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Corrosion behaviour of vitrified heavy metals from industrial waste

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Abstract. The vitrification process is an attractive route for the inertization treatment of hazardous industrial wastes. The corrosion resistance of this kind of materials is one of the most important requirements to ensure the long term retention of the toxic metals. In this work, silicate glasses with various waste concentrations were obtained using a galvanic sludge from metallurgical activities and glass forming rejects from ceramic activities. Glasses with several galvanic waste concentrations were obtained. The corrosion behaviour of the vitrified materials under various pH media was evaluated. The FTIR technique was used to investigate the glass structural modifications. Glasses containing 40 wt.% galvanic waste additions show higher resistance to corrosion media than those without waste additions.

Introduction

The adequate and safe management of hazardous industrial wastes involve complex aspects of many orders, such as sanitary, environmental, economic, industrial and cultural. In the specific case of the galvanic solid rejects, which contain transition and toxic heavy metals such as Nickel and Chromium, the legislation in most countries forbids their simple deposition on the ground. Vitrification has been proposed as an inertization alternative.

The vitrification process used for industrial wastes is more complex than the simple dilution of the waste in a glass matrix. During melting, the waste may contribute with some metal oxides to the random glass network and the transition and heavy metal oxides, associated with the glass, may act as glass network formers or modifiers [1].

This behavior may be explained as follows: in a pure silica glass structure, each silica tetrahedron is linked with four other by the corner oxygen atoms (bridging oxygen, BO). Thus, all oxygen atoms are BOs and every Si atom is named Q^4 species. When modifier cations (R^+ and/or R^{++}) are added to the glass composition, some oxygen atoms will bond with the modifier cations, becoming non-bridging oxygens (NBOs), and some Si atoms are named Q^n species. The presence of modifier cations in the glass network usually changes the glass characteristics, such as the melting point and the glass chemical durability. A characteristic behavior can occur with cations with coordination number higher than four, such as those generally present in the galvanic wastes. The Q^n abundance is also affected by the presence of Boron or Aluminum, given that Al^{3+} and B^{3+} show a strong tendency to replace Si^{4+} in the Q^4 species. The use of the vitrification process for toxic metals immobilization is based on the assumption that the chemical durability of the resultant glasses will reduce the contamination of the environment. Although one of the most important characteristics of a glass is its chemical durability, glasses cannot be considered rigorously inert. The glass chemical durability can be evaluated as corrosion resistance to water attack (hydrolytic resistance), acid attack and alkaline attack. The dissolution process is irreversible [2] and the presence of impurities and the complexity of the glass composition will have a strong influence in the dissolution behavior [3,4]. The aim of this work was to study the feasibility of using only industrial rejects of different origins to obtain glasses capable of immobilizing transition and heavy metals. Such capability was evaluated as chemical resistance to various corrosive media.

Experimental

Three different industrial rejects were used as raw materials, namely, rejected fine silica powder from the milling process, as collected by sleeve filters (particle size <0.074mm), galvanic waste (GW) produced in the spent water treatment in a galvanic metal coating plant, and a dried granite sludge produced in the sawing process of ornamental stones. The silica powder, given its very fine grain size, is considered harmful to human and animal health; the GW, mostly due to its chemical characteristics, has also been classified as environmentally very hazardous solid waste. The granite sludge is non-hazardous but can cause serious environmental problems [5].

A boron modified soda-lime glass base composition (labeled C00 in Table 1) was calculated from the Na_2O–CaO–SiO_2 and CaO–B_2O_3–SiO_2 phase equilibrium diagrams [6]. The base composition C00 was prepared using the fine silica powder and the granite sludge, complemented by other reagents, namely: alumina (Alcoa A-1000), sodium hydroxide (97 wt.%, Aldrich), calcium oxide (97 wt.% Nuclear), potassium carbonate (99 wt.%, Carlo Erba) and boric acid (97 wt.%, Química Moderna). To this base composition, 10 and 40 wt.% GW additions were made (respectively, compositions C10 and C40 in Table 1).

Table 1. Chemical compositions of the glasses investigated [wt.%].

