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SOLID GALVANIC WASTES INCORPORATION IN GLASS MATRICES

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ABSTRACT

Among the industrial solid residues, the galvanic wastes have been received special attention, due to the nature of its components. These residues in general present a high concentration of alkaline and transition metals. When discarded or stored inadequately, they can be released for the environment, causing ecological and health damages. An interesting alternative to recycle those wastes is to remove them from the environment, through its incorporation in silicate glasses matrices.
This work proposes the obtaining of amorphous structures, glasses or frits, from formulations with industrial solid galvanic wastes, with good chemical stability.
A characterization study of the residue and primary materials, as commercial silica and feldspar and investigations about the formation of amorphous phases, galvanic wastes incorporation and chemical stability of the obtained products, were made. With these results, it was possible to formulate compositions that allow the obtaining of frits for ceramic enamels, with 23 % in weight of solid galvanic waste incorporated and good coating characteristics.

INTRODUCTION

The recycling and valuation of wastes coming from industrial processes has become, a worldwide concern, very important in the last years. One of the possible forms to inertize and recycle effluents of dangerous nature is through its vitrification, given that the glass, for presenting an open amorphous structure, can incorporate in the same one, with certain easiness, a great number of elements of the periodic table.
For this work, the interest residues had been the galvanic effluents from the galvanoplasty industry that, in accordance with the Brazilian legislation[(1)], belong to the category of the industrial non-inert solid residues. These residues present a series of metals in their composition and other composites that directly make impracticable the discarding right thru the environment. This work presents a study of incorporation of these galvanic residues in a glass matrice based in a commercial composition with silica and feldspar, focusing the attainment of compositions that can be used for the manufacture of frits and ceramic enamels.
The silicate glasses are the most common glasses used for applications like windows, plates, glasses for packings, incandescent light bulbs, etc. Its basic structure is formed by silicon-oxygen tetrahedrons, in which the silicon atom, with valence 4^+, is co-ordinate in tetrahedrons with 4 oxygen atoms, forming an amorphous structure that allows to the incorporation of modifiers elements. These elements can contribute for the improvement of properties, lower temperatures of processing and improvement of viscosity and chemical resistance [(2)].

The silicate glasses accept the incorporation of modifiers oxides that may cause partial ruptures in the silica network, diminishing the cohesion, the stability and the temperature of the fabrication process. We decide to adopt the vitrification line because the glass, showing an amorphous and opened structure, allows to incorporate and inertizate the metals present in the galvanic residue, being able to submit the glasses to the environment without risk to liberate the non-inert elements.

EXPERIMENTAL PROCEDURE

In this work the solid galvanic residue dry (SGR), the silica and the feldspar, both commercial ones were used as the start materials The chemical analyses of these materials were conduced by X-ray fluorescence spectroscopy (RIGAKU model RIX 3000) and by the pattern XRD (RIGAKU model DMAX 200). Thermal behavior of the samples was studied using a simultaneous TGA/DTA (NETZCH equipment). The heating treatments were conducted on powder samples and on the fused materials. The experiments were performed by heating samples until the temperature of 1400 °C, at the heating rate of 20°C/min and synthetic airflow. The residue was dried in an oven at 110°C / 24hs, desegregated in a ball mills and classified by sieving at 200 mesh (< 75 μm).

Two series of compositions were evaluated. The first one with SGR, silica and feldspar and the second series with sodium carbonate additions, in detriment of the amount of feldspar, aiming at to diminish the temperatures of process and improve the viscosity of the glasses.

The mixing of the start materials for melting glass experiments were performed in a balls mill, with a plastic bottle and alumina balls as media, to improve the homogenization step.

The compositions based on the system CaO - Na_2O - SiO_2 were calculated, considering the residue stability variation with temperature increase. The concentration of SiO_2 was kept constant and the relation feldspar/residue was varied, aiming to get adequate characteristics of fluidity. With the variation of the feldspar concentration, the temperature of glass formation could be varied, due to presence of fluxes and stabilizers (Al_2O_3). It was possible to study the incorporation/inertization in the mass of the glass, varying their concentration in the residue.

RESULTS

The chemical analysis for X-ray fluorescence showed silica with 99.6 wt.% of SiO_2, and a potassic feldspar, with 5.7 wt.% of K_2O. The majority components present in the SGR were Cr: 18.5%, Ca: 17.9%, Zn: 15.4%, Mg: 7.1% (in weight %).

