

Article

Experiments Using Different Types of Waste to Manufacture Ceramic Materials: Examples on a Laboratory Scale

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Abstract: Reusing waste as raw materials to produce other materials can entail a decrease in production costs and in the abusive use of natural resources. Furthermore, it can even improve the properties of the end product or material. In this sense, a review of the most relevant literature published in recent decades shows that numerous solutions have been proposed or implemented, such as its use to produce construction materials, catalysts, pigments, pozzolana, refractory materials, glass-ceramic products, etc. Our research group has verified the viability of using different types of waste as secondary raw materials to obtain several types of ceramic, glassy and glassceramic materials, as well as frits. This article highlights several types of industrial waste that have both non-toxic (Li, Ca and Mn) and highly toxic (Cr VI) differentiating elements that can be used in sintering and vitrification industrial processes to immobilise them or render them inert. We studied the compositions and characterised the various materials obtained, conducting toxicity and leaching tests on waste/materials designed with high amounts of chromium. A suggestion for future lines of research has been proposed.

Keywords: waste; immobilisation; render inert; reuse; ceramics; glass-ceramics; construction materials



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1. Introduction

Society's concern over protecting the environment and implementing a self-sustaining industrial system has increased in recent years [1]. As a result, one of the most topical issues, due to its impact on the environment, is without question the issue of contamination from waste, immobilising it and rendering it inert, or treating it to potentially recover resources from said waste, using it as secondary raw material [2,3]. Furthermore, the EU has implemented mandatory directives that require a minimisation of waste and, specifically, that (with a very optimistic outlook) tailing ponds should disappear from the EU by 2017 (Directive of the European Parliament 2006/21/CE EUR-Lex-Europa.eu and EU classification criteria based on their dangerousness), which has not occurred. This waste is currently stored in special tanks or containers inside the factories that create them. Occasionally, it is dumped in uncontrolled landfills. This is why, for several years now, experts have been developing processes that make it possible to recycle waste by transforming it into useful materials [4,5]. From an economic point of view, reusing waste as raw materials to produce other materials can entail a decrease in production costs and in the abusive use of natural resources. Furthermore, it can even improve the properties of the end product or material. Numerous solutions have been proposed in this sense [5–8], such as using it to produce construction materials, catalysts, pigments, pozzolana, refractory materials, glass-ceramic products, etc. (Table 1). Therefore, interest in using most industrial waste as a raw material is increasing, proving the viability of using it as a secondary raw material to obtain various types of ceramic, glassy and glass-ceramic materials, as well as frits [5–8]. Other products obtained through thermal treatments and/or sintering processes [8] include those that can be used in agriculture as slow-release fertilisers (bioglasses produced using biomass) and biosolids.

Table 1. Types of waste used as secondary raw materials to manufacture ceramic and glassy products.

Waste	Material	Use
Concrete from demolitions	Fired clay ceramics	Construction
Glass containers: bottles, flat glass, TV screens and PCs	Gresites	Coatings (facades, tunnels, balconies, shops, gymnasiums, etc.)
Sludge: Hydrometallurgical, from wastewater treatment plants, estuaries, lakes, natural stone, etc.	Porcelain stoneware tiles, bricks, roof tiles	Flooring and coating
All types of slag: from smelting, plasma arc, etc.	Glassceramics, tiles, porous materials, etc.	Building and public works
Fly ash from municipal solid waste incinerators or thermal power stations	Bricks, traditional slabs, frits, glass-ceramics	Facades, producing enamels
Composite materials (fibreglass composites)	Sintered tiles from fibres	Flooring and coating

