



NOI MATRICI VITROCERAMICE PENTRU IMOBILIZAREA UNOR DEȘEURI DE CROM

NEW GLASS-CERAMIC MATRIX FOR THE CHROMIUM WASTES IMMOBILIZATION

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The present paper proposes an alternative recycling method for two common glass wastes: window panes and funnel CRT glass, together with Bojidar kaolin as new glass matrix for chromium waste immobilization. The kaolin was previously used as adsorption support for the soluble Cr^{6+} waste from residual waters. Three different weight ratios glass waste:kaolin (60:40, 70:30 and 80:20) were used for the glass-ceramic synthesis. The raw materials as powders (granulometric fraction under 0.1 mm) were mixed together and then pressed into cylinders having the diameter and height around 35 mm. The heat treatment was conducted at three different temperatures 900, 1000 and 1100°C respectively for 60 minutes. The compactness of the obtained glass-ceramic samples was characterized using their apparent porosity and apparent density. The obtained values range from 0 to 22.93% for the apparent porosity and from 1.93 to 2.25 g/cm³ for the apparent density respectively, depending on the glass waste type and heat treatment temperature. The microporous structure was illustrated using SEM. The phase composition of the studied samples was established by RX diffraction, cristobalite, diopside, tridymite and wollastonite being the main crystalline phases. The compressive strength of the obtained glass-ceramic products was measured and correlated with the heat treatment temperature. The highest values range from 136 to 175 N/mm², corresponding to the samples obtained at 1000°C. The hydrolytically stability and chromium leachability were determined according to the ISO 719/1985 and American Extraction Procedure Toxicity Test respectively. All the studied samples completely immobilized the chromium ions in the glass-ceramic matrix so that no chromium extraction was recorded for the acid and neutral mediums. The glass ceramic matrix have a low sensibility to the alkaline medium, the total chromium extracted being less than 0.014% after 28 days. The obtained results suggest that the immobilization of the chromium wastes adsorbed on kaolin in glass ceramic matrix is a viable solution having multiple economic advantages.

Lucrarea de față propune o alternativă de reciclare a două deșeuri de sticlă comune: geam și partea conică a tubului cinescop, împreună cu caolinul de Bojidar sub forma unei matrici vitroceramice pentru fixarea unor deșeuri de crom. Caolinul a fost în prealabil utilizat ca mediu adsorbant pentru reținerea Cr^{6+} solubil dintr-o apă reziduală uzată. Pentru sinteza probelor au fost folosite trei rapoarte gravimetrice deșeu de sticlă:caolin (60:40, 70:30 și respectiv 80:20). Materiile prime pulverulente (fracțiunea granulometrică sub 0,1 mm) au fost omogenizate împreună și apoi presate sub formă cilindrică având diametrul și înălțimea de cca. 35 mm. Tratatul termic s-a realizat la trei temperaturi diferite (900, 1000 și 1100°C), timp de 60 minute. Compactitatea probelor obținute a fost caracterizată pe baza porozității aparente și respectiv a densității aparente. Acestea variază între 0-22,93% în cazul porozității aparente și respectiv între 1.93-2.25 g/cm³ pentru densitatea aparentă, în funcție de tipul deșeurii de sticlă utilizat și de temperatura de tratament termic. Structura microporoasă a probelor a fost ilustrată folosind imagini SEM. Compoziția fazală a materialelor obținute, stabilită prin difracție RX a pus în evidență ca faze cristaline principale cristobalitul, diopsidul, tridimitul și wollastonitul. Rezistența la compresiune a fost corelată cu temperatura de sinteză, cele mai bune valori, între 136-175 N/mm², corespunzând probelor obținute la 1000°C. Stabilitatea hidrolitică și respectiv capacitatea de imobilizare a cromului au fost determinate pe baza ISO 719/1985 și respectiv American Extraction Procedure Toxicity Test. Toate probele sintetizate au imobilizat complet ionii de crom astfel că nu au fost identificate pierderi de crom, în mediile acid și neutru. Matricile vitroceramice sintetizate prezintă o sensibilitate redusă față de agresiunea mediului bazic, pierderile de crom prin solubilizare fiind mai mici de 0,014% după 28 de zile. Rezultatele obținute sugerează că imobilizarea unor deșeuri de crom adsorbite pe caolin sub forma unor matrici ceramic-vitroase reprezintă o soluție viabilă cu multiple avantaje economice.

