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Reuse of incinerator bottom and fly ashes to obtain glassy materials

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Abstract

Bottom and fly ashes coming from the urban wastes incineration represent a by-product nowadays landfilled. By mixing different amount of these residues with others inert materials, such as glass cullet and feldspar waste, two vitrifiable mixtures are tailored. Glasses, obtained by means of vitrification process, are chemically stable with low leachability of contaminants and show comparable properties to those of commercial soda-lime glasses. Moreover, from the thermal and mechanical characterisation the tendency of these glasses to crystallise, for their transformation into glass-ceramic materials, has been evidenced.

Keywords: Incineration; Wastes; Vitrification

1. Introduction

In 2005 about 31.7 millions tonnes of municipal solid wastes are produced in Italy. 48.8% of this amount (15.4 millions tonnes) has been landfilled, while only 3.2 millions tonnes have been incinerated. Besides this latter quantity, about 611,000 tonnes of refuse-derived fuel (RDF), 514,000 tonnes of special wastes and 40,000 tonnes of sanitary wastes, have to be added. The total amount of incinerated wastes is around 4.4 million tonnes [1].

Even though from 2000 to 2006 the incinerator number is increased of 7 units (from 43 to 50 and others 9 are under construction), an efficient integrated system for the waste management, from a technical and economical point of view, is not reached. The Agency for Environmental Protection and Technical Services (APAT), claims that at least 25% of the produced wastes should be incinerated with energy recovery [1]. The potential expansion of the incineration process leads to a corresponding increase of the bottom and fly ashes amounts which have to be landfilled.

From the incineration of municipal wastes, bottom ash with volume ranged between 10 and 12% of the starting volume of the waste and weight between 20 and 35% of the starting weight of the waste, are obtained. On the other hands, fly ash are obtained with a percentage of 2–5 wt% [2,3]. According to this data the annual production of municipal incinerator bottom and fly ashes (starting from 3.2 millions tonnes of municipal solid waste incinerated) could be, respectively estimated in about 1,200,000 and 150,000 tonnes, significant amount which is mainly landfilled. In this context it is important to develop new recovery processes in order to increase the application field of these residues.

The vitrification process, which fixes toxic elements present in chemically unstable compounds, has been successfully experimented in the inertization of nuclear wastes [4]. It is possible, by mixing different wastes, to tailor vitrifiable mixtures, which can be melted and transformed into chemically stable glasses with low leachability of the contaminants. This kind of materials can be exploited in the construction field.

In the present research, glassy compositions containing incinerator bottom and fly ashes, glass cullet and feldspar wastes have been tailored and prepared. The obtained materials have been characterised in order to evaluate their reuse.

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2. Experimental procedures

The materials used in this research are municipal waste incinerator bottom and fly ashes, glass cullet from the municipal recycling program and feldspars extraction waste. The fly ash characterisation has needed pre-treatments such as washing with distilled water to separate and quantify the soluble fraction. From this analysis results that the soluble fraction corresponds to 14.5% and the insoluble fraction 85.5%. The results point out that in the soluble fraction chlorines has the higher percentage (11%), followed by K_2O (5%), Na_2O (3.7%), CaO (1.4%), NO_3^- (0.006%), SO_4^{2-} (0.44%). The lost of ignition of the fly ash, performed at 970 °C is 8.4%. In Table 1 the chemical composition, analysed by X-fluorescence (Philips PW 2004), of the insoluble fraction calcined at 970 °C has been reported.

For the bottom ash some pre-treatments such as magnetic separation and grinding (particle size <0.4 mm) have been necessary. The chemical analysis has been performed by X-fluorescence on the sample calcined at 1100 °C (higher temperature causes the melting of the sample) (Table 1) and the lost of ignition is 11 wt%. In order to inertize the incinerator residues, a vitrification process has been performed. In particular two ternary mixtures have been tailored: (V1) 50% bottom ash, 5% fly ash and 45% glass cullet and (V2) 53% bottom ash, 4% fly ash and 43% feldspars residue. The choice of these formulations is related to the different characteristics of glass cullet and feldspar waste and to the necessity of balancing the ratio of Si/Al/Ca in the final glass. Glass cullet, in fact, contains high amount of calcium oxides, capable to favour crystal growth in the glass, and feldspar wastes, particularly rich in alumina, renders the glass network more resistant to chemical reagents.