The results achieved for ATG and ATG analysis showed constant loss of mass with the increase of the temperature, until 650 ºC. In this temperature, the ATD data indicated an endothermic peak, pointing the release or reordenation of some species present in the residue; around 1100°C, initiates an endothermic behavior, possibly indicating some reordering or volatilization of some components. With the increase of the temperature, the loss of mass continued to occur, however in minor rates, until the temperature of 1100°C, where it comes back to increase again, tending to stabilize at 1400°C. These data are indicative of the possible temperature intervals to treating the SGR, without significant loss for the environment by volatilization.[4]

After heat thermal treatments at 1450 and 1550°C for 3 hours, the XRD patterns of the residue showed well defined crystalline phases (Figure 1), constituted of the majority

components present as dichromates, magnesium, oxides, etc and the residue, without fluxes additions, practically did not suffer melting.
In the FIG.2 are presented the results for the SGR X-Ray analysis, gotten from calcined samples at 1450 and 1550°C for 3 hours. After thermal treatment at 1450°C, occurred the presence of Cr and Zn composites, MgO and CaO. However, when the residue was calcined at 1550°C, a relative reduction in the intensity of the referring $Zn_2Cr_2O_4$ peaks occurred, indicating possible incorporation to the amorphous phase, that begins to increase after treatment at 1550 °C, where the data showed that the waste didn't melt.

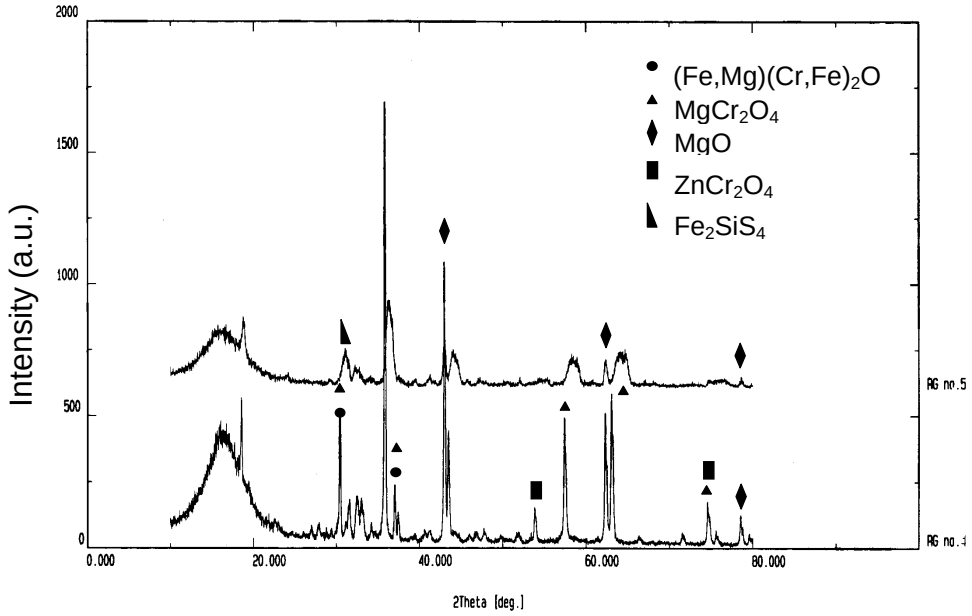

FIGURE 1: SGR X-Ray analysis data, at 1450°C and 1550°C

A group of glass compositions was studied at 1400 °C/1h and the results showed that, in remaining constant the silica concentration at 47% (in weight) and varying the SGR and feldspar concentrations, occurred the formation of a glass with low viscosity. It was observed that the glass could be poured with easiness, for a composition containing 23% SGR max and 30% feldspar.

The FIG.2 shows the results for X-Ray Diffratometry analysis in samples after melting at 1400 °C/1h.

