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RECYCLING OF INORGANIC WASTE IN MONOLITHIC AND CELLULAR GLASS-BASED MATERIALS FOR STRUCTURAL AND FUNCTIONAL APPLICATIONS

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Introduction

Any form of management of inorganic waste, from landfill disposal to recovery, implies a stabilisation step applied through several chemical and physical processes, including vitrification. The most common applications of this technology concern waste from metallurgical industrial processes, from the demolition of buildings and civil infrastructures, or from combustion processes, particularly from municipal solid waste (MSW) incineration.¹

Vitrification generally consists of the dissolution of metal oxides from hazardous waste in molten glass, at high temperatures; the metal ions are then “frozen” into the vitreous structure following the cooling of the melt. Waste-derived glasses offer high chemical stability, in a vast range of compositions, with the only constraint of adequate content of SiO₂, essential for glass formation.^{1,2} This requirement is generally fulfilled by mixing waste with minerals or glass cullet from recycling operations or even by considering waste mixtures. In some cases, the stabilisation does not rely on the dissolution of waste, but simply on the thermal destruction, by high temperature processing: as an example, for asbestos-containing waste (not containing heavy metal oxides), vitrification is recommended essentially for the dismantling of the characteristic hazardous fibrous structure.¹

In general, vitrification compares poorly with other management options, if followed simply by landfilling. Direct landfilling, backfilling in salt mines, neutralisation of waste acid, use as filler material in asphalt, *etc.* may be more convenient for energy consumption and air emissions.³ The cost/benefits balance may be improved if an extra revenue is achieved, by use of waste-derived glasses as raw material for high-value products.¹ These products (mostly) consist of monolithic glass-ceramics for structural applications, as an alternative to natural stones or ceramic tiles, or foams (*e.g.* cellular glass-ceramics) for thermal and acoustic insulation.

Both classes of glass-based products actually depend on the application of a secondary thermal treatment, implying extra costs. Again, the cost/benefits balance may be adjusted favourably, typically by: (i) engineering the conversion process from waste-glass to products thermal treatment; (ii) integrating the processing of glass-based products in whole 'waste management chain'. As reported Gomez *et al.*,⁴ waste-glass may correspond to the final output of plasma heating of waste, providing both gasification of organics, by pyrolysis (thermal treatment in non-oxidative atmosphere), and metal separation upon melting (under reducing conditions). Avoiding landfill charges combined with the energy production from waste-derived gas ('syngas'), the recovery of metals together and the added value from glass products, improves the commercial viability of the approach.

The integration is essential for Enhanced Landfill Mining approaches, and constitutes the basis of the current MSCA-ETN NEW-MINE European project.⁵ The present paper aims at providing an up-to-date overview of the technology of glass-based products as an effective solution for the upcycling of the inorganic residue from thermochemical conversion of landfill wastes. The added value will be put in correlation with both structural and functional properties.

Inorganic waste as raw materials for glass-based products

Inorganic residues, in the view of conversion into glass-based products, can be divided according to the content of glass formers, notably silica. In fact, silica-rich waste materials can be vitrified by themselves or with limited quantities of additives, such as recycled glasses. Silica-poor wastes, on the contrary, cannot lead to glass-ceramics or glass-foams, without additional raw materials; however, silica-poor wastes may have a significant impact on the functionalities of the final products.¹

Ashes from different combustion processes represent a fundamental example of silica-rich waste.⁶ Coal fly ashes (FA) from thermal power plants vary their composition as function of the type of coal used, the combustion conditions or the provenance, as shown in Table 1.⁷ Molten coal fly ashes may form glass directly, but more commonly some additional oxides are added to lower the viscosity, from minerals or from glass cullet.^{8,9}

Ashes from incineration of municipal solid waste (MSW) should be considered as belonging to two distinct categories: (a) MSW incinerator bottom ashes (BA); (b) MSW incinerator fly ashes. Bottom ashes (consisting of glass, magnetic metals, minerals, synthetic ceramics, paramagnetic metals and unburned organic matter) are known to be poorly hazardous, especially in form of coarse particles.¹⁰ On the contrary, MSWI fly ashes constitute a significant form of hazardous waste, since they

contain dioxins or furans, to be destroyed, as well as leachable heavy metals (Cd, Cr, Cu, Pb), to be immobilised.¹¹

The high temperatures required by vitrification cause the destruction of organics,^{1,2} but gaseous emissions must be verified in terms of chlorine and volatile heavy metal oxides. Preliminary treatments (washing, mixing with additives) are feasible, but they may determine a new disposal problem.² Ashes actually derive from any process for energy recovery, reduction of waste volume and destruction of possible organic pollutants. The ashes produced vary in their composition according to the different waste incinerated. Rice husk ash, produced in biomass power plants that use rice husk as fuel, has been used as a silica precursor since it contains around 85–90% of amorphous or crystalline silica depending on the combustion conditions.² Sewage sludge fly ash, paper sludge ash, oil-shale ash or meat and bone meal ashes feature are interesting since they contain significant amounts of other glass forming oxides, such as P₂O₅.²

