

INERTIZAREA ÎN MATRICE VITROASE A AMESTECURILOR REACTIVE EPUIZATE PROVENITE DIN ÎNDEPĂRTAREA Cr(VI) CU Fe⁰ ÎN EXPERIMENTE PE COLOANĂ

INERTIZATION IN VITREOUS MATRIX OF EXHAUSTED REACTIVE MIXTURES RESULTED FROM THE REMOVAL OF Cr(VI) WITH Fe⁰ IN CONTINUOUS-FLOW SYSTEM

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The present paper proposes an innovative way to Harness the exhausted reactive mixtures resulted from the removal of Cr(VI) with Fe⁰ in continuous-flow system (column experiments), by vitrification using two types of common waste glasses: window panes and cathode ray tubes (CRT). The melting of the two types of wastes (glass and the reactive mixture containing chromium), conducted in economically advantageous conditions at 1000°C for 180 minutes generates very viscous melts that were difficult to process. Therefore it was considered necessary to use borax as a flux in order to improve the fluidity of the melted glasses. The RX diffraction was used to confirm the vitreous character of the samples, validating the purposed melting conditions. The hydrolytically stability, determined according to the ISO 719/1985, classify all the investigated glasses in the most stable class of glasses HGB1. The chemical stability and chromium and iron ions leachability were determined and American Extraction Procedure Toxicity Test respectively. The chemical stability of the glasses expressed by measuring their dissolution rate show two different behaviors: one for acidic and neutral mediums and another for alkaline medium, corresponding to two different attack mechanisms on the glass matrix. At pH = 5.5 and pH = 7.0 the glasses dissolution rates are very low, between 0.013-0.059 µg/h, while at pH = 8.5 the values rise to 0.143-0.492 µg/h. The amounts of chromium and iron ions leached from all the investigated glasses regardless the environment's pH and the considered time are very low, between 0-0.0104 % of the total chromium and between 0-0.0042 % of the total iron brought by the exhausted reactive mixtures. The obtained results confirm the viability of the suggested solution for immobilizing the exhausted reactive mixtures containing chromium together with common waste glasses in order to obtain glasses having very high chemical stability with multiple economic advantages.

Lucrarea de față propune o metodă inovativă de valorificare a amestecurilor reactive epuizate provenite din îndepărtarea Cr(VI) cu Fe⁰ în experimente pe coloană prin vitrificare folosind două tipuri de deșeuri de sticlă comune: geam și tub cinescop (CRT). Topirea celor două tipuri de deșeuri (amestec reactiv epuizat conținând crom și respectiv deșeu de sticlă) în condiții economic avantajoase la 1000°C timp de 180 minute duce la obținerea unor topituri foarte vâscoase, greu de procesat. De aceea s-a considerat necesară folosirea boraxului datorită efectului său fondant pentru creșterea fluidității topiturilor. Difractometria RX a fost utilizată cu scopul de a confirma caracterul vitros al probelor investigate, validând alegerea condițiilor de sinteză. Stabilitatea hidrolitică, măsurată conform ISO 719/1985, califică toate probele studiate în cea mai stabilă clasă de sticle, HGB1. Stabilitatea chimică și respectiv pierderile de ioni de crom și fier în urma agresiunii chimice au fost determinate în conformitate cu American Extraction Procedure Toxicity Test. Stabilitatea chimică, exprimată prin gradul de solubilizare a sticlei, prezintă comportări diferite în mediu acid și neutru și respectiv în mediu bazic datorită mecanismelor diferite de atac chimic asupra rețelei vitroase. La pH = 5,5 și respectiv pH = 7,0 gradul de solubilizare a sticlelor studiate este foarte redusă (0,013-0,059 µg/h), valorile crescând la 0,143-0,492 µg/h în cazul agresiunii alcaline (pH = 8,5). Cantitatea de ioni de crom și fier solubilizată din matricea vitroasă în urma atacului chimic este foarte redusă, cuprinsă între 0-0,0042 % și respectiv 0-0,0042 % din cantitatea totală de crom și fier adusă de amestecul reactiv epuizat. Rezultatele obținute confirmă viabilitatea soluției propuse pentru imobilizarea amestecurilor reactive epuizate conținând crom alături de cele două deșeuri de sticlă sub forma unor mase vitroase cu rezistențe chimice foarte ridicate în condiții economic avantajoase.

Keywords: wastes vitrification, waste glasses, glass recycling, chromium wastes.

