Chemical durability of glasses obtained by vitrification of industrial wastes

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Abstract

The vitrification of zinc-hydrometallurgy wastes, electric arc furnace dust (EAFD), drainage mud, and granite mud was shown to immobilize the hazardous components in these wastes. Batch compositions were prepared by mixing the wastes with glass-cullet and sand to force the final glass composition into the glass forming region of the SiO_2–Fe_2O_3–(CaO, MgO) system. The vitrification was carried out in the 1400–1450°C temperature range followed by quenching in water or on stainless steel mold. The United States (US) Environmental Protection Agency (EPA) toxic characterization leaching procedure (TCLP) test was used as a standard method for evaluating the leachability of the elements in the glasses and glass-ceramics samples made with different percentages of wastes. The results for EAFD glasses highlighted that the chemical stability is influenced by the glass structure formed, which, in turn, depends on the Si/O ratio in the glass. The chemical durability of jarosite glasses and glass-ceramics was evaluated by 24 h contact in NaOH, HCl and Na_2CO_3, at 95°C. Jarosite glass-ceramics containing pyroxene (J40) are more durable than the parent glass in HCl. Jarosite glass-ceramics containing magnetite type spinels (J50) have a durability similar to the parent glass and even lower in HCl because the magnetite is soluble in HCl. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

The stabilization treatment of waste-streams generated in primary raw material refining and metallurgical plants is particularly difficult because of the complex composition and high content of regulated heavy metals. Vitrification of hazardous wastes has been established as an environmentally compatible stabilization process because of the high chemical resistance of the glass product in most environmental conditions. Glasses demonstrate high resistance in most chemical media because the hazardous components, usually heavy metals, are atomically bonded in the glass network [1,2]. By properly selecting raw materials and other wastes as additives, products such as glass fibers and glass-ceramic tiles with chemical and mechanical properties comparable or better than commercial ones can be obtained [3–5] thus giving perspectives of recycle market exploitation.

In order to comply with current regulations for landfill disposal, either in the USA or in Europe, a low leachability of hazardous components from the glass or glass-ceramic matrix must be achieved, i.e. the vitrified waste must acquire an inert behavior towards environmental leaching conditions. However, this is a difficult property to assess because it requires: the selection of adequate corrosion test procedures simulating natural long term conditions, such as ASTM C1285 and NEN 7349, a knowledge of disposal or use conditions, a comprehensive corrosion data base, an understanding of the corrosion mechanism and a verification of predicted long-term performance.

The absence of co-ordinated and common regulation leads to the existence of a multitude of leaching procedures for waste characterization, in relation to assessments of their actual or potential environmental impact when utilized or deposited, many of which differ only slightly from each other. The existing leaching procedures for granular wastes and industrial sludge commonly used in various countries, including for regulatory testing, can be grouped into: column leaching test, such as NEN 7343 and Nordtest Procedure column test, batch leaching test, such as DIN 38414 SA, AFNOR X31-210, TCLP method and availability tests, such as NEN 7341. Moreover, new leaching procedures are

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currently being developed such as tank leaching test for compacted granular waste developed by the Netherlands Energy Research Foundation (ECN) in cooperation with Rutgers University in New Jersey [6].

In this scenario, the selection of the adequate leaching test has a key role for landfill disposal purposes, product reutilization and comparison.

The wastes investigated in the present work include jarosite, electric arc furnace dust (EAFD), drainage mud and granite mud. Jarosite is an iron-rich waste that results from the roast-leach-electrolysis process used in producing zinc [7]; the investigated samples came from a Spanish plant. EAFD is a waste by-product from steel-making operations [8]; the sample analyzed was produced in an Italian stainless steel plant. They are both classified as hazardous wastes. Drainage mud arises from canal drainage while granite mud is the result of the sawing of the blocks carried out in Sardinia. They contain fractions of heavy metals, in the first case, and metallic iron in the second. Combinations of these wastes were vitrified on a laboratory scale and by means of a pilot plant [9]. The batch compositions were defined with the objective of stabilizing the highest quantity of waste and recycling the glass or glass-ceramic products in the construction industry. The United States (US) Environmental Protection Agency (EPA) toxic characterization leaching procedure (TCLP) has been selected as the batch leaching test because it simulates conditions under a landfill that has acid drainage. It has been applied, with no practical modifications, by the Italian norm in order to classify the wastes and to verify the wastes inertization processes [10–12].

The chemical durability of the glass and glass-ceramic tiles was investigated by weight loss per surface unit employing NaOH, HCl and Na_2CO_3 aqueous solutions, at 95°C.

2. Experimental

The waste compositions were determined by means of an X-ray fluorescence (XRF) Xepos spectro instrument. Table 1 shows the compositions of the investigated wastes expressed as wt.% of the oxide.

The particle size distributions of wastes and glasses were determined by means of standard sieves and Marven series 2600 laser diffraction techniques.

The raw wastes and the corresponding waste made glasses were subjected to the TCLP test by putting them in contact with distillate water for 24 h. The pH of the solution was kept constant to 5 by addition of diluted acetic acid [10,11]. The analyses were carried out on the liquid extraction phase by means of atomic adsorption (Varian Spectra 200) spectroscopy.