Keywords: glass wastes, glass recycling, chromium wastes, glass ceramic

1. Introduction

The preoccupation and concern for the environment, greatly affected by the recent industrial development, resulted in the adoption of systematic treatment processes for solid, liquid and gaseous waste generated by the industrial production [1]. The recycling of glass wastes become a very attractive

concept in the last decades due to the multiple economic and ecological advantages [2]. Using recycled glass in the production process saves important quantities of raw materials, conserving the natural resources and also decreases the energy consumption for the melting process, so that less CO₂ is emitted into the atmosphere. Also, in the landfilling sites the waste volume is reduced,

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allowing as much domestic waste as possible to be recycled [3]. Although the glass recycling has as major drawback the expensive separation process of the glass scraps from other materials such as ceramics or metals contaminants [4]. The recycling process is even more complicated for the cathode ray tubes (CRT) wastes, knowing that these glasses contain large amounts of heavy metals [5, 6].

Chromium is a common pollutant generated from many industrial processes: tanneries, electroplating, textile, dyeing, and metal finishing etc. [7] The oxidation states having a major environmental impact are Cr(III) and Cr(VI). Trivalent chromium is an essential ion, involved in the protein, lipid and glucose metabolism of mammals [8]. The hexavalent chromium has a severe toxicity acting as carcinogens, teratogens and mutagens in biological systems, is classified by the Agency for Toxic Substances and Diseases Registry as the top sixteenth hazardous substance [9, 10].

The adsorption of chromium(VI) from residual waters using clays is a matter of great interest in the recent years [11 -14]. This paper propose a new way to transform the chromium rich clay into a non-hazardous product by vitrification having the advantages of reducing the waste volume, destroying the residual organics and immobilizing heavy metals [15]. The main economic disadvantages: energy and capital intensive, may be counterbalanced by the further conversion of the glasses obtained from wastes into marketable products: glasses [16, 17], glazes [18], glass foams [19, 20], glass-ceramics [21, 22], or glass fibres [23].

2. Experimental Procedure

2.1. Sample preparation

The glass wastes used in this paper were window panes and funnel CRT glass. The compositions of the precursor glasses, determined by X ray fluorescence using a Niton XL 3 analyzer, are presented in Table 1.

The Bojidar kaolin composition [24] before chromium adsorption is presented in Table 2.

The kaolin was previously used as adsorption support for the soluble chromium waste

from residual waters containing 2.4 g/L Cr⁶⁺. The adsorption conditions were:

- residual water pH = 5,
- shaking time: 120 minutes,
- solid:liquid ratio 1:100.

Chromium concentration in the supernatant were determined by Atomic Absorption Spectroscopy using a Varian SpectrAA 110 spectrometer. The content (%) of hexavalent chromium adsorbed by kaolin was determined from the difference between initial C_i and final C_f concentrations of hexavalent chromium ion in the residual water, before and after contact. The following equation was used for calculations:

$$\%Cr(VI) = \frac{C_i - C_f}{C_i} 100$$

The chromium retention efficiency of the process was over 99%, the resulting kaolin contains 33 % Cr⁶⁺.

The weight ratios glass waste:kaolin were used for the glass-ceramic synthesis are presented in Table 3.

Table 3

Batch composition of the studied glass ceramics [wt. %]
Compoziția amestecului de materii prime [% greutate]

Sample	Waste glass [%]		Kaolin [%]
	Window pane	Funnel glass	
P1	60	-	40
P2	70	-	30
P3	80	-	20
P4	-	60	40
P5	-	70	30
P6	-	80	20

The raw materials as powders (granulometric fraction under 0.1 mm) were mixed together and then pressed into cylinders having the diameter and height around 35 mm. The heat treatment was conducted at three different temperatures 900, 1000 and 1100°C respectively for 60 minutes.

