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Minimization of Pb content in a ceramic glaze by reformulation the composition with secondary raw materials

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Abstract

In this study a commercial ceramic glaze composed by both olivine (magnesium iron silicate, $(Mg,Fe)_2SiO_4$) and commercial frits, rich in lead (about 30 wt%), was reformulated by using secondary raw materials (CRT cone glass and municipal solid incinerator post-treatment bottom ashes before and after vitrification). The waste-based products were characterized and, compared to the standard glaze, showed better acid resistance, comparable aesthetic characteristics and slightly lower stainless 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.

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1. Introduction

Ceramic glazes have essentially two functions, technical and aesthetical. The former is to render the surface of the ceramics products completely waterproof, making it easy to remove any substance liable to cause dirt or stains. The second is to give to the ceramic product a glossy, colourful surface which would be difficult to achieve in any other way [1]. In ceramic industries the glazes are typically applied by deposition from a water-based suspension. The solid fraction of glaze suspensions is composed of different types of raw materials: oxides, pigments, feldspars and frits. The frits, which are the glassy fraction, are the main components and are obtained from mixtures of silicates and carbonates which are melted and rapidly cooled in water.

In ceramic tiles production fluxing and matt frits that can contain different percentages of Pb are used. Lead glazes are most commonly used on earthenware, porcelain and tiles. They are reliable, easy to control, durable for most purposes and they produce attractive glazes. When the glazes are properly formulated and fired at a high temperature, the lead is sealed. However, if they are not properly prepared and fired, lead may leach (i.e. move from the glaze) into the environment. These days, raw or free lead is rarely used. The lead is compounded with silicate into a frit, which is less dangerous, in fact Pb frits is bound inside of the glass structure. In catalogues, manufacturers label the glazes containing lead and use terms such as lead-free, non-toxic and dinnerware-safe to identify lead-free glazes. The lead frits most diffuse are monosilicates, bisilicates, rocaille and monoboron, where the Pb percentage is between 60 and 80%. The reason for use these frits resides in the property developed: they improve the fusibility, give particular brightness, facilitates the development of colour and helps to reduce the coefficient of expansion, modulus of elasticity and the tendency to devitrification. The current trend is to replace the lead frits by other fluxing agents, such as boric oxide, in order to reduce lead frits production, not because frits are harmful, but to avoid the dangerous handling of lead compounds [2].

In this study lead frits used in production of commercial ceramic glazes are replaced by the secondary raw material cone CRT glass (provided by waste of electrical an electronic equipments (WEEE)) and a silicate glaze component rich in Mg, Fe (olivine) is substituted by pre-treated incinerator bottom ash in order to valorise them.

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The waste of electrical and electronic equipments (WEEE) is an emerging problem as well as a business opportunity of increasing significance, given the volume generated and their content of both toxic and valuable material. In fact WEEE contains substantial quantities of reusable materials such as metals, plastics and glass, which can be recovered in the form of secondary raw materials. For this reason, industrial activities disassembling End of Life (EOL) electronic equipments have been started in Europe in order to avoid the final disposal. Existing technologies allow the recovery and recycle of various components from WEEEs, by separation of plastics, rubbers, electronic circuits, metals and glasses. After this step, some of these components result ready to use, while others deserve further processing before their use as secondary raw materials [3].

The Decision of European Communities 2005/32/EC classifies the WEEE as hazardous wastes. 80% of these residues are constituted by television sets and monitors. It is estimated that approximately 65% of the weight of a television set or a computer monitor is constituted of cathode ray tube (CRT) glasses. In Italy in 2008 the amount of WEEE produced was about 800,000 tons/years with a recovery percentage limited at 12% [4]. The CRTs are normally made of several glass components divided into four typologies (screen or panel, cone or funnel, neck and frit junction), each of them presenting different chemical composition and properties [5]. Glasses like cone and neck contain principally Pb (16–50%) instead panel glass has other hazardous metals as Ba (around 8–10%) and Sr (5–10%). In cone glass, Pb is present in high percentage to stabilize the glass and to protect monitor and TV set users against X-ray radiation emitted by the electron gun, but the same measure is not possible for panel glass, because of the browning phenomenon. This phenomenon is caused by a reduction of metal ions in the glass by electron beams and the generation of metal colloids according to the reaction $Pb^{2+} + 2e^{-} \rightarrow Pb^{0}$ [5,6]. For these reasons, there is an increasing urgency to develop new applications for recovered CRT glass in agreement with Directives 2002/96/EC regarding the recyclability and 2003/108/EC on WEEE management and 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipments (RoHS – Restriction of hazardous substances).

In this framework, the cone glass that contains significant quantities of Pb (around 16%) can be an important secondary raw material for the production of new eco-compatible Pb containing ceramic products, where it is necessary its introduction as melting agent or to emphasize the colouring. The cone glass can help to reproduce commercials compositions.

