

RECYCLING AND VALORISATION OF STEEL FLY ASH IN DIFFERENT GLASSES AND GLASS-CERAMICS

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Abstract

Thermally stable and chemically inert glass-ceramics were prepared from surface nucleated basaltic glasses obtained by inserting up to 10 wt% steel plant fly ash into different kinds of inorganic matrices. Three different matrices were tested: municipal incinerator grate ash, glass cullet and a low cost CMAS devitrifiable glass. The results confirmed the capability of recycling and valorisation of the steel fly ash by the vitrification/devitrification technique with the advantage to reduce the waste volume and to transform it into new marketable materials with good technological properties.

Introduction

In the past the recovery efforts were impeded by low prices for primary raw materials, sufficient landfill capacities and hence low prices for depositing the wastes, chemical inhomogeneity and reactivity of the solid residuals and negative image of products made from waste materials. On the contrary, in the future the development of recycling technologies will become economically advantageous because refuse disposal is becoming very rare and expensive, legal restrictions for treatment of residuals are getting more and more severe and the amount of products to be recycled will strongly increase. In particular, it has been seen that many kinds of wastes and/or by-products undergo to a vitrification process [1-5] in order to reduce the waste volume, to destroy the organic components, to immobilise toxic elements and minerals by a structural incorporation in a solid state lattice. Moreover, during vitrification the recovery of the remaining valuable oxides for further use as secondary raw materials can be achieved. The good weather resistance of the glass obtained during vitrification offers the possibility to immobilise wastes of different origin in a single process thus increasing the homogeneity and the chemical composition reproducibility (necessary requirement for obtaining reliable products for general applications). Hence, vitrification is in line with general effort to recover and reuse valuable raw materials produced from industrial processes or waste treatment technologies. However, this technology, which requires additional process costs mainly due to the melting, can be fully justified if high-quality products can be put into the market.

The most effective way for improving the mechanical and physical properties of the vitrified products is to form glass-ceramics by controlled crystallisation [6-8]. These materials appear promising, not only because of their outstanding properties, but also because the production process involves conversion of quite common silicate raw materials into substances with superior properties. The characteristics of glass-ceramic materials basically depend on the properties of the finely separated crystalline phase and residual glass which make up the glass-ceramic material. The kind of crystalline phases and thus also the final properties of the glass-ceramic material can be controlled by the initial glass composition and by its heat treatment. In this way an almost unlimited number of types of glass-ceramic material can be prepared with various combinations of properties, many of which are useful in practice.

In this work a fly ash coming from the filtering operations of an Italian carbon steel plant has been mixed together with other waste raw materials, municipal incinerator grate ash and glass cullet, and then transformed into new amorphous and semicrystalline materials. Furthermore,

the effect of the addition of the steel dust on the main properties of a previously studied [9] CMAS (CaO-MgO-Al₂O₃-SiO₂) glass-ceramic system has been investigated.

Experimental

Original glasses from carbon steel plant fly ash, municipal incinerator grate ash, glass cullet and a low cost CMAS glass-ceramic system (Table 1 and 2) were obtained at about 1450°C in refractory crucibles by heating the starting mixtures in an electrically heated furnace from room to melting temperature.

By considering the high iron and zinc oxides content into the steel waste dust and the role played both by iron that provides colours and zinc that can lighten or darken the colours and provide a variety of decorative appearances, 1, 2, 5 and 10 wt% of this waste has been added to the CMAS glass-ceramic above mentioned.

The following characterisation was performed on the glassy samples. Differential thermal analysis tests, DTA (Netzsch DSC 404), were performed on powders heated at 10°C/min in static air fired from 20 to 1400°C. Thermomechanical analysis was performed with a dilatometer Netzsch 402 EP on glassy specimens of 4x0.5x0.5 cm in size heated at 10°C/min from room temperature to the softening point. Durability was tested in water (ISO 719); release test in acetic acid according to the Italian regulation [10], and finally the chemical analysis of the leaches solutions by an Induction Coupled Plasma Varian Liberty 200. Density was determined by the hydrostatic method at room temperature (Gibertini Balance E42-E31). Vickers microhardness was determined by a Digital Micro Hardness Tester Matsuzawa DMH 2 with a load of 50 g and a load time of 15 s. Colour measurements were performed using a UV-VIS spectrophotometer (Perkin Elmer, Lambda 19) with CIELab method [11]. Finally, X-ray powder diffraction patterns (Philips PW 3710) were collected on bulk heat-treated samples of dimension 1x1x0.5 cm in the 5°–60° 2θ range was.

