



Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/gexplo

Vitrification of urban soil contamination by hexavalent chromium

S. Ballesteros^a, J.Ma. Rincón^b, B. Rincón-Mora^c, M.M. Jordán^{c,*}^a Industrial Engineering Department, Tecnológico Nacional de México, Instituto Tecnológico de Tijuana, Av. Universidad s/n, Tijuana, BC, Mexico^b Instituto de Ciencias de la Construcción Eduardo Torroja, Consejo Superior de Investigaciones Científicas, c/Serrano Galvache s/n, Madrid, Spain^c Department of Agrochemistry and Environment (GEA-UMH), Miguel Hernández University, Elche, Alicante, Spain

ARTICLE INFO

Article history:

Received 20 June 2016

Accepted 9 July 2016

Available online xxxx

Keywords:

Soil remediation

Vitrification

Hexavalent chromium

Mexico

ABSTRACT

This research describes the characteristics, formation mechanisms, and leaching of Cr⁶⁺ wastes that are contaminating a Mexican urban soil. By means of a vitrification process, a method has been proposed that transforms Cr⁶⁺ to Cr³⁺ and achieves effective immobilization of this highly toxic industrial waste affecting an urban area. By various physicochemical and microstructure characterization techniques, such as XRD, DTA, and SEM/EDS, carrying out complete characterization of these new materials was possible. The final vitrified or glassy products of silicate composition lead to a glass ceramic material that is environmentally very stable, showing high chemical and mechanical stability where all Cr⁶⁺ was reduced to Cr³⁺ in the residual glass network, as well as other chromium oxidation states confined in the crystalline phases formed in the final glass-ceramic. The leaching tests on samples stabilized by vitrification have shown that the release of ions from the structure of these new materials was negligible, yielding values <0.5 mg/l with respect to current international and domestic environmental regulations. The final glass-ceramics obtained by vitrification and controlled crystallization showed adequate mechanical resistance properties.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In Mexico, some areas are highly contaminated by heavy metals. Currently, there are >75,000 tons of untreated residues in the form of slags and sludges containing high concentrations of hexavalent chromium, Cr⁶⁺, in densely populated zones very near Mexico City (Ballesteros and Rincón, 2005; Ballesteros et al., 2010; Ballesteros, 2014). For decades, the toxic substances in these residues have represented a threat to both human health and the environment. Cr⁶⁺ is toxic, carcinogenic, highly soluble in water, and very corrosive (Ladrón de Guevara and Moya, 1995). As such, its presence and the forms of treating it continue being an unresolved challenge today. Environmental laws worldwide are becoming ever stricter, and the tendency towards sustainable development is leading to research on safe and stable storage alternatives for these residues to diminish their environmental impact. Despite tremendous efforts to stop soil and subsoil contamination, it has been confirmed that confinement does not definitively resolve the potential risk of its release during transport or from leachate that this type of residue represents.

The residues produced at industrial facilities that manufacture chemical products of chromium, such as sodium chromate (Na₂CrO₄), represent serious environmental problems if they are not properly stored. Though nowadays there are hydrometallurgical extraction methods for efficient control of chromate, risk of environmental contamination exists

if control measures are not taken for the control of slags coming from the production of sodium chromates (Ballesteros, 2014).

The traditional methods for obtaining sodium chromate on a commercial scale were developed for operating in open rotary kilns with limited production efficiency. The residue produced contains values that exceed the recommended range of 0.1–0.2% of hexavalent chromium. The treatment for reducing Cr⁶⁺ to a less toxic chemical species is difficult because it involves expending financial resources without providing, in most cases, attractive commercial options. The areas contaminated by these residues or by controlled confinement are today the greatest source of Cr⁶⁺ contamination (Kumar and Shripad, 2015).

Chromate compounds present in the residue with Cr⁶⁺ solubilize with the passage of time at concentrations of 0.7–5% of Cr⁶⁺, even subsequent to carrying out efficient extraction of the chromate in the very process. After decades, this residue forms various types of chromium salts (calcium chromate, CaCrO₄; calcium aluminochromate, 3CaO·Al₂O₃·CrO₄; tri-basic calcium chromate, [Ca₃(CrO₄)₂]; and basic iron chromate, [Fe(OH)CrO₄]), which are slowly soluble in water, then form Cr⁶⁺ due to water filtration in the subsoil (Ballesteros, 2014; Tinjum et al., 2008).

Capillary migration of Cr⁶⁺ and its concentration towards the surface at landfill or confinement sites is variable due to the presence of slowly soluble chromium salts and changes in meteorological conditions. Due to these phenomena, concentrations a few centimeters from the ground surface can vary from just a few parts per million to percentage levels that are many times greater than the concentration at the very confinement site. At these sites, chromate enrichment is evident at the subsoil surface or confinement areas as outcrops in the form

* Corresponding author.

E-mail address: manuel.jordan@umh.es (M.M. Jordán).

of greenish-yellow stains extending along constructed walls and confinement installations or processing areas (Meegoda et al., 2000).

Cr^{6+} harms health when it exceeds the levels of environmental regulation established by many of the world's countries. According to the Sodium Dichromate Listing Background Document for the Inorganic Chemical Listing Determination report by the Environmental Protection Agency (EPA), chromate residues are considered dangerous. This residue exceeds the limits of the Toxicity Characteristic Leaching Procedure (TCLP) for chromium (US EPA, 1998) and as reported also for other materials in Romero et al. (2009). Before their confinement, these residues generally go through a neutralization process in tanks containing a ferric chloride solution as an agent that reduces Cr^{6+} to trivalent Cr^{3+} , making it precipitate by adding lime, thus preventing the residue from harming the environment.

Currently, two possible safe and final storage methods exist for chromate residues: one is dumping in landfills, and the other, in the best cases, is confinement in sealed containers. These methods are the simplest and cheapest solutions, but not the safest from the long-term environmental protection point of view. Given the current state of caring for the environment, in terms of handling and disposal, storage in containers until subsequent transfer for duly authorized confinement is used most frequently. However, this alternative continues to pose a risk to subsoil and groundwater contamination (Palmer and Wittbrodt, 1991).

