

Potential of tungsten tailings as glass raw materials

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ABSTRACT

Glasses from different types of tungsten mine tailings were obtained and studied to determine their ability to be used as raw materials of commercial glass. Tailings of granitic composition from Barruecopardo, of calc-silicate wastes from Morille, and of schists and quartz from Panasqueira, were used as raw materials. The addition of CaCO_3 and NaCO_3 was necessary for the manufacture of the glass. Samples were characterised by XRF, XRD, HSM and DTA-TG. Furthermore, the expansion coefficient, Vickers microhardness and leaching properties were measured. The results show that all the tungsten mine tailings used were suitable for the manufacture of commercial glass, with the addition of calcium and soda. The calc-silicate tailing needs less additive content to produce a glass. Also, they present lower workability temperatures and higher durability. Glasses obtained from all the tested tailings retain the potentially toxic elements in their structure and prevents the environmental pollution.

Keywords: Recycling, Tailings, Tungsten, Glass.

1. Introduction

Tungsten is a critical material for the European Union, which contributes to the opening of new mines in Europe, where tungsten occurs mainly in granitic and calc-silicate deposits. Usually, minerals rich in potentially toxic elements, such as sulphides,

accompany tungsten ores [1,2]. Thus, the generated tailings constitute an environmental problem that requires short-term solutions to carry out these mining activities in a more environmentally-friendly way.

Vitrification is a technology that stabilizes hazardous wastes, since it renders them in a stable glass or glass-ceramic commercial product [3,4]. On the other hand, there are mining wastes with a high potential as raw materials in the production of ceramic, glass and glass-ceramics [5,6]. An advantage of these materials is that they have already been processed industrially, and then often have a good homogeneity and a fine particle size. In addition, the costs of extraction are low and this application could be an additional income for mining activities.

In this work, glasses obtained from different types of tungsten mine tailings were studied to determine their ability to be used as raw materials for commercial glass production.

2. Materials and methods

2.1 Materials

Materials used for this study came from tailings of the most common types of tungsten deposits. Tailings of granitic composition from Barruecopardo (Spain) were previously investigated [7] and here they are compared with wastes from the tailing of veins hosted in schists from Panasqueira (Portugal) and calc-silicate materials from the skarn-type deposit of Morille (Spain).

Dry homogeneous wastes and reactive CaCO_3 (PANREAC, cod.121212), and Na_2CO_3 (PANREAC, cod.131648) were used to prepare the original glasses.

2.2. Experimental procedure

The chemical composition of raw wastes and glasses was determined by X-ray fluorescence (XRF). After evaluating the chemistry of the waste, the original glasses were formulated using a mixture of tailings, CaCO_3 and Na_2CO_3 (Fig. 1).

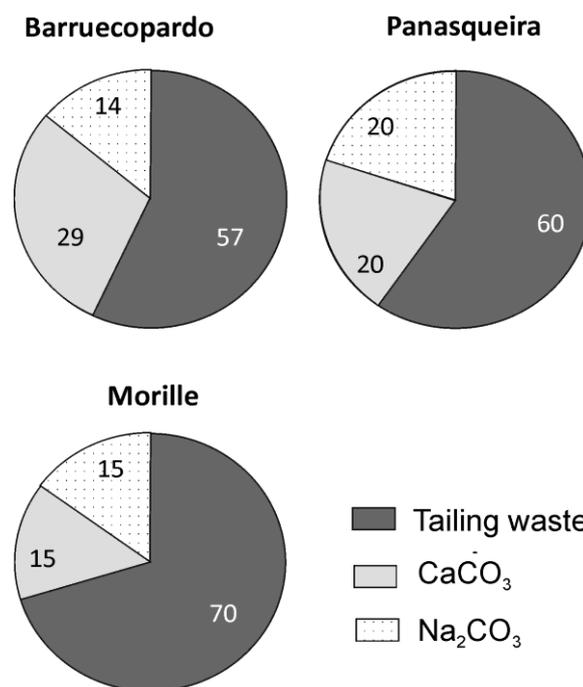


Fig. 1. Composition of the prepared glasses.

