Characterization of fly ash, slag and glass hull for the obtaining of vitreous materials

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Abstract. This article presents the structural and thermal characterization of fly ash, the waste from blast furnace slag and the glass hull, generated as common residues in industry, which cannot be recycled easily or destroyed in a simple and fast way. In the particular case of fly ash, at present are being used as a lightweight aggregate in the production of cement, concrete and additive in the production of glass and glass ceramics. As far as the slag and hull, are being used as additives for the asphalt and concretes, however its use still is restricted, reason why its use in alternative ways are necessary. Initially the chemical composition of residues was established, determining that the fly ashes contains SiO₂, Al₂O₃ and Fe₂O₃ oxides; 90% of the total composition, was confirmed by X-ray diffraction analysis. As minor constituents, small percentages of Mg, P, S, K, Na and Ti were found. For the slag case, the phases of Fe₂O₃, Ca₂Mg (SiO₂)₂ and Ca(MgAl)(Si,Al)₂O₆ were identified, observing the presence of amorphous phase higher than 94% of the total phase of the system. Meanwhile, the glass hull sample showed a higher percentage of 95% amorphicity, mainly identifying a weak signal associated with silicon oxide SiO₂. The thermal analyses of the samples, exhibit a decrease in mass for samples between 25-1000°C was observed, which can be attributed to different physical-chemical events that occur in the materials. The heat flow for each sample is related with the removal of the water retained by the physisorption processes around 92-110°C in all cases. With this previous characterization of the precursors, a sample was composed using 70% fly ash, 10% slag and 20% of glass hull was composed and treated at 1200°C/1.5 hours, obtaining a dense black glassy material for potential applications in field of the glass ceramics.

1. Introduction
The fly ash is a raw waste material mainly generated by the coal combustion process for energy production [1]. This material has received special attention in recent years, due to the increased research related to the study of its physiochemical properties, focused on the use as an aggregate in the manufacture of concrete and reinforced cements, due to its crystalline mineral compounds, carbon particles and glass aluminosilicates, each with levels of reactivity, stability and specific composition that allow to achieve diverse properties [2,3]. This material can provide a strong support for the obtaining of applications in construction field as low-cost adsorbents for the removal of organic compounds, gas treatment, light aggregates, mine fillings, road sub-base, zeolite synthesis, solidification of waste and the manufacture of geopolymers among others [3-5], demonstrating that the chemical composition of these materials is satisfactorily robust to be used in design of value-added products [6]. The main components of a fly ash are the SiO₂, Al₂O₃ and Fe₂O₃ oxides (with values around 70%, classified as class F ashes), the presence of different concentrations of MgO, CaO, Na₂O and K₂O as minor components could be an important factor in reducing costs in the glassmaking process due to the
possibility of reducing evolving temperatures in the synthesis of glass materials. In addition, this effect of reducing energy costs can be enhanced by the addition of secondary components related to slag and glass hull, which allow the production of a wide variety of vitreous materials for thermal induction systems, and decorative materials between others according to the literature [6-9]. In this sense, the manufacture of vitreous derivatives related to the recycling of industrial waste presents a series of benefits such as the reduction of the electric consumption, the improvement of the quality of the material, the reduction of the emissions of greenhouse gases and the cost of Transport of raw materials [10]. Reason justifying the development of the current work in the development of an experimental methodology for the production of vitreous material with the use of fly ash, slag and glass hulls from the region of Boyacá, Colombia. Materials that have been characterized to ensure the homogeneity of the process and the possibility of obtaining value-added materials [11,12].

2. Methodology
The design of the synthesis process was initiated with the physical processing and standardization of the raw materials of fly ash, slag and glass hull by an initial stage of milling using a standard 200 US mesh. The morphology and surface characteristics of materials were evaluated by scanning electron microscopy (SEM-EDX) on a Q600 SDT V20.9 Build 20 equipment. For the analysis, the samples were coated with platinum for a better resolution images in a sputtering QUORUM Q150R ES instrument. The elemental composition of the raw materials was analysed by X-ray fluorescence (XRF), using a PANanalytical MiniPal 2 spectrometer operated at 20KeV. The structural analysis was performed in an X-ray diffraction equipment, PANanalytical X-Pert PRO 2.2, using the Cu Kα radiation at (1.54Å), with steps 0.020° (2θ) in a continuous mode from 10-90°. Based on the characterization, a percentage composition of the starting materials 70% ash, 10% slag and 20% glass hull were employed to evaluate the characteristics of the vitreous material in accordance with previous works. The results of thermal stability and transition temperature (Tg) were validated by thermal analysis (TGA-DSC), which were performed on a SDT Q600 20, DSC-TGA Standard instrument, using a heating rate of 10°Cmin⁻¹ under argon flow conditions (100 mLmin⁻¹), from room temperature to 1100°C. The results were analysed by the enthalpy values associated to the main thermodynamic transitions shown by the obtained vitreous material.