Results and Discussion

The most significant properties are reported in Table 3.

The addition of 10 wt% of steel fly ash to both the municipal incinerator grate ash and CMAS system causes a decrease either in the glass transition (T_g) or in the softening (T_s) temperatures so rendering the glass less viscous because of the decrease in SiO₂ content (former oxide) and the increase in ZnO content (modifier oxide). A shift of the crystallisation temperature (T_c) toward a lower value can also be observed, this last effect can be attributed to the decrease in silicon oxide and/or the iron oxide nucleating effect. This last oxide is also

responsible for a second exothermic peak near 990°C in the grate ash-containing sample, S9P1, corresponding to the formation of Fe-containing crystalline phases. In the glass cullet-containing series, the addition of fly ash induces crystallisation since a weak exothermic event is recorded at about 800°C. Such a peak, absolutely absent in V10 sample, can be again attributed to the increase in iron content.

The linear thermal expansion coefficient, α , determined in the 100-500°C range decreases from the glass-cullet-containing samples to CMAS system-containing ones because of the increase of the bivalent cations (characterised by a high field strength) with respect to the monovalent ones

As regards to water durability test, the values obtained divide the glasses into categories where the lower the category number the better the durability. Results listed in Table 3 underline a worsening in the steel added glass (S9P1) with respect to the matrix (S10). The highest values correspond to the glass cullet-containing series where the higher Na⁺ content with respect to other series renders the glass more subjected to leaching processes. Furthermore, by considering the particular nature of the starting materials, the release test in acetic acid has been also carried out to simulate the behaviour of the waste incorporated in the glassy matrix when exposed to the leaching both of the rain and of the percolates from organic and inorganic mixed dumps. For all the compositions very low release values for metallic micropollutants have been obtained, all in the range allowed by the Italian regulations, necessary condition for their reutilization as product of a inert waste.

The slight increase in the density value (D), corresponding to the introduction of the steel dust in all the compositions, is probably due to the higher atomic mass of Zn and Fe than other main elements present.

Vickers microhardness (H_V) values remain constant with a global decrease with respect to pure silica glass (about 7 GPa) because of the presence of the alkaline-earth oxides weakening the glassy network.

Since the addition of steel fly ash, in which iron is the main component, in the glass cullet and CMAS series causes a variation in the colour of the colourless base systems (being S10 composition already dark brown), the colour analysis on the CMAS9P1 and V9P1 samples was performed. It is known that the same Fe₂O₃ percentage introduced in a silicate matrix can confer a different coloration dependently upon the acid-basic character of the glasses [12]. The acidobasicity of a glass depends on the non-bridging oxygens concentration in the glassy network, which is related to the amount of the alkaline oxides that play the role of modifiers cations [13]. Hence, it is possible to foresee a colour variation in glasses, containing the same

amount of iron, as a consequence of a change in the alkaline content. For this reason Figure 1 shows the a^* and b^* parameters as a function of the $\text{Na}_2\text{O-SiO}_2$ ratio for V9P1 and CMAS9P1 compositions containing the same steel dust percentage (10 wt%). Thus, with the increase of Na_2O content (V9P1) it has been noted a slight shift from green to red for a^* parameter (negative and positive values indicate the predominance of the green and red colour, respectively) and a more marked shift from blue to yellow for b^* parameter (negative and positive values indicate the predominance of the blue and yellow colour, respectively).

As far as the devitrification tendency is concerned, the steel waste dust acts as a promoter for the crystallisation process when added to incinerator grate ash and to glass cullet, respectively (Figure 2). In general, the XRD patterns recorded on the above mentioned samples presented a change in the diffraction peaks attributed to the different crystalline phases present depending on the glass-ceramic composition and thermal treatment performed (maghemite Fe_2O_3 , magnetite Fe_3O_4 , anorthite sodian $(\text{Ca,Na})(\text{Si,Al})_4\text{O}_8$, wollastonite CaSiO_3 and franklinite ZnFe_2O_4). The pyroxene crystals, augite $\text{Ca}(\text{Fe,Mg})\text{Si}_2\text{O}_6$ and/or diopside $\text{Ca}(\text{Mg,Al})(\text{Si,Al})_2\text{O}_6$, resulted to be the thermodynamically most favoured phase, being present in all the studied compositions (except for V10 since it does not crystallise).

