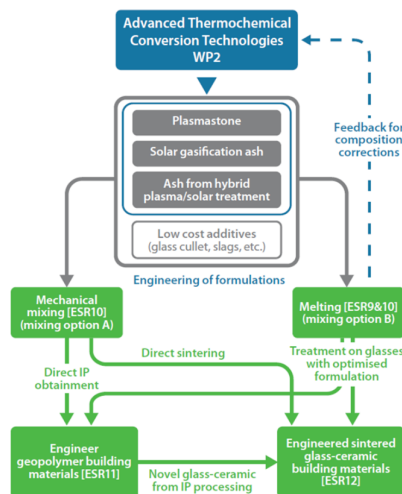




EU TRAINING NETWORK FOR RESOURCE RECOVERY THROUGH ENHANCED LANDFILL MINING

# European Training Network for Resource Recovery Through Enhanced Landfill Mining (NEW-MINE)

## D3.1 Final report on WP advanced upcycling



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Confidential

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## 1. Introduction and objectives

A milestone in circular economy is undoubtedly represented by the concept of ‘end of waste’. A certain waste stream can be conveniently used, as an example, for energy generation, exploiting the organic fraction, subjected to combustion (direct generation) or thermochemical conversion (indirect generation, by synthesis of new fuels), but, in general, its ‘pollution potential’ does not disappear. In fact, inorganic fractions remain as a fundamental by-product, with even enhanced hazardousness, due to the concentration of noxious compounds, namely including heavy metals. A truly circular approach cannot neglect the treatment of the by-products, by transformation into safe and useful products.

The term *upcycling* is by itself a guiding light. It specifies the act of reusing waste as raw material for *valuable* new products, distinct from the original ones [1]. Safety and generic utility must be integrated by economic attractiveness, realized when the properties of the new products match with (or even exceed) those of commercial products, but with savings in the overall processing.

Specifically concerning landfill waste, the work package #3 (WP3) had the following scientific and technological objectives, pursued by early stage researchers ESR9, ESR10, ESR11 and ESR12, supported by respective partner institutions (RWTH Aachen University, KU Leuven, Italcementi and University of Padova):

- To develop energy-efficient and environmentally sustainable, electro-thermal and mechanical techniques for the conditioning of by-products from the thermochemical conversion of RDF (ESR9, ESR10);
- To develop innovative building materials, with a low carbon footprint, chemically stable and exhibiting multiple functionalities, from the unconditioned and conditioned by-products of the thermochemical conversion of RDF (ESR11, ESR12).

The first point reminds that the upcycling potential of inorganic waste may be even enhanced, by separation of metallic and non-metallic components; in fact, metal extraction is doubly convenient, in the perspective of replacement of conventional ores and development of a glass residue with specified chemistry, in turn favoring the obtainment of further products. The second point reminds the challenge in applying any upcycling option, concerning the balance between energy/emissions inputs and outputs. New cementitious materials (‘inorganic polymers’) and cellular glass-ceramics were specifically targeted as *references for a low carbon economy*: while inorganic polymers are attractive in replacing ordinary Portland cement, produced by means of a CO<sub>2</sub>-intensive process [2], cellular glass-based materials, in configuring highly durable thermal insulators [3], offer significant savings during their service life.

## 2. Methods

The starting point for WP3 activities consisted of the selection of appropriate reference materials. Ideally, WP3 activities could be applied only *after* the completion of those in WP1-2, since upcycling technologies were expected to deal with (mostly) inorganic residues from preliminary separation and thermochemical treatments on the organic fraction of landfill waste. The upcycling options (pursued mainly by ESR11 and ESR12) were progressively refined on models of the outputs from WP1-2:

- **Plasmastone:** *glass* from industrial plasma-assisted processing of municipal solid waste (from Scanarc Plasma Technologies AB, Hofors, Sweden [4]), already realizing both transformation of organics (as combustible synthetic gas, SynGas) and separation of molten metal alloy (owing to reducing conditions); this glass configured a preliminary hypothesis of integration between WP1-2 and WP3, *after* application of a specific electro-thermal technology; the industrial process, however, *did not allow for compositional control*;



- **Municipal solid waste incinerator bottom ash (MSWI BA):** the residue configured a model for the output of WP1-2 *before* the application of electro-thermal and mechanical techniques, realized by ESR9 and ESR10, by means of large scale experiments, leading to a new generation of waste-derived glasses (VBA, vitrified bottom ash);

It can be noted that *glass is essential in the overall methodology of WP3*. When properly formulated, glass collects a multitude of inorganic non-metallic components (i.e. oxides, dominated by  $\text{SiO}_2$ ) and permanently stabilizes noxious pollutants, such as heavy metal ions, trapped by chemical bonds inside an amorphous network [5]. As an example, waste-derived glasses belonging to the  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  system, possibly including also  $\text{Fe}_2\text{O}_3$ , date back to the 1960s [6]. Waste-derived glasses are *intermediate products*, since only their use as raw material for new marketable products would imply adequate revenues to compensate the costs of waste conversion ('vitrification'). Interestingly, they are also *attractive intermediates*, since they may lead to products by application of low temperature treatments, such as *alkali activation* and *viscous flow sintering*.

A milestone in ESR9 activity consisted of the application of *submerged arc furnaces* (SAF) for the smelting of inorganic waste. The previously mentioned ashes were first dried, and later on, metallic pieces were recovered using magnetic and eddy-current separators. SAF conditions were defined through the study of the material and the thermodynamic conditions necessities for reducing metal oxides and eliminating hazardous such as chlorides, sulphates, dioxins and heavy metals. Metals were recovered either by liquid metal collection after coagulation or by volatilisation via the gas/ flue dust output. The by-products produced in melting trials were comminuted and characterised. The chemistry of non-metallic fraction ('mineral by-product') could be kept quite constant, as an effect of the mixing of ashes with fluxes, such as  $\text{CaO}$  or  $\text{MgO}$ , and additional waste, such as MSW incineration fly ash (IFA). An overview of the 'conditioning' operations is provided by Fig.1.

