

# Physical-chemical characterization of a galvanic sludge and its inertization by vitrification using container glass

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## Abstract

Several industrial processes produce large amounts of heavy metals-rich wastes, which could be considered as “trash-can raw materials”. The incorporation in ceramic systems can be regarded as a key process to permanently incorporate hazardous heavy metals in stable matrixes. In particular the aim of this work is to prepare and evaluate environmental risk assessment of coloured glass and glass-ceramic with the addition of chromium(III) galvanic sludge having a high content of  $\text{Cr}_2\text{O}_3$  (15.91 wt%). Trivalent chromium compounds generally have low toxicity while hexavalent chromium is recognized by the International Agency for Research on Cancer and by the US Toxicology Program as a pulmonary carcinogen. The sludge has been characterized by ICP –AES chemical analysis, powder XRD diffraction, DTA, SEM, leaching test after different thermal treatments ranging from 400°C to 1200°C. Batch compositions were prepared by mixing this sludge with glass containers. The glass container composition is rich in  $\text{SiO}_2$  (69.89 wt%),  $\text{Na}_2\text{O}$  (12.32 wt%) and  $\text{CaO}$  (11.03 wt%), while the sludge has a high amount of  $\text{CaO}$  (42.90 wt%) and  $\text{Cr}_2\text{O}_3$  (15.91 wt%). The vitrification was carried out at 1450°C in an electrical melting furnace for 2 h followed by quenching in water or on graphite mould. Chromium incorporation mechanisms, vitrification processability, effect of initial Cr oxidation state, and product performance were investigated. In particular toxic characterization by leaching procedure and chemical durability studies of the glasses and glass-ceramics were used to evaluate the leaching of heavy metals (in particular of Cr). The results indicate that all the glasses obtained were inert and the heavy metals were immobilized.

*Keywords: chromium electroplating sludge, thermal behaviour; vitrification, chemical glass durability.*



## 1 Introduction

Chromium has been used in industry for various applications over a century, including steel production, plating, anodising of aluminium, leather tanning, wood preservation, water-cooling, etc. The use of chromium (VI) containing solutions ( $\text{CrO}_3$  250g/l and  $\text{H}_2\text{SO}_4$  2,5 g/l) as deposition metal is the unique technique employed in the plating industry [1], despite of its high toxicity [2]. After electroplating is completed, the plated parts are rinsed with water. Eventually this rinse water becomes highly contaminated with plating solution and must be replaced. This fact presents a serious environmental problem since the water is highly concentrated in chromate ions. The hazardousness of this galvanic waste is not only due to Cr(VI) presence but also to the high concentration of heavy metals, as Ni, Ti, etc. This chromium rich solution needs a chemical treatment based on a two-stage process: the first stage reduces hexavalent chromium Cr(VI) to a harmless  $\text{Cr}_2(\text{SO}_4)_3$  by using chemical agents as sodium bisulfate ( $\text{NaHSO}_3$ ), sodium or calcium meta-bisulfite ( $\text{Na}_2\text{S}_2\text{O}_5$ ). In the second stage trivalent chromium and other metals are precipitated by the addition of calcium or sodium hydroxide in their hydroxide form, which can be easily separated and disposed in landfills. Nowadays the cost of landfill disposal and the decrease in the number of disposal sites have led to considerate stabilization of waste into a glassy matrix or ceramic materials an accepted treatment process [3, 4]. In the last 30 years it has been reported many examples about recycling of industrial waste in cement, glass, and metallurgy industry [5], but few works can be found in literature regarding recycling of galvanic chromium sludge [6] into glassy matrixes or ceramics compounds [7].

The aim of this work is to characterize the chromium galvanic sludge and to study the vitrification process as an efficient method to immobilize the hazardous components of this galvanic waste. In particular it is investigated the stabilization process evaluating the chemical resistance of the obtained glasses and glass-ceramics compounds.

## 2 Experimental

The electroplating sludge employed in this investigation has been collected from a local plant, while the glass is from container waste. These wastes have been characterized by ICP -AES technique (Varian, Liberty 200). Galvanic sludge previously milled for 40 min in a porcelain jar was added in the percentages of 0.5, 1.5, 3, 6 wt% corresponding to  $\text{Cr}_2\text{O}_3$  content of 0.12, 0.25, 0.5 and 1 wt% to the container glass composition and the dry mixtures were ground in a ball-mill for 20 min. The mixture was fired in mullite crucibles at 1450°C for 1 h in electrical melting furnace. The melts have been quenched in water to obtain the frits or poured into a graphite mould and quenched in air to obtain a bar shape glass. The glass shape were heated at 750°C with 1 h of soaking time to eliminate the internal stresses due to the fast cooling rate in air. Frits can facilitate and reduce the time required to ground in the preparation of glass ceramics. The container glass and frits in the above reported composition have



been humidified with 6 wt% of water and pressed in order to obtain cylindrical samples. Subsequently these pellets were fired at different temperatures from 600 to 1000°C obtaining glass ceramics.

