

Section 5. Applications and biomaterials

Silicate glasses obtained from fine silica powder modified with galvanic waste addition

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Abstract

This work presents a study of waste incorporation in silicate glass process based on the formulations of soda-lime glass compositions using two different industrial solid residues. Glass silicates were produced from the residue of silica powders retained in the filter sleeves of sanitary ceramic factories. An other waste also used as the starting material was the solid galvanic residue from metallurgical processes. Besides part of the silica contents was replaced by boron oxide to improve melting of the glasses and the behavior of both the formulations was analyzed. The temperatures for the fusion were selected based on the equilibria diagrams and the flux characteristics of the melting as a function of the glass compositions. Temperatures up to 1500°C and annealing treatments were used. The composition and the structure of the glass specimens were studied using X-ray fluorescence and X-ray diffraction methods. The resistances of the glasses at environmental conditions by hydrolysis, acid and alkaline attack experiments were analyzed. Glasses with up to 40wt% of added galvanic solid waste and 28wt% of fine silica powder with a good chemical resistance were obtained.

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1. Introduction

The recycling and valuation of wastes coming from industrial processes has become, a worldwide concern, very important in the last few years and claims for a solution in the near future.

The vitrification process simulates the natural phenomenon of the glassing from volcanic rocks (ex. Basalt). These natural glasses contain toxic materials in their structure that have shown environmental inert as the time. These elements are absorbed in the chemically stable vitreous matrix [1]. The vitrification of hazardous residues has been industrially applied as the treatment

of radioactive wastes [2] as the inertization of ashes from urban garbage incinerators [3–5].

Glass has been used due to its chemical and physical–chemical characteristics such as good behavior during fusion, homogeneity, durability and stability to several environmental conditions [1]. In addition, glass shows an open amorphous structure and can easily be incorporated with a great number of elements of the periodic table. These characteristics are also interesting to the inertization of galvanic waste in the glass matrix that contains several different metals in its composition [6].

This process is available to incorporate simultaneously wastes from different sources in glass matrix. Besides the wastes may contribute with glass formers and improve its chemical resistance properties.

In this study fine silica powder restrained in industrial filters and galvanic solid waste from metallurgical process were chosen as the starting material to obtain glass silicate with a good chemical stability.

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2. Experimental

2.1. Raw materials

Fine powder of silica waste: restrained waste in filter sleeves of milling process (particle size < 0.074 mm). Fine silica powder is an environmentally inert material, but silica dust, due to its very fine grain size is harmful to human and animal health being classified as a very harmful waste according to Brazilian standard NBR-10004 [5]. Although fine grain size, silica (< 0.1 mm) is not a raw material to produce glass because it can improve the viscosity [8] of the melt and hence the refining time, the vitrification of this material is an interesting way to inertize it.

Galvanic waste (GW): obtained from the served water treatment in a plant of galvanic metal coating process, due to its physical–chemical characteristics this material has also been classified as a very environmentally hazardous solid waste, in accordance with the Brazilian standard NBR-10004 [7].

Industrial Feldspar: obtained from milling of granite rocks.

Other reagents also used were aluminum oxide (Alcoa A-1000), sodium hydroxide (97 wt% – nuclear), calcium oxide (97 wt% – química moderna), potassium carbonate (99 wt% – carlo erba) and boric acid (97 wt% – química moderna).

2.2. Glass preparation

2.2.1. Formulation

The adjustment of the compositions include the following stages:

1. Attainment of a soda-lime glass using phase equilibria diagram for the CaO–NaO–SiO₂ [9] system (Fig. 1) with a low viscosity at the melting temperature. In this composition we used only fine powder of silica and pure reactants. This composition was labeled as mixture K (Table 1). Part of the pure oxides was substituted by feldspar and it was labeled KF composition.
2. Using phase equilibria diagram for the CaO–B₂O₃–SiO₂ [10] system (Fig. 2), part of the silica content in compositions K and KF was replaced by boron, to have lower melting temperatures. The finish compositions were respectively labeled N and NF (Table 1). The other reagents had been added aiming at the necessary adjustment of the compositions.
3. Galvanic waste (GW) was incorporated in the mixtures KF and NF in concentrations of 10%, 20%, 30% and 40% in mass. For these mixtures, considered the contributions in glassing, such as silica and calcium oxide among others. The resultant mixtures were labeled as KFR10, KFR20, KFR30, KFR40, NFR10, NFR20, NFR30 and NFR40 (Table 1).