The building industry is an excellent industry for the absorption of large quantities of solid wastes and by-products. The ceramic floor and wall tile sector are the most important sector for ceramic products in Spain due to its high production and marketing, which implies a high economic scope and a great technological effort in its innovations and especially in its designs, which has led Spain to occupy a leading place in this type of products in the past decades. Ceramic products and, principally, bricks and tiles are very heterogeneous on having been formed by clay by a wide margin of composition. Due to this, these materials can tolerate the presence of different types of residues in a considerable quantity, which can help to reduce construction costs. The fundamental idea is that this type of waste can have applications as a “secondary raw material” in agricultural products (in the case of biosolids) or in construction (in the case of rustic ceramics, glass and glass-ceramics, or in the vitrification process itself as a means of inerting certain toxic or hazardous wastes). Our research group is formed by scientists involved in glasses from wastes (vitrification processing). The disordering of structures (amorphous or pseudo-amorphous) facilitates the hosting or immobilization of a wide range of industrial wastes. In the last decades, this research group has resolved some problems, such as the following: differences to immobilize specific type of wastes, the determination of the most efficient treatment by vitrification, the use of glasses and waste glasses as precursors for geopolymer production, etc.

The goal of this review article was to prove, through experiments conducted by our research group, that certain types of industrial waste can be rendered inert, specifically, industrial waste that is characterised by its differential amounts of Li, Ca, Mn and Cr, as well as having high amounts of aluminium and iron silicates. These types of waste are located in several areas in Spain and one of them is located in Mexico. They come from the following types of industries: wastewater treatment, natural stone quarries and sawmills, quarries for extracting pegmatites with lithium, municipal solid waste (MSW) incinerators, metallurgic industries (in this case regarding ferroalloys) and, lastly, others from the chemical industry that are highly toxic (such as sludge that has chromium VI).

The specific objectives were as follows: (i) conduct a full physical-chemical characterisation of the waste selected, (ii) design ceramic pastes using waste from the marble industries in the area of Novelda (Alicante, Spain), formulated with ash from MSW incinerators, to obtain (by sintering) traditional ceramic tiles, (iii) investigate the components of an abnormal deposit located on a beach in Galicia and try to establish its origin and interest (due to its high levels of Mn) to obtain glassy and glass-ceramic materials with uses in the optical, and dye and pigment industries, (iv) define the nature of the additions

of Cr_2O_3 , as a nucleating agent, to a ‘model glass, $\text{Li}_2\text{O}-\text{SiO}_2$ binary system’ to obtain traditional glass-ceramic materials, and (v) research how to render highly toxic waste inert, such as the waste from a chemical industry that produces compounds with chromium and with significant amounts of Cr (VI), which would enable a traditional industrial process, transforming this waste into a secondary raw material for the production of other materials.

2. Materials and Methods

2.1. Traditional Ceramic Covering Tiles Obtained by Recycling Marble Waste and MSW Fly Ash

Following the chemical (XRF) and mineralogical (XRD) characterisation of the clay ceramics used and the waste from marble dust and fly ash, we designed several compositions with ternary mixtures of conventional clay, fly ash from MSW incinerators and marble dust waste [1]. The initial compositions had the following amounts: fly ash from MSW = 0 (control), 1, 2, 3, 4, 5 and 10 (% of the weight) and marble dust = 0 (control), 15, 20, 25, 30 and 35 (% of the weight), respectively. The initial dust pastes were pressed axially in a semi-automatic Mignon-S Nanetti press at 40 MPa and in disc-shaped moulds measuring 20 mm in diameter and 5 mm in thickness, weighing around 3.5 g.

The firing was conducted under the common conditions used by the industries that use fast firing: 0–500 °C: 2 h+ 500–650 °C: 2 h+ 650 °C—Tmax: 2 h; Tmax: 4 h, maintaining the following maximum temperatures: Tmax at 975°, 1000°, 1025° and 1050 °C for 4 h [1,2].

We then established the linear shrinkage and water absorption capacity of the ceramic tile bodies obtained as well as the flexural strength using INSTRON 1011 machinery and by way of three-point bending [9–14].

2.2. Characterisation and Glass-Ceramic Capabilities of Glassy Slag Rich in Manganese Oxide

The chemical composition of the initial samples (Figure 1) was determined by X-ray fluorescence (XRF) (Brücker equipment). The crystalline phases were characterised in powdered samples by X-ray diffraction (XRD) and Cu $K\alpha$ radiation (40 kV and 30 mA), scanning a range of Bragg angles between 5° and 60°. The microstructure was initially studied at low amounts of magnification using transmission light microscopy with polarised light with a Nikon Eclipse E400 POL microscope on thin, uncovered samples [15,16].

