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Recycling of pre-stabilized municipal waste incinerator fly ash and soda-lime glass into sintered glass-ceramics

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ABSTRACT

A recent method, based on the use of amorphous silica, allows for the inertization of MSWI fly ash, avoiding expensive vitrification. The present paper demonstrates that glass-ceramics, i.e. the most established products from waste-derived glasses, are feasible by direct, inexpensive viscous flow sintering of pre-stabilized fly ash mixed with clay and recycled soda-lime glass. The sintering treatment did not compromise the chemical stabilization of fly ash, as confirmed by leaching test and by cell culture studies (with mouse embryonic fibroblasts used to assess possible cytotoxicity), applied on sintered glass-ceramics. Optimized glass-ceramic tiles, processed at 1050 °C for 30 min, not only featured attractive aesthetic appearance and low water absorption (<2%), but also exhibited a remarkable specific strength (~3.6 $MPa^{0.5}$ cm^3/g).

1. Introduction

Vitrification is considered to be the safest technology for the treatment and remediation of non-combustible hazardous waste, among the various technologies for the disposal of inorganic waste (U.S. Environmental Protection Agency, 1992). Despite the soundness of the approach, implying both thermal destruction of waste and immobilization of pollutants (e.g. heavy metal ions) in a matrix with high chemical stability, vitrification remains highly energy and capital intensive (Colombo et al., 2003). When environmental safety has not an absolute priority over cost, like in the case of radioactive waste (Lee et al., 2006), vitrification is sustainable only if high value products, such as monolithic and cellular glass-ceramics, for structural and functional applications, are obtained from the developed waste-derived glasses (Rawlings et al., 2006; Chinnam et al., 2013).

It must considered that some types of waste pose additional limits to vitrification; as an example, municipal solid waste incinerator fly ash deserves a particular attention, due to the presence of compounds, such as chlorides, having a poor solubility in glass melts (Kim and Kim, 2004; Lee et al., 2006). Recent experiences, however, have demonstrated that the stabilization of this specific waste (i.e. the entrapment of heavy metals) may be achieved without vitrification, by direct reaction with colloidal silica, even at room temperature (Bontempi et al., 2010; 2013). The resulting material, named COSMOS® ("COlloidal Silica Medium to Obtain Safe Inert"), may be washed and soluble salts can be recovered from solution simply by crystallization (Bontempi et al., 2010).

COSMOS has been already employed as a filler for mortars, bitumen, resins and plastics; in particular, promising properties have been shown for polypropylene matrices (Besco et al., 2013). No application has been reported so far regarding the reuse of COSMOS in ceramics, including glasses. The possible removal of chlorides by washing would certainly help the vitrification (in analogy with what proposed by Kim and Kim, 2004), but any melting step would not be economically justified, after the treatment with colloidal silica (simple but not inexpensive).

Glass-ceramics, i.e. the most established waste-derived glass-based products, may be obtained even avoiding an expensive vitrification step, by direct sintering of inorganic waste mixed with recycled glass powders (Lin et al., 2009). In some cases, when clay is added, as a binder, glass-ceramic products ('glass-based stonewares') may be obtained, in terms of overall processing, in good analogy with traditional stoneware ceramics (Bernardo et al., 2009), but with the significant advantage of much lower sintering

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temperatures, due to the intensive fluxing ability of glasses (Lin, 2007). The stabilization of shrinkage normally provided, in conventional stoneware ceramics, by the formation of mullite (aluminium silicate, from thermal transformation of clays) within the liquid phase from molten feldspars, is attributed, in glass-based stonewares, to the crystallization of other silicates. In fact, Ca-rich silicates may form as an effect of glass devitrification and/or reaction of glass with CaO, e.g. introduced as hydroxide (Bernardo et al., 2009). In the present investigation COSMOS, due to its formulation, will be basically intended as an alternative source for CaO, together with an inert fraction: optimized formulations actually led to lightweight glass-ceramics possessing microstructural homogeneity and high specific mechanical properties, to be used as low cost building material, with no negative impact on the chemical stability already achieved with COSMOS.

The chemical stability of the produced glass-ceramics was assessed by a novel method, i.e. by combination of a conventional leaching approach (EN 12457−3; for comparison purposes, the same process was applied to COSMOS) and an *in vitro* cytotoxicity test (ISO 10993-5:2009), usually considered for biocompatibility tests of materials (Amaral et al., 2009). Indeed very few previous reports dealing with waste-derived materials (Boccaccini et al., 1997; Huang et al., 2008) have considered such a combination of tests including cell culture studies to assess the material biocompatibility or safety.

2. Experimental procedure

2.1. Materials preparation and characterization

COSMOS material was obtained by mixing three different types of fly ashes: ashes coming from MSWI (65 wt% in the composition), residues from coal desulfuration (FGD fly ash) (20 wt%) and ash from coal combustion (15 wt%) (Bontempi et al., 2010). The specimens were prepared by adding to the mixture of the three powders 25 wt% of colloidal silica solution, wetting with water, and mixing for 1 h.