In the specific case of chromate residue contamination at the Cromatos de México plant in Tultitlán, no appropriate measures have ever been taken to handle this type of residue. Initially, this was because no well-defined environmental regulations existed during the 1970's and 80's, and then later because the effects from these residues on human health were either unknown or ignored (Ladrón de Guevara and Moya, 1995). The recovery of chromium is another method by which the problem of the residues can be minimized. In the center of Mexico, the locations detected with Cr^{6+} contain >75,000 tons. It is therefore evident that there is a great need to research and understand this problem with the objective of developing a treatment process that is suitable to current needs, thus improving environmental conditions, and not only in the indicated location, but also in other locations within that country that present environmental problems similar to those aforementioned. The residue, prior to its treatment, contains 15–20% Cr_2O_3 , 0.3–1% Cr^{6+} as sodium chromate, pH = 8.7, 30% moisture and 70% solids without volatile matter. This type of residue normally contains total chromium at a level of 109,000 mg/kg (10.9% wt).

Therefore, this research studied and analyzed the characteristics and formation mechanisms of pyrometallurgical residues containing Cr^{6+} , and a vitrification process is proposed as a definitive treatment for the contamination problem that the deposits of this type of residue pose. The process consists in neutralizing the Cr^{6+} produced by the Cromatos de México Corporation, which has remained in the same location for over three decades, by developing a vitrification process followed by controlled devitrification (Ballesteros et al., 2006).

Vitrification followed by crystallization of an original vitreous product (bulk glass or frit) has been widely proposed in recent decades for the immobilization of industrial wastes and even for recycling as a secondary raw material (Rincón and Zayas M^a, 1994). Thus, in the case of ashes, this technology was proposed for recycling them in porcelainized stoneware (Hernandez-Crespo et al., 2006). Aineto et al. (2006) used the same procedure over slags coming from gasification power plants. In recent decades, these ceramic and vitrification methods have been applied by Rincón (2016) for all types of industrial residues and even for hydrometallurgical mud wastes, as was seen in previous papers on chromium wastes by Ballesteros et al. (2006) and Ballesteros and Rincón (2011). On the other hand, it is also well known that chromium oxide (Cr_2O_3) has been a usual nucleating agent for promoting crystal growth or controlled devitrification in glasses (Rincón-Mora et al., 2016), even at very low concentrations in the composition of glasses susceptible to be transformed into glass-ceramics.

To accomplish this, dolomite-silica gravel was used as an additive to form calcium and magnesium silicate glasses of a composition similar to that of natural basaltic rocks. This was done because it has been well known for quite some time that these glasses are very stable over the long term, and considering that with the chromium (Cr^{6+}) concentrations in the residues investigated here (approximate to 3 wt%), they are the most suitable for neutralization due to their inclusion in a glassy matrix followed by a crystallization process. Said process creates highly stable materials due to the formation of spinels high in chromium oxides, pyroxene, and augite, with substitutions in their crystal lattice and other heavy metals existing in these types of wastes (Morse, 1994). The final vitreous ceramic materials that are obtained present technological properties that are improved in comparison to traditional vitreous ceramic material, they are environmentally stable, and furthermore, can be used in the construction industry in various applications due to their characteristics and appearance similar to those of natural stones (Rincón et al., 2001).

2. Materials and method

For the experimental development of this research, three 5-kg samples were chosen: M1, which came from contaminated ground (soil) from areas of the plant; M2, which was the most contaminated as it had endured for years in confinement (slags and sludges from storage vaults in situ); the third sample, M3, less toxic, was obtained from concrete fragments of plant structures or adjacent buildings, already abandoned due to the contamination they showed (Fig. 1). All samples are the property of Cromatos de México in the city of Tultitlán, Mexico. Thus, the identification of the chosen samples was as follows:

- M1 → Soil contaminated with hexavalent chromium.
- M2 → Slag processing with hexavalent chromium.
- M3 → Demolition residues with hexavalent chromium.

In all cases, the samples were taken from surface outcrops of chromate (very evident due to the presence of yellow and greenish-yellow stains) except for the extraction of sample M2, which was taken at a depth of up to 3 m.

Chemical characterization of the samples was performed using various analysis techniques: X-ray fluorescence (XRF), atomic absorption, ICP, and C and S combustion analysis. Mineral phases in both the residues, as well as the molten glasses, were analyzed by the X-Ray diffraction technique (XRD) with a Rigaku Model D max 210 operating at 30 kV and 16 mA, utilizing Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) with a 5° radiation incidence angle.



Fig. 1. Various aspects of the soil and location contaminated by chromates in Lechería and Tultitlán (México) (Ballesteros, 2014).

Physical characteristics were analyzed by various methods in the contaminated residues in order to determine the particle size, moisture, density, pH, and water soluble fraction.

TCLP (toxic characteristics leaching procedure) was utilized to evaluate the lixiviation of the toxic substances in the residues (Strachan, 2001; Romero et al., 2009). In the preliminary evaluation of the TCLP test, 5 g of residues were added to 95.5 ml of distilled water and subjected to magnetic shaking. The pH was determined to be above 5. Then, 3.5 ml of 1 N HCl were added, the solution was heated to 50 °C, and this temperature was maintained for 10 min. The definitive extraction stage used 100 g of sample (in triplicate), added at a 2:1 ratio, with the appropriate TCLP solution and placed in a hermetically sealed laboratory glass recipient that was spun at 30 RPM for 20 h. Once the shaking cycle finished, the solution was filtered with a fiberglass mesh to remove solids from the sample, and the pH of the solution was measured.

The toxicity test with distilled water for samples of residues M1, M2, and M3, and also for molten glasses, was in accordance with the ASTM D 3987-12 standard in order to learn the leaching behavior in both types of samples before and after vitrification. Thus, 70 g of sample were added to 1400 ml of distilled water and continuously shaken for 18 h at 23 °C. The mixtures were filtered with a vacuum filtering device, and afterwards the pH of the solution was determined. The Cr⁶⁺ concentrations of the obtained leachates from the TCLP extract and ASTM D 3987-12 were measured following the UV colorimetric method included in this standard.

