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The recycling of MSWI bottom ash in silicate based ceramic

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Abstract

The possibility of recycling the Municipal Solid Wastes Incinerated (MSWI) bottom ash by its incorporation in ceramic tiles was investigated. The MSWI bottom ash was introduced both in untreated (previous deironization) and vitrified condition. The sintering of the different products was investigated by determining water absorption and linear shrinkage. To evaluate possible variations due to the presence of different amount of bottom ash, mineralogical and microstructural examinations by quantitative X-ray diffraction and scanning electron microscopy, were performed. While the untreated bottom ash, till an amount of 5 wt%, did not seem to affect the above characteristics of selected materials, the vitrified bottom ash, 5–10 wt%, as strong fluxing agent, promoted the sintering of porcelain stoneware. Leaching results allow to assert that the fired samples are not dangerous.

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1. Introduction

In 2008 about 32.5 millions tons (0.2% less respect to 2007) of municipal solid wastes (MSW) have been produced in Italy. 44.9% of this amount (16 millions tons) has been landfilled without pre-treatment, while only the 10.9% of MSW (4.1 millions tons) have been incinerated (MSWI). Besides this latter quantity, about 450 thousand tons of special wastes and 39 thousand tons of sanitary wastes, have to be added. The total amount of incinerated wastes in MSW incinerator is around 4.1 million tons [1].

From the incineration of municipal wastes, bottom ash with volume ranged between 10% and 12% of the starting waste volume and weight between 20% and 35% of the starting waste weight, is obtained [2,3]. According to this data, in Italy, the annual production of MSWI bottom ash could be estimated in about 797 thousand tons, a significant amount of which is landfilled (about 49.2%) [4].

The aim of this study has been to evaluate the possibility of recycling bottom ash in ceramic tiles as a secondary raw material (SRM). The bottom ash was also vitrified with the main scope of sealing several pollutants in a higher chemically stable glassy material. The environmental benefit of waste stabilization could be coupled with economic advantages, if the waste glass represents a valid SRM.

Ceramic bodies, such as tiles, are heterogeneous materials, consisting mostly of natural raw materials mixes having a wide range in composition. It means that, these products can tolerate the substitution of different types of waste materials rather well, even in high percentages [5–7]. The relatively high firing temperature normally adopted (>1000 °C), should promote effective incorporation of wastes into ceramic matrix. Moreover, strongly reactive heavy metals and transition metals, often contained in wastes, tend to promote sintering process. The incorporation of wastes in ceramic body mixes can have a positive effect on the firing process, by saving energy as a consequence of the reduction of sintering temperature. Besides, the final products frequently do not show hazardous leaching characteristics [8–10].

In the present work, untreated and vitrified bottom ash denoted in the following U and V, respectively, have been used in the preparation of different body mixes, starting from two industrial mixes, i.e. porcelain stoneware and porous single firing ("monoporosa") tiles.

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Porcelain stoneware tile, characterized by very low water absorption, <0.5% [11], and high values of density and mechanical strength, represents the best product, in terms of technical performances, developed in the field of ceramic tiles. This product is the result of an industrial processing of a mix of raw materials, rich in fluxing agents that, fired at high temperature, around $1200\,^{\circ}\text{C}$, develops a large amount of glassy phase able to strongly densify the material. A typical composition contains 25-50% of kaolinitic and ball clays, 50-60% of feldspar sand and 5-10% of quartz sand.

Porous single firing is characterized by relatively high water absorption, >10% [11]. In comparison with porcelain stoneware, it is a product with lower density and mechanical strength. It is a useful product suitable for wall covering, resulting from an industrial processing of a mix of raw materials with lower added value. A typical composition contains 30-40% of ball clays, 20-50% of feldspar sand and 10-15% of carbonate.

Different porcelain stoneware compositions, using both U and V bottom ash, have been tailored, while for porous single firing, only U bottom ash was considered, due to: (1) the vitrifying costs that do not justify its use in a low added value product; (2) the porous characteristic of the product that does not need a sintering precursor as vitrified bottom ash.

The modified compositions have been characterised to evaluate their performance in comparison with the current products. To assess the environmental impact in accordance with the Italian regulation implementing the EU directives, leaching tests have been carried out both on the materials and the U and V bottom ash.

