Vitrified galvanic waste chemical stability

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Abstract

Chemical stability evaluation is the main parameter to harmful industrial waste treatment process for legal ratification process. The inertization by glassing is an interesting technological option for the treatment of galvanic solid environment harmful wastes mainly due to the possibility to avoid its heavy metals content toxic action. In this study a vitrification process for galvanic waste incorporation with good chemical stability was presented. Glasses with up to 40 wt.% of galvanic solid waste by modifications in the basic composition of soda-lime glasses were prepared. After fusing at temperatures up to 1300 °C the glasses were characterized by FT-IR, XRF and XRD methods. The chemical stability was evaluated by hydrolytic, alkaline and acid attacks assays. Glasses with homogeneous and high chemical stability were obtained.
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1. Introduction

The vitrification process is widely applied for radioactive waste storage and recently has been studied for many wastes class inertization, as urban and industrial residues.[1–3] In present study, galvanic solid residue (that contains heavy metals ions) with silica and feldspar filter wastes from the ceramic industries was utilized. All compositions were calculated based on the soda-lime glasses compositions. Vitreous materials for these applications are used because of the structural arrangement that support easily the incorporation of many kinds of chemical elements, as the heavy and transition metal ions. The glass usually also shows a good environment chemical stability, that is a very interesting characteristic to residues inertization.[4]

The waste vitrification process is more complex than the simple dilution of the waste components in the glassy matrix. The melting high temperature effect can reduce some melt components to their oxides forms. In this sense it is inevitable that the oxides from the harmful waste, as the galvanic solid residue, interact with the oxides from the glass raw materials resulting a modified glass.

Residual materials usually show very complex chemical compositions, i.e., they are composed of many chemical species and some of them show one or more coordination numbers.

The pure silica glass makes a continuous random chain with some local coordination order, i.e., several silicon–oxygen tetrahedral atomic arrangements (basic glass structural unit, SU) covalent linked by the oxygen atoms (bridging oxygen, BO) without result in a long term crystalline order. When modifiers cations are added, part of the BOs are interrupted and in several chain positions will end up as non-bridging oxygen (NBO). In an ordinary soda-lime glass is usually the SU oxygen linked with a Na^+ modifier cation that low the melting point or Ca^{2+} modifier is added to improve the chemical resistance. When the mono-coordinated cations (R^+) are added and break the BO, the result is a network terminal point NBO, linked by ionic bonds. On the other hand, if the modifier cations show a number of coordination equal to 2, these modifier cations can make a bridge with two NBO that improves the glass network coherence and, consequently, the glass chemical resistance. The same concept may be applied for the modifier cations that show coordination number higher than 4, as the Nickel and Chrome from the galvanic waste. In this case they can promote the link with two or more units like as SU and NBO. As a consequence, the waste introduction in the glass can determine an improvement in chemical resistance.[5]

The notation utilized to indicate the relationship whit the BO and NBO for the network formers (SU), are shown in Fig. 1.

The dissolution of the glass is basically influenced by the pH values of the attack media,[6] and may be defined by: (1) glass matrix water diffusion—with the modifier ions changed by water hydrogen free ions; (2) network hydrolyses—when the structural

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SU (structural unit)	Q^4	Q^3	Q^2	Q^1	Q^0
BO (bridge oxygen)	4	3	2	1	0
NBO (non-bridging oxygen)	0	1	2	3	4
Representation					

Fig. 1. Silicate glass basic local structural units[5].

unit links are broken; (3) amorphous superficial layer formation (alkalis/modifier poor); (4) OH^- glass network attack[6–9].

The glass dissolution in strong acid or alkaline media, in general is higher for glasses with the NBO-modifier bonds (ionic) than to the BO bonds (covalent) ones.

2. Experimental

2.1. Raw materials

2.1.1. Fine powder of silica waste

Restrained residue in the filter sleeves of the milling process of this material (particle size < 0.074 mm). The fine powder of the silica is an environmental inert material, but silica dust, due to its very fine hard grain size is harmful to the human and animal health being classified as a very harmful residue according to the Brazilian Standard, NBR-10004.[10] Although silica with fine grain size (less than 0.1 mm) is not used as raw material to produce glass, because it can improve the viscosity of the melt[9] beside the longer refination time is always required, the vitrification of this material may be an interesting way to its inertization.

