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Innovative Glass Recipes Containing Industrial Waste Materials

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The growth of the industrial production generates a high volume of waste materials. These products have a significant impact on the environment. Therefore, the valorization of industrial wastes, especially those produced in huge quantities, is an important social and ecological issue. Waste reuse and recycling could help to develop new products and aggregate value to materials that would have been previously discarded. Furthermore, it could reduce the consumption of natural resources and pollution. Blast furnace slag and fly ash are waste materials largely used in concrete production, mainly as an aggregate, and road construction, as porous asphalt and in other contexts. These wastes contain many elements that are also present in typical glass formulas, such as CaO, SiO_2, Al_2O_3, and Fe_2O_3. However, these elements are highly refractory, and their presence in complex compositions leads to a high tendency to crystallize and to high working temperatures. For this reason, it is a challenge to get transparent materials at reasonable temperatures from these waste products. Glass is a material that allows large amounts of various elements in solution, and is suitable for assimilating the complex materials in its compositions. In this work, we produced transparent glass samples incorporating amounts up to 35% (in weight) of blast furnace slag or fly ash. The compositions were adjusted in order to allow for chemically durable glasses in relatively low melting temperature: the samples were successfully submitted to water durability tests and were obtained in melting temperatures between 1100°C and 1350°C, depending on the composition. The melting conditions were optimized in order to achieve a higher transparency. The optical, mechanical and thermal properties of the samples were measured and compared to the standard borosilicate and soda-lime glasses.

Keywords: Phosphate glass, Fly Ash, Slag, Industrial waste, recycling, glass.

1. Introduction

Industrial waste management is an urgent issue in a society that witnesses a growing industrial production. Expanding populations, urbanization and increased wealth are ramping up the global production of solid waste. Factors like population and per capita gross domestic product (GDP) are used to measure the total global municipal solid waste (MSW) production (Hoornweg et al. 2015). Some predictions about the world population suggest that the population will reach the highest point during this century. The waste production rates per capita usually grow with wealth, despite the fact that there is a tendency toward anti-materialism in the wealthiest countries. The junction of these aspects points to a scenario in which over the next decades the global waste generation will probably also peak (Hoornweg et al. 2015).

About 5 to 7% of the global greenhouse gas emissions originate from the manufacture of ordinary Portland cement (OPC), constituting a huge burden for the global environment (Hendriks et al. 1998). Geopolymer is a promising technology; it is an ecological binding material that functions as an alternative to Portland cement. Usually, the geopolymer is formed by the reaction of a geologically generated aluminosilicate compound, like clay and metakaolin, or of industrial by-products, like fly ash and ground granulated blast furnace slag with an alkaline solution (Neupane 2016). The two principal environmental advantages that derive from substituting the geopolymer binder for the Portland cement are the significant decrease in greenhouse gas emissions and the use of industrial by-products to develop building materials. Using slag cement or ground granulated blast furnace slag (GGBS) as a concrete additive are other ways to develop building materials using waste products.

On average, the generation of 1t Portland cement creates about 1.2t of CO_2 in Europe. At the same time, the production of 1t blast-furnace slag cement composed of 50 wt.% GGBS brings only 0.54t CO_2 (EUROSLAG Technical Leaflet No. 1, 2003). In 2016, the concentrations of CO_2 in the Earth's atmosphere reached a record. According to the World Meteorological Organization (WMO), the record increase in the annual mean from 2015 to 2016 was 50% higher than the average of the past 10 years (WMO, 2017).

Hence, future emission reduction is necessary. The use of slag is a very efficient and economical way to reduce the CO_2-emissions and the energy used in manufacture processes.

Despite a large number of products developed from waste materials, most of them consist of non-transparent materials, partly because it is a challenge to get transparent materials at reasonable temperatures from these waste products. Slag and fly ash contain many elements that are also present in typical glass formulas. For instance, the elements found in higher amounts in the compositions of standard silicate glasses are SiO_2, Na_2O, CaO, K_2O, MgO, Al_2O_3, Fe_2O_3 (Zschimmer 2013). All those elements are found both in slag and in fly ash compositions. Their compositions are listed in Table 1. Some of those elements are highly refractory and their presence in complex compositions means they are highly likely to crystallize and have high working temperatures. However, glass is a material that allows large amounts of various elements in solution, being suitable to assimilate complex materials in its compositions.

