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Mercury leaching from hazardous industrial wastes stabilized by sulfur polymer encapsulation

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ABSTRACT

European Directive 2013/39/EU records mercury as a priority hazardous substance. Regulation n° 2008/1102/EC banned the exportation of mercury and required the safe storage of any remaining mercury compounds. The present work describes the encapsulation of three wastes containing combinations of HgS, HgSe, $HgCl_2$, HgO_2, $Hg_3Se_2Cl_2$, HgO and Hg^0, according to patent of Spanish National Research Council WO2011/029970A2. The materials obtained were subjected to leaching tests according to standards UNE-EN-12457 and CEN/TS 14405:2004. The results are compared with the criteria established in the Council Decision 2003/33/EC for the acceptance of waste at landfills. The Hg concentrations of all leachates were <0.01 mg Hg/kg for a liquid/solid ratio of 10 l/kg. All three encapsulated materials therefore meet the requirements for storage in inert waste landfills.

1. Introduction

European Directive 2013/39/EU (2013/39/EU, 2013) regards Hg as a priority hazardous substance. Indeed, a world-wide effort is now underway to reduce both the supply and demand of Hg. EU Council and European Parliament (2008/1102/EC, 2013) ban the exportation of Hg and its compounds and address the safe storage of metallic Hg. The export ban came into force on 15 March 2011 and affects metallic Hg, cinnabar ore, Hg_2Cl_2, and mixtures of metallic Hg with other substances, including Hg alloys, with a mercury concentration of at least 95% weight. As a result, all excess Hg must be stored in safe conditions in secure places until definitive stabilization policies are established (2008/1102/EC, 2013).

The legal basis for pre-treatment technologies for metallic mercury is collected in Regulation 1102/2008 (2008/1102/EC, 2013). It lies down that metallic mercury resulting from specific sources (e.g. chlor-alkali-plants) has to be considered as waste from 15 March 2011. In combination with the mentioned export ban of metallic mercury from 15 March 2011 a safe storage for considerable amounts of surplus mercury has to be ensured within the Community to prevent the metallic mercury from re-entering the market. Disposal of elemental mercury presents due to its liquid phase and high vapor pressure several emission risks. To reduce these risks, solidification of elemental mercury shall be considered as a possible alternative. Article 8 (2) of the Regulation foresees that the Commission shall keep under review ongoing research activities on safe disposal options, including solidification of metallic mercury.

In section (18) this researches to solidify metallic mercury is described to involve "techniques for stabilization or other ways of immobilizing mercury". Decision 2000/532/EC (2000/532/EC, 2000) defines stabilization and solidification in the following way: "stabilization processes change the dangerousness of the constituents in the waste and thus transform hazardous waste into non-hazardous waste. Solidification processes only change the physical state of the waste by using additives, (e.g. liquid into solid) without changing the chemical properties of the waste".

A huge number of researches have been carried out for the treatment of liquid mercury and mercury-containing wastes, as consequence of the European policies, as amalgamation, vitrification and stabilization/solidification (Busto et al., 2011; Randall and Chattopadhyay, 2004; Roussat et al., 2008; Zhang et al., 2009). Apparently the best technology to be applied seems to be stabilization/solidification, mainly sulfur polymer stabilization solidification, chemically bonded phosphate ceramics, cement mixtures... (Chattopadhyay, 2003; Chen et al., 2009; Fuhrmann et al., 2002).

The process patented by the Spanish Research Council (CSIC following its Spanish initials) (López et al., 2011a), developed as part

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of the MERSADE LIFE project, covers the conversion of elemental Hg into HgS by milling at room temperature. Equal quantities (by weight) of Hg and S (according to a stoichiometric excess of 45 wt%) are brought into contact in a ball mill containing stainless steel balls. The impact and friction forces of milling reduce the size of the Hg droplets (producing microspheres) and lower the surface tension to allow S grains to become adhered at the reaction interface, leading to the formation of metacinnabar. Milling is performed at 400 rpm for 15 min to 3 h. After 60 min of milling, the metacinnabar formation reaction is more than 99.99% complete. The process followed minimizes the oxidation of mercury to mercuric oxide because metacinnabar formation is carried out at low temperature, and also minimizes the amount of mercury which has not reacted in the first stage thanks to the extra sulfur content in the medium in the second stage (Lopez-Delgado et al., 2012b).

Encapsulation via the formation of sulfur polymeric cements (SPC) (Lin et al., 1995; Mohamed and Gamal, 2009; Vlahovic et al., 2011) containing sand and gravel has been successfully used for the immobilization of elemental Hg (Lopez-Delgado et al., 2012b) and phosphogypsum (García-Díaz et al., 2013b; López et al., 2011a), and in the utilization of waste ilmenite (Contreras et al., 2013). Different UNE (European Standard) and RILEM (Reunion Internationale des Laboratoires et Experts des Materiaux, Systemes de Construction et Ouvrages) standard tests have been used to examine the immobilization of elemental Hg in this way. Samples with very high Hg contents (up to 30% w/w, the maximum currently available) show no capillarity, their resistance to alkaline and acidic media is very high, they show good resistance to spray salt mist and freeze-thaw and dry-wet conditions, and the fire hazard of samples at low heat output is negligible (Lopez-Delgado et al., 2012a). The SPC developed to date have some applications as construction material (García-Díaz et al., 2013a; Tayibi et al., 2011a,b). However, the encapsulation of Hg and S described in this paper allows for a waste content of 60–70 wt%. Destined for storage in land-fills, and containing no sand or gravel, this material therefore allows much larger amounts of waste to be incorporated. The absence of gravel also reduces the costs associated with the treatment.