The most significant production of iron-rich wastes derives from the iron and steel industry. Blast furnace (BF) slag is undoubtedly easier to process than other slags, due to the high contents of silica and alumina, usually accompanied by CaO and, in a lower amount, MgO, as reported in Table 1. However, being a well-known pozzolanic material, BF slag is often reused for not-glass-based products, such as concrete and geopolymers.² Other slags, such as basic oxygen furnace slag (BOF) and electric arc furnace (EAF) slag, dust from an electrostatic precipitators, on the contrary, may find applications only after composition correction and vitrification.¹ Finally, iron-rich waste arise also from non-ferrous metallurgy processes (separation of copper from ores, zinc hydrometallurgy, aluminium extraction aluminium hydroxide, in turn deriving from bauxite after separation of the well-known 'red mud'), each leading to specific waste compositions.²

Plasma heating of waste from excavated landfills yields, besides syngas from anaerobic gasification of organics, a solid residue falling in an intermediate position between silica-rich waste and iron-rich waste,^{12,13} as shown by Table 1. However, the addition of low cost additives (such as recycled glasses, mine tailings) and conditioning treatments, notably pyrometallurgical processes – for the separation of valuable metals -, may make the chemical composition closer to the ranges for the most established waste-derived glass-ceramics (Slagstittals, see later) and favour the manufacturing of chemically stable, dense or porous products.

Table 1: Typical chemical compositions of selected waste and commercial waste-derived glass-ceramics (Slagsitalls) - adapted from the literature^{1,2,7}

Oxide	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	Na ₂ O	K ₂ O	Others (main)
Coal FA	18.1-75.6	7.6-55.5	0.8-37.8	3.5-9.0	3.1-9.9	0.2-2.6	0.6-2.4	2.5 - 18.2 SO ₃
MSWI FA	7.3-27.5	3.2-11.0	16.6-19.5	2.6-3.1	1.4-5.0	13.1	11.2	9.8 SO ₃ 10.3 - 22.0 Cl ⁻
MSWI BA	30.3-47.4	9.9-13.0	18.8-23.1	2.8-2.9	4.3-10.2	1.9-4.5	0.9-1.0	1.2 - 1.9 P ₂ O ₅
MBM *	2.3	0.2	46.4	1.3	8.7	8.7	3.5	34 P ₂ O ₅
Sewage ash	39.5	17.2	7.2	2.1	11.1	1.2	2.7	1.9 P ₂ O ₅
Oil shale ash	31.9-34.7	9.1-9.4	27.6-27.7	3.4-5.9	3.8-4.4	0.2-0.3	4.2-7.4	
Rice husk ash	90.7	0.06	1.2	0.8	0.3		1.6	3.6 P ₂ O ₅
BF slag	34.4-37.0	14.5-14.8	26.6-41.7	6.5-6.7	0.3-0.6	0.2-1.4	0.4-0.7	
BOF slag	10.3-13.7	1.1-3.9	38.7-40.4	7.4-8.2	11.2-12.9			2.0 P ₂ O ₅
EAF dust	4.4-5.9	0.7-1.5	7.5-20.7	5.2-9.6	24.3-52.8	0.9-6.6	1.0-1.8	1.1 - 15.9 Cr ₂ O ₃ 7.6 - 13.8 ZnO
Cu extraction waste	24.8-24.9	0.8-0.9	0.6-0.8	0.3-0.5	67.6-67.7		0.4-0.5	2.7 - 2.8 ZnO
Red mud	7.8	17.1	11.7	0.6	44.1	3.2	0.1	
Plasmastone	26.2-42.2	6.7-17.3	14.3-26.6	1.9-4.0	11.9-27.3	0.5-4.2	0.4-1.3	1-1.7 TiO ₂
Soda-lime glass cullet (SL)	71.6	1.0	9.0	3.9	0.1	13.5	0.4	
Boro-alumino silicate glass cullet (BS)*	72.0	7.0	1.0			6.0	2.0	12.0 B ₂ O ₃
Slagsitalls	49.0 - 63.0	5.4 - 10.7	22.9 - 29.6	1.3 - 12.0	0.1 - 10.0	2.6 - 5.0		5.0-10.0 P ₂ O ₅ 3.0-6.0 TiO ₂

* MBM=meat and bone meal ash; ** from discarded pharmaceutical vials

Monolithic glass-ceramics

Selected glass compositions may lead to controlled crystallisation, with formation of the so-called glass-ceramics, by a double step heat treatment. A glass component (shaped into the desired form) is heated first to the temperature of maximum nucleation and then to the temperature of maximum crystal growth (slightly higher than the previous one), with a holding time at each temperature, before cooling. Discovered in the late 1950s, the technology has been applied to waste-derived glasses since the early 1960s.⁷ As a consequence, the manufacturing of glass-ceramics must be considered as the most established valorisation way for inorganic waste, supported by an extremely vast literature, and by extensive industrial production, under trade names such as “Slagsitalls” and “Slagceram”.^{2,7}

