RECENT ADVANCES IN THE STABILIZATION OF HEAVY METALS FROM INDUSTRIAL WASTES INTO CERAMIC MATRICES

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ABSTRACT

The stabilization/solidification (S/S) of industrial wastes into clayey raw materials used in ceramic manufacturing represents an important environmental challenge. Such secondary resources can, actually, be considered as substitute materials in standard ceramic production, as they contain useful oxides. However, the presence of heavy metals in many industrial solid by-products is a significant environmental issue. Therefore, potential stabilization of these elements into ceramic matrices can be beneficial for protecting human and environmental health. Otherwise, possible leaching of pollutants caused by rain from clay-based ceramics incorporating industrial powders would possibly lead to contamination of surface and sub-surface water, thus arising critical environmental concerns.

In the present work, recent progress in the immobilization of potentially toxic heavy metals from various industrial waste by-products including coal/lignite fired power plant fly and bottom ashes, steel industry electric arc furnace dust and various sludges, into fired ceramic materials is reviewed. The environmental behavior of these ceramics during several leaching tests and ecotoxicological analyses is studied, in order to assess the potential for retention of such pollutants into clay-based ceramics towards their safe use as building products. These objectives are in line with Green Chemistry principles. Moreover, the aim of safely turning waste from one industry into useful feedstock for another one towards industrial symbiosis and ample coordination is strongly encouraged by current European Union environmental policies.

In fact, stabilization of potentially pollutant factors of industrial solid wastes, such as heavy metals, into environmentally-friendly clay ceramics can be achieved and appears a suitable alternative, as concentrations of these elements in the leachates, which depend on the leaching method employed and system parameters, can remain within acceptable limits.

Keywords: heavy metals, stabilization/solidification, leachability, industrial wastes, ceramics, solid wastes management.

1. Introduction

The stabilization/solidification (S/S) of industrial wastes into clayey raw materials used in standard ceramic manufacturing, placing special emphasis on resources optimization, to minimize uncontrolled waste disposal (Lyberatos and Nzihou, 2009) - a significant potential source of release of several environmentally sensitive elements to the environment - and also to reduce exploitation of natural raw materials, towards eco-friendly building materials production, will contribute to environmental protection and sustainable development. Moreover, value-added ceramic products will be obtained that can satisfy quality and technical requirements for a market of increasing competitiveness.

Actually, industrial solid by-products can be considered as substitute materials in ceramics fabrication due to their valuable oxides content. However, the presence of heavy metals, including As, Hg, Cd, Co Cr, Br, Sr, Pb, Se, Sn and Zn, constitutes a significant environmental issue. So far, the environmental compatibility of several industrial secondary resources, such as fly and bottom ashes produced in huge quantities in thermal power plants fed with high ash content low quality coals, and also steel industry electric arc furnace dust, various sludges from different origins, etc., has been evaluated by various leaching tests, including EN12457-2, TCLP, DIN38414-S4, NEN7341, AFNORX31-210, NBR10005 and JST-13. Apparently, the leachability of the compounds depends on the leaching test employed. Moreover, ecotoxicological characteristics of some industrial solid wastes have been determined using bioassays (Baba *et al.*, 2010; Badanoiu *et al.*, 2015; Kim and Lee, 2015; Orešanin *et al.*, 2007, Sebag *et al.*, 2009; Tsiridis *et al.*, 2012). Because of the mobility and bioavailability of many of the aforementioned elements upon water extraction, possible leaching of pollutants caused by rain can lead to contamination of surface and sub-surface water, which represents a critical environmental concern. Certainly, the mobility of most elements contained in combustion ashes is dominated by pH, which in turn is strongly influenced by the amount of calcium in fly ash (Izquierdo and Querol, 2012; Leuven and Willems, 2004; Tsikritzis *et al.*, 2013; Van Breemen and Vermij, 2007; Yuan *et al.*, 2010). The physicochemical processes and interrelationships of environmental contaminants including heavy metals into soil and subsurface have been extensively studied for predicting the fate of the pollutants and the risk they pose to human and ecological receptors so far (Kalavrouziotis *et al.*, 2009; Karapanagioti *et al.*, 2012).

