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# DEVELOPMENT AND CHARACTERISATION OF DENSE WASTE-DERIVED GLASS-CERAMICS

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## Introduction

Landfilling of waste has been employed for centuries as a low-cost manner for managing waste, which can provoke known serious issues to environment and society such as long-term methane emissions and local pollution issues.[1] Enhanced Landfill Mining (ELFM) has a potential to be a solution not only for the management of existing landfills, but also for current problems related to the limited availability of resources and energy production. *Ex situ* ELFM consists of excavating landfills and seeks maximum resources recovery in an efficient way. In addition, the fraction of waste that cannot be recovered can be used to generate energy by employing clean technologies such as plasma gasification.[2] During this process, a vitrified residue named plasmastone is generated, which can then be upcycled for developing building materials such as inorganic polymer binder.[2,3] Plasmastone can contain a high content of iron oxide which aids in the nucleation and crystallisation of glass during sintering.[4] Therefore, this glassy material could also be applied in the development of glass-ceramic materials without adding a nucleating agent by sintering with concurrent crystallisation (sinter-crystallisation).[5] However, as plasmastone is easily crystallised, its densification can be hindered due to an increase of the apparent viscosity of the glass caused by the formation of crystals during firing.[6] An option to produce dense glass-ceramics made with a glass sensitive to crystallisation is to introduce another glass that is hardly crystallised and can be easily densified by viscous flow, such as soda-lime glass (SLG).[7] Based on this, this paper reports the production, characterisation and environmental impact assessment of dense glass-ceramics made with a mixture of fine powders of plasmastone, recycled SLG and kaolin clay by cold pressing and sinter-crystallisation to be employed as tiles.

## Materials and Methods

Plasmastone (particle size < 75 µm) was provided by Scanarc (Sweden) with the following main composition: $SiO_2$: 37.3 (wt%); CaO: 22.9; $Fe_2O_3$: 20.9; $Al_2O_3$: 12.8;

MgO: 2.4 and $Na_2O$: 1.1. In addition, this material also contained metals like Cu (7124 ppm), Cr (406 ppm) and Ni (203 ppm), which exceed the Austrian limit values to be used as secondary resource in building materials. SLG (mean particle size of 30 µm) was provided by the company SASIL SpA (Italy). SLG, a fine powder, composes the residual waste glass fraction obtained after colour selection and removal of metallic and polymeric residues in glass recycling.[8] The main composition of this glass was $SiO_2$: 71.9 (wt%); $Na_2O$: 14.3; CaO: 7.5; MgO: 4.0; $Al_2O_3$: 1.2.[9] Sintered plasmastone derived glass-ceramics were obtained by uniaxially pressing a fine mixture of powders of 45 wt% plasmastone/45 wt% SLG/10 wt% white kaolin clay at 50 MPa in a steel die of squared section (50 mm). The green tile was dried overnight at 75°C and fired at 1000°C for 30 min with heating and cooling rates of approximately 40°C/min.

The mineralogical composition of powdered glass-ceramics was determined by X-Ray diffraction (XRD) (Bruker D8 Advance, Germany). The density was measured according to the Archimedes' method and water absorption according to the boiling method. The dynamic elastic modulus was measured using non-destructive dynamic resonance (E). Vickers microhardness was measured applying a load of 9.8 N and porosity was determined using the software ImageJ on micrographs obtained by scanning electron microscopy.

A four-point bending test (32 mm outer span, 8 mm inner span) was performed using an Instron 1121 UTS instrument (Instron, USA) on 15 specimens (35.1 ± 1 mm X 3.5 ± 0.2 mm X 3.1 ± 0.1 mm) with cross-head speed of 1 mm/min. Weibull statistics was applied according to Barsoum,[10] obtaining the Weibull modulus ($m$) and the characteristic strength ($\sigma_0^{4pt}$). The equivalent strength for three-point configuration was estimated by using scaling equations based on Weibull modulus and under the hypothesis of flaws happening with a volume ($Vf$) or surface ($Sf$) distribution.[11]

Leaching tests were performed following the ÖNORM EN 12457-4 (waste) with a liquid (distilled water) to solid ratio of 10. A commercial tile of "Ceramiche di Sassuolo" (Gruppo B II b) was used as control, as the use of recycled materials is only allowed as it can be proved that the environmental impact of the recycled product is not worse than that of a competing product from primary raw materials, according to Austrian Waste Management 2002. Inductively coupled plasma mass spectrometry and ion chromatography were used to measure the contents of heavy metals in the leachates and the Austrian Recycling Building Materials Ordinance was used as a reference.