Table1: Chemical compositions of fly ash and blast furnace slag deduced from X-ray fluorescence and expressed in mass%.

	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	L.O.I.
BFS	34.40	11.53	39.17	7.81	1.42	1.6	0.23	0.58	-	-	1.15
FA	54.28	23.32	4.23	1.62	8.01	0.64	0.85	1.97	1.23	0.54	3.37

In this work, we aimed to create new glass recipes incorporating waste materials into their compositions. Furthermore, we aim to create transparent materials at relatively low working temperatures. To reach these conditions, the elements, as well as the melting conditions, were optimized. The optical, mechanical and thermal properties of the samples were measured and compared to the standard borosilicate and soda-lime glasses.

2. Methods

A recent estimation concluded that over 200 000 non-crystalline solids (NCS) have been made during the 6000 years of glass history (Zanotto et al. 2004). This number is impressive; however, many possibilities still remain. Almost the totality of the periodic table could hypothetically be incorporated into the glass. Considering the possible combinations of the 80 most useful elements from the periodic table, an equation was developed to calculate how many NCS can be theoretically formed by them. The result showed that an astronomical number of years would be necessary to synthesize all these 1.3×10^{52} compositions (Zanotto et al. 2004).

Consequently, choosing random elements to prepare glass is not an efficient option. The many possible combinations could lead to diverse properties far from the expected ones. Two main methodologies are currently used for glass production. The so-called "cook and look" technique has been used for a long time. Via this technique, a starting composition is developed based on available data, compositions previously reported and intuition. This composition is experimentally prepared at the laboratory, and its properties are characterized and measured. The determined properties are compared with the desired ones; based on the difference, the researcher develops more samples in an attempt to fine-tune the composition and get closer to the target (Mauro 2017). On the one hand, this technique has already yielded in fruitful results which originated many commercial products. On the other hand, the large number of tested compositions can be expensive and results in a long process, especially if the choice of the starting composition is made without careful criteria and its properties are very far from the target.

Another technique is based on the use of predictive modelling tools to facilitate the design of new glass compositions. Quantitatively precise models have already been developed for different properties. However, each model is only appropriate to solve a certain type of problem. There is still no model that is able to address every property simultaneously (Mauro 2017). Topological constraint theory and atomistic simulations are examples of cases in which precise predictions of properties are made based on the chemical makeup of the glass. However, as the glass is a non-crystalline material, its atomic positions are not known with absolute certainty. They should be described using probability distribution functions, which makes the predictions more complex. An ideal application of this approach would require modellers working closely with experimentalists. Although the use of predictive modelling becomes each day more unavoidable the selection and implementation of the models is still a long process that requires interdisciplinary work. Collaboration among professionals skilled in chemistry, physics, and materials can facilitate the selection and implementation of models.

In this study we used the first technique, starting from an initial glass composition. The elements were weighted using an analytical balance and ground using a ceramic mortar. This mixture was transferred to a platinum crucible and melted for 1.5 hours. Melting temperatures ranged from 1100ºC to 1350ºC, depending on the glass composition. The melted mixtures were poured into a stainless steel mould preheated to around 450°C and were annealed at this temperature for 3 hours before cooling to room temperature inside the furnace. These glass samples were then ground and polished. The steps of this process are illustrated in Figure 1.

Fig. 1 Scheme of the glass samples production.

Phosphate was used as a glass former, being obtained from the element KH_2PO_4 (potassium dihydrogen phosphate), which in high temperatures transforms into KPO_3 (potassium metaphosphate) and H_2O. Aluminium oxide (Al_2O_3) was added in order to improve the chemical durability of the glasses. Fly ash and blast furnace slag were also incorporated in amounts as high as possible.These waste materials were used in the powder form, and they can be observed in Figure 2.

Fig. 2 The raw waste materials, fly ash and slag.