From the chemical composition of the residues, compositions with the addition of a dolomite and silica gravel were selected within the quaternary system CaO–MgO–Al₂O₃–SiO₂ (Morse, 1994) and following previous research about crystallization from melted basalts (Hidalgo et al., 1988; Vicente-Mingarro et al., 1992a; Vicente-Mingarro et al., 1992b). To carry out the laboratory-scale immobilization by vitrification of the residues investigated here, fusions of the residue mixtures were made with gravel in graphite crucibles in a high temperature (1600 °C) Superkhanthal vertical electric furnace (model SWEDISH AB pob 505) equipped with a EUROTHERM 818P4 temperature controller. A silica-based additive was added to sample M2 because it contained a low concentration of it; the remaining two samples were handled without adding any type of silica additive. Each crucible melted 500 g of sample. Afterwards, the samples were cooled slowly, inside the oven, to prevent the stress fractures that are produced from sudden temperature changes when melts are exposed to air, and which are common in the cooling process subsequent to casting a molten mass (Turkdogan, 1983; Vicente-Mingarro et al., 1992a). The mixtures were cast into brass molds, and discs with 120 mm diameters some 12 mm thick resulted. An additional series of molten samples with the corresponding M1, M2, and M3 formulations were cooled directly in water, causing rapid

cooling to ensure complete vitrification, and therefore afford them the conditions so they could be examined by the differential thermal analysis technique (DTA).

The thermal methods used (TGA/DTA) enabled learning the exo- and endothermic reactions, as well as the phase transformations, glass-transition temperature (T_g), recrystallizations, and fusion phenomena. In all glasses, the thermal behaviors were tested in volume samples or in coarse grains, and furthermore in pulverized samples with 60 μm grain sizes. These thermal methods allowed knowing better the nucleation and crystal growth phase transformations from the original vitreous samples at several heating velocities (Ballesteros, 2014). With this procedure, determining the respective glass transformation (T_g), nucleation (T_n), maximum crystal growth (T_c) and fluxing (T_f) temperatures can be possible. According to Uhlmann (1980), from these temperatures, it is possible to evaluate the relative stability of these glasses with respect to their devitrification (Rincón, 1992).

Observation by SEM/EDS was carried out on samples directly embossed in epoxy resin, polished and metallized with gold in vaporizing equipment by Emscope sputter coating, as well as by direct observation in fresh fractures. The epoxy embossing, and its subsequent polishing and metallization, were necessary, in addition to the more precise microanalyses of the crystallized phases by energy-dispersive X-ray spectroscopy (EDS) (Rincón, 1990). Various types of equipment were used: a SEM/EDS Jeol and a Philips XL-30, and, in some cases, a Hitachi FESEM/EDS (Field Emission). All of these operated at 25 kV with EDS spectrometers by the firms of Oxford and Edax. For the energy dispersive spectroscopy (EDS) microanalysis, several areas were analyzed depending upon the size of different or vitreous phases and by using semi-quantitative software by considering the (ZAF) correction method due to the effects of atomic number (Z), absorption (A), and fluorescence (F) (Hren et al., 1979).

3. Results and discussion

The chemical analyses of the compounds, and the major, minor, and residual elements present in the residues are shown in Table 1. The compositions of the residues in M1 and M3 indicated percentages of 42.82 and 40.69 wt% of SiO₂, which suggest that these residues can be directly processed by vitrification and obtain the corresponding glasses. In contrast, the SiO₂ content in sample M2 was 18.97% w/w, corresponding to a low value, so adding silica gravel additives was necessary to adjust the SiO₂ composition in the residue before melting it and converting it to glass. Samples M1 and M3 containing Cr⁶⁺, mainly due to the diffusion of chromium chemical compounds and their leaching over time, gave rise to strongly contaminated areas close to the production plant. In contrast, M2 corresponds to both components:

Table 1
Chemical analysis of contaminated soil and chromium waste samples used for vitrification.

Oxides wt%	M1 contaminated soil	M2 processing slag	M3 demolition construction waste	Additive dolomitic rock gravel
SiO ₂	42.82	18.97	40.69	66.42
Al ₂ O ₃	12.8	11.87	11.86	7.21
Fe total (Fe ₂ O ₃)	5.42	16.86	4.45	11.69
CaO	16.74	24.37	26.27	7.18
MgO	2.08	8.0	1.95	2.92
TiO ₂	0.53	0.59	0.3	–
Na ₂ O	13.28	9.23	8.89	3.24
K ₂ O	2.21	1.0	2.12	1.18
P ₂ O ₅	0.24	0.2	0.16	–
C	2.38	4.10	2.82	–
S	–	–	0.17	–
Cr total (Cr ₂ O ₃)	1.39	4.58	0.33	0.01
MnO	–	0.24	–	0.12
NiO	–	–	–	0.023
ZnO	0.12	–	–	–

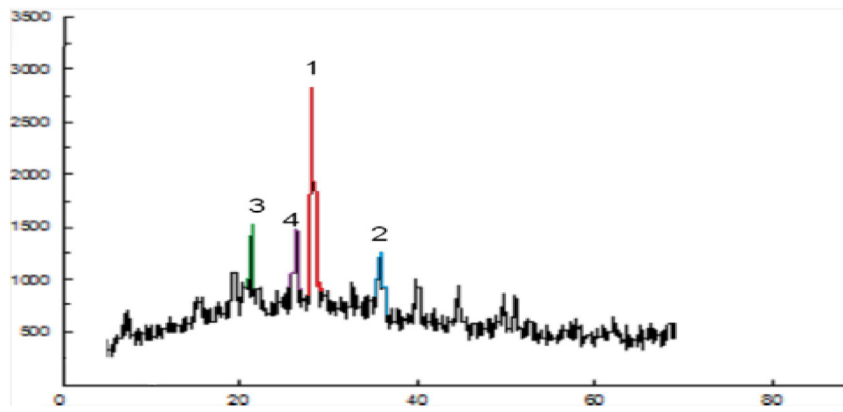


Fig. 2. XRD diffractogram from sample M2 (slag contaminated with hexavalent chromium). 1: chromium spinel; 2: hematite; 3: albite; 4: gehlenite.

a slag comprised of Cr_2O_3 and chromate that had progressively leached over time.