On laboratory scale vitrification experiments jarosite was calcined at 800°C for 2 h; by this treatment, about

Table 1
Composition of the wastes in weight percentage of the oxides after drying at 105°C

Oxides	Jarosite	EAFD	Drainage mud	Granite mud	Glass cullet
	wt.%				
SiO_2	3.7	4.1	50.0	72.8	72.5
Al_2O_3	0.3	1.0	8.0	13.2	0.5
Na_2O	n.d.	6.0	0.6	3.5	13.4
K_2O	n.d.	1.0	2.0	4.2	0.2
MgO	0.2	9. 0	1.0	0.4	4.0
CaO	0.1	20.2	9.0	3.4	8.7
P_2O_5	n.d.[a]	n.d.	0.7	n.d.	n.d.
PbO	3.6	0.5	n.d.	n.d.	n.d.
ZnO	5.6	7.0	n.d.	n.d.	n.d.
MnO	n.d.	4.0	0.2	0.1	n.d.
CuO	n.d.	n.d.	n.d.	n.d.	n.d.
CdO	n.d.	n.d.	n.d.	n.d.	n.d.
Fe_2O_3	49.3	23.0	6.0	3.0	0.1
Cr_2O_3	n.d.	18.0	0.1	n.d.	n.d.
LOI	37.2	5.0	21.0	0.1	n.d.
Sums	100.0	98.8	98.6	100.7	99.4

[a] n.d. = Not detected.

96% of the sulfur content was removed. Different batch compositions were prepared by mixing the wastes with the addition of glass-cullet and sand in ratios so that the overall composition of the glass was in the glass forming region of the systems SiO_2–Fe_2O_3–(CaO, MgO) [13]. Fusion was carried out in corundum crucibles (99.8% Al_2O_3) by means of an electric furnace in the 1400–1450°C temperature range. Metal evaporation was shown to be negligible due to the oxidizing conditions and the high volume to surface ratio.

On a pilot plant scale, a 1 ton/day glass melter was employed. The vitrification pilot plant, projected for melting glass batches up to 1450°C and operated by LPG combustion has been described elsewhere [9]. Raw jarosite was employed and the sulfur recovered by the gaseous effluent treatment system of the plant. Dusts were recovered in the baghouse filters and reintroduced in the glass batch so that no other wastes were produced by the vitrification process. Dusts contained zinc and lead in variable amounts as a function of the batch composition, melting conditions and cold trap efficiency. XRF analyses of the glass showed that between 10 and 20% of zinc evaporated during melting and about 0.2% of sulfur was retained in the glass. Part of the melt was quenched in a stainless steal mold to obtain tiles and part in water to obtain glass frit.

Glass-ceramics were obtained by means of a one-step heat treatment of the glass at 720°C for 1.5 h [14]. The percentage crystalline phase formed was determined by quantitative XRD technique, using a Philips-1830 apparatus and CuK_α radiation, by comparing the areas of amorphous and crystalline phases in the XRD spectrum [15]. Transmission electron mycroscopy and

energy dispersion spectroscopy by means of a Jeol 2010 URP apparatus was employed to analyze the crystal grain dimensions and morphology as well as the distribution of the elements between the amorphous and crystalline phases [16].

In order to assess the leachability of the glass and glass-ceramic tiles, these were subjected to leaching tests in hot acid and basic media. A 5% NaOH, 5% HCl and 0.02 N Na_2CO_3 at constant temperature of 95°C were selected on the basis of literature data for comparison [17–19]. The EN 122 test for evaluation of ceramic tiles chemical resistance was considered inappropriate for product in which 50% of the composition is made of hazardous waste. In performing these experiments, the glass-ceramic tiles were cut into regular shapes, lapped and the surface area of each sample measured by Image Analyzer technique. The samples were immersed in each of the thermostated and magnetically agitated solutions and, at fixed time intervals, they were removed from the solution, washed, dried at 105°C, weighed, and then placed in the respective solutions again. The test-time was fixed at 24 h.

3. Results and discussion

3.1. TCLP test on vitrified wastes

The wastes are made of fine powder having the following specific surface: 4.36 m^2/g for EAFD wastes, 11.03 m^2/g for jarosite wastes. The wastes were subjected to US EPA TCLP tests to determine the leachability of the regulated heavy metals in the raw waste. The concentration of elements in the leachate of the EAFD wastes and jarosite were compared with the Italian and EPA limits. The results highlighted that in the EAFD a 23.0 mg/l chromium leachate concentration exceeds the limits of both regulations while a 0.5 mg/l zinc is at the limit allowed by the Italian regulations. In jarosite, zinc (15.5 mg/l) and lead (4.0 mg/l) concentrations largely exceed the Italian limits.

The glasses were labeled with a letter (D or J); letters indicate the main type of waste (D = EAFD and J = jarosite) and digits indicate the waste loading in the glass. In Table 2 the oxide weight percentage of the glass compositions are listed.

In order to assess the stabilization of the hazardous waste into an inert glass matrix, all glasses were subjected to US EPA TCLP test. As far as EAFD glasses are concerned, Fig. 1 shows the plots of aluminum, zinc, lead and silica concentrations in the leachate solutions as a function of EAFD percentage in the glass. It is observed that when there is more than 40% of EAFD in the glass batch, the glass silica network dissolves in the acetic acid solution and heavy metals are released in the solution at concentrations exceeding the regulatory limits.