The sample was analysed for distribution of main and trace elements using microprobe analysis (Jeol JXA 8200 Superprobe) after polishing the materials using 1 µm-sized diamond suspension and diamond spray followed by coating with a fine layer of carbon. Main and trace elements were measured in five points of each phase. These phases have been previously found in the XRD pattern and then identified by EDS.

## Results and Discussion

XRD analysis (Figure 1) reveals that presence of the following phases in plasmastone-derived glass-ceramics: Fe rich silicate (hedenbergite, $Ca(Fe_{0.821}Al_{0.179})(SiAl_{0.822}Fe_{0.178}O_6)$ PDF no. 78-1546), wollastonite ($CaSiO_3$ PDF no. 84-0655), hematite ($Fe_2O_3$ PDF no. 89-2810), magnetite ($Fe_3O_4$ PDF no. 89-0691), quartz ($SiO_2$ PDF no. 83-0539) and cristobalite ($SiO_2$ PDF no. 89-3607). The silica phases are originated from kaolin clay.

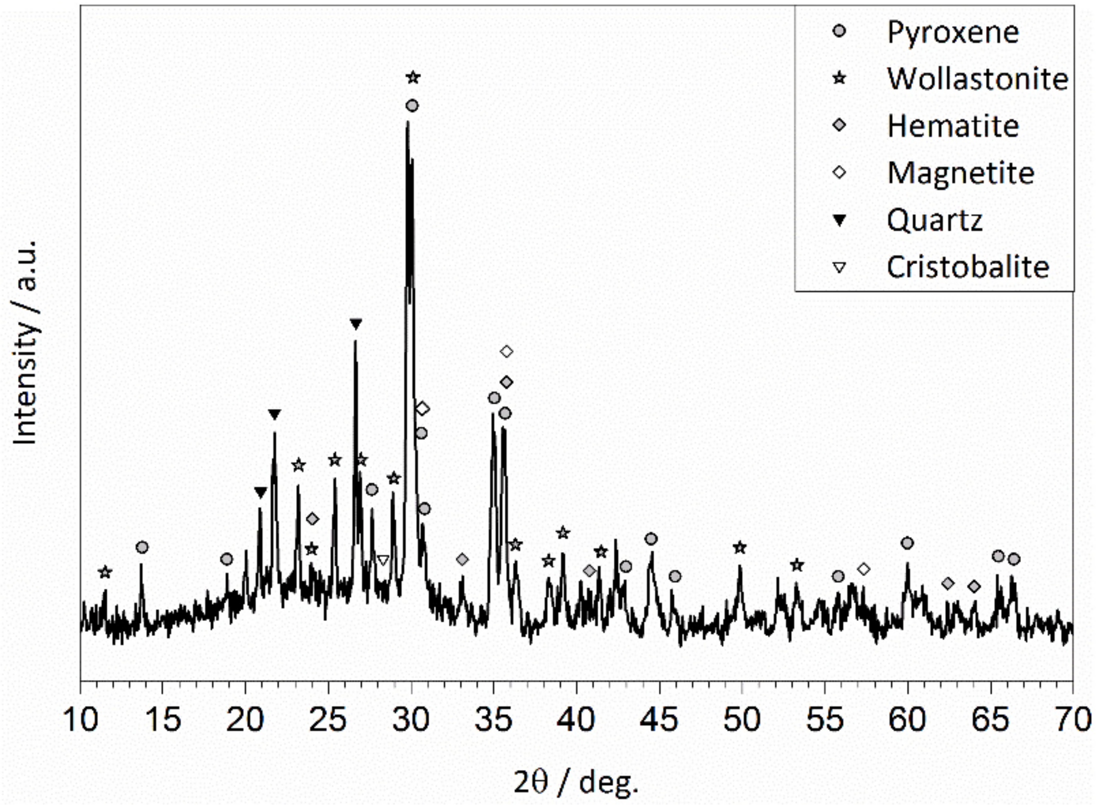

**Figure 1:** XRD pattern of dense plasmastone based glass-ceramic

The results from XRD are consistent with the micrograph (Figure 2) which shows the crystalline phases embedded in residual glassy phase, which helps in sealing the iron silicate rich zones. In addition, silicon oxide and iron oxide phases can be identified as well as a closed porosity, similar to industrial tiles.