Another important problem is represented by recovery of bottom ash of municipal solid waste incineration (MSWI). In Italy, in 2007, the generation of municipal solid waste (MSW) was 32.55 millions tons and the amount of incinerated waste was around 4.5 million tons [4]. Solid outputs of incineration are represented by fly and bottom ashes that in the case of MSWI ranges from 3–5 to 20–35% by weight of the original quantity of waste for fly and bottom ash, respectively [7,8]. In the past years in Italy some companies became active and specialized in post-treatment technology of bottom ashes. The objective is minimizing waste production by transforming it in secondary raw materials. The treatment starts from a complex process of selection and physical/mechanical treatment (ageing, sieving and washing) of incineration bottom ashes. After the process, an inert material with silica-based matrix, rich in iron, calcium and aluminium oxides is obtained. This material can be successfully applied mainly in cement as secondary raw materials (SRM), substituting extracted raw materials or in the ceramic sector [9–11].

Several studies with MSWI ashes were carried out in recent years, focussing on their vitrification/devitrification [12–16], on the structure and properties of bulk glass-ceramics [14,17–19], as well as on the possibility of obtaining sintered glass-ceramics from powdered MSWI glasses [19–25]. This is because vitrification is a known technology for the inertisation of different industrial residues [26,27].

Many investigations have been performed by the authors regarding the valorisation of post-consume residues [28–31], in particular in the traditional ceramic sector, that consumes large quantities of raw materials obtaining added-value products with low environmental impact. This is achieved by the reduction in the use of raw materials, transport, energy consumption, waste processing and by the recycling of high-quality secondary raw materials.

In the present work the authors have focused their attention on the reformulation of a commercial ceramic glaze by using cleaned cone CRT glass and bottom ash with o without vitrification in order to exploit some characteristics of these secondary raw materials and to obtain environmental benefits.

2. Materials and experimental procedure

2.1. Secondary raw materials

In this study SRM (Table 1) used for the reformulation of commercial glaze were:

- Bottom ash in two fractions: coarse (diameter around 2–8 mm) and fine (diameter lower than 2 mm) as supplied by a physical treatment plant.
- Both the fractions of bottom ash after vitrification at 1400 °C for 1.5 h using corundum crucible and quenched in water.
- Reclaimed CRT cone glass (diameter around 5–7 mm).

The ceramic glaze chosen for the reformulation is based on olivine, zirconium components (zirconium oxide and silicate), clays, tin oxide and lead-rich frits (total quantities of lead oxide around 30 wt%). This glaze has ochre colour and is used for the production of ceramic tiles “tipo cotto”. The lead presence emphasizes its colour.

In view of the presence of chromophore elements (in particular iron) in MSWI bottom ash, vitrified and not, and the presence of lead in the CRT cone glass, these two secondary raw materials were chosen as potential substitutes of olivine and commercial frits rich in lead, respectively.

Table 1
SRM chemical analysis (wt%) determined by inductively coupled plasma (ICP-Varian Liberty 200). BAF: fine bottom ash; BAL: coarse bottom ash; respective glasses: fine GF and coarse GL; cone glass. The associate error evaluated by the instrument is ±0.5 ppm.

Oxide	BAF	GF	BAL	GL	Cone glass
SiO_2	30.31	35.09	47.40	48.47	47.09
Al_2O_3	13.03	13.64	9.95	11.12	3.45
Fe_2O_3	10.02	11.53	4.38	4.48	0.13
CaO	23.05	26.06	18.80	19.52	3.54
MgO	2.83	3.73	2.91	4.00	1.62
Na_2O	1.94	2.44	4.53	4.95	13.86
K_2O	0.94	1.45	0.98	1.81	9.21
TiO_2	1.07	1.71	0.75	1.29	0.12
MnO	0.18	0.17	0.11	0.15	–
ZnO	0.73	0.54	0.34	0.61	0.14
PbO	0.36	0.17	0.31	0.12	16.94
BaO	0.08	0.40	0.09	0.34	2.29
SrO	–	–	–	–	0.92
P_2O_5	1.96	1.90	1.26	1.96	–
CuO	0.68	0.83	0.47	0.60	–
Others	1.06	0.10	1.17	0.11	0.36
L.O.I[a]	11.70	–	5.58	–	–
Total	99.94	99.76	99.03	99.53	99.67

[a] Lost of ignition.

Different compositions using MSWI bottom ash before and after vitrification were formulated. No additives were used to vitrify the bottom ash (fine and coarse fraction).

2.2. Preparation of glazes

Glazes compositions containing MSWI bottom ash (22–32 wt%) of both coarse and fine fractions, cone glass (29–33%) and the other typical raw materials were prepared by wet milling (35 wt% of water, 40 min) using a laboratory ball mill (residue <2% at 45 μm). The same procedure was performed for the compositions containing vitrified MSWI bottom ash (17–41%) of both coarse and fine fractions and cone glass (29–33%). After milling, the density of the glaze slurries were measured by picnometry and adjusted by water to the reference density value (1.715 g/cm^3). The wet-milled glaze was applied in laboratory by a doctor blade on a green single-firing ceramic support. Firing of the glazed support was made in a semi-industrial electric roller kiln at the reference glaze firing temperature (1170 °C) with a cycle of 40 min. In order to remain within the compositional range of olivine $(Mg,Fe)_2SiO_4$) Fe/Mg ratio of fine MSWI bottom ash was balanced by addition of talc ($Mg_3Si_4O_{10}(OH)_2$). After preliminary tests four glazes, two with fine MSWI bottom ash (labelled A and B) and two with fine vitrified MSWI bottom ash (labelled C and D) were selected for the characterization; the total content of SRM in these formulations is presented in Table 2.