Fine powders of recycled soda-lime glass (SiO_2: 72.3 wt%, Na_2O: 12.0, CaO: 10.0, MgO: 2.0, Al_2O_3: 2.2, Fe_2O_3: 0.3, TiO_2: 0.1) and pure kaolin clay (SiO_2: 43.5 wt%, Al_2O_3: 39.0) were considered, in analogy with a previous investigation (Ponsot and Bernardo, 2013). Glass and clay were mixed with washed COSMOS powder in four different weight proportions, labelled C1 (glass/clay/COSMOS = 50/25/25), C2 (55/20/25), C3 (60/15/25) and C4 (65/10/25), and added with water (35%–40% of the total solid), thus obtaining aqueous slips, later homogenized in an agate planetary ball milling system at 400 rpm, for 30 min. The slips were cast in wide glass containers and left at 110 °C overnight. The dried mixtures were directly pressed at 40 MPa in rectangular steel dies, to obtain tiles of dimensions 50 mm × 30 mm × 3 mm, or discs of dimensions ~30 mm in diameter × 2 mm in height. Pressed samples were sintered in air, at a temperature varying from 800 to 1100 °C, with heating rate of 40 °C/min and a holding time of 30 min, followed by natural cooling. For the evaluation of the mechanical properties, small beams of 40 mm × 3 mm × 2 mm were cut from bigger tiles and carefully polished up to a 5 μm finish and chamfered at the edges, by using diamond tools.

The densities of all sintered samples were measured according to Archimedes' principle. Immersion in boiling water was used for the evaluation of water absorption, according to current standard ISO 10545-3.

Mineralogical analysis was conducted by X-Ray Diffraction analysis (XRD) on powdered samples (Bruker D8 Advance, Karlsruhe, Germany – CuKα radiation, 0.15418 nm, 40 kV-40 mA, 2θ = 10–60°, step size = 0.05°, 2 s counting time). Phase identification was performed by means of the Match!® program package (Crystal Impact GbR, Bonn, Germany), supported by data from PDF-2 database (ICDD-International Centre for Diffraction Data, Newtown Square, PA).

The elastic modulus was measured by non-destructive resonance frequency testing (GrindoSonic Mk5, Leuven, Belgium). Four-point flexural strength tests were carried out by using an Instron 1121 UTS (Instron, Danvers, MA), operating with a cross-head speed of 1 mm/min; each data point represents the average of ten individual tests.

Selected samples were studied by means of scanning electron microscopy (ESEM Quanta 200, FEI Company, Eindhoven, The Netherlands), in order to investigate the microstructural development. The release of heavy metals was evaluated by application of TCLP leaching test according to the guidelines of standard EN 12457-3: 15 g of small fragments (300 μm < dimensions < 3.35 mm, obtained from bending strength tests) were placed in 150 cl distilled water, in a liquid to solid ratio of 10, and stirred for 24 h at 25 °C. The resulting solutions were acidified with nitric acid up to pH = 2, filtered through a 0.6 μm filter and analysed by using inductively coupled plasma mass spectrometry (ICP-MS, SPECTRO Analytical Instruments GmbH, Kleve, Germany).

For the cytotoxicity study, six disc-shaped samples were considered (three for the direct method and three for the indirect method, see below). 0.5 g of dry powder mixture were pressed at 30 MPa using a 13 mm diameter mould, then directly heated (i.e. direct insertion in the furnace at high temperature and cooling in air) at 1050 °C, for 30 min, to obtain pellets of 2 mm thickness. Samples were then gradually polished up to a 350 nm finish by using diamond tools.

2.2. Cell culture assay procedures

In order to assess the cell compatibility of the materials, direct and indirect cell culture methods were applied which have been described elsewhere (Hoppe et al., 2011). Mouse embryonic fibroblasts (MEF) were cultured for 24 h in a Dulbecco's Modified Eagle Medium (DMEM) containing 10% Foetal Bovine Serum (FBS) and 1% of penicillin-Streptomycin, at 37 °C, in a humidified atmosphere (air, with 5% CO_2). In the indirect method (elution test), extracts were obtained by placing the test and control (soda-lime glass as typical window glass) specimens in separate cell culture media under standard conditions. Each fluid extract (supernatant from the samples) obtained after 1, 2 and 3 days of incubation was then

Table 1
Results of leaching test on several samples of fly ashes and COSMOS powder.

Element	Ashes MSWI (ppm)	Ashes FGD (ppm)	Ashes of carbon (ppm)	COSMOS (ppm)
P	n.d.	n.d.	0.3 ± 0.1	n.d.
S	n.d.	1.1 ± 0.9	67 ± 6	98 ± 9
Cl	2477 ± 234	980 ± 93	n.d.	3522 ± 288
K	433 ± 46	6.6 ± 0.8	6.6 ± 0.6	479 ± 41
Ca	1850 ± 171	794 ± 97	173 ± 14	2318 ± 177
V	n.d.	n.d.	0.29 ± 0.02	n.d.
Cr	n.d.	n.d.	0.031 ± 0.004	n.d.
Fe	0.18 ± 0.08	n.d.	0.29 ± 0.02	n.d.
Zn	3.7 ± 0.3	0.03 ± 0.01	0.013 ± 0.002	1.6 ± 0.1
As	n.d.	n.d.	0.048 ± 0.004	n.d.
Se	n.d.	n.d.	0.96 ± 0.07	n.d.
Br	33 ± 3	4.4 ± 1	0.012 ± 0.001	71 ± 6
Rb	n.d.	n.d.	0.012 ± 0.002	n.d.
Sr	n.d.	1.8 ± 0.1	2.4 ± 0.19	n.d.
Ba	n.d.	n.d.	0.19 ± 0.02	n.d.
W	n.d.	n.d.	0.053 ± 0.005	n.d.
Pb	13 ± 1	n.d.	n.d.	n.d.