Glass	SiO_2	B_2O_3	Na_2O	CaO	K_2O	Al_2O_3	MgO	Fe_2O_3	Cr_20_3	NiO	CuO	ZnO	PbO
C00	54.0	6.0	28.4	8.6	1.0	3.0	-	0.1	-	-	-	-	-
C10	50.8	5.6	26.7	8.0	0.9	2.0	0.4	0.2	2.1	1.3	0.7	0.5	0.1
C40	40.7	4.5	21.4	6.5	0.8	1.6	1.4	0.5	8.4	5.2	2.8	1.9	0.5

The compositions were melted in alumina crucibles at a constant melting temperature of 1300ºC during 2h [7]. The molten glasses were poured and shaped as (10 x 10 x 50) mm bars, naturally cooled in air down to 500ºC and then annealed at this temperature for 2h.

The amorphous character of the glasses was confirmed by powder X-ray diffraction analysis (XRD, Brunker-AXS model D8, Advance Powder diffractometer). The powder specimens were mounted on a glass sample holder and the XRD patterns were recorded in the 10–80º 2θ range [1].

The hydrolytic resistance of the glasses was determined by the Day method [8] modified with the use of a soxlet distillation column. The glass bars were sliced into 1 mm thick samples, which were polished down to 63 μm. During the hydrolytic resistance test, the glass sample was continuously washed with distilled water and the dissolved species were removed with the leaching solution to the boiler recipient. The resistance to alkaline attack was measured using the method described by Navarro [9], modified by the use of (1 x 10 x 10) mm specimens. In this method, the sample is attacked for 3h by a 1.0 M equimolar solution of sodium hydroxide and sodium carbonate, heated at 100ºC. This method was also used for the acid attack resistance studies. In this case, the samples were attacked for 6h by a 6.0 N solution of hydrochloric acid heated at 100ºC. In all cases, the test results are expressed in terms of mass loss referred to the initial surface area of the sample. During the tests, the samples weight changes were recorded after 24, 72, 168 and 336 hours using a precision analytical balance ($\pm 5x10^{-5}$ g). After 336 hours leaching, the samples surface layer was removed and analyzed by FTIR spectroscopy. Also for FTIR analysis purposes, similar corrosion tests were carried out with milled glass fine powders (<210 μm) bagged in Whatmann 40 filter paper.

The FTIR spectroscopy determinations were carried out using a Thermo Nicolet–Nexus 870 FTIR spectrometer. The samples were dispersed in spectrometric grade KBr (Merck p.a.) discs. Literature data [10-12] were used to interpret the results. Statistical standard deviation methods were applied to determine measurement errors [13].

Results

The XRD patterns of all compositions show amorphous structures. However, for high GW concentration (glass C40), small intensity peaks attributed to chromium and sodium silicate compounds can be observed in the diffraction pattern, suggesting a tendency for the devitrification of the glass.

Fig. 1 shows the FTIR spectra obtained for the unattacked glasses. All spectra show the three characteristic peaks of a silicate glass, near 1010 cm^{-1} (SiO_4 tetrahedron surface), 780 cm^{-1} (SiO_4 tetrahedron bonding) and 460 cm^{-1} (Q^4 tetrahedral Si-O-Si). The presence, in all samples, of peaks at 900-920 cm^{-1} (Si-O Q^1 NBO) is indicative of the existence of silicon oxides without BOs. All glasses show discontinuous sites in the glass network. Peaks observed near 670 cm^{-1} are related to (Si-O-B) bonds within the glass random network of silica tetrahedra. The segregation of boron oxide is illustrated by peaks near 1406 cm^{-1} (B-O). The 1470 cm^{-1} peak possibly corresponds to the Na^+ terminal sites in the glass network. The low intensity peaks observed near 780 cm^{-1} and 1010 cm^{-1} may be related to the formation of GW metal silicates (mainly chromium and nickel silicates). No peaks near 500 cm^{-1} were observed, which would indicate the segregation of metal oxides. Probably, the metal cations are completely bonded within the glass network. Peaks at 1750 cm^{-1} (H-O-H) and 3470cm^{-1} (-O-H) indicate the presence of structural water. The 1600 cm^{-1} peak is characteristic of free water and can be attributed to the samples moisture.

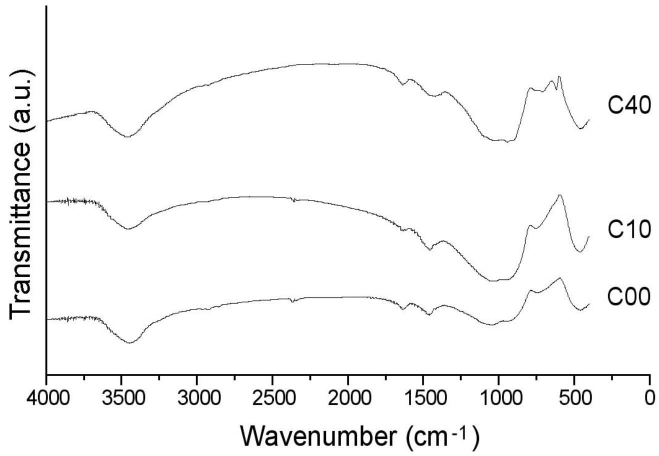

Figure 1. FTIR spectra of samples C00, C10 and C40.