2.1.2. Galvanic waste (GW)

Obtained from the served water treatment in a plant of galvanic metal coating process, due its physical–chemical characteristics this material also has been classified as an environmental very hazardous solid waste, in accordance with the standard NBR-10004.[10]

2.1.3. Feldspar waste

Restrained residue in the filter sleeves of the raw milling process.

Others reagents as aluminum oxide (Alcoa A-1000), sodium hydroxide (97 wt.%, Nuclear), calcium oxide (97 wt.%, Quimica Moderna), potassium carbonate (99 wt.%, Carlo Erba) and Boric Acid (97 wt.%, Quimica Moderna) also were used.

2.2. Glasses formulation

The adjustment of the compositions included the following stages:

Table 1
Composition planned for fusion studies based on equilibria diagrams (wt.%)

Composition	B.00	B.10	B.20	B.30	B.40
SiO_2	54.0	50.8	47.3	44.0	40.7
B_2O_3	6.0	5.6	5.3	4.9	4.5
Na_2O	28.4	26.7	24.9	23.2	21.4
CaO	8.6	8.0	7.5	7.0	6.5
K_2O	1.0	0.9	0.9	0.8	0.8
Al_2O_3	3.0	2.0	1.9	1.7	1.6
MgO	–	0.4	0.7	1.1	1.4
Fe_2O_3	0.21	0.2	0.3	0.4	0.5
Cr_2O_3	–	2.1	4.2	6.3	8.4
NiO	–	1.3	2.6	3.9	5.2
CuO	–	0.7	1.4	2.1	2.8
ZnO	–	0.5	0.9	1.4	1.9
PbO	–	0.1	0.3	0.4	0.5

(1) Attainment of a soda-lime glass using phase equilibria diagrams for the $CaO–NaO–SiO_2$[11] and $B_2O_3–CaO–SiO_2$[12] systems with low viscosity at the melting temperature. This composition was labeled as mixture B. Fine powder of silica, feldspar and pure reactants were used.
(2) Galvanic waste (GW) was incorporated in the mixture B.00 in the concentrations of 10, 20, 30 and 40 mass%. For theses mixtures, were considered its contributions in glassing, such as the silica and calcium oxide among others. The resultant mixtures were labeled as B.10, B.20, B.30 and B.40 (Table 1).

2.3. Glass fusion

The compositions were homogeneized and heat treated in electric furnace at normal atmosphere, for 2 h in Alumina crucibles. The melting temperatures were selected as function of the flux behavior of the melting. The glasses were conformed in bars mold (10 mm × 10 mm × 50 mm) and annealing at 500 °C for 2 h following the natural cooling own the furnace.

2.4. X-ray powder diffraction (XDR)

X-ray powder diffraction (XRD) measurements of the obtained glasses were carried out using a Brunker-AXS model D8 Advance powder diffractometer, with a Cu Kα X-ray source, at 40 kV and 25 mA. The powder samples were mounted on a

glass sample holder. The XRD patterns were recorded over a 2θ range of 10–80°.

2.5. X-ray fluorescence (XFR)

X-ray fluorescence (XFR) chemical characterization of the raw materials and the obtained glasses were carried out using a Rigaku X-ray Rix 2000 apparatus.

2.6. Hydrolytic resistance

The hydrolytic resistance of the glasses were carried out using the method described by Day et al.[13] modified by the use of a Soxlet distillation column. The samples with dimensions of 1 mm × 1 mm × 10 mm were continually washed with distilled water and the dissolved specimens from the glasses samples were carried with the leaching solution to the boiler recipient. This modified method was used to avoid that the dissolved specimens back to the surface of the glass and the influence of the same pH variations of the leach solution on the glass dissolution rate. The time leaching test was fixed at 1, 3, 7 and 14 days. The weigh variations of the samples and the pH of the leach solution were measured by use of the analytical precision balance (±0.00005 g) and the precision pHmeter, respectively.