The mineralogical analysis of the galvanic sludge and glass-ceramics has been carried out by an X-ray ( $\text{CuK}\alpha$ ) powder diffractometer, XRD (Philips PW 3710, Holland). The XRD patterns were collected in the  $5\text{-}60^\circ$  ( $2\theta$ ) range at room temperature. The thermal behaviour of chromium galvanic waste has been characterized by means of differential thermal analysis (DTA and TG) (Netzsch DSC 404). Scanning electron microscopy (SEM) (PHILIPS XL 40) has been performed on representative samples of sludge and glass-ceramics to observe phase distribution and microstructural features. Furthermore the assessment of the chemical durability in water, acid (HCl 6M boiling, 3h) and alkaline ( $\text{NaCO}_3$  0.5 M and NaOH 1 M. boiling, 1h) conditions was carried out on representative specimens of the manufactured glasses following ISO/R 719, ISO/R 695 and DIN 12116 standards [8].

### 3 Results and discussion

#### 3.1 Thermal behaviour of chromium electroplating sludge

The chemical analysis of galvanic waste indicates the following composition in wt%: 0.81  $\text{SiO}_2$ , 0.8  $\text{Al}_2\text{O}_3$ , 42.50 CaO, 1 MgO, 6.1  $\text{Na}_2\text{O}$ , 0.5  $\text{K}_2\text{O}$ , 1.3  $\text{Fe}_2\text{O}_3$ , 0.01  $\text{TiO}_2$ , 0.2 NiO, 0.5 CuO, 0.2 MnO, 15.91  $\text{Cr}_2\text{O}_3$ , 0.02 CoO, 0.02 CdO and the L.OI is 30% Figure 1 illustrates the TG and DTA curves of the galvanic sludge during the heating process.

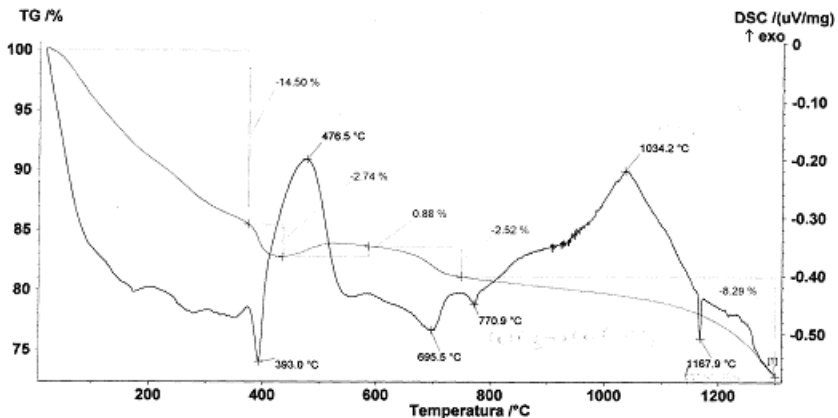


Figure 1: DTA and TG curves of as-received galvanic sludge.

The DTA curve shows exothermic peaks at 476.5 and 1034.2°C, while endothermic peaks appeared at 393, 695.5, 770.9 and 1167.9°C. The total weight loss is 28%. This result is in close agreement with that obtained from

calculations based on chemical analysis and calcination at 1200°C (about 30%) It is presumed that the weight loss is related to CO<sub>2</sub>, H<sub>2</sub>O. The exothermic peak at 393°C is probably related to the release of crystallization water; the peak at 770.9°C corresponds to the CaCO<sub>3</sub> decomposition and 1034.2°C could be due to a crystallization. The endothermic peak at 475°C represents the organic compound combustion and the one at 1167.9°C could be a melting reaction. X-ray diffraction was performed in the as received waste and in samples previously submitted to different isothermal treatments from 400 to 1200°C with 1h of soaking time. Fig. 2 resumes the XRD data showing CaSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, CaCrO<sub>4</sub> and CaCO<sub>3</sub> as main constituents, labelled a, b, c, and d respectively.