The BOs hydrolysis and the network breakdown will be verified by the changes in the peaks near 1100 cm^{-1} (Si-O Q^3 NBO) and 1200 cm^{-1} (Si-O Q^4), for all samples. The hydrolysis process product (formation of the amorphous surface layer) is evidenced by a peak at 940 cm^{-1} (Si-OH).

Fig. 2 shows the changes in the weight loss rate during the hydrolytic attack tests. It can be observed that the samples with high GW contents show higher resistance to water attack.

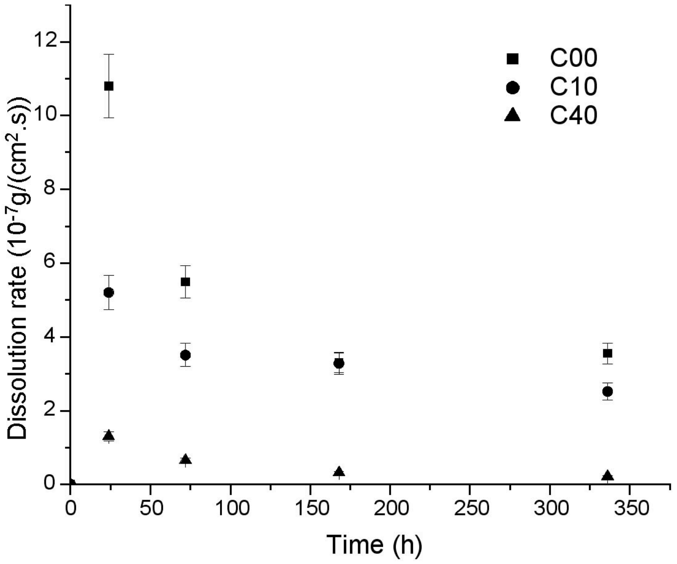

Figure 2. Dissolution rate [10^{-7} g/(cm^2.s)] of glasses C00, C10 and C40 in water.

The increase of the dissolution rate over the test first few hours is an indication that the glass sample dissolution begins (initial stage) with the preferential extraction of alkalis from the glass surface [9,10]. The sample with the highest GW content shows a low rate of alkali release. In the next hours of attack, a silica rich surface layer is formed, which may contribute to improve glass resistance stabilization as it slows down the dissolution rate. This can clearly be seen in samples C00 and C10. According to some authors [6,10,15] the presence of this layer indicates that the dissolution of these glasses is due to the hydrolysis of the Si–O bonds.

After 336 hours (14 days) leaching, the samples surface layer was removed and FTIR spectra were obtained from the resulting powders. The structural vitreous silica signature (1010 cm^{-1}, 780 cm^{-1} and 460 cm^{-1}) can be seen in both C00 and C10 samples (Fig. 3). In sample C40, a silica rich layer was not observed. This result indicates that in these glasses with high GW contents, the hydrolysis reaction of the Si–O bonds occurs with less intensity. Fig. 3 shows that non leached material is segregated in both C00 and C10 samples, given the absence of peaks at 900-920 cm^{-1} (Si-O Q^1 NBO). The BOs hydrolysis and the network breakdown are confirmed by the presence of peaks near 1100 cm^{-1} (Si-O Q^3 NBO) and 1200 cm^{-1} (Si-O Q^4). The hydrolysis process product is evidenced by the peak at 940 cm^{-1} (Si-OH). These results indicate the BOs hydrolysis contribution to the formation of the amorphous surface layer. Boron oxide corrosion is indicated by the peak at 670 cm^{-1} (Si-O-B).