On the other hand, the addition of the waste in the percentage of 1, 2, 5 and 10 wt% to the CMAS glass-ceramic no changes substantially the thermal behaviour of the base system except for the lowering of the characteristic temperatures as shown in Figure 3. This is probably related to the iron and zinc oxides which playing the role of structure modifiers lower the glass viscosity and favour the crystallisation kinetics without affect the mechanism (surface) and the mineralogy (pyroxene) of the material.

As regards the release test in acetic acid, Table 4 shows that also CMAS glasses release amounts of micropollutants in the range allowed by the Italian regulations. In particular the iron ion, present as main constituent, is completely immobilised into the glassy matrix without interacting with the environment.

Colourless CMAS glass becomes yellow, green or brown depending on fly ash content. Such coloration is due to the presence of the main cromophore element present, i.e. iron. The shift of L^* parameter toward lower values passing from CMAS to CMAS+P10 composition designates a brightness decrease which is no longer affected by addition of fly ash above 5 wt% (Figure 4). Moreover, for all the samples studied, the b^* parameter values show the predominance of the yellow colour on the blue.

4 Conclusions

The steel fly ash coming from an Italian carbon steel plant has been successfully mixed together with other wastes (municipal incinerator grate ash or glass cullet) or a low cost CMAS glass-ceramic system to produce stable and inert glasses transformed into the corresponding glass-ceramics by controlled heat treatments. All the glasses obtained have a good water durability, a release of metallic micropollutants in the range allowed by the Italian regulations and a Vickers microhardness typical of silicate glasses containing alkaline-earth oxides. The main elements present in the dust, i.e. Fe and Zn, play their role of glass network modifiers lowering the glass viscosity and favouring the surface formation of pyroxene crystals. Moreover, when the steel dust is added to the above mentioned CMAS glass-ceramic system, because of the iron chromophore high content, its most significant effect is the appearance of a different coloration (yellow, green or brown) depending on the amount introduced without affecting the other properties of the base system. The results reached may allow to recycle and valorise this kind of waste both as starting material for the production of marketable glasses and glass-ceramics and as colouring agent in place of a pure iron oxide into a colourless base system.

References

1. C. Cantale, S. Castelli, A. Donato, D. M. Traverso, P. Colombo and G. Scarinci "A borosilicate glass for the Italian high level waste. Characterization and behavior", *Rad. Waste Manag. and the Nuclear Fuel Cycle*, **16** (1991) 25-47.
2. G. Scarinci, C. Morosato, P. Canu and L. Angelin "Inertizzazione mediante vetrificazione di residui da inceneritori di R.S.U.", in Atti del 7 Convegno Nazionale "*Inquinamento dell'aria e tecniche di riduzione*", Padova 17-19 novembre 1997, pp. 499-507.
3. L. Barbieri, T. Manfredini, I. Queralt, J. Ma. Rincòn and M. Romero, "Vitrification of fly ash from thermal power stations", *Glass Technol.* **38**(5) (1997) 165-170.
4. S. Hregich, F. Nicoletti "Inertization of inorganic solid wastes by vitrification" in Proceedings of the 1st National Congress Valorisation and Recycling of Industrial Wastes, Series of Monographs on Materials Science, Engineering and Technology, Ed. by M. Pelino and G. C. Pellacani, Mucchi Editore – Modena (1998), pp. 155-167.
5. G. Scarinci, G. Brusatin, L. Barbieri, A. Corradi, I. Lancellotti, P. Colombo, S. Hreglich, and R. Dall'Igna, "Vitrification of industrial and natural wastes with production of glass fibers", *J. Europ. Ceram. Soc.*, accepted.
6. L. Barbieri, I. Lancellotti, G. C. Pellacani, P. Pozzi, J. Ma. Rincòn e M. Romero "Use of thermoelectric power plant fly ash in the production of low cost glasses and glass-