Sheeted and pressed Slagsitalls have been produced for the last 50 years in more than twenty billion square meters and used in construction, chemical, mining and other branches of industry. The base glasses for both Slagsitalls and Slagceram products belong to the systems CaO-Al₂O₃-SiO₂ (CAS) and CaO-MgO-Al₂O₃-SiO₂ (CMAS) (see Table 1), and are obtained from slags of ferrous and non-ferrous metallurgy, ashes and waste of mining and chemical industries, with minor compositional adjustments with glass-forming oxides.^{1,2}

Quite constant glass compositions may be achieved adjusting the ratios between different wastes, when variations in the composition of a single component occur. In any case, changes in the overall glass composition are tolerated, considering the nature of the crystal phases developed, *i.e.* calcium silicates and aluminosilicates, forming a number of solid solutions (wollastonite, CaO·SiO₂; anorthite, CaO·Al₂O₃·2SiO₂; gehlenite, 2CaO·Al₂O₃·SiO₂ *etc.*).² The high percentage of crystals, distributed uniformly in the whole volume, with sizes varying from 0.1 to 1 mm, leads to good mechanical strength and excellent abrasion resistance, coupled with good chemical durability.

A key feature of waste-derived glasses, on the contrary, is the availability of nucleating agents, such as iron oxides. The crystallisation of iron-rich glasses begins with the separation of small magnetite (Fe₃O₄) crystals, but the surface oxidation of Fe²⁺ to Fe³⁺ may cause the formation of hematite (Fe₂O₃), thus decreasing the crystallisation degree. Operating with Fe-rich waste glasses, usually dark and exhibiting poor thermal conductivity by radiation, has some significant drawbacks. The removal of gas bubbles from the glass melt requires high temperatures and long holding times (refining step). Many pores in the base glass, frozen upon crystallisation, strongly limit the mechanical properties of the final glass-ceramics. In

addition, waste-derived glass-ceramics are generally aesthetically poorer than natural stones and traditional ceramics.^{1,2}

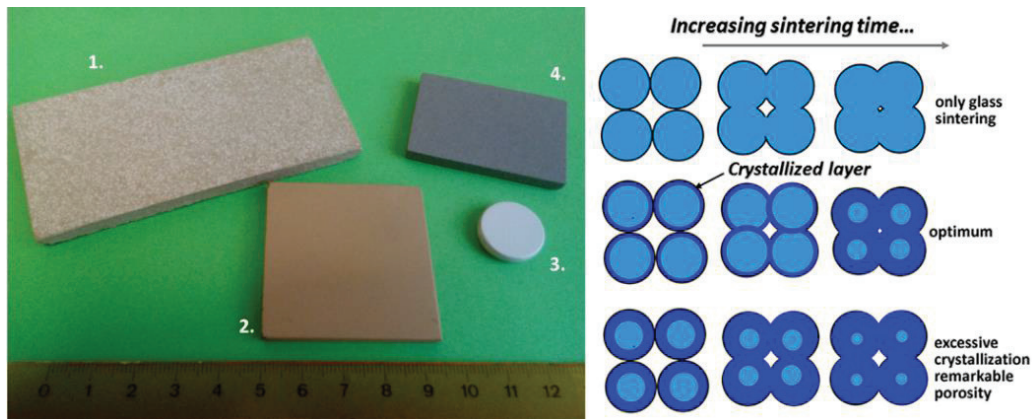


Figure 1: Examples of waste-derived sintered glass-ceramics (Slagsitall-type composition): 1. starting from coarse glass granules; 2. starting from fine glass powders (<50 μm); 3. starting from fine glass powders sintered after mixing with zircon white pigment; 4. material from direct sintering of a soda-lime glass/MSWI BA mixture (left); mechanism of simultaneous sintering and crystallisation (right)

The sinter-crystallisation process, consisting of the viscous flow sintering of glass frits with concurrent crystallisation, provides valid solutions for the above-mentioned drawbacks. Originally applied for the first time during the 1970s, for the manufacturing of marble-like tiles (used in the building industry), the process has been progressively transferred to the valorisation of waste glasses.¹ When applying the sintering route, there is no need to refine the melt before casting into a frit, thus reducing cost and gaseous emissions. In fact, the vitrification may be applied in small plants and in particularly short times, favouring the immobilisation of components that could vapourise with longer heat treatments. The ground glass powder is later pressed and heated to a certain temperature, at which viscous flow and crystallisation occur simultaneously. The crystallisation, generally starting at the contact points between adjacent glass granules¹⁴, gives a pleasant visual appearance to the products (see Figure 1, left part). More significantly, a relatively high degree of crystallisation may be achieved in very short times, the surface of glass being a preferred site for nucleation. In some cases, the sintering may be performed with very fast heating rates (even by direct insertion of glass powder compacts in furnaces set at the sintering temperature), thus configuring a fast sinter-crystallisation.¹⁵