3.1. Mineralogy of phases in obtained residues and vitrified products

The crystalline phases were identified by XRD in both the residues and the vitrified products. Thus, the peaks of the crystallographic phases found in the residue of sample M2 (processing slag) were evident. Note the presence of peaks from the crystallographic phases of hematite (Fe_2O_3) and associated to the presence of the chromates; a complex spinel of various elements $(\text{Mg, Fe, Mn, Cr})_3\text{O}_4$, a phase of calcium hydroxide $\text{Ca}(\text{OH})_2$, and an albite-type feldspathic phase $\text{Na}(\text{AlSi}_3\text{O}_8)$ were found (Fig. 2).

In the case of XRD, peaks characteristic of spinel of the (Mg, Fe) ($\text{Fe, Al, Cr})_2\text{O}_4$ and augite types ($\text{CaMgAl}_2\text{Si}_2\text{O}_6$) were detected in the diffractogram of the V2 glass (Fig. 3). Furthermore, the presence of an initial phase of augite in glass (V1) is observed, and it can be seen that increasing the content of chromium oxides in sample V2 gives rise to a mixture of phases of augite + spinel along with the intensification of the formation of the hematite phase (Fe_2O_3). The formation of the wollastonite phase (CaSiO_3) was predominant in the V3 glass, which

had the highest SiO_2 content due to the concrete included in the demolition waste.

3.2. Thermal analysis (DTA) in vitrification samples

In Fig. 4, the peak of the powder sample is shown (curve in red), indicating that the nucleation occurs on the surface, given the characteristics of the sample and that its effect is spontaneous, defining a first peak at $802\text{ }^\circ\text{C}$. In contrast, the granule glass sample behaved in such a way that a longer time was required to achieve crystallization and crystal growth, forming the first crystallization peak at $832\text{ }^\circ\text{C}$. In Fig. 4, note the behavior of this glass (V2) in both the powder and granule sample; in both samples, it is very similar. A high tendency of crystallization is observed, indistinctly whether the sample is pulverized or bulk (Figs. 5 and 6).

That preceding means that the tendency to crystallize is strongly influenced by the presence of nucleating agents as a part of the original raw material until the formation of the glassy matrix. Therefore, the crystallization of this glass is in volume, which means that the nucleating agents present in the sample, such as chromium and iron, are in sufficient quantities to be able to promote crystallization in this glassy material obtained from residues rich in chromium and iron. The

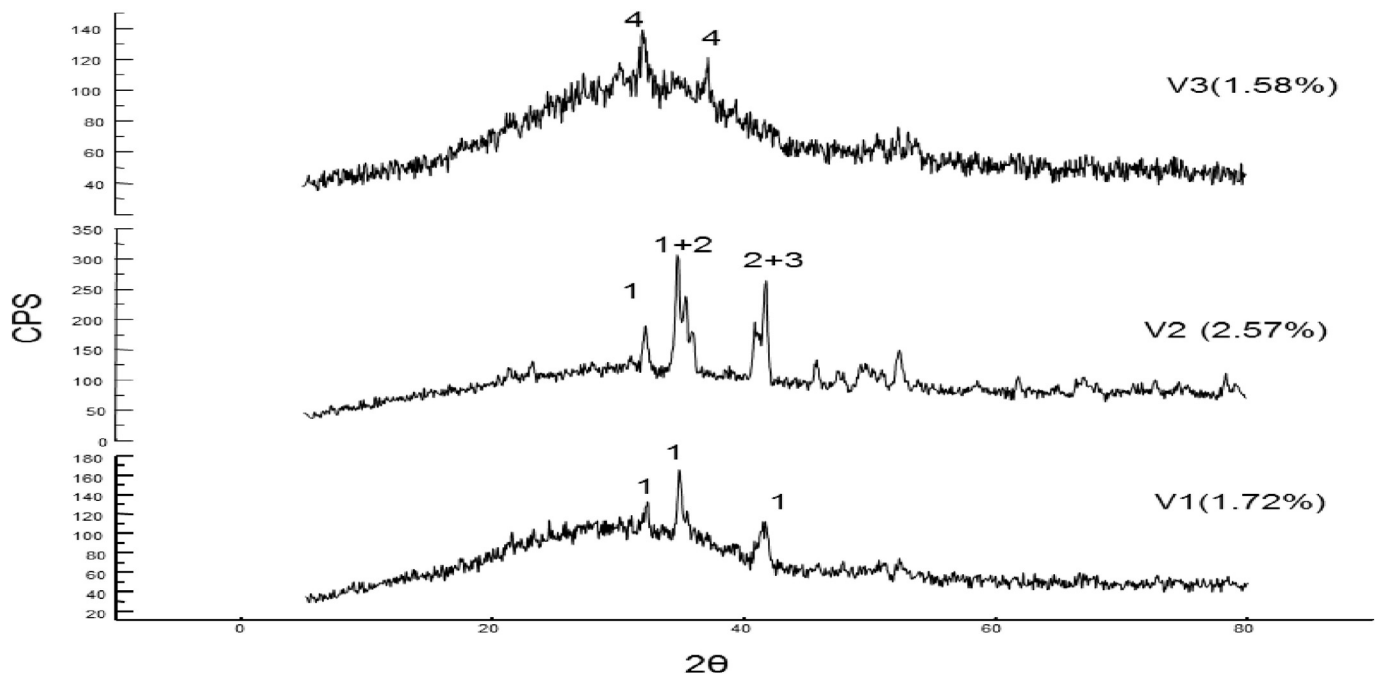
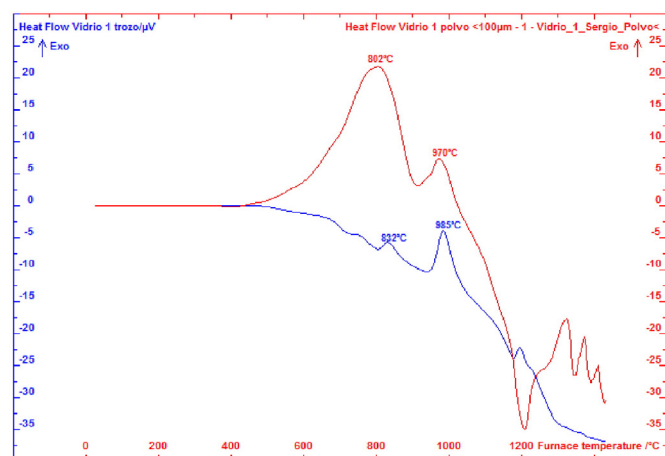
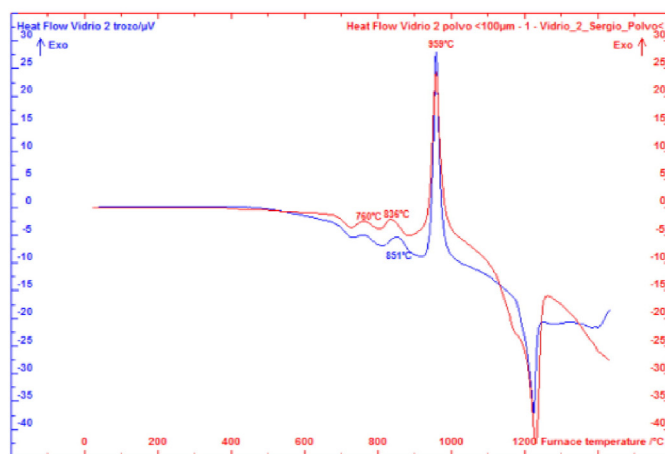