Table 2
Calculated oxide composition of the glasses

Oxides	D25	D40	D45	D50	J30	J40	J50
	wt.%						
SiO_2	56.15	46.30	50.57	39.40	50.71	52.90	47.38
Al_2O_3	0.73	0.83	0.80	0.99	3.91	4.10	3.37
Fe_2O_3	5.89	8.80	10.62	11.87	19.60	23.90	28.33
Cr_2O_3	3.79	7.30	6.90	7.74	0.05	n.d.	n.d.[a]
P_2O_5	n.d	n.d.	n.d.	n.d.	0.28	n.d.	n.d.
MgO	5.30	6.10	5.30	6.70	2.15	1.80	1.76
MnO	1.32	1.92	2.23	2.46	0.11	n.d.	n.d.
CuO	n.d.	n.d.	n.d.	n.d.	0.10	0.10	0.15
CdO	n.d.	n.d.	n.d.	n.d.	0.01	0.01	0.01
CaO	11.71	13.44	11.48	14.64	8.50	5.20	4.70
ZnO	1.81	3.02	3.32	3.69	2.60	2.70	3.25
PbO	0.12	0.20	0.22	0.24	1.55	1.70	2.05
Na_2O	12.07	11.32	6.76	10.30	4.80	6.40	6.00
K_2O	0.57	0.73	0.84	0.96	1.00	1.10	0.90
Sums	99.46	99.96	99.04	98.99	95.37	99.91	97.90

[a] n.d. = Not detected.

This behavior can be explained by recalling that the chemical stability of a glass is influenced by the polymerization of the glass structure formed, which mainly depends on the Si/O ratio [20–22]. For comparison, in Table 3 the values of the Si/O ratio for several silicate structures are listed. It can be seen that when this ratio is less than 0.33, the network obtained is not polymerized and is made up of isolated tetrahedra. Stevels [20] defines the glasses with a ratio of less than 0.33 as "invert glass" that show low chemical resistance and properties independent from the percentage of SiO_2 in the glass composition. In the EAFD glasses investigated, the limit is 40% EAFD i.e. Si/O ratio at about 0.31. In D45 glass, part of the glass cullet was replaced with sand thus obtaining a Si/O ratio of about 0.34. This glass composition shows a chemical resistance higher than D40 and all the analyzed element concentrations are within the EPA Universal Treatment Standard regulatory limits for TCLP test.

The results in Table 4 highlighted that all the analyzed elements for D and J glasses, are within the USA and Italian regulatory limits with the exception of the D50 composition. For the last composition, the results of the test could be improved by substituting the glass cullet with sand thus achieving a Si/O ratio up to 0.32. However, the viscosity at the melting temperature would be increased.

3.2. Chemical durability of glasses and glass–ceramics

The possibility of the reutilization of glasses obtained by the vitrification of hazardous wastes is mainly driven by economical evaluations and normative aspects. In the case of EAFD from stainless steel production, due to the relative small quantity of production, the landfill
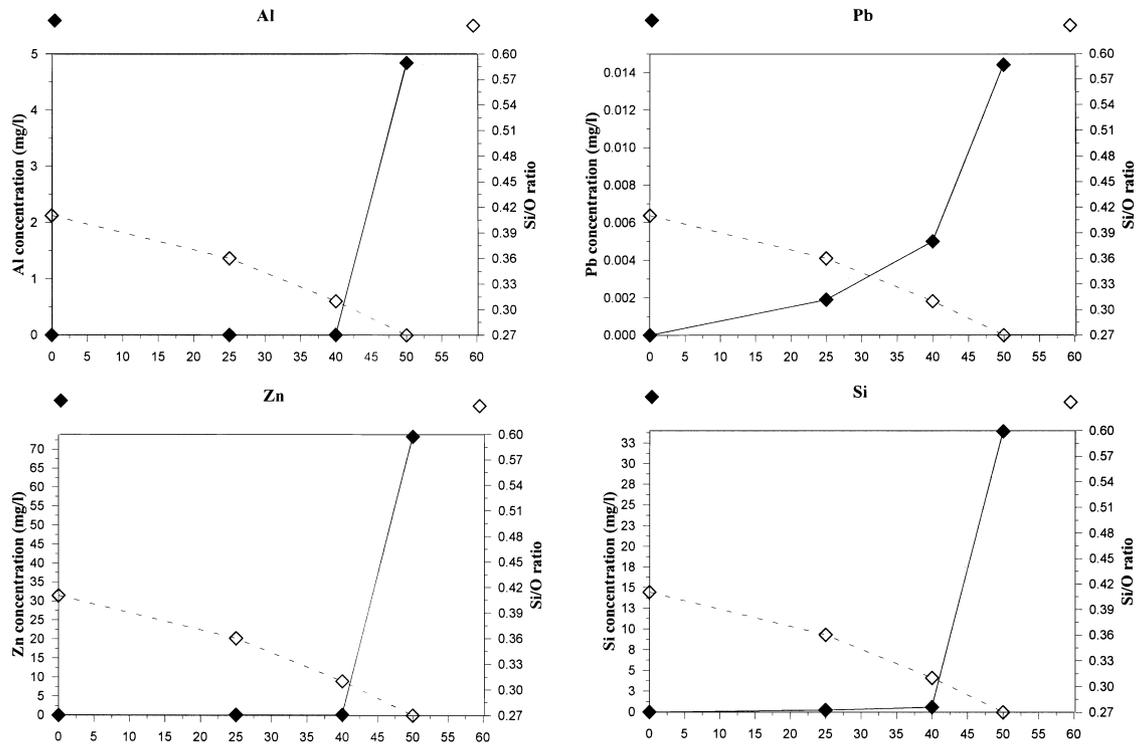
Fig. 1. Aluminum, lead, zinc and silicon concentrations in the TCLP leachates as a function of EAFD% in the glasses.