For the inertization, the patent procedures (01.305245) of the Stazione Sperimentale del Vetro [5] has been followed (melting at about 1400 °C). The aim of the patent is to consider the inorganic waste as raw material employed in the formulation of batches with at least 95% of waste. These batches are suitable for the production of glass from which it could be possible to make products with commercial added value. Glasses have been subjected to 24 h test according to UNI 10802 ("Rifiuti liquidi, granulari, pastosi e fanghi—Campionamento manuale e preparazione ed analisi degli eluati" October 2004 [6] derived from the European norm EN 12457 "Characterisation of waste-Leaching-Compliance test for leaching of granular waste materials and sludges"). Sample was placed in bidistilled water with a leaching volume/material weight ratio of 10 l/kg and maintained for 24 h. After filtration, the chemical composition of the eluate has been analysed by ICP (ICP-AES—Thermo Jarrell Ash, Iris Advantage with vaporizer Cetac Technologies U5000AT+) and pH (pHmeter Crison—Basic 20) and conductivity analysis (Radiometer Analytical—Meterlab CDM210) have been performed. The thermal properties of the prepared materials have been studied by means of differential thermal analysis (Netzsch DSC 404) (heating rate 10 °C/min, particle size <25 μm) in order to investigate glass transition temperature and crystallisation temperature, dilatometry and optical heating microscopy (MISURA 3.32) in order to evaluate linear expansion coefficient α, sintering and softening temperatures. For dilatometry (Netszch model EP 402) the samples were glass bars of 15 mm × 5 mm × 5 mm heated at 50 °C/min. For optical heating microscopy, glass powders were manually pressed and formed to obtain a cylindrical samples with a diameter of 2 mm and height 3 mm successively heated at 50°C/min. In order to evaluate the technological characteristics of these glasses, Vickers microhardness, with a load of 25 gf (H_v), fracture toughness (K_{Ic}) (REMET HX-1000) and dry abrasion resistance (Ceramic Instruments AP/87 abrasimeter) measurements have been conducted. This last test was conducted at 7, 14 and 21 revs using alumina FEPA 80 with mean diameter around 180 μm as abrading agent. A flux of this alumina falls tangentially to a rotating steel disk (diameter of 200 mm), pressed by a fixed load against the tested surface. In order to make the measurements comparable, the abraded volume (V expressed in mm^3) is normalized by the overall distance L (in m) covered by the disk in its N revolutions, which is equal to $L = 2\pi dN$. Thus, the measurement is expressed as normalized volume $V_N = V/L$ (in mm^3/m).

As regards the fracture toughness test, a Vickers indentation was carried out with a load so high (300 gf) to produce measurable fractures starting from the indentation vertexes; in this way by appropriate equations the value of this property can be obtained. The Evans and Charles equation, suitable for glassy materials, was used in this study [7]:

$$K_{IC} = \frac{0.0824P}{c^{3/2}}$$

where P is the indentation load, in N, and c is the fracture length measured from the middle of the indentation in μm.

SEM analysis has been conducted (SEM Philips XL 30 coupled with energy dispersion spectroscopy EDAX 9900) on the glass samples in order to investigate the abrasion mechanism and to measure the fracture length in the indentation vertexes.

Table 1
Chemical composition of the used raw materials (wt%)

Oxide	Fly ash	Bottom ash	Feldspar residue	Glass cullet	V1	V2
SiO_2	18.5	46.7	65.1	72.1	54.4	52.6
Al_2O_3	7.37	6.86	18.2	2.2	5.41	12.1
BaO	0.139	0.109	–	–	0.159	0.134
Fe_2O_3	2.26	4.69	1.54	0.29	3.84	4.36
TiO_2	1.56	0.77	0.14	–	0.584	0.611
MgO	2.74	2.22	1.06	2.48	2.47	1.77
CaO	37.5	26.3	1.89	9.87	20.3	17.3
Na_2O	2.93	4.62	7.8	12.9	8.17	5.88
K_2O	2.03	0.888	1.1	0.7	1.12	1.06
P_2O_5	1.56	0.855	0.1	–	0.461	0.516
MnO	0.129	–	–	–	–	–
SO_3	14.4	2.18	–	–	0.456	0.354
Cl	0.867	0.176	–	–	0.376	0.402
SnO_2	0.123	–	–	–	–	–
ZnO	2.07	0.714	–	–	0.407	0.521
CuO	–	0.281	–	–	0.198	–

3. Results and discussion

The effectiveness of the vitrification process on the incinerator residues has been evaluated by means of the 24 h leaching test (Table 2). From the results appears evident the low leaching percentage of metals, confirmed by the low conductivity of the eluates which are only five times higher with respect to bidistilled water and significantly less with respect to bottom and fly ashes without vitrification (Table 3). pH values also confirm the less amount of leached ions in the solutions of vitrified materials with respect to the as-received fly and bottom ash, where a high basicity is showed. The similar pH and conductivity of the V1 and V2 glasses show that the vitrification process renders very stable and homogeneous the compositions despite of both the difference of the starting raw materials and the glass composition.