- ceramics”, in Proceedings of the 1st National Congress Valorisation and Recycling of Industrial Wastes, Series of Monographs on Materials Science, Engineering and Technology, Ed. by M. Pelino and G. C. Pellacani, Mucchi Editore – Modena (1998), p. 183-190.
7. L. Barbieri, I. Lancellotti, T. Manfredini, I. Queralt, J. Ma. Rincòn and M. Romero, “Design, obtainment and properties of glasses and glass-ceramics from coal fly ash”, *Fuel* **78** (1999) 271-276.
 8. L. Barbieri, A. M. Ferrari, I. Lancellotti, C. Leonelli, J. Ma. Rincòn and M. Romero “Crystallization of (Na₂O-MgO)-CaO-Al₂O₃-SiO₂ glassy systems formulated from waste products”, *J. Am. Ceram. Soc.*, accepted.
 9. C. Leonelli, T. Manfredini, M. Paganelli, P. Pozzi and G. C. Pellacani, “Crystallization of some anorthite-diopside glass precursors” *Journal of Materials Science* 26 5041 (1991).
 10. Italian Regulation D.I. 14 July 1986.
 11. Ruth M. Johnston, *Pigment Handbook*, Vol. 3, Ed. Temple C. Patton, Vol. 3., John Wiley and Sons, USA, 1973, p. 229.
 12. M.B. Volf, *Chemical Approach to Glass*, Elsevier, 1984, pp. 350-351
 13. Arun K. Varshneya, “Fundamentals of Inorganic Glasses”, Academic Press Inc. (1994), New York State College of Ceramics pp. 468-471.

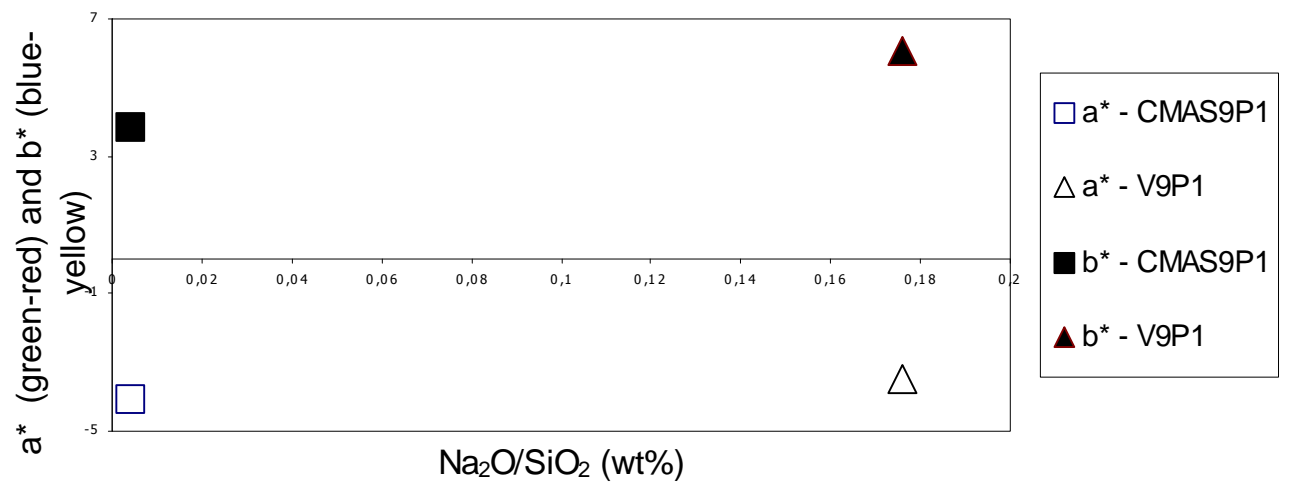


Figure 1 - a* and b* parameters as a function of the Na₂O-SiO₂ ratio for the steel added compositions.