disposal of the glass frit as inert material was shown to be the most economical and environmentally sound way to manage EAFD. The jarosite (as well as goethite, the other zinc hydrometallurgy waste stream) [4] production of a zinc plant is about $130–160 \times 10^3$ ton/year and the

total European Union (EU) production varies between $600–700 \times 10^3$ ton/year. Since cement stabilization followed by landfill disposal of the cement-mix is not considered an efficient long term waste treatment, vitrification and re-utilization of the glass could represent an economically pursuable alternative.

One possibility of reutilization of the glasses has been the production of glass-ceramic paving tiles. J40 and J50 compositions were investigated because of the low viscosity and melting point and high waste content. Details about the glass characterization and crystallization behavior are reported elsewhere [23].

In Fig. 2, the XRD spectra of the J40 and J50 glass-ceramics are reported. It can be observed that pyroxene

Table 3
Ratio Si/O of silicate crystalline structures

Structure	Formula	Si/O
Three-dimensional	$[SiO_2]$	0.5
Two-dimensional	$[SiO_{5/2}]^{1-}$	0.4
Mono-dimensional	$[SiO_3]^{2-}$	0.333
Isolated Si tetrahedra	$[SiO_4]^{4-}$	0.25

Table 4
TCLP results leachate element concentrations and EPA and Italian limits

Metals	D25	D40	D45	D50	J30	J40	J50	Italian limits	U.S.E.P.A characteristics	U.S.E.P.A UTS limits[c]
Fe	0.004	0.405	0.080	0.630	< 0.001	0.020	0.030	2	nr[a]	nr
Cr	< 0.010	0.011	< 0.010	< 0.010	n.d.[b]	n.d.	n.d.	2	5	0.60
Zn	0.095	0.170	0.170	3.300	< 0.001	0.009	0.014	0.5	nr	4.30
Al	0.003	0.005	< 0.010	1.090	< 0.001	0.051	0.074	1	nr	nr
Mn	< 0.010	0.138	n.d.	n.d.	n.d.	n.d.	n.d.	2	nr	nr
Cd	n.d.	n.d.	n.d.	n.d.	n.d.	< 0.010	< 0.010	0.02	1	0.11
Cu	0.023	0.027	< 0.010	< 0.010	< 0.001	< 0.010	< 0.010	0.1	nr	nr
Pb	0.002	0.005	< 0.010	0.020	0.001	0.060	0.104	0.2	5	0.75

[a] nr = Not regulated.

[b] n.d. = Not detected.
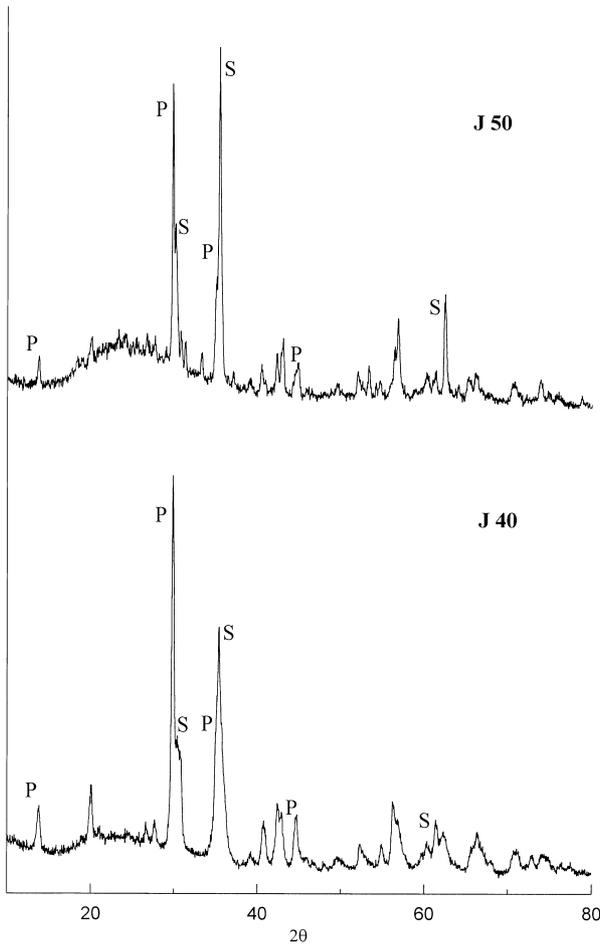
[c] Federal Register V63#100, 28 May 1998.