2. Materials and experimental

For present investigation a bottom ash from an incinerator plant placed in north of Italy, which only treats municipal wastes, was considered. In particular, U and V bottom ash were used, in order to verify the possibility of conditioning them in ceramic tiles. For this purpose two typologies of industrial mixes were selected for: (i) porcelain stoneware and (ii) porous single firing tiles.

2.1. Characterization of U and V bottom ash

The bottom ash used in this research is classified as special not hazardous waste and it is codified by the European Waste Catalogue (EWC) as 190101.

The U material was submitted to the following preliminary treatments: deironization by passing a simple magnet on the layered powder, drying at about 105 $^{\circ}$ C for 24 h to eliminate the humidity content, grinding in a laboratory ball mill to obtain a powder ($d_{90} < 300 \ \mu m$).

To evaluate the chemical composition of U, total metals content was determined. About 500 mg of powder samples were directly inserted into microwave closed vessels (PTFE) with 8 ml of HNO3/HCl Suprapur (ratio 1/3) at 210 °C for15 min in microwave oven (Multiwave 3000 – Anton Paar). After cooling down, digests were transferred to glass

volumetric flasks and the volumes were made up to 50 mL with deionised water. Then, elemental analysis (Al, As, Cd, Co, Cr, Cu, Fe, K, Mn, Na, Ni, Pb, Zn) was performed by means ICP/AES (Thermo Jarrell Ash, Iris Advantage with vaporizer Cetac Technologies U5000AT+, US).

Glass with bottom ash has been obtained, without adding others components, by melting at about 1400 $^{\circ}$ C in an electric furnace (Lenton, mod. EHF 17/17, UK) with a heating gradient of 5 $^{\circ}$ C/min up to 500 $^{\circ}$ C and 10 $^{\circ}$ C/min from 500 $^{\circ}$ C to the maximum temperature with 1 h of soaking time. The chemical composition (oxides wt%) of the MSWI bottom ash, U and V, was analysed by atomic emission spectroscopy (Philips ICP – AES Varian Liberty 200, NL).

X-ray diffraction analysis was carried out by a powder diffractometer (PW3830, Philips, NL) with Ni-filtered CuK α radiation in the 5–70 $^{\circ}$ 2 θ range on both U and V powders (30 μ m particle size).

The compliance leaching test has been performed on U and V, according to the Standard EN 12457-2 [12]. The samples, which originally and after a pre-treatment had a size below 4 mm, were put in contact with distilled water in capped bottles. Liquid to solid ratio was 10/1 and the suspension was agitated for 24 h at room temperature, 20 ± 5 °C. Solid residue was separated by filtration and on each eluate pH (pH meter Crison – Basic 20, S) and conductivity (Radiometer Analytical – Meterlab CDM210, F) were determined. Furthermore, after acidification (pH 2 using HNO₃) metals content was analysed by ICP/AES.

To prepare the ceramic mixes, U and V were ground by using a zirconia jar mill to an average dimension of 40 μ m (d_{50}), controlled by laser granulometer (Master-Size 2000, Malvern, UK).

2.2. Samples preparation and characterization

The porous single firing body mix, denoted M, was composed by 40% of illitic-kaolinitic clay, 25% of Na-feldspar, 25% of feldspathic sand and 10% of dolomite. A modified body mix, denoted M5U, was obtained by adding 5 wt% of U to the raw materials.

The porcelain stoneware body mix, denoted P, was composed by 40% kaolinitic and illitic clays, 40% Na-feldspar sand, 20% K-feldspar sand. Two modified body mixes were prepared, replacing 2 and 5 wt% of Na-feldspar sand, with the same percentages of U, denoted P2U and P5U, respectively. Other two body mixes denoted P5V and P10V, respectively, were obtained by substituting 5 and 10 wt% of Na-feldspar sand, with V.

Chemical analyses were determined by inductively coupled plasma optical emission spectroscopy (ICP–OES Optima 3200 XL, Perkin-Elmer, US).

Porous single firing and porcelain stoneware mixes were prepared by milling the raw materials in a porcelain jar mill for 1 h, with 30 wt% of water and 1 wt% of a deflocculant (FLUICER CF907, Ceramco, Zwischer and Schwarz Group, D). To obtain powders suitable for shaping, the slips were dried overnight in an oven at 110 $^{\circ}$ C, crushed and sieved to pass at 125 μ m screen. Test specimens were then prepared in form of

Table 1 Chemical composition (oxides wt%) of U, V and ceramic mixes.

