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Transition metals in glass formation

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Abstract

The structure of silicate glasses gets its charge stability through SiO_2, R_2O_3, R^{2+} and R^+ groups arrangement. In these glassy structures, transition metals are usually used as dopants in small amounts. However, in soda-lime glass systems, transition metals can take part in the glassy network in larger quantities as secundary former or modifier, insted R^{2+} groups, if the charge balance conditions are made favorable by R_2O_3 groups additions. This paper studies transition metals (Cr, Ni, Fe, Cu, Zn, Pb, Ru) soda-lime-borosilicate glass network incorporation. This process was applied for many kinds of toxic metals containing vitrification waste. The glasses were obtaind by melt at temperature of 1300°C, and characterized by FT-IR and XRD techinics. The chemical stability was evaluated by hydrolytic attack test. The glasses showed a high chemistry and environmental stability like the soda-lime glass.

1. Introduction

The control of the hazardous wastes emitions to biosphere is very important to attain the sustainable development. Harzardous waste are not only generate during production process but in the product cicle end life too. The deposition of galvanic wastes, e-waste and nano-waste is obviously a potential risk to public health due to the possibility of toxic metal (Cr, Ni, Cu, Zn, Pb, Pb, Ru, etc) lixiviation.

New trends in environmental regulation, such as the European directive WEEE (Waste Electrical and Electronic Equipment) bring to the manufacturer the responsibility for mitigating the environmental impact of their product not only during the production process, but also throughout product life, and after the obsolescence and disposal of it. These trends involve waste material reverse logistics and environmental compliance practices.

According to sustainable economy, these trends are based on the principle of Arthur Cecil Pigou [(1)], where the final price of the product should reflect the actual cost of the product, which is the sum of its production cost and the potential impact cost on environmental degradation and the harm for public health. By environmental and public health points of view, the reduction of the economic advantage obtained using unsustainable and unethical practices aims to establish a balance between price and actual sustainable cost.

The operation of such nature diretive involves the development of new technologies to apply in reverse logistic processes directed to the recovery of raw materials or treatment and processing of waste generated. The heavy and transition metals and rare earth recovery is undoubtedly the best alternative, though it is not always technically applicable and in specific cases, the recovery process results in more environmentally damage than the simple disposal of waste. Thus, waste treatment and processing technics should also be developed. Among the technology options for this purpose, the vitrification process of these materials can become an interesting option, seeing that they are widely studied and for many kind of hazardous waste, such as the nuclear industry, generated from electroplating plants, steel production and mining processes have been developed [(2-5)].

The present work compares the results obtained by the author's studies of galvanic waste, computers electronic board (e-waste) and catalysts for the reforming of ethanol for use in fuel cells (nano-waste) vitrification [(3-7)].

The vitrification process presented here differs from the usual processes by replacing calcium in soda-lime glass by cations of the metals contained in waste. The accommodation of metals in the glassy network is facilitated by the use of boron with the function to change the charge balance in the random structure of these glasses. Boron also has the function of raw material melting temperature lowering (1300°C) avoiding metal sublimation and making the process environmentally friendly.

2. Experimental Procedure.

Waste containing Cr, Ni, Cu ,Zn and Pb from metal electroplating plant (São Paulo, Brazil), calcinated (1100°C) computers electronic board (Fe, Al, Cu, Zn, Ni and Pb containing), and Pt/Ru carbon suported catalysts for the reforming of ethanol for use in fuel cells were used as raw materials. Filter sleeve Silica (98 wt%) retained in a milling process of a ceramic sanitary industry plant (São Paulo, Brazil) and SiO_2, Al_2O_3 and Na_2O containing sludge from cutting and polishing ornamental granite (São Paulo, Brazil) were used to avoid analitical grade reactants use. The raw material's chemical compositions (data no show) were determined by X-ray fluorescence (X-Ray Rix2000, Rigaku Corporation, Tokyo, Japan). The adjustment of composition waste attained with analytical grade reactants as Al_2O_3, NaOH, CaO and H_3BO_4.

The formulation of glass was carried out following the criterion of melting temperatures ≤ 1300 ° C in order to avoid the sublimation of Ni, Cu, Pb and Zn [3-5] two compositions of soda-lime-borosilicate glass using phase equilibrium diagrams of the systems $CaO\text{-}Na_2O\text{-}SiO_2$ [8] (Fig. 1-a) and $CaO\text{-}B_2O_3\text{-}SiO_2$ [9] (Fig. 1-b) were calculated. The concentration of CaO (oxide modifier R^{2+}) ranged from 15 to 20% by weight. These compositions were called T15C and T20C in according to the contents of CaO and are also represented in Figure 1. These glasses are here labeled as the TC series.