Fig. 2. X-Ray spectra of J40 and J50 glass-ceramics. S = spinel, P = pyroxene.

solid solution is the main crystal phase in the J40 glass-ceramic while magnetite (Fe_3O_4) and franklinite ($ZnFe_2O_4$) spinel is the main crystalline phase in the J50 glass-ceramic, the difference being the higher iron content of the latter composition. The percentage of crystal phase, calculated comparing the areas of amorphous and crystalline phases in the XRD spectrum resulted as being: 54% in J40 with a pyroxene/magnetite ratio of about 3 and 44% in J50 with a pyroxene/magnetite ratio of about 0.8, respectively; therefore, less Fe_2O_3 creates more pyroxene.

The chemical durability of J40 and J50 glasses and glass-ceramics was tested in Na_2CO_3, NaOH and HCl solutions at 95°C. In Figs. 3 and 4, the weight losses (in mg/cm^2) are reported as a function of time for J50 glass and glass-ceramic respectively. The interaction between the leaching medium, the surface of the glass, the crystalline phases, expressed as weight-loss as a function of time experimental data, were interpolated by means of a third degree polynomial function. The solid lines, in Figs. 3 and 4, are the interpolating mathematical functions. Similar curves were obtained for J40 glass and glass ceramic.

In explaining the experimental data two possible mechanisms, i.e. ion-exchange leaching and matrix dissolution, were considered to explain the release of cations from the glass structure in different aqueous solutions. The leaching mechanism involves the replacement of Na and K with a hydrogen-bearing ion from the solution leading to the formation of a leached layer, i.e. alkali depleted layer. Therefore, in neutral and acid media, the initial stage of the reactions is the diffusion
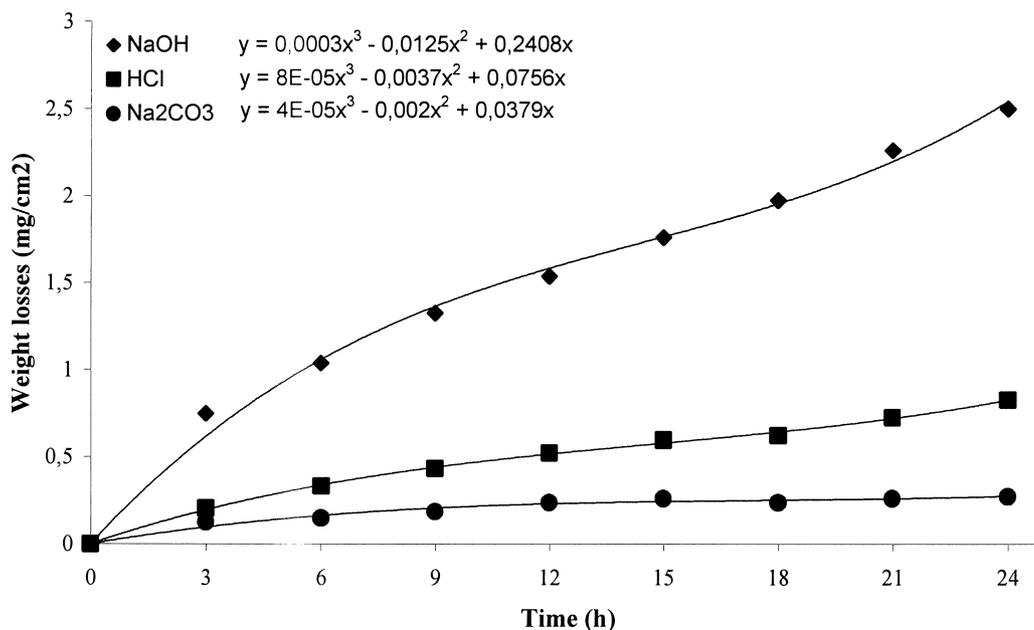

NaOH $y = 0{,}0003x^3 - 0{,}0125x^2 + 0{,}2408x$
HCl $y = 8E\text{-}05x^3 - 0{,}0037x^2 + 0{,}0756x$
Na2CO3 $y = 4E\text{-}05x^3 - 0{,}002x^2 + 0{,}0379x$