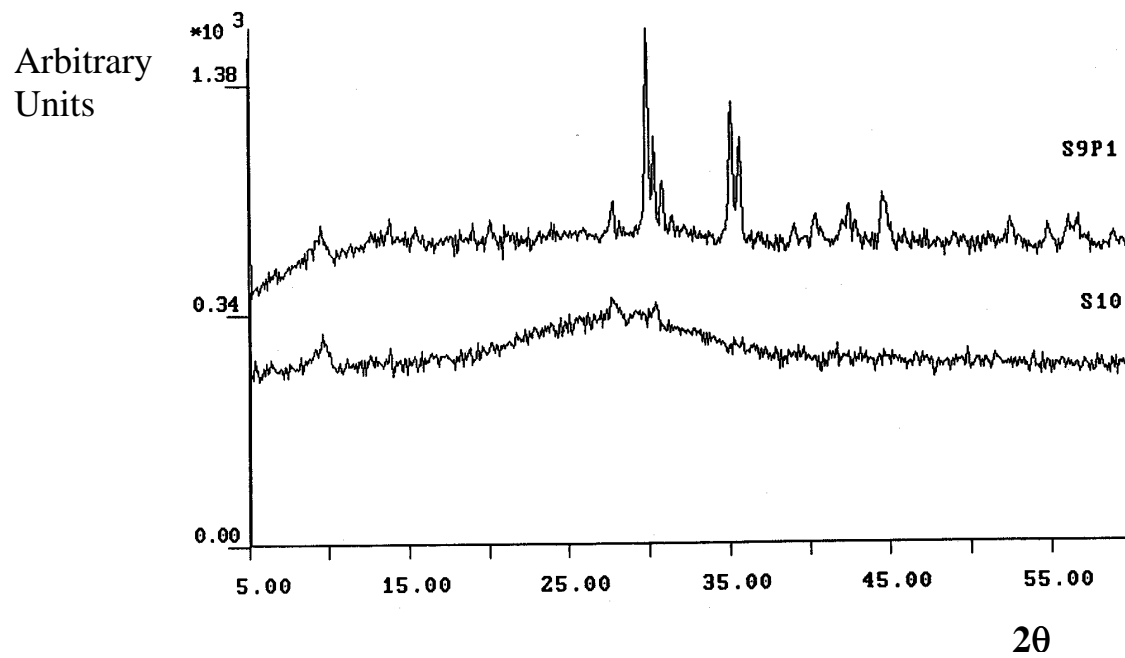


Figure 2 - XRD patterns of the S10 and S9P1 glass-ceramics obtained at 1000°C for 1 hour.

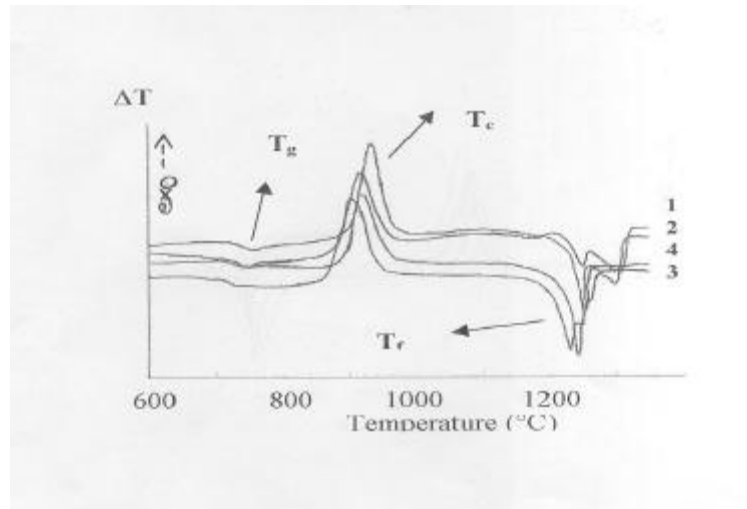


Figure 3 - DTA curves of the compositions (1)CMAS, (2) CMAS + P2, (3) CMAS + P5 and (4) CMAS + P10.

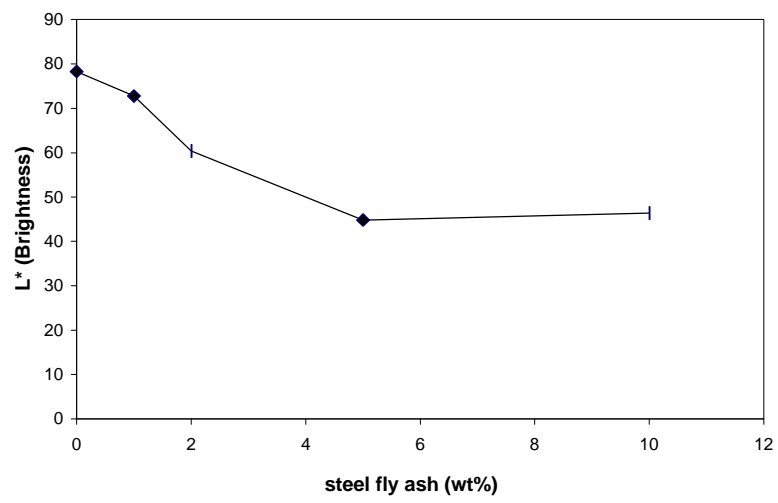


Figure 4 - Variation of the L* parameter as a function of the composition for the CMAS + P series

