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Cathode ray tubes glass wastes used for vitrification of iron oxide rich waste resulted from the groundwater treatment

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Abstract. This paper presents a new solution to use the cathode ray tube glass wastes for iron oxide rich waste vitrification. The obtained glass-ceramics, synthesized at three heat treatment temperatures: 800, 900 and 1000 °C were characterized in terms of the effect of the CRT waste glass addition upon the dimensional stability, apparent porosity and density, chemical stability and lead barium and iron ions retention capacity.

***Keywords*:** CRT wastes; cathode ray tube; sludge waste; glass ceramics.

1. Introduction

A major challenge in many countries around the world is the appropriate disposal of solid wastes containing heavy metals, generated by industry and agriculture, posing a serious risk to the human health and the ecological environment [1-3]. The insufficient land-filling space and the increasing cost for land disposal, generates an increasing interest for recycling these industrial waste [4] and providing alternative materials that facilitate the reduction in the depletion rate of natural materials [5]. Solid wastes recycling into ceramics, cement aggregates, concrete, geopolymers, has been mentioned by many researchers [6, 7].

In this context, glass recycling become a very attractive concept in the last decades having some major advantages: quality conservation [8], energy savings [9,10], waste reduction [11], reduction in raw material extraction and decrease of the environmental contaminant [12].

The glass wastes recycling by vitrification is known as an energy consuming process, economically viable only if it generates new glass-based products having high market impact, such as glass or glass-ceramic matrix composites [13, 14], glazes [15], glass foams [16, 17], etc.

Cathode ray tubes (CRT) have disappeared from the market in the developed countries, being replaced with modern TV screens but the number entering the waste stream is yet to peak in Europe [18]. The presence of lead and barium in CRT glass, the ceramic industry [19, 20] and construction materials [21-23] seem to be the most promising outlets for CRT glass recycling.

This research offers a new alternative to recycle the CRT wastes together with an iron oxide rich waste prepared by calcination of the sludge from the settling tanks that collect wastewater from washing the filters from the iron removal step of groundwater treatment process by vitrification together kaolin as glass-ceramic products able to immobilize iron and heavy metals (barium and lead) ions in their structural matrix.

2. Experimental

The oxidic composition of the two precursors is presented in Table 1. The CRT waste composition was determined by RX fluorescence using a Niton XL 3 analyzer while the kaolin oxidic composition was provided by a local ceramic company (S.C. IPEC S.A. Timisoara).

Table 1. Oxidic composition (weight %) of the raw materials

Oxide	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3	BaO	PbO	TiO_2	P.C.
CRT	60.92	8.96	7.44	0.67	0.14	2.07	0.15	10.80	8.85	-	-
Bojidar kaolin	49.29	0.14	0.87	0.56	0.44	35.18	0.78	-	-	0.43	12.31

The iron oxide rich waste (IOR) results from the sludge accumulated in the settling tank that collect the water resulted from the filters washing process from the iron removal stage from the local groundwater treatment plant (S.C. Aquatim S.A. Timisoara). After a prior natural drying for 72 hours, the dried sludge was calcined at 750 ºC for 6 hours. The heat-treated waste composition, determined by RX fluorescence is 83.00 % Fe^{3+}, 10.03 % Mn^{2+} and 5.41 % Ca^{2+} respectively.

The CRT waste powder (100 µm mesh) was obtained by wet grinding at a 1:2:1 material-balls-water ratio using a Pulverisette type laboratory mill, then dried at 105 °C for 24 hours and then sieved. The batch compositions used for the glass-ceramics synthesis are presented in Table 2.

The precursors were dry mixed together and then pressed into cylindrical shapes using a Greisinger

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Electronics M.P 150 D hydraulic press. The obtained cylinders having a diameter of 10 mm and a height of 30 mm were heat treated in an electric furnace (NABERTHERM 300-1300°C) at 800, 900 and 1000 °C for 60 minutes at the maximum temperature and then cool slowly to room temperature in order to avoid thermal stress.

Table 2. Batch recipes (weight %) used for the studied glass-ceramics

Sample	Batch composition [weight %]		
	CRT waste	IOR waste	Bojidar kaolin
1	60	0	40
2	50	10	40
3	40	20	40
4	30	30	40

The dimensional stability of the studied samples was determined considering the volumetric shrinkage after firing, determined using an electronic caliper. The apparent densities and apparent porosities of the obtained glass-ceramics were measured using the liquid saturation method under vacuum with water as working liquid.

The chemical stability was determined using 100 mL deionized water maintained at a temperature of 20 °C. The samples having a previously measured mass m_i, were immersed for 28 days and then dried in an oven for 6 hours at 110 °C to reach the constant m_f mass. The dissolution rate D_r was calculated using the relation:

$$D_r = \frac{\Delta m}{t} \quad [\mu g/h] \qquad (1)$$

where: $\Delta m = m_i - m_f$ is the weight loss leached by deionized water after the time t.

The barium, lead and iron ions immobilization capacity in the glass-ceramic matrix was determined using leaching tests performed according to the American Extraction Procedure Toxicity Test [24]. Deionized water was used as extraction medium at a constant temperature of 20 ± 2 °C, ions leachability analysis being measured after 28 days using a Bruker Aurora ICP-MS.