Table 1

Oxidic composition of the recycled glasses used as precursors / Compoziția oxidică a deșeurilor de sticlă folosite ca precursori

Waste glass	Composition (weight %)								
	SiO ₂	Na ₂ O	K ₂ O	MgO	CaO	Al ₂ O ₃	Fe ₂ O ₃	PbO	BaO
Window pane	71.86	13.13	0.02	5.64	9.23	0.08	0.04	-	-
Funnel glass	58.00	7.03	8.57	2.18	3.64	4.12	-	12.99	3.47

Table 2

Oxidic composition of the Bojidar kaolin / Compoziția oxidică a caolinului de Bojidar

Bojidar kaolin	Composition (weight %)								
	SiO ₂	Na ₂ O	K ₂ O	MgO	CaO	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	PC
	49.29	0.14	0.87	0.44	0.56	35.18	0.78	0.43	12.31

2.2 Characterization methods

The apparent density and apparent porosity of the obtained glass ceramics was measured using the liquid saturation method under vacuum with water as working liquid.

The microporous structure of the glass ceramic matrix was analyzed by SEM, using an Quanta FEG 250 microscope.

The compression strength of the investigated samples were determined using a U-test compression machine.

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

The hydrolytic stability of the glass ceramic 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 deionized 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 Na₂O extracted. The chromium 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. 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). 2 g of each sample were taken and shaken with 250 ml of ammonia–acetate buffer solution for different time periods at a constant

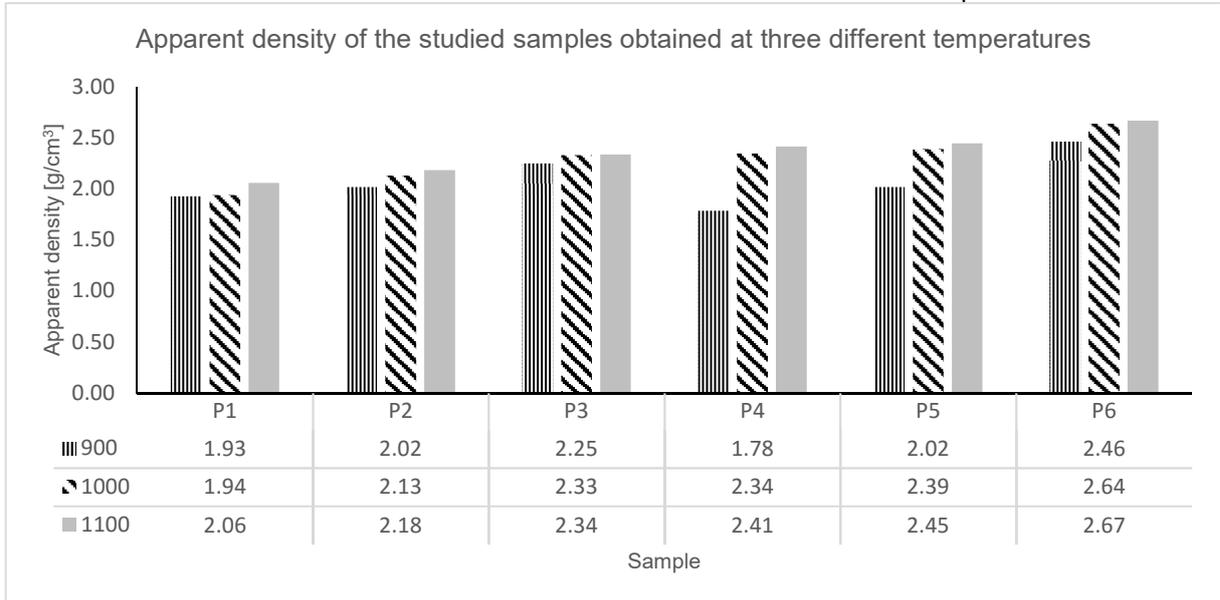


Fig. 1- The apparent density of the studied glass ceramic samples sintered at 900, 1000 and 1100°C / Densitatea aparentă a maselor vitroceramice studiate sinterizate la 900, 1000 și 1100°C.