From the DTA analysis of the two glass compositions (Fig. 1), glass transition temperatures of $T_{gV1} = 580\,^{\circ}C$, $T_{gV2} = 620\,^{\circ}C$ are evidenced, crystallisation temperatures of $T_{cV1} = 824\,^{\circ}C$ and $T_{cV2} = 922\,^{\circ}C$ and melting temperatures (T_m) around at $1100\,^{\circ}C$ are identified. V1 shows lower T_g due to the lower amount of network forming oxides ($SiO_2 + Al_2O_3 = 59.81$ wt%) and a higher amount of modifying oxides ($Na_2O + K_2O = 9.29$ wt%) with respect to V2 ($SiO_2 + Al_2O_3 = 64.7$ wt% and $Na_2O + K_2O = 6.94$ wt%). These differences in the composition leads to a lower polymerization degree in the glassy lattice of V1 due to the higher number of non-bridging oxygen generated by the presence of alkaline metals.

Table 2
Metals concentration in the eluates of glasses

	V1 (mg/kg)	V2 (mg/kg)	V1 (% leached)	V2 (% leached)
Al	5.5	5.6	0.039	0.018
As	0.092	0.12	0.27	0.40
Ca	35	51	0.024	0.041
Cd	0.002	0.014	0.023	–
Co	0.004	0.022	0.051	0.28
Cr	0.012	0.082	0.004	0.051
Cu	0.60	0.40	0.038	0.052
Fe	1.7	4.8	0.013	0.031
K	25	36	0.54	0.81
Mg	2.2	6.5	0.014	0.061
Mn	0.02	0.078	0.008	0.025
Na	13	32	0.042	0.15
Ni	0.074	0.066	0.21	0.16
Sb	0.006	0.016	0.007	0.021
Zn	0.23	1.2	0.007	0.028

Table 3
Conductivity of studied samples

Sample	Conductivity (μS/cm)	pH
Bidistilled water	4.9	6.8
Bottom ash	5500	12.46
Fly ash	2990	12.59
V1	19.1	8.9
V2	26.9	9.2

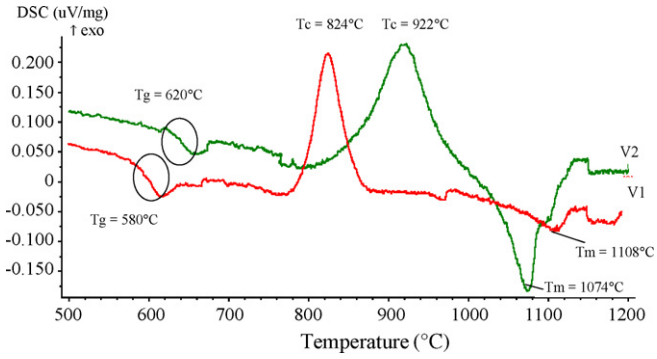

Fig. 1. DTA curves of the glasses V1 and V2.

The different chemical composition of the two glasses influences also the α value. This property is inversely proportional to the strength of bonding in materials structure; therefore higher amount of modifying ions allows wider thermal vibrations with isotropic expansion of the cavities of the network [8]. Accordingly with this behaviour of the silicate glasses, the V1 α value is higher with respect to V2 ($\alpha_{V1(20–400^{\circ}C)} = 9.1 \times 10^{-6}\,^{\circ}C^{-1}$, $\alpha_{V2(20–400^{\circ}C)} = 7.8 \times 10^{-6}\,^{\circ}C^{-1}$). Based on the relationship between the temperatures measured by hot stage microscopy

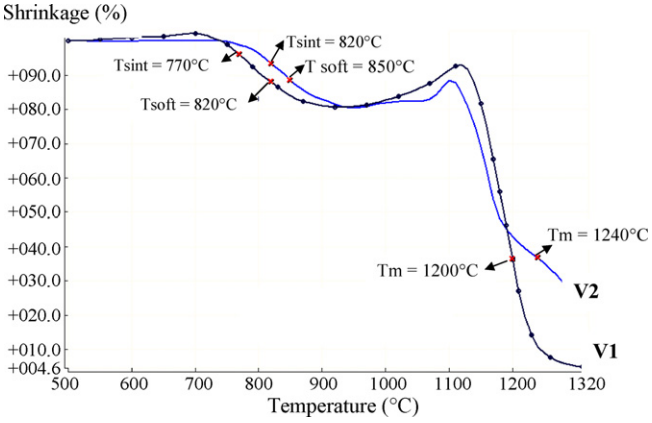

Fig. 2. Comparison of the sintering curves of the V1 and V2 glasses.