1. Introduction

The effect of the industrial production upon the environment is a well-known concern underlie by the latterly rapid alteration of the ecosystem. The pollution with heavy metals resulted from mining, smelting or different other

industries affects the health of aquatic and terrestrial organisms [1] Chromium is a major heavy metal pollutant which is released mainly from industrial processes: tanning, electroplating, dyeing, metallurgy, wood preserving etc. [2] Chromium can exist in different oxidation states ranging from (-IV) to (+VI), Cr(III)

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and Cr(IV) being the two thermodynamically stable states having a major environmental impact [3]. Trivalent chromium, the naturally occurring element, play an essential role in the protein, lipid and glucose metabolism of mammals [4]. The hexavalent chromium is mainly a result of human activities. In contrast to Cr(III), Cr(VI) is highly toxic to humans being regarded by the Agency for Toxic Substances and Diseases Registry as a Group A human Carcinogen due to its high toxicity and great mutagenicity [5-7]. A large number of methods are mentioned in literature for the abatement of Cr(VI) aqueous pollution: treatment with metallic iron (Fe⁰) [8], electrochemical removal [9], electrocoagulation [10], membrane separation, chemical precipitation, reverse osmosis, ion exchange [3], adsorption [11 - 13] reduction using organic gels [14] etc. However, in the last three decades, considerable volume of research has been carried out to investigate the use of Fe⁰ for the removal of a wide range of pollutants from contaminated waters, including heavy metals [15]. One of the most important questions which rise in Fe⁰-based treatment technology, like in many other water treatment technologies, is what to do with the wastes resulted from the treatment process? This paper proposes an innovative way to harness the exhausted reactive mixtures resulted from the removal of Cr(VI) with Fe⁰ in continuous-flow system (column experiments), by vitrification using waste glasses. The column filling used for the removal of Cr(VI) was composed of Fe⁰ and sand, in accord with recent theoretical studies which indicated that mixing Fe⁰ with non-expansive materials will sustain the Fe⁰ - systems efficiency by delaying the cementation of Fe(OH)_n colloids inside the Fe⁰ filter [16].

Glass recycling have economical and ecological advantages by saving important quantities of raw materials, conserving the natural resources and decreasing the energy consumption for the melting process resulting less CO₂ emissions [17]. The main drawback of the recycling process is associated with the expenses for the separation phase of the glass scraps from other materials such as ceramics or metals contaminants [18], especially for the cathode ray tubes (CRT) wastes, due to the large amounts of heavy metals [19, 20]. The main advantages of the proposed vitrification solution: immobilization of heavy metals, destroying the residual organics and reducing the waste volume

[21] can counterbalance the economic disadvantages by developing the obtained glasses as new marketable products: bulk glasses [22, 23], glazes [24], foam glasses [25, 26], glass materials for heat transfer processes [27], fillers in bubble columns for polymerization or esterification processes [28, 29], packing materials in fractionation columns [30] etc.

2. Experimental Procedure

2.1. Sample preparation

The immobilization of the exhausted reactive mixtures was realized by vitrification together with two types of common waste glasses: window panes and cathode ray tubes (CRT). The compositions of the precursor waste glasses, determined by X ray fluorescence using a Niton XL 3 analyzer, are presented in Table 1.

Table 1
Oxidic composition of the recycled glasses used as precursors (% weight) / *Compoziția oxidică a deșeurilor de sticlă folosite ca precursori (% greutate)*

Oxide	Window pane	CRT
SiO ₂	71.86	60.92
Na ₂ O	13.13	8.96
K ₂ O	0.02	7.44
CaO	9.23	0.67
MgO	5.64	0.14
BaO	-	10.80
PbO	-	8.85
Al ₂ O ₃	0.08	2.07
Fe ₂ O ₃	0.04	0.15

The two waste glasses were powdered by wet grinding using a Pulverisette laboratory mill then dried and sieved so that the granulometric fraction under 100 μm was kept in order to be used as glass precursor.

The composition of the exhausted reactive mixture and the corresponding retained chromium from each column is presented in the Table 2.

The exhausted reactive mixtures were dried at 105°C for 24 hours and then mixed together with the waste glass precursors.

