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Vitrification of incinerated tannery sludge in silicate matrices for chromium stabilization

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ABSTRACT

The vitrification process was applied for the stabilization and solidification of a rich in chromium ash that was the by-product of incineration of tannery sludge. Six different batch compositions were produced, based on silica as the glass former and sodium and calcium oxides as flux agents. As-vitrified products (monoliths) were either composed of silicate matrices with separated from the melt Eskolaite (Cr_2O_3) crystallites or were homogeneous glasses (in one case). All as-vitrified products were thermally treated in order to transform them to partially crystallized, i.e. devitrified products. Devitrification is an important part of the work since studying the transformation of the initial as-vitrified products into glass-ceramics with better properties could result to stabilized products with potential added value. The devitrified products were diversified by the effective crystallization mode and separated crystal phase composition. These variations originated from differences in: (a) batch composition of the initial as-vitrified products and (b) thermal treatment conditions. In devitrified products crystallization led to the separation of Devitrite ($\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$), Combeite ($\text{Na}_4\text{Ca}_4\text{Si}_6\text{O}_{18}$) and Wollastonite (CaSiO_3) crystalline phases, while Eskolaite crystallites were not affected by thermal treatment. Leaching test results revealed that chromium was successfully stabilized inside the as-vitrified monoliths. Devitrification impairs chromium stabilization, only in the case where the initial as-vitrified product was a homogeneous glass. In all other cases, devitrification did not affect successful chromium stabilization.

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1. Introduction

Currently, most of the global leather production utilizes chromium salts for leather tanning (Alibardi and Cossu, 2016; Mao et al., 2016; Celary and Sobik-Szołtysek, 2014). During the tanning process 60% of total chromium reacts with raw hides and animal skin, while the remaining 40% is discharged diluted in the wastewater. The processing of one metric ton of raw hide/skins produces 50 m^3 of wastewater (Kolomaznik et al., 2003), which contains 500–5500 mg/L trivalent chromium (Pathe et al., 2005). According to Kanagaraj et al., 2006, in annual basis about 6.5 million tons of wet salted hides are being processed, producing 300–500 million m^3 of wastewater annually, on global scale (Jaghava Rao et al., 2003).

Tannery sludge is the by-product from the processing of this wastewater through chemical precipitation achieved by the addition of lime and inorganic coagulants (Dhal et al., 2013). Through

this treatment almost all chromium is removed from the wastewater, forming a sludge with varying moisture content. The tannery sludge cannot be freely deposited due to its high organic carbon and trivalent chromium content. Additionally, high environmental risks stem from the potential transformation of trivalent chromium to hexavalent chromium, which is highly mobile, carcinogenic and toxic (Chen et al., 2012). Different methods of Cr stabilization/solidification have been proposed to further treat tannery wastes such as encapsulation, solidification or vitrification which are able to transform the sludge in pigments, cementitious, ceramics, and vitrificates (Chen et al., 2015; Celary and Sobik-Szołtysek, 2014; Montanes et al., 2014; Abreu and Toffoli, 2009) that could be either safely landfilled or even used in building applications (Xu et al., 2013).

Vitrification concentrates a significant number of advantages, which render it one of the most effective methods of solidification/stabilization of municipal and industrial solid wastes (Pisciella et al., 2001) including chromium containing wastes (Celary and Sobik-Szołtysek, 2014; Lazău and Vancea, 2014; Sobiecka and Szymanski, 2014). Its place in the field of solid waste

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management has been crucial since early 1960s, when it started developing as the method for immobilization of high-level radioactive wastes (Ojovan and Lee, 2014). A short list of vitrification's advantages comprises of (a) the high chemical stability of the end products, (b) their endurance with time, (c) their attractive physical characteristics (e.g. superior mechanical properties), (d) its versatility with respect to the broad range of wastes it can immobilize (Colombo et al., 2003), (e) the ability for complete decomposition of organic content and (f) the significant volume reduction of the waste varying from 20% up to 97% (Bernardo et al., 2012).

These significant advantages stem from the nature of the vitrification products and the conditions demanded for their synthesis. More specifically, numerous toxic elements can be incorporated in oxide glass matrices (LaGrega et al., 2001), while waste content can reach 60 wt.% of the batch materials (Kavouras et al., 2003a). Oxide glass structures have excellent chemical stability and durability, i.e. they are highly resistant against attack from water or other chemical agents. Consequently, vitrification products have low environmental impact and can potentially be deposited in landfills without any problems (Conner and Hoeffner, 1998). Additionally, in most cases the existing overarching framework of glass science can be utilized without the need to produce novel basic knowledge.