3. Results and discussion

3.1. Choosing the compositions

Traditionally, most glass used as a building material is constituted of borosilicate or soda-lime. Both these glasses have SiO_2 as a glass former, in concentrations between 71%-80% in weight (Zschimmer 2013). The waste materials already have high melting temperatures, and SiO_2 melts around 1722°C (Rumble 2018), a mixture of these wastes and SiO_2 would result in products with very high viscosity and working temperatures.

Phosphate glasses possess relatively low working temperatures, low liquidus viscosity, high UV transparency and high solubility for other glass modifiers or intermediaries (de Lima et al. 2015). Pure P_2O_5 melts around 562°C (Rumble 2018). One of their major drawbacks is that these glasses are usually hygroscopic and not stable under room atmosphere. However, in the last decades, the compositions were adjusted and phosphate glasses with high stability against devitrification were developed (de Lima et al. 2015).

For this reason, phosphate was used as a glass former in this study. The element KPO_3 was chosen as the phosphate source. In high temperatures, KPO_3 can be obtained from the decomposition of the element KH_2PO_4 (Potassium phosphate monobasic), as presented in Equation 1. The element KH_2PO_4, in its turn, results from the synthesis of the elements K_2O (Potassium Oxide), P_2O_5 (Phosphorus pentoxide) and H_2O, as shown in Equation 2.

$KH_2PO_4 \rightarrow KPO_3 + H_2O$ (1)

$K_2O + P_2O_5 + 2H_2O = 2KH_2PO_4$ (2)

The first melting attempts aimed to obtain samples from a binary mixture of KPO_3 and slag or fly ash. However, they produced non-transparent materials, as can be observed in Figure 3.

Fig. 3 Non-transparent samples containing 80KPO3-20Slag and 70KPO3-30Slag, respectively.

3.2. Water resistance

The addition of Aluminium oxide (Al_2O_3) yielded transparent glass samples. Furthermore, existing literature points out that the incorporation of Al_2O_3 is linked to higher chemical durability in the samples (Inaba 2016). This relation was reinforced by the water resistance tests conducted in this study. The results of the first tests (Series 1), in which samples were kept underwater for just for 24 hours, are found in Table 2. The results showcase samples with a low water durability, the binary samples or ternary samples with a very low Al_2O_3 content present the lowest durability.

Table 2: Samples of series 1 that remained 24h under demineralized water.

Sample	Final Mass
*B270	100%
$75KPO_3$-12.5Slag-$12.5Al_2O_3$	100%
$77.5KPO_3$-10Slag-$12.5Al_2O_3$	100%
$80KPO_3$-10Slag-$10Al_2O_3$	96.7%
$80KPO_3$-$20Al_2O_3$	99.78%
$85KPO_3$-10Slag-$5Al_2O_3$	42.59%
$90KPO_3$-10Slag	0%
$90KPO_3$-$10Al_2O_3$	0%

*B270 is a commercial Borosilicate glass used here as a reference.

Concentrations of Al_2O_3 lower than 12.5% cannot improve the chemical durability. Therefore, the Al_2O_3 was added to the samples in concentrations between 12.5% and 20%. These samples are named Series 2. The samples listed in Table 3 had their water resistance tested for a period longer than that of the first test. They were kept under demineralized water for 30 days without any mass loss.

These glasses present high water resistance in relation to general phosphate glasses. As an example, the reported compositions $54.5P_2O_5$-$20.5K_2O$-$20.5Cs_2O$-$4.5Al_2O_3$ and $50P_2O_5$-$16.7Na_2O$-$16.7K_2O$-$16.7Cs_2O$ show a mass loss of 19.3% and 100%, respectively, when dipped in water at 18°C for only 1 hour (Inaba 2016).

Table 3: Compositions in weight of Series 2 samples that remained under demineralized water for 30 days with no mass loss.

KPO_3	Fly Ash	Slag	Al_2O_3
60	25	-	15
70	15	-	15
75	12.5	-	12.5
60	20	-	20
55	35	-	10
65	20	-	15
60	30	-	10
70	-	15	15
60	-	20	20
65	-	17.5	17.5

3.3. Colouration

For the samples containing slag, we obtained transparent materials with a maximum concentration of 15% of this waste material. The samples consisting of 12.5% of slag show blue colouration, while the ones consisting of 15% have amber colouration. It is also possible to obtain samples with a higher concentration of slag; however, they are not transparent. All the samples are illustrated in Figure 4.