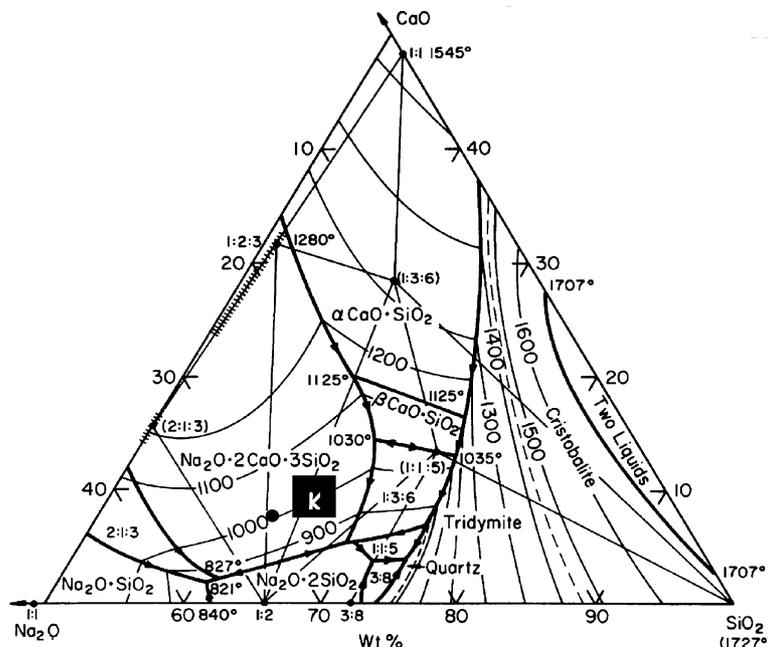


Fig. 1. K Composition formulated on the CaO–NaO–SiO₂ [9] system.

Table 1
Formulated compositions (wt%) (error $< 5 \times 10^{-5}$)

Compositions	K	KF	KFR10	KFR20	KFR30	KFR40	N	NF	NFR10	NFR20	NFR30	NFR40
SiO ₂	60.4	59.4	54.0	51.8	48.0	44.2	54.0	54.0	50.8	47.3	44.0	40.7
B ₂ O ₃	–	–	–	–	–	–	6.0	6.0	5.6	5.3	4.9	4.5
Na ₂ O	28.5	29.1	26.7	25.9	24.4	22.9	28.4	28.4	26.7	24.9	23.2	21.4
CaO	8.6	8.7	7.8	7.0	6.2	5.7	8.6	8.6	8.0	7.5	7.0	6.5
K ₂ O	1.1	1.2	0.9	1.1	1.0	0.9	1.0	1.0	0.9	0.9	0.8	0.8
Al ₂ O ₃	2.6	3.2	2.4	3.0	3.3	2.5	2.0	3.0	2.0	1.9	1.7	1.6
MgO	–	–	0.4	0.7	1.1	1.4	–	–	0.4	0.7	1.1	1.4
Fe ₂ O ₃	0.2	0.2	0.3	0.4	0.5	0.5	0.1	0.1	0.2	0.3	0.4	0.5
Cr ₂ O ₃	–	–	2.1	4.2	6.3	8.4	–	–	2.1	4.2	6.3	8.4
NiO	–	–	1.3	2.6	3.9	5.2	–	–	1.3	2.6	3.9	5.2
CuO	–	–	0.7	1.4	2.1	2.8	–	–	0.7	1.4	2.1	2.8
ZnO	–	–	0.5	0.9	1.4	1.9	–	–	0.5	0.9	1.4	1.9
PbO	–	–	0.1	0.3	0.4	0.5	–	–	0.1	0.3	0.4	0.5