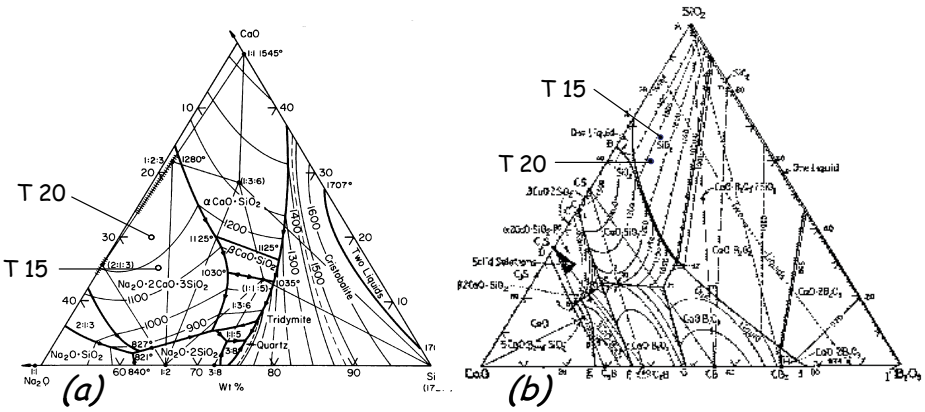

Figure 1 - (a) $Na_2O:CaO:SiO_2$ [8] and ; (b) $B_2O_3:CaO:SiO_2$ [9] phase diagrams with T15C and T20C compositions indication.

To incorporate the waste (Galvanic-waste, e-Waste or nano-waste) in this series of glasses, Ca^{2+} was replaced in the formulation by oxides of transition metals present in it, considering the equivalent mole of cations and the valence typical of these metals, the glass (Fe^{3+}, Al^{3+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, $Pb^{2+}$and Ru^{4+}) for example, 1.0 mol Fe^{3+} equivalent to 1.5 mol of Ca^{2+}; 1.0 mol Cu^{2+} equivalent to 1.0 mol of Ca^{2+}, etc. These compositions were respectively labeled as T15G and T20G (containing galvanic wastes), T15N and T20N (nano-waste) and T15E and T20E (e-waste). The median was about 30wt% waste in the T15 glass and 40 wt% waste in the T20 glass. All compositions are presented in Table 1. It is possible to note in this table that the difference in mass between the glass of reference and their derivatives waste containers is due to difference in mass between the CaO and the replacing metals, maintaining the molar ratio of formulation in adopted criteria. The compositions were melted at 1300°C for two hours in high alumina crucibles in a vertical furnace. The glasses were cast into bars (10x10x50mm) and annealed 500°C for 2 h.

Table 1 – **Glass compositions (wt%)**

Composition	T15C	T15G	T15N	T15E	T20C	T20G	T20N	T20E
SiO_2	**47,6**	**47,6**	**45,4**	**43,8**	**43,5**	**43,5**	**41,0**	**39,2**
B_2O_3	**6,9**	**6,9**	**6,6**	**6,4**	**8,0**	**8,0**	**7,5**	**7,2**
Na_2O	**27,5**	**27,5**	**26,2**	**27,3**	**25,5**	**25,5**	**24,1**	**23,0**
Cão	**14,9**	**14,9**	**7,2**	**4,0**	**19,9**	**5,7**	**9,5**	**5,9**
K_2O	**1,0**	**1,0**	**1,0**	**1,0**	**1,0**	**1,0**	**0,9**	**0,9**
Al_2O_3	**2,0**	**2,0**	**1,9**	**1,8**	**2,0**	**2,0**	**1,9**	**2,4**
MgO	**0,0**	**0,0**	**0,0**	**0,0**	**0,0**	**1,4**	**0,0**	**0,0**
Cr_20_3	**0,0**	**0,0**	**0,0**	**0,0**	**0,0**	**8,5**	**0,0**	**0,0**
Fe_20_3	**0,0**	**0,4**	**0,1**	**5,8**	**0,0**	**0,5**	**0,1**	**7,6**
RuO_2	**0,0**	**0,0**	**9,2**	**0,0**	**0,0**	**0,0**	**12,2**	**0,0**
Pt	**0,0**	**0,0**	**0,6**	**0,0**	**0,0**	**0,0**	**0,8**	**0,0**
NiO	**0,0**	**0,0**	**0,0**	**0,3**	**0,0**	**5,2**	**0,1**	**0,3**
CuO	**0,0**	**0,0**	**0,0**	**7,4**	**0,0**	**2,8**	**0,0**	**9,6**
ZnO	**0,0**	**0,0**	**0,0**	**1,0**	**0,0**	**1,9**	**0,1**	**1,3**
Others	**2,0**	**1,6**	**1,7**	**1,2**	**2,2**	**5,6**	**0,8**	**2,6**