The mixed powders were melted in a Pt-Ir crucible at 1450 °C for 4 h and quenched in a Cu plate. X-ray powder diffraction (XRD) was used to verify the amorphous structure of the glass and the mineralogy of the neoformed mineral phases induced in thermal treatment. Glass-transition temperature (T_g) analysis and the coefficient of linear expansion were measured by a horizontal dilatometer. The glasses thermal evolution was determined by differential thermal analysis (DTA), using Pt-Rh crucibles, under an air flow of 80 ml/min, and heated at 10°C/min. The density of the glass was measured in toluene using the Archimedean method. The viscosity-temperature curves have been plotted from fixed viscosity points determined by hot stage microscopy (HSM) [8] using a Hot-stage processing software [9]. Microhardness was measured on a Galileo Isoscan OD Vickers micro-indenter with a load of 200 g. The chemical stability of the glasses was investigated according to the DIN 38 414 S4 method [10], then the analyses were performed by inductively coupled plasma optical emission spectrometry (ICP-OES) and ICP-mass spectrometry (ICP-MS).

3. Results and discussion

3.1. Raw tailing characterization

The chemical composition of tailing materials and original glass is shown in Table 1a. The highest alkali content is found in the calc-silicate Morille tailing, and the lowest occurs

in the schist-rich Panasqueira. Barruecopardo has the lowest Fe₂O₃ content, 1.12 wt. %, which is important for obtaining a clear glass.

3.2. Mechanical properties of glass

The amorphous structure of the glasses was corroborated by XRD. T_g is 642 and 664 °C for Barruecopardo and Panasqueira, respectively, whereas it is 569 °C in Morille.

The coefficient of linear expansion between 20 and 400 °C is similar in all the cases, being 9.1x10⁻⁶ °C⁻¹ for the Pasqueira glass, 11.9x10⁻⁶ °C⁻¹ for Barruecopardo and 12.5x10⁻⁶ °C⁻¹ for Morille, and are slightly lower than for a soda-lime glass, which is 9.1x10⁻⁶. These results relatively correlate with an Appen's theoretical expansion coefficient (R²=0.9997) [11].

Density is one of the most important properties for industrial glass production. This is 2.48 g/cm³ for the Barruecopardo glass, 2.52 g/cm³ for the Panasqueira glass, and 2.57 g/cm³ for the Morille glass, which are slightly higher values than a soda lime glass (2.44 g/cm³).

The Vickers microhardness (Hv) are 6.7 (±0.5), 6.9 (±0.5) and 7.4 (±0.4) GPa, for Morille, Barruecopardo and Panasqueira glasses, respectively, which are higher than the typical 5.36 GPa of conventional silica glasses [12].

3.3. Thermal evolution

DTA curves (Fig. 2) show two single exothermic peaks corresponding to the crystallisation temperature (T_{Cr}). The formation of new crystalline phases in the Barruecopardo glass occurs at 771 and 963 °C and is due to the crystallization of wollastonite and nepheline. In the Morille glass these peaks occur at 776 and 1047 °C, and nepheline, wollastonite and melilite-group minerals formed. In the Panasqueira glass, the two events are close at 873 and 905°C, mainly corresponding to nepheline and a minor content of plagioclase. The endothermic peak occurs between 1132 and 1246°C and is attributed to melting of neoformed minerals.