The fact that vitrification involves high temperature processing brings forth the only disadvantage of this process: its relatively high implementation cost. To this argument, several counter-arguments can be raised: (a) International, regional and State regulatory systems progressively become stricter on issues including classification of waste streams, maximum permissible extraction levels for toxic elements, and prerequisites for new landfill areas (Tchobanoglous et al., 1993). (b) Increasing social pressure. (c) There are several cases where solid wastes or their solid residues cannot be safely deposited in land filling areas, leaving no alternative apart from vitrification (Bernardo et al., 2012). (d) The ongoing transition from a linear to a circular approach of waste management strategies. After the application of urban mining concept in municipal and industrial waste streams (Baccini and Brunner, 2012), the residues should be placed in geological repositories, closing in such a way the material cycle (Cossu, 2012). (e) Vitrification products can be easily transformed into glass-ceramic materials, whose physical properties can be tailored, e.g. chemical resistance, appearance, mechanical properties (Strnad, 1986). These products result from the thermal treatment of vitreous materials and due to their enhanced properties could lead to the fabrication of value-added products for building or decorative applications, (Rawlings et al., 2006) lowering the cost of the total process. Vitrification technology as a remediation method for waste treatment has been practiced in many countries, particularly the United States. In the present work the vitrification method was applied in a laboratory scale, in order to stabilize/solidify a chromium-loaded ash that was the residue of incineration of chromium-containing tannery sludge with high organic carbon and trivalent chromium content. The scope was to investigate the ability to synthesize vitrified monoliths using chromium-loaded ash, considering chromium's low solubility in silicate melts and the subsequent production of glass-ceramics through controlled thermal treatment and crystallization of the initial as-vitrified products. The work was dictated from the fact that composition, shape and spatial distribution of the separated ceramic phases can be relatively easily controlled, by tuning devitrification conditions (Kavouras et al., 2003b). In connection, it has been proved that they straightforwardly affect chemical, morphological and mechanical properties (Pisciella et al., 2001). The novelty of this work lies upon the utilization of reagent grade raw materials in the vitrification step and the subsequent production of glass ceramics that would improve the properties of the vitreous products and potentially lower the cost of vitrification as they are proposed as added value

materials. In addition, research on the devitrification routes of all initial as-vitrified monoliths has depicted the role of the devitrification temperature and time on the stability, the microstructure and the properties of the end glass-ceramics. Special attention was paid on the fate of chromium after every treatment step, which was monitored through leaching tests.

2. Materials and methods

The initial waste was recovered from the industrial zone of Thessaloniki in northern Greece in the form of dried sludge. The sludge was pretreated in order to remove as much organic content as possible, while avoiding oxidation of chromium from the trivalent to the hexavalent form. The pretreatment step was composed of incineration at starved air conditions for 90 min at 500 °C. These conditions have been proved to remove 80% of sludge's organic content, while preventing chromium oxidation (Kavouras et al., 2015). The resulting ash was subsequently homogenized by mechanical action in a Fritsch Pulverizette 6 planetary mill.

Batch mixtures were prepared by mixing silica (SiO₂), soda ash (Na₂CO₃) and lime (CaCO₃) reagent grade powders in various proportions as it is listed in Table 1. SiO₂ is the glass forming oxide, while Na₂O and CaO glass modifying oxides (flux agents). Powder mixtures were co-melted for 120 min in a platinum crucible at 1400 °C and 1500 °C, depending on the batch composition, in order to achieve a homogenous melt. The melt was casted in air on a refractory stainless steel plate and cooled rapidly.

As-vitrified products were subsequently thermally treated, in order to foster crystallization and produce devitrified products. The vitreous nature of the as-vitrified products and the respective thermal treatment temperatures were determined by Differential Thermal Analysis (DTA) applied by a Setaram TG-DTA SetSys 1750 °C instrument in air. Heating and cooling rates were set at 10 °C/min and the samples were placed in Al₂O₃ crucibles.

All as-vitrified and devitrified products were structurally characterized by X-ray diffraction (XRD) technique with a Rigaku powder diffractometer, using CuKα1 radiation. Morphological characterization was made by optical microscopy and Scanning Electron Microscopy (SEM). The respective instruments were a Zeiss Axiolab-A metallographic microscope and a JEOL JSM-840A electron microscope. Elemental analysis for all products was made by Energy Dispersive Spectrometry (EDS) with an OXFORD ISIS-300 EDS analyzer, attached on the SEM instrument. Morphological observations were conducted on mirror-like polished or chemically etched surfaces of the products, depending on the type of characterization needed. Polishing was made by wet grinding utilizing SiC papers. The final finishing was achieved with 5.0 μm and 0.3 μm Al₂O₃ pastes. Chemical etching was made by attacking the samples' surface by HF 10% w/v solution, for duration of 5 min.

To get a first estimation on their environmental impact and the efficiency of the specific waste treatment processes used, the stabilization of Cr at the as-vitrified and devitrified products was verified by leaching tests. The standard leaching test EN 12457-4 (liquid per solid ratio – L/S 10 L/kg) was used to characterize the solidified materials. According to this test, as-vitrified and devitrified products were crashed to form pieces of less than 10 mm in diameter and were placed in bottles with deionized water (leaching solvent) for 24 h rotational mixing at 10 rpm. Total Cr in the leachates was determined using a Perkin Elmer Analyst 400 atomic absorption spectrophotometer and the examined solidified products were characterized based on the EU decision 2003/33/EC,¹

¹ Council of the European Union, 2003/33/EC: Council decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC, Official Journal of the European Communities, Brussels, 2003.

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