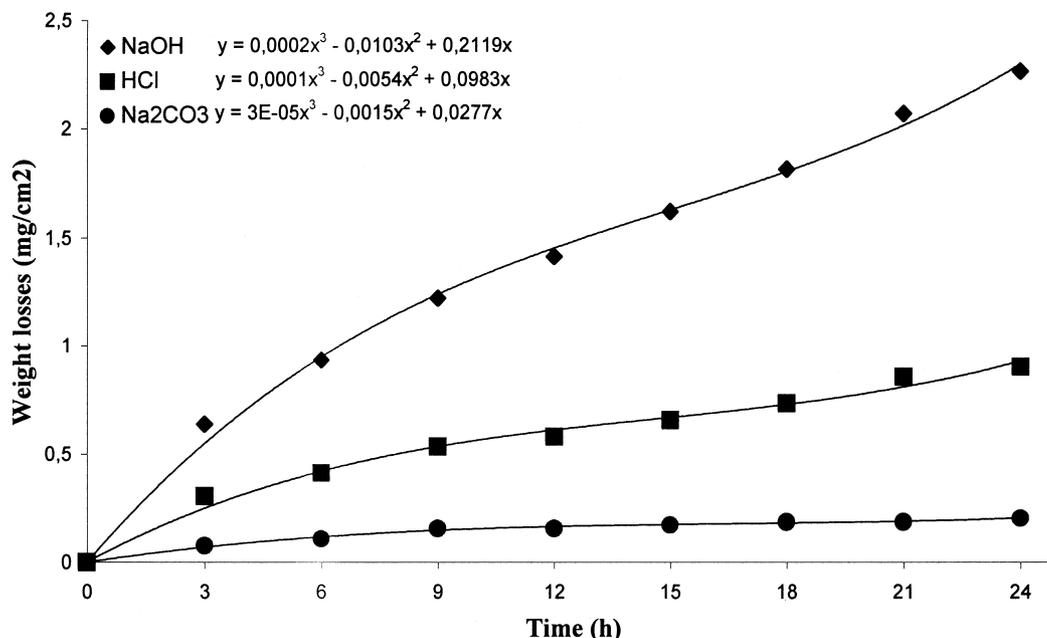Fig. 3. Weight losses vs time for J50 glass and glass-ceramic respectively in differentmedia at 95°C.

Fig. 4. Weight losses vs time for J50 glass and glass-ceramic respectively in differentmedia at 95°C.

of alkali ions through the glass network and across the leached layer into the solution. The diffusion rate of alkali ions gradually slows down as the leached layer becomes thicker and this behavior is represented by a parabolic type of relation [24]. The leaching of the alkali from the glass creates pathways that facilitate the subsequent removal of Pb^{2+}, Fe^{2+}, Zn^{2+} ions. The removal of these latter ions requires that two H^+ from the aqueous solution must replace each cation. The local rise of solution pH could facilitate the dissolution of the glass Si-tetrahedra.

The matrix dissolution reactions implies the dissolution of the Si-network by which the glass dissolves directly into the solution either after leaching or without leaching. This type of chemical reaction is characteristic of alkaline media and leads to a higher weight loss as a function of time, as highlighted by the NaOH plot shown in Figs. 3 and 4 for the glass and glass-ceramic respectively. The overall effect of the interaction between a glass structure and a solution is dictated by the rates at which the two mechanisms take place.

In the present study, due to the extreme experimental conditions (temperature and pH) the aggression on the surface is complex and the experimental third degree polynomial curves could be divided into three stages

Table 5
Weight losses of jarosite glasses and glass-ceramics for 24 h in NaOH, HCl and Na_2CO_3 at 95°C

Samples	J40 glass	J40 glass-ceramic	J50 glass	J50 glass-ceramic
	mg/(cm² day)			
HCl	0.471	0.215	0.827	0.901
NaOH	2.190	1.628	2.500	2.261
Na_2CO_3	0.373	0.103	0.274	0.203

Fig. 5. TEM picture of J50 glass-ceramic at 142,000 magnification.

corresponding to different mechanisms. In the first stage the leaching of the sample surface prevails and the ion removal proceeds with the square root of the time. In the second stage, the weight loss increases linearly by a matrix dissolution mechanism due to the removal of silica clusters from the surface. In the third stage, the surface of the sample becomes rough and cracked [25] and the specific surface of the glass and the matrix dissolution rate increase.

In Table 5 the weight losses of J40 and J50 glasses and relative glass-ceramics after 24 h contact with NaOH, HCl and Na_2CO_3 solutions are summarized. The data show that J40 glass-ceramic acquires a durability four times better than the parent glass because pyroxene is a stable crystal phase whose structure is made up of silica chains and Fe^{2+} and Ca^{2+} cations positioned between the chains.