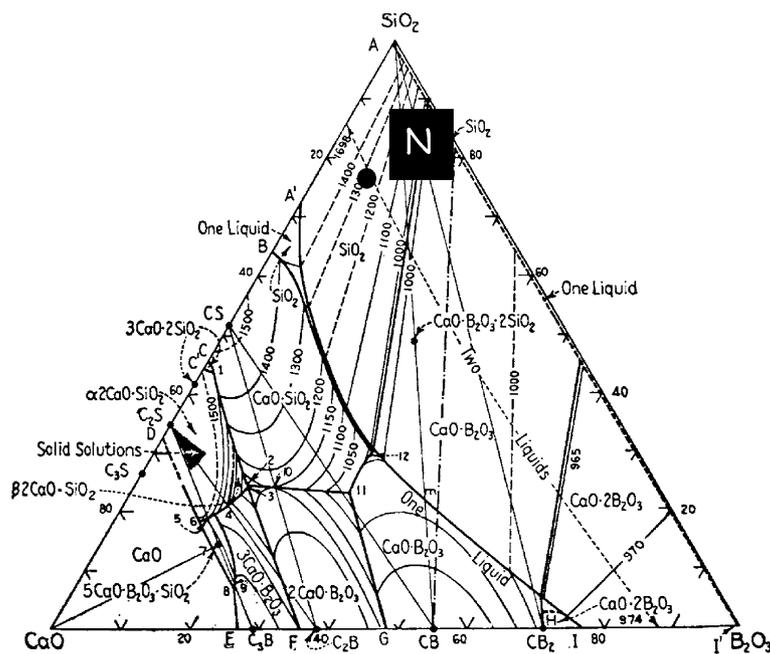


Fig. 2. Indication of N composition in the CaO–B₂O₃–SiO₂ [10] system.

Sodium or calcium carbonates normally used as fluxants in glass manufacture were replaced by sodium oxide and calcium oxide to avoid strong gas formation and its undesirable consequences.

2.2.2. Glass sample preparation

All compositions were prepared and heat treated in an electric furnace at normal atmosphere in alumina crucibles. The time of melting at the temperature studied was fixed as 2 h [11]. The fusion temperatures were selected based on the equilibria diagram [9,10] and on the melting flux behavior. The fused glasses were molded in to rods (10 × 10 × 50) mm, at normal cooling in air until 500 °C and then they were annealed at this temperature during 2 h. The specimens for the hydrolytic, alkaline and acid attack tests were cut in to 10 × 10 × 1 mm and polished at 0.063 mm [12]. The specimens were pow-

dered (<0.025 mm) by milling in a mill attritor using hard metal balls before chemical and structural analysis.

2.3. X-ray powder diffraction (XRD)

The 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-K_α 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 2 range of 10–80°.

2.4. X-ray fluorescence (XFR)

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

variations for all the analysis were calculated using the fundamental parameter methods with a relative deviation less than 10%.

2.5. Hydrolytic resistance

The hydrolytic resistance measurements of the glasses were carried out using the method described by Day [12] modified by using a soxhlet distillation column. Samples with dimensions of (1 × 1 × 10) mm were continually washed with distilled water and the dissolved specimens from the glass samples were carried with the leaching solution to the boiler recipient. The main target to introduce this modification on the Day's method is to avoid that the part of the dissolved ions of the samples return on its surface and to avoid too the pH variations in the attack solution. The time leaching test was fixed at 1, 3, 7 and 14 days. The weight variations of the samples were measured by using an analytical precision balance ($\pm 5 \times 10^{-5}$) g.

2.6. Alkaline attack resistance

The alkaline attack resistance measurements were carried out using the method described by Navarro [8] and modified here by the use of specimens with dimensions of the (1 × 1 × 10) mm. In this method the sample is attacked by a mixture of equal parts of sodium hydroxide 1.0M and sodium carbonate 1.0M heated at 100°C for 3h. The results are expressed in terms of the mass loss by the initial superficial area of the sample.

2.7. Acid attack resistance

The acid attack resistances were carried out using the method described by Navarro [8] modified by the use of samples with dimensions of (1 × 1 × 10) mm. In this method the samples are attacked by a solution of Chloridric acid 6.0N heated at 100°C for 6h. The results are expressed by the rate between mass loss and the initial superficial area of the sample.

