Stabilization of heavy metals using low-grade magnesia, Portland and Sorel cement

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Abstract

In this study, the stabilization/solidification of two common industrial solid wastes, i.e. Electric Arc Furnace Dust (EAFD) and Pb-ReFining Dust (Pb-RFD) was investigated. EAFD and Pb-RFD cannot be disposed even in waste landfills, because the leached concentrations of Pb from EAFD and of Sb from Pb-RFD exceeded the respective limit concentration values for disposal in hazardous waste landfills; therefore, these wastes have to be appropriately treated (stabilized) before the disposal. The stabilized wastes were prepared by mixing each one with low grade MgO, or Portland cement, or MgO with $MgCl_2$ (known as Magnesium oxychloride cement, or Sorel cement) at ratios 5-25 wt%. The respective control-leaching tests were conducted following the EN 12457-4 standard leaching test and the stabilized samples were classified according to the 2003/33/EC Decision, referring to the disposal of solid wastes in landfills. The leachates of stabilized EAFD with Sorel cement presented lower concentrations, than the regulation limits for disposal even in non-hazardous waste landfills. However, the stabilized EAFD-MgO and EAFD-Portland cement wastes cannot be disposed even in hazardous waste landfills. All differently stabilized Pb-RFD wastes can be further disposed in hazardous waste landfills.

Keywords: Stabilization; Electric Arc Furnace Dust; Pb-Refining Dust; Magnesia; Sorel cement; Portland cement

1. Introduction

Stabilization/solidification (S/S) is an effective technique for the treatment of large amount of wastes that are difficult to be treated by the application of other methods, such as recover/reuse or simply disposal in controlled landfills [1]. This technique can limit the solubility or mobility of hazardous substances and maintains them in their least mobile or toxic form [2]. Stabilisation refers to those techniques that reduce the hazardous behaviour of wastes by means of chemical reactions, whereas solidification refers to techniques that can generate a monolithic solid of high structural integrity [3]. As a result, the stabilized/solidified wastes can be safely disposed of in landfills with minimal risk of leaching toxic substances and polluting soil, surface or ground waters [4]. Portland cement, hydrated lime, phosphoric compounds, pozzolanic materials, such as fly ash, have been commonly examined/used as stabilizing additives in the S/S processes [4, 5].

Cement-based S/S is a widely used treatment process for immobilizing heavy metals. Toxic elements could be fixed in the resulting hydrated compound through the respective hydration reaction. The mechanism of S/S in this case can be written in a simplified way as [6]:

$A + B + H_2O \rightarrow H(M)OH_2$, where:

A: Portland cement

B: waste containing heavy metals

M: heavy metal

$H(M)OH_2$: hydrated compound containing M.

Magnesium Oxychloride Cement (MOC), also known as Sorel cement, is considered as non-hydraulic cement. MOC is produced by mixing MgO with $MgCl_2$ [7]. The bonding phase of MOC is created according to the following chemical reactions:

$3\ MgO + MgCl_2 + 11\ H_2O \rightarrow 3\ Mg(OH)_2.MgCl_2.8H_2O$ (phase 3)

$5\ MgO + MgCl_2 + 13\ H_2O \rightarrow 5\ Mg(OH)_2.MgCl_2.8H_2O$ (phase 5)

In this study, an efficient s/s process, that can allow the safe disposal of EAFD and Pb-RFD wastes in appropriate landfill sites, is proposed. An interesting approach, aiming to reduce the environmental and health impact of EAFD and of Pb-RFD wastes is the s/s by using MOC. Low-grade MgO and Portland cement were also examined in this work for the stabilization of EAFD and Pb-RFD wastes, in order to compare the results with those from EAFD and Pb-RFD stabilization, when using MOC.

2. Materials and Methods

Low-grade magnesia (MgO) is product of Grecian Magnesite S.A. (microcrystalline caustic calcined MgO) of 83.4% nominal purity, while Ordinary Portland Cement (OPC) is CEM II type with high resistance (42.5 MPa). $MgCl_2.6H_2O$ is a reagent of industrial grade, which contains 47% $MgCl_2$.