3. Results discussion
Initially, the scanning electron microscopy (SEM) images, show the presence of particles of all possible morphologies, related to the basic conformations of these materials as shown in Figure 1.

![Figure 1. Images obtained by scanning electron microscopy at 10μm for the (a) fly ash, (b) slag, and (c) Glass hull samples.](image)

The micrographs reveal the existence of heterogeneous particles separated from each other, on which it was possible to perform the morphological identification of a total of 10000 particles, which were selected in the automatic configuration of the scanning electron microscope, satisfying the statistical criteria in the analysed samples. The particle size evaluation in all cases using the Image J software, permitted to establish a variable distribution as indicated in the histograms of Figure 2. In the case of
the fly ash sample, the results showed a homogeneous granulometric distribution around 100-150μm, whose composition is mainly associated with the presence of aluminosilicates derived from coal combustion processes, which confers to this material a low density and a high mechanical resistance as has been established by Żyrkowski et al. [12]. In the case of the slag sample, the results showed the presence of particles behaving as agglomerates with a size of about 125-150μm, indicating condensation of droplets by vapours’ and collection of liquid or powder in the process of the blast furnace of the steel industry [13]. On the other hand, the glass hull sample shows the presence of embedded glass silica, which demonstrates its low tendency to be incorporated into the glass material with high variability in particle sizes between 70-225μm showing a high heterogeneity without a tendency defined, taking into account that the source is not unique, making this type of distribution in size and composition very variable. According to the work of García-Fraile et al., Alabama et al., and Shaheen et al. [4,14], the characteristics of the raw materials can be exploited in favour of a better incorporation of the individual components for the manufacture of glass products, allowing the improvement of the synthesis process to consolidate an optimal physical interaction with low porosity and excellent levels of compaction. Accordingly, the work by Matsunaga et al. [15], indicate that the quality of glass materials obtained from raw materials having a particle size distribution very close to about 150±50μm, allow the generation of a large number of applications for structural purposes and of sieving for the adsorption of gases, treatment of organic compounds and of mercury among others [3,16,17], confirming the potential of these raw materials for the development of value-added vitreous materials with excellent results.

![Figure 2. Percentage distribution histograms particle size for fly ash, slag and glass hull samples.](image)

The basic composition results measured by X-ray dispersive spectroscopy (EDX), show that in the case of fly ash, the elements of highest contribution by weight are Si and Al represented in about 85% of the total composition, while the other 15% corresponds to minor elements of K, Fe and Ca oxides as shown in Figure 3. For the slag sample, the results indicate a very varied composition related with transition elements, however the greatest contributions are related with the presence of the SiO₂, CaO and Al₂O₃ oxides, which conform at least the 85% of the total weight, the remaining percentage is discriminated in transition elements, relevant to the process of steelwork, this result indicates a relevant pozzolanic reactivity that allows it to be considered as an effective additive in the production of cement mixtures in accordance with Wang et al. [17].
The glass hull sample exhibit a marked presence of calcium and aluminium oxides with minor transition elements related to the typical dyes of this raw material as indicated in Table 1. Although the high content of silica in two of three precursors of raw materials (fly ash and glass hull), represent a high viscosity in the final vitreous material, this represent the possibility of obtention of low-porosity materials with a high bulk density in accordance with Żyrkowski et. al [12], although other oxide precursor components may generate a decrease in viscosity, this can be compensated by the effect of alumina (Al₂O₃), which reduce the concentration of oxygen in the final material, enabling the devitrification processes and increasing the chemical stability to sulfide attack and the mechanical strength of vitreous materials [3,6,8,11,13,16,19].

The results of the structural analysis performed by X-ray diffraction in the precursor materials are shown in Figure 4, where the characteristic signals associated to the main identified crystalline phases are identified, which were analysed and processed by the X’Pert High Score software in the ICDD databases.

**Table 1.** Percentage values of elemental composition of precursor materials associated with fly ash, slag and glass hull.

| Element Weight (%) | Fly ash |           |           |           |           |           |           |           |           |           |           |
|--------------------|---------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| O                  | 29.39   | Al        | 18.25     | Si        | 37.3      | K         | 2.88      | Ca        | 3.12      | Fe        | 9.06      | Mg        | -         | Ti        | -         | Mn        | Zn        | Na        |
| Slag               | O       | 9.06      | Al        | 6.55      | Si        | 13.38     | K         | 0.19      | Ca        | 19.33     | Fe        | 1.65      | Mg        | 1.81      | Ti        | 0.22      | Mn        | 0.91      | Zn        | 1.44      | Na        |
| Glass hull         | O       | 45.87     | Al        | 0.46      | Si        | 36.18     | K         | -         | Ca        | 6.32      | Fe        | -         | Mg        | -         | Ti        | -         | Mn        | -         | Zn        | 8.78      | Na        |

Figure 3. X-ray dispersive spectroscopy patterns for (a) fly ash, (b) slag, and (c) glass hull samples.

