

Inertization of Galvanic Waste in a Silicate Glass

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Abstract. Among the industrial solids residues of galvanic wastes have been paid special attention justified by their compositional characteristics that constitute a source of environmental contamination due their high heavy metals content. In this paper, an alternative low cost method in order to inertize and incorporate directly a galvanic waste in a silicate glass matrix was proposed. Some different compositions were calculated from the starting material aiming to obtain an environmentally stable silica glass with maximum waste (23 wt%) incorporation at temperatures around 1450°C.

Introduction

Industrial development over the last decades has generated large amount of toxic and hazardous inorganic wastes. In the light of environmental norms residues generated from the galvanic process in metallurgical industry is a tight of attention due appreciable heavy and hazardous metals present with several reagents as sulfates, chlorites and others [1]. The complexity of the composition hinders a clear classification as well as the definition of only processes for reusing or incorporating of the same ones in manufactured products. To convert this complex composition in to an inert waste by an economically feasible route is nowadays a challenge.

The glass is the material that possesses the highest chemical stability and it can homogeneously incorporate into its structure virtually any element of the periodic table or several at same time (the wastes usually have a very complex chemical composition) [2]. The main objective is to obtain glasses whose characteristics allow commercial applications such as materials for building site, decoration, or stretched in fiber forms, which have applications as insulating and/or reinforcements of materials [1, 2, 3].

Ceramic industries also produce significant quantity of residues during the processing of the raw materials. The silica is one of the basic components present in the composition of great majority industrialized ceramic products for the most varied application fields. However, in many of the production processes, before being used, the silica (SiO_2) is submitted to a conditioning step that includes the grinding operations and sieving for the size classification. These operations are accomplished for seeking the adaptation of the particle size in agreement with the characteristic specifications of each process. As result, the fine of grinding, in this case fines from the silica powder (SiO_2), are drag to the filters of air at the draught exit of the mills. The normal way to reduce the fines consists in its incorporation to the production line. However, in the usual processing of ceramic products, the starting components and the particle size distribution admit, in general, little variation. In this regard, the excessive presence of fines from any component may affect the process, for instance, the amount of formed vitreous phase, the shape and volume of the final product, etc. So only a small amount of these fines is at present recycled in the same process. Besides extremely pollutant, the largest inconvenience of the presence of this type of particles, in suspension in the air, is to provoke lung illnesses.

Experimental

Industrial solid residue from the galvanic process, silica from filters of the ceramic industry and commercial feldspar were used. The residue composition was determined using X-ray fluorescence (Spectrometer RIX 3000-RIGAKU) and inductively coupled plasma (ICP-Atomic Emission Spectroscopy) methods. The oxidation studies and mass loss due to volatile species and structural changes with the increase of the temperature were accomplished until 1400°C with a heating rate of 20°C/min and synthetic air flow (5L/h) using thermal differential and thermo-gravimetric analyzes (DTA/TGA, Netzsch) and X-ray diffraction (XRD). The fines of the silica also was analyzes by powder XRD. These techniques were also used in the fusion studies and formation of the glasses. The start compositions used for the fusion of the glasses were calculated considering the majorities components present on the residue whose the characteristics could have possible influence on the glass production such as refractory oxides, glass forming, melting, etc. Initially the global compositions were preformed considering the residue components in form of the oxides. The investigated compositions are listed in Table 1. Before the fusion experiments the samples were homogenized by rotating a bottle with same balls. From the data obtained from DTA and TGA curves, samples in pellets shaped were prepared for melting in alumina crucibles in temperature range of 1300-1550°C at hold time up 4 hours, using an electrical vertical furnace. When the viscosity was low enough to flux, the melt (~20g) was poured on to metal plate or in the carbon die. In order to verify the glass transition temperature (T_g) and also investigate the influence of the residue content on the behaviour of the glass resultant, differential thermal analysis (DTA) measurements were performed on powders samples (<100µm).

Table 1. Compositions of mixtures studied in weight %.