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	MnO	PbO	ZnO	CuO	L.I.a
Bottom o	ash												
U	33.70	13.31	1.52	5.37	35.00	4.62	1.66	2.27	0.14	0.33	0.27	0.11	1.70
V	34.22	13.46	1.54	5.73	35.58	4.67	1.68	2.29	0.14	0.32	0.26	0.11	0.00
Porous s	ingle firing												
M	61.29	17.73	0.67	0.53	4.24	2.06	1.69	2.97	0.00	0.00	0.00	0.00	8.49
M5U	59.87	17.49	0.71	0.78	5.74	2.18	1.69	2.93	0.01	0.02	0.01	0.01	8.15
Porcelair	n stoneware												
P	72.36	17.15	0.48	0.49	0.68	0.25	1.85	3.53	0.00	0.00	0.00	0.00	3.19
P2U	71.31	17.23	0.51	0.60	1.37	0.34	1.79	3.54	0.00	0.01	0.01	0.00	3.22
P5U	69.10	17.18	0.55	0.75	2.38	0.47	1.68	3.52	0.01	0.02	0.01	0.01	3.22
P5V	69.88	17.36	0.56	0.76	2.41	0.48	1.70	3.56	0.01	0.02	0.01	0.01	3.15
P10V	67.32	17.34	0.63	1.02	4.13	0.70	1.54	3.36	0.01	0.03	0.03	0.01	3.17

^a L.I. = loss on ignition.

disks (40 mm in diameter), by pressing the powders after an addition of 6 wt% of water, at 52 and 30 MPa for porcelain stoneware and porous single firing body mixes, respectively. Firing was performed in an electrical muffled furnace (MAB, FM76, I), following four scheduled thermal cycles, adopting a heating rate of 5 °C/min and a natural cooling to room temperature. While for porous single firing mixes three maximum temperatures, 1100, 1120 and 1140 °C, were chosen, for porcelain stoneware mixes, four temperatures were adopted, 1120, 1140, 1160 and 1180 °C. The firing behaviour of the specimens was evaluated on the basis of their linear shrinkage. Water absorption and bulk density were determined according to the test method recommended for ceramic tiles, reported in the Standard ISO 10545-3, 1997 [13]. The total porosity was also calculated on the basis of absolute density of powdered fired samples, following the Standard ASTM C329-88 [14].

The quantitative mineralogical compositions of fired samples were determined by X-ray diffraction analysis (PW3830, Philips, NL). Powdered specimens, diluted with 10 wt% of corundum NIST 676 as internal standard, were side loaded to minimize preferred orientation. Data were collected in the angular range $10-80^{\circ}$ 2θ with steps of 0.02° and 5 s/step and the Rietveld refinements were performed, using GSAS-EXPGUI [15,16].

The microstructure of the fired materials was analysed by scanning electron microscope, SEM (Zeiss EVO 40, D), equipped with energy dispersion X-ray attachment, EDS (Inca, Oxford Instruments, UK).

To establish the environmental risk in the use of MSWI bottom ash, leaching tests were performed on the fired samples, M5U, P2U and P5U, containing U, according to the standard EN 12457-2 [12]. The searched elements were those indicated in the Italian regulation used to classify the granulated and monolithic residues for landfilling (D.M. 30/08/05) [17].

3. Results and discussion

3.1. Untreated and vitrified MSWI bottom ash

The chemical composition (Table 1) of U shows SiO₂, Al₂O₃ and CaO as main components and a content of about 4 wt% of

alkali oxides which can behave as fluxing agents. This composition promotes, with clays and others raw materials, the formation of a silicatic matrix. Furthermore the presence of chromophore oxides (Fe₂O₃, TiO₂, MnO and CuO) is also evident (about 6 wt%) and this raw material feature limits the amount of introduction, in particular in porcelain stoneware.

From the data reported in Table 1, the similar composition of MSWI bottom ash before and after vitrification, U and V, may indicate that neither volatilization nor crucible interaction phenomena occur during the thermal treatment.

XRD spectra shown in Fig. 1 were made on air dried U and V powders. U material shows the presence of quartz (SiO₂) as main phase, calcite (CaCO₃), gehlenite (CaAl₂SiO₇), anorthite (CaAl₂Si₂O₈) and traces of gypsum (CaSO₄·2H₂O), thenardite (Na₂SO₄) and mirabilite (Na₂SO₄·10H₂O), a hydration product of thenardite. The little amount of mirabilite is induced by relative humidity present in the atmosphere [18]. V material resulted completely amorphous as it is evident by the broad band between 20° and 30° in the pattern.