Table 2
Percentage of secondary raw materials (SRM) added in selected formulations.

	% Bottom ash fine	% Bottom ash fine vitrified	% Cone glass	% SRM total
Glaze A	22	–	32	54
Glaze B	32	–	29	61
Glaze C	–	25	31	56
Glaze D	–	39	23	62

2.3. Characterization of glazes

The aesthetic aspect (colour) of the glazes after firing was measured by CIELab method using a spectrophotometer (COROB – Colour Engineering) with Illuminant D65 and Observer 10°. According to this method the following parameters were measured: L^* (lightness) from absolute white $L^* = 100$ to absolute black $L^* = 0$, a^* (red-green) and b^* (yellow-blue) elaborated from the visible spectra.

Acid (HCl 3 vol%) and stain resistance tests have been performed in the glazes according to UNI EN ISO 10545.13 and UNI EN ISO 10545.14, respectively. In the staining resistance test, the green staining agent (paste prepared with 40 wt% Cr_2O_3 in light oil) was used. The classification was made by visual inspection after the cleaning procedure.

In order to check the environmental characteristics of the studied glazes, a leaching test was performed following UNI EN ISO 10545.15. In this case, cubic samples prepared with the glaze compositions studied and fired using the industrial cycle described above were immersed in acetic acid solution (4 vol%) for 24 h. The concentration of Pb released in the solution was measured by inductively coupled plasma (ICP-Varian Liberty 200).

The characteristics temperatures and the thermal expansion coefficient of glazes were measured by Optical Dilatometer (model Misura 3, Expert System). The thermal expansion coefficients were determined in the range 50–400 °C. X-ray diffraction measurements at room temperature were carried out on glazes surface in 5–70° 2θ range, using a diffractometer for thin coatings (X-Pert Philips, Ni-filtered Cu Kα radiation with sample holder MPSS) in order to identify the crystalline phases developed. Moreover, to analyse the formation of crystalline phases on powdered glaze samples as a function of the

Table 3
Chemical composition in oxide % of the reference glaze and formulations with SRM.

Osside	Reference	A	B	C	D
SiO_2	31.46	42.64	41.29	42.24	40.80
Al_2O_3	2.43	4.33	5.41	4.65	6.25
Fe_2O_3	0.92	2.64	3.62	2.93	4.45
ZrO_2	19.62	18.45	16.31	17.82	13.36
CaO	0.85	5.92	7.70	6.44	9.16
MgO	4.27	5.26	4.99	5.18	5.90
Na_2O	0.55	2.72	2.63	2.69	2.42
K_2O	0.49	2.02	1.90	1.99	1.71
TiO_2	1.94	2.60	2.43	2.55	2.13
ZnO	1.98	0.26	0.33	0.28	0.38
PbO	30.44	5.13	4.58	4.97	3.80
BaO	–	1.32	1.18	1.28	0.98
SrO	–	0.64	0.57	0.62	0.47
B_2O_3	3.36	0.07	0.10	0.08	0.12
SnO_2	1.00	1.18	1.05	1.14	0.86
Others	–	1.31	1.71	1.44	2.14
L.O.I	0.68	3.48	4.16	3.68	5.06
Total	99.99	99.97	99.96	99.98	99.99

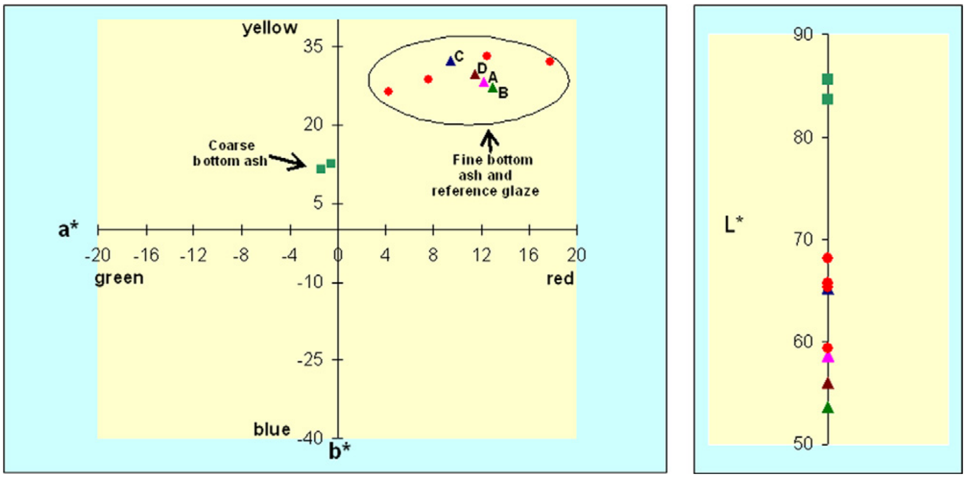

Fig. 1. CIELab system plot for the reference glaze at different tonalities (spheres) and the formulations prepared with SRM (triangles: fine vitrified bottom ash and not; square: coarse bottom ash).

temperature, a XRD heating chamber (HTK 16) was used. Powders of these glazes (<40 μm) were heated on platinum bar from room temperature, and reaching the following temperatures of 600, 800, 900, 1000, 1100 and 1200 °C where the XRD scanning was performed. In order to reproduce the industrial cycles a heating rate of 50 °C/min was used and the patterns were collected also during cooling cycle at 900 and 25 °C to control the effect of cooling on the glaze crystalinity. The X-ray diffraction patterns at each temperature were obtained over a range of diffraction 10–70° 2θ with time per step equal to 27 s.