2.7. Resistance to the alkaline attack

The resistance to the alkaline attack was carried out using the method described by Navarro[7] and based in the standard DIN 12116 (1976)[14] modified by use of specimens with dimensions of the 1 mm × 1 mm × 10 mm. By this method the sample is attacked by a mixture of equal parts of sodium hydroxide 1.0 M and sodium carbonate 1.0 M heated at 100 °C during 3 h. The results are expressed by the mass loss in relation to the initial superficial area of the sample.

2.8. Resistance to the acid attack

The resistance to the acid attack was carried out using the method described by Navarro[7] and based in the standard ISO 695-1984 (1991)[15] modified by use of samples with dimensions of 1 mm × 1 mm × 10 mm. In this method the sample is attacked by a solution of cloridric acid 6.0 M heated at 100 °C during 6 h. The results are expressed by the rate between mass loss and the initial superficial area of the sample.

2.9. Infrared spectrometry (FT-IR)

Infrared spectrometry (FT-IR) measurements of the obtained glasses and the leached glass superficial thin layer after hydrolytic attack were carried out using a Thermo Nicolet-Nexus 870 FT-IR spectrometer. The samples were grindered to fine power and prepared in KBr spectrometric grade (Merck P.A.). Many IR spectrum found in the literature.[16–18]

Table 2
Raw materials main constituent oxides (wt.%)

Element	GW	Silica	Feldspar
SiO_2	22.0	98.0	72.0
Al_2O_3	0.9	0.9	16.0
CaO	14.0	0.1	0.6
K_2O	0.2	0.2	6.2
Na_2O	1.2	0.2	4.9
MnO	0.1	–	0.1
Cr_2O_3	21.0	–	–
CuO	6.9	–	–
NiO	13.0	–	–
ZnO	4.7	–	–
PbO	1.3	–	–
Fe_2O_3	1.1	0.2	0.7
P_2O_5	1.2	–	–
SO_3	7.4	0.1	0.1
MgO	3.5	–	–

3. Results and discussion

The main constituents present in the galvanic and silica waste and in the feldspar are shown in Table 2.

For the conformation purpose the compositions (B.00, B.10, B.20, B.30 and B.40) which attained a good flux behavior of the melting at the 1300 °C were selected. In spite of the fines of the silica waste is not useful for the glass manufacture in all compositions studied its efficiency as glass former were observed.

The XRD patterns results are shown in Fig. 2 for all compositions studied. In general the nature of amorphous materials was observed in all the analyzed samples. Although when high galvanic waste concentration was used, like as for samples B.30 and B.40, the initial tendency to crystallization of some metals specimens were verified.

The obtained fused glass samples were by XFR analyzed. The lost of some metals specimens (Cr, Ni, Cu, Zn and Pb) contents was verified. Fig. 3 shows the difference with the determined values and the respectively start calculated compositions. These variations indicate possible oxides sublimation because of the melting temperature (1300 °C).
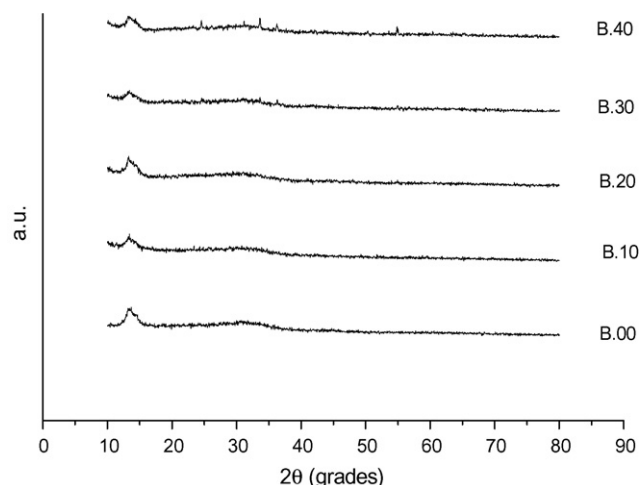