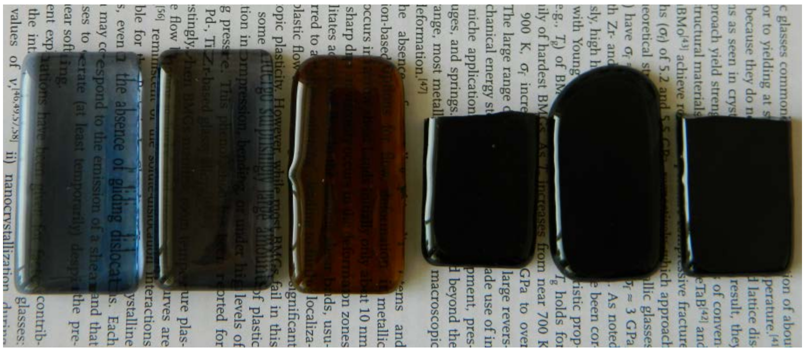

Fig. 4 The samples containing slag.

The samples containing slag were very sensitive to some melting conditions and small variations in the compositions. Phase separations were observed in those samples, while the samples containing fly ash retained homogeneity after all the tests. The sample consisting of 12.5% slag exhibits different colourations depending on the temperature at which is melted. Melted at 1150°C, the sample shows a homogeneous blue colouration. At 1250°C it is heterogeneous and reveals two different patterns of colouration, blue and transparent. At 1350°C the sample is homogeneous and transparent. The visual aspects of the sample melted at the three temperatures are found in Figure 5.

The sample consisting of 15% slag presents homogeneity and amber colouration. Tests were made adding Boron oxide (B_2O_3) at the composition, in an attempt to decrease its thermal expansion. The introduction of 10% of B_2O_3 modifies the visual aspect of the sample, which becomes heterogeneous and transparent with light yellow areas. Further addition of 10% B_2O_3, totalizing 20%, generates two phases, one transparent and one blue. The three samples are shown in Figure 6.

Fig. 5 Samples consisting of 12.5% slag melted at different temperatures: 1150°C, 1250°C, and 1350°C, respectively.

Fig. 6 Samples consisting of 15% slag, without the addition of B_2O_3, with the addition of 10% B_2O_3 and 20% B_2O_3, respectively.

For the samples containing fly ash, transparent samples with a maximum concentration of 35% of fly ash were obtained. The samples consisting of 35% fly ash show green colouration and were produced at 1350°C. The samples consisting of 15% fly ash are yellow and can be produced at lower temperatures (1100°C). The samples become darker for higher concentrations of fly ash, as illustrated in Figure 7. The melting temperature also increases with the fly ash concentration. No tests were conducted for fly ash concentrations higher than 35%. It is probably possible to produce glass samples at temperatures higher than that. However, these temperatures would be higher than 1400°C and the samples would present a very dark colouration, which is not useful for the purposes of this work.

Fig. 7 The samples containing fly ash

Further studies will be conducted in order to understand the origin of these different phases and colourations. The fact that a composition is so susceptible to changes in melting conditions and to the introduction of further elements, generates glass with interesting and unique colouration. However, this is a drawback if we intend to manufacture glass on a commercial scale. The presence of impurities in the melting or the use of a furnace with a non-tightly-controlled temperature would produce glasses with undesirable properties. Considering this point, the manufacture of glasses containing fly ash is more beneficial than the ones containing slag.

3.4. X-ray diffraction patterns

The samples containing the most waste materials had their structures analyzed by X-ray diffraction (XRD). This analysis confirmed the amorphous character of the samples, even the darkest ones, because they exhibit the large bump characteristic of amorphous materials, as can be observed in their XRD patterns in Figures 8 and 9.