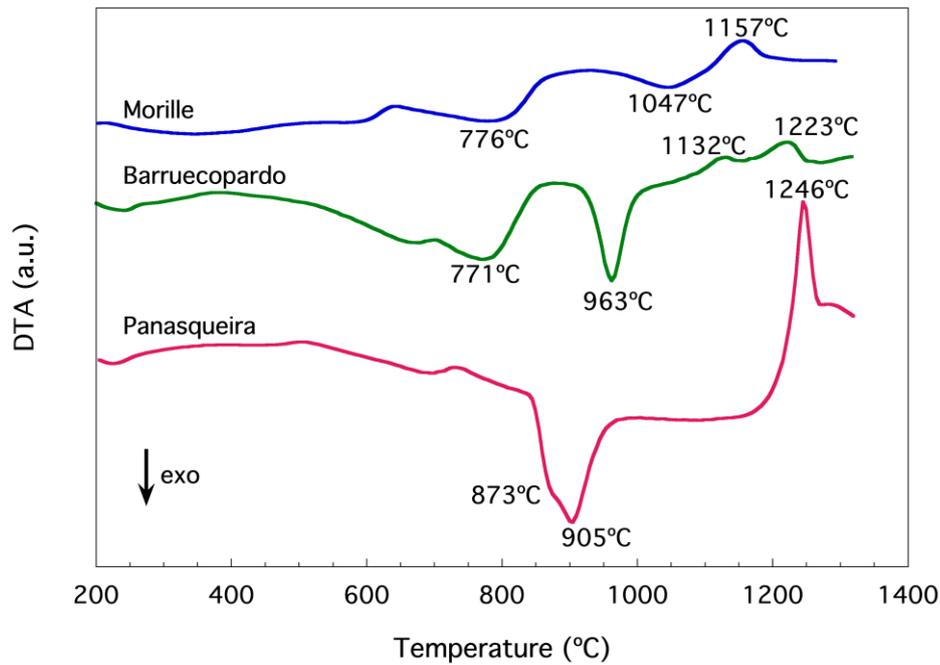


Fig. 2. DTA curves from original glasses.

The rheological behaviour of the studied glasses, as well as the comparison with a soda-calcium common glass, is presented in Fig. 2. The decrease in viscosity with increasing temperature is non-Arrhenius and deviates from the normal behaviour of a viscous flow as the compositions enter into the crystallization range (especially remarkable below 10^8 Pa·s). Hence, the reported values correspond to the apparent viscosities of crystal-glass-melt mixtures. The melts of modified mine waste compositions are sensibly more viscous than the soda-lime melt.

Working temperatures to produce the Morille glass are lower than in the other two samples. Thus, the energy consumption necessary for the temperature treatment will be lower to produce the Morille glass than the other two glasses.