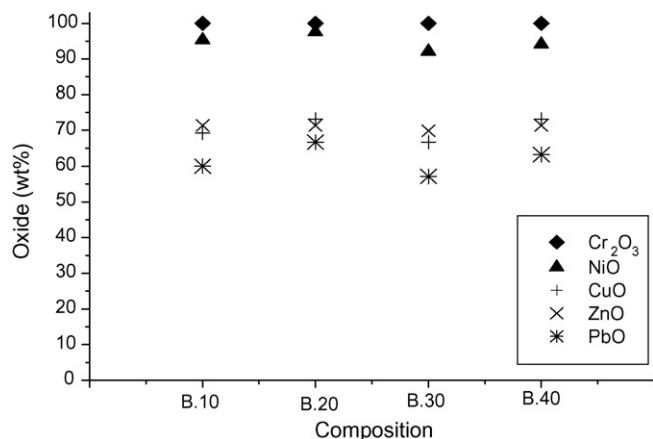Fig. 2. B.00, B.10, B.20, B.30 and B.40 XRD analysis.

Fig. 3. Comparison between the calculated glass galvanic waste oxides mass composition and the same oxides founded in obtained glasses, by XRF.

The obtained results by FT-IR analysis from fused glass samples (B.00, B.10 and B.40) are shown in Fig. 4. These results were interpreted from the literature.[16–18]

The vibration modes found are similar to usual silica glasses, those are, $1200 \, cm^{-1}$ (Si–O,[Q^4]) near $1010 \, cm^{-1}$ (SiO$_4$ stretching), $780 \, cm^{-1}$ (bridging oxygen) and $460 \, cm^{-1}$ (Si–O–Si bending). In all samples were also observed peaks at $1100–1150 \, cm^{-1}$ (Si–O[NBO], [Q^3]) and peaks at $850–880 \, cm^{-1}$ (Si–O[NBO][Q^0]), that indicates NBO's presence and characterize the random network discontinuation points that are corrosion susceptible.

The near $500 \, cm^{-1}$ peaks absence indicates that metallic oxides are not segregated. These results possibly indicate that the metallic oxides will be completely linked with the silicate structure. The low intensity peaks observed at the 780 and $1010 \, cm^{-1}$ energy bands, may indicate the initial silicate formation with the involved metals.

The near $670 \, cm^{-1}$ (Si–O–B) presence indicates that part of the total boron oxide takes place in random glass network
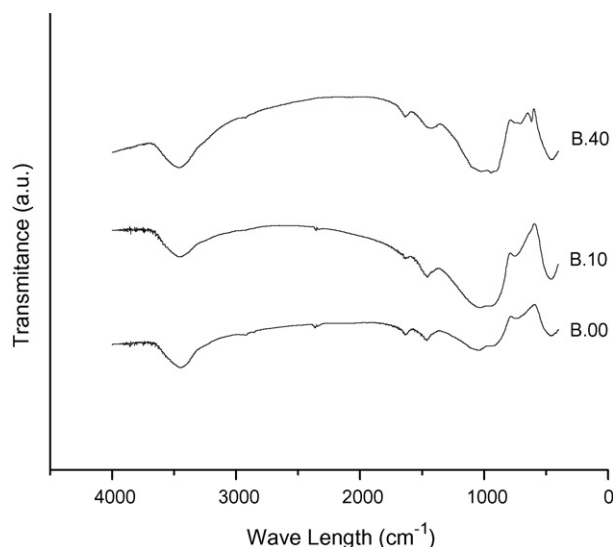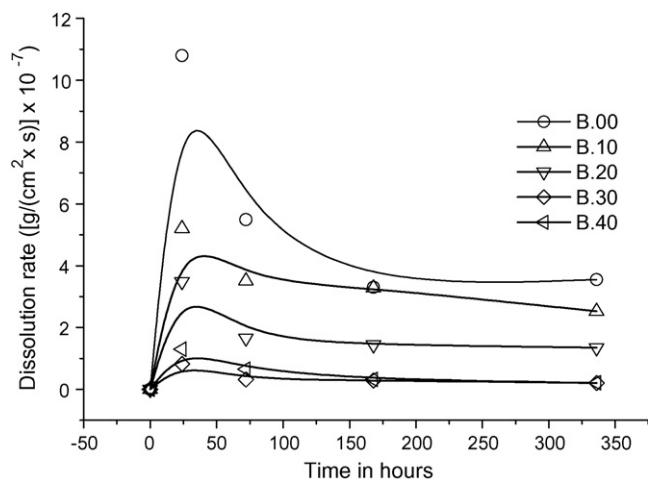