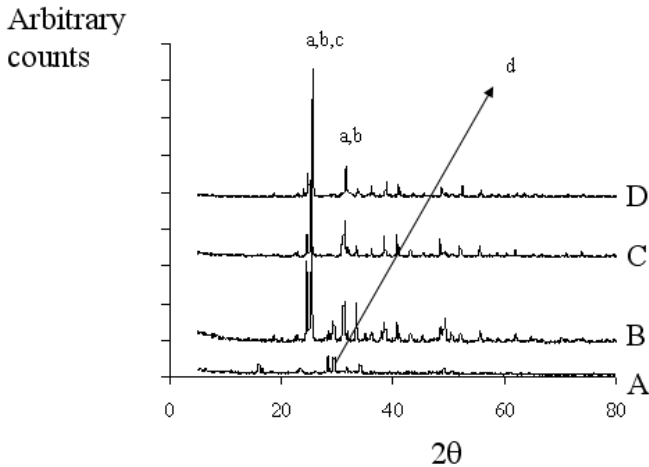


Figure 2: XRD spectra of galvanic sludge dried at 105°C (A) and thermally treated at 500°C (B), 800°C (C) and 1200°C (D) respectively

It is important to observe, in agreement with the DTA results, that the CaCO<sub>3</sub> peaks disappear at 800°C. The elementary analyses performed on the dried samples and on those obtained at 700 and 800°C show a decrease in C, confirming the CaCO<sub>3</sub> decomposition, as Table 1 reports.

Table 1: Elementary analysis of galvanic sludge dried at 105°C and thermally treated at different temperatures from 700°C up to 1200°C.

Sample	N %	C %	H %	S %
105°C	0.00	1.76	1.91	10.99
700°C	0.00	0.64	0.00	9.59
800°C	0.00	0.00	0.00	9.50
1000°C	0.00	0.00	0.00	6.53
1200°C	0.00	0.00	0.00	6.39

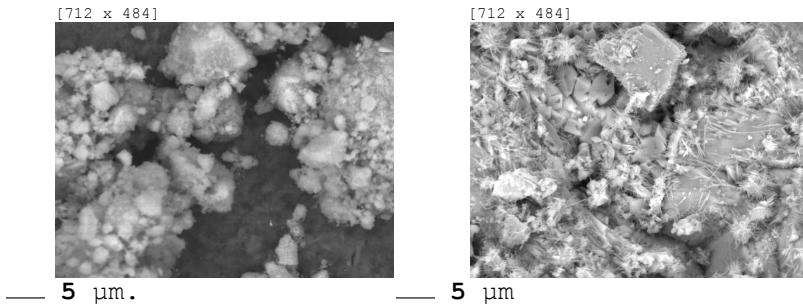


Figure 3: SEM micrographs of dried galvanic sludge and thermally treated at 1100°C.

### 3.1.1 Glasses and glass ceramic characterization

Table 2 reports the chemical composition from theoretical calculations and the ICP chemical analysis of the V1 and V2 glasses. It is evident from these results that a very low crucible refractory contamination occurs. In fact, it can be observed an increase in the amount of  $\text{Al}_2\text{O}_3$ . It is important to remark that no significant variation of the  $\text{Cr}_2\text{O}_3$  percentage is recorded. This fact indicates that vitrification could be considered a good alternative to stabilize wastes with a high content of heavy metals.

Table 2: Chemical composition from theoretical calculations of V1, V2, V3 and V4 and the ICP chemical analysis of the V1 and V2 glasses.

Oxide	V1	V2	V3	V4	ICP	ICP
	Theoret. wt%	Theoret. wt%	Theoret. wt%	Theoret. wt%	V1 wt%	V2 wt%
$\text{SiO}_2$	69.57	69.21	68.52	67.18	68	68.5
$\text{Al}_2\text{O}_3$	2.64	2.62	2.6	2.55	6.2	7.1
$\text{CaO}$	11.28	11.56	12.1	13.50	10.57	11.50
$\text{MgO}$	2.24	2.24	2.23	2.20	1.92	2.22
$\text{Na}_2\text{O}$	12.27	12.24	12.2	12.10	11.61	12.30
$\text{K}_2\text{O}$	1.48	1.47	1.46	1.45	1.51	1.42
$\text{Fe}_2\text{O}_3$	0.12	0.12	0.13	0.15	0.19	0.13
$\text{BaO}$	0.13	0.13	0.13	0.13	0.12	0.11
$\text{ZrO}$	0.13	0.14	0.14	0.13	0.13	0.13
<b><math>\text{Cr}_2\text{O}_3</math></b>	<b>0.12</b>	<b>0.25</b>	<b>0.49</b>	<b>0.96</b>	<b>0.11</b>	<b>0.22</b>

The water chemical durability of the obtained glasses remains constant with respect to container glass up to 3% in waste showing a medium resistance [8].