The sinter-crystallisation process relies on a delicate balance between viscous flow sintering and surface crystallisation. As shown by Figure 1 (right), if the crystallisation at the glass surfaces is too intensive, the densification may be incomplete; on the contrary, for a glass not prone to surface crystallisation, the viscous flow sintering

predominates, with the formation of a sintered glass body. An optimum balance may be obtained by engineering the glass composition (Slagsitalls formulations provide a good reference), but also by adopting a hybrid approach, implying the use of mixtures of a glass particularly sensitive to surface nucleation with a glass not prone to crystallisation (*e.g.* waste-derived glass combined with soda-lime glass).²

Cellular glass-ceramics

Cellular glasses generally offer high surface area, high permeability, low density, low specific heat, high thermal and acoustic insulation and high chemical resistance.¹⁶ If mostly closed-celled, they can be termed as “foams”. In most cases, glass-based foams represent a further variant of glass sintering. If sinter-crystallised glass-ceramics depend on a delicate balance between viscous flow sintering and crystallisation, glass foams rely on a similarly delicate balance between viscous flow sintering and gas evolution. Crystallisation may occur as well.²

The gas evolution depends on oxidation or decomposition reactions of additives mixed with glass powders.¹⁶ Oxidation reactions cause the release of CO_x gas (carbon monoxide or carbon dioxide) from C-containing compounds, *e.g.* carbon black, graphite, SiC, organic substances, reacting with oxygen from the atmosphere. Decomposition reactions are those provided by carbonates (mainly Na- and Ca-carbonates) or sulfates, leading to the release of CO₂ or SO_x; a special variant comes from oxides of metals undergoing transition from high to low valence state and releasing oxygen gas (*e.g.* MnO₂ being transformed into MnO). Oxidation and decomposition may even overlap, with nitrides, transformed into oxides with release of nitrogen.¹⁶

Foaming additives, such as SiC, may be quite expensive and have a negative impact on the overall cost/benefit balance. Improvements are expected from the adoption of a new method – developed recently –¹⁷, based on alkali activation, as shown by Figure 2. Soda-lime glass suspensions, in weakly alkaline aqueous solutions (2.5 M NaOH, or KOH), undergo progressive gelification at low temperature (80°C). Before complete hardening, an extensive foaming may be achieved by vigorous mechanical stirring, with the help of a surfactant. The hardening to the formation of hydrated calcium silicate compounds (C-S-H), in analogy with conventional Portland cement.

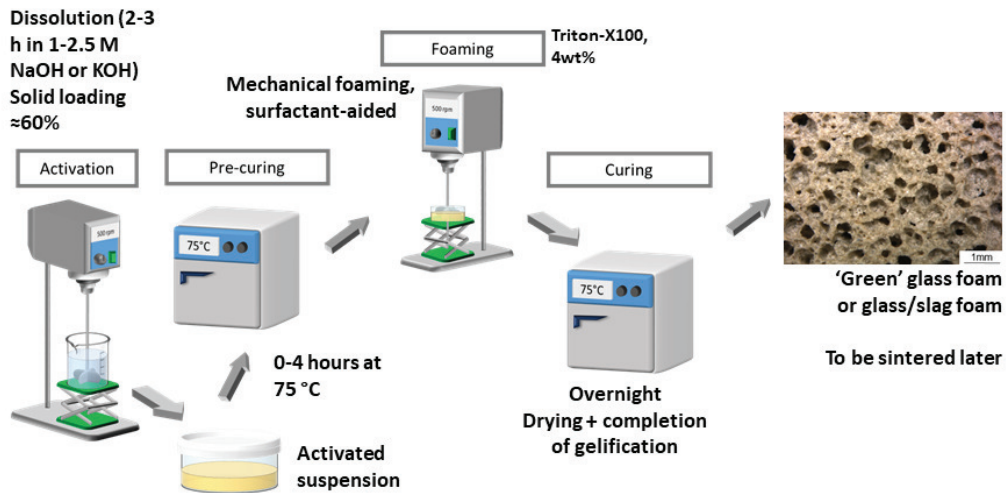


Figure 2: Schematic representation of the manufacturing of glass-based foams according to “weak alkali activation” (before sintering)