	RSF10	RSF20	RSF30	RSF40	RSF50
Residue	43	33	23	13	3
Silica	47	47	47	47	47
Feldspar	10	20	30	40	50

Results and Discussion

Table 2 shows the composition of the solid galvanic residue where Cr, Ca, Zn, Mg, Fe and S are the major components determined. Some elements, when in oxidizing form show same characteristics that should be considered in the formulation and processing of the glassy. For instance, the chrome, in the oxide form (Cr_2O_3) presents low solubility in the silica. However, if it is present in the form of salts then it will to participant in the net of the glass, to act as colorant also assuming other oxidation states. Zinc in the oxide form can volatilises with the increase of the temperature. Insoluble metallic sulphites as zinc or iron sulphates may be formed.

Table 2. Chemical compositions of the solid galvanic waste (in wt.%).

Element	[wt. %]	Element	[wt. %]	Element	[wt. %]	Element	[wt. %]
Cr	18,5	Mg	7,1	Si	3,9	Cl	0,86
Ca	17,9	S	6,9	F	1,7	Al	0,20
Zn	15,4	Fe	6,3	Mn	1,2	Zr	0,15

DTA/TGA results show the residue weight loss with the increase in temperature until to 1400 °C (maximum temperature of the experiment). The DTA shows an exothermic peak at 700 °C is related with the same volatilisation reaction. Besides the XRD patterns of the heat-treated samples

at 1400 and at 1550 °C reported in Fig.1 where the crystalline phases with metals content are observed. After a heat treatment at 1550°C the elements initially present in the residue are detected. Consequently, these glasses may melt around this temperature without loose the releasing considerable volatiles specimens with metals to atmosphere.

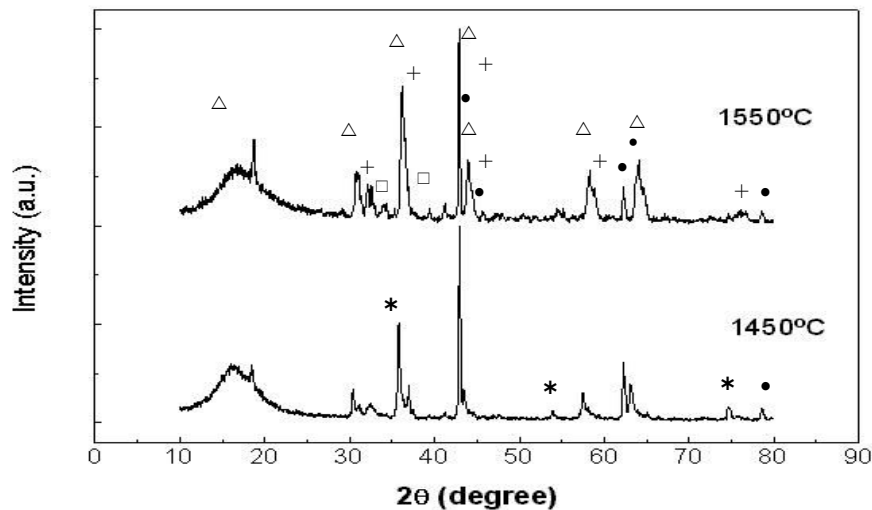


Figure 1. XRD pattern of the samples of residue after heat treatment at 1450°C and at 1550°C, The indexed peaks were identified as: (Δ) $(\text{Fe,Mg})(\text{Cr,Fe})_2\text{O}_4$; (\bullet) MgO ; (+) MgCr_2O_4 ; (\square) Fe_2SiS_4 ; ($*$) ZnCr_2O_4 .

The DTA and TG curves until 1400 °C in air atmosphere at a heating rate of 10 °C/min corresponding to compositions RSF 10 and RSF 20 are shown in Fig. 2. For both compositions, a similar behaviour was observed. Considering the different components in the formation of the glass, it is observed that endothermic and exothermic peaks have an open shaped even for a heating rate relatively low (10 °C/min.).