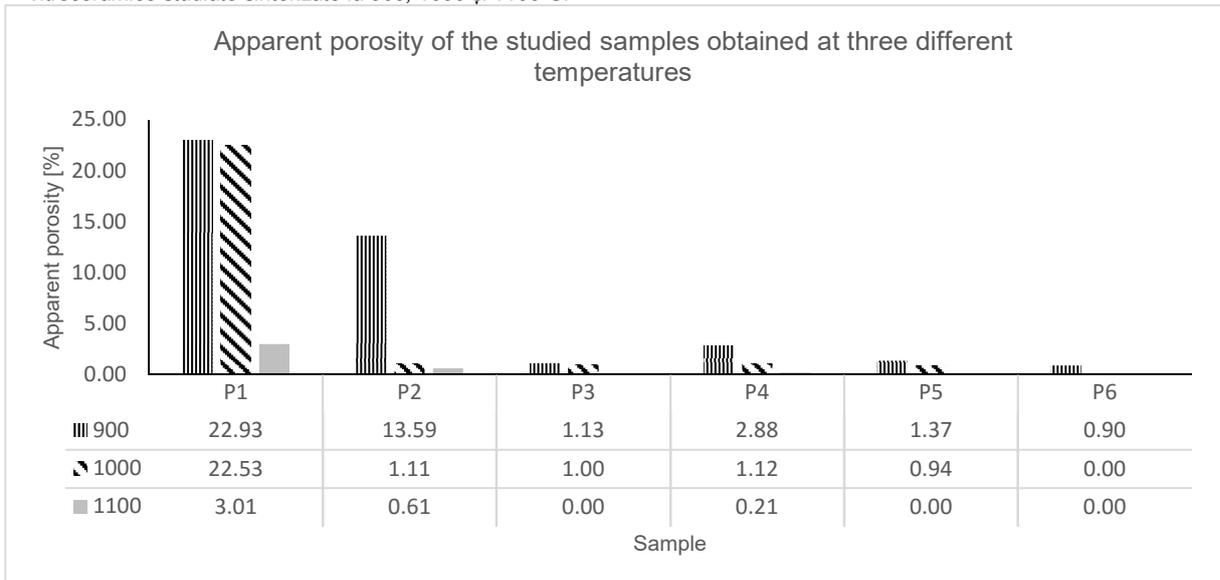


Fig. 2 - The apparent porosity of the studied glass ceramic samples sintered at 900, 1000 and 1100°C / Porozitatea aparentă a maselor vitroceramice studiate sinterizate la 900, 1000 și 1100°C.

temperature of $20 \pm 2^\circ\text{C}$. The chromium concentration in the extraction mediums was measured using a Varian SpectrAA 110 atomic spectrometer fitted with the Mark 7 flame atomization system.

3. Results and discussion

3.1. Glass ceramic apparent densities and apparent porosities

The apparent density and the apparent porosity of the investigated glass ceramic compositions are illustrated in Figure 1 and Figure 2 respectively.

For all the six samples, increasing the sintering temperature generates to a larger amount of melted glass that fills the pores, leading to a higher apparent density and a smaller apparent porosity of the glass ceramic matrix. The funnel glass wastes, having PbO , generates higher amounts of liquid phase at lower temperatures due to the fusibility effect of the lead oxide, leading to lower values of the apparent porosity compared to

windows panes wastes. This behavior is illustrated in Figure 3 by comparing the SEM pictures of the samples P1 and P4 having similar amounts of the 2 glass wastes. Sample P1, containing window panes glass wastes presents an inhomogeneous microstructure, having irregular large pores with a high scattered dimensional distribution compared to the sample P4.

3.2. Glass ceramic compression strength

Considering the target utilization for these glass ceramics as floor tiles, the compression strength is an important parameter. The influence of the sintering temperature upon the compression strength values for the six investigated samples is illustrated in Figure 4.

The behavior of the mechanical compression strength is similar for all the samples, having a maximum value at 1000°C corresponding to the optimal sintering temperature. At 900°C the incomplete sintered matrix cannot generate enough mechanical strength and at 1100°C the fragile behavior of the large amount of glass has a