In contrast, the durability of the J50 glass ceramic is similar to the parent glass and even lower in HCl. In Fig. 5 the TEM picture of a J50 glass-ceramic is shown in which the spinel crystals are evident in the glassy matrix. The distribution of elements, by EDS analysis, in the amorphous and crystal phases of the glass-ceramic (reported in Fig. 6) shows that Fe and Zn are mainly concentrated in the crystals, Si is uniformly distributed throughout the material, Na and Ca are concentrated in the remaining glass. Pb seems to be uniformly distributed, with a slight preference for the glassy phase. Therefore, the possible explanation of the reduced durability of the J50 glass ceramic compared to the parent glass could lie in the fact that the major crystal phase (magnetite type spinels) are soluble in HCl and this reduces the overall chemical resistance of the glass-ceramic. In Table 6, the concentrations of the
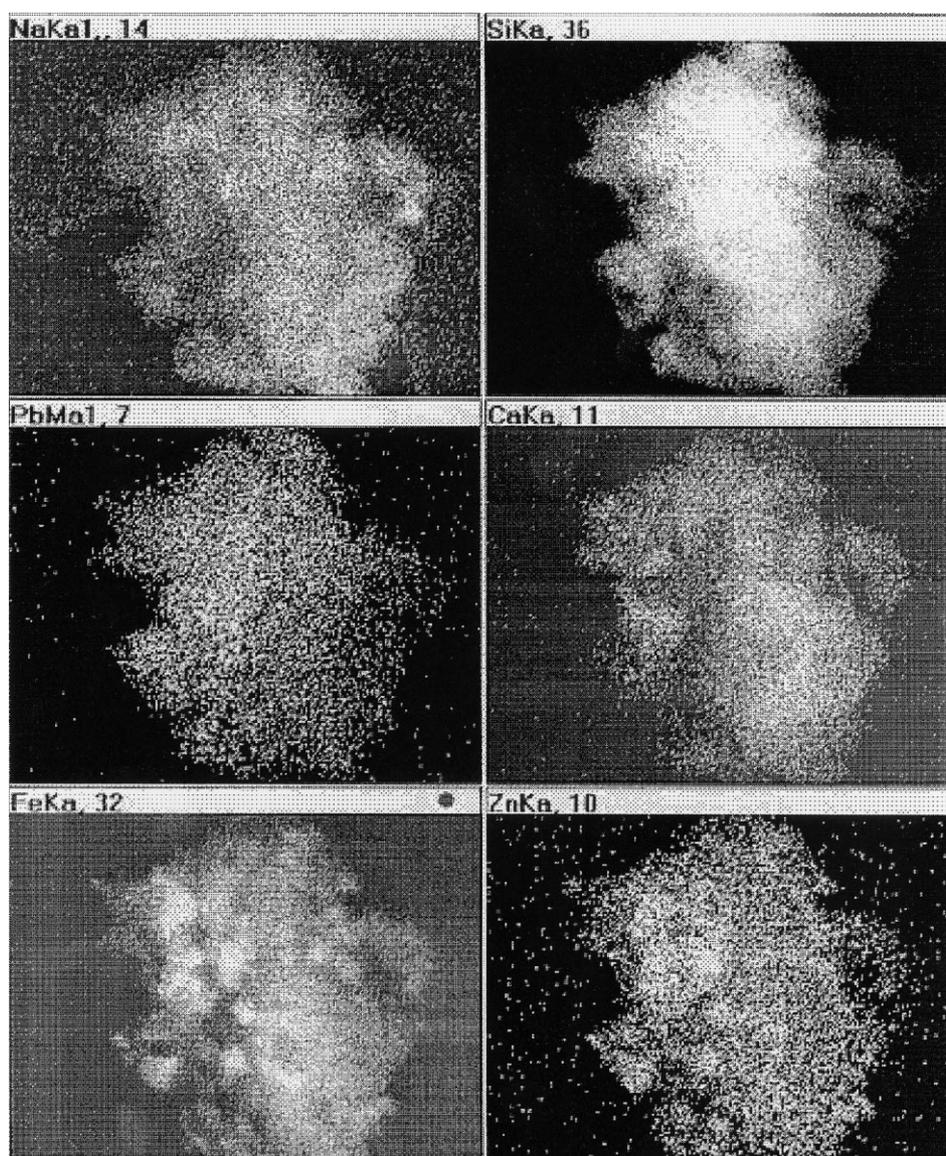

Fig. 6. EDS-map of major elements for J50 glass-ceramic.

Table 6
Leachate element concentrations of jarosite glass and glass-ceramic in NaOH, HCl and Na_2CO_3 at 95°C after 24 h

	J50 glass			J50 glass-ceramic		
	NaOH	HCl	Na_2CO_3	NaOH	HCl	Na_2CO_3
	mg/l					
Al	15.01	3.37	2.14	10.07	3.47	1.75
Cu	0.13	0.11	0.01	0.23	0.08	< 0.05
Pb	3.26	0.85	0.11	3.84	0.60	0.17
Zn	1.50	0.96	0.09	1.11	0.82	0.05
Fe	0.59	3.61	0.24	1.35	6.01	0.13

Table 7
Comparison of chemical durability of jarosite and commercial glasses and glass-ceramics based on weight loss measurements

Samples	NaOH 5% (6 h)	HCl 5% (24 h)	Na_2CO_3 0.02 N (6 h)
	mg/cm^2		
Soda-lime glasses [17]	0.80	0.05	1.50
Basalt glass [17]	1.10	0.90	0.10
Basalt glassceramic [17]	1.20	0.32	1.01
J40 glass	1.80	0.47	0.31
J40 glassceramic	1.31	0.21	0.08
J50 glass	1.04	0.83	0.15
J50 glass-ceramic	0.94	0.91	0.11

main elements in the leaching media are reported for the J50 glass and glass-ceramic. The results confirm the low chemical resistance of the magnetite based glass-ceramics in HCl.

Finally, for the sake of comparison, the chemical durability data for jarosite glasses and glass-ceramic together with a basalt glass and a soda-lime glass [17], are reported in Table 7. They show that the waste-made glass durability is comparable to that of commercial glasses.

4. Conclusions

The results of this study highlighted the possibility of incorporating as much as 45% of EAFD wastes and 50% of jarosite wastes into glassy products. The durability of the glass batch compositions can be estimated by the Si/O ratio. If the glass network is stable the hazardous components are stabilized in the amorphous structure and the glass easily passes the US and Italian regulatory limits for TCLP test.