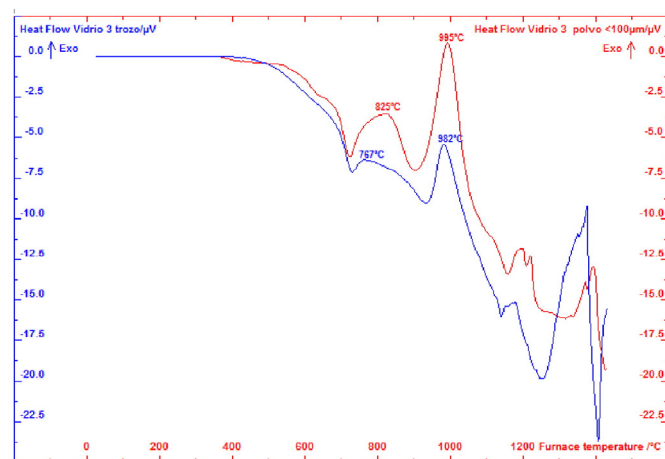
Fig. 3. X-ray diffraction for vitrified samples with different Cr_2O_3 percentages, expressed in weight % Cr_2O_3 . 1: chromium spinel; 2: hematite; 3: albite-anorthite; 4: wollastonite.



a)



b)



c)

Fig. 4. DTA trace analysis of the glasses in the case of bulk and powdered glass (size smaller than 60 μm) for glass samples V3 (a), V2 (b), and V1 (c).

behavior of glass (V3), under the same experimental conditions used in the DTA test for glasses V1 and V2, resulted in thermal behavior very similar to the samples of glass V1 in that the predominant nucleation and crystallization is that of the peak of the powder sample, which tends to surface crystallize more than in volume (Ballesteros et al, 2009; Ballesteros, 2014).

3.3. Leaching tests on residues contaminated by hexavalent chromium

The results of some characteristics of the powder of chromite residues for different samples are shown in Table 2. Solutions with pH in the basic range of 10–11 result when these leach into water due to the presence of calcium oxide in the residue. The soluble fraction due to the presence of salts in chromite residues is 27.1%, while for the soil residues on the corporation's property it is 23%, and 10% for the demolition residues (Table 3).

The results from the TCLP extract and ASTM D 3987-12 for the residues investigated here are shown in Fig. 3. It demonstrates that all the residues are classified as “hazardous materials” according to what EPA regulations (TCLP and ASTM D 3987-12) mark. One difference was found in the chromium concentration in the solution of distilled water (ASTM D 3987-12 standard) when compared to the concentration of the TCLP extract, with the Cr^{6+} concentration relatively lower, as a more standardized leaching method (TCLP) was used, capable of being applied for various analysis techniques and the subsequent determination of distinct species, elements, and compounds present in a leaching extract.

All the leachates from the ASTM D 3987-12 tests were yellow basic solutions whose pH ranged from 9 to 11. For the TCLP test, they were acidic and had a faint dark yellow color. Furthermore, the same tests were carried out on the V1, V2, and V3 vitrified materials in order to determine the Cr^{6+} concentration in original glasses and materials stabilized by vitrification. The Cr^{6+} concentrations in the original glasses with the ASTM D 3987-12 and TCLP extract tests were $<0.026\text{ mg/l}$ for the three indicated glasses.

3.4. Observations and microanalysis of phases in the vitrified material

In the glass samples, which were cooled inside the furnace and then heat treated, there was formation of various crystalline phases. The spinel phases of iron and magnesium (Mg, Fe) $(\text{Fe, Al, Cr})_2\text{O}_4$, enriched in Cr and the equiaxial type, is a disperse phase throughout the entire microstructure, not major but containing a percentage of up to 65.78% in the crystals in the form of Cr_2O_3 .

Other phases found in the form of very small crystals with a white contrast and only observed in the backscattered electron mode correspond to the metallic phase in the shape of Fe–Cr microspheres, deriving from oxide reduction reactions during the vitrification process proposed here; in the crystals in the shape of a cross, the analyzed composition is very stable, not varying from one crystal to the others and similar to the stoichiometric composition of $\text{CaO} \cdot \text{MgO} \cdot (\text{Al}_2\text{O}_3) \cdot 2\text{SiO}_2$ augite; crystals forming dendrites in the shape of feathers that in most cases grow around the crystals of augite (indicated by number 3 in Fig. 4).

The crystal composition is almost the same among several crystallites of augite (pyroxenes). In the case of feldspar crystallization, the crystals are smaller in size, showing strong variations in composition between several areas of the microstructure.