The melting process was conducted at 1000°C for 180 minutes using a Nabertherm HTC08/16 electric furnace. The vitrification of the two types of wastes (glass and the reactive mixture containing chromium) in this economically advantageous conditions led to very viscous melts that were

Table 2
The composition of the exhausted reactive mixture and the corresponding retained chromium from each column [g]. / *Compoziția amestecului reactiv epuizat și cantitatea de crom reținută pe fiecare coloană [g].*

Column	Fe ⁰ particles size 1-2 mm	Sand particles size 0.5-1.25 mm	Sand particles size 1.25-2 mm	Retained chromium
1	40	58.4	7.4	18.3·10 ⁻³
2	80	43.8	7.4	26.3·10 ⁻³
3	100	36.5	7.4	33.6·10 ⁻³
4	120	29.2	7.4	44.6·10 ⁻³
5	160	14.6	7.4	56.1·10 ⁻³

Table 3
The composition of the studied glasses [weight ratio] / *Compoziția sticlelor sintetizate [raport gravimetric].*

Sample	Column	Exhausted reactive mixture	Glass waste		Borax
			Window pane	CRT	
I.1G	1	1	1	-	2
I.2G	2	1	1	-	2
I.3G	3	1	1	-	2
I.4G	4	1	1	-	2
I.5G	5	1	1	-	2
I.1C	1	1	-	1	2
I.2C	2	1	-	1	2
I.3C	3	1	-	1	2
I.4C	4	1	-	1	2
I.5C	5	1	-	1	2

difficult to process. Therefore it was considered necessary to use borax as a flux in order to improve the fluidity of the melted glasses. The optimal ratio exhausted reactive mixture-waste glasses-borax after several preliminary tests was considered 1:1:2, the resulting compositions for the studied glasses being presented in Table 3.

The melts were press-quenched between two stainless steel blocks and annealed to remove stress. The obtained rectangular samples having around 10x25x4 mm were used for further investigations.

2.2. Characterization methods

The phase composition of the studied glass samples was determined using a Rigaku Ultima 4 diffractometer.

The hydrolytic stability of the glass samples was determined according to ISO 719-1985, using 2 grams of product, having particles size less than 500 μm, kept for 60 min in 50 mL de-ionized water at 98°C. A volume of 25 mL of the obtained solution was titrated against 0.01 mol/l HCl solution. The volume of HCl needed for neutralization is recorded in order to express the equivalent R2O extracted and the corresponding stability class.

The chemical stability of the glasses was investigated by measuring the dissolution rate of the samples immersed in three extraction mediums having pH 5.5, 7.0 and 8.5 respectively for 28 days. The buffer solutions from 5.5, 7.0 and 8.5 pH were prepared by taking 2.5% v/v glacial acetic acid in water and by adding concentrated ammonia solution until the desired pH value was reached. The pH of the solution was measured using a digital pH meter (Type E-500). The volume of the utilized solutions of 100 mL was maintained constant during the considered determination time at a constant temperature of 20 ± 2°C. After 28 days the samples were dried for 6 hours at 110°C until they reach constant mass. The dissolution rate of the glass samples is expressed as weight loss in time as it is presented by the following

equation:

$$Dr = \frac{\Delta m}{t} = \frac{m_i - m_f}{t} \quad [\mu\text{g/h}]$$

where: m_i is the initial sample mass, m_f the final sample mass and t represents the considered experimental time of 28 days.

The chromium and iron immobilization capacity of the studied glasses was investigated by measuring the chromium ions extraction using leaching tests performed according to the American Extraction Procedure Toxicity Test [25]. Three extraction mediums having pH 5.5, 7.0 and 8.5 respectively were used, analysis being performed after 1, 14 and 28 days respectively. Two grams of each sample were taken and shaken with 250 ml of ammonia-acetate buffer solution for different time periods at a constant temperature of 20 ± 2°C. The chromium concentration in the extraction mediums was measured using a Bruker Aurora M90 Inductively Coupled Plasma Mass Spectrometer.

3. Results and Discussion

3.1. Phase composition

The vitreous character of the glass structure was tested for two glass samples containing the highest amount of sand (I.1G and I.1C), knowing that the sand has the slowest rate of incorporation into the glass matrix. The obtained diffraction spectra are presented in Figure 1.

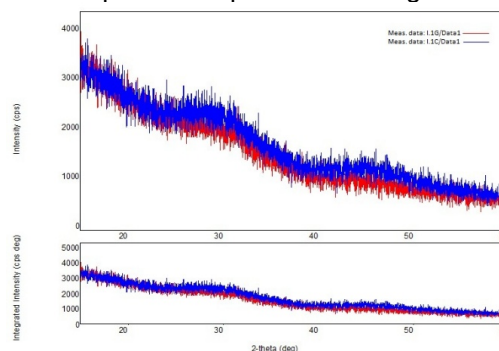


Fig.1 - Diffraction spectra of the samples I.1G and I.1C / Spectrele de difracție ale probelor I.1G și I.1C.