2.8. Error calculation

The statistical standard variation methods were applied to determine the measure errors [13].

3. Results

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

For the purpose conformation the compositions that attained a good melting flux behavior according to the temperature of the fusion were at 1300°C N, NF,

Table 2

Main constituent of the start materials in mass% ($\pm 0.01\%$)

Element	Galvanic waste	Silica	Feldspar
SiO ₂	22.0	98.0	72.0
Al ₂ O ₃	0.9	0.9	16.0
CaO	14.0	0.1	0.6
K ₂ O	0.2	0.2	6.2
Na ₂ O	1.2	0.2	4.9
MgO	3.5	–	–
Cr ₂ O ₃	21.0	–	–
CuO	6.9	–	–
NiO	13.0	–	–
ZnO	4.7	–	–
PbO	1.3	–	–
Fe ₂ O ₃	1.1	0.2	0.7
P ₂ O ₅	1.2	–	–
SO ₃	7.4	0.1	0.1

NFR10, NFR20, NFR30 and NFR40 and at 1500°C were K, KF, KFR10, KFR20, KFR30 and KFR40.

The XRD patterns results are shown in Figs. 3 and 4 for all compositions studied.

Fig. 5 shows the mass loss verified during the fusion for each composition studied, in metal oxide forms expressed comparing the XRF analysis before and after fusing the glasses.

The alkaline and acid attack resistance results after 3 and 6h of attack respectively are presented in Fig. 6.

Figs. 7 and 8 show the mass loss rate behavior for K (soda-lime) and N (soda-lime with boron) groups respectively during the hydrolytic attack experiments. For all analyzed compositions we observed the mass loss rate decrease with the time of the attack in both groups of the samples (Figs. 7 and 8), respectively.

Figs. 9 and 10 show the leach extracts pH variations during the hydrolytic attack experiments for series K

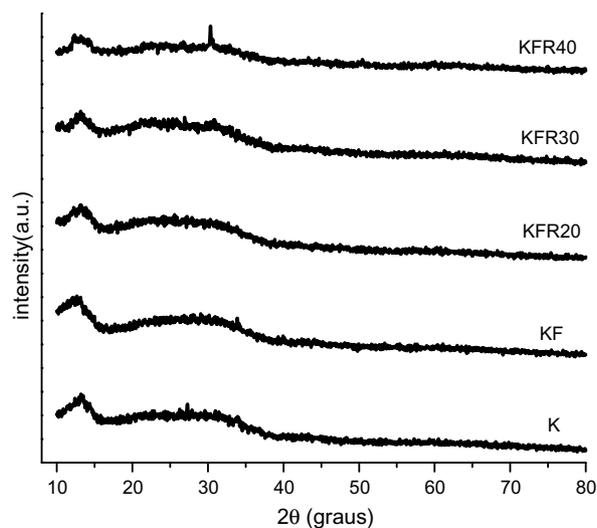


Fig. 3. XRD specters of the glasses samples K, KF, KFR20, KFR30 and KFR40.

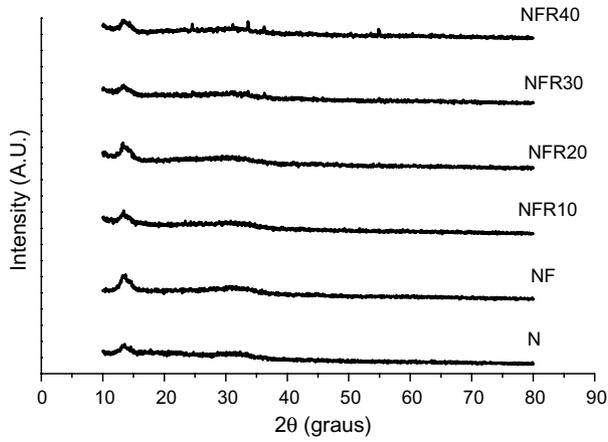


Fig. 4. XRD patterns from the N, NF, NFR10, NFR20, NFR30 and NFR40 glasses samples.