EAFD is a by-product of steel production in scrap recycling facilities [8], while Pb-RFD is produced during secondary lead (re-smelting) production [9]. The standard leaching test EN 12457-4 (i.e. leaching by using as solvent deionized water at liquid per solid ratio (L/S) 10 L/kg) was selected to characterize initial and stabilized EAFD and Pb-RFD wastes. Each waste was mixed with MgO, or OPC, or MgO with $MgCl_2$ (i.e. MOC) at ratios 5-25 wt%, and deionized water was accordingly added. The solid mixtures were subjected to the leaching test EN 12457-4 after aging for 15 days. The classification of initial wastes, as well as of the finally stabilized mixtures, was based on the 2003/33/EC Decision, regarding the acceptance of wastes in appropriate landfills [10]. The metal concentrations in leachates were determined by using Atomic Absorption Spectrophotometer (AAS), either with flame (Perkin Elmer Analyst 400), or with graphite furnace (Perkin Elmer Analyst 800).

3. Results and Discussion

The initial characterization of raw EAFD and of Pb-RFD waste is presented in Table 1. As shown in this table, the leached Hg and Se concentrations from EAFD, i.e. 1.5 mg Hg/kg and 1.2 mg Se/kg, exceed the respective limit concentration values for disposal in non-hazardous waste landfills (0.2 mg Hg/kg and 0.5 mg Se/kg, respectively). Furthermore, the leached concentration of Pb, i.e. 650 mg Pb/kg, exceeds the limit value for disposal even in hazardous waste landfills (which is 50 mg Pb/kg). Therefore, EAFD cannot be accepted for disposal even in hazardous waste landfills. The leached As, Cd, Hg, Pb and Se concentrations from Pb-RFD, i.e. 4.5 mg As/kg, 2.2 mg Cd/kg, 1.5 mg Hg/kg, 11 mg Pb/kg and 4.3 mg Se/kg, exceed the respective limit concentration values for disposal in non-hazardous waste landfills (2.0 mg As/kg, 1.0 mg Cd/kg, 0.2 mg Hg/kg, 10 mg Pb/kg and 0.5 mg Se/kg, respectively), according to the 2003/33/EC Decision, while the leached Sb concentration, i.e. 12 mg/kg, exceeds the limit value for disposal even in hazardous waste landfills (5 mg Sb/kg). Consequently, the Pb-RFD waste cannot be accepted for disposal even in hazardous waste landfills.

Table 1: EAFD and Pb-RFD wastes' leaching characteristics, by using the EN 12457-4 standard leaching test

	EAFD	**Pb-RFD**	**Detection limit**	**Regulation limits**		
				Inert waste	**Non-hazardous waste**	**Hazardous waste**
pH	12.3	11.2	-	-	-	-
EC (mS/cm)	18.0	17.6	-	-	-	-
Redox (mV)	+41.0	+456	-	-	-	-
mg/kg						
As	0.08	**4.5***	0.01	0.5	2	25
Ba	2.9	1.0	1	20	100	300
Cd	ND	**2.2***	0.01	0.04	1	5
Cr	4.4	0.6	0.1	0.5	10	70
Cu	ND	0.4	0.1	2	50	100
Hg	**1.5***	**1.5***	0.01	0.01	0.2	2
Ni	ND	ND	0.1	0.4	10	40
Pb	**650****	**11***	0.1	0.5	10	50
Sb	0.03	**12****	0.01	0.06	0.7	5
Se	**1.2***	**4.3***	0.01	0.1	0.5	7
Zn	ND	ND	0.1	4	50	200

ND: Not Detected

**Values which exceed the regulation limits for disposal in non-hazardous waste landfills according to Council Decision 2003/33/EC*

***Values which exceed the regulation limits for disposal in hazardous waste landfills according to Council Decision 2003/33/EC*