Furthermore, presence of water soluble salts into ceramics can cause efflorescence phenomena, which are among the most frequent problems, especially on face bricks, affecting their aesthetic quality (Ana Andrés, 2009, Cultrone and Sebastián, 2008).

In the present study, recent progress in the immobilization of heavy metals from various industrial by-products into fired ceramic materials is reviewed. Possible immobilization of these potentially toxic elements into ceramic matrices encapsulating industrial powdery residues, will avoid leaching, water resources contamination and bioaccumulation of trace pollutants, thus, it can be much beneficial for protecting human and environmental health. The environmental behavior of these ceramics upon subjection to several leaching tests and ecotoxicological analyses is studied, in order to assess the potential for retention of such pollutants into clay-based ceramics, towards their safe use as building products. These objectives are in line with, at least, two of the Twelve Green Chemistry Principles, particularly with the 3rd paragraph (“Less Hazardous Chemical Syntheses”) and the 7th one (“Use of Renewable Feedstocks”) (Anastas and Warner, 1980). It should also be emphasized that the aim of turning waste from one industry into useful feedstock for another one is strongly encouraged by current E.U. environmental policies.

2. Stabilization/solidification of heavy metals from industrial solid wastes into ceramic matrices

Several studies are reported in recent literature on leaching behavior of heavy metals from different industrial solid waste by-products that have been stabilized/solidified in standard clayey raw materials used in the manufacture of resource efficient and lower cost ceramics, with physico-mechanical and chemical properties not significantly affected by the incorporation of the industrial by-products. In most cases, pH of the medium, varying with the leachant used according to the evaluation test employed, appears a determinant parameter for dissolution of metals, governing their release from the solid phase into solution. Indicatively:

Environmental properties of ceramics sintered via conventional technology or microwave radiation starting from extruded clayey mixtures encapsulating industrial powdery by-products, specifically from fly and bottom ashes derived from conventional burners and also circulating fluidized bed combustion (CFB) ash, were recently investigated, including the leaching properties followed by ecotoxicological analyses, to assess the potential for their safe use as building products. The ceramics so-produced would not be characterized as ecotoxic, since the ecotoxic effect of the leachates of crushed materials on the photobacterium *Vibrio fischeri* does not exceed 20% (Karayannis *et al.*, 2015; Karayannis *et al.*, 2013). Petrurgic method at 950°C for a mixture of fly ash and bottom ash was also proposed as a simple, inexpensive and energy saving method for the development of possible engineering and construction applications, as confirmed by the concentration of heavy metals upon leaching tests (Vu *et al.*, 2012).

Electric arc furnace dust (EAFD), generated upon steel scrap melting for steelmaking, from the volatilization of metals that are oxidized and subsequently solidified and detained in form of fine powder in specially designed filters, can also be regarded as a material of no environmental concern, by stabilization in non-metallurgical industries such as in structural clay ceramics. In fact, EN12457 standard leaching tests of mixtures of clay with 2.5 and 5 wt.% EAFD content, fired at 850, 900 and 950◦C, showed that the quantities of heavy metals leached from crushed blocks are within regulatory limits (Stathopoulos *et al.*, 2013). Other researchers also implied that using steelmaking dust in the manufacture of ceramic construction materials, such as clay bricks, ceramic ware and cement bricks, is both possible and reasonable (Karayannis, 2014; Lis and Nowacki, 2012). Moreover, utilization of other by-products of the electric arc furnace steelmaking process, specifically of electric arc furnace slag (EAFS) and ladle furnace slag (LFS), as admixtures into clay-based ceramic construction products fired at various temperatures, which can be used for protection from electromagnetic environmental pollution, is possible, since leaching test performed showed stabilization of all studied toxic elements within the sintered ceramic structure (Bantsis *et al.*, 2011). Environmentally-friendly incorporation (up to 9 wt.%) of mill scale, another steel industry waste, produced during the milling process from the rapid oxidization of the hot iron products, as an efficient secondary resource into red ceramics is also feasible (Spiliotis *et al.*, 2014).