3. Results and discussion

3.1. Samples dimensional stability after the heat treatment

The dimensional stability of the samples is affected by the shrinkage due to the structural changes that occurs during the firing process. The evolution of the volume contractions vs. CRT waste amount used in the glass-ceramic synthesis for the three firing temperatures is illustrated by Figure 1.

The samples obtained at 800 °C show the lowest shrinkage values, ranging between 0.96 - 3.40 % while firing at 1000 °C generates higher shrinking, between 4.02 - 7.87 %. Higher heat treatment temperatures generate larger amounts of liquid, more fluid phase increases, able to occupy the glass-ceramic structural pores, generating a lower dimensional stability of the samples. The substitution of the CRT with IOR waste decrease the contractions during firing due to a lower amount of vitreous phase thermal generated, less important at a temperature of 800 °C but more pronounced at 1000 °C.

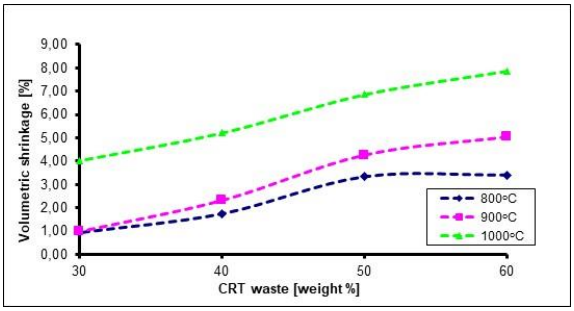

Figure 1. Evolution of volume contractions vs. CRT amount for the obtained glass-ceramics

3.2. Apparent porosities and apparent densities of the samples

The evolution of apparent glass ceramics porosity and density with the CRT amount is illustrated in Figures 2 and 3. The apparent porosities are between 38.50 - 56.02 % for the samples fired at 800 °C, higher compared to sintered at 1000 °C ranging between 23.97 - 33.41 %. The samples apparent density range between 1.21 - 1.56 g/cm^3 at 800 °C and 1.83 - 1.98 g/cm^3 at 1000 °C respectively.

Increasing the heat treatment temperatures generate larger amount of melted phase able to fills the pores, leading to a lower apparent porosities and higher apparent densities. Replacing the CRT waste with IOR waste generates a lower amount of melt at the same firing temperature leading to lower apparent densities and higher apparent porosities.

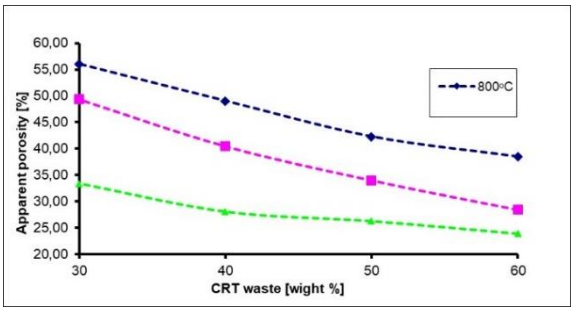

Figure 2. Evolution of apparent porosity vs. CRT amount for the obtained glass-ceramics

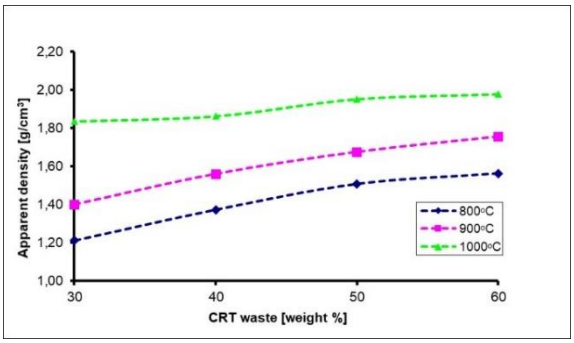

Figure 3. Evolution of apparent density vs. CRT amount for the obtained glass-ceramics

3.3. Chemical stability of the samples

The evolution of chemical stability expressed as dissolution rate after 28 days upon the CRT waste

amount used to synthesize the studied samples is presented in Figure 4.

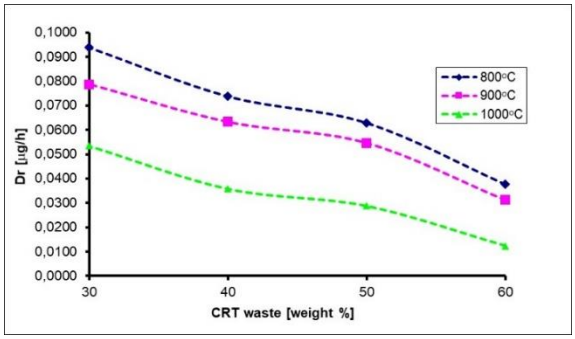

Figure 4. Evolution of dissolution rate after 28 days vs. CRT amount for the obtained glass-ceramics

The values obtained confirm the good resistance to hydrolytic attack even at the term of 28 days for all samples. The dissolution rates range between 0.038 - 0.094 mg/h for the samples fired at 800 °C and decrease as the heat treatment temperature increases down to 0.012 - 0.053 mg/h at 1000 °C. Lowering the CRT amount used for sample synthesis leads to an increase of the dissolution rate and therefore a decrease of the hydrolytic stability due to lower amounts of vitreous phase formed during the heat treatment, knowing that the glass phase have a higher hydrolytic stability compared to that of the ceramic phase composing the glass-ceramic matrix.