The present work describes the encapsulation of three wastes containing combinations of HgS, HgSe, $HgCl_2$, HgO_2, $Hg_3Se_2Cl_2$, HgO and Hg^0, following the process outlined in patent CSIC WO2011/029970 (López et al., 2011b). The encapsulates obtained were subjected to leaching tests according to standards UNE-EN-12457 (AENOR, 2003) and CEN/TS 14405:2004 (CEN, 2004).

2. Methods and materials

2.1. Origin of the examined wastes

The examined materials included: (1) an Hg-containing waste produced during the extraction of alumina from bauxite (sample ARS); (2) an Hg-containing waste from a mercury slurry derived from the wet purification of the gases produced during the roasting of sulfited zinc minerals (sample GTS); and (3) the Hg-containing powder from spent fluorescent lamps (sample SFL).

2.2. Experimental procedures

2.2.1. Waste characterization

Chemical composition of the different wastes were analysed by X-ray fluorescence using a Bruker S4 Pioneer system. A 1 g aliquot of each dry sample was mixed with 10 g of $LiBO_4$ and 5 drops of 20% LiI. The samples were thus turned into homogenous glass "pearls" for analysis. Mineralogical compositions were determined by X-ray diffraction using a Bruker D8 Discover diffractometer with Kα Cu radiation (40 kV, 30 mA). The patterns of diffraction were obtained in the 2θ scanning range from 10° to 100°, using a 3 s scan step time. True densities were determined using a AccuPyc II 1340 helium pycnometer. Granulometries were measured using a Malvern Instruments Ltd. Mastersize 2000 APA 2000 apparatus.

A representative amount of each sample was placed in water for 24 h to disintegrate the original matrix. Each sample was then introduced into a magnetic separator at a constant speed of 700 rotations min^{-1} to homogenize the matrix. Aliquots were then collected and the Hg concentrations determined using a LECO Instruments AMA 254 Mercury Analyzer.

2.2.2. Encapsulation

The three wastes were encapsulated in three steps:

(1) *Transformation of Hg into HgS (metacinnabar)*: The ARS, GTS and SFL samples were milled in a ball mill at 400 rpm for 1 h, along with the quantity of S required according to the stoichiometric equation below:

$$Hg + S \rightarrow HgS \quad (1)$$

(2) *Addition of further S*: The HgS obtained in the above step was mixed with 10 g of Rubber Soul 10 (grain size <60 μm) elemental S (Repsol IPF, Madrid, Spain) per kg of mercury wastes to produce a plastic material homogenate. This mixture was then pre-heated to 130 °C.

(3) *Encapsulation*: The hot mixture was kneaded, heated to 140 °C, and a modified sulfur-containing polymer (STX™, supplied by Starcrete™ Technologies Inc. Québec, Canada) added (5 wt% of the total final S content). This final mixture was placed in 16 × 4 × 4 cm molds and left to cool. Once room temperature had been reached, the casts – monoliths of encapsulate – were taken out of their molds and stored for later analysis. Fig. 1 summarizes the process. Fig. 2 shows

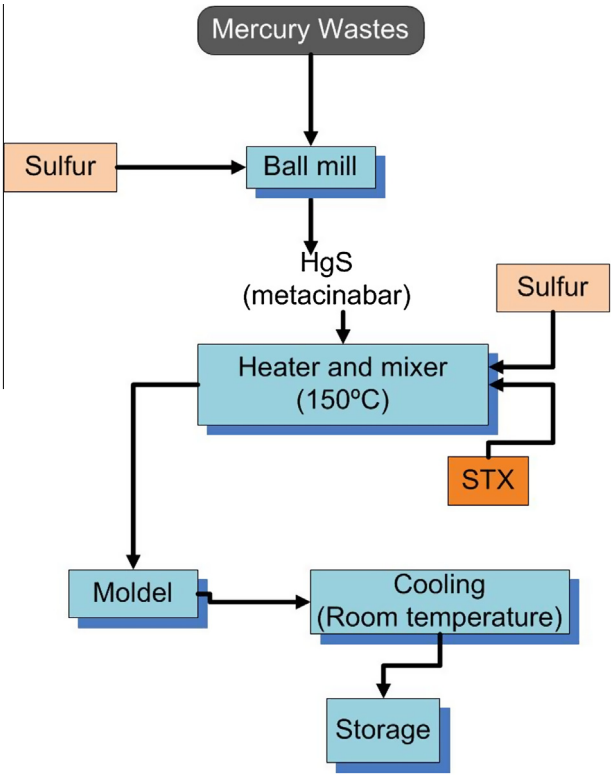

Fig. 1. The encapsulation process.