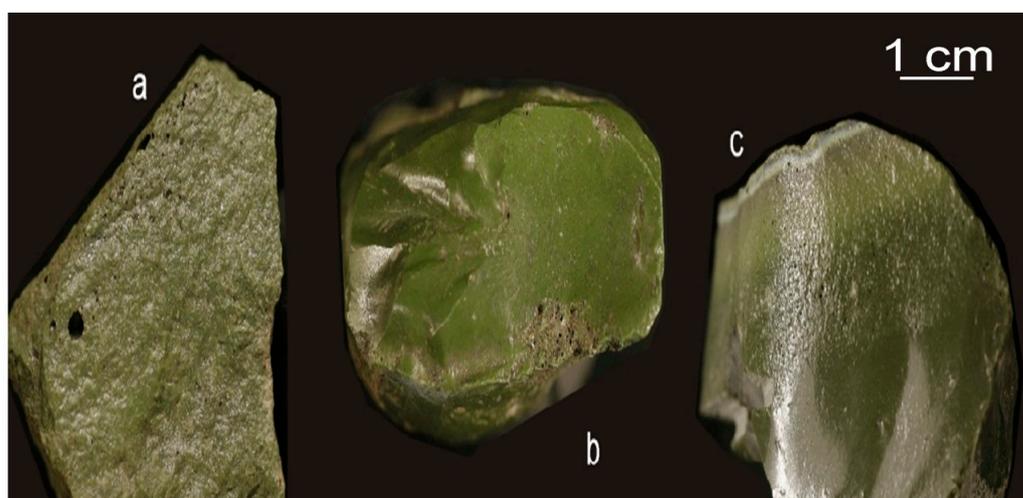


Figure 1. Deposited material, found on a beach, showing the general appearance of the samples taken during the sampling process and which can be classified into two types according to its visual features: (a,b) glassy-crystalline material and (c) glassy material with conchoidal fractures and a glassy shine [16].

To research the phase transformations of this material when it is heated at high temperatures, we conducted thermal differential and thermogravimetric analyses (DTA/TGA) using SETARAM® equipment with a heating speed of 10 °C/min in an inert atmosphere.

In addition, we studied the samples with hot stage microscopy (HSM, Misura equipment), also with a heating speed of 10 °C/min [16–22]. We then performed a waste melting experiment, heating it after crushing it into grains of 0.5–1 mm at 1450 °C in a Superkhantal resistance furnace at a heating speed of 20 °C/min, stabilising the melting temperature for 60 min and cooling it by directly straining the molten mass into a brass mould [22–24] to obtain prismatic glass bars (parallelepipeds measuring 30 × 5 × 5 mm). The black opal-opaque glass samples were observed through scanning electron microscopy and energy dispersive X-ray spectroscopy using JEOL SEM/EDS equipment (JEOL Ltd., Boston, MA, USA) (Figure 2).