The glass characterization was performed using the techniques of X-ray diffraction (XRD) for powdered glass samples (Bruker AXS D8 Advance, USA). The measurements of the infrared spectra were performed using Thermo Nicolet - Nexus 870 FT-IR spectrometer. USA, from samples of powdered glass (dispersion in KBr pellets, spectrophotometric grade - Merck PA). The chemical resistance evaluation (hydrolytic resistance test) was performed as described by Day [10].

3. Results and Discussion

In the X-ray diffraction patterns corresponding to the TC glass series (modified with calcium – Fig.2-a), amorphous structures characteristic for silicate glasses were indicated. However, as obtained TE glass series (e-waste) diffractograms analysis (Fig. 2-e), indicate that for both glasses, there is a glassy amorphous phase and a crystalline phase corresponding to iron oxide (FeO, PDF89-0687). Analyzing the XRD patterns corresponding to the TG glass series (galvanic waste) presented in Fig. 2-b, can be observed a glass amorphous fase and the presence of crystalline phases Cr_2O_3, Ni_3S_2, Cu_2S, $Ca_3(CrO_4)_2$, $Ni(Cr_2O_4)$ and (PDF 71-2488, 76-1870, 83-0730, 88-0108). The crystalline fases peaks are more intense in T20G glass.The XRD patterns corresponding to TN glass series (nano-waste) are shown in Fig. 2-c. In this patterns is possible to observe that beyond the glassy amorphous phase a crystalline phase corresponding to silicate ruthenium (PDF880898) is present. This phase is better defined for glass T15N. T20N on the glass, that apparently occurs a transition to the crystalline ruthenium (PDF060663). Platinium correspondet peacks are not observed. These results indicate that nearly 15 and 20 wt% of residue incorporated, there is a glass matrix saturation, where the metal absortion as part of the glass random structure ceases and crystalline phases will form preferentially. Interestingly, these crystalline phases in general are chemically and environmentally stable and can also add interest characteristics to the glass, in accordance with the technological application that can give to the same.

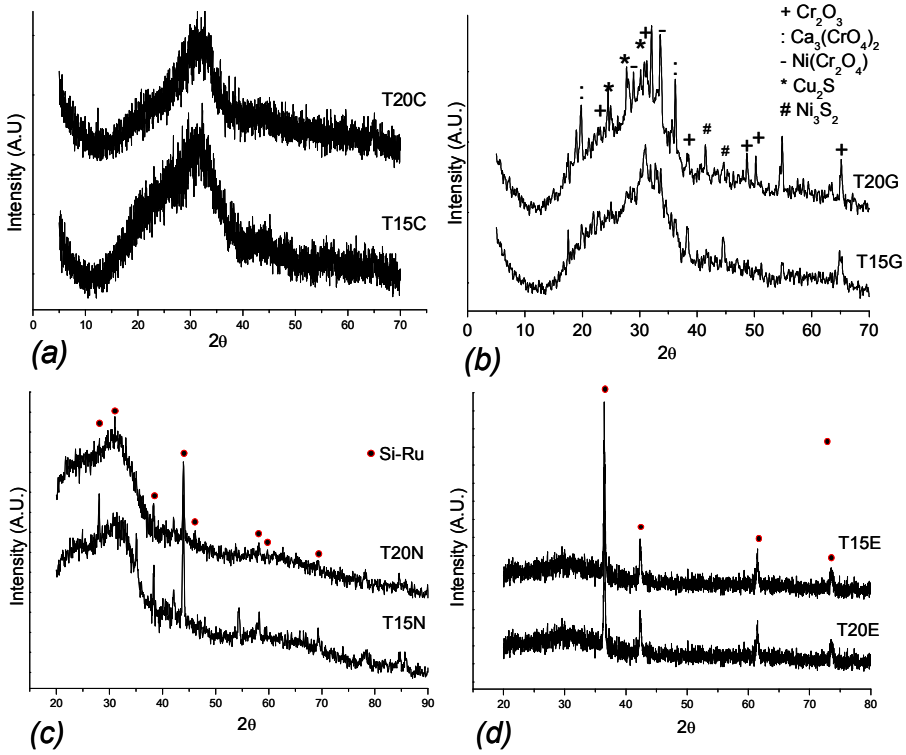

Figure 2 - XRD patterns corresponding to: a) Calcium glasses; b) Galvanic waste glass ; c) Nano-waste glasses ; and. d) e-Waste glasses