The degree of sintering and the microstructure and morphology of the crystals in the glazes were observed by Scanning Electron Microscopy (ESEM, Quanta-200, FEI Co., equipped with an EDS).

3. Results and discussions

Table 3 reports the chemical composition in oxides of the reference glaze and the selected formulations with SRM: A, B, C and D. It is possible to note that the formulations show a higher content of Si, Al, Ca, K, Na and Fe oxides with respect to reference glaze – in agreement with the chemical composition of MSWI bottom ash added – but considerably lower amount of lead oxide. The higher LOI (Lost of Ignition) of the formulated glazes with respect to reference one can be attributed to the use of not vitrified bottom ash and talc in A and B while to the use of talc only in C and D where bottom ash are previously vitrified.

The reference industrial glaze used in this study contains olivine (around 20%), which is a magnesium iron silicate $(Mg,Fe)_2SiO_4$ that confers particular colour and surface effect. The olivine is an isomorphic mixture of fosterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4), both soluble in all proportions, where Mg^{2+} and Fe^{2+} ions can substitute each other in the crystalline network. The chromatic effect is due to the ions dissolved in the glass. The CRT cone glass has was used also the function of melting agent to improve Mg^{2+} and Fe^{2+} ions dissolution.

Preliminary tests emphasized that the formulations with coarse bottom ash (vitrified and not) do not develop the desired colour (Fig. 1), and therefore they were discarded. On the other hand, for the compositions with fine bottom ash (vitrified and not) the results obtained were good, but the addition of talc was necessary to reach the optimum Fe/Mg ratio as explained in Section 2.2.

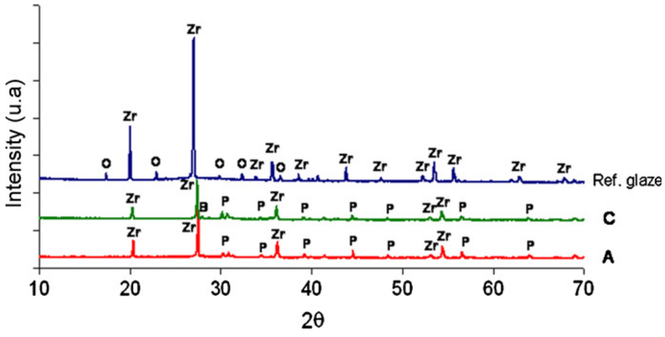

Fig. 2. XRD spectra of the glaze A (analogous glaze B), C (analogous glaze D) and reference glaze. Zr = zircon; P = pyroxene; O = olivine; B = baddeleyite.

Fig. 1 shows CIELab parameters of the glazes produced, where the region covered by reference glaze hues and those of fine and coarse bottom ashes formulations are evident. The reference glaze can present various hues as shown by spheres symbols in Fig. 1. The formulations A, B, C and D (by triangles

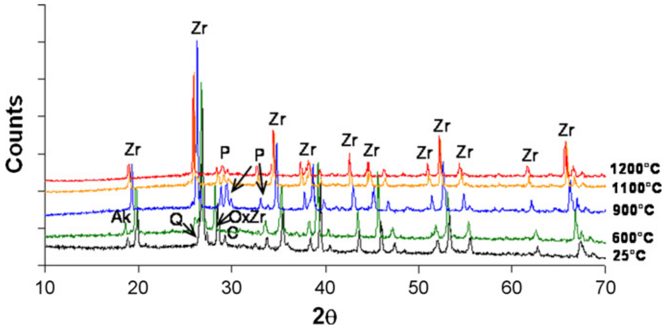

Fig. 3. XRD spectra of the glaze A at different temperatures. Q = quartz, Ak = akermanite, C = calcite, P = pyroxene and Zr = zircon.

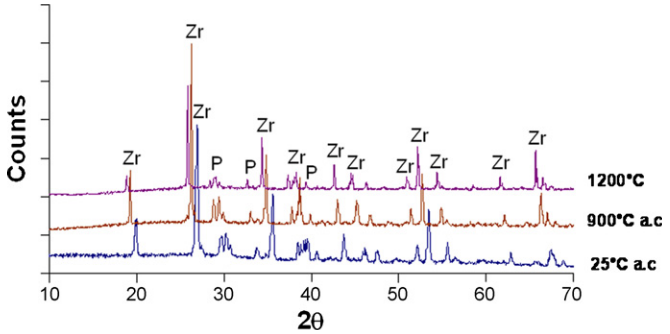

Fig. 4. XRD spectra of the glaze A after cooling at 900 and 25 °C compared to 1200 °C spectrum. Zr = zircon and P = pyroxene.

symbols) lie inside the region delimited for reference glaze tonalities; on the contrary the formulations with coarse ash are localized outside (in the region of green colour). Regarding L^* values, it is possible to note that fine ash compositions show lower lightness (intense colour) than the reference glaze tonalities while the coarse ash compositions show high lightness (light colour).