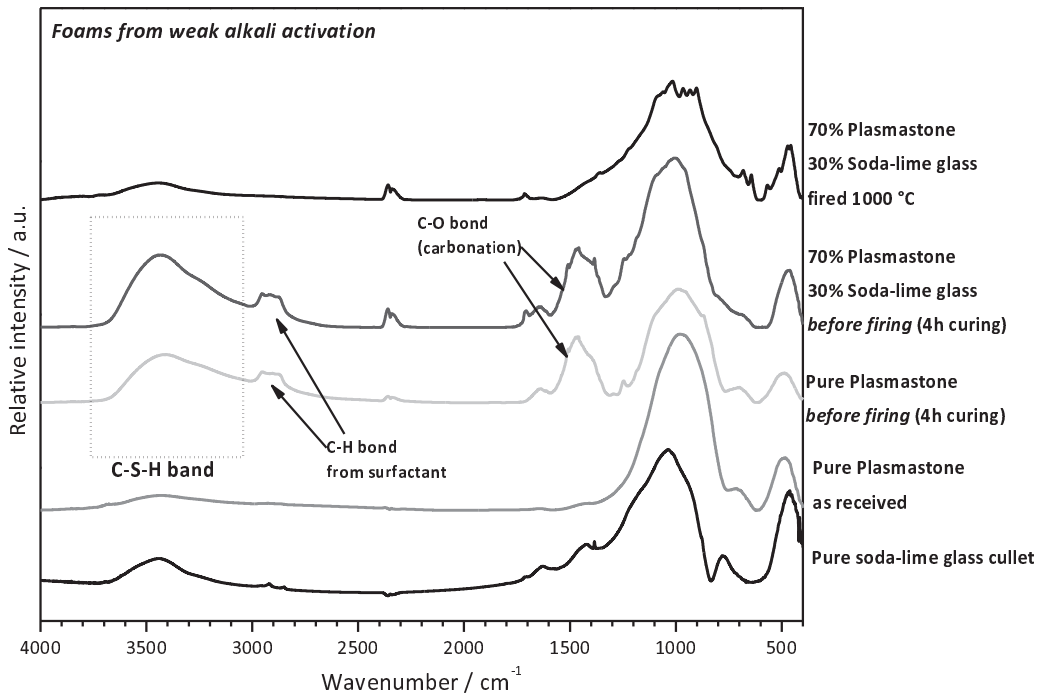


Figure 3: FTIR spectra of selected waste glasses before and after weak alkali activation/gelification/mechanical foaming

As shown by the FTIR spectra in Figure 3, plasmastone, owing to its high CaO content, exhibits a well visible absorption band centred at about 3400 cm^{-1} . The band is even enhanced when the waste-derived glass is considered after mixing with soda-lime glass (also rich in CaO). The band, not visible in the as-received conditions, disappears

after firing above 700°C. The water release associated with the decomposition of hydrated compounds is thought to contribute to the cellular structure (“secondary foaming”), upon firing. A slight contribution could actually come also from CO₂ release (the formation of carbonates is testified by the peak at 1400 cm⁻¹). The surfactant, visible from peaks attributable to vibrations of C-H bonds (C-H₂ stretch at about 2800 cm⁻¹), does not provide any contribution, upon firing, being completely decomposed below 400°C.⁷¹

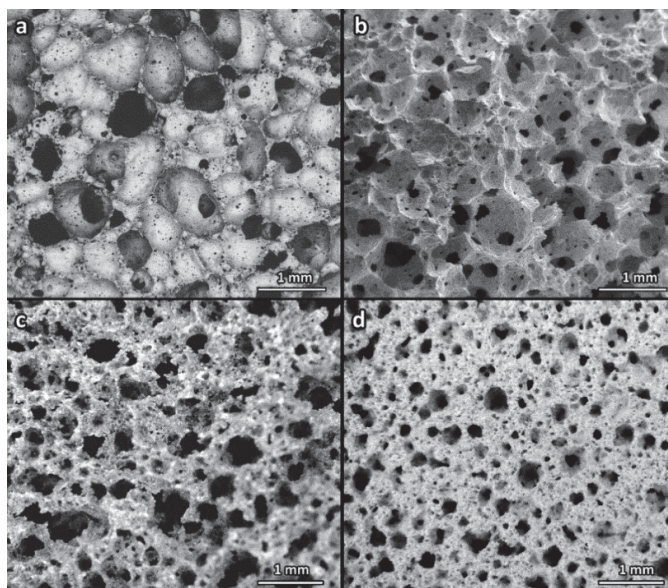


Figure 4: Example of glass-based foams resulting from weak alkali activation/gelification/mechanical foaming/sintering: a) soda-lime glass (3 h dissolution in 2.5 M NaOH solution; 4 h at 75°C; foaming with 4% Triton X-100 surfactant; firing at 700°C, 1 h); b) Ca-Mg silicate bio-glass (dissolution in 1 M NaOH; foaming with surfactant; firing at 900°C, 1 h); c) plasmastone 70%-soda-lime glass 30% (dissolution in 2.5 NaOH/KOH solution; foaming with surfactant; firing at 900°C, 1 h); d) glass from vitrification of MSWI BA (dissolution in 2.5 NaOH solution; 1 h at 75°C; foaming with surfactant; firing at 900°C, 1 h)

For soda-lime glass, the sintering step, aimed at stabilising the cellular structures, may be performed just at 700°C, *i.e.* at a much lower temperature than those required by foaming with C-containing additives (well above 850°C). A typical microstructure is shown in Figure 4a. The approach is so flexible that it can be applied, besides pure soda-lime glass, to (CaO-rich) bioglasses (Figure 4b)¹⁸, mixtures of soda-lime and iron-rich slag from copper metallurgy, Plasmastone (pure and with addition of soda-lime glass, Figure 4c) and glass from the melting of MSWI bottom ash (Figure 4d). The extensive crystallisation upon firing (*e.g.* occurring from glass-slag interaction) is not an issue, since it may freeze the open-celled morphology of the starting alkali-activated, foamed glass suspensions, leading to materials not simply

suitable for thermal and acoustic insulation, but also as scaffolds for tissue engineering, catalytic supports and filters.