The diffuse pattern of both spectra confirm the vitreous character of the samples, validating the purposed melting conditions.

3.2. Glasses hydrolytic stability

The resistance of the studied glasses towards water aggression was analyzed according with ISO 719-1985, the results being presented in Table 4.

Table 4

The hydrolytic stability and the corresponding hydrolytic class of the investigated glasses / *Stabilitatea hidrolitică și clasa de stabilitate corespunzătoare pentru sticlele studiate*

Sample	Alkali oxide leached [□g/g glass]	Stability class
I.1G	15.45	HGB1
I.2G	18.6	HGB1
I.3G	22.25	HGB1
I.4G	25.8	HGB1
I.5G	30.55	HGB1
I.1C	13.95	HGB1
I.2C	16.05	HGB1
I.3C	20.15	HGB1
I.4C	23.25	HGB1
I.5C	27.65	HGB1

All the studied glasses belongs to the most stable class of glasses HGB1. A major influence upon the hydrolytic stability of the synthesized glasses is that of the SiO₂ amount brought as sand within the exhausted reactive mixture as it is presented in Figure 2.

All the studied glasses show a quasilinear dependence of their hydrolytic stability upon the quantity of sand brought with the exhausted reactive mixture used as precursor. The explanation of this behavior is based on the stabilization effect of SiO₂ upon the vitreous matrix knowing that this oxide is a glass network former.

3.3. Glasses chemical stability

The values of the dissolution rate for the studied samples after 28 days are summarized in the Figure 3.

Two different behaviors can be observed, one for acidic and neutral mediums and another for alkaline medium. At pH = 5.5 and pH = 7.0 the glasses dissolution rates are very low, between 0.013-0.059 μg/h. This can be explain by the leaching of the alkali oxides from the glass surface in acidic and neutral mediums that lead to an enrichment in SiO₂ at the surface level. Consequently it creates a passivation effect that causes the lower dissolution rates values.

The alkaline environment aggression leads to dissolution rate values higher than in the previous case, between 0.143-0.492 μg/h because of the absence of the passive layer [31 - 33].

3.4 Chromium and iron ions immobilization in glasses

The chromium ions leached from the studied glasses in the three chemical aggressive environments for the three considered periods of time, expressed as percent chromium measured in the lixiviate from the total ion amount in the glass are illustrated in the Figure 4.