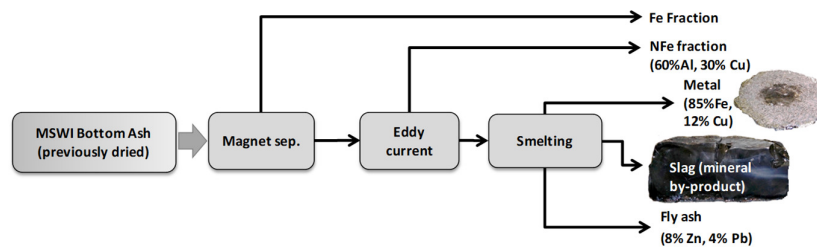


Fig.1 - Scheme of ash conditioning (example: MSWI BA)

ESR10 focused on alternative electro-thermal treatments for the obtainment of a glassy inorganic residue. SAF technology is undoubtedly energy-intensive, but it relies on a substantial recovery of metals. *Vitrification is somewhat integrated with a metallurgical treatment* (a waste-derived glass is obtained in analogy with what traditionally occurring in blast furnaces, with molten metal topped by a layer of lighter vitreous slag [5]; this is reminded by Fig.1, where the non-metallic by-product is termed as 'slag'). Conventional vitrification, without substantial metal recovery, is evidently less sustainable, but there is room for improvement specifically in the heating method. In particular, the ESR considered *microwave heating*, which has demonstrated advantages over conventional heating methods. The ability of microwaves to heat selectively, and quite often volumetrically, depending on the microwave process equipment, results in high heating rates and energy savings [7]. In the specific case, the microwave response of MSWI BA had to be tuned through the measurement of dielectric properties. As a second step, the microwave vitrification of BA was realized using a single-mode microwave cavity, operating at 2.45 GHz.

The core of ESR11's activity consisted of *alkali activation* as nearly room temperature option for the transformation of glassy by-products into construction materials. Alkali-activation is actually receiving a growing interest in defining binders alternative to Portland cement, but also monoliths.



Usual alkali-activated materials (AAMs), generally known as ‘geopolymers’, are produced through the dissolution of an aluminosilicate reactive compound in a concentrated aqueous solution of alkali hydroxide or silicate [8]. The dissolution causes the release of ‘inorganic oligomers’ (molecules with few  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  ions mutually bonded by bridging oxygens, with OH terminations) in the aqueous solution, later subjected to condensation reactions, with water release and formation of a gel, at low temperature (room temperature or typically a temperature below 100 °C). Typical reactive aluminosilicates, such as metakaolin, are known to yield a ‘zeolite-like’ gel, consisting of a continuous, three-dimensional aluminosilicate network, amorphous or semi-crystalline [8]. The alkali ions remain substantially ‘trapped’ in the aluminosilicate network, for an optimum  $\text{Al}_2\text{O}_3/\text{SiO}_2$  balance in the raw materials, with the achievement of chemically stable products, also when industrial by-products are used as raw materials [9].

It should be noted that a gel is formed even from formulations with different  $\text{Al}_2\text{O}_3/\text{SiO}_2$  balances; in addition, CaO-rich formulations do not yield a ‘zeolite-like’ gel, but provide a condensation product that could be termed ‘tobermorite-like’ gel, given the analogy with the products of cement hydration [8]. The term *inorganic polymer* (IP) may be used to identify the products, independently from the structure [8,10]. The concept of alkali activation and ‘inorganic polymerization’ is open also to glasses, as raw materials. Glasses with engineered chemical composition (aluminosilicate glasses) can be used as precursors for geopolymer-like materials [11-13], to be used as new binders for the building industry, according to the formation of sodium aluminosilicate hydrate (N-A-S-H) and calcium aluminosilicate hydrate (C-A-S-H) gels. ESR11 specifically explored the fundamental processing parameters affecting the reaction mechanism involved in the formation of Ca-Fe-rich IPs and their correlation with the final properties of the developed materials.

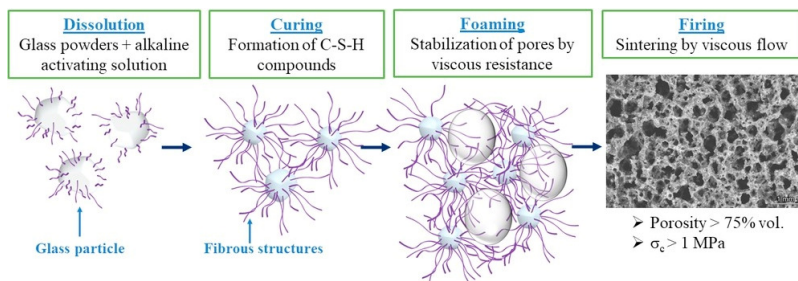


Fig.2 - Scheme of manufacturing of glass-based foams from alkali activation and mechanical stirring

ESR12 pursued the upcycling of vitreous by-products by extensive application of viscous flow sintering. Compared to crystalline ceramics, glasses feature a distinctive advantage in the possibility of sintering at moderately high temperatures. In fact, fine glass powders may coalesce and form a ‘pyroplastic’ mass when put above the so-called dilatometric softening point, in turn placed slightly above the transition temperature,  $T_g$  [5]. The preliminary milling and the reheating determined additional costs, but the properties of the resulting product could be enhanced by the simultaneous crystallization of glass (‘sinter-crystallization’), leading to glass-ceramics. Interestingly, alkali activation and sinter-crystallization could be combined (Fig.2) for the manufacturing of *highly porous glass-ceramics*. In this case, the activation was not intended at extensive glass dissolution, but at the formation of surface gels (mainly based on hydrated calcium silicate compounds) by *partial* dissolution, operated by much diluted alkaline aqueous solutions (‘weak’ alkali activation), leading to progressive hardening [14]. An extensive direct foaming may be achieved by mechanical stirring of partially gelled suspensions, comprising also a surfactant. Sintering is applied just to consolidate ‘green’ foams resulting from dried suspensions (first stabilized by the viscous resistance offered by surface gels). The process is reputed to be less expensive and more environmentally friendly than the





## 2. Conditioning of ashes by microwave heating

The conditioning of ashes by microwave irradiation (KU Leuven) was assessed through dielectric properties measurements up to 1060°C (Fig.4). BA is a low loss microwave (2.45 GHz) absorber up to 320°C, above which the dielectric properties were dominated by the pyrolysis of organic matter and the production of char resulting in an instantaneous thermal runaway of 500°C/min; high temperatures (>1400 °C) were achieved in a few minutes (Fig.5). The identified phase changes in the BA during microwave processing were the formation of pyroxene group minerals, liquid phases and the gradual transformation of hematite ( $\text{Fe}_2\text{O}_3$ ) to magnetite ( $\text{Fe}_3\text{O}_4$ ), wüstite ( $\text{FeO}$ ) and metallic iron. Air quenching yielded a high amount of amorphous phase (94 wt%) with minor amounts of crystalline phases, such as anorthite, corundum, pyroxene, wollastonite, quartz and metallic iron. Despite the much different processing, glass from microwave treatment still fell close to industrial waste-derived glasses; the absence of metal extraction reflected, however, in a substantially higher  $\text{Fe}_2\text{O}_3$  content, as reported in Tab.1.