The T15C and T20C glasses FTIR spectra are show in Figures 4 and 5 respectively. In both glass, the silica tetrahedral distribution consists in Q^4, Q^3, Q^2 and Q^1 structural arrangements (indicated respectively by 1, 8, 7 and 6 in figures) [11] alkali metals and alkaline earth metals silicates formation can be observed (indicated by 4 in the figures). The sodium presence in the random structure which is easily observed (indicated by 10 in the figures). The boron oxide participation in glass network is discrete (indicated by 3 and 9 in the Fig. 3).

However, in T15E and T20E (e-waste), T15G and T20G (galvanic waste) and T15N and T20N (nano-waste) glasses, the silica tetrahedra distribution in glass structure are Q^3 and Q^2 arrangements types (indicated by 8 and 7 in the figures 6 and 7 respectively) and metals silicates participation is increased (indicated by 4 in the figures), in these glass the boron oxide participates in the main structure (indicated by 3 in the figures). Such configuration is indicative of transition and heavy metals participation in glass structure. In these glasses the boron oxide are distributed in tetrahedral and trigonal forms, with preference for the latter [3]. The tetrahedral boron contributes to the formation of sequences Q^3 and Q^2 by replacing silica tetrahedra chains. The trigonal boron participation in glassy structure is indicative of its charge compensator function similarly to alkaline earth metals, thus allowing the occurrence of sites where transition-metals participation in structure is stable. How preferably, such positions are occupied by alkaline earth metals, second the ionic field discretion [3-5], thus the presence of calcium in T15E and T20E glasses lead to iron cations excess and in consequence FeO precipitate in lower concentrations than in other waste containing glass, as observed in XRD patterns shown in Figures 3-3b. Thus, the waste containing glass network consists of small segments of silica tetrahedra, interconnected by the boron and transition metals.

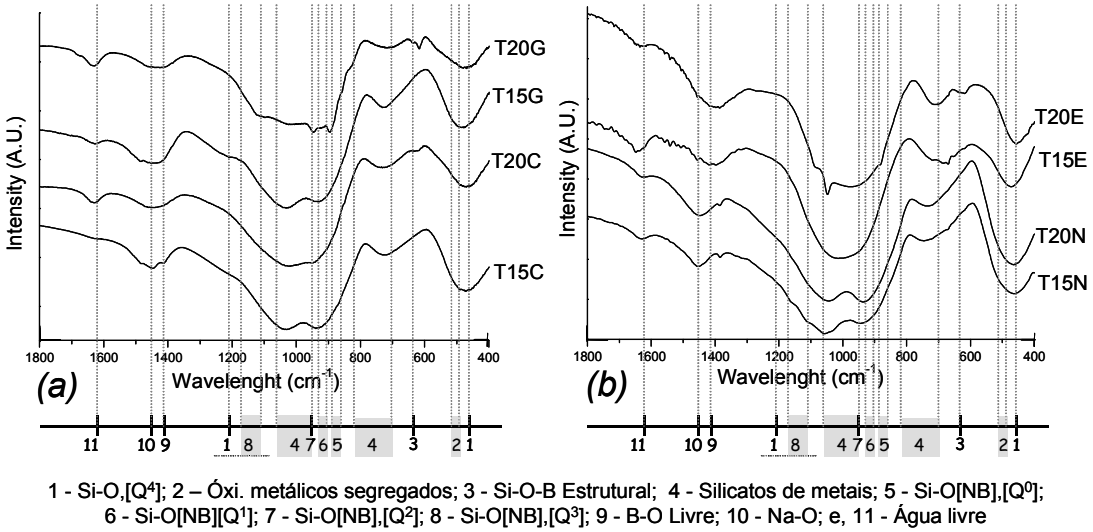

Figure 3 – Glasses FTIR spectrograns a) T15C, T20C, T15G and T20G; b) T15N, T20N, T15E and T20E

In Fig. 4, the dissolution rate during the hydrolytic attack, is shown for the glass control (T15C and T20C) and the other glass with the residues incorporated (T15G, T20G, T5E, T20E, T15 N and T20N).

