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# Vitrified medical wastes bottom ash in cement clinkerization. Microstructural, hydration and leaching characteristics



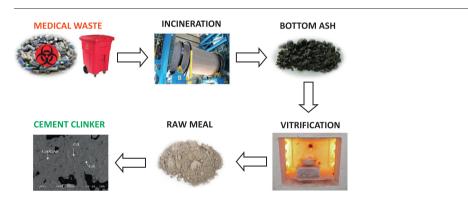
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#### HIGHLIGHTS

## G R A P H I C A L A B S T R A C T

- Medical wastes incinerator bottom ash was vitrified (VMBA) with recycled glass.
- VMBA was used in the raw meal for Portland cement clinkers production.
- All syntheses satisfied the requirements for strength class 52.5 (EN 197-1).
- Trace elements of VMBA and hydrated cements were well below regulatory limits.



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## ABSTRACT

The present investigation focuses on the utilization of medical wastes incineration bottom ash (MBA), vitrified with soda lime recycled glass (SLRG), as an alternative raw material in cement clinkerization. Bottom ash is recovered from the bottom of the medical wastes incineration chamber, after being cooled down through quenching. It corresponds to 10-15 wt% of the initial medical wastes weight and since it has been classified in the category of hazardous wastes, its safe management has become a major environmental concern worldwide. MBA glasses of various syntheses were initially obtained during the MBA vitrification simultaneously with various amounts of silica scrap (20, 25 and 30 wt% correspondingly). The produced MBA glasses were in turn used for the production of Portland cement clinker, after sintering at 1400 °C, thus substituting traditional raw materials. Both evaluation of vitrification and sintering products was carried out by chemical and mineralogical analyses along with microstructure examination. The final cements were prepared by clinkers co-grinding in a laboratory ball mill with appropriate amounts of gypsum ( $\approx$ 5.0 wt%) and the evaluation of their quality was carried out by determining setting times, standard consistency, expansibility and compressive strength at 2, 7, 28 and 90 days. Finally, the leaching behaviour of the vitrified MBA and hydrated cements, together with the corresponding of the "as received" MBA, was further examined using the standard leaching tests of the Toxicity Characteristic Leaching Procedure (TCLP) and the EN 12457-2. According to the obtained results, the quality of the produced cement clinkers was not affected by the addition of the vitrified MBA in the raw meal, with the trace elements detected in all leachates measured well below the corresponding regulatory limits.

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## 1. Introduction

The safe treatment and disposal of medical wastes, generated during health-care activities mainly in Health Units is one of the major environmental concerns in modern societies. They include a wide range of inorganic and organic-based materials, mentioned in the European Waste Catalogue - EWC (2001) of the Annex of the European Communities Decision, such as used syringes or needles, blood, body parts, chemicals, diagnostic samples, pharmaceuticals, medical devices, radioactive materials, etc. Although their hazardous content, according to the World Health Organization (WHO), is relatively low and has been estimated at about 20 wt%, it appears that several properties such as toxicity, infectivity, carcinogenicity, radioactivity etc. require special treatment. The remaining 80 wt% presents similar properties with the corresponding of municipal solid wastes (WHO, 1999a, 2010).

The main available treatment methods used today in developed countries worldwide, instead of disposal in sanitary landfills, are the alternatives of sterilization, such as thermal or chemical disinfection (mainly in case of lower pathogen load) as well as the corresponding of thermal treatment (incineration, pyrolysis, gasification) (Blenkharn, 2006; Matsui et al., 2003; Nema and Ganeshprasad, 2002; Park et al., 2009). Among the proposed methods, incineration (the process of wastes conversion into ashes and gases during their dry oxidation carried out at high temperatures) has been established as one of the best option for the management of the health-care hazardous wastes, both because of all their pathogen thermal elimination and the significant wastes weight/volume decrement (about 70 wt% or 90 v/v%) (Anastasiadou et al., 2012; Zhao et al., 2008a). When incineration is combined with energy recovery (electricity or heating recovery facilities) it could be considered, technically and economically, as the one of the most feasible solutions for most hospitalization wastes management (Alvim-Ferraz and Afonso, 2005; Shaaban, 2007; Xie et al., 2009). On the other hand, its main disadvantages, are the potential emissions of hazardous air pollutants (when the incinerator is not working properly), the relatively high operation and maintenance costs as well as the requirement for the produced ashes (fly and bottom ashes) special management (Jang et al., 2006; Lee et al., 2004; Ruoyan et al., 2010). Also, incineration is not considered a preferred treatment method for specific types of medical wastes such as radioactive and batteries (WHO, 1999b).