The amount of chromium ions leached from

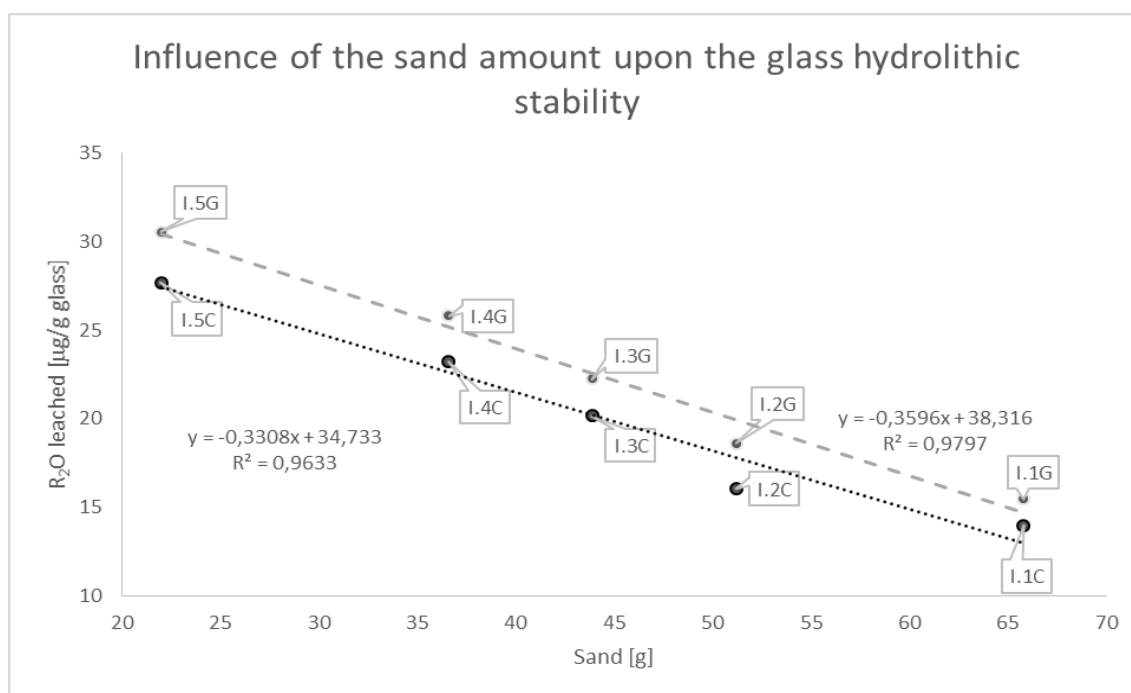


Fig.2 - The influence of the sand amount upon the hydrolytic stability of the studied glasses / *Influența cantității de nisip asupra stabilității hidrolitice a sticlelor studiate.*

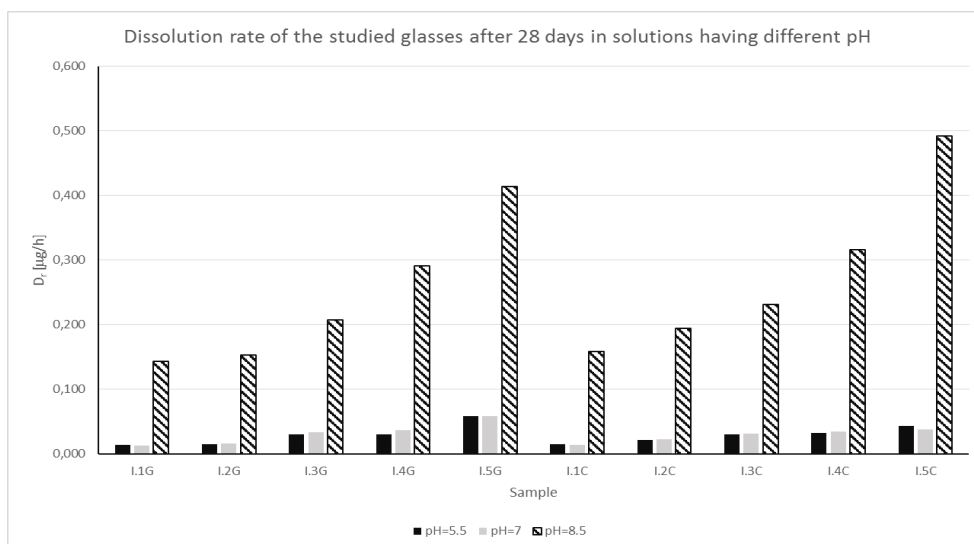


Fig.3 - Dissolution rates of the studied glasses / Rata de solubilizare a sticlelor studiate.

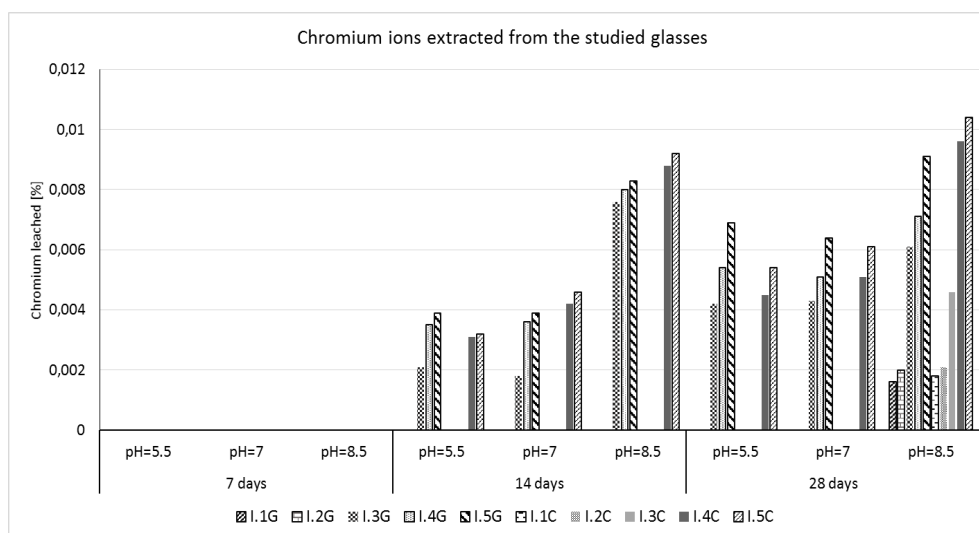


Fig.4 - Chromium ions losses from the studied glasses / Pierderile de ioni de crom din probele studiate.