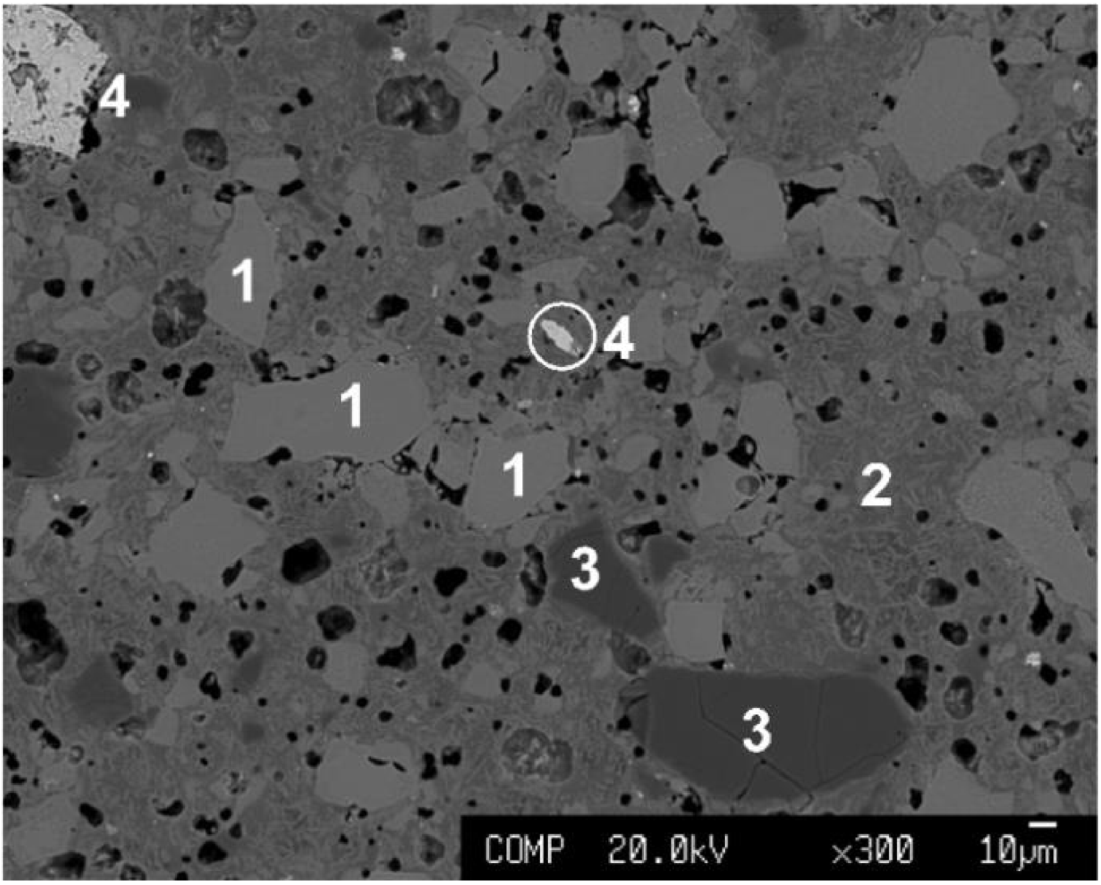

**Figure 2:** Micrograph of dense glass-ceramic: 1) iron silicate rich zone; 2) glass/wollastonite zone; 3) silica; 4) iron oxide

The mechanical properties of the glass-ceramic (Table 1) are in the same range as the mechanical properties of commercially available material: the elastic modulus is comparable to the one measured for a commercial porcelain stoneware,[12] while the microhardness is similar to other waste-derived glass-ceramics.[13,14] The equivalent strength $\sigma_{eq}^{3pt}$ in a three-point configuration of a sample with standard geometry (cross-section of 3 mm x 4 mm and loading span of 40 mm) was calculated as 76 MPa. In addition, the equivalent strength for bigger tiles $\sigma_{eq}^{L}$ (cross-section of 8 mm x 300 mm and loading span of 300 mm) exceeded the lower strength limit (35 MPa) for materials to be applied as tiles (BIa group).[15]