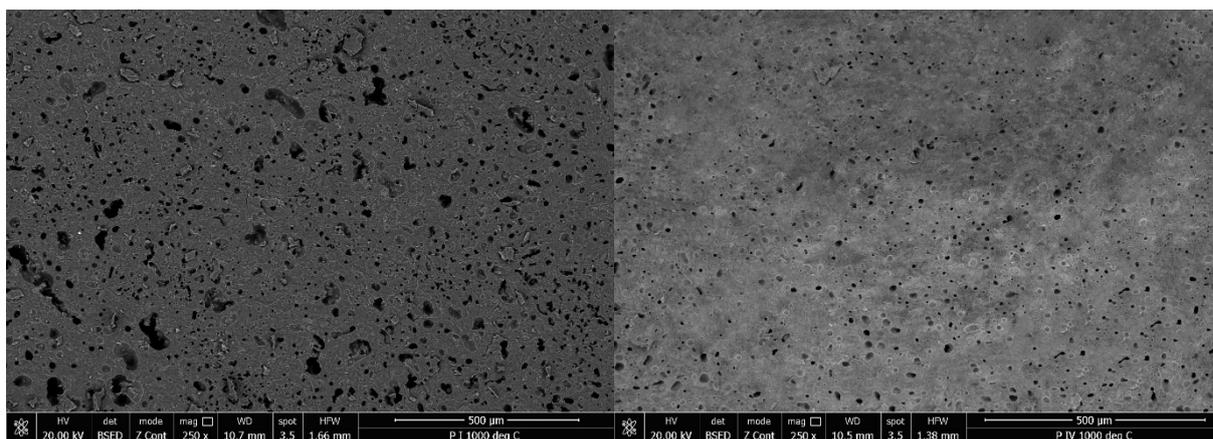


Fig. 3 - Porous microstructure of P1 and P4 samples at 1000°C / Structura microporoasă a probelor P1 și P4 sinterizate la 1000°C .

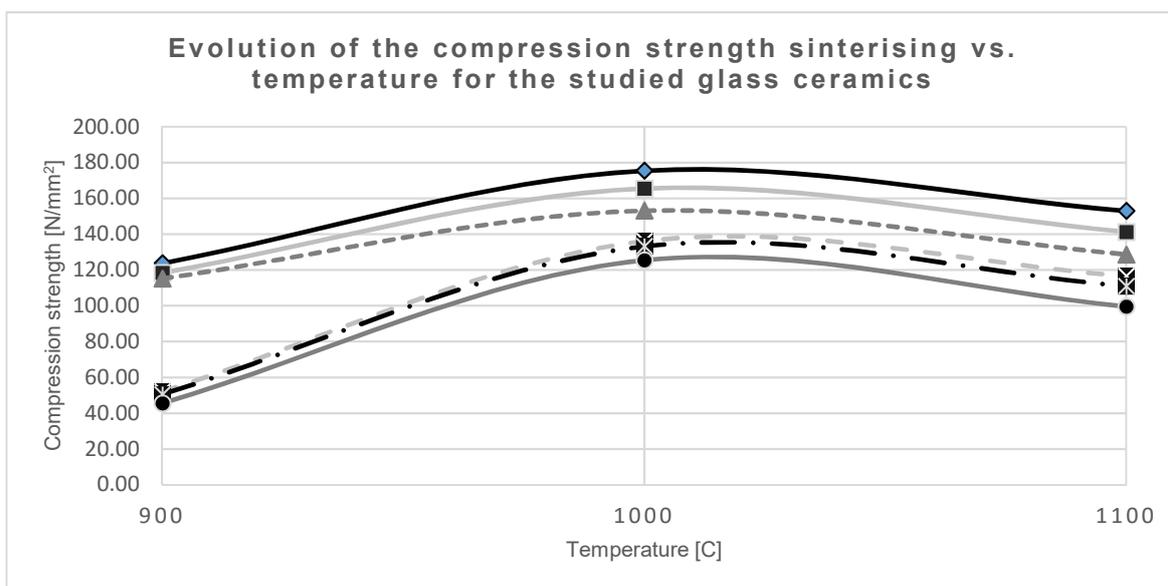


Fig. 4 - The compression strength of the studied samples at 3 sintering temperatures / Rezistența la compresiune a probelor studiate la cele trei temperaturi de sinterizare.