These results are in agreement with the increase of pH and conductivity observed with the increasing waste percentage. The damage of the glass network lead to a release of  $\text{OH}^-$  and therefore to an increase in pH, while an increase of

the mobile ions  $\text{Na}^+$  and  $\text{K}^+$ , which are easily leached, causes an increase in conductivity. The examined glasses are slightly attacked in basic and acid medium. The weight loss of the glass containing 6 wt% of galvanic waste, expressed as weight loss per surface unit, is equal to  $174 \text{ mg}/100 \text{ cm}^2$  and  $2.69 \text{ mg}/100 \text{ cm}^2$  in alkali and acid respectively [8].

In order to verify the possibility to obtain a semi-crystalline technologically interesting such as glass-ceramics different thermal treatments have been performed on the glassy samples. XRD analysis shows the presence of crystalline phases dispersed in the glassy matrix, in particular wollastonite is the main crystalline phase (Fig.4).

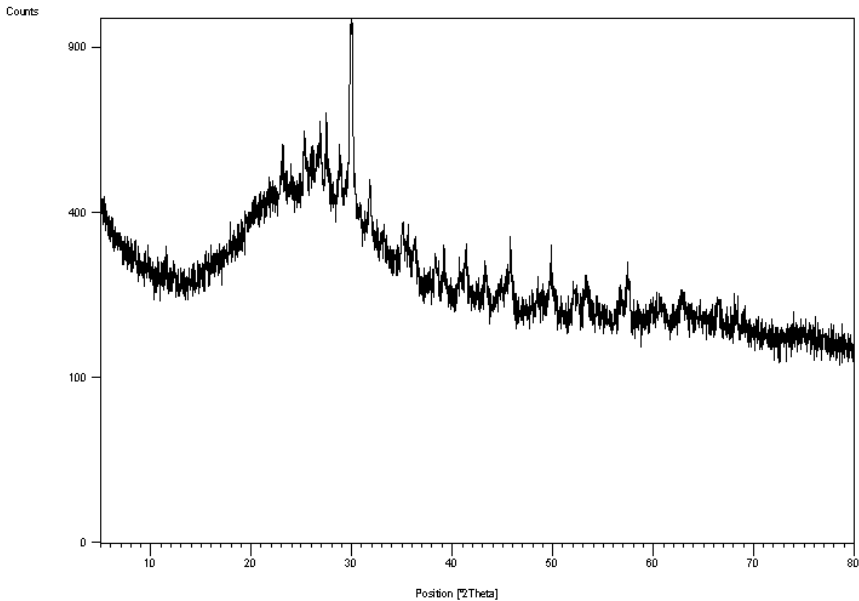


Figure 4: XRD spectrum of a sample fired at  $900^\circ\text{C}$  showing wollastonite as main crystalline phase.

Figure 5 shows a SEM micrograph of a sample of these glass-ceramics compounds showing a microstructure where needle grains of a crystalline phase, that could be wollastonite, are embedded in an amorphous glassy matrix. These needle like grains are presented in the glass-ceramic microstructure from  $750^\circ\text{C}$  (Fig.5). The porosity of these glass-ceramic results low, which could be an indication of good mechanical properties.

## 4 Conclusions

The results of this investigation highlight the possibility of incorporating galvanic waste as economical raw material in glassy products. Adequate thermal

treatments could lead to the production of glass-ceramic products. Therefore vitrification and devitrification could represent adequate techniques for inertization of industrial sludge with heavy metals content and alternatives to the disposal in landfills. In future more studies will be performed both on glasses and glass ceramics to evaluate the influence of an increase in the amount of galvanic sludge on the chemical and mechanical properties of the products and to better analyse the sintering process.

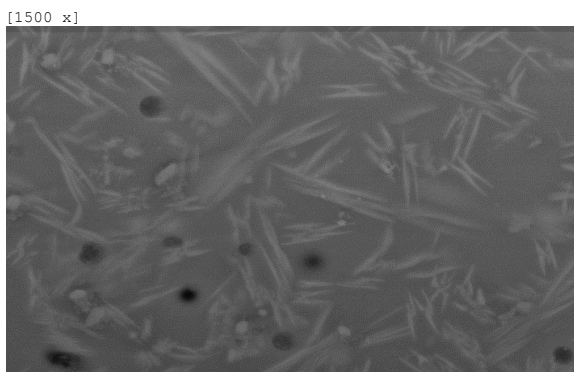


Figure 5: SEM micrograph of a sample fired at 750°C showing needle-like grains of wollastonite crystalline phase.

## Acknowledgement

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