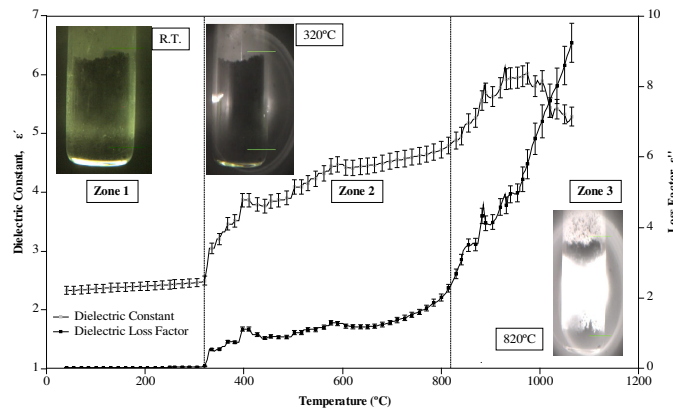


Fig.4 - Measured dielectric properties of DBA as a function of temperature. The images in each temperature range, depict the photos of DBA taken by the video camera during the dielectric properties measurements.

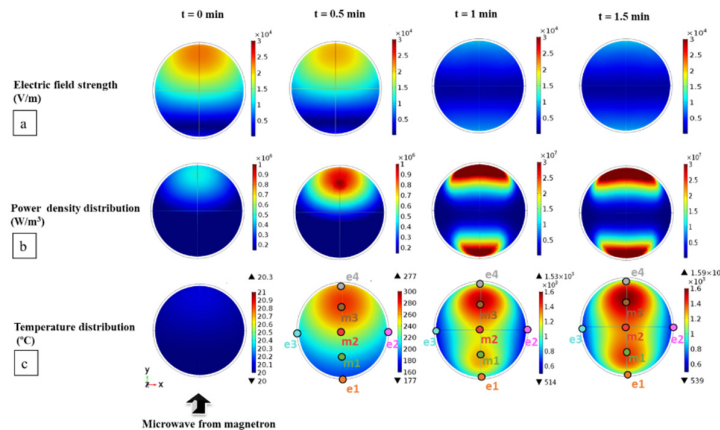


Fig.5 - Simulated electric field strength (a), power density distribution (b) and temperature distribution (c) for BA microwave vitrification performed at 800 W for 0 min, 0.5 min, 1 min and 1.5 min processing time.

## 3. Manufacturing of inorganic polymers with engineered properties

A broad range of IP materials with engineered properties were produced and optimized (at Italcementi in cooperation with KU Leuven and University of Padova). Significant efforts were made in developing predictive models, in optimizing mixture proportions and in minimizing the shrinkage of





IP binders and mortars. Optimized products characterized by a high dosage of residues in their composition (> 90 wt% of solids), increased volumetric stability, excellent mechanical properties, and good residual characteristics after exposure to high temperatures were developed.

IP 'binders' (cementitious matrices without any 'inert' phase embedded) derived from a substantial dissolution of Plasmastone powders in alkali activated aqueous solutions [15]. This was due to the use of fine powders (>90% below 100  $\mu\text{m}$ ), immersed in high molarity (14M) KOH solutions. The  $\text{K}_2\text{O}/\text{SiO}_2$  balance was adjusted by addition of silica fume ad/or potassium silicate, as shown by Tab.2. Monoliths could be obtained simply by casting suspensions in metallic mouldings, followed by curing in controlled conditions ( $20 \pm 0.5^\circ\text{C}$  and  $95 \pm 1.0\%$  relative humidity) for 24 h.

Tab.2 - Overview of formulation of Plasmastone (PS)-derived IPs

Experimental plan	Code	Mixture portion (wt %)					Solid/liquid wt ratio	Molar ratios	
		PS	SF	K-silicate (aq.)	KOH (aq.)	$\text{H}_2\text{O}$		( $\text{SiO}_2/(\text{Al}_2\text{O}_3+\text{Fe}_2\text{O}_3+\text{CaO})$ )	$\text{K}_2\text{O}/\text{SiO}_2$
1	F11	66.3	5.2	0.0	17.5	11.0	2.50	1.00	0.20
	F12	66.3	5.2	0.0	23.0	5.6	2.50		0.26
	F13	52.4	4.1	0.0	13.9	29.6	1.30		0.20
	F14	52.4	4.1	0.0	18.2	25.4	1.30		0.26
2	F11	66.3	5.2	0.0	17.5	11.0	2.50		0.20
	F21	67.4	4.1	4.8	16.9	6.9	2.50		0.20
	F12	66.3	5.2	0.0	23.0	5.6	2.50		0.26
	F22	67.4	4.1	4.8	22.4	1.4	2.50		0.26

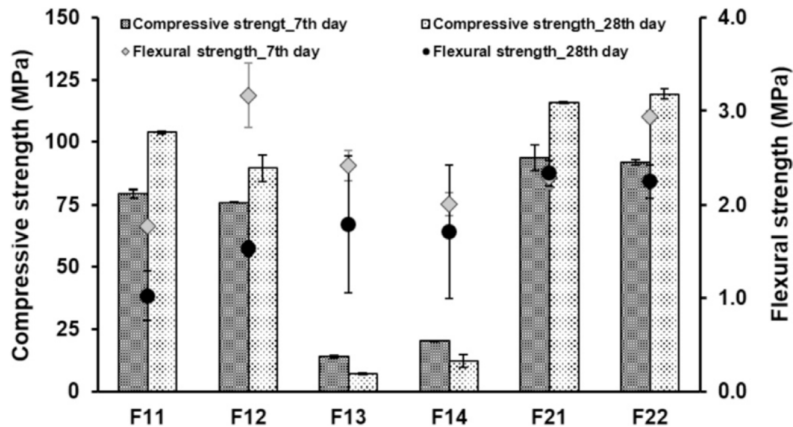


Fig.6 – 7 and 28 day physical properties of Plasmastone (PS)-derived IPs

The reaction kinetics and the structural development of Ca-Fe-rich IPs were mostly affected by the solid-to-liquid and  $\text{K}_2\text{O}/\text{SiO}_2$  ratios the most influential ones. The introduction of soluble silicates in the activating solutions positively impacted on the reaction kinetics and favoured the formation of denser microstructures, with a positive repercussion on the mechanical performance, summarized in Fig.6. Progressive refinements (by use of soluble silicates, see Fig.7a) led to even enhanced properties, such as low open porosity and water absorption (<5%) and high flexural (up to 7 MPa) and compressive strength (up to 175 MPa).