Fig. 2 shows the XRD spectra of the glaze A (analogous at glaze B), C (analogous at glaze D) and reference glaze. From the X-ray analysis conducted on glazed samples after firing, the following crystalline phases were identified in the reference glaze: zircon ($ZrSiO_4$) and olivine ($Mg_{1.77}Fe_{0.23}(SiO_4)$. New glaze formulations A and B presented only zircon and pyroxene (solid solution of diopside ($CaMgSi_2O_6$) and augite ($Ca(Fe,Mg)Si_2O_6$)) in agreement with the chemical composition of MSWI bottom ash added, rich in calcium and iron oxides. In the compositions C and D (vitrified bottom ash) the crystalline phases identified were: zircon, pyroxene and baddeleyite (ZrO_2), used in the composition as raw material.

XRD spectra at different temperatures of the glaze A during heating are reported in Fig. 3. The choose of glaze A was due to the characteristic of the containing raw materials used – MSWI

Table 4
Tests of acid and staining resistance for the glazes studied.

Sample	Acid ResistanceCLASS[a]	Stain ResistanceCLASS[b]
Reference glaze	B	5
Glaze A	A	4
Glaze B	A	3
Glaze C	A	1
Glaze D	A	1

[a] A = no visible effect; B = light change in aspect; C = visible effect and material displaced.

[b] 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.

Table 5
Lead concentration (ppm) in solution and release percentage for the glazes studied.

Sample	Pb (ppm)	% Pb released
Reference Glaze	50.66	0.167
Glaze A	0.68	0.013
Glaze B	1.51	0.033
Glaze C	0.48	0.008
Glaze D	1.52	0.048

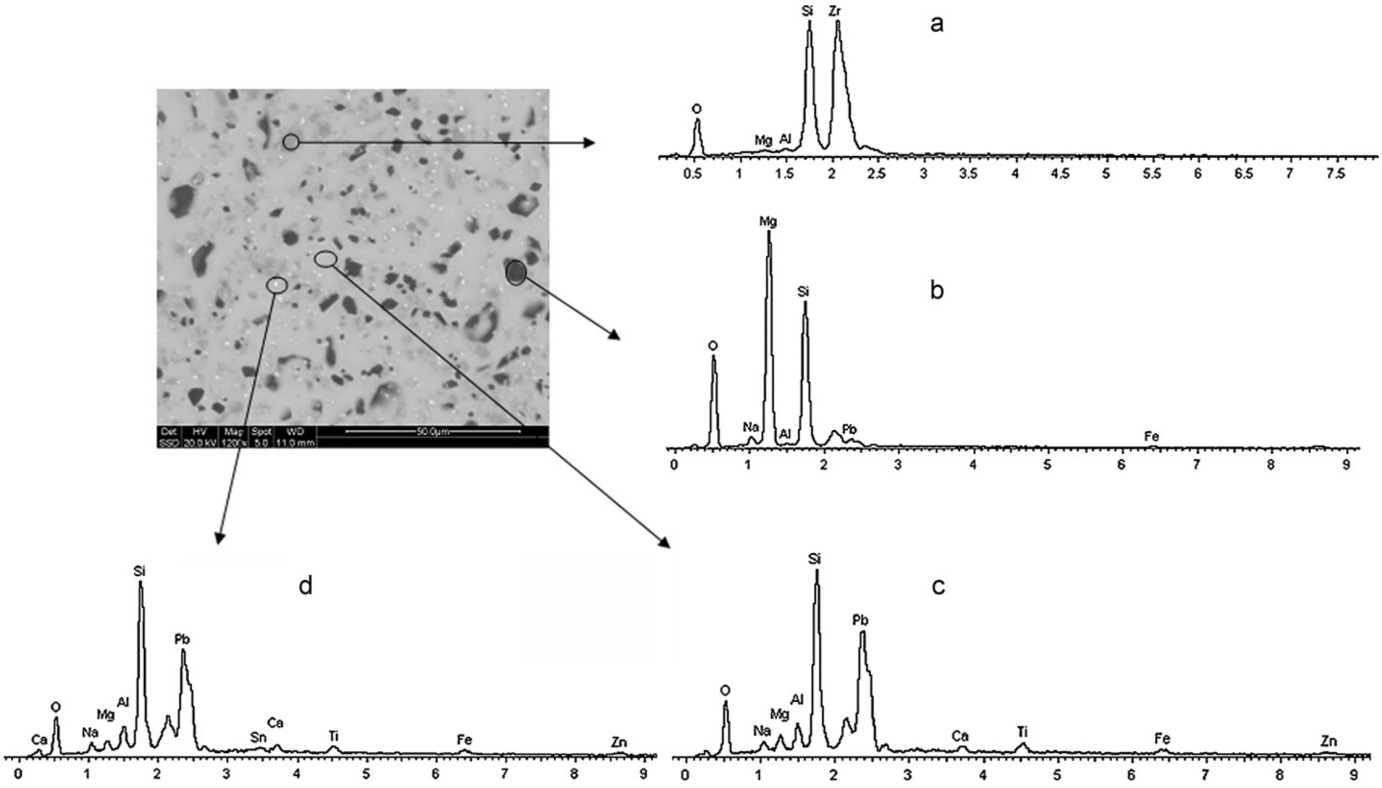

Fig. 5. SEM surface micrograph of reference glaze and EDS spectra analysis of (a) zircon; (b) olivine; (c) glassy matrix and (d) tin oxide particles in the glassy matrix.