The composition of this phase does vary from one zone to another. Due to the respective Na and Ca contents, the formation of an albite-anorthite solid solution between both types of feldspars ($\text{NaAlSi}_3\text{O}_8$ – $\text{CaAl}_2\text{Si}_2\text{O}_8$) is possible. The formation of this solid solution is very frequent in basalt glass-ceramics. Hence, the variation observed in the composition. It is evident that the slower cooling rate results in the growth formation of elongated crystals with increased spacing between one other, with the augites one of the most predominant phases in the samples of the glass/glass-ceramic material obtained here.

3.5. Extraction of Cr^{3+} and Cr^{6+} species in the vitrified products

The results of the determination of hexavalent chromium and total chromium by UV/Vis spectrometry, wet chemistry, and ICP spectrometry in vitrified samples are shown in Table 4 for each of the analyzed samples. The colorimetric method to determine Cr^{6+} and Cr^{3+} was

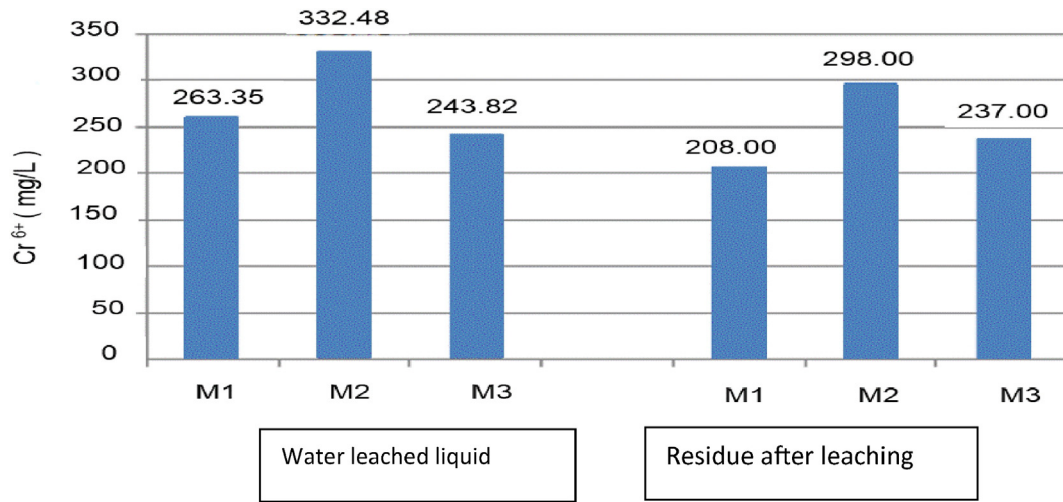


Fig. 5. Cr⁶⁺ concentrations in distilled water in accordance with ASTM D 3987-12 and the leached residue TCLP extract (the three columns on the left correspond to the leached water solution and the three columns on the right correspond to the residual solid from the vitreous product).

carried out just as the specification states in a manner that the dissolution was complete in both the samples and the MCR (BAM S0004) commercial standard of reference. This ensured that the Cr⁶⁺ and Cr³⁺ species of chromium were present in the resulting solution. The characteristic color of hexavalent chromium is an intense pink, as was observed in the stages of sample titration.

One of the determinant effects in the leaching method with mixtures of NH₄HF₂/H₂SO₄ and Mohr's salts was to protect the bond or valence states of chromium. The objective of this is to prevent interference or promoting redox phenomena between the Fe²⁺ and Cr⁶⁺, like has been discussed in household glass (Fernández Navarro, 1985). The nature of the vitrified products that were obtained here from the original