Regarding incineration bottom and fly ashes nature, it can be either calcareous or siliceous, containing also other metal oxides (aluminum, magnesium or iron) in lower quantities. Although their organic content is very low, representing no more than 1.0 wt% of the total (usually with no detectable content of Polychlorinated dibenzofurans (PCDFs) and Polychlorinated dibenzodioxins (PCDDs), being almost completely destroyed during the combustion process), they are always enhanced with metallic substances. All heavy metals, with the exception of mercury (that remains in vapour state) are entrapped in the produced ashes, as they cannot decamp along with the off-gases. Heavy metals (and metalloids) such as Ba, Zn, Ag, Cd and As, detected in the incineration ashes of medical wastes, are mainly originated from drugs and photographic or diagnostic materials. The corresponding quantities of Cu, Sn, Pb and Au are usually derived from medical instruments. The origin of metals such as Fe, Cr, Mo, Ni and Mn is mainly attributed to the stainless steel medical tools and other related instruments (ferritic or austenitic) while Ti and V are usually originated from the artificial implants burning (Zhang et al., 2002; Zhao et al., 2008b). Finally rare earths, together with Si and Al are constituents found in ceramics, electrodes, camera lenses and semiconductors. Taking into account the significant medical wastes weight reduction (about 70 wt%) during the incineration process, the final ashes heavy metals content is always higher than that of the initial medical wastes (Anastasiadou et al., 2012; Jung et al., 2004).

MBA is recovered from the bottom of the incineration chamber, after being cooled down through quenching. The latter corresponds to 10–15 wt% of the initial medical wastes weight and it is usually stored in closed drums or containers. Since MBA has been classified in the category of hazardous wastes, according to the EWC, its safe management has become a major concern worldwide (Chang and Wey, 2006). The option of landfilling, the most common and widely used practice today, is directly associated with the risk of hazardous substances leaching originated from the ashes to soil and ground water. In this sense, it has been suggested the control of heavy metals content through stabilization/solidification processes, prior to final disposal, thus minimizing their solubility and leachability, either by physical (encapsulation and immobilization in a binder matrix) or chemical transformation to more stable forms, generally in such levels that convert the incinerations ashes to an environmentally acceptable waste form for landfilling (Anastasiadou et al., 2012; Sobiecka et al., 2014; Tzanakos et al., 2014).

Although the common practice of disposal in secured landfills is nowadays substantially controversial, there are very few studies regarding the use of the alternative waste management method of valorization in MBA, mostly laid in its possible utilization as an additive in cement mortars (Filipponi et al., 2003; Genazzini et al., 2003, 2005), a filler material in road bases construction (Azni et al., 2005), as a raw material in ceramic industry, or as a filler material in concrete (Al-Mutairi et al., 2004; Tay, 1987).

In the published literature so far, has been given little attention to the bottom ashes inactivation through vitrification process, which could produce stable outgrowths that can be suitable for raw materials in the cement industry. In this context, the present investigation aims to the MBA utilization, after vitrification, as a raw material for the production of Portland cement clinker. According to the proposed experimental approach, MBA has been subjected in two different high temperatures processes; the first vitrificated at 1300 °C along with recycled glass, and the other corresponding to the raw meal clinkerization at 1400 °C. The latter process is targeting to hazardous content elimination at the highest degree, mainly through phase's transformation and incorporation reactions between elements.