Direct sintering and Layered glass-ceramics

Glass-ceramics from direct sintering rely on the formation of silicate and aluminosilicate crystals, similar to those produced by crystallisation of waste glasses, by interaction of recycled glasses with inorganic waste, upon sintering. This fact supports the use of the term “glass-ceramic”, despite the absence of any melting step.² The direct sintering is advantageous for reducing the volatilisation of some pollutants; on the other hand, the products lack homogeneity, so that some pollutants could remain concentrated in some areas. The leachability of sintered residues could be in any case lower than that of untreated waste (Zacco *et al.* specifically mention the viability of direct sintering of incinerator residues).¹¹

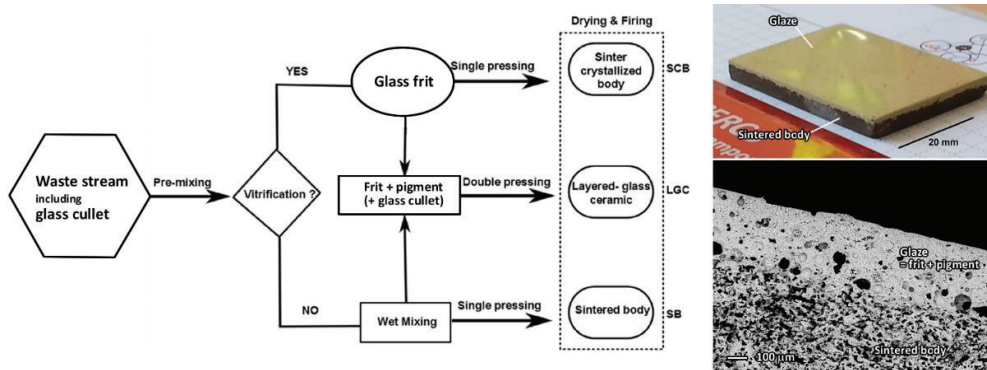


Figure 5: Schematic representation to different approaches to waste-derived glass-ceramics, with overall appearance (top right) and typical cross-section detail (bottom right) of a layered glass-ceramic tile

Layered glass-ceramics (LGCs), shown in Figure 5, object of more recent investigations, may be seen as an evolution of directly sintered glass-ceramics. They refer to a specific market need, in the field of building materials, *i.e.* that for lightweight tiles, with low water absorption (below 2%, for optimised frost resistance), to be placed vertically. Anchored to metal frames, in turn fixed on main building walls, these tiles constitute the so-called ventilated façades. The air gap between the tiles and the wall contributes positively to the thermal insulation (minimising thermal losses, in winter, and minimising overheating, in summer). In layered glass-ceramics, a single-step treatment causes the direct sintering of a base body formed by a glass/waste mixture and the sinter-crystallisation of a glaze, obtained from a glass in turn derived from the same starting materials.² The high residual porosity (in the order of 30-35%), the high water absorption, the poor visual appearance and the limited chemical homogeneity of the base body are not

significant issues. In fact, mechanical strength, colour and stabilisation of pollutants depend on the much denser glaze (the glazed side is that to be exposed to the environment). Strength, colour and shrinkage of the glaze can be adjusted by using additives, like pigments and other glasses. Vitrification of waste is reputed to be sustainable, since it is applied only to a limited amount of starting materials; the single firing reduces the costs associated to the deposition of a glaze.

Table 2: Strength-density correlations for selected glass-ceramic foams

Formulation	Sintering T (°C)	Total porosity (vol.%)	Shape factor (ϕ)	Compressive strength, σ_{cr} (MPa)	Calculated strength, σ_{fs} (MPa)
SL glass foam, amorphous (Fig. 4a)	700	86	0.8	3.2 ± 0.5	89.7
Bioglass CEL2, crystallised (4b)	900	75	1	2.4 ± 0.2	102.9
Plasmastone/SL glass 70-30, crystallised (4c)	1000	80	1	1.4 ± 0.1	78.2
Plasmastone/BS glass 70-30, crystallised	1000	75	1	2.2 ± 0.3	88.0
Vitrified BA, crystallised (4d)	900	81	1	6.2 ± 0.7	374.3
Soda-lime glass + Cu slag (6c)	900	82	0.8	1.3 ± 0.1	30.0

Structural and functional properties

Most of glass-ceramic foams exhibit a quite favourable compromise between thermal conductivity (good if low) and strength (good if high). The strength of glass-based foams can be actually tuned according to cell morphology and crystallisation. In general, the crushing strength of a cellular material depends on the bending strength of the solid, with a scaling factor. This factor is a function of the relative density (ρ_r , ratio between density of the porous body and density of the solid phase, or “true density”), according to the well-known Ashby’s model:²

$$\sigma_{cr} = \sigma_{fs} \cdot [0.2 \cdot \phi \cdot \rho_r^{1.5} + (1 - \phi) \cdot \rho_r] \quad (1)$$

Where ϕ defines the fraction of solid at the cell edges ($1 - \phi$ represents the fraction of solid at the cell faces), σ_{cr} is the compressive strength and σ_{fs} is the bending strength of the solid phase. A closed-cell morphology corresponds to significant contribution from the linear term, absent for open-celled foams (or “sponges”, with $\phi = 1$).