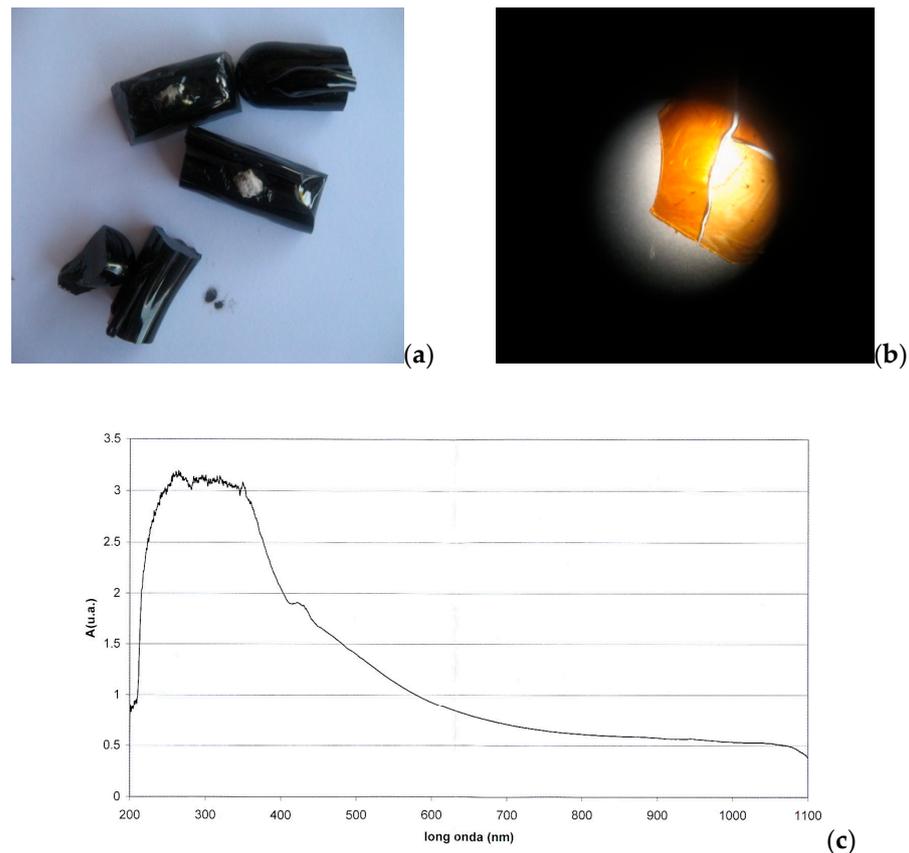


Figure 2. Appearance of a thin sheet of the glass obtained by melting the material rich in manganese oxide at 1450 °C, observed through a binocular loupe (a) and showing its amber colour when thinned (b); and (c) the optical absorption spectrum, which shows a 95% transmission for wavelengths greater than 700 nm.

2.3. Vitrification of a Soil Contaminated by Cr (VI) from a Nearby Urban and Industrial Area

We gathered three samples weighing 5 kg each to complete the experimental development of this research: Sample 1 from contaminated earth or soil from the area around the plant; Sample 2, which is more contaminated and has been confined for years (slags and sludge from ‘in situ’ storage vaults); and Sample 3 (less toxic), obtained from fragments of concrete from the walls of buildings in the contaminated location. All the samples (Table 2) come from the same venue, ‘Cromatos de México’ [25–29]. The chemical characterisation of the samples was performed with several analytical techniques: X-ray fluorescence (XRF), atomic absorption with inductively coupled plasma (ICP) and establishing their C and S contents through combustion. From the chemical composition of these types of waste, we designed and synthesised silicate-type glasses within the following ternary composition system: CaO–MgO–Al₂O₃–SiO₂ [25,26].

Table 2. Samples taken in this research and the resulting new vitrified materials.

Initial Sample Contaminated with Cr ⁶⁺	Formulating the Glasses	Glass Samples (Quenched)	Glass-Ceramic Samples
S1 (soil)	S1 + added feldspar gravel (70-25-5% of coke ash)	G1	GC1
S2 (slag)	S2 + S1 (soil)+ added feldspar gravel	G2	GC2
S3 (concrete from construction and demolition waste)	Milled as received	G3	GC3

These formulations required the addition of a silica feldspar-dolomitic gravel to produce calcium silicate glasses and reach compositions similar to those of natural basalt rocks, as it is well known that the latter are very stable glasses in the long term [27–30]. The mineralogical phases of both the different types of waste and melted glasses were analysed using X-ray diffraction (XRD) through the powder method, using Rigaku Model D max 210 equipment operating at 30 kV and 16 mA, using K α radiation of Cu ($\lambda = 1.5406 \text{ \AA}$) with a 5° angle of incidence to obtain information on the structure of the polycrystalline or amorphous materials analysed in this study. The physical features of the contaminated waste were analysed following various methods in order to determine the particle size, humidity, density, pH and the fraction that was soluble in water. The TCLP (Toxic Characteristics Leaching Procedure) test of the EPA was used to assess the leaching of the waste's toxic substances. The toxicity test with distilled water was used for waste samples S1, S2 and S3, and the melted glasses were analysed following ASTM Standard method D 3987-06 to learn the leaching behaviour of both types of samples before and after the vitrification [26–33].

