 8).

4.4. Final consideration and the benefits of this innovative green solution

In this project we tested the production of high-quality ceramic glazes exploiting secondary raw materials. The glazes created in our project can be considered "green" products because they contain more than 50 wt % of secondary raw materials. In particular, we tested the use of the so called Re.Wo -corresponding to the thermal inertization product of rock wool - and recovered boric glass - 100 % recycled material as defined on section 7.8.1.1 c, UNI EN ISO 14021 and deriving from laboratory glassware. Rock wool represent a category of man-made vitreous fibres widely used in several sectors like that of construction. A key point is the potential health hazard of these materials. This means that the challenges associated with managing and disposing of these fibres are similar to those for asbestos-containing materials. The inertization of these materials offer the opportunity to recycle them as secondary raw materials. The outcomes could have a considerable economic effect for both the inertization system provider and the end user. For the company managing the inertization process, there will be a benefit in avoiding waste disposal costs while also gaining the opportunity to sell the treated materials. Meanwhile, the user company will benefit from a reduction in the need for natural raw materials.

Many formulations were tested and after the optimization process, the final samples show a good aesthetic quality, good stain resistance and a surface with no defects. Moreover, the realized glazes resulted to be stable under chemical attack and in good dilatometric agreement with the supports they are supposed to be glazed. Therefore, considering all these data, this study show that is possible to use waste instead of commercial expensive frits in the production of ceramic dark glazes.

CRediT authorship contribution statement

Mattia Sisti: Writing – original draft, Investigation, Data curation. **Davide Guidetti:** Investigation, Data curation. **Fabiana Altimari:** Writing – original draft, Investigation, Data curation. **Fernanda Andreola:** Writing – review & editing, Validation, Methodology, Investigation, Data curation, Conceptualization. **Luisa Barbieri:** Writing – review & editing, Validation, Supervision, Investigation, Funding acquisition, Conceptualization. **Isabella Lancellotti:** Investigation, Writing – review & editing. **Lara Casini:** Investigation. **Francesco Colombo:** Investigation. **Rossella Arletti:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Funding acquisition, Conceptualization. **Riccardo Fantini:** Methodology, Investigation. **Alessandro F. Gualtieri:** Writing – review & editing, Validation, Supervision, Resources, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Alessandro F. Gualtieri is inventor of an Italian patent protecting the inertization process of the exhaust wool: Italian Patent N. 102021000002246 "*Apparato* per *il trattamento di rifiuti contenenti lana minerale*", Inventors: I. Zanatto, A.F. Gualtieri. Repository date: February 2, 2021.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ceramint.2024.11.396.

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