**Table 1:** Physical and mechanical properties of the dense sample

| Water absorption (%) | Density (g/cm$^3$) | Porosity (%) | *E* (GPa) | *m* | Strength (MPa) | | | $H_v$ (GPa) |
|---|---|---|---|---|---|---|---|---|
| | | | | | $\sigma_0^{4pt}$ | $\sigma_{eq}^{3pt}$ | $\sigma_{eq}^{L}$ | |
| 0.65 ± 0.12 | 2.52 ± 0.01 | 5 | 76.79 ± 2.5 | 11 | 69.8 | $76.6^{Vf}$ | $39.3^{Vf}$ | 5.3 ± 0.04 |
| | | | | | | $76.4^{Sf}$ | $43.1^{Sf}$ | |

Leaching tests (Table 2) shows that the samples are within the Austrian regulation for classes U-A and U-B with respect to leachability, despite the fact that the total contents of Cu, Cr and Ni exceeded the Austrian limit values for recycled building materials. U-A and U-B refer to quality classes for recycled construction materials used in unbound or (hydraulically/bituminously) bound applications as aggregate. On the other hand, the sample cannot be classified as D (which is relevant for slags), due to the quantity of Mo leached. However, it should be noted that even the control sample cannot be classified as D due to leaching of Co and W.

**Table 2:** Results of the leaching test of dense materials (mg/kg DM)

| | U-A | U-B | D | Control | Sample |
|---|---|---|---|---|---|
| Cr | 0.6 | 1.0 | 0.3 | 0.017 | 0.088 |
| Cu | 1.0 | 2.0 | | 0.19 | 0.33 |
| Ni | 0.4 | 0.6 | | 0.042 | 0.019 |
| Cl | 800 | 1000 | | 5.9 | 3.4 |
| $SO_4$ | 2500 | 6000 | | 19 | 32 |
| Ba | | | 20 | 0.029 | 0.13 |
| Cd | | | 0.04 | 0.001 | 0.0015 |
| Co | | | 1 | 2.9 | 0.018 |
| Mo | | | 0.5 | 0.12 | 1.5 |
| Tl | | | 0.1 | <0.0010 | 0.0041 |
| V | | | 1 | 0.26 | 0.064 |
| W | | | 1.5 | 2.8 | 0.18 |
| F | | | 10 | 4.2 | 2.6 |

Low leaching of heavy metals can be explained by the incorporation of heavy elements in stable mineral phases, as indicated by electron microprobe analyses (Table 3). They show that Cu is mainly bound in Fe oxide, Cr in iron silicate rich zones, whereas Zn and Ba are evenly distributed among iron silicate rich zones and glass/wollastonite zones (due to the resolution of the microprobe, it was not possible to perform the quantitative analysis separately in these phases). Mo, which is the only problematic element with respect to leaching, is mainly distributed among the glass/wollastonite zone. It is possible that the higher leaching of Mo is caused by dissolution of residual glassy phase: one of the reactions that occur when SLG is exposed to water is ion exchange reaction. In this class of reaction, protons or others cations replace Na (or other modifiers cations), which can cause the enhancement the pH of the solution, favouring network dissolution.[16] If indeed the glassy phase is dissolved, then other pollutants bond to it should also have been leached. However, Cu is present in a high quantity in glassy phase/wollastonite and its leaching is very low. One hypothesis is that Cu may be only bond to wollastonite, which apparently is not dissolved. Another hypothesis could be that Cu is indeed leached, but then a copper zinc silicate is precipitated which is not dissolved. This assumption comes from the identification of these silicates in others plasmastone based glass-ceramics developed by the group.

**Table 3:** Results of the microprobe analysis

| **Phase** | **Mo (%)** | **Fe (%)** | **Cu (%)** | **Ba (%)** | **Zn (%)** | **V (%)** | **Cr (%)** |
|---|---|---|---|---|---|---|---|
| Iron silicate zone | 0.01 | 13.3 | 0.20 | 0.03 | 0.06 | 0.04 | 0.13 |
| Silica | 0.01 | 0.18 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| Glass/ wollastonite zone | 0.03 | 3.50 | 0.25 | 0.03 | 0.05 | 0.01 | 0.03 |
| Iron Oxides | 0.00 | 62.1 | 0.41 | 0.00 | 0.03 | 0.02 | 0.10 |

## Conclusion

We may conclude that dense plasmastone derived glass-ceramics were successfully produced by sinter-crystallisation. The glass-ceramics present low water absorption and mechanical properties comparable to those of commercial ceramic tiles and natural stones. Concurrently, heavy metal leaching experiments indicated that the glass-ceramic have low leachability when compared to commercial ceramic tiles. However, Mo leaching was above Austrian regulation values. Separation of metals should thus be considered in the ELFM value chain prior to or during plasmastone production before its use in glass-ceramics.

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