The undesirable, substantial drying shrinkage (water loss in the pores, resulting in significant capillary stresses) could be controlled by addition of organic compounds, leading to pore generation. 2-Methyl-2,4-Pentanediol was found to be the more effective shrinkage reducing agent and slight less detrimental to strength development. As an alternative, additions of commercial normalized sand ('inert' coarse aggregates, >100  $\mu\text{m}$ , leading to mortars) and calcium-rich admixtures (granulated blast furnace slag) were found to be a simple and relatively inexpensive method to minimize shrinkage





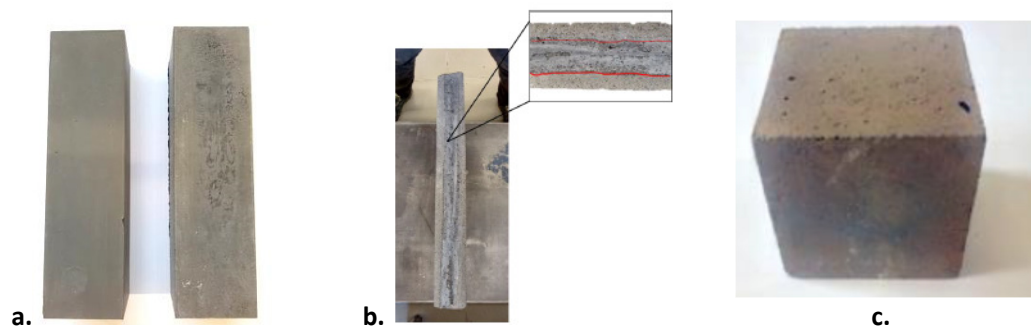
[16,17]. Increasing dosages of calcium-rich admixtures up to 3.0 wt% were able to reduce shrinkage by more than 60 %. By combining multiple shrinkage mitigation strategies, highly dense mortars with a total slag content that exceeded 85 wt% were developed presenting low shrinkage values ( $\approx 1$  mm/m) and, high flexural (up to 8 MPa) and compressive strength ( $> 55$  MPa).

The functionalization of IP mortars was addressed, and the effects of incorporating phase change materials (PCM) [18] in the mix design investigated. Lightweight IPs were developed using different processing routes, and their mechanical and thermal properties examined. Pre-made foams, in-situ foaming, and lightweight aggregates were used to produce thermal insulating lightweight materials with broad range properties. The parameters affecting each processing route were examined, and the materials optimized in terms of apparent density, compressive, and thermal conductivity.

The use of small-size lightweight aggregates was found the most adequate to develop insulating AAMs able to be compliant with structural requirements. The optimized materials presented compressive strength exceeding 4 MPa, apparent density near  $0.50 \text{ g/cm}^3$  and, thermal conductivity lower than  $0.10 \text{ W/m}^\circ\text{K}$ . For non-structural purposes, the combined use of gas releasing, air-entraining, and stabilizing agents was found promising. By adequately tailoring the mix design, IPs could be engineered to present extremely low apparent density and thermal conductivity,  $280 \text{ kg/m}^3$ , and  $0.06 \text{ W/m}^\circ\text{K}$ , respectively.

The addition of PCM (commercial microencapsulated paraffin Nextek\_24D, Microtek Laboratories) to the mortars formulation could effectively reduce temperature gradients, proving thermal buffering features to the developed materials. Such results indicate that IPs can be functionalized to act as passive thermal regulators able guarantee adequate levels of comfort in near-zero energy buildings.

The high-temperature resistance of the developed AAMs was also demonstrated (Fig.7c). The results have shown that IP mortars have superior thermal performance relative to those of mainstream construction materials. Post-heating properties are determined by the maximum temperature of exposure and heating rate. Lower heating rates have a beneficial effect on AAM's mechanical performance, while steepest heating processes promote severe deterioration processes and result in extensive crack development. Those harmful effects limited the use of the developed materials to  $900^\circ\text{C}$  if high heating rates would be experienced. Nonetheless, independently of the heating rate tested, the thermal features of benchmark materials (e.g., OPC-based products) were clearly surpassed [19].



*Fig. 7 – a) Specimens of optimized dense IP binders (thickness = 60 mm);  
b) Multifunctional composite panel prototype (total thickness =85 mm; dense layers 15 mm thick);  
c) Cubic sample (size: 60 mm) treated at  $900^\circ\text{C}$  ( $1^\circ\text{C/min}$ )*

Finally, a precast multifunctional composite panel was produced. The motivation for this research was to develop high performance sustainable sandwich panels (Fig.7b) with the potential to replace conventional precast insulating solutions. The challenge was to demonstrate the feasibility of



producing thermally-responsive and insulating sandwich panels at a semi-industrial scale and identify possible criticalities in future upscaling stages. The production of optimized IP mortars, with or without containing phase change materials, was shown to be a robust process that does not suffer significant scaling effects. Conversely, the production of foamed IPs was found to be more sensitive to scaling, which can be challenging in industrial contexts.

#### 4. Manufacturing of dense and porous glass-ceramics

As specified above, glasses feature a distinctive advantage in the possibility of sintering at moderately high temperatures. With specific formulations, sintering occurs with simultaneous crystallization ('sinter-crystallization'), thus forming glass-ceramics [5,6]. Owing to the formation of a multitude of silicate and alumino-silicate crystals, embedded in a residual glass matrix, dense glass-ceramics are generally much stronger than glasses (fully amorphous) and they can be used as structural materials, e.g. as a replacement of natural stones (marble, granite) or traditional ceramics (such as porcelain stoneware) in claddings and floors [5,6]. Interestingly, the previously mentioned waste-derived glasses belonging to the  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  system (possibly including also  $\text{Fe}_2\text{O}_3$ ) are among the most suitable for the application of sinter-crystallization treatments [5], with the possibility to achieve nearly full density and substantial crystallization (Fig.7), starting from fine powders ( $<50\text{ }\mu\text{m}$ ), by fast heating treatments (30 min at  $900\text{-}1000^\circ\text{C}$ , with high heating rates).