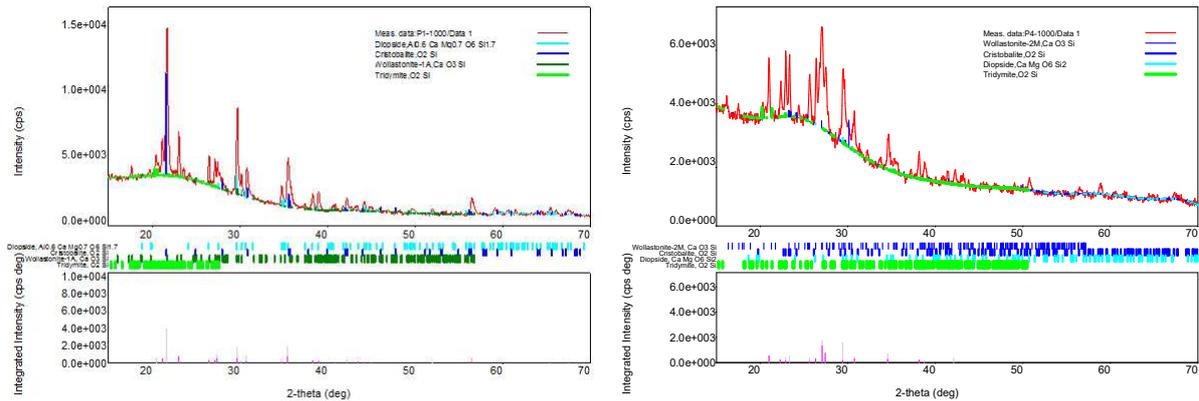


Fig. 5 - RX diffraction spectra for the samples P1 and P4 at 1000°C / Spectrele de difracție RX pentru probele P1 și P4 sinterizate la 1000°C.

negative influence over the compression strength values. The glass ceramics having window panes waste glass as precursor have better compression properties compared to that based on funnel waste glass due to the higher amount of fragile glass generated by PbO in the second matrix.

3.3. Glass ceramic phase composition

The main phases present in samples P1 and P4, having the best compression strengths at 1000°C, are illustrated in Figure 5.

The main crystalline phases in both samples, having different glass waste precursors, are wollastonite, tridymite, diopside and cristobalite. The presence of tridymite can be accounted for the sand that comes with the kaolin while the cristobalite is generated by the recrystallization process of the amorphous SiO₂.

3.4. Glass ceramics hydrolytic stability

The chemical properties of the investigated glass ceramics were studied for the samples sintered at 1000°C, having the highest mechanical compression strength. The resistance of the studied glasses towards water aggression was analyzed according with ISO 719-1985, the results being summarized in Table 4.

Table 4

The hydrolytic stability and the corresponding hydrolytic class of the investigated glass ceramics
Stabilitatea hidrolitică și clasa de stabilitate corespunzătoare pentru probele vitroceramice studiate

Sample	Extracted Na ₂ O equivalent [μg/g]	Stability class
P1	23	HGB1
P2	35	HGB2
P3	62	HGB2
P4	30	HGB1
P5	42	HGB2
P6	55	HGB2

The main source for the alkali extracted by water chemical attack is the vitreous phase, therefore the glass ceramics hydrolytic stability decrease with the increase of the glass waste amount. The two glass wastes precursors generate similar behaviors regarding the stability of the glass ceramics towards water aggression.

3.5. Chromium immobilization in the glass ceramic matrix

The leaching test had a duration of 1, 14 and 28 days respectively, after which the solid and the liquid were separated by filtration. The lixiviate was chemically analyzed using a Varian SpectrAA 110 atomic absorption spectrophotometer. The obtained values, expressed as percent chromium measured in the lixiviate from the total ion amount in the glass, are presented in Figure 6.

The lixiviation values for chromium range between 0 and 0.014 % for all the investigated samples. The pH of the attack solution influence the chromium leachability, the glasses being more sensitive to the alkaline medium aggression for all the studied periods of time. The acid and neutral mediums does not extract any chromium from the glass ceramic matrix, even after 28 days. The values presented in the figure 6 can be explain based on the glass composition and compactness. The similar behavior for the two groups of samples can be explained considering the glass-kaolin ratio, larger kaolin amounts generating higher values for extracted chromium. The samples P1-P3, having windows panes glass wastes as precursor, generates a lesser encapsulation of the ceramic phase and therefore a higher susceptibility to lixiviation. The samples P4-P6, having a more fluid melted phase due to the presence of lead oxide increase the encapsulation of the ceramic phase generating matrix less sensible to lixiviation.