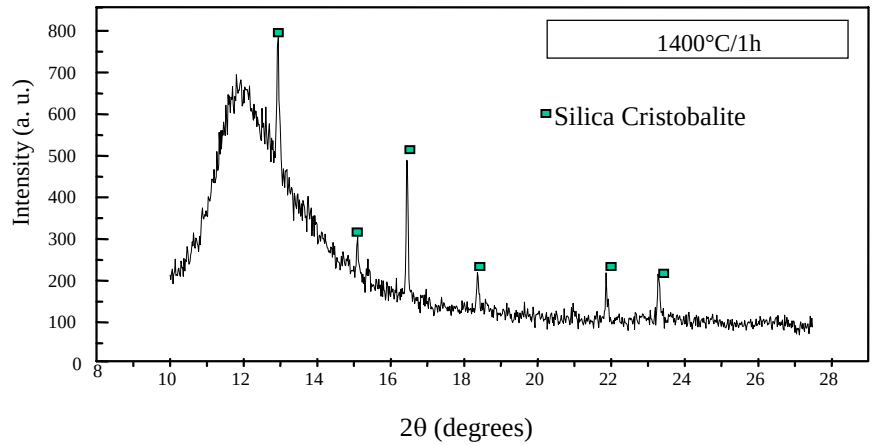

FIGURE 2 : Difratogram: sample with 23% SGR, 47% sílica, 40% feldspar, after melting at 1400°C/1h.

These results allow to conclude that, increasing the feldspar concentration up to 40% in weight in the initial composition of the glass, it was possible to detect stable cristobalite silica, after thermal treatment at 1400 ºC. Assuming that the feldspar is a silicate, always when its concentration increases, the silica content also increases. With these results, it was possible to incorporate up to 23% in weight of the solid galvanic residue in a glass.

To improve the glass fluidity, the Na content was increased, through the addition of Na_2CO_3, (in the range of 5 to 25% in weight); keeping fixed the contents of SGR and SiO_2 and varying the feldspar concentration in the range of 5 to 25% (in weight), in a way that the sum of contents of Na_2CO_3 and feldspar totalizes 30% (in weight) of the glass composition. With this procedure, the best results were achieved for the compositions contained 10% feldspar, 20% Na_2CO_3 and 5% feldspar, 25% Na_2CO_3, while the contents of SGR (23%) and silica (47%) remained fixed for both compositions. By extrapolation of these compositions in the CaO - NaO - SiO_2 phase equilibrium system, it was possible to see that the glasses obtained were located in the same region correspondent to commercial glasses compositions (FIG.3).

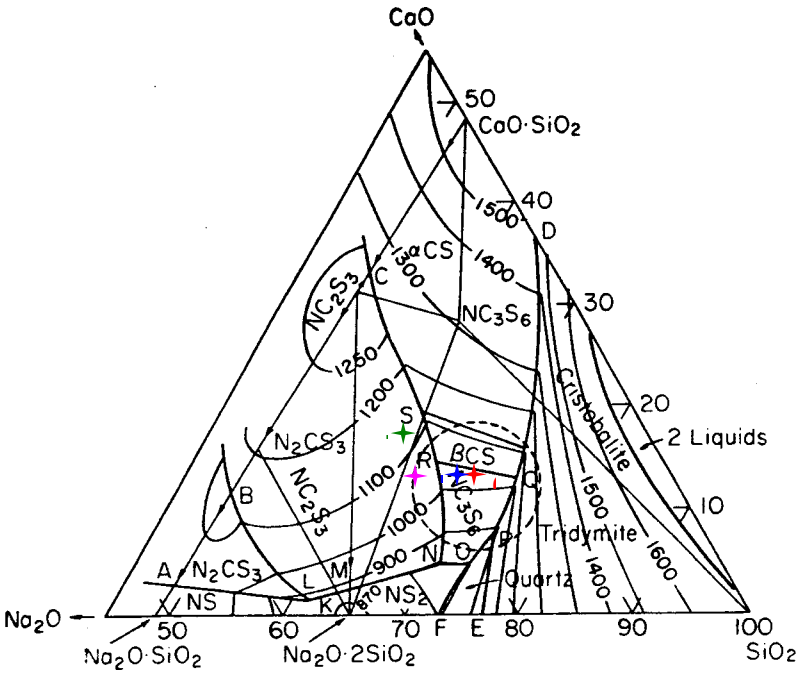

FIGURE 3: CaO - NaO - SiO_2 phase equilibrium system, showing the obtained compositions right into the circled region of commercial glass compositions.

X-Ray Diffratometry analyses were made in samples with the 2 compositions above and the results showed no formation of crystalline phase, stating that the residue components were incorporated in the glass matrices.