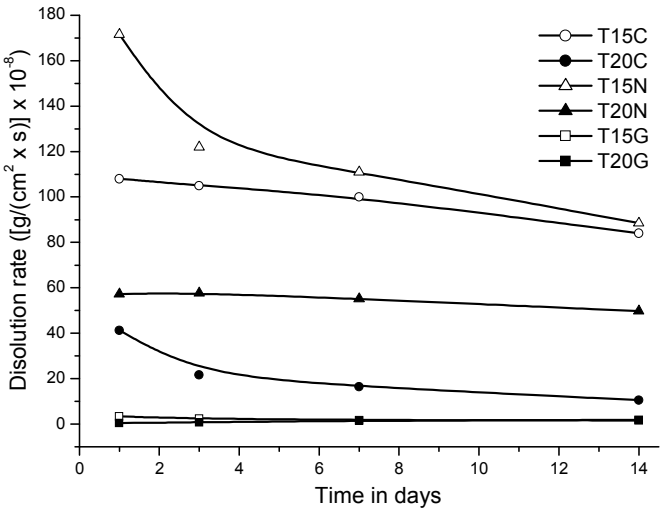

Figure 4 – Hydrolytic resistance test curves (dissolution rate versus time) obtained from the glasses T15C, T15N, T15G, T20C, T20N and T20G

In general, all glasses showed an increase in hydrolysis resistance as increasing the concentration of modifiers (CaO and / or metals). The CaO replacement by ruthenium results in small changes in chemical resistance of the samples (T15N and T20N). This fact indicates the participation of Ru in the random network of glass, offsetting the lower calcium content. Even with the ordering of the crystalline silicates in the form of metal (Fig.2), part of ruthenium content takes part in the amorphous phase. In the other hand, for galvanic waste containing glasses (T15G and T20G) the chemical resistance increased significantly. This fact may indicate that the presence of different transition and / or heavy metal cations (Cr, Ni, Cu, Zn, Pb) in the same glass, facilitates it's accommodation in random structure, allowing the incorporation of higher concentrations of waste before crystallization. This result is in accordance with the XRD diffractograms in Fig. 2.

4. Conclusions

The transition metals participation in the glass structure hypothesis was demonstrated for all studied glasses for different metals such as Cr, Ni, Cu, Zn, Pb, Fe and Ru. The participation of platinum in this structure remains inconclusive. The metals does not replace calcium as a modifier, but also can improve the chemical resistance of glass. To accommodate the metals is necessary the presence of the trigonal coordenated boron in order to act as a charge compensator and maintain the stability of the glassy network. There is a saturation limit in glass structure from which it can not hold more metals, precipitating the same in crystalline form. The saturation of the structure appears to be related to the metal ionic radius field and if different metals accommodated in a same glass the saturation limit increase in regards to accommodation of a single type of metal.

This technology presents an interesting possibility for improvement of the usual processes of vitrification of waste as well as in the production of glasses doped with metals.

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References

[1] A.C. Pigou, *The Economics of Welfare*. Nova York: MacMillan, 1920.
[2] M. Romero, J. M. Rincón, R. D. Rawlings, I. Boccaccini, Mat. Res. Bull., v. 36, p. 383–395, 2001.
[3] A.C. Silva, S. R. H. Mello-Castanho, F. Guitian, I. Montero, A. Esteban-Cubillo, I. Sobrados, J. Sanz, J. S. Moya, J. Am. Ceram. Soc., v.91, n.4, p.1300–1305, 2008.
[4] A.C. Silva, S.R.H. Mello-Castanho, J. Non-Cryst. Sol., v.348, p.211–217, 2004.
[5] A.C. Silva, S.R.H. Mello-Castanho, J. Eur. Ceram. Soc., v.27, p.565–570, 2007.
[6] A.C. Silva, O. Julio-Junior, S.R.H. Mello-Castanho, 19° Congresso Brasileiro de Engenharia e Ciência dos Materiais. November 21 to 25, 2010, Campos do Jordão - Brazil
[7] A.C. Silva, L. Pidone, S.R.H. Mello-Castanho, 55° congresso Brasileiro de Cerâmica. May 29 to June 01, 2011, P. de Galinhas - Brazil
[8] K.A. Shahid, F.P. Glasser, Phys. Chem. Glasses, v.12 , n.2, p.50-57, 1971.
[9] E.P. Flint, L.S. Wells, , J. Res. Natl. Bur. Stand. v.17, n.5, p.727-752, 1936.
[10] D.E. Day, Z. WU, C.S. Ray, P. Hrma, J. Non-Cryst. Solids, v.241, p.1–12, 1998.
[11] S.A. MAcDonald, C.R. Schardt, J.H. Masiello, J.H. Simmons, J. Non-Cryst. Solids. v. 275, p. 72-82, 2000.

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