Fig. 5. Resistance to hydrolytic attack with the time for all composition studied.

with the silica. The non-incorporated boron oxide presence is indicated by near $1406 \, cm^{-1}$ (B–O) peaks.

A possible sodium oxide indicative was revealed by a peak near at $1470 \, cm^{-1}$. This peak is more intense in the glass without galvanic waste. This fact maybe indicates that part of Na$^+$/NBO linkages were replaced by metal ions from galvanic waste. These metals ions usually show coordination number bigger than one, and because of these, they are able to link with different tetrahedron NBO, improving the glass network structural coherence and consequently the chemical resistance.

Fig. 5 shows a hydrolytic attack the mass loss rate behavior for all compositions studied where the reductions in the loss mass rate with the time were observed. In this figure is possible to observe that the samples with high GW contents are most water attack resistant. This fact indicates that the galvanic waste metals ions are collaborating to the glass network structural coherence and improving the chemical resistance.

A superficial layer rich in silica was formed in the samples B.00 and B.10 at the following hours of attack. This layer may contribute to improve both the glass resistance and the pH solution stabilization. In agreement with some authors[7,16,19] the presence of this layer is an indicative that the dissolution of these glasses were attained by the alkalis extraction and hydrolyses of the Si–O bonds process. In the samples B.20, B.30 and B.40, that show high chemical stability, a rich silica layer was not observed. This result indicates that in these glasses with high GW contents, the hydrolysis reaction on the Si–O bonds occurs slowly.

The combination of these interesting results shows that the glasses with concentrations of solid galvanic residues up to 20 mass% had presented a higher resistance to the hydrolytic attack than the basic glasses composition ones. In these experiments, only the resistance of the glasses in relation of its basic composition without GW was studied. The toxicity of the leach extract was not evaluated.

Fig. 6 shows the leach extracts pH variations during the hydrolytic attack experiments. The pH stabilization of the leach solutions with the time was observed for all compositions. The increase of the pH in the first hours of the treatment is an
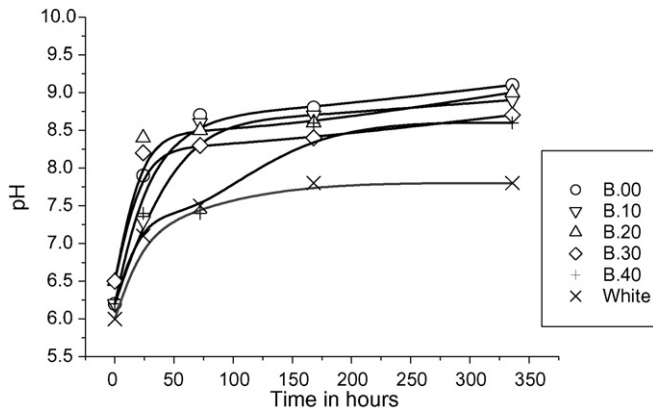

Fig. 4. FT-IR analyses from the glasses compositions B.00, B.10 and B. 40.

Fig. 6. pH variation behavior with the time of the hydrolytic attack leach extracts.

Fig. 8. Mass loss variation with the time from glasses samples after alkaline and acid attack.

indicative of the initial stage of glass sample dissolution. The preferential extraction of alkalis on the surface of the glasses occurred as pointed by the literature.[20] The samples with high GW content show low rate of alkalis release as B.30 and B.40.