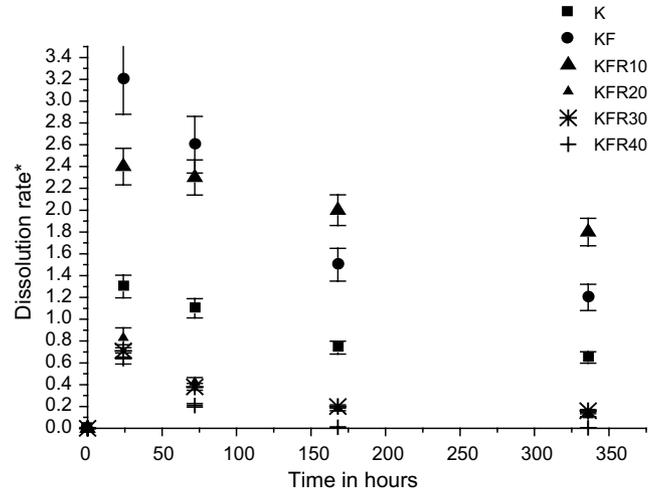


Fig. 7. Group 'K' glass dissolution rate under water attack in function of the time of test ($*[g/(cm^2 \times s)] \times 10^{-7}$).

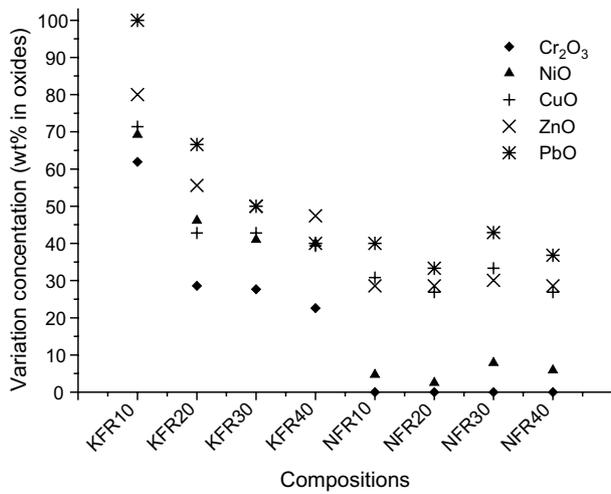


Fig. 5. Variation of concentration in glasses samples for each oxide specimens initially present in GW.

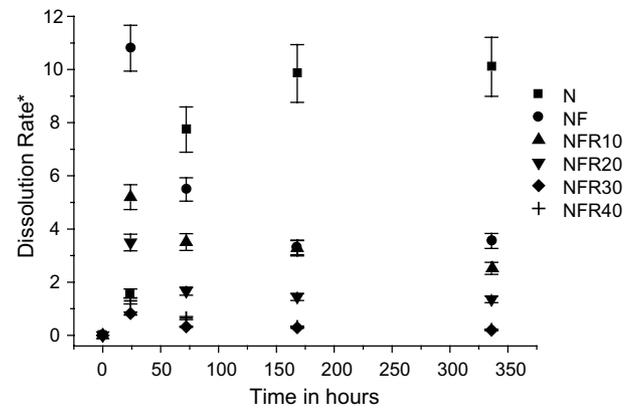


Fig. 8. Group 'N' glass dissolution rate under water attack by the time of test ($*[g/(cm^2 \times s)] \times 10^{-7}$).

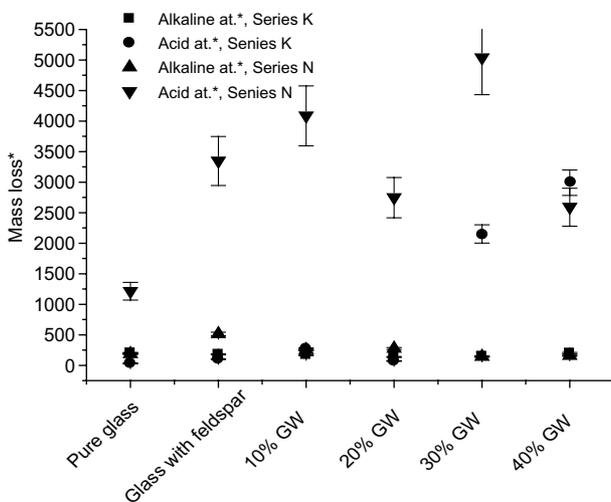


Fig. 6. Alkaline and acid attack resistances (mg/dm^2).