bottom ash non-vitrified (lower cost of management) and higher content of lead glass – capable to better develop the hue. At room temperature are observed raw materials as quartz (SiO_2), baddeleyite (ZrO_2), akermanite ($Ca_2MgO_7Si_2$) and calcite ($CaCO_3$) derived from addition of bottom ash. It is evident the formation of pyroxene starting from 900 °C (crystalline phase responsible of the ochre colour in this glaze). At 1200 °C (temperature similar to the industrial firing cycle) the crystalline phases present are zircon and pyroxene only. In Fig. 4 are reported the spectra collected during cooling at 900 °C and 25 °C compared to one at 1200 °C. A small shift in 2θ range is observed in 1200 °C and 900 °C after cooling (a.c.) due to the holder expansion during heating. From the patterns it is possible to observe that the same crystalline phases are present after cooling, but a higher crystallinity is noted for both zircon and pyroxene phases (higher relative intensity in 900 °C a.c and 25 °C a.c.) compared to 1200 °C.

The results of chemical and staining resistance tests are reported in Table 4. From all the results reported in this table appears evident that 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. However, chemical durability is closely related to the crystalline phases in the surface. Staining resistance tests showed that in case of industrial glaze the stain was eliminated using water, while for the compositions A and B the stains were eliminated with blear and strong agent, respectively. In case of compositions C and D, it was not possible to remove the stains. This behaviour is probably due to the different surface characteristics of the SRM samples (roughness, porosity, etc.). This will be confirmed by the surface microstructural observation. In particular regarding acid resistance, the glazes with secondary raw materials do not present any change in the visible aspect (class A), while the reference glaze shows a light modification in the aspect (class B). The acid resistance improvement in the formulated glazes can be attributed to the pyroxenes development. This class of minerals has a good chemical resistance as evidenced by many authors [32,33].

The new formulations have very low contents in lead oxide with respect to reference glaze as shown in Table 3. In the reference glaze, it corresponds to around 30 wt%, while in A, B and C formulations it is present around 5 wt%, and only 4 wt% in D formulation. In Table 5 the values of leaching test (lead concentration in the eluates and their respective release percentage) are reported showing a strong decrease of Pb leaching due to the raw materials used. The new glazes A and B show a lead release percentage around 13 and 5 times lower than the reference glaze, while C and D glazes show 20 and 3 times lower, respectively.