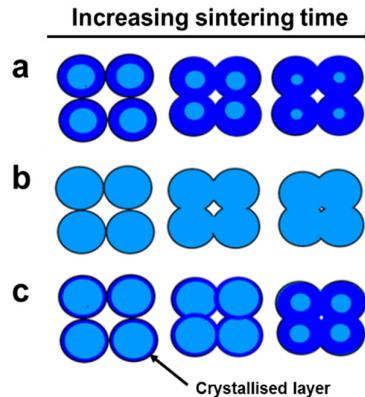


Fig.8 - Scheme of sinter-crystallisation: a) excessive crystallisation; b) only glass sintering; c) optimised condition.

Plasmastone, as expressed by Tab.1, did not fall within the compositional range of 'comfortable'  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  glasses. Owing to the remarkable  $\text{Fe}_2\text{O}_3$  content, sintering was accompanied by a too intensive crystallization (stimulated by the preliminary separation of iron oxide phases), impeding densification (Fig.8a); in other words, Plasmastone powders crystallized before viscous flow sintering could take place [20]. The balance between sintering and crystallization, however, could be tuned by addition of waste soda-lime glass (discarded fine powders from the recycling of glass containers, not accepted in the manufacturing of new container for the presence of heterogeneous plastic and ceramic contaminations), generally leading to crystallization-free sintering (Fig.8b). The glass additive effectively underwent viscous flow (promoting densification), but it also reacted with Plasmastone, leading to significant changes in the developed crystal phases (calcium rich silicates instead of silica-poor calcium alumino-silicates). The Plasmastone-soda lime 'hybrid' substantially behaved like a homogeneous glass undergoing optimized sinter-crystallization (Fig.8c)

Dense glass-ceramics were obtained (at University of Padova) from uniaxial pressing of powder mixtures of 45 wt% Plasmastone, 45 wt% soda-lime glass and 10 wt% kaolin clay (used as binder) [20], as shown by Fig.7. The firing treatment was performed at  $1000^\circ\text{C}$  for 30 min with heating and cooling rates of approximately  $40^\circ\text{C/min}$ , mimicking that of industrial ceramic tiles (generally fired well above



1100 °C). The fast treatment promoted itself the viscous flow, preventing the crystallization before reaching the maximum firing temperature. In this way, dense glass-ceramics with water absorption below 0.7% could be achieved (small sample for sintering test shown in Fig.9a; a pleasant bronze-brown colour was accompanied by an absolute control of shape, except an uniform shrinkage of ~8%). The elastic modulus was equal to  $76.8 \pm 2.5$  GPa, whereas the bending strength (calculated for big tiles, with a dimension of 300 mm x 300 mm x 8 mm, from statistical treatment of experimental data, collected on small bars) approached 40 MPa, well above the lower strength limit (35 MPa) for commercial ceramic tiles. Furthermore, the specific bending strength was 16 MPa cm<sup>3</sup>/g, highly exceeding the milestone value (2 MPa cm<sup>3</sup>/g, originally set on the values of natural stones). Finally, the environmental impact assessment performed on these materials showed that the leaching of hazardous elements was particularly limited (cooperation University of Padova-Montanuniversität Leoben), and mostly attributable to alkali-enriched residual glass phase (Fig.9b).

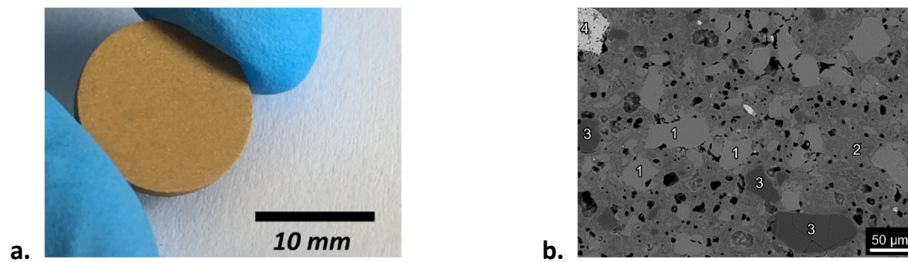


Fig. 9 – a) Aesthetic appearance of optimised dense waste-derived glass-ceramic; b) polished section with characteristic phases: 1) hedenbergite; 2) glass/wollastonite zone; 3) silica; 4) iron oxide

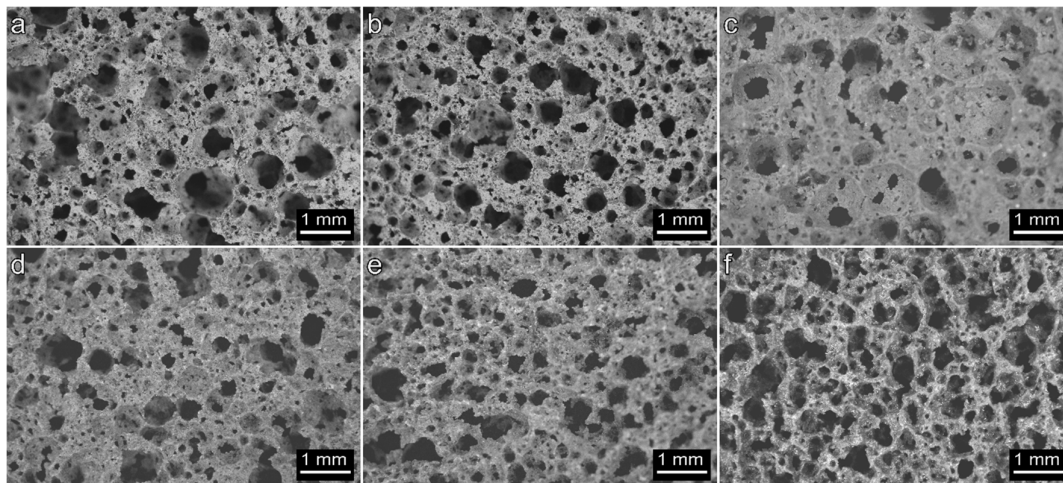


Fig. 10 - Micrographs of Plasmastone-derived foams fired at 1000 °C: a) Pure Plasmastone; b) 10SL; c) 20SL; d) 30SL; e) 40SL; f) 30BAS.