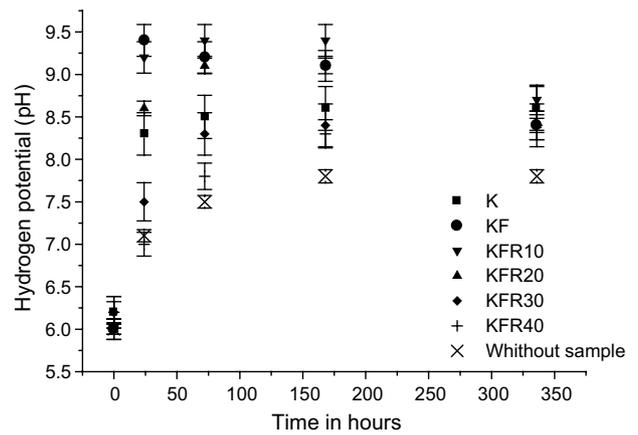


Fig. 9. Group 'K' leach solution pH variation by the assay time.

and N respectively. The pH stabilization of the leach solutions with time was observed for all compositions.

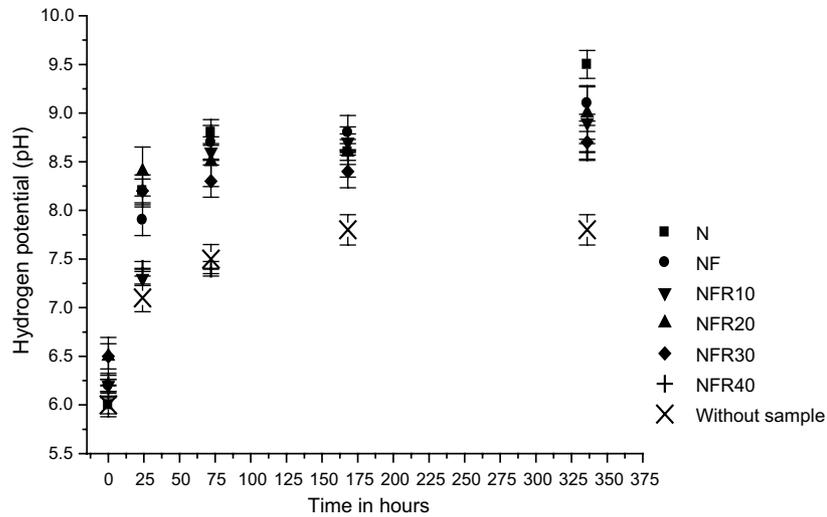


Fig. 10. Group 'N' leach solution pH variation with the assay time.

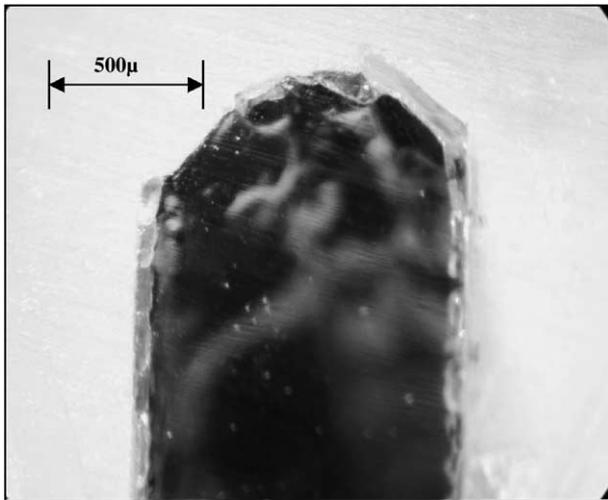


Fig. 11. Picture (magnification about 100×) obtained from KFR10 transversal section sample (around 1.0mm thickness) after 14 days hydrolytic attack.