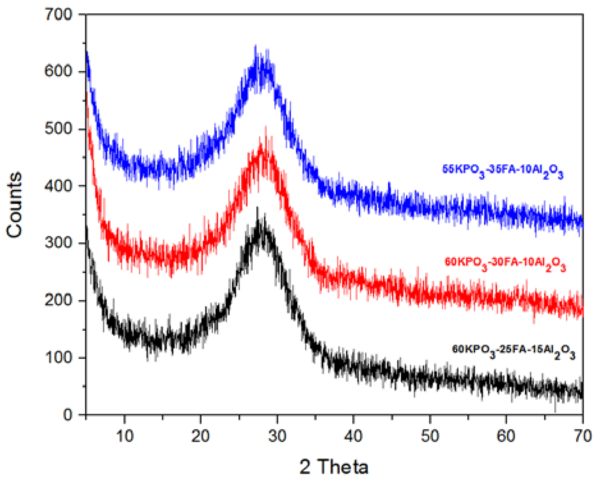

Fig. 8 X-ray pattern of the samples with high concentration of fly ash.

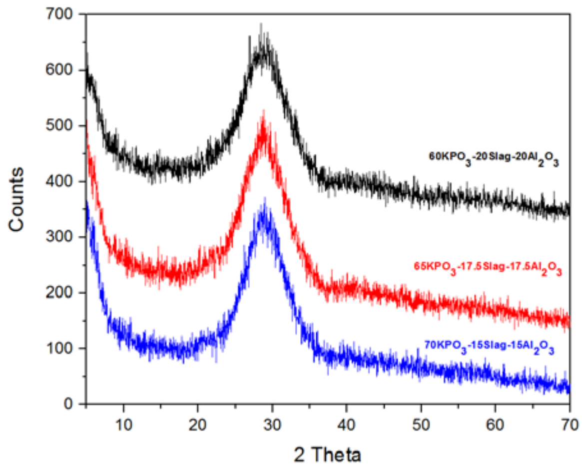

Fig. 9 X-ray pattern of the samples with high concentration of slag.

3.5. Thermal and mechanical properties

The glasses consisting of waste materials were melted at a minimum temperature of 1100°C, and maximum of 1350°C. The melting temperatures increase for higher amounts of waste materials. Even the maximum melting temperature is low in relation to commercial glasses, as the borosilicate glass, that melts around 1650°C. Thermal analysis shows the characteristic temperatures for one sample consisting of 12.5% slag and a commercial borosilicate glass. While in the 12.5% slag sample the range of glass-liquid transition temperatures (T_g) is around 443°C, for the commercial glass it is around 545°C. Both areas are circulated in Figure 10. Crystallization peaks (T_c) are found for both samples. The glass consisting of slag presents a peak with a higher intensity, around 638°C, which was expected due to the high tendency of crystallization of waste materials, rich in various oxides.

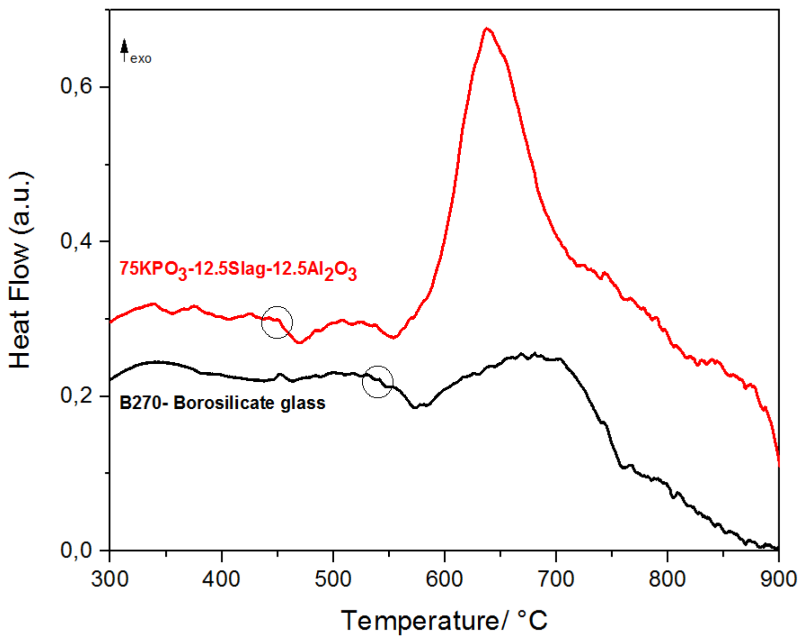

Fig. 10 Thermal analysis curves of a borosilicate glass and a glass consisting of 12.5% slag. Glass transition regions are highlighted.