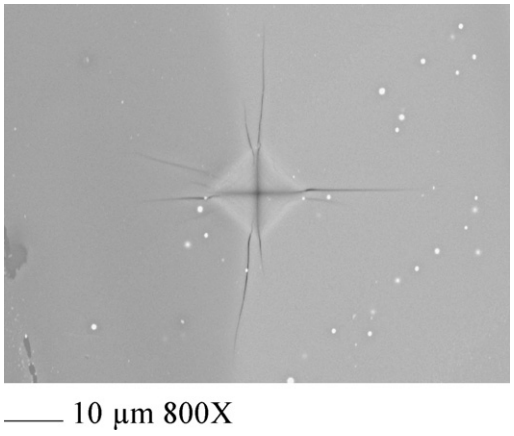

Fig. 3. SEM micrographs of Vickers indentation on V2 glass.

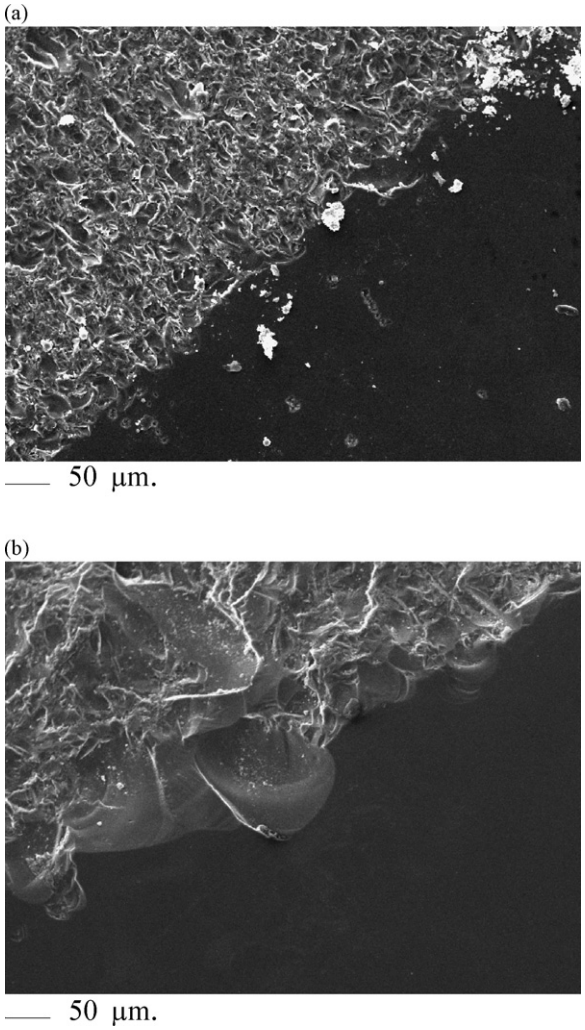

Fig. 4. SEM micrographs (130×) showing abrasion mechanism of (a) V1 and (b) V2 glasses.

and their corresponding viscosities Scholze [9] defined some characteristic points of viscosity (dPa s):

(a) the first shrinkage (or sintering temperature): the temperature at which the pressed samples starts to shrink ($\log \eta = 10.0$);
(b) softening point: the temperature at which the first sign of softening are observed ($\log \eta = 6.1$).

Optical heating microscopy has been evidenced that V1 shows lower sintering and softening temperatures than V2 ($T_{sintV1} = 770\,^{\circ}C$, $T_{sintV2} = 820\,^{\circ}C$, $T_{softV1} = 820\,^{\circ}C$, $T_{softV2} = 850\,^{\circ}C$). This trend is related to the lower degree of polymerization of the V1 glass network. Moreover, the sintering curve (Fig. 2), which reports the material shrinkage ($\Delta L/L_0 \times 100$) as a function of temperature, shows a plateaux between 900 and 1000 °C for V1 and between 950 and 1050 °C for V2. This plateaux, where the shrinkage remains constant, corresponds to the crystallisation interval of these glasses in which the densification is inhibited [10]. In Table 4 dry abrasion resistance, Vickers microhardness and fracture toughness