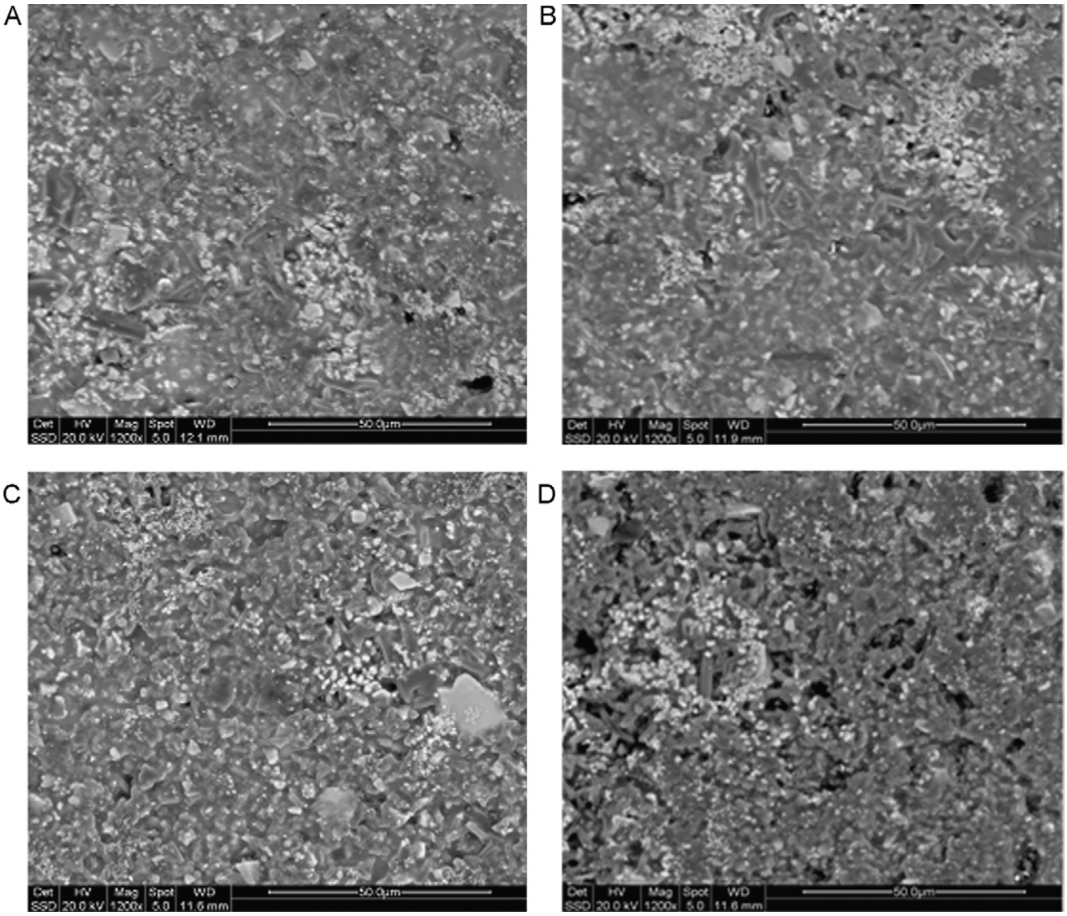

Fig. 6. SEM surface micrograph of four formulations tailored. A and B compositions with bottom ash and cone glass; C and D compositions with vitrified bottom ash and cone glass.

Table 6
Characteristic temperatures and thermal expansion coefficients for the reference glaze and glazes studied.

Sample	T (°C) Sintering	T (°C) Softening	T (°C) Melting	$\alpha \times 10^{-7}\,°C^{-1}$
Reference glaze	660	900	1020	65.18
Glaze A	950	1130	1210	65.41
Glaze B	1050	1150	1230	65.86
Glaze C	750	1111	1181	72.50
Glaze D	1060	1141	1190	72.44

As shown in Table 6, notwithstanding the different crystalline phases, the glazes A and B have a thermal expansion coefficient similar to reference one ($65 \times 10^{-7}\,°C^{-1}$), ensuring the same applicability of the industrial product. Conversely, the glazes C and D show thermal expansion coefficient significantly higher (around $72 \times 10^{-7}\,°C^{-1}$). This change is probably due to superior quantity of glass materials introduced, since in this case the bottom ashes were vitrified.

The characteristic temperatures of the tailored glazes are presented in Table 6. It is evident that in formulations with addition of SRM, the sintering, softening and melting temperatures are higher than those of reference glaze, due the lower quantities of lead oxide present in these compositions. It is important to highlight the low melting role of the lead oxide into the formulations.

Fig. 5 shows the SEM surface micrograph of the reference glaze, presenting a fine distribution of crystals embedded in a glassy phase. EDS analysis shows crystals with different composition and morphology, embedded in a matrix particularly rich in Si, Pb, and with significant amounts of Al, Mg, Na, Ti, Zr and Ca (Fig. 5(c)). The large light grey crystals have composition rich in Si and Zr corresponding to zircon (Fig. 5(a)), while dark grey crystals with polygonal shape (Fig. 5(b)) are rich in Mg and Si corresponding to olivine, both these crystalline phases were added as raw materials and detected also by XRD. Further, small white crystals rich in Si and Pb and containing Zr, Sn and Zn are evident (Fig. 5(d)).

The four glazes tailored with SRM show different surface microstructures with respect to the reference one (Fig. 6). Glaze A has a more homogeneous surface. B and D glazes show an irregular open porosity higher than glazes A and C. This is probably due to the lower amount of the low melting cone glass in the formulation as also evidenced by the characteristics temperatures which shows a refractory behaviour of these glazes. This microstructure is in agreement with the results of both staining resistance (Class1) and Pb release which is higher for B and D glazes.

