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Fabrication of glass-based products as remediation alternative for contaminated urban soils of Barcelona

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ABSTRACT

Contaminated soils from an area previously occupied by a metal smelting industry of Barcelona city were used as raw material for making glass. Vitrification was investigated as a possible remediation technique. The main pollutants in these soils are Cu, Pb and Zn. Glass was formulated using 80 wt% of soil and 20 wt% of Na_2CO_3. The mixture was molten at 1450 °C. Crystallisation temperatures, obtained by Differential Thermal Analysis, were 790 °C, 842 °C and 879 °C. Nepheline, diopside and rhönite crystallized from glass treated at exothermal peaks. The endothermic peak at 1259 °C corresponds to the melting temperature. Glass transition temperature, determined by dilatometry was 632 °C. Viscosity-temperature curve was used to calculate the relevant temperatures for the process. The conformation range is between 995 °C and 1298 °C, and the workability interval ranges from 1293 °C to 1302 °C. The contents of the elements leached from the glass are well below the limits established by the European legislation. Thus, the vitrification is an effective remediation technique for contaminated soils.

1. Introduction

Vitrification has proven to be a good immobilization technique for potentially toxic elements in soils that has been used as an in situ technique for years [1]. More recently, vitrification of polluted soils has been proposed as an ex-situ technique where soils are used as raw materials in the manufacture of glasses and glass-ceramics [2]. In this case, in addition to solving the environmental pollution problem, an economic benefit could be obtained. This technique has already been successfully applied to urban soils [3].

In the present work polluted soils of Barcelona city (Catalonia, Spain) located in an area that previously was occupied by a metal smelting industry were used as raw material for making glass. The aim of this research is to evaluate the vitrification as the first step to sustainable remediation with a land reuse and an energy efficiency in highly polluted soils where other techniques, as phytoremediation or organic amendments stabilization, are not possible.

2. Materials and methods

2.1. Materials

The raw soils are located in the Sants district of Barcelona. It is situated in the flat alluvial plain of Barcelona, characterized by quaternary sediments with carbonate levels. The soil shows a basic pH with secondary $CaCO_3$ accumulation in all depths. The organic carbon content was low as a result of rapid mineralization of organic matter under semiarid conditions, which decreases with depth. Sandy-loam and loamy texture classes are observed in the topsoil and subsoil, respectively [4]. This urban place was an industrial area in the last century occupied by a metal smelting industry. Because of industry activities, this soil shows artefacts having more than 20 vol% in the upper soil horizon. For the experimental procedure, 30 kg of the uppermost 50 cm of soil in a 60 m^2 area was sampled and subsequently mixed.

2.2. Methods

Chemical composition of raw soils and glasses was determined by X-ray fluorescence. Dry soils (80 wt%) and reactive Na_2CO_3 PANREAC,

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Table 1a
Chemical composition (in wt.%) of the soil and the formulated glass.

Sample	SiO_2	Al_2O_3	CaO	K_2O	Na_2O	Fe_2O_3	MgO	MnO	P_2O_5	ZnO	PbO	LOI
Soil	54.59	9.71	14.43	1.85	0.79	15.42	1.42	0.14	0.67	0.53	0.17	26.25
Glass	47.63	8.47	12.59	1.61	13.44	13.45	1.24	0.12	0.58	0.46	0.15	–

cod.131648 (20 wt%) were used to make the glass. The mixed powders were homogenized and melted in a Pt-Ir crucible at 1450 °C, with a holding time of 2 h. A part of the casting was quenched in a Cu plate and the other part has been annealed at 540 °C to obtain test pieces.

Physical properties of glass have been determined. Density was measured in toluene using the Archimedean method UNE-EN 993-2:1996 [5]. Colour was determined using a Spectrophotometer CM-700d Konica-Minolta. Visible spectrum was observed with a Shibuya spectroscope and the refractive index was obtained using a Shibuya MC-601 refractometer.

The thermal evolution of glass was determined by differential thermal analysis (DTA), using Pt-Rh crucibles, under an air flow of 80 mL/min, heating at 10 °C/min. The glass was treated at the temperatures of the DTA peaks during two hours to determine the mineral phases formed. X-ray powder diffraction (XRD) was used to verify the amorphous structure of the glass and the mineralogy of mineral phases induced in thermal treatment. Glass-transition temperature (T_g) and the coefficient of linear expansion (between 20 and 400 °C) were measured by a Lynseis horizontal dilatometer using the annealed samples. The viscosity-temperature curves have been plotted from fixed viscosity points determined from quenching glass using a hot stage microscopy (HSM) using a specific software [6].

