



Contents lists available at ScienceDirect

## Journal of Geochemical Exploration

journal homepage: [www.elsevier.com/locate/gexplo](http://www.elsevier.com/locate/gexplo)

## Vitrification of urban soil contamination by hexavalent chromium

S. Ballesteros<sup>a</sup>, J.Ma. Rincón<sup>b</sup>, B. Rincón-Mora<sup>c</sup>, M.M. Jordán<sup>c,\*</sup><sup>a</sup> Industrial Engineering Department, Tecnológico Nacional de México, Instituto Tecnológico de Tijuana, Av. Universidad s/n, Tijuana, BC, Mexico<sup>b</sup> Instituto de Ciencias de la Construcción Eduardo Torroja, Consejo Superior de Investigaciones Científicas, c/Serrano Galvache s/n, Madrid, Spain<sup>c</sup> 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  $\text{Cr}^{6+}$  wastes that are contaminating a Mexican urban soil. By means of a vitrification process, a method has been proposed that transforms  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  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  $\text{Cr}^{6+}$  was reduced to  $\text{Cr}^{3+}$  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,  $\text{Cr}^{6+}$ , 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.  $\text{Cr}^{6+}$  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 ( $\text{Na}_2\text{CrO}_4$ ), 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  $\text{Cr}^{6+}$  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  $\text{Cr}^{6+}$  contamination (Kumar and Shripad, 2015).

Chromate compounds present in the residue with  $\text{Cr}^{6+}$  solubilize with the passage of time at concentrations of 0.7–5% of  $\text{Cr}^{6+}$ , 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,  $\text{CaCrO}_4$ ; calcium aluminochromate,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CrO}_4$ ; tri-basic calcium chromate,  $[\text{Ca}_3(\text{CrO}_4)_2]$ ; and basic iron chromate,  $[\text{Fe}(\text{OH})\text{CrO}_4]$ ), which are slowly soluble in water, then form  $\text{Cr}^{6+}$  due to water filtration in the subsoil (Ballesteros, 2014; Tinjum et al., 2008).

Capillary migration of  $\text{Cr}^{6+}$  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](mailto: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).

$\text{Cr}^{6+}$  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  $\text{Cr}^{6+}$  to trivalent  $\text{Cr}^{3+}$ , 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  $\text{Cr}^{6+}$  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%  $\text{Cr}_2\text{O}_3$ , 0.3–1%  $\text{Cr}^{6+}$  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  $\text{Cr}^{6+}$ , 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  $\text{Cr}^{6+}$  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<sup>a</sup>, 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 ( $\text{Cr}_2\text{O}_3$ ) 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 ( $\text{Cr}^{6+}$ ) 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 $\alpha$  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).

Download English Version:

<https://daneshyari.com/en/article/5754502>

Download Persian Version:

<https://daneshyari.com/article/5754502>

[Daneshyari.com](https://daneshyari.com)