The durability tests in alkali and acid at 95°C demonstrate that:

(a) a controlled crystallization treatment may improve the durability of glasses if the crystalline phase has a better chemical resistance than the parent glass in the contact solution. (b) the weight losses as a function of time for waste-made glasses and glass-ceramics are comparable to that of commercial products based on gross weight loss measurements.

The vitrification and recycling process of hazardous wastes is a combined process that could represent a suitable solution to the environmental impact of several industrial activities and open opportunities for giving value to the wastes.

References

[1] Compton KL, Bennert DM, Bickford DF. Regulatory issues in vitrification research: a case study of circuit board reclamation. In: Proceeding of the symposium on Environmental and waste management issues in the ceramic industry at the 95th annual meeting of the American Ceramic Society. Cincinnati: Mellinger G.B. American Ceramic Society, 1993. vol. 39: p. 3–12.

[2] Festa D, Gudagnino M. Chemical properties of glasses. Part I. Rivista della Stazione Sperimentale del Vetro 1995;5:189–93.

[3] Pelino M, Cantalini C, Sun HT. Glass-ceramic materials obtained by recycling of industrial wastes. In: Glass ceramic materials. Fundamentals and application. Series of monographs on materials science, engineering and technology. Italy: Mucchi Editore, 1997. p. 223–242.

[4] Pelino M, Cantalini C, Abbruzzese C, Plescia P. Treatment and recycling of goethite waste arising from the hydrometallurgy of zinc. Hydrometallurgy 1996;40:2087–94.

[5] Paul BQ, Douglas EC, Lawrence DM. Application of slag technology to recycling of solid wastes. Paper presented at the AIME SME annual meeting, Denver, Colorado, USA, 25–28 February 1991.

[6] Van der Sloot HA, Heasman L. Quevauviller Ph. Harmonization of leaching/extraction tests. Amsterdam: Elsevier, 1997.

[7] Pelino M. Recycling of Jarosite waste in the production of glass and glass-ceramics materials. Interceram 1998;47(1):22–6.

[8] Aota J, Morison L, Mikhail SA, Chen TT, Liang DT. Immobilisation of hazardous elements in EAF dust by vitrification process. Waste Processing and Recycling :335-49.

[9] Pelino M. Recycling of zinc hydrometallurgy wastes in glass and glass-ceramic materials. Waste Management 2000;20:561–8.

[10] US Environmental Protection Agency, Toxicity Characteristic Leaching Procedure (TCLP), 40 CFR 268, Appendix I, US Federal Register.

[11] US Federal Register 28 May 1998; 100 (63): 28748–9.

[12] G.U. 13 Settembre 1984, n.253. De. C. I. 27/07/84 art.5 D.P.R. 10 Settembre 1982, n. 915.

[13] Chick LA, Swanson JL, Goldman DS. Nuclear waste glass composition limitation, Fuel reprocessing and waste management. Paper presented at the American Nuclear Society International Topical Meeting, August 1984.

[14] Karamanov A, Pelino M. Evaluation of the degree of crystallization in glass-ceramics by density measurements. Journal of European Ceramic Society 1999;19(5):649–54.

[15] Kim H, Rawligs R, Rogers P. Quantitative determination of crystal and amorphous phases in glass-ceramics by X-ray diffraction analysis. British Ceramic Transaction Journal 1989;88:21–5.

[16] Pelino M, Cantalini C, Tazzi M, Ullu F. Re-utilization of zinc-hydrometallurgy wastes and granite mud for production of glass-ceramic materials. Proceedings of XX International Mineral Processing Congress. Aechen, Germany: Heinz Hoberg and Harro von Blottnitz, 1997; 5: 597–605.

[17] Beall GH, Rittler HL. Basalt glass-ceramics. American Ceramic Society Bulletin 1976;55(6):579–82.

[18] Tanaka Yoshimi, et al. Aichi-Ken Kogyo Shidosho Hokoku 1978;14:65–70.

[19] Li JP, Quian WJ, Li XT. Wuji Cailiao Xuebao 1992;7(2):251.

[20] Appen AA. The chemistry of glasses. Himiq: Leningrad, 1974.

[21] McMillan PW. Glass ceramics. London: Academic Press, 1979.

[22] Pegg IL, Saad EE, Feng X, Adiga RB, Freeborn WP, Macedo PB. Product models for the vitrification of waste valley high-level wastes. Material Research Society Symposium Proceedings. Berlin: Werner Lutze, Rodney C. Ewing, 1989; 127: 215–22.

[23] Karamanov A, Cantalini C, Pelino M, Hreglich A. Kinetic of phase formation in jarosite glass-ceramic. Journal of European Ceramic Society 1999;19:527–33.

[24] Ahmed AA, Abbas AF, Youssof IM. Attack of lead crystal glass by aqueous solution of ethyl and methyl alcohol. Proceedings of XVII International Congress on Glass. Beijing: Chinese Ceramic Society, 1995; 3: 239–44.

[25] Zwicky HU, Grambow B, Magrabi C, Aerne ET, Bradley R, Barnes B. et al. Corrosion behaviour of British Magnox waste glass in pure water. Material Research Society Symposium Proceedings. Berlin: Werner Lutze, Rodney C. Ewing, 1989; 127: 129–36.