Fig.5 - Iron ions losses from the studied glasses / Pierderile de ioni de fier din probele studiate.

all the investigated glasses regardless the environment's pH and the considered time is very low, between 0-0.0104 % of the total chromium brought by the exhausted reactive mixtures.

All glasses show a very good immobilization after 7 days with no discernable losses of chromium, regardless of the environment's pH. At the 14 days term, the samples I.1G and I.2.G containing window panes waste glass and I.1C-I.3C containing CRT waste glass show no chromium losses. With increasing the amount of exhausted reactive mixture amount more chromium ions are leached since the mixture is the ion bearing vector. The corresponding decrease of the SiO₂ amount generates a lower encapsulation of the chromium ions in the glass network. The CRT glass generates at the synthesizing temperature a more fluid melt comparing to window pane glass and therefore increase the chromium immobilization.

All the obtained glasses show higher chromium losses in alkaline environment compared to acid and neutral environments, due to the passivation effect discussed in the previous chapter.

The iron ions losses, expressed as percent iron measured in the lixivate from the total ion amount in the glass for all the investigated samples are illustrated in the Figure 5.

The amount of iron ions leached from all the investigated glasses regardless the environment's pH and the considered time is very low, between 0-0.0042 % of the total iron brought by the exhausted reactive mixtures.

At the 7 and 14 days terms, the samples I.1G and I.2.G containing window panes waste glass and I.1C and I.2C containing CRT waste glass show no chromium losses regardless of the environment's pH. Only after 28 days these samples show very low iron losses in the alkaline medium, between 0.0010-0.0023 %.

The samples I.3G and I.3.C generate iron losses only after 14 days while the samples I.4G and I.5.G containing window panes waste glass and I.4C and I.5C containing CRT waste glass shows very low iron ions losses after 7 days regardless of the environment's pH.

For all the glasses, increasing the amount of iron and decreasing the amount of SiO₂ leads to a lesser encapsulation of the iron ions in the glass network and consequently generates a lower immobilization.

Similarly to the previous sets of samples, all glasses are more sensitive to the alkaline environment as it was explained before.

4. Conclusions

The focus of this research is to immobilize the chromium and iron ions retained on exhausted reactive mixtures resulted from the removal of

Cr(VI) with Fe⁰ by vitrification together with two common waste glasses: window panes and cathode ray tubes.

For economic reasons regarding the melting process, the use of borax as a flux was necessary. Different ratios exhausted reactive mixture- waste glasses -borax was tested, the optimal value for the ration being established at 1-1-2.

The hydrolytic stability of the studied glasses was measured. All the glasses belong to HGB1 stability class, the best one according to ISO 719-1985. A quasilinear dependence of the hydrolytic stability upon the amount of SiO₂ brought with the exhausted reactive mixture was established.

The chemical stability of the glass samples was established by measuring the dissolution rate after 28 days in mediums having different pH. The low values recorded confirm the very good stability conferred by the glass matrix. The glasses present a high chemical stability towards the acidic and neutral environments, the recorded losses being between 0.013-0.059 μg/h. All the studied samples are more sensitive to the alkaline medium, the corresponding dissolution rates ranged from 0.143-0.492 μg/h. due to the absence of the passivation layer.

The amount of chromium ions leached in the three aggressive environments after 7, 14 and 28 days according to the American Extraction Procedure Toxicity Test was very low, ranging from 0-0.0104 % of the total chromium brought by the exhausted reactive mixtures.

The amount of iron ions leached from all the investigated glasses regardless the environment's pH and the considered time is very low, between 0-0.0042 % of the total iron brought by the exhausted reactive mixtures.

The higher amount of losses of both chromium and iron ions are generated by the alkaline environment that leach SiO₂ and B₂O₃, both network former oxides, generating a continuous destabilizing attack on the vitreous matrix.

The CRT glass generates at the synthesizing temperature more fluid melts comparing to window pane glass and therefore increase the chromium and iron ions immobilization.

The obtained results confirm the viability of the suggested solution for immobilizing chromium contained in the exhausted reactive mixtures together with common waste glasses in order to obtain glasses having very high chemical stability with multiple economic advantages.

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