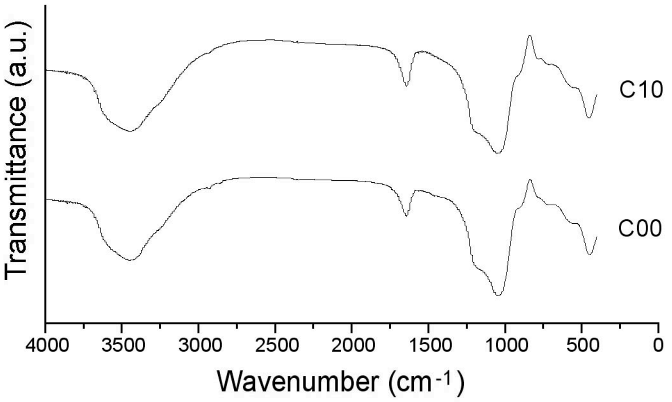

Figure 3. FTIR spectra of the C00 and C10 glasses surface layer, after 336 hours of hydrolytic attack.

Fig. 4 shows the changes in the FTIR spectra of the three glasses C00, C10 and C40 with the duration of the hydrolytic attack. For all samples, leaching is stronger at the beginning of the hydrolytic attack (*i.e.* during the first 24 hours). Peaks observed near 1010 cm^{-1}, 780 cm^{-1} and 460 cm^{-1} (Q^4) indicate that in all samples the glass random network was not attacked. The presence of peaks at 780 cm^{-1} and 1010 cm^{-1} in all samples, shows that the metal silicates from the added galvanic waste were not removed during the hydrolytic attack. Segregated metal oxides peaks at 500 cm^{-1} are not observed. These results indicate that the metal silicates were not involved in the corrosion process. Peaks observed in all samples near 670 cm^{-1} (Si-O-B) indicate low dissolution of structural boron oxide. For composition C00 (Fig. 4-a), the peaks near 1406 cm^{-1} (B-O) reveal segregated boron oxide extraction. The peaks near 850-880 cm^{-1} (Si-O Q^0 NBO) and 900-920 cm^{-1} (Si-O Q^1 NBO) in sample C40 (Fig. 4-c) indicate glass network dissolution, resulting in segregated silica tetrahedra and amorphous surface layer formation. The Si-O Q^0 NBO and Si-O Q^1 NBO seem to be extracted to the leach solution in samples C00 and C40 (Fig. 4-a and c, respectively).

The addition of galvanic waste to the base glass also modifies its resistance to alkaline attack. Once again, composition C40 showed higher resistance values when compared with compositions with lower GW contents, as shown in Fig. 5.

As expected, all samples presented high solubility in acid environment, given their high alkali content. However, in this experiment, it is interesting to note that the resistance to the acid attack decreases with increasing GW additions.