Table 2 reports some estimations of the bending strength of the solid phase for the foams shown in Figure 4, based on ϕ values of at least 0.8. Any glass-based cellular

material, in fact, is not “ideally closed-celled”, in its mechanical behaviour; membranes between adjacent cells (visible in Figure 4a, for soda-lime glass foams) do not collaborate in full, for the presence of pores, so that a good fitting of data is given by relatively high ϕ values. The effect of partial crystallisation on the crushing strength of glass-ceramic is not straightforward. On the one hand, it may increase the bending strength of the solid phase (visible from CEL2 and vitrified BA); on the other hand, the crystallisation may increase strongly the apparent viscosity of the glass, limiting any reshaping of pores upon firing and leading to poorly homogeneous materials. The structural disuniformity (see the foam from plasmastone/glass mixture, Figure 4c) may compromise the reinforcing effect. Finally, as brittle materials, porous glass-ceramics are subjected to a size effect, so that beyond differences in the distribution of solid phase between edges and faces, the strength increases with decreasing cell size (see the foam from vitrified BA, Figure 4d, exhibiting a particularly remarkable compressive strength).

Some crystal phases do not affect the strength, but are interesting for the functional properties. In particular, iron-rich phases, such as magnetite (Fe_3O_4) and other ferrites (oxides with the general formula $\text{M}^{2+}\text{O}\cdot\text{Fe}_2\text{O}_3$), are well known for their ferri-magnetic behaviour, that could be tuned by changing composition, processing temperature, annealing time, particle size (for frit-derived glass-ceramics), heating and cooling rates. As an example, Francis studied the annealing of a glass, from the melting of furnace slag and flue dust, for 2 h at 800 to 1000°C, and found that saturation magnetisation decreases as a consequence of the transformation of the magnetic species into non-magnetic phases.¹⁹

The ferri-magnetism implies the dissipation of electromagnetic energy, owing to magnetisation hysteresis, that could be exploited in many applications. As an example, Ponsot *et al.* obtained ferrimagnetic glass-ceramics, from the sintering of borosilicate waste glass with iron-rich slags (from copper and lead metallurgy), that could reach high temperatures (exceeding 300°C) after the application of an alternating magnetic field for very limited times (60 s).²⁰ The glass-ceramics could configure innovative heating elements (for cooking tops), considering the resistance to thermal shock (due the low expansion coefficient of the borosilicate glass matrix) and the chemical stability (confirmed by cytotoxicity studies). Further studies, *e.g.* in the field of electromagnetic shielding, are currently in progress on foams from alkali activation/gel casting/firing based on plasmastone-based foams, sintered at low temperature (800°C, Figure 6a) and mixtures of soda-lime glass and Cu metallurgy slag (see Table 1, Figure 6b). In particular, Cu slag leads to glass-ceramic foams owing to interaction between constituents, in turn causing the precipitation of Ca-Fe silicate (pyroxene) and iron oxides, in form of magnetite and hematite (Figure 6c), upon firing at 900°C. For an optimum slag content of 20 wt% the glass-ceramics exhibit some

potential in electromagnetic shielding, owing to the observed absorption band at 2.4 GHz (Figure 6d); the obtained glass-ceramics could find a valuable application, despite the relatively low strength (see Table 2).

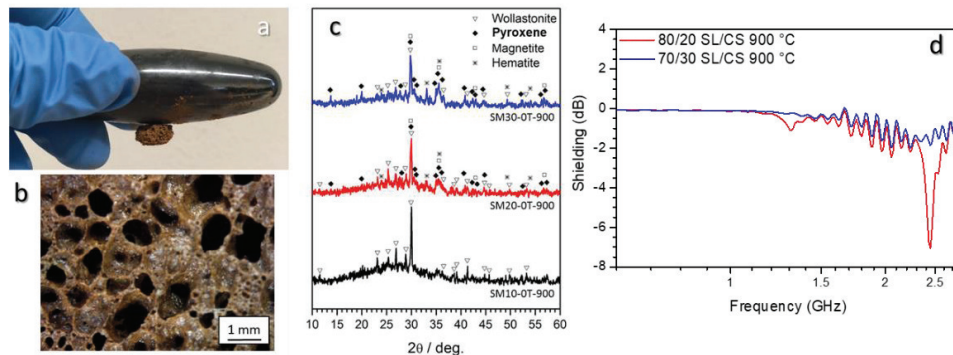


Figure 6: Obtainment of ferri-magnetic glass-ceramics: a) magnetic behaviour of plasmastone-based foam sintered at 800°C; b) microstructure of a foam from soda-lime glass and Cu slag (20%), obtained by alkali activation/gel casting, fired at 900°C; c) crystal phases as a function of Cu slag content; d) electro-magnetic shielding tests on selected foams