Various by-products of other metallurgical industrial activities, currently being problematic wastes rather landfilled, are also under consideration for stabilization/solidification into ceramic matrices. In particular, leaching tests lead to conclusion that 50 and even 70 wt.% of red mud, an alkaline leaching waste from bauxite processing plant, is proper for being used by pressing with clay in the production of heavy clay ceramic bodies sintered at 900°C to 1190°C (Hildebrando *et al.*, 2013). Also, improvements in potential leachability of some pollutants can be attained by the incorporation of Waelz slag and foundry sand into clay-based bricks fabricated in a semi-scale industrial trial, incorporating additions to less than 30 wt.% to meet regulatory leaching limits for Mo (Quijorna *et al.*, 2012). Furthermore, by recycling metallurgical waste mixtures, including foundry sands, exhaust metallurgical dust, spent galvanic glass microspheres and acid inertization salt, into ceramic materials containing 75-85% of the industrial wastes and fired at 950-1010°C, heavy metals leaching and solubility remain hundreds of times less than those permitted by the national standards of Brazil, due to formation of a glassy structure with inclusion of newly formed minerals (Mymrin *et al.*, 2014). Moreover, the leachability of relatively large amounts of toxic metals found in industrial sludge generated in a hot-dip galvanizing process after wastewater neutralization reduces to a negligible level upon utilization of the sludge as raw material fired at 1020°C for possible use in masonry industry (Arsenovic *et al.*, 2012).

Sludges from textile industry wastewater treatment plants are often contaminated with heavy metals of dyestuffs and chemicals, and, therefore, they are considered hazardous. Mixing with clay can be an eco-friendly solution for the management of textile laundry wastewater sludge, incorporated up to a 20 wt.% to produce safe and inert bricks for civil construction, according to the results of the heavy metals leaching and solubilization tests (Herek *et al.*, 2012). Incineration techniques can also be used for as much as 80% textile sludge volume reduction and destruction of the hazardous elements. Then, stabilization/solidification of up to 10-20 wt.% of the incinerated ash into ceramic tiles and blocks can be achieved (Iqbal *et al.*, 2014).

Besides, geopolymerization is proposed as an alternative, environmentally-friendly and sustainable method for stabilization/solidification of industrial solid residues, making beneficial use of some of their typical characteristics, such as alkalinity and expressive aluminosilicate contents, leading to solid materials with similar properties to usual traditional ceramics, so that they can be used as construction materials. Specifically, geopolymer bricks from bauxite residue compositions, fired at 800°C, reach a leaching resistance closer to common pressed clay bricks (Bitencourt *et al.*, 2012). In other study, the leaching analyses applying the first order reaction/diffusion model, after immersion in pH 4 and 7 solutions, show that the heavy metals are effectively immobilized in mine tailings-based geopolymer bricks, which is attributed to the incorporation and immobilization of heavy metals into the geopolymer network. According to the experimental data, the leaching behavior is controlled to an extended degree by the solubility/reaction rate (Ahmari and Zhang, 2013). Furthermore, possible inertization of hazardous elements such as heavy metals in ferronickel slag geopolymers, in order to improve sustainability of the respective industrial sector, is influenced by monovalent and divalent anions, such as sulphate and nitrates (Komnitsas *et al.*, 2013).

3. Concluding remarks

Stabilization of potentially pollutant factors such as heavy metals of industrial solid wastes, including power station ashes, steelmaking by-products and various metallurgical wastes, into clay-based bricks is feasible. The results reported in several relevant studies show an affinity between clay and ash leading to manufacture of ceramics with relatively low lixiviation levels, as concentrations of these elements in the leachates remain within acceptable limits, thus providing an alternative to minimize the environmental impacts caused by several industrial activities.

Solubility appears an important factor controlling the leaching behavior. The potential of heavy metals to be transferred to the liquid phase depends upon:

- the leaching method used and
- the pH of the medium, which varies with the leachant used and appears a determinant parameter for the dissolution of the elements.

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