The method for immobilising/vitrifying waste [34–36] with hexavalent chromium on a laboratory scale was conducted in graphite crucibles with mixtures of waste and additives in a Superkanthal electrical shaft furnace, specifically the SWEDISH AB pob 505 model, at high temperatures (1600 °C), and it was equipped with the temperature controller model EUROTHERM 818P4. We added feldspar-dolomitic silica gravel to samples S1 and S2 to make up for the low amounts of silica that this type of waste has. The amount of each mixture subjected to gradual heating until melting at 1400 °C was around 500 g in each crucible. They were then cooled slowly inside the furnace to remove any breaking strains caused by the sudden change in temperature that occurs when straining the molten substance in the open and which, as is well known [23,24], are common in the cooling process after pouring the molten mass. We obtained glass-ceramic disks with a diameter of 120 mm and 12 mm of thickness. Another series of melted samples for formulations S1, S2 and S3 were cooled directly in water, as in the processes to obtain frits for glazes. This caused severe hardening, and the material ended up as glass shards or needles, which were turned to powder for the DTA/TGA.

The morphology of the phases present in the vitrified and devitrified products was determined by observing them with SEM microscopy and an EDS microanalysis. The thermal analysis methods used (DTA/TGA) made it possible to learn the exothermic and endothermic reactions that matched the phase transformations that took place in the initial glasses when heating them at high temperatures [26]. They also made it possible to determine, roughly, the temperatures of the glass transformation (T_g), recrystallisation and melting phenomena. The mechanical strength properties were established by subjecting the glassy and glass-ceramic materials studied to flexural strength tests, conducting both three- and four-point bending tests after precision-grinding the tile bodies. We also obtained data on mechanical strength with indentation hardness tests with diamond tips (microhardness tester Matsuzawa MHT 2, with a maximum load of 1 kg), applying the load for 10 s [26].

3. Results

3.1. Traditional Ceramic Covering Tiles Obtained by Recycling Marble Waste and MSW Fly Ash

Using ash from MSW incinerators and waste from marble sawmills (specifically using the ones generated in the area of Novelda, Alicante) makes it possible to obtain traditional-looking coating materials (roof tiles or tiles) for construction activities. The fly ashes of the MSW analysed have a high reactivity to the minerals in clay and the quartz in the raw material customarily used to produce traditional ceramic materials, making it easier to sinter them at lower temperatures. In these types of products or materials, the heavy elements (mainly the Cd) from ashes from MSW are immobilised. The water absorption capacity of the traditional products obtained increases in a linear way with the addition of fly ash waste (Figure 3). This makes it possible to define an optimal proportion of addition in order not to surpass the percentages required by the standards and depending on the functionality of each product [1].

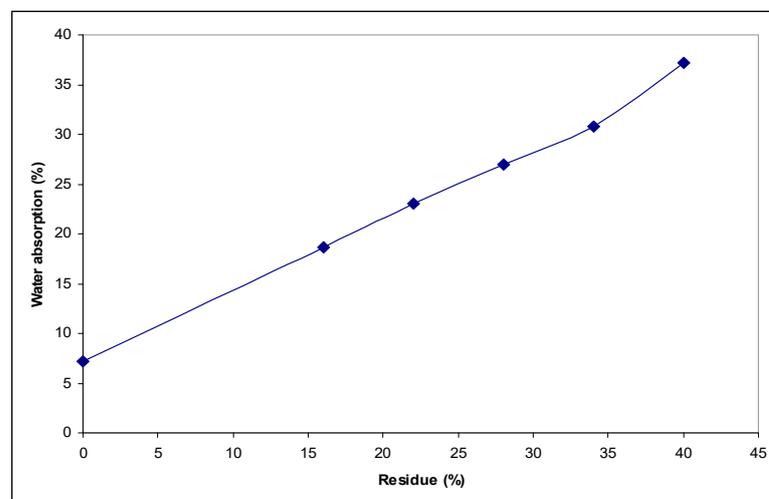


Figure 3. Variation in the water absorption of the tiles obtained as a function of the residue content added in the formulation of the original paste [1].