To evaluate if the firing process influences the recycling of bottom ash, an investigation of waste chemical composition and harmful substance mobility was performed. The presence of metals has been determined by direct comparison of the leaches before and after vitrification. The results presented in Table 2,

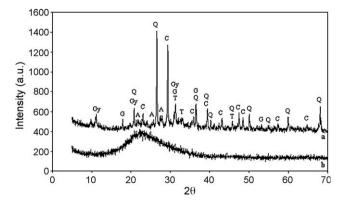


Fig. 1. Comparison between U (a) and V (b) XRD spectra: Q, quartz; C, calcite; G, gehlenite; A, anorthite; Gy, gypsum; T, thenardite and M, mirabilite.

Table 2 Metals content in U and leaching values for U and V.

Metals	U metals content (mg/kg)	U metals released (mg/l)	V metals released (mg/l)	Limit value inert wastes ^a (mg/l)	Limit value not hazardous wastes ^a (mg/l)
Cu	1,041	0.480	0.320	0.2	5.0
Zn	903	0.019	0.073	0.4	5.0
Co	14	< 0.003	< 0.003	_	_
Ni	45	< 0.003	< 0.003	0.04	1.0
As	16	0.033	0.003	0.05	0.2
Cd	92	0.008	< 0.001	0.004	0.02
Cr	119	< 0.001	< 0.001	0.05	1.0
Pb	4,552	0.530	0.150	0.05	1.0
Al	30,600	90.4	0.100	_	_
Fe	8,653	< 0.01	0.170	_	_
Mn	518	< 0.003	0.007	_	_
Na	11,200	151	0.310	_	_
K	9,980	52.8	0.260	_	_

^a [17].

in which the first column reports the metals content in U, show a heavy metal burden with high concentrations of Pb, Cu and Mn.

The results of leaching tests show that U is characterized by a conductivity 1490 µS/cm and 11.16, while V by 11.4 µS/cm and 6.32, respectively. U shows a high release of heavy metals and solubilisation of alkaline metals (Table 2). This residue derives from the waste combustion and it is constituted also by an unburned fraction that can causes DOC (Dissolved Organic Carbon) leaching and enhancing mobilization of metals because of complexation.

By analysing the different materials leaching, it can be observed that V material shows lower values with respect to the waste before thermal treatment, due to the mobility of metals, i.e. Pb is lower. The bottom ash vitrification reduces the leachability of the hazardous species present, confirming that the amorphous structure fixes metals by chemical bonds in an aluminium silicate network. In fact Al, which takes part to the glassy phase, is not released, highlighting that the glass lattice is not solubilised. Soluble metals such as Na and K are also embedded in the glassy phase, showing low releases and confirming a near to neutral value of pH. A further confirmation of the vitrification effectiveness is evidenced by the reduction, about two orders of magnitude, of the glass eluate conductivity. Since the value of Cu and Pb releases are higher than the limits established by the Italian regulation that implements the EU directives about the waste landfilling [17], both the U and V materials cannot be classified as "inert wastes", but can be considered "not hazardous wastes". On the basis of these remarks, the vitrification process can be important but not sufficient to classify the material as inert.

3.2. Porous single firing mix

The addition of 5 wt% of MSWI bottom ash in porous single firing mix, did not give rise to a significant variations in the chemical composition. Respect to the reference material, M, the modified mix, M5U, shows only a small increase of CaO and a concomitant decrease of SiO₂ (Table 1). From Fig. 2, it is clear that these changes are not sufficient to cause a different firing behaviour. Both the samples, at all firing cycles, are characterized by water absorption >10 wt% (Fig. 2a) and they can be considered belonging to BIII Group [11]. In particular, at 1120 and 1140 °C, the water absorption values are rather similar (about 14 and 12 wt%, respectively) for both the samples M and M5U. Also the linear shrinkage (Fig. 2b) follows a similar trend.

By SEM images of the fracture surfaces of M and M5U, both fired at 1120 °C (Fig. 3), it is possible to note the considerable level of interconnected porosity. Their physical characteristics, reported in Table 3, confirm that porous single firing samples show very close values of bulk and apparent density and a high level of open porosity typical of this class of products.