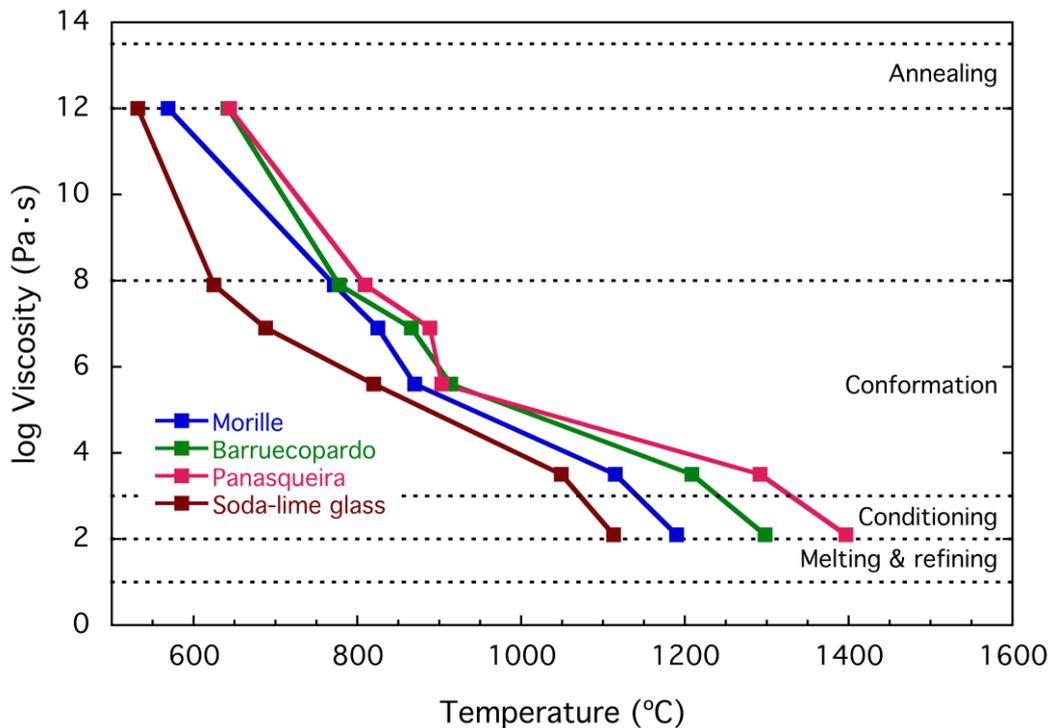


Fig. 3. Viscosity–temperature curves and workability intervals of the studied glasses, as well as comparison with a soda-lime glass.

Depending on the rheological behaviour of glass in the working viscosity interval, 10^6 - 10^3 Pa·s, glasses can be classified into short and long types [13], depending on whether this interval of temperature is lower or higher than 400 °C, respectively. Short glasses are more suitable for processing in an automatic system due their narrow viscosity range. In this work, the temperature intervals are 333°C, 285 °C and 236 °C for the Panasqueira, Barruecopardo, and Morille glasses, respectively all of which are appropriate for automatic processing.

3.4. Leachability

Tailings from Barruecopardo [1] and from Panasqueira [2,14] produce runoff waters with high metal concentrations. In contrast, the metal contents of leachates from the obtained glasses (Table 1b) are lower than the one indicated in the DIN 38 414 S4 to be considered as inert [9]; hence, the metals were fixed in the structure of these glasses.

Table 1a

Chemical composition of the tailing raw materials and the formulated glasses.

Oxide (wt.%)	Bp-t	Mo-t	Pan-t	Bp-g	Mo-g	Pan-g
SiO ₂	73.98	62.50	66.90	55.96	53.21	51.13
Al ₂ O ₃	13.41	13.35	15.05	10.15	12.99	11.50
TiO ₂	0.14	0.55	0.75	0.11	0.40	0.57
Fe ₂ O ₃	1.12	3.76	6.29	0.84	3.55	4.81
MnO	0.01	0.18	0.05	0.01	0.11	0.04
Na ₂ O	2.77	1.99	0.92	8.09	11.46	15.12
MgO	0.26	1.63	1.94	0.19	1.88	1.48
CaO	0.51	9.6	0.33	20.38	14.58	12.69
K ₂ O	5.29	1.03	3.22	4.00	1.19	2.46
P ₂ O ₅	0.36	1.18	0.19	0.27	0.64	0.15
LOI	2.19	2.05	2.49	-	-	-

Bp, Barruecopardo; Mo, Morille; Pan, Panasqueira; t, tailing; g, glass.

Table 1b

Chemical composition (ppb) of leachates from the glasses.

Metal (ppb)	TL	Mo-lx	Pan-lx	Bp-lx
Zn	4000	12.7	19.8	8.9
Cd	40	0.1	0.1	0.1
Pb	500	47.2	203.1	3.2
As	500	2.7	31.4	10.8
Cu	2000	18.6	17.9	17.2
Cr	500	1.78	2.9	0.9
Ni	400	4.7	3.4	11.0
W	-	9.7	10.2	13.8
Sn	-	0.7	0.3	0.1

TL, threshold limits according to the DIN 38414-S4 method.

4. Conclusions

All the tungsten mine tailings used were suitable for making glass, with the addition of calcium and sodium. However, those with calc-silicate composition have several advantages:

- (1) They need a lower content of additives.
- (2) The workability temperatures are lower than in the other glasses, which means that lower energy consumption is necessary for the temperature treatment during the glass manufacture.
- (3) These glasses show a lower Al₂O₃/Na₂O ratio, which is indicative of greater durability.

Glasses obtained from all the tested tailings retain the potentially toxic elements and prevent the environmental pollution. Then, the production of glass using these wastes can be useful to avoid pollution of tailings after the ore processing.

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