Figure 1(a) shows the Pb leached concentrations from the stabilized EAFD waste after 15 d allowed for aging at different proportions of the three examined additives, while Figure 1(b) shows the respective Se leached concentrations. The concentrations of Hg in these leachates, produced from the stabilized EAFD waste with different additives, are presented at Table 2. Hg concentrations were below the respective limit values for disposal in non-hazardous waste landfills and for all the examined stabilization processes; however, Pb and Se concentrations were found below these limit values (Pb 10 mg/kg and Se 0.5 mg/kg, respectively), but only at MOC s/s process. The EAFD waste treatment by using MgO and $MgCl_2$ (Sorel cement, MOC) was found to reduce significantly the leaching of heavy metals, as the pH values of the mixtures were ranged around 9.5–10.0, where the solubility of heavy metals is minimized [11]. Thus, the re-dissolution of heavy metals that can occur in higher (alkaline) pH values, e.g. by using certain alkaline additives, such as MgO or OPC, was avoided in this case. When mixing EAFD with MOC in proportions greater than 10%, that was resulted in the production of stabilized wastes, acceptable even in non-hazardous waste landfills, according to the 2003/33/EC Decision.

Table 2: Hg leaching behavior from stabilized EAFD

Additive	MOC	MgO	OPC
wt%		mg/kg	
5	ND	0.01	ND
10	ND	0.01	ND
20	ND	ND	ND
25	ND	ND	ND

ND: Not Detected

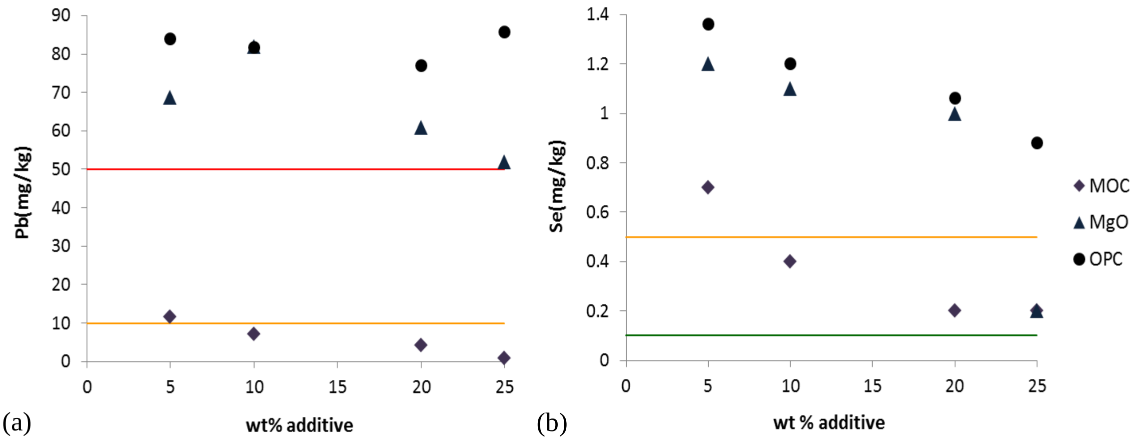

Fig. 1 (a) Pb, and (b) Se leaching behavior from the stabilized EAFD waste

Figure 2 shows the respective Se and Sb leached concentrations (as Fig. 2a and 2b) from the stabilized Pb-RFD waste after 15 d allowed for aging, by using different proportions of the three examined additives, while Table 3 presents the concentrations of As and Cd in the leachates and Table 4 shows the respective Hg and Pb leached concentrations. Specifically, As, Cd, Hg and Pb concentrations were below the respective limit concentration values for disposal in non-hazardous waste landfills and for all the examined stabilization processes, while Se and Sb concentrations were below the limit values, but only for disposal in hazardous waste landfills. According to the leaching results, all mixtures can be accepted for disposal in hazardous waste landfills. However, the mixing of Pb-RFD waste with MOC in proportion greater than 20% has resulted in the production of stabilized waste, acceptable even in non-hazardous waste landfills, according to the 2003/33/EC Decision.