The quantitative mineralogical composition of porous single firing samples, fired at 1120 °C, reported in Table 4, confirms

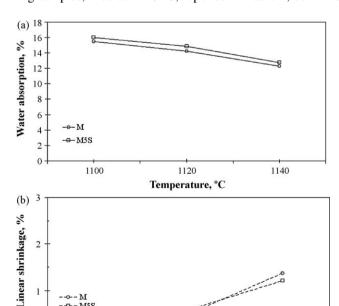


Fig. 2. Water absorption (a) and linear shrinkage (b) of porous single firing samples containing and not U as a function of temperature.

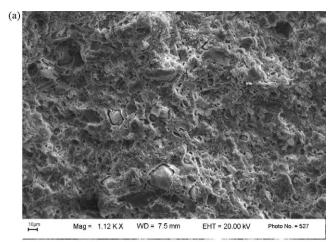
1120

Temperature, °C

1140

-- -- M5S

1100



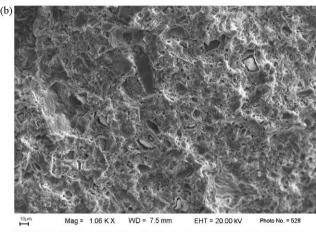


Fig. 3. SEM micrographs of fracture surfaces of porous single firing samples: (a) M and (b) M5U, fired at $1120\,^{\circ}$ C.

once again that the addition of 5 wt% of bottom ash does not cause significant changes. The amounts of quartz, plagioclase (bytownite type) and alkali feldspar (anorthoclase type) coming from the raw materials, are practically the same and also the amorphous phase does not change.

3.3. Porcelain stoneware mix

The substitution of Na-feldspar with different percentages, 2 and 5 wt%, of U and 5 and 10 wt% of V, gives rise to some

changes in the chemical composition of porcelain stoneware material in comparison with the reference, P (see Table 1).

In particular, it is important to note a progressive increasing of CaO and the concomitant decreasing of SiO_2 , a slight increase of chromophore oxides (Fe_2O_3 , TiO_2) while other oxides, such as, MgO and K_2O , do not vary significantly.

The effect is different, depending on the condition of added MSWI bottom ash, U and V. This is evident, considering the firing behaviour of porcelain stoneware samples containing 2 and 5 wt% of U and 5 and 10 wt% of V (Fig. 4).

The reference material, P, reaches a water absorption value $<\!0.5$ wt% at $1160\,^{\circ}\mathrm{C}$ (0.02 wt%) and has to be considered belonging to BIa Group [11]. The replacement of Na-feldspar sand with 2 wt% of U, P2U, does not influence significantly the water absorption, as it appears evident comparing the behaviour of P and P2U, in Fig. 4a. A higher amount of U, 5 wt%, causes, at the same temperatures, a slight decrease of the sintering, see the values of water absorption.

On the other hand, the introduction of 5 and 10 wt% of V in porcelain stoneware mix, favours the firing process. Already at $1140\,^{\circ}\text{C}$, both P5V and P10V, present values of water absorption <0.5%, 0.30 and 0.37 wt%, respectively. It has to be noted that the reference material reaches the same condition at $1160\,^{\circ}\text{C}$ (Fig. 4a).

From Fig. 4b it is clear that P reaches the maximum shrinkage at 1160 °C and its behaviour is rather stable also at higher temperatures. Also samples P2U and P5U, reach the maximum shrinkage at the same temperature, even if the material P5U results slightly less stable at higher temperatures. In samples P5V and P10V, the dimensional stability results to be quite compromised and, at temperature >1160 °C, a significant expansion happens.

The physical characteristics of fired samples, reported in Table 3, are supported by SEM observations. The reference material P, fired at 1140 °C, shows a microstructure characterized by a rather widespread porosity essentially interconnected (Fig. 5a) in agreement with the still high water absorption. Increasing the firing temperature, till 1160 °C, the larger development of liquid phase allows to close the open pores, resulting in a more compact microstructure (Fig. 5b). At the same temperature, 1160 °C, the presence of 2 and 5 wt% of U, make it possible to obtain a similar compact microstructure (Fig. 6a and b). Nevertheless, even if the closed porosity is similar, in P5U

Table 3
Physical characteristics of the fired porous single firing and porcelain stoneware samples.