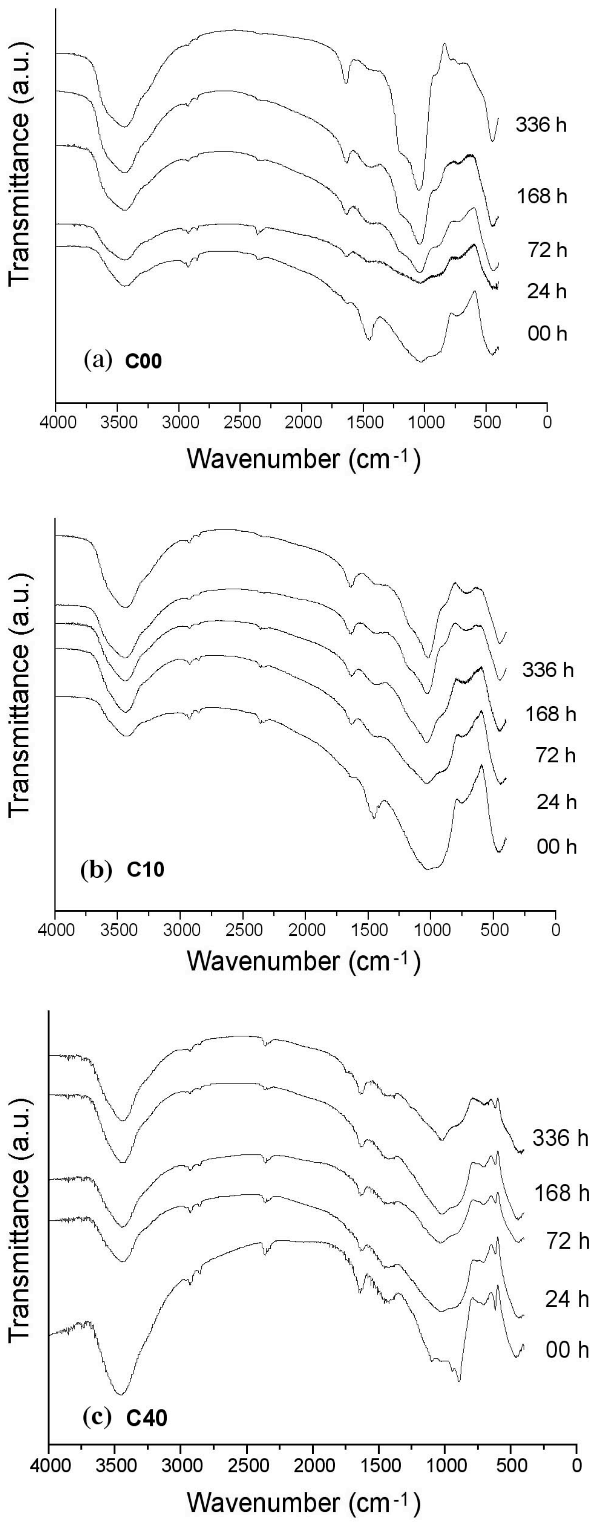

Figure 4. FTIR spectra of glass powders subjected to hydrolytic attack for 1, 3, 7 and 14 days: (a) composition C00; (b) composition C10; and (c) composition C40.

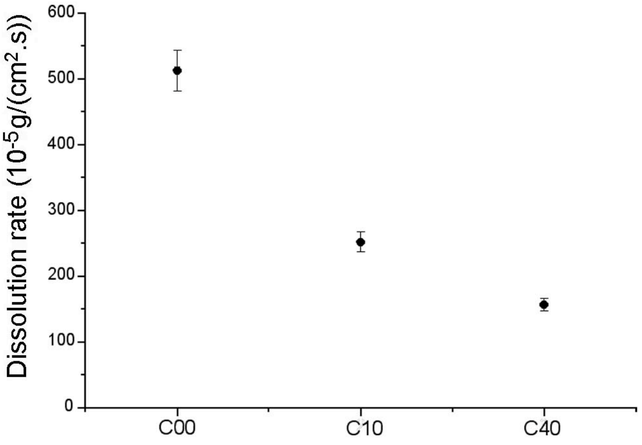

Figure 5. Dissolution rate [10^{-5} g/cm^2] of glasses C00, C10 and C40, after 3 h alkaline attack.

Discussion

Multi-oxide glass terminal points in the random network were observed, as expected. Evidences of GW metal oxide crystal clusters were observed in low intensity only in the sample containing 40 wt.% GW. The GW metal oxides appear to be incorporated in the random glass network. The chemical resistance improved with the presence of the GW in the glass composition. One possibility is that the metal oxides bond with two or more NBOs, *i.e.* the GW metal oxides promote "bridges" between NBOs, thus reducing the number of terminal points in the random glass network. The main reason for the improved chemical resistance is probably the smaller number of terminal points.

The dissolution during acid attack of the glass with the highest GW concentration may be explained by the fact that BOs bonds are stronger than the (Si-O-R) bonds formed by the GW metal oxides, and the protonic attack is more intense in the acid environment than in water. In the hydrolytic attack, the formation of a surface layer in the less resistant glasses may contribute to the improvement of the glass resistance stabilization.

The hydrolysis of the Si–O bonds in these layers was observed. Combination of these interesting results explains why the glasses containing 40 wt.% solid galvanic waste presented higher resistance to the hydrolytic attack.

Conclusions

Silicate glasses were obtained from the selected wastes (galvanic waste, granite sludge and fine silica powder) based on compositions calculated from the appropriate phase equilibrium diagrams. The galvanic waste containing glass compositions showed a dissolution behavior similar to that observed for the base glass, but less intense. The FTIR spectroscopy results suggest that the metal ions present in the galvanic solid waste (*e.g*. chromium and nickel) are incorporated in the glass network, which explains the improved corrosion resistance. Moreover, the glasses with high concentrations of galvanic waste presented interesting characteristics such as high resistance to hydrolytic attack, medium resistance to alkaline attack and low resistance to acid attack. All glasses showed good resistance to all corrosion media and, based on the results obtained, it can be said that galvanic waste additions generally lead to the improvement of the glass chemical resistance. Thus, the inertization and the reduction of the health hazard potential of all waste materials were achieved. In these experiments, only the corrosion resistance of the glasses was studied in comparison with the base composition without GW additions. The toxicity of the leach extract was not evaluated.

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