Similarly, the addition of fly ashes from MSW entails a linear decrease in flexural strength values (Table 3). Therefore, as in the earlier case, it is possible to establish an optimal amount to add to the waste, depending on the standards for each type of product [1,5].

Table 3. Flexural strength of the raw paste and samples fired at their sintering temperature.

% (Weight) of Waste Added	Flexural Strength (MPa)	
	Raw Paste	Sintered Paste
0	3.5 ± 0.1	13.5 ± 3
16	1.9 ± 0.2	12.3 ± 2
22	1.5 ± 0.1	10.0 ± 1
28	1.0 ± 0.1	9.5 ± 2
34	1.2 ± 0.3	8.7 ± 1
40	1.1 ± 0.2	6.9 ± 2

3.2. Characterisation and Glass-Ceramic Capabilities of Glassy Slag Rich in Manganese Oxide

It is a glassy and/or glass-ceramic material that has precipitated crystallites of gehlenite, wollastonite, aluminosilicates and manganese sulphide. It melts at around 1400 °C, following a prior exsolution of hydrogen sulfide gases (Figure 4).

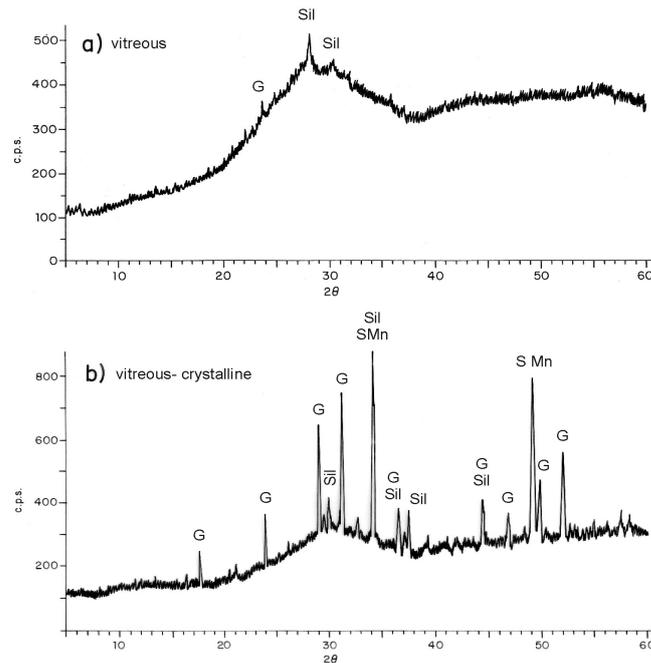


Figure 4. XRD of the samples of the material rich in manganese oxide: (a) glassier sample (G: gehlenite, Sil: replaced aluminium silicate); (b) XRD diffractogram of the glass-ceramic sample (G: gehlenite; Sil: replaced aluminium silicate; and SMn: manganese sulphide).

The study of the thermal behaviour at high temperatures reveals that it would be a good matrix for the production of frits and/or glass-ceramic materials, with uses in the flooring and ceramic coatings industry, as the crystallisation activation energies (Figure 5) in both the glassy and semi-crystalline materials are not particularly high [37,38].