Any valorisation option has no actual sense if the developed materials do not exhibit an absolute stabilisation of pollutants from the adopted waste. The reference to a standard composition, provided by Slagsitalls (already recognised as stable materials), is specifically intended to optimise the chemical durability. The leaching performances of glass-ceramics, in fact, may be hard to predict, with some ions embedded in the crystal phases or in the residual glass phase. The previously mentioned “hybrid” approach may be helpful if a waste-derived glass is already available and remelting would not be possible and/or convenient. Glass from dismantled pharmaceutical vials (see Table 1), as an example, may be considered as an additive for plasmastone-based foams obtained by weak alkali activation/gelcasting. The practical absence of CaO determines some difficulties in the low temperature hardening (the amount of C-S-H developed is attributable only to plasmastone dissolution; 30% recycled glass means a reduction of 30% of the phase responsible for the hardening), but the chemical durability is much higher than that exhibited by foams with soda-lime glass as additive. Figure 7, in particular, shows the release of selected heavy metals (V, Cr, Mo), upon leaching tests, normalised on the thresholds for class D (=inert) materials, according to the Austrian Recycling Building Materials Ordinance.²¹ Contrary to soda-lime glass-containing foams, the foams from the use of pharmaceutical glass can be considered as perfectly “safe”: V and Mo are nearly one order of magnitude below the threshold; Cr remains closer to the threshold, but more than one order of magnitude below compared to the leaching of materials deriving from soda-lime glass. The durability is favourably

affected by the overall reduction of alkali and by the enhancement of oxides with a stabilising action, such as B_2O_3 and Al_2O_3 .

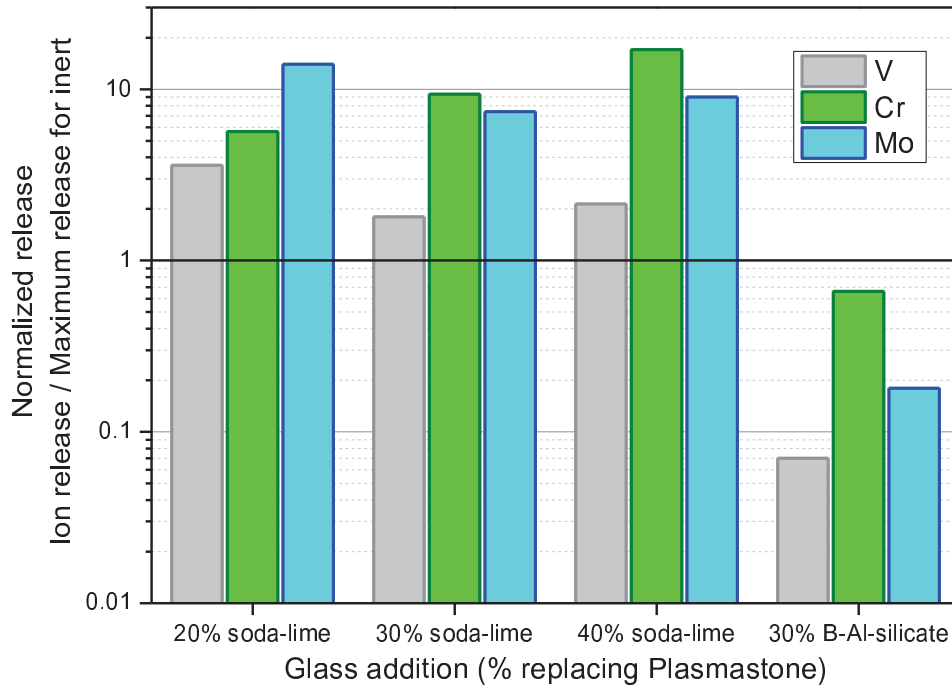


Figure 7: Leaching of selected heavy metals from glass-ceramic foams (according to Austrian Recycling Building Materials Ordinance) derived from plasmastone/recycled glass mixtures

Concluding remarks

The continuously increasing production of hazardous and toxic wastes undoubtedly favour the manufacturing of both monolithic and cellular glass-based materials, by application of viscous flow sintering. The extra costs for these treatments may be limited by a careful engineering of chemical compositions and well compensated by integrating the processing of glass-based products in a comprehensive “waste management chain”, according to which the starting glasses are not the only result of waste stabilisation, but are available as side products of gasification/metal extraction operations. The mixing of waste-derived glasses with recycled glasses generally provides some control on viscous flow sintering, crystallisation and chemical durability even *a posteriori*, i.e. not operating on the starting formulations. Finally, chemical components that could represent an issue for the overall processing of glass-ceramics, such as iron oxides, may actually be turned into an opportunity for extending the functionalities of the final products.

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