Chemical stability of glasses was investigated according to the DIN 38 414 S4 method [7] and analyses were performed by inductively coupled plasma optical emission spectrometry (ICP-OES) and ICP-mass spectrometry (ICP-MS).

3. Results and discussion

3.1. Chemical composition

The composition of the raw soil (Table 1a) shows an adequate content of framework oxides; with SiO_2 and Al_2O_3 of 54.59 wt% and 9.71 wt %, respectively, a high content in Fe_2O_3, 11.37 wt%, and CaO, 14.43 wt % but low content in alkalis, being Na_2O 0.79 wt% and K_2O 1.85 wt%.

The main pollutants are Cu, Pb and Zn with about 930, 1330 and 5379 ppm, respectively. The established background upper limits in this area are Cu 145 ppm, Pb 91 ppm and Zn 326 ppm [8]. In this case, the high heavy metal content reduces the efficiency of the phytoremediation or organic amendments stabilization [4].

3.2. Physical properties of glass

In the obtained glass density is 2.69 g cm^{-3}, which is a slightly higher than in soda-lime silica glasses (2.44 g cm^{-3}). This is due the richness in metals, as it happens in glasses obtained from tailings [9]. The coefficient of linear expansion is $10.95 \cdot 10^{-6}$, higher than in a soda-lime glass, which is between $8 \cdot 10^{-6}$ and $9 \cdot 10^{-6}$ [10].

The refractive index is 1.586 and the spectroscopic absorption lines are in dark yellow, red and blue regions, which are attributed to iron contents.

The glass colour is evidenced from the CIELAB colorimetric coordinates (L*, a*, b*, C*, H) [11]. The lightness, L* vary between 0, which corresponds to black and 100, which is the white. +a* is the red axis, −a* is the green axis, +b* is the yellow axis and −b* is the blue axis. In the Barcelona glass L* is 45.35. a* is 0.62 and b* is 1.89, which plots between yellow and red. This could be due the high Fe contents (Table 1a). The chroma C* measures the purity and in this glass it is1.99 and the hue angle H measures the intensity of colour 71.84.

3.3. Thermal evolution

The DTA curve (Fig. 1a) shows a slight change in slope at 657 °C related to T_g, followed by three single exothermic peaks corresponding to the crystallisation temperature (T_{Cr}) of different mineral phases. The first event is slightly pronounced at 790 °C and is attributed to the crystallization of nepheline ($Na_3K(Al_4Si_4O_{16})$ as the XRD pattern of the treatment at this temperature evidences (Fig. 1b). This event is followed by two well-defined peaks at 842 °C and 879 °C corresponding to the crystallization of diopside ($CaMgSi_2O_6$) and rhönite ($Ca_4[Mg_8Fe^{3+}{}_2Ti_2]O_4[Si_6Al_6O_{36}]$). The XRD patterns indicate that rhönite increases with temperature whereas diopside is gradually reduced until disappear at 1100 °C. The transformation of diopside into röhnite with the increase of temperature has been reported in other glasses [12]. Finally, the

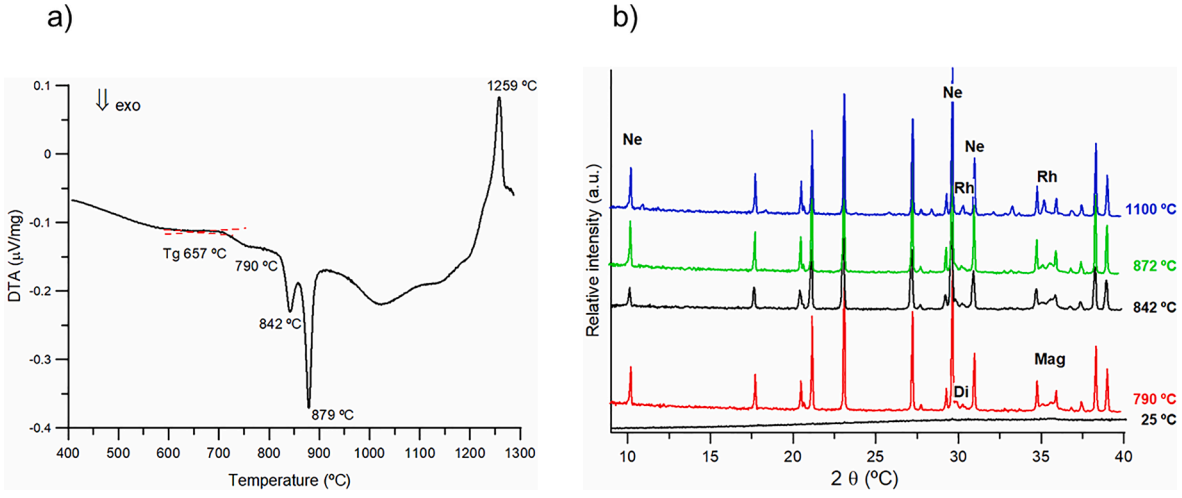

Fig. 1. a) DTA curves of the obtained glasses. b) XRD pattern showing the phases formed during the thermal evolution. At 25 °C the amorphous structure of glass is evidenced. Di, diopside; Mag, magnetite; Ne, nepheline; Rh, rhönite.