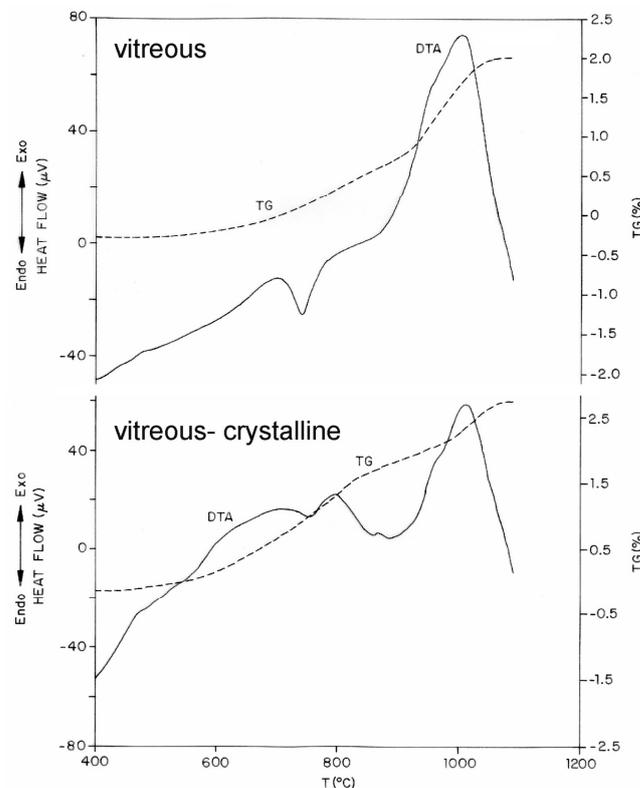


Figure 5. DTA/TG traces from the vitreous and vitro-crystalline sample [6].

In thin sheets, the glasses obtained by fully melting the deposited material (slag) are amber, and the corresponding optical absorption spectrum has a wide band resulting from the overlap of the Mn^{2+} and S_2^- bands. This makes it possible to deduce that despite the volatilisation of the sulphur from the slag sulphides, some sulphur does remain tied to the structure of these types of glasses.

3.3. Vitrification of an Urban Soil Contaminated by Cr (VI) from a Nearby Urban and Industrial Area

A soil that is highly contaminated with Cr^{6+} from an industrial area close to urban areas has been vitrified, formulating a glass with a basalt matrix that has then been subjected to a controlled devitrification or crystallisation process, which leads to glass-ceramic materials that are stable in the environment.

The concentrations of hexavalent chromium obtained by leaching the glassy and glass-ceramic materials are <0.022 mg/kg, which is less than the 5 mg/kg established by the global regulation for waste with Cr^{6+} [16,34–37]. The thermal tests conducted by DTA/TGA on the initial glasses have made it possible to define the temperatures at which the crystallisations that occur within the initial glasses form. They are pyroxenes (augite) and form in the 800–850 °C range.

Chromium and iron spinels are also formed, corresponding to the exothermic peaks observed at around 950 °C, which is the phase that essentially stores the Cr^{6+} , achieving its immobilisation [16,34–37].

We have verified that the relative thermal behaviour among these types of glasses follows the following trend regarding both bulk and surface crystallisation: $G1 > G3 > G2$ (Figure 6).

The flexural strength of this type of glass-ceramics is, on average, 70 MPa (three-point bending), whereas the strength of the materials obtained in this study is around 255 MPa (four-point bending), values that are relatively high compared to conventional glass-ceramic materials and much higher than those obtained with traditional ceramic and flooring materials, or even with natural stones used in construction systems [9,38–40].