*Porous glass-ceramics* were considered as an even more promising target than dense tiles, for the possible exploitation in thermal insulation and in lightweight constructions. As mentioned before, highly porous materials could be achieved without applying the current procedures for the manufacturing of glass-based foams, based on glass powders – with specified chemical composition – mixed with foaming agents, which decompose and release gases at temperature well exceeding the glass softening point [6]. Foams actually exploited a recently established method based on a ‘weak’ alkali activation and gel casting [14]. Glass powders were cast in low molarity solutions (NaOH and KOH<3M), leading to highly loaded suspensions (55-65% solid content) which underwent progressive hardening (at 75°C), by formation of surface gels. Before complete setting, the suspensions, added



with a surfactant, could be directly foamed (by intensive mechanical stirring), dried and finally subjected to viscous flow sintering (at 800-1000°C).

The correction of Plasmastone with soda-lime glass (SL) did not simply support the sinter-crystallization, but it also favored the gelation (by formation of calcium silicate hydrated compounds). Highly homogenous foams (porosity of 75-80 vol%, with compressive strength >1 MPa), as shown by Fig.10, could be easily obtained and further tuned, in terms of chemical stability, phase development and functionalization. Firing in air, for Plasmastone coupled with soda-lime glass, led to products with limited but not negligible leaching of Cr, Mo, V; a complete stabilization of heavy metals could be achieved by replacement of soda-lime glass with another glass, namely boro-alumino-silicate (BAS) from dismantled pharmaceutical vials [21]. The new glass addition determined a different crystal phase assemblage, by interaction with Plasmastone, resulting in a more stable (i.e. more silica-rich) residual glass matrix, even for treatments at 800 °C [22].

Low temperature sinter-crystallization of porous glass-ceramics had a significant impact on additional functionalities. It specifically promoted the separation of iron oxide in form of magnetite phase ( $\text{Fe}_3\text{O}_4$ ); the consequent magnetic functionality disclosed additional applications, in *electromagnetic shielding* (in the GHz range) [22]. Such effect could be highly enhanced by firing in inert (nitrogen) atmosphere, leading to chemically stable materials even for soda-lime glass addition (simultaneous ‘stabilization and functionalization’), at only 800 °C [23]. The increased electromagnetic shielding (above 3 dB in a wide spectral range, see Fig.11a,b) actually derived from the overlapping of magnetism (absorption due to magnetic hysteresis), at high frequency, and electrical conductivity (above 2 S/m), at low frequency. The origin of electrical conductivity is still under investigation, but it reasonably derived from the overlapping of electronic conductivity of iron oxide phases (well-known semiconductors) and ionic conductivity of the glass-ceramic matrix.

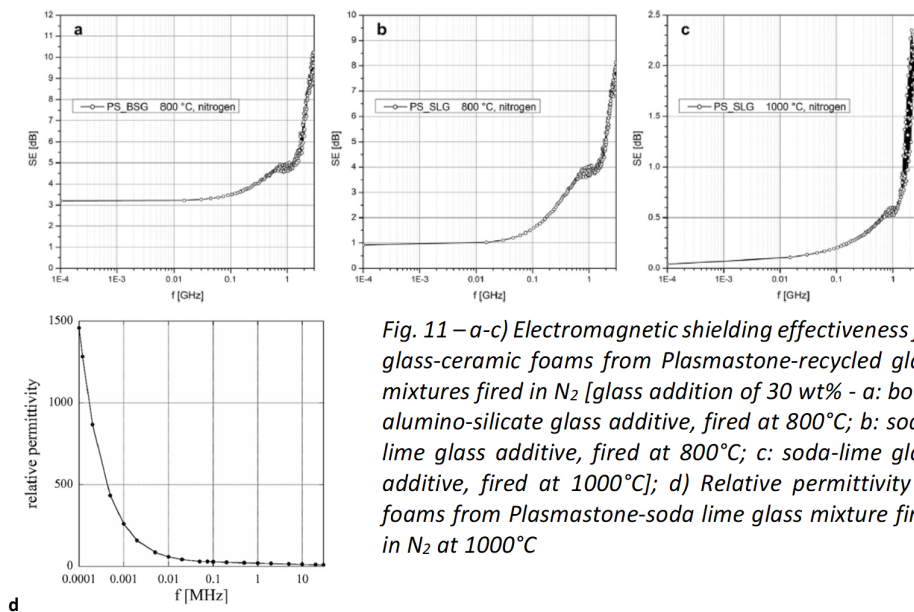


Fig. 11 – a-c) Electromagnetic shielding effectiveness for glass-ceramic foams from Plasmastone-recycled glass mixtures fired in  $\text{N}_2$  [glass addition of 30 wt% - a: boro-alumino-silicate glass additive, fired at 800°C; b: soda-lime glass additive, fired at 800°C; c: soda-lime glass additive, fired at 1000°C]; d) Relative permittivity of foams from Plasmastone-soda lime glass mixture fired in  $\text{N}_2$  at 1000°C

The application of treatments in nitrogen cannot be an extensive solution, but it triggers *high value secondary ‘niche’ applications*, as further ways of ‘advanced upcycling’. The coupling of electrical conductivity and presence of iron oxide phases could be exploited, as an example, in the field of electrocatalysis. Moreover, the electrical conductivity could be even tuned: increasing the firing temperature up to 1000 °C transformed glass-ceramic foams into insulators (conductivity  $<10^{-2}$  S/m), not leading to significant shielding (Fig.11c); however, iron oxide ‘islands’ exhibited a substantial





*polarization*, leading to materials with particularly high dielectric permittivity (Fig.11d), that could be applied in super-capacitors (for short term energy storage) [23].

Sinter-crystallization of vitrified ashes was somewhat more straightforward. Highly porous glass-ceramics could be obtained again by weak alkali activation and sintering, even without secondary glass addition [24]. The glass addition could be useful only to reduce the alkali activator (1 M NaOH instead of 2.5 NaOH) [25]. In general, foams exhibited a high strength-to-density value, exceeding in most cases the milestone value of 5 MPa cm<sup>3</sup>/g (for porosity >70 vol%), as shown by Tab.3, coupled with stabilization of pollutants (no release of heavy metals above thresholds for inert materials, upon leaching tests), for all conditioning strategies.

Tab. 3. Mechanical properties and porosity of the porous glass-ceramics.