Figure 4. X-ray diffraction patterns of the three raw materials of fly ash, slag and glass hull.
In the case of fly ash, the characteristic signals associated with silicon oxide as quartz SiO₂ (Q), mullite Al₄Si₂O₁₀·₆H₂O (M) and hematite Fe₂O₃ (H), which are common materials to this type of samples have been identified extensively in the literature [15,19]. Detailed analyses of the slag sample, identify the presence of a hematite Fe₂O₃ phase, like the final stage of oxidation processes of iron in the steel industry. Additionally, were identified the crystalline phases related to the merwinite Ca₃Mg(SiO₄)₂ (MW) and diopside Ca(Mg,Al)(Si,Al)₂O₆ (D) phases, being clear that the presence of amorphous material exceeds the 94% of the total phase, indicating a strong vitrification process in the sample. These features, allow to establish the prevailing presence of MgO₂ and SiO₂ compositions, which favours the obtaining of vitreous material with application in the adsorption of gaseous pollutants NOx, SOx, organic compounds, mercury in air, dyes and organic compounds in wastewater, in accordance with the development of multifunctional vitreous materials [3,16,20,21]. Meanwhile, the glass hull sample showed a high percentage amorphicity around 95%, in which was possible to identify a weak signal associated with silicon oxide SiO₂ as shown in Figure 4.

The thermal analysis of the raw materials shown in Figure 5, indicate a decrease in mass of samples between 25-1200°C. This mass loss can be attributed to different physicochemical events that arise in these materials as have been well-known by Pavas and Molina et al. [20]. Initially, the heat flow for each sample present several endothermic and exothermic signals related with the removal of water retained by the physical adsorption process around 92-110°C in all cases.

![Thermal analysis between 25 and 1200°C for raw materials of (a) Fly ash, and (b) Slag.](image)

The region between 120-200°C, can be attributed to elimination of organic matter mainly represented by oils and other substances derived from the physical manage of raw materials. The zone between 200-600°C, represent the elimination of carbonates and oxo-carbonates species, which are common contaminants of Na, K, Ca, and Mg oxides that represent at least a 70% of weight in all samples [22]. Finally, the zone around 600-1200°C represent different stages of melting and volatilization of minor species of low melting point oxides, characterized by strong exothermic signals and a weight loss around 65% in all cases. The exothermic signal observed at 700°C can be attributed to the oxidation of iron and magnesium compounds present in the three materials [23]. These materials present several exothermic signals that allow us to see the nucleation and crystallization points when subjected to thermal treatments, and which could contribute to the production of vitreous materials.

With the results of the physicochemical characterization of the raw materials, a composition of 70% of fly ash, 10% of slag and 20% of glass hull could be established, with the objective of forming a glass material for potential applications and obtaining of a value added product. To this end, the mixture was subjected to a thermal process according to the thermogravimetric analysis performed in the sample (Figure 6(a)) at 1200°C for 90 minutes using a heating chute of 2°C/min, with a slow cooling step, obtaining A black and dense vitreous material according to the process developed by Savante et al., Alabama and Oziel Méndez [23,24]. As indicated in Figure 6(a) the mixture prior to heat treatment
presented endothermic and exothermic signals between 1000°C and 1100°C, which indicate the temperature of nucleation and crystallization of the mixture. The corresponding structural characterization by X-ray diffraction shown in Figure 6(b), confirm the obtaining of an amorphous material of at least (95.3%) in phase content, without evidence of surface crystallization in accordance with the obtaining of a vitreous material [23-26].

![Figure 6. TGA-DSC prior to thermal treatment and curves X-ray diffraction pattern of vitreous material obtained at 1200°C for 90 min.](image)

This shows that coal fly ash, blast furnace slag and glass hull waste have a wide range of industrial and technological applications.

4. Conclusions
The three characterized raw materials of fly ash, slag and glass hull, shown from point of view of surface, composition and structural conformation an optimal characteristic for use as components in design of vitreous materials for potential applications. The XRD results of mixture in percentage (70% fly ash, 10% slag and 20% glass hull), confirm the obtaining of an amorphous material without presence of the main diffraction signals associated with the raw materials confirming the evolution of a chemical reaction between main components in accordance with the objective of current work. The thermal analysis of vitreous sample, confirm the presence of an exothermic signal around 1200°C related with a vitreous transition in accordance with the obtaining of a material for potential applications in field of vitreous add-value products. With current results, is clear that is necessary to complement present work with the aim to reveal the effectiveness of proposed methodology to obtaining of new and advanced vitreous materials for potential applications.

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