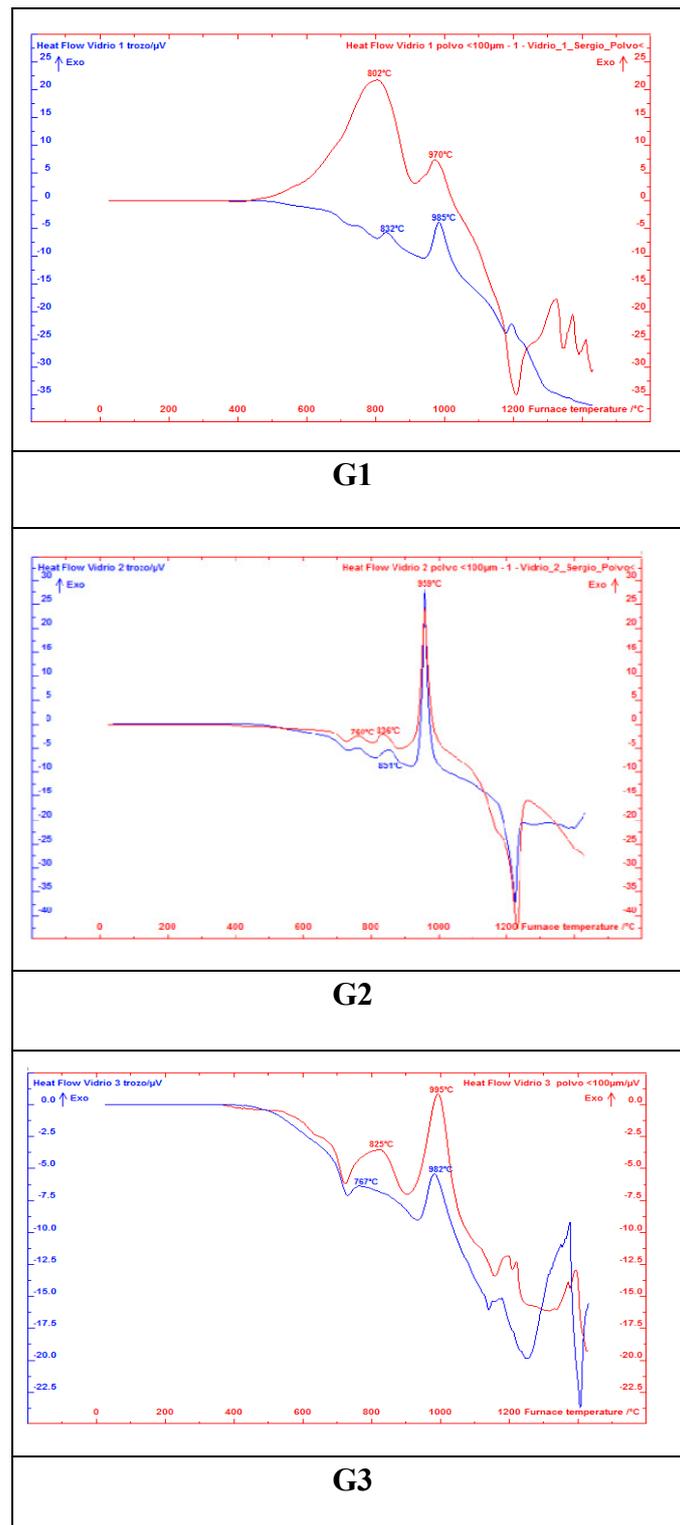


Figure 6. Thermal behaviour (DTA) for G1, G2 and G3 glass samples.

4. Conclusions

We have verified that it is possible to apply both sintering and vitrification industrial processes to several types of industrial waste that have both non-toxic (Li, Ca and Mn) and highly toxic (Cr VI) differentiating elements, to immobilise them or render them inert. At the same time, this research has shown that it is possible to obtain products in construction systems (ceramic and/or glass-ceramic tiles). However, it is essential to advance with a

comprehensive study of these and other types of waste. A new edition of a book published in 2019 [39] and a new book published in 2021 [40] explore new glass-ceramic materials and properties and review the expanding fields related to applying these materials. Other papers, such as one published recently in 2024 [38], contain current information on glass/glass-ceramic forming using traditional raw materials and by-products. Undoubtedly, this field of research is very interesting, as it deals with an essential issue that must be addressed in the coming years in a sustainable economy that is committed to a circular economy and zero waste.

5. Suggestion for Future Lines of Research

We propose conducting surface slip resistance tests in line with the Technical Building Code (CTE, in Spanish). Furthermore, additional tests required by the current regulation must also be conducted, such as resistance to stains, compression strength, frost resistance (if the formulated pastes are used for brickwork or tiles), abrasion resistance, surface wear, etc. In addition, the Time-Temperature-Transformation (TTT) curves must be calculated for glasses obtained with waste enriched with Mn. Furthermore, due to the special optical properties that Mn provides to the structure of glasses, solarisation measures should be taken with these glasses; furthermore, their possible properties as luminescent glasses should be studied (a topic that is currently of great scientific and technological interest). It is also highly interesting to investigate the effect of adding Cr_2O_3 as a crystallisation, nucleating agent in more complex, glassy matrices that are the bases of glass-ceramics obtained from other types of industrial waste, such as those composed of the following systems: $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{Li}_2\text{O-K}_2\text{O-CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$. Lastly, work is being conducted on sintering frits obtained from vitrified materials formulated with Cr (VI), with the aim of obtaining single-firing coloured ceramic tiles.

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