A standard borosilicate glass has an elastic modulus of approximately 63 GPa and a hardness of 6.4 GPa while for a soda-lime glass these values are 74 GPa and 5.5 GPa, respectively (Chorfa et al. 2010). The glasses from Series 1 with high water resistance had some mechanical properties measured using the nanoindentation method, the results are listed in Table 4. There is a trend of increasing both properties with amounts of slag and Al_2O_3. The values are quite low in relation to the standard glasses. The properties of the Series 2, consisting of higher amounts of slag and fly ash, were also measured.

Table 4: Average elastic modulus and hardness of Series 1 determined by nanoindentation.

Sample	Composition	Average E (GPa)	Average H (GPa)
1	$77.5KPO_3$-10slag- $12.5Al_2O_3$	39.3	3.27
2	$75KPO_3$-12.5slag- $12.5Al_2O_3$	41.6	3.42
3	$80KPO_3$-10slag- $10Al_2O_3$	40	2.28
4	$80KPO_3$-$20Al_2O_3$	36.7	2.67

The Series 2 presented higher elastic modulus and hardness than the first series. The results of the samples consisting of slag are shown in Table 5, and the results of the samples consisting of fly ash are presented in Table 6.

Table 5: Average elastic modulus and hardness of the samples of Series 2 consisting of slag.

Sample	Composition	Average E (GPa)	Average H (GPa)
1	$70KPO_3$-15Slag-$15Al_2O_3$	43.7	4.19
2	$50KPO_3$-$20B_2O_3$-15Slag-$15Al_2O_3$	45.5	4.67
3	$65KPO_3$-17.5Slag-$17.5Al_2O_3$	46.7	4.59
4	$65KPO_3$-20Slag-$15Al_2O_3$	49.2	4.85
5	$60KPO_3$-20Slag-$20Al_2O_3$	52.6	5.14

Considering samples with a same amount of KPO_3, the addition of waste is more effective to increase both properties than the addition of Al_2O_3. It can be observed comparing samples 3 and 4 from Table 5 or samples 1 and 2 from Table 6. Comparing Table 5 and Table 6 it is noticeable that glasses consisting of slag possess much higher elastic modulus and hardness than the glasses consisting of fly ash. The different compositions of the raw waste materials could be a possible explanation for this difference. The slag contains 39.17% of CaO (Calcium oxide), while the fly ash contains 4.23% of the same element. The hardness of a phosphate glass can increase with the CaO content due to densification (Rao et al. 2014). Furthermore, the CaO is easily crystallized, and it could explain the fact that materials consisting of slag can form glass in a shorter range of compositions than the ones consisting of fly ash.

Table 6: Average elastic modulus and hardness of the samples of Series 2 consisting of fly ash.

Sample	Composition	Average E (GPa)	Average H (GPa)
1	$60KPO_3$-20FA-$20Al_2O_3$	41.6	3.94
2	$60KPO_3$-25FA-$15Al_2O_3$	42.3	3.99
3	$55KPO_3$-35FA-$10Al_2O_3$	43.5	4.18
4	$60KPO_3$-30FA-$10Al_2O_3$	45.2	4.56
5	$40KPO_3$-$20B_2O_3$-25FA-$15Al_2O_3$	48.4	5.02

4. Conclusions and perspectives

We proved that it is possible to develop new glass compositions using industrial waste. There were produced materials consisting of up to 35% of fly ash, and 20% of slag and their vitreous structures were confirmed using X-ray diffraction. Thermal analysis and nanoindentation techniques were applied to compare the properties of these new glasses with commercial glasses used in building engineering. The water resistance of the samples was improved with changes in the compositions, achieving high water resistance. The colouration of the samples varies depending on the composition and melting temperatures. Besides to form glass in a larger range of compositions, the samples consisting of fly ash are also less susceptible to changes in melting conditions and to the introduction of further elements. Therefore, the manufacture of glasses containing fly ash is more profitable than the ones containing slag. As next steps, the thermal expansion of these glasses will be determined and the nanoindentation measurements will be concluded for all the samples. The most promising samples will be cast as glass bricks.

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