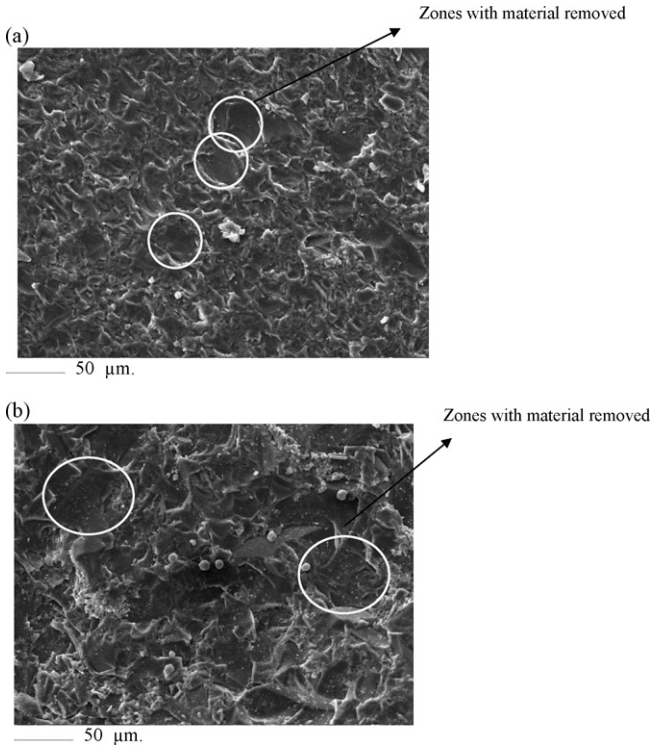

Fig. 5. SEM micrograph (260×) showing the abraded microstructure of (a) V1 and (b) V2 glasses.

Table 4
Dry abrasion resistance and mechanical properties of V1 and V2 glasses

Glass	V (mm^3)	V_N (mm^3/m)	H_v (kg/mm^2)	K_{IC} (MPa m$^{1/2}$)
V1	61.0 ± 0.7	4.62 ± 0.05	568 ± 7	0.53 ± 0.06
V2	58.6 ± 1.4	4.43 ± 0.11	585 ± 29	0.57 ± 0.07

are reported. The samples do not show significant differences between surface and cross-sectional Vickers microhardness, therefore only the latter has been reported. From the values it appears evident that the glasses shows similar mechanical characteristics and comparable to those of soda-lime glasses ($H_v = 550$ kg/mm^2, $K_{IC} = 0.75$ MPa m$^{1/2}$) [11,12]. The higher standard deviation of the V2 Vickers microhardness can be caused by not complete homogeneity of this material due to its chemical composition. In V2 glass, in fact, the easily meltable glass cullet, which favours the atoms mobility in the melt and the homogenisation process are substituted with the feldspar waste, which increases the viscosity during the melting.

In Fig. 3 a Vickers indentation is reported, where the fractures used for the K_{IC} calculation are shown. The cracks are in the range of 5–20 μm.

The dry abrasion resistance is evaluated in terms of material volume cut out V (in mm^3) and normalized volume $V_N = V/L$ (in mm^3/m). From the table it appears evident that the V1 and V2 samples show similar values and comparable with glasses belonging to the $CaO–Al_2O_3–SiO_2$ system ($V_N = 5.044$ [13]).

In order to have more information about the abrasion mechanism, the samples are studied by means of SEM analysis (Figs. 4 and 5). From the morphology of the abraded surface

it appears evident that the two glasses have a different fracture mechanism (Fig. 4) notwithstanding they show very similar abraded volumes. The pressure of abrasive grains against the surface of the material cause a peak stress at a depth of a few micrometers, which originates crack propagating themselves up to the surface with subsequent material removal. V1 glass has a very corrugated surface with a fine microstructure (Fig. 5a) characterized by small zones of material removal, while V2 glass shows an abrasion mechanism characteristic of brittle materials with large smooth depressions and coarse microstructure (Fig. 5b). The abrasion resistance mostly depends on fracture toughness and in glasses the abrasion is mainly due to brittle fracture and not due to plastic deformation; this explains both mechanical properties of these two glasses and the similar abrasion resistance values.

4. Conclusions

From the present study emerges that the vitrification process applied to the tailored mixtures is a useful technique to valorise the incinerator bottom and fly ashes. The obtained glasses show low metals release percentages and less ions releases with respect to the incinerator ashes. From the mechanical characterisation it appears that Vickers microhardness, fracture toughness and abrasion resistance are comparable with similar commercial glassy systems. From the thermal characterisation it appears that the materials are also suitable for the obtainment of glass-ceramic materials.

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