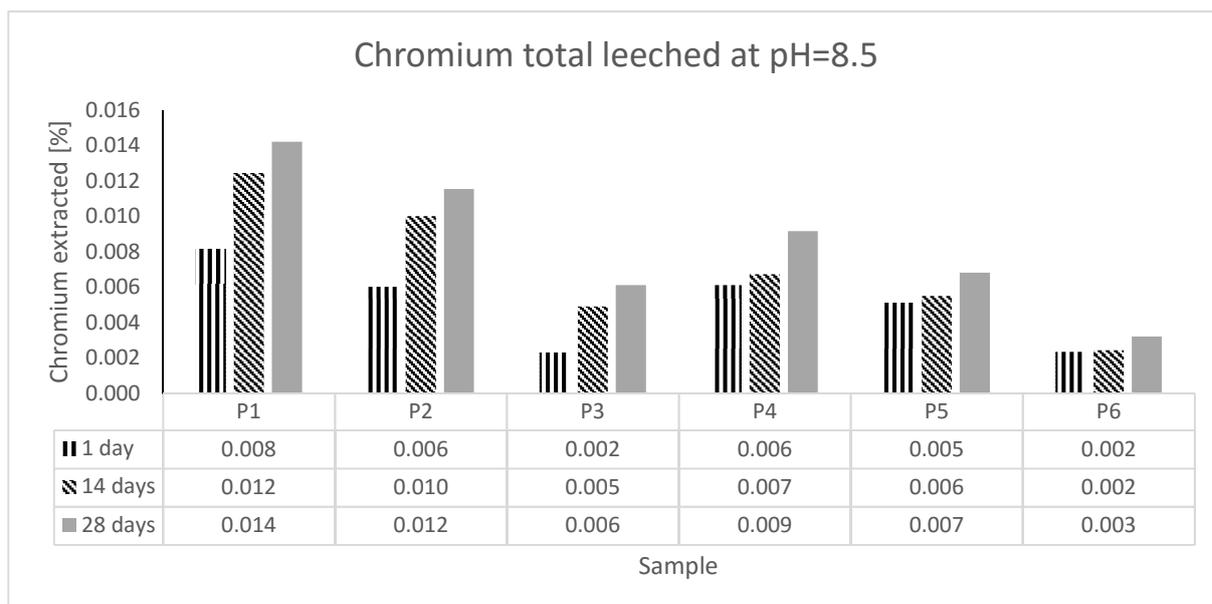


Fig. 6 - Total chromium leached from the studied samples at pH=8.5 / Cromul total solubilizat din probele studiate la pH=8,5.

4. Conclusions

The chromium in kaolin used to remove Cr^{+6} from a residual water can be immobilized by vitrification using window panes and funnel waste glasses, providing multiple economic advantages.

The apparent density of the investigated samples range between $1.78\text{-}2.67\text{ g/cm}^3$, while the apparent porosity values are between 0-23.19% depending of the sintering temperature. The PbO present in the funnel waste glass precursor generates more fluid melts compared to those obtained using windows wastes glasses and therefore the obtained glass ceramics have higher densities and lower porosities.

The compression strength of the obtained samples is affected by the sintering temperature, the higher values correspond to 1000°C . The glass-kaolin ratio also influences the compression strength, higher glass amounts in the glass ceramic matrix generates more fragile structures.

The main crystalline phases in all the glass ceramic samples are wollastonite, tridymite, diopside and cristobalite.

The chemical properties of the studied glass ceramics were studied for the samples sintered at 1000°C , having the highest mechanical compression strength. The hydrolytic stability of the products, according with ISO 719-1985, qualifies them as HGB1-HGB2 glasses, having very good resistance to water.

The investigated glass ceramic matrix immobilized chromium very well. Only the alkaline medium generates very low chromium lixiviation, less than 0.014% after 28 days. The most stable samples were P4-P6, where the fluid melt generates a better encapsulation of the chromium rich ceramic phase.

The obtained results confirm the viability of the suggested solution for immobilizing soluble chromium wastes, retained in kaolin as adsorption support, into glass ceramic matrix using glass wastes as precursor materials, with multiple economic advantages.

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