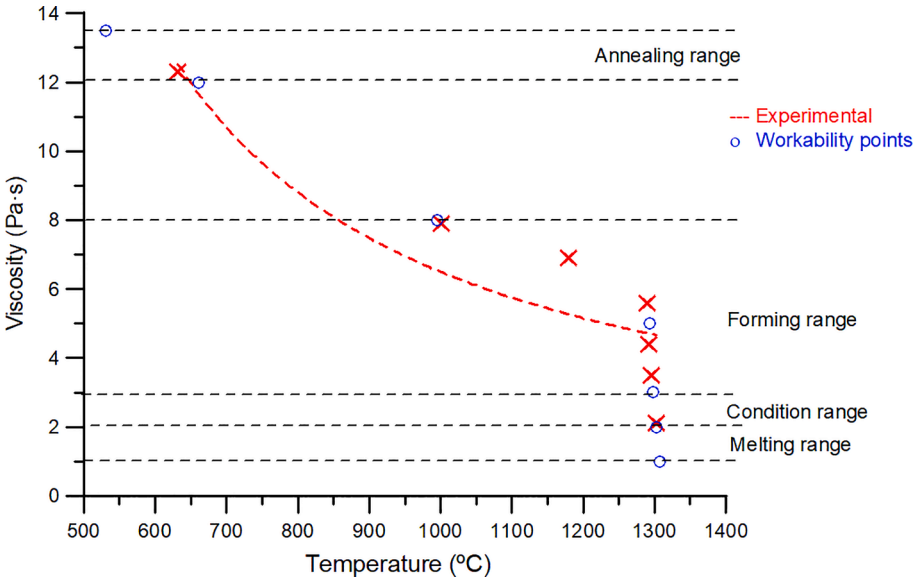

Fig. 2. Viscosity–temperature curves and workability intervals of the studied glasses.

Table 1b
Content of potentially toxic elements (in ppm) of glasses and their leachates.

Sample	Cu	Zn	Pb	As	Cr	Ni	Cd	Hg
Glass	744	4303	1064	–	96	53	5	–
Leachate	0.006	0	0.0005	0.0001	0.0001	0	0	0.0001
TL leachates	2.00	4.00	0.50	0.50	0.50	0.40	0.04	0.01

TL, threshold limits [6]; LOI, loss of ignition.

pronounced endothermic peak occurs at 1259 °C and is attributed to the melting of phases formed during the thermal treatment.

The dilatometric softening point, T_d, is 685 °C and T_g is 632 °C whereas the calculated value in the DTA is 647 °C. This discrepancy of several °C occurs because the dilatometric T_g indicates the beginning of the transition and the T_g from DTA indicates the end of the transition [13].

The viscosity-temperature curves of the glass show differences between the theoretical one, which is obtained from the chemical composition [14] and the experimental one elaborated with the viscosity fixed points obtained from the dilatometric T_g and HSM (Fig. 2). The theoretical temperatures are much lower than the experimental ones and fits into the Vogel–Fulcher–Tammann equation [15]. However, the experimental curve does not fit into the equation because the low viscosity temperatures are close each other. This can be attributed to the crystallization phases with the increase of temperature [16] whereas in the case of the theoretical curve this crystallization is not taken into account. The conformation range (10^8-10^3 Pa·s) is between 995 °C and 1298 °C, and the workability interval (10^5-10^2 Pa·s) ranges from 1293 °C to 1302 °C.

3.4. Leachability

The content in potentially toxic elements of leachates from the obtained glass (Table 1b) is lower than the indicated in the DIN 38 414 S4 to be considered as inert [7]. This suggests that these elements were fixed in the structure of these glasses.

4. Conclusions

The polluted soils of Barcelona are suitable for making a stable glass with the addition of sodium. The glasses crystallize at temperatures corresponding to the exothermal DTA peaks, with the formation of nepheline, diopside, rhönite and magnetite. The workability interval is 1293 °C–1302 °C.

Glasses obtained from the Barcelona soils retain the pollutant elements. Therefore, a sustainable remediation of the soils could be their use as raw materials in glass manufacturing.

CRediT authorship contribution statement

Núria Roca: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. **Maite Garcia-Valles:** Methodology, Software, Resources, Validation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. **Pura Alfonso:** Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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