The influence of the samples' apparent porosity upon the hydrolytic stability is illustrated by Figure 5.

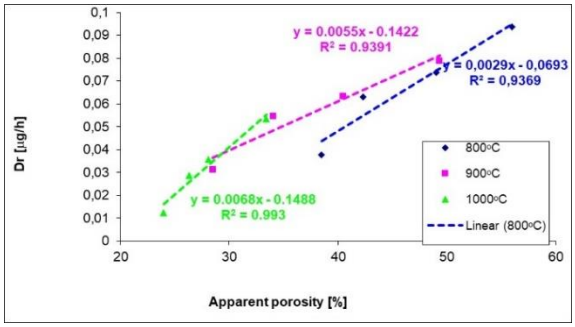

Figure 5. Influence of the obtained glass-ceramics porosity upon their hydrolytic stability

The hydrolytic attack upon the glass-ceramic matrix occurs through the material-water interface. Higher porosities generate larger interfaces and higher dissolution rates. Increasing the firing temperature leads to lower porosities due to the higher amounts of melting phase that occupy the available pores and therefore better chemical stability. It is interesting to observe a quasilinear dependence between the apparent porosity and chemical stability of the investigated samples.

3.4. Ions immobilization in the glass ceramics matrix

No lead or barium ions dissolution from the studied glass ceramics after 28 days can be measured using the Bruker Aurora ICP-MS equipment. This can be explained based on the fact that those ions come in the samples structure via the glass CRT vector, less susceptible to hydrolytic attack.

The iron ions leachability vs. the CRT amount is presented in Figure 6.

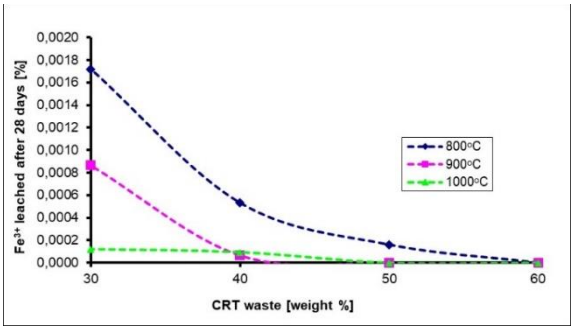

Figure 6. Evolution of iron ions amount leached after 28 days after 28 days vs. CRT amount for the obtained glass-ceramics

All the synthesized samples show a very good immobilization of the iron ions in the glass-ceramic matrix, the leached iron quantities after 28 days being extremely low, ranging between 0 - 0.0017 % of total iron contained by the sample. A higher firing temperature leads to a lower iron dissolution due to the larger amounts of glass phase generated during the heat treatment, able to encapsulate the iron IOR waste vector.

Higher amounts of CRT waste used for the glass-ceramic synthesis at the same firing temperature leads to larger amounts of melting phase able to protect the IOR waste against the hydrolytic attack.

4. Conclusions

New glass-ceramics were synthesized using cathode ray tubes wastes Bojidar kaolin and an iron oxide rich waste generated in the filters washing process used for groundwater treatment.

The samples dimensional stability after the heat treatment process range between 0.96-3.40% at 800 °C and 4.02-7.87% at 1000 °C. The substitution of the CRT waste with IOR waste increase the dimensional stability during firing due to a lower amount of vitreous phase thermal generated.

The apparent porosities of the samples range between 23.97 - 56.02% and the corresponding apparent densities between 1.21-1.98 g/cm^3, depending of the firing temperature. Replacing the CRT waste with IOR waste generates lower amount of liquid phase at the same firing temperature leading to lower apparent densities and higher apparent porosities.

The dissolution rates range between 0.038 - 0.094 mg/h for the samples fired at 800 °C and decrease as the heat treatment temperature increases down to 0.012 - 0.053 mg/h at 1000 °C. Reducing the CRT amount due to the increase in the amount of IOR used for sample synthesis leads to a decrease of the hydrolytic stability due to lower amounts of vitreous phase formed during the heat treatment. A quasilinear dependence between the apparent porosity and chemical stability of the investigated samples was established.

No lead or barium ions dissolution from the studied glass ceramics after 28 days can be highlighted. The synthesized glass-ceramics show a very good iron ions immobilization, the lixiviation values after 28 days ranging between 0 - 0.0017 % of the total iron content. Higher amounts of CRT waste have a favorable effect upon the iron ions immobilization at the same firing

temperature due to a better iron encapsulation in the glass-ceramic matrix.

The obtained results recommend the viability of the proposed alternative to use cathode ray tube glass waste for iron oxide rich waste immobilization in glass-ceramic matrix having multiple economic advantages.

Conflict of interest

Authors declare no conflict of interest.

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