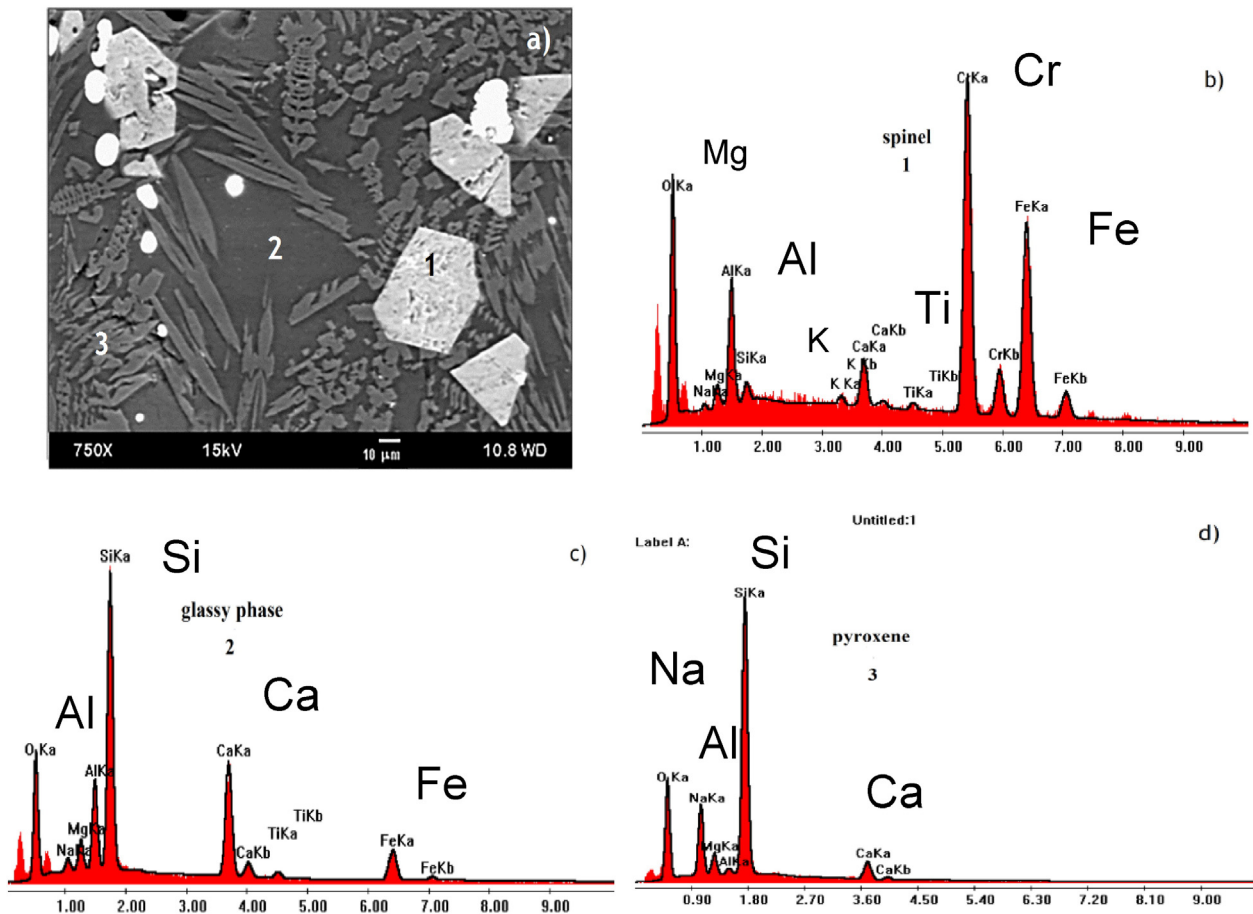


Fig. 6. a) Selected SEM micrograph obtained by the cross section of one of the glass-ceramic samples (from V2 original glass) exhibiting various sizes and shapes of polygonal spinel crystals together with other acicular and dendritic crystal growth of augite and pyroxene phases. Microanalysis EDS spectra are shown in: b) spinel crystal (labeled in the micrograph as number 1); c) residual glass phase (labeled number 2); and d) acicular and dendritic crystallizations (labeled number 3).

Table 2

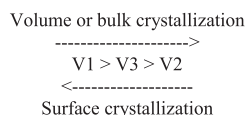
Physical characteristics of samples of residues contaminated by hexavalent chromium from the Cromatos de México Corporation.

Property	Contaminated soil	Slag	Demolition waste
	M1	M2	M3
Particle size (mm)	5	25	35
Moisture (% w/w)	52	5	5
Density (gr/cm ³)	1.21	1.22	1.2
pH	11	11	10
Water-soluble fraction (% w/w)	27.12	23	10

design of the glass has shown in the results of this paper the existence of chromium and iron spinels with valences in the trivalent state (Cr³⁺ and Fe³⁺), preventing the promotion of redox phenomena that affect actual readings in the determination of hexavalent chromium in the vitrified material.

4. Conclusion

The method for vitrification of a soil in an urban contaminated area containing high levels of hexavalent chromium adapted and developed here, for this research, represents a powerful and reliable tool for immobilizing this toxic chemical component. In the final products, both glass and glass-ceramic materials, the leached Cr⁶⁺ after etching determinations were evaluated. The hexavalent chromium concentrations obtained in the glass/glass-ceramics VC1, VC2, and VC3 produced values <0.22 mg/kg, values lower in comparison to the 5 mg/kg that the worldwide regulation specifies for releasing species of Cr⁶⁺ after leaching tests. Differential thermal analysis provide data about the thermal stability and phase transformation by crystallizations taking place in the original glasses (V1, V2, and V3), indicating DTA peaks of augite crystalline formation at 837 °C and chromium and iron spinel at 948 °C embedded in a residual silicate vitreous matrix. From the DTA results, the following relative thermal behavior between the synthetic laboratory glasses was verified, prepared with different concentrations of chromium residues:



Acknowledgement

The authors thank J. Cano for SEM Lab assistance at the Center of Wood Research in Castilla-la Mancha, Toledo, Spain, and Ballesteros thanks the IETcc-CSIC for allowing several stays throughout 2008–2010 in order to complete his doctoral thesis. Many thanks are also due to Paul Nordstrom from the Linguistic Support Unit at the Miguel Hernández University of Elche for carefully reviewing the English from the original manuscript.

Table 3

SEM/EDS average microanalysis of all crystalline phases obtained from all glass-ceramics obtained from the V1, V2, and V3 original glasses.

Oxide (weight %)	Diopside (CaMgSi ₂ O ₆)	Augite (Pyroxene) (CaMgAl ₂ Si ₂ O ₆)	Albite–Anorthite (NaAlSi ₃ O ₈ –CaAl ₂ Si ₂ O ₈)	Spinel (MgCr ₂ O ₄)
Na ₂ O	1.21	0.70	11.38 (8.23–13.56)	–
MgO	13.32	10.89	3.11	20.22
Al ₂ O ₃	5.26	11.17	19.36 (15.62–24.44)	9.89
SiO ₂	53.35	48.00	48.02	1.47
K ₂ O	–	–	1.25	–
CaO	22.31	22.40	14.84 (6.27–24.53)	–
TiO ₂	2.27	2.67	0.82	1.15
Fe ₂ O ₃	–	–	–	1.50
Cr ₂ O ₃	2.18	4.17	1.21	65.78

Table 4

Chromium (VI) determination and total chromium from UV/Vis and ICP spectrometry after leaching of vitrified products obtained from contaminated soil and close area sample specimens.

Original samples from contaminated areas	Name of vitrified product (glass)	Microstructure after controlled devitrification	mg/kg Cr ⁶⁺	mg/kg total Cr
M3 Construction demolition waste with Cr ⁶⁺	V3	Residual glassy phase, wollastonite, anorthite, and chromium spinel	<0.022	11.095
M2 Processing slag + soil with Cr ⁶⁺ + silica gravel	V2	Chromium spinel + augite, pyroxene + residual glassy phase	<0.022	13.730
M1 soil with Cr ⁶⁺ + silica gravel	V1	Chromium spinel + augite, pyroxene and residual glassy phase	<0.022	8.228
Conventional commercial glass as reference	BAM-S004 ^a	Glassy phase in solution + Cr ⁶⁺	448	463

^a National Bureau of Standards reference glass material.