Table 1. Average chemical composition (wt%) of the starting materials (ICP analysis)

<i>Oxide</i>	<i>Steel fly ash</i>	<i>Incinerator grate ash</i>	<i>Glass cullet</i>	<i>CMAS glass- ceramic</i>
SiO ₂	3.8	45	70	53
Al ₂ O ₃	1.1	9.7	1.2	9.2
CaO	5.8	19	9.4	25
MgO	3.2	2.2	4.1	13
Na ₂ O	1.4	4.6	13	-
K ₂ O	0.76	1.3	0.33	-
Fe ₂ O ₃	45	3.8	0.27	-
ZnO	25	0.32	0.10	-
TiO ₂	0.080	0.93	-	-
MnO	3.1	-	-	-
Cr ₂ O ₃	0.61	0.040	0.020	-
PbO	2.7	0.010	0.040	-
CdO	0.070	-	-	-
NiO	0.12	-	-	-
CuO	0.49	-	-	-
SnO ₂	0.12	-	-	-
BaO	0.11	0.17	0.060	-
ZrO ₂	-	0.29	-	-

Table 2. Wt% components ratio in the studied compositions

<i>Composition</i>	<i>Steel fly ash</i>	<i>Incinerator grate ash</i>	<i>Glass cullet</i>	<i>CMAS glass- ceramic</i>
S10	-	100	-	-
S9P1	10	90	-	-
V10	-	-	100	-
V9P1	10	-	90	-
CMAS10	-	-	-	100
CMAS9P1	10	-	-	90

Table 3. Thermal, chemical, physical and mechanical properties of the glasses studied

<i>Parameter</i>	<i>T_g (DTA)</i> (°C)	<i>T_c(DTA)</i> (°C)	<i>T_S (DIL)</i> (°C)	<i>a₁₀₀₋₅₀₀ · 10⁶</i> (°C ⁻¹)	<i>Water</i> <i>durability*</i>	<i>D</i> (kg//m ³)	<i>H_V</i> (GPa)
<i>Composition</i>							
S10	648	937	702	9.0	1	2.71	6.2
S9P1	635	871; 990	716	9.2	2	2.96	6.9
V10	540	none	623	10.9	3	2.51	6.2
V9P1	547	807	653	10.3	2	2.60	6.6
CMAS10	720	932	814	8.0	1	2.73	6.6
CMAS9P1	685	889	775	7.9	1	2.88	6.0

*1 = Very high resistance, 2 = High resistance, 3 = Medium resistance

Table 4. Micropollutants release (mg/l) in acetic acid compared to both the limit values of the Italian regulation and the theoretical release of 2g of glass when completely leached

Composition	<i>Al (mg/l)</i>	<i>Fe (mg/l)</i>	<i>Zn (mg/l)</i>	<i>Mn (mg/l)</i>	<i>Pb (mg/l)</i>
	1mg/l*	2mg/l*	0.5mg/l*	2mg/l*	0.2mg/l*
	<i>Th/Exp</i>	<i>Th/Exp</i>	<i>Th/Exp</i>	<i>Th/Exp</i>	<i>Th/Exp</i>
CMAS	98/0.09	-/0.00	-/0.00	-/0.00	-/0.00
CMAS+P1	123/0.04	9/0.00	5.2/0.00	-/0.00	0.56/0.05
CMAS+P2	142/0.02	20/0.00	10/0.00	0.62/0.00	0.93/0.01
CMAS+P5	119/0.15	34/0.14	23/0.15	3.1/0.01	1.1/0.04
CMAS+P10	117/0.15	63/0.06	44/0.22	5.7/0.01	2.8/0.05

*according to [5]