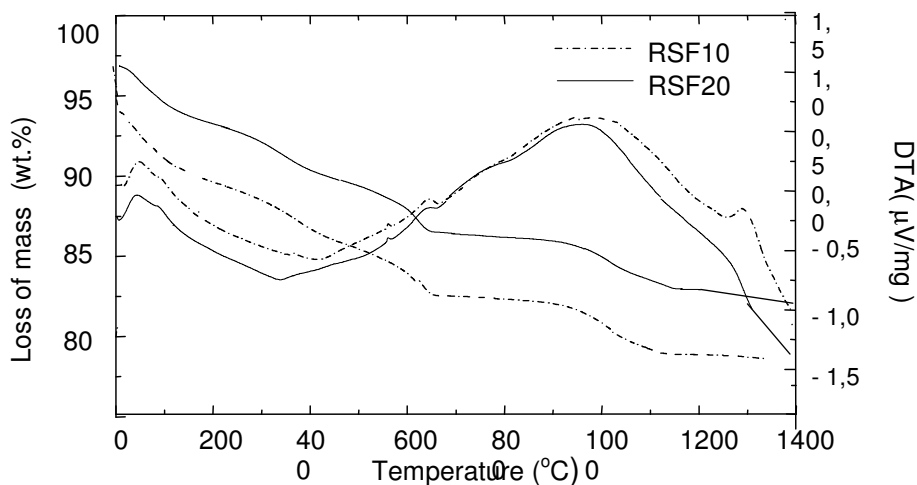


Figure 2. DTA/TG curves for RSF10 and RSF20 compositions in air atmosphere.

In both compositions it is possible to verify two endothermic peaks at 1000 and 1300°C respectively related to the transition temperatures of the glass formation. The behaviour of the mass loss with the increase of the temperature in all compositions analysed was analogous with the behaviour observed for the pure residue. These results show that the variations in the residue composition with the temperature will (not significantly) interfere in the thermal behaviour of the mixtures. These thermo-gravimetric variations are attributed to possible elimination of the volatile species initially presents in the solid galvanic residue as the anionic species (sulphates, chlorates, and some fluorites). The differences observed are attributed to the initial proportions of these species in the studied mixture as reported in Table 1. Keeping the concentration of silica constant (47 wt%) and increasing the feldspar the glasses with lower viscosity were observed. The glass flowed with easiness when the composition RSF30 (23 wt% in residue) was used. The X-ray diffraction patterns (Fig. 3) showed the amorphous nature of the obtained for RSF10, RSF30 and RSF40 glass composition. The RSF10 specimen shows more crystalline phases from the residue than others compositions after vitrification. RSF40 specimens whose have less residue concentration show high amorphous phase content despite peaks of cristobalite were also present. These results allow to conclude that increasing the feldspar concentration up to 40 wt% in the initial composition of the glass, the cristobalite phase remains stable until 1400°C. Taking into consideration that the feldspar is a silicate, once its concentration is increased, the silica content in the glass is also increased. With this results, it was possible to incorporate up to 23 wt% in weight of galvanic solid residue in a silicate glass.

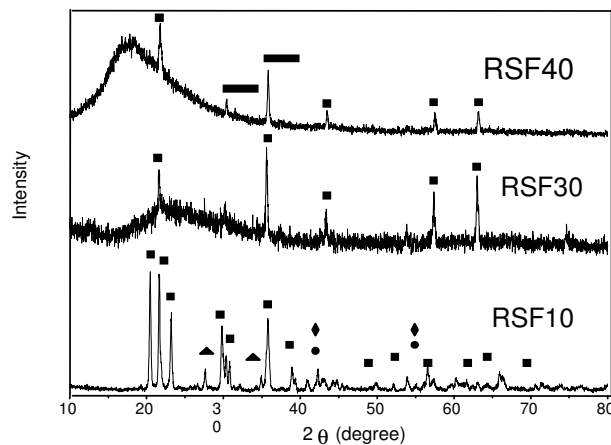


Figure 3. X-ray diffraction pattern of the different melted compositions.
 Legend: (■) cristobalite; (▲) $(K,Na)(Si,Al)_4O_8$; (◆) $ZnCr_2O_4$.

Conclusions

The residue studied preserves its initial constituents until 1400°C. Reductions in the mass with the increase of the temperature were observed. A good flowing was obtained by incorporating 23 wt % of solid galvanic residue in the glass matrix.

References

- [1] M. Romero, R.D. Rawlings, J.M. Rincón: *J. of Non-Crystalline Solids* 271 (2000) 106-118.
- [2] L. Barbieri, T. Manfredini, I. Queralt, J.M. Rincón, and M. Romero: *Glass Technology*, 1997, 38(5), 165-170.
- [3] M. Ferraris, M. Salvo, F. Smeacetto, L. Augier, L. Barbieri, A. Corradi and I. Lancellotti: *J. Eur. Cer. Soc.* 21(2001) 453-460.

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