References

- Aineto, M., Acosta, A., Rincón, J.M., Romero, M., 2006. Las escorias de la central térmica GICC ELCOGAS Como materia prima Para la síntesis de materiales vitrocerámicos. Parte 2: Síntesis y caracterización de los materiales vitrocerámicos. Boletín de la Sociedad Española de Cerámica y Vidrio 45 (1), 28–32.
- Ballesteros, S., 2014. Síntesis y caracterización de residuos con alto contenido en Cr (VI) a través de un método de vitrificación propuesto para la obtención de materiales vitro-cerámicos inertes. Ph.D. Thesis. Instituto Tecnológico de Saltillo, Coahuila, México.
- Ballesteros, S., Rincón, J.M., 2005. Vitrification of a Mexican chromium sludge with the production of a basalt like petrugral glass ceramic. International Congress on Valorization and Recycling of Wastes. VARIEREI 2005 (6 pp).
- Ballesteros, S., Rincón, J.M., 2011. Microstructure and Microanalysis of Porous Glass Obtained by Sintering of Vitreous Powders From Cr-Ni Sludge. 17, 2 pp. 1904–1905.
- Ballesteros, S., Parga, J.R., Romero, M., Rincón, J.M., 2006. Vitrification of a Mexican sludge with the production of a basalt like petrugral glass ceramic. In: Torres, L. (Ed.), 3rd International Symposium of Hybridized Materials with Super 3D Functions. Japan-Mexico Joint Meeting 1. University of Nuevo Leon, Monterrey (217 pp).
- Ballesteros, S., Parga, J.R., Delgado, A., Cano, J., Rincón, J.M., 2009. Electron microscopy study of vitrified materials from chemicals containing chromium contaminated soil and confined mud waste with chrome III and VI. Joint Meeting of the Spanish and Portuguese Microscopies Societies 1. IE University, Segovia, pp. 289–290.
- Ballesteros, S., Parga, J., Rincón, J.M., 2010. Vitrificación para inmovilizar residuos peligrosos. Ciencia y Desarrollo, CONACYT Ed., México. 243 (36), 6–11.
- Fernández Navarro, J.M., 1985. El Vidrio: constitución, fabricación, propiedades. CSIC Ed, Madrid.
- Hernandez-Crespo, M.S., Romero, M., Rincón, J.M., 2006. Nucleation and crystal growth of glasses produced by a generic plasma arc-process. J. Eur. Ceram. Soc. 26, 1679–1685.
- Hidalgo, M., Callejas, P., Rincón, J. Ma., J. Pask, J., 1988. Microstructure characterization of basalt glass-ceramics. In: Evans, A. (Ed.), Ceramic Microstructures '86. The Role of Interfaces 1. Plenum Publishing Corp. Berkeley, California, pp. 117–126.
- Hren, J.J., Goldstein, J.I., Joy, A.C., 1979. Introduction to Analytical Electron Microscopy. Plenum Press (Ed.).
- Kumar, M.D., Shripad, P.K., 2015. Recent advances in silica-based materials for the removal of hexavalent chromium: a review. J. Chem. Eng. Data 60, 2521–2540.
- Ladrón de Guevara, J., Moya, V., 1995. Toxicología Médica (Clínica e Industrial). McGraw-Hill Interamericana, Aravaca, Madrid (700 pp).
- Meegoda, J.N., Kamolpornwijit, W.K., Charleston, G., 2000. Construction use of vitrified chromium contaminated soils. Practical Periodical of Hazardous, Toxic and Radioactive Waste Management, pp. 89–98.
- Morse, R.E., 1994. Basalt Phase Diagrams. Heidelberg, Springer-Verlag, New York (493 pp).
- Palmer, C.D., Wittbrodt, P.R., 1991. Processes affecting the remediation of chromium-contaminated sites. Environ. Health Perspect. 92, 25–40.
- Rincón, J.M., 1990. Analytical electron microscopy as quality control for tiles. Tile Brick Int. 6 (4), 24–27.
- Rincón, J.M., 1992. Principles of nucleation and controlled crystallization of glasses. Polym.-Plast. Technol. Eng. 31 (3–4), 309–357.
- Rincón, J.M., 2016. Vitreous and ceramic processing for the recycling of industrial wastes. Key Eng. Mater. 663, 11–22.
- Rincón, J.M., Zayas M^a, E., 1994. Recycling of industrial wastes as glass-ceramic eco-products. 1st part. Técnica Cerámica 223, 220–229.
- Rincón, J.M., Romero, M., Jordán, M.M., Gutiérrez, J.P., 2001. Materiales Inorgánicos en la Construcción. UMH and IETcc-CSIC. XV CEMCO, Madrid-Elche (250 pp).
- Rincón-Mora, B., Jordán, M.M., Rincón, J.M., 2016. Chromium oxide additions in the lithium disilicate glass crystallization. Mater. Lett. 179, 138–141.

- Romero, M., Hernandez-Crespo, M.S., Rincón, J.M., 2009. Leaching behaviour of a glassy slag and derived glass ceramics from arc plasma vitrification of hospital wastes. *Adv. Appl. Ceram.* 108 (1), 67–71.
- Strachan, D.M., 2001. Glass dissolution: testing and modeling for long-term behavior. *J. Nucl. Mater.* 298, 69–77.
- Tinjum, J.M., Benson, C.H., Edil, T.B., 2008. Mobilization of Cr(VI) from chromite ore processing residue through acid treatment. *Sci. Total Environ.* 391, 13–25.
- Turkdogan, E.T., 1983. Crystal growth in undercooled liquids and glasses. *Physico-chemical properties of molten slags and glasses*. London: The Metals Society. 1 (373 pp).
- Uhlmann, D.R., 1980. Nucleation, crystallization and glass formation. *J. Non-Cryst. Solids* Volumes 38–39 (part 2, May–June), 693–698.
- US EPA, 1998. Toxicological Review of Hexavalent Chromium (In Support of Summary Information on the Integrated Risk Assessment System).
- Vicente-Mingarro, I., Callejas, P., Carda, J., Sales, M., Rincón, J.M., 1992a. TEM/STEM/EDX investigation of glass-ceramics obtained from Canarian álcali-basalts. In: Lopez-Galindo, A., M.I., R.-G. (Eds.), *Electron Microscopy 92. EUREM 92 2*. Universidad de Granada, Granada, Spain, pp. 405–406.
- Vicente-Mingarro, I., Rincón, J.M., Bowles, P., Rawlings, R.D., Rogers, P.S., 1992b. Viscosity measurements on glasses obtained from Canary Islands alkali volcanic rocks. *Glass Technol.* 33 (2), 49–52.