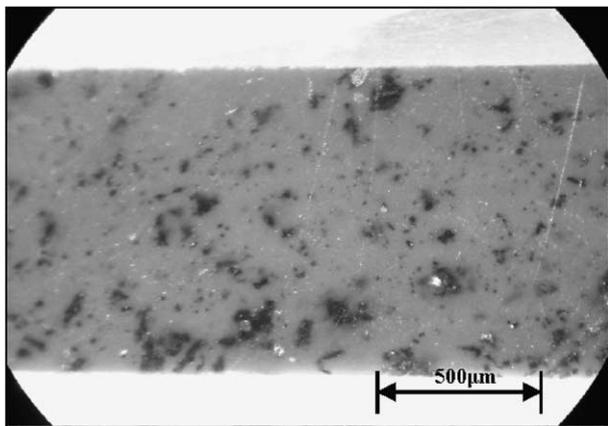


Fig. 12. Picture (magnification about 100×) from KFR40 transversal section sample (around 1.0mm thickness) after 14 days hydrolytic.

Figs. 11 and 12 show the cross section of the samples from different series composition illustrating the surface aspect after the hydrolytic attack assay.

4. Discussion

The use of the powdered silica waste as glass former raw material on all studied compositions was improved.

In general, all the glass samples analyzed by the XRD method (Figs. 3 and 4), were amorphous in nature. Although when high galvanic waste concentration was used as for samples KFR30, KFR40 and NFR40 the tendency of some metal specimens to crystallize was verified. In these diffraction patterns the small peaks at 31.9° and 51.6° may be related to Ni_2O_3 crystals formation. The presence of Cr_2O_3 was not detected even its low solubility in silica melt [8].

The loss of some metal specimens (Cr, Ni, Cu, Zn and Pb) contents were verified in the results obtained by XFR analyses from fused glass samples. Fig. 5 shows the values determined and the calculated starting compositions.

The addition of galvanic solid wastes in glasses increase their resistance to alkaline attack. The compositions KFR20 (GW 20 wt%), KFR30 (GW 30 wt%) and NFR20 (GW 20 wt%), showed higher resistance values than others, in comparing with compositions without GW shown in Fig. 6. All the samples had presented high solubility in acid environment, as expected, justified by the high alkali content in the considered glass compositions. It is interesting to observe in this experiment that the resistance to the acid attack decreases with the GW additions for all compositions considered.

During the hydrolytic attack tests, reductions in the mass loss rate with time were observed. Comparing

Figs. 7 and 8 it is possible to observe that the samples with high GW contents are more resistant to water attack. Highest hydrolytic resistance in glasses without boron was also observed, as expected.

The pH stabilization of the leach solutions with time during the hydrolytic attack experiments was observed for all compositions (Figs. 9 and 10). The increase of the pH in the first few hours of the treatment is indicative at the initial stage of glass sample dissolution the preferential extraction of alkalis on the surface of the glasses occurred as pointed by the Refs. [14–19]. The sample with a high GW content shows a low rate of alkali release as KFR30, KFR40 and NFR 40 compositions.

In the following hours of attack a superficial layer rich in silica was formed in the samples K, KF, KFR10, N, NF, NFR10 and NFR20. These layers, as illustrated in Fig. 11, may contribute to improve both glass resistance and the pH solution stabilization. In accordance with some authors [8,17,18] the presence of this layer indicates that the dissolution of these glasses was attained by the hydrolysis of the Si–O bonds. In the samples KFR20, KFR30, KFR40, NFR30 and NFR40, a rich silica layer was not observed (Fig. 12). This result indicates that in these glasses with high GW contents, the hydrolysis reaction on the Si–O bonds occurs more slowly.

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

5. 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.
3. The studied glass compositions with high concentrations of galvanic solid waste had presented interesting characteristics like high resistance to the hydrolytic attack, medium resistance to the alkaline attack and low resistance to the acid attack.
4. The glasses with a high concentration of galvanic waste incorporated show a better resistance to the hydrolytic and alkaline attack than the common glass with the same basic composition.
5. The glasses with high GW contents show a poor acid environment resistance.
6. The glasses without boron addition show the best resistance in all attack conditions.
7. The boron glass content shows a better resistance to loose metal specimens during the melting.
8. Complete inertization or 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.

Acknowledgments

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