	Bulk density (g/cm ³)	Apparent density (g/cm ³)	Open porosity (vol.%)	Closed porosity (vol.%)
Porous single firing				
M, 1120 °C	1.90	2.64	28.30	0.42
M5U, 1120 °C	1.95	2.60	24.86	1.88
Porcelain stoneware				
P, 1140 °C	2.39	2.47	3.18	1.49
P, 1160 °C	2.43	2.43	0.01	2.66
P2U, 1160 °C	2.45	2.45	0.12	2.02
P5U, 1160 °C	2.44	2.44	0.12	2.42
P5V, 1140 °C	2.43	2.43	0.07	2.35
P10V, 1140 °C	2.41	2.41	0.03	3.06

Table 4
Quantitative mineralogical composition (wt%) of fired porous single firing and porcelain stoneware samples.

	Quartz	Mullite	Plagioclase	Anorthoclase	Glassy phase
Porous single firing					
M (1120 °C)	23.0 ± 0.2	_	31.3 ± 0.4	5.4 ± 0.4	40.3 ± 1.2
M5U (1120 °C)	24.8 ± 0.2	_	30.0 ± 0.5	5.4 ± 0.5	39.8 ± 1.3
Porcelain stoneware					
P (1160 °C)	21.4 ± 0.1	5.3 ± 0.5	$3.4 \pm 0.4^{\rm a}$	_	69.9 ± 1.2
P2U (1160 °C)	20.6 ± 0.1	5.7 ± 0.4	10.5 ± 0.8	_	63.2 ± 2.2
P5U (1160 °C)	19.1 ± 0.1	4.4 ± 0.4	15.6 ± 0.7	_	60.9 ± 2.1
P5V (1160 °C)	18.0 ± 0.1	4.6 ± 0.4	17.4 ± 0.7	_	59.9 ± 2.1
P10V (1160 °C)	14.5 ± 0.2	3.3 ± 0.3	25.3 ± 0.6	_	56.8 ± 2.0

Agreement factors for all the refinements: wRp 0.08-0.07; χ^2 5.4-3.7.

material, the pores size seems to be larger and their distribution does not appear homogeneous (Fig. 6b).

Also in the samples containing V, P5V and P10V, fired at 1140 °C, the closed porosity is not significantly different if compared with the reference material P fired at the same temperature. Microstructural observations (Fig. 7a and b) reveal the presence of round and rather large pores. Since, after vitrification of bottom ash, a refinement is not foreseen, the closed porosity could be attributed to the development of gasses, trapped in the material during firing [19]. Moreover, the composition of the glassy phase may change upon devitrification, [20,21] limiting the solubility of dissolved gas and promoting the nucleation of bubbles.

The quantitative mineralogical analysis (Table 4) points out that the replacement, in increasing percentages, of the feldspathic fluxes with both U and V, promotes the crystal-

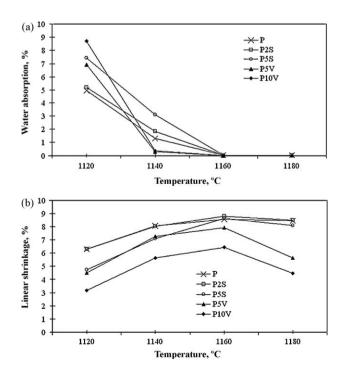


Fig. 4. Water absorption (a) and linear shrinkage (b) for porcelain stoneware samples containing U and V as a function of temperature.

lization of plagioclase, in particular of Ca-plagioclase (bytownite type), according to the increased content of CaO due to bottom ash (Table 1). On the other hand, the presence of plagioclase (Na-plagioclase) present in the standard composition comes from incomplete melting of the raw materials [22]. On the contrary, the amount of mullite decreases, due to the consumption of SiO_2 and Al_2O_3 by the crystallization of feldspars. Because of the higher crystallization, the amorphous

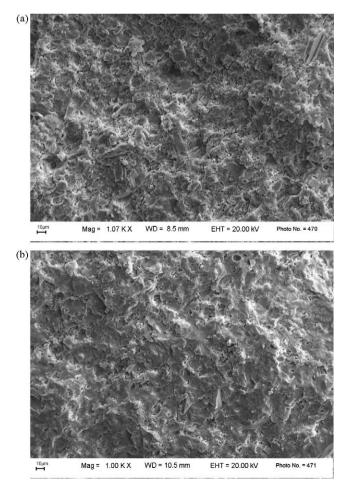


Fig. 5. SEM micrographs of fracture surfaces of porcelain stoneware reference material P: (a) fired at $1140\,^{\circ}$ C and (b) at $1160\,^{\circ}$ C.