Metal extraction/vitrification strategy	S1	S2	S3	S4
<b>Density determinations</b>				
$\rho_{\text{geom}}$ (g/cm <sup>3</sup> )	0.76 ± 0.03	0.54 ± 0.01	0.63 ± 0.01	0.66 ± 0.01
$\rho_{\text{apparent}}$ (g/cm <sup>3</sup> )	2.45 ± 0.00	2.70 ± 0.01	2.50 ± 0.03	2.55 ± 0.01
$\rho_{\text{true}}$ (g/cm <sup>3</sup> )	2.70 ± 0.00	2.81 ± 0.00	2.68 ± 0.00	2.64 ± 0.01
$\rho_{\text{rel}}$	0.281	0.193	0.233	0.252
<b>Porosity distribution</b>				
Total porosity (vol%)	71.9	80.7	76.7	74.8
Open porosity (vol%)	68.9	79.9	75.0	73.9
Closed porosity (vol%)	2.9	0.8	1.7	0.9
<b>Strength determinations</b>				
$\sigma_{\text{comp}}$ (MPa)	3.8 ± 0.9	3.0 ± 0.5	2.9 ± 0.9	4.2 ± 0.7
Specific $\sigma_{\text{comp}}$ (MPa cm <sup>3</sup> /g)	5.0	5.6	4.7	6.3

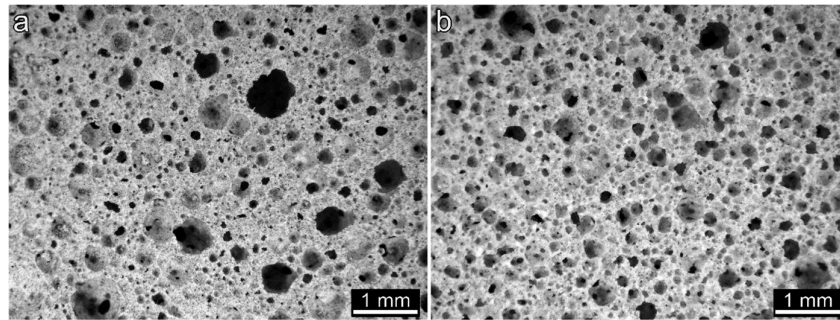


Fig. 12 - Micrographs of recycled vitrified bottom ash-based foams: a) foams made with only ground S1 foams; b) foams made with addition of 30% soda-lime glass.

Tab. 3 - Mechanical properties and porosity of 'recycled' porous glass-ceramics.

Group of samples	VBA recycled foams	70% VBA/30% SL glass recycled foams
<b>Density determinations</b>		
$\rho_{\text{geom}}$ (g/cm <sup>3</sup> )	0.68 ± 0.01	0.66 ± 0.00
$\rho_{\text{apparent}}$ (g/cm <sup>3</sup> )	2.66 ± 0.03	2.59 ± 0.01
$\rho_{\text{true}}$ (g/cm <sup>3</sup> )	2.72 ± 0.00	2.63 ± 0.00
<b>Porosity distribution</b>		
Total porosity (vol%)	75.0	74.8
Open porosity (vol%)	74.4	74.5
Closed porosity (vol%)	0.6	0.3
<b>Strength determinations</b>		
$\sigma_{\text{comp}}$ (MPa)	1.0 ± 0.1	4.9 ± 1.2



Foams from vitrified bottom ash could be actually considered as **permanent materials**, e.g. materials enabling further recycling after being dismantled (*'end of waste' fully achieved*). As shown by Fig.12a finely powdered glass-ceramic foams could be used as raw materials for another 'weak' alkali activation/sinter-crystallization cycle, still leading to homogeneous and chemically stable foams. Interestingly, while direct recycling led to generally weaker foams (compared to the ones from the first cycle), foams obtained by using mixtures of powders from dismantled primary foams and soda-lime glass (Fig.12b) exhibited an even increased strength-to-density ratio (attributable to transformation in the crystal phases arising upon reactive sintering), as reported by Tab.4 [26].

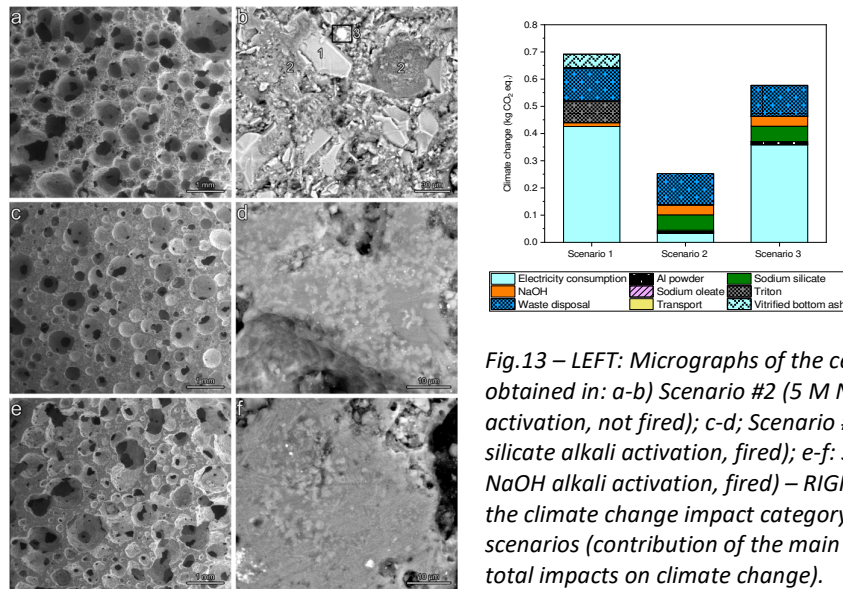


Fig.13 – LEFT: Micrographs of the ceramic foams obtained in: a-b) Scenario #2 (5 M Na-silicate alkali activation, not fired); c-d) Scenario #3 (5 M Na-silicate alkali activation, fired); e-f) Scenario #1 (1 M NaOH alkali activation, fired) – RIGHT: Results for the climate change impact category for three scenarios (contribution of the main processes to the total impacts on climate change).