Table 3: As and Cd leaching behavior from the stabilized Pb-RFD waste

	As			Cd		
Additive	**MOC**	**MgO**	**OPC**	**MOC**	**MgO**	**OPC**
wt%	**mg/kg**			**mg/kg**		
5	ND	0.08	0.24	ND	0.01	0.04
10	ND	0.05	0.17	ND	0.01	0.13
20	ND	ND	0.26	ND	ND	0.26
25	ND	0.17	0.15	ND	ND	0.15

ND: Not Detected

Table 4: Hg and Pb leaching behavior from the stabilized Pb-RFD waste

	Hg			Pb		
Additive	**MOC**	**MgO**	**OPC**	**MOC**	**MgO**	**OPC**
wt%	**mg/kg**			**mg/kg**		
5	ND	0.01	ND	ND	8.7	9.2
10	ND	ND	ND	ND	8.1	9.6
20	ND	ND	ND	ND	6.9	4.9
25	ND	0.01	ND	ND	5.9	8.0

ND: Not Detected

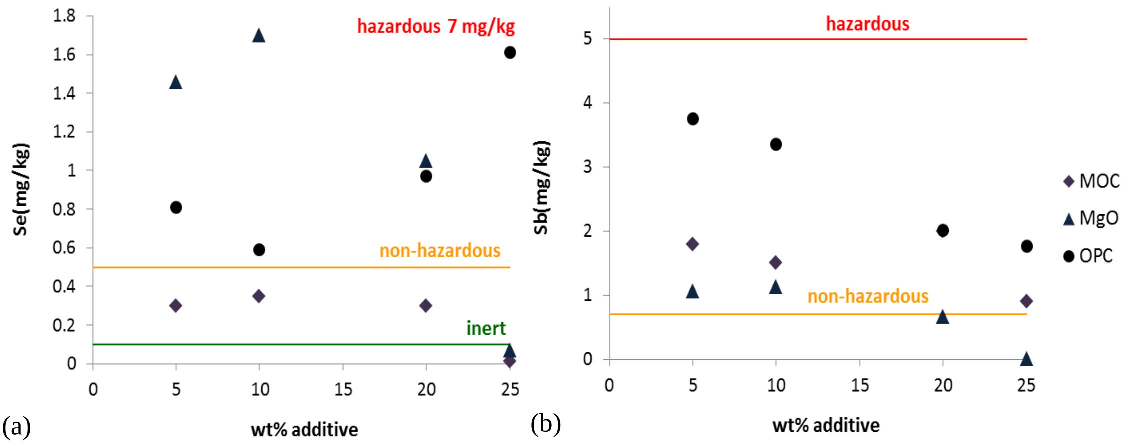

Fig. 2 (a) Se, and (b) Sb leaching behavior from the stabilized Pb-RFD waste

4. Conclusions

Several additives, i.e. low-grade magnesia (MgO), Sorel cement (MOC) and Portland cement (OPC) were examined to stabilize the heavy metals content in two common industrial solid wastes (EAFD and Pb-RFD), in order to be able to dispose them in the respective waste landfills, according to the Decision 2003/33/EC. The stabilized EAFD waste with MOC addition at 10 wt% can be disposed of even in non-hazardous waste landfills, according to the EC regulation, since the concentration of leached Pb was below the respective limit value for disposal in non-hazardous waste landfills, while the addition of OPC or MgO did not manage to limit the leaching of heavy metals bellow the limit concentration values for disposal even in hazardous waste landfills. The effectively stabilized Pb-RFD waste with MOC addition at 20 wt% can be disposed of even in non-hazardous waste landfills, while the addition of MgO or OPC was found to stabilize heavy metals in Pb-RFD, allowing it to be disposed of but in hazardous waste landfills, because the respective Se and Sb leaching concentrations did not exceed the limit values, but for disposal in hazardous waste landfills only.

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