### 2. Experimental

### 2.1. Vitrification process

The bottom ash used in the present investigation has been generated during the incineration process of medical wastes in a rotary kiln, carried out in the temperature range of 1100–1200 °C, with excess of air (about 70 wt%). The combustion residue, after being mechanical removed from the bottom of incinerator chamber, is directly cooled down through water-quenching, thus forming an amorphous black glassy cohesive matter, rich in silica (Anastasiadou et al., 2012;

Table 1	
Chemical analysis of raw materials and vitreous p	products.

Oxides	Raw materials analyses (wt%)					
	MBA	SLRG	VMBA <sub>20</sub>	VMBA <sub>25</sub>	VMBA <sub>30</sub>	
$\begin{array}{c} \text{SiO}_2\\ \text{Al}_2\text{O}_3\\ \text{Fe}_2\text{O}_3\\ \text{CaO}\\ \text{MgO}\\ \text{K}_2\text{O}\\ \text{Na}_2\text{O}\\ \text{SO}_3\\ \text{Cr}_2\text{O}_3\\ \text{ZrO}_2\\ \text{MnO}\\ \end{array}$	$\begin{array}{c} 57.52\pm0.1\\ 7.32\pm0.03\\ 1.18\pm0.01\\ 19.34\pm0.04\\ 1.83\pm0.05\\ 0.92\pm0.01\\ 6.50\pm0.2\\ 0.03\pm0.001\\ 0.42\pm0.005\\ 0.92\pm0.004\\ 0.04\pm0.002\\ \end{array}$	$\begin{array}{c} 71.87 \pm 0.1 \\ 2.05 \pm 0.03 \\ 0.48 \pm 0.01 \\ 9.74 \pm 0.04 \\ 2.14 \pm 0.05 \\ 0.45 \pm 0.01 \\ 12.62 \pm 0.2 \\ n.d.^a \\ 0.08 \pm 0.005 \\ n.d. \\ n.d. \\ 0.08 \pm 0.005 $	$\begin{array}{c} 62.35 \pm 0.1 \\ 6.51 \pm 0.03 \\ 1.02 \pm 0.01 \\ 17.75 \pm 0.04 \\ 1.97 \pm 0.05 \\ 0.83 \pm 0.01 \\ 7.57 \pm 0.2 \\ \text{n.d.} \\ 0.34 \pm 0.005 \\ 0.71 \pm 0.004 \\ 0.03 \pm 0.002 \end{array}$	$\begin{array}{c} & & \\ 63.05 \pm 0.03 \\ 6.05 \pm 0.03 \\ 0.87 \pm 0.01 \\ 17.46 \pm 0.04 \\ 2.02 \pm 0.05 \\ 0.80 \pm 0.01 \\ 8.11 \pm 0.2 \\ \text{n.d.} \\ 0.30 \pm 0.005 \\ 0.68 \pm 0.004 \\ 0.03 \pm 0.002 \end{array}$	$\begin{array}{c} 5.3\\ 63.58\pm 0.1\\ 5.85\pm 0.03\\ 0.83\pm 0.01\\ 16.89\pm 0.04\\ 2.05\pm 0.05\\ 0.75\pm 0.01\\ 8.38\pm 0.2\\ n.d.\\ 0.28\pm 0.005\\ 0.63\pm 0.004\\ 0.02\pm 0.002\end{array}$	
TiO <sub>2</sub> Cl <sup>-</sup> LOI <sub>1000</sub>	$\begin{array}{c} 0.61 \pm 0.005 \\ 0.38 \pm 0.001 \\ 3.95 \pm 0.05 \end{array}$	$0.07 \pm 0.005$ n.d. $0.17 \pm 0.05$	$0.59 \pm 0.005$ n.d. n.d.	$0.48 \pm 0.005$ n.d. n.d.	$0.35 \pm 0.005$ n.d. n.d.	

<sup>a</sup> n.d. = Not detected.

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