Tab. 4 – Overall comparison of upcycling options

Group of samples	Scenario #1	Scenario #2	Scenario #3
Total LCA results per FU (panel 1000 cm <sup>3</sup> )	0.0031	0.0014	0.0030
Normalised LCA	1.00	0.46	0.96
Average leaching (L)	0.03	0.10	0.04
Normalised L	0.34	1.00	0.38
Strength, $\sigma_{comp}$ (MPa)	2.9	1.6	2.9
Normalised ( $1/\sigma_{comp}$ )	0.54	1.00	0.54

Glass from vitrified bottom ash (S#3) was actually tested for LCA studies (cooperation with ESR13, KU Leuven, WP4) aiming at comparing the manufacturing of highly porous foams (all with porosity ~70 vol%, Fig.13) obtained by different methods [27]:

- weak alkali activation, gel casting and sintering at 1000 °C (Scenario #1);
- inorganic polymerization (a 'strong' form of alkali activation) and pore generation by addition of reactive aluminum powder, without any additional firing treatment (Scenario #2);
- inorganic polymerization (a 'strong' form of alkali activation) and pore generation by addition of reactive aluminum powder, with additional firing treatment at 1000 °C (Scenario #3).

Fig.13 (right) shows that the enhanced energy consumption upon firing (Scenario #1) was nearly balanced by the enhanced use of alkali and synthetic alkali silicates in inorganic polymerization (Scenario #2). Scenario #1 was only nominally less sustainable, since LCA considered an expensive





synthetic surfactant used in the experiments ('Triton'), which could be replaced, in the perspective of industrial upscaling, by naturally derived surfactants. A more reasonable comparison concerns Tab.4, showing that fired products were generally stronger and with a lower 'average leaching' (average of the ratios between leachates and threshold leaching limits of all significant pollutants). A substantial equivalence of advanced upcycling options can be envisaged.

Finally, weak alkali activation, gel casting and sintering (at 800-900 °C) was applied also to VBA resulting from microwave heating [28]. Although not particularly strong (compressive strength not exceeding 3 MPa, for a porosity of 65-70 vol%), the foams could exhibit again a successful coupling of stabilization (leaching well below threshold levels for inert materials) and functionalization, with specific attention to electrical properties. The electrical conductivity was constant in the whole frequency range (75 kHz-30 MHz) at  $0.9 \pm 0.1$  S/m, a value of the order of that of Si and Ge semiconductors [26,28]. The relative permittivity evidenced particularly high levels (exceeding 50000), with a marked increase with decreasing frequency (a huge permittivity exceeding 200000 was noted at 50 Hz).

Apart from the production of porous glass-ceramics, the microwave-vitrified BA was also used as a precursor for the porous inorganic polymers. Mixing the precursor with a sodium silicate solution of high alkalinity, avoiding the use of any thermal treatment, resulted in the formation of highly porous materials with up to 4.8 MPa compressive strength (for a porosity of 65 vol%). Due to the inherent metal content of microwave-vitrified BA, the use of any metal gas releasing agent - typically used in the case of porous inorganic polymers, such as aluminum powder (fine metal particles oxidize in alkaline aqueous solutions, with hydrogen release) – could be avoided.



Fig. 14 - Lightweight aggregates; b: Internal structure of the aggregate.

Tab. 5 - Particle density, water absorption and peak load of the lightweight aggregates.

Firing temperature	$\rho_a$ (g/cm <sup>3</sup> )	$\rho_{rd}$ (g/cm <sup>3</sup> )	$\rho_{ssd}$ (g/cm <sup>3</sup> )	WA (%)	Peak load (N)
750 °C	0.8	0.7	0.8	9.2	150 ± 2
800 °C	0.8	0.8	0.8	10.2	202 ± 5
850 °C	0.9	0.7	0.9	19.2	174 ± 4
900 °C	0.9	0.7	0.9	26.6	150 ± 2

A final remark concerns again porous glass-ceramics (cooperation University of Padova-Italcementi). A moderate alkali activation (aqueous solution 5M NaOH/KOH) could be exploited for complete gelation of suspensions of waste-derived glass (Plasmastone) mixed with soda-lime glass (30 wt%), with drying at 75°C, for 40 min. The hardened suspensions could be hand crushed into fragments, subsequently fired at 750-900 °C (30 min, direct insertion of 'green' granules in the furnace, for 'instantaneous heating'). Porous *spheroidal aggregates* ('granules', Fig.14) were formed by viscous flow sintering accompanied by gas generation, deriving from the decomposition of the hydrated compounds responsible for the gelation. All four groups of lightweight aggregates (depending on sintering temperature, see Tab.5) were found to be quite light, with particle density below 2 g/cm<sup>3</sup>, thus fulfilling the Norm EN 13-055 for lightweight aggregates (*BS EN 13055:2016 Lightweight*



*aggregates*, 2016). Preliminary tests have already shown that these aggregates could be used in lightweight (cement-based) mortars, with low thermal conductivity, comparable to lightweight mortars produced with granulated foam glass. Further efforts will be likely applied, in the future, in the perspective of *extensive industrial exploitation*. A production of granules beyond the lab scale would be useful for the preparation of composites with waste-derived glass granules bound by a waste-derived inorganic polymer matrix.

#### 4. Conclusions and lessons learnt

The conversion of waste-derived glasses into inorganic polymers or glass-ceramics is confirmed to involve a number of mature and reliable upcycling technologies. The reliability mainly resides in the stabilization of pollutants, so that the obtained materials - to be variously applied in the building industry -, configure a real 'end of waste'. Alkali activation (realizing a more or less substantial dissolution of waste-derived glasses) is recognized as a fundamental processing step, in developing both inorganic polymers and porous glass-ceramics.

The obtainment of a glass from landfill waste triggers the upcycling technologies. The sustainability of this intermediate step (involving high temperature conditioning of *inorganic residues* from the pretreatment of waste) resides on its coupling with metal extraction or on the revision of the heating conditions, e.g. adopting non-conventional vitrification techniques, based on microwave irradiation.

The coupling of vitrification with metal extraction offers an interesting control of the chemical formulation of the waste-derived glasses, maximizing the chemical stability and the physical properties (namely mechanical properties) of the products from application of upcycling technologies. However, the upcycling technologies are so flexible to compensate 'deviations' from the glass formulations most likely leading to high quality products. This was effectively tested with Plasmastone, successfully combined with glass additives (other types of waste).

Glasses with formulations not fully corresponding to those most likely leading to high quality products (e.g. with extremely high  $\text{Fe}_2\text{O}_3$  content) are actually an opportunity, more than an issue. Engineered processing conditions, in fact, may lead to (still stable and safe) products with extended functionalities, to be used even beyond constructions.

Given their reliability and flexibility, the upcycling technologies outlined in NEW-MINE most likely constitute a reference in the whole field of valorization of inorganic residues. Further extensions (e.g. production of lightweight glass-ceramic granules, bound by an inorganic polymer matrix) are envisaged.

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