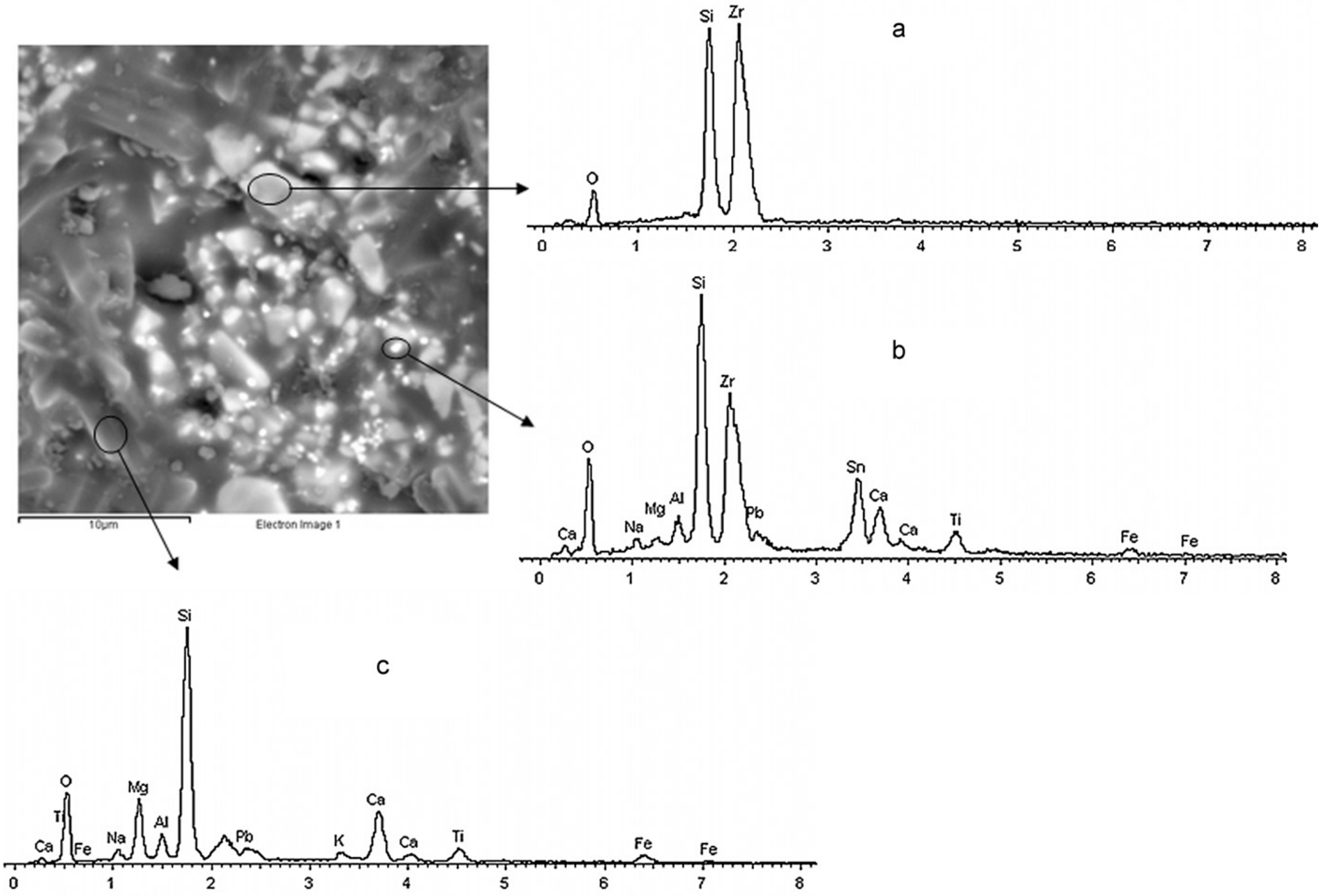

Fig. 7. SEM micrograph of surface of glaze A and EDS analysis of (a) zircon; (b) tin oxide particles in the glassy matrix and (c) pyroxene.

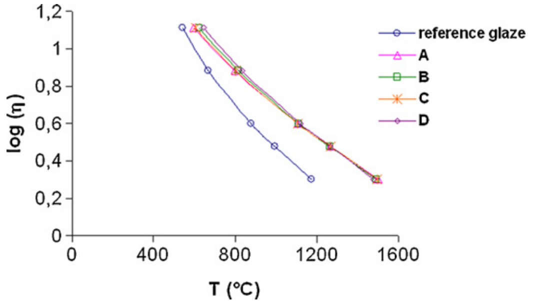

Fig. 8. Lakatos viscosity versus the temperature for the new glazes compositions compared to the reference one.

In Fig. 7 is reported a magnified view of glaze A surface. From the EDS spectra it is possible to observe zircon (Fig. 7(a)) and small white crystals rich in Sn (Fig. 7(b)) dispersed in a glassy matrix as observed previously in the reference glaze. Further crystals rich in Si, Ca, Mg, typical composition of pyroxene, are evident. This is the new phase formed by the bottom ash contribution into the glaze and it is responsible of the colour development in these glazes.

In order to further investigate the thermal behaviour, optical dilatometry measures were performed. The optical dilatometry and SEM measures evidence that the formulations have different sintering behaviour (Table 6), probably due to the changes of viscosity during firing. In particular B and D formulations shows higher sintering and softening temperatures confirming the more porous surface microstructure evidenced by SEM. In order to support this hypothesis, a theoretical calculation of Lakatos viscosity as a function of the temperature has been performed for both the reference glaze and the formulations using SRM. The method is based on the linear dependence between the glass constituent concentrations expressed in mol% and viscosity (standard deviation ~3.0 °C). In this theory the interactions among the glass constituents have not been considered [34].

In Fig. 8, the calculated log viscosity–temperature curves have been plotted in the range of viscosity 10^2–10^{13} poise. A higher viscosity is observed in the new formulations with respect to reference glaze within the analyzed temperature range (20–1500 °C), thus confirming the SEM and Optical Dilatometer results above described.

4. Conclusions

The results obtained demonstrated the possibility to minimize Pb content by reformulating a commercial ceramic glaze with secondary raw materials (MSWI bottom ash and CTR cone glass). In particular, the glazes reformulated showed better acid resistance than the standard glaze and good aesthetic characteristics. With these formulations it is possible to obtain glazes with significantly lower Pb content respect to reference glaze, and consequently the release percentage. The interesting findings encourage an industrial further investigation thanks to both good technological results and environmental advantages. The valorisation of the selected secondary raw materials in the studied application implies: reducing of natural raw materials use, energy saving (for the avoided use of commercial frits) and reduction of lead in the new compositions according to the European REACH directive. Moreover considering the high percentage (50–60%) of secondary raw materials used in these formulations, good opportunities for LEED (Leadership in Energy and Environmental Design) certification are foreseen.

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