Thermal analysis of the same compositions showed no significative variations in mass and ATD results showed that the composition contained 10% feldspar, 20% Na_2CO_3, 23% SGR and 47% silica presented a glass with higher stability until 1450°C, when compared to the other composition with 5% feldspar, 25% Na_2CO_3, 23% SGR and 47% silica. (FIG. 4)

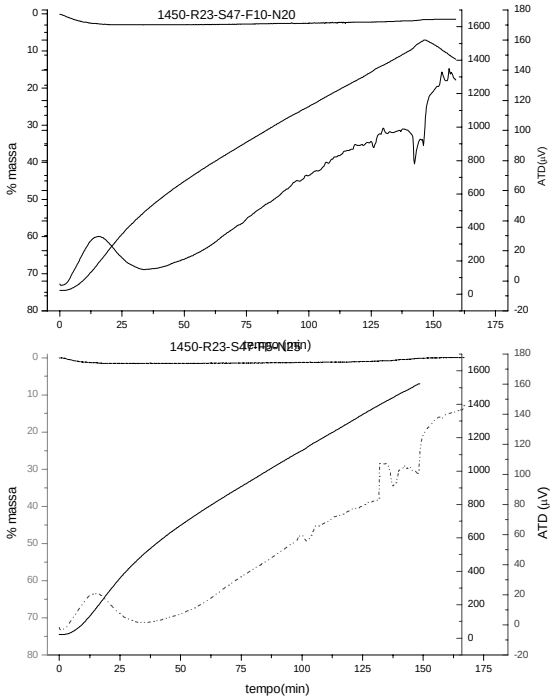

FIGURE.4: ATD and ATG data for compositions with 5% feldspar, 25% Na_2CO_3 and 10% feldspar, 20% Na_2CO_3 (both with 23% SGR)

The samples were submitted to chemical resistance tests during 14 days in a watery way and the results did not shown significant variations of mass or pH, evidencing the chemical stability of glasses.

Using the composition containing 10% feldspar, 20% Na_2CO_3, 23% SGR and 47% silica (% in weight), chosen for its greater stability until the temperature of 1450°C, were obtained frits, by pouring the casting glass in water in the ambient temperature, under agitation. After milling (<75µm), a ceramic enamel, based on a commercial composition in enamels for ceramic coatings was prepared: 91.8% of frits, 8.0% of kaolin and 0.2% of CMC (carboximetilcelulose), as dispersant. The enamel was prepared and homogenized in watery way. The enamel suspension was deposited over a sinterized alumina plate, to verify its power of covering and behavior during the burning. After drying the piece in an electric furnace (110°C/6h), the specimen was thermally treated at 1200°C/1h. Of this form, it was possible to manufacture a ceramic enamel, with good stability to the hydrolytic attack, with 23% of SGR incorporated in its structure.

CONCLUSIONS

The studies with the SGR demonstrated that it is a residue with low solubility in water and presents stable components until the temperature of 1400°C.

The procedures carried through in this study allowed to transform the solid galvanic residue class II (not inert) into class III (inert).

Between the studied compositions, the ones that demonstrated a good behavior of melting, incorporation and resistance to the hydrolytic attack, were formulated with 23 % of solid galvanic residue, 47% of silica, 5% of feldspar and 25% of Na_2CO_3 and

the composition presenting 23 % of solid galvanic residue, 47% of silica, 10% of feldspar and 20% of Na_2CO_3 (% in weight).
The addition of 23% in weight of solid galvanic residue to a silicate structure constitutes a significant amount in terms of incorporation of a non-inert residue in a product, pointing a possibility to reintegrate residues generated in a productive cycle.
The studied compositions presented stability until their temperatures of melting, and the composition with 23 % of solid galvanic residue, 47% of silica, 10% of feldspar and 20% of Na_2CO_3 (% in weight), presented stability until the temperature of 1450ºC.
The enamels elaborated from frits with 23 % of solid galvanic residue, 47% of silica, 10% of feldspar and 20% of Na_2CO_3 (% in weight), presented good properties of covering and brightness, after burned at 1200°C/1 h.
It was obtained a ceramic enamel with 23% in weight of solid residue from industrial galvanic processes, totally incorporated, presenting good resistance to the hydrolytic attack and with good characteristics of covering.

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