^a Na-plagioclase residual from the raw materials.

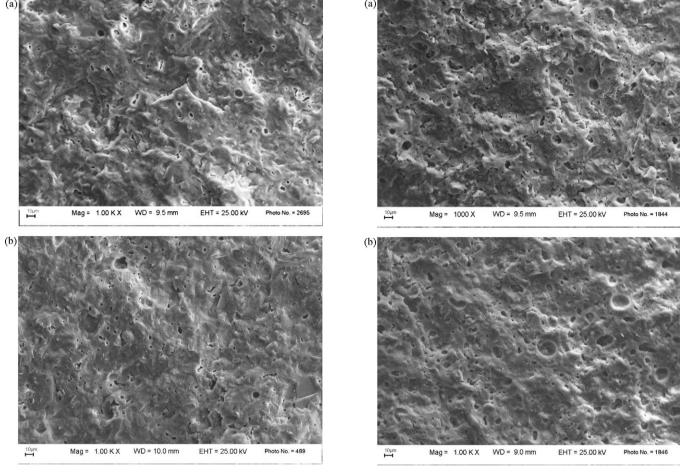


Fig. 6. SEM micrographs of fracture surfaces of porcelain stoneware samples containing U: (a) P2U and (b) P5U, fired at $1160\,^{\circ}$ C.

Fig. 7. SEM micrographs of fracture surfaces of porcelain stoneware samples containing V: (a) P5V and (b) P10V, fired at $1140\,^{\circ}$ C.

phase content decreases, increasing the bottom ash in the mix. It has to be noted that the mineralogical composition of P5U, containing 5 wt% of U and P5V, containing the same percentages V, are not so different.

Leaching tests have been performed on the samples containing U, in particular M5U fired at 1120 °C, and P2U and P5U both fired at 1160 °C. It has to be underlined that, at the moment the Italian environmental legislation does not contemplate a test to check the leaching of final products such as ceramic tiles obtained by recycling different type of wastes.

Therefore it was seemed reasonable to adopt the methodology for granular and monolithic residues with moderate and irregular shape, specified in the Standard UNI 10802 [23].

The results reported in Table 5, confirm that the firing at high temperatures $>1000\,^{\circ}\text{C}$, allows the development of a silicatic matrix able to incorporate and block inside the amorphous phase the dangerous elements, as it was found for the vitrified bottom ash, previously described. In particular, the soluble heavy metals are embedded in the matrix, giving rise to a very low release and allowing to classify these materials as "inert

Table 5
Leaching test results of fired samples containing U.

	M5U (1120 °C) (mg/l)	P2U (1160 °C) (mg/l)	P5U (1160 °C) (mg/l)	Limit value inert wastes ^a (mg/l)
Cu	0.006	0.005	0.015	0.2
Zn	0.004	0.001	0.006	0.4
Co	0.000	0.000	0.000	_
Ni	0.015	0.016	0.012	0.04
As	0.000	0.000	0.000	0.05
Cd	0.000	0.000	0.000	0.004
Cr	0.039	0.000	0.000	0.05
Pb	0.005	0.004	0.008	0.05
SO_4	1.211	0.000	0.000	100

^a [17].

wastes" [17]. Moreover, even if the leaching tests were carried out on granulated materials, more reactive than the monolithic samples, it is important to underline that, the leaching values obtained for heavy metals, are very low.

4. Conclusions

The recycling of untreated and vitrified bottom ash, U and V, into traditional ceramic tiles is technologically feasible. While the addition of 5 wt% of U to porous single firing mix did not give rise to significant changes in comparison with the reference material, the substitution >5 wt% in a porcelain stoneware mix favoured a higher crystallization. The substitution in porcelain stoneware mix of both 5 and 10 wt% of feldspar with V favoured not only an incipient crystallization, but helped also the sintering process, allowing a reduction of the maximum firing temperature of about 20 °C.

Leaching tests performed on bottom ash showed that its vitrification is important to decrease the heavy metal release. However the thermal treatment is not sufficient to classify the resulting material as inert. In any case the vitrified bottom ash is more suitable to be used as SRM in the silicate based ceramics, in particular in porcelain stoneware tiles.

The present work suggests that the ceramic tiles industry might represent an opportunity to recycle untreated and vitrified bottom ash.

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