The superficial layer formed in the glass B.00 and B.10 was removed and analyzed by FT-IR[21] technique (Fig. 7). The absence of peaks ranging from 900 to 920 cm^{-1} (Si–O[NBO][Q^1]) indicates the strong dissolution of the Q^1 species.

The hydrolyses process in the BO links were evidenced by the increase in the peaks near 1100 and 1150 cm^{-1} (Si–O[NBO]Q^3), indicating the break of the glass network. The peak at 940 cm^{-1} (Si–OH) shows the hydrolysis process product. The minor intensity peak at 670 cm^{-1n} (Si–O–B) may indicate the break of this kind of linkage.

The alkaline and acid attack resistance results are presented in Fig. 8. The additions of galvanic solid residues in glass increase the alkaline attack resistance. All the samples had presented high solubility in acid environment, as expected, justified by the high alkali content in the considered glass compositions.

The high acid medium (hot 6 M HCl) solubility indicates a strong proton (H$^+$) attack in the NBO with metal ions linkages,
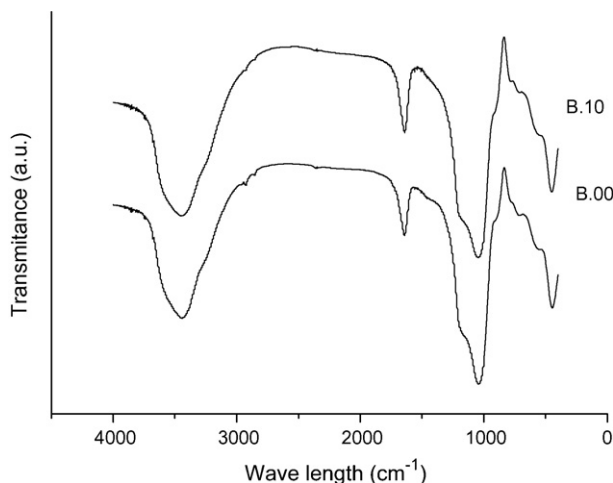
important is to note that these conditions are several times more rigorous than the environment conditions.

4. Remarks

1. A soda-lime silicate glass from silica fine powder was obtained.
2. By using the phase equilibria diagrams it is possible to find the best fusion condition compositions with boron additions.
3. Glasses with 75.1 mass% combined wastes were obtained.
4. The studied glasses compositions with high galvanic solid waste content had presented interesting characteristics like as high resistance to the hydrolytic attack, medium resistance to the alkaline attack and low resistance to the acid attack.
5. The glasses with a high concentration of galvanic waste incorporated show better resistance to the hydrolytic and alkaline attack than the common glass with the same basic composition.
6. The glasses with high GW contents show a poor acid environment resistance.
7. The inertization and the decrease of the health harmful potential of both residues, the galvanic waste and the fine powder of silica for all the studied compositions were attained.
8. There are indications that the galvanic solid residue metal ions have outstanding participation in the glass network.

Acknowledgements

Fig. 7. FT-IR analysis of the superficial layer from the B.00 and B.10 glasses compositions after 14 days under hydrolytic attack.

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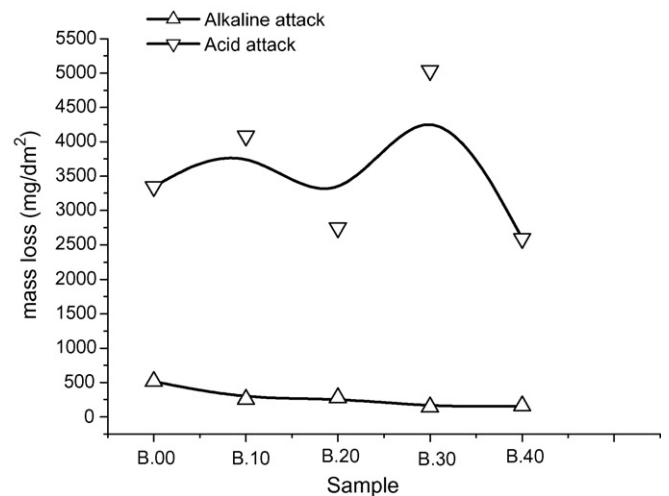
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