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IMMOBILIZATION OF ELECTRIC ARC FURNACE DUST TOXIC ELEMENTS WITHIN THE MATRIX OF CONCRETE BASED PRODUCTS

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ABSTRACT
Electric Arc Furnace Dust (EAFD) generated through the production of carbon and alloy steel products is classified as environmentally hazardous waste mainly because of its relatively high levels of Pb, Cd and Cr. The aim of the present work was to investigate the effect of the EAFD addition on the properties of concrete building products (e.g concrete bricks) and to stabilize the toxic elements contained in EAFD in order to get environmentally accepted products. Concrete specimens were prepared by vibration and press-forming of mixtures containing cement, sand, dolomite, calcium stearate with water and the addition of different percentages of EAFD. For the immobilization of the toxic elements of EAFD within the matrix of the specimens, different percentages of each one of NaH_2PO_4, H_3PO_4 and of a mixture of H_3PO_4 - $FeSO_4.7H_2O$ were added successively to each one of the mixtures as stabilizing materials. Modulus of rupture (MOR) and water absorption (WA) tests showed that the specimens produced had specifications within accepted limits for relevant products. Leaching tests applied on the specimens proved the compliance with imposed leachate Maximum Acceptable Limits (MAL), since the practiced stabilizing materials effectively immobilize toxic elements within the prepared specimens.

KEYWORDS: EAFD; Concrete products; Metals immobilization; Stabilization; Leaching; Phosphates; Ferrous salts.

1. INTRODUCTION

The EAFD production is increasing proportionally to the increase of steel production by Electric Arc Furnace (EAF) process. The specific dust portion per ton of crude steel in the electric steel process is about 10 to 15 kilos or approximately 1.5% of the scrap steel charged to the EAF (Menad *et al.,* 2003; Mager *et al.,* 2000). The average range of Electric Arc Furnace Dust (EAFD) is about 10 kg per ton of steel melt. The worldwide output of EAFD exceeded the $3.7x10^6$ tn/year as was forecasted (Mager *et al.;* 2000). The EAFD produced annually in Greece from the five plants producing steel by EAF process was estimated to be approximately $3x10^4$ tons (Sidenor, 2008).

EAFD is classified as an environmentally hazardous waste in most regions of the world, mainly because of its relatively high levels of Pb, Cr, Cd and halides and in general because of its chemical and physical properties (Mitrakas *et al.,2007;* Cheng, 2003; Mager *et al.,* 2000). Among other parameters (Sikalidis *et al.,* 2006; Franco *et al.,* 2005) air pollution by EAFD particulates was reported to be connected to cancer (Adamson *et al.,* 2000; Valavanidis *et al.,* 2008). The chemical composition of EAFD depends on the quality of steel scrap processed, the type of steel being produced, the technological and operating conditions and the degree of dust recycling into process (Rocabois *et al.*, 2000; Delalio *et al.,* 2000; Sofilić *et al.,* 2004).

Most of the so far developed and commercialized processes are predominantly applied to the recovery of heavy metals from the EAFD, the re-cycling of EAFD and to a lesser extent to its inactivation prior to permanent disposal to landfills (Zunkel and Schmitt, 1995).

Currently, about 55% of EAFD is processed by high temperature metal recovery processes, mainly for Zn and Pb recovery. Although these methods and also the hydrometallurgical ones have high cost, are used because of the limited number of approved process alternatives for treating these hazardous wastes. Although developed and emerging technologies are available to stabilize EAFD for burial in landfills, the long term interest of industry and state will be better served by technologies that are utilizing EAFD in a way to result to profitable economics. Alternative processes have been developed to produce industrial products by using EAFD. Pisciella *et al.* (2001) used EAFD together with other industrial wastes to produce glasses. Sikalidis and Mitrakas (2006) completely stabilize EAFD within a sintered ceramic body and developed environmentally accepted ceramic products which resulted to profitable economics.

Almost all the rest 45% of the EAFD is disposed in landfills. EAFD must be stabilized for safe disposal in accordance to the environmental regulations, since it has been designed by the USEPA as a hazardous waste (K061). Many treatments have been applied for EAFD stabilization. Pereira *et al.* (2001) used coal fly ash as the fundamental raw material and main binder in EAFD solidification/stabilization process. The concentration of metals in leachate from the solidification/stabilization products was a strongly pH dependent; thus, the final pH of the leachate is the most important variable in reaching the imposed limits and therefore in meeting the stabilization goals. To assure that the Pb, Zn, Cr and Cd concentration limits are not exceeded in leachates, the final pH of the leachate must be within a range of values corresponding to the minimum solubility of the metals in the leaching medium. This is normally achieved in the pH range 8.0-11.3 for TCLP leachates and in the pH range 9.4-10.3 for DIN leachates. However, toxic wastes' leachate must fulfill the Maximum Acceptable Limits (MAL) for landfill disposal, which has already set for certain chemical parameters by the European Community (2003). In an attempt to reduce metals leachability of EAFD various acidic materials as immobilization materials were investigated (Mitrakas *et al.*, 2007). Among them H_3PO_4 proved the most effective one, since the concentration in leachate of all EAFD metals, especially that of Pb, was found almost two order lower than MAL in a wide range of pH (7-11.5).

The aim of the present work was to convert the toxic industrial waste EAFD, to a useful raw material for the production of environmentally accepted concrete building products by stabilizing the toxic elements that contains using phosphate acidic materials.

2. MATERIALS AND METHODS

2.1. Samples Preparation

Concrete based brick specimens were prepared by vibration and press-forming of mixtures containing cement, river sand and crushed dolomite with water and the addition of different percentages of EAFD and NaH_2PO_4, H_3PO_4 and a mixture of H_3PO_4 and $FeSO_4.7H_2O$ as acidic materials for heavy metals immobilization. The formula of the mixture, the preparation parameters and the groups of specimens prepared are given in the Table 1.

Table 1. Formula of the mixture and preparation parameters for the concrete based brick specimens

Formula of the mixtures		Preparation parameters	
River sand (0 -2 mm)	64 % w/w	Water to cement ratio	0.35
Dolomite (0-1mm)	15 % w/w	Frequency of vibration	3000 sc min^{-1}
Cement I 42.5N	21 % w/w	Amplitude of vibration	0.4 mm
Calcium stearate 66g /100 kg of the batch		Pressure applied	100 kg cm^{-2}
EAFD[1]	0, 5, 10 and 15 % w/w	Size of the specimens, cm	
(in substitution of the sand)		16x4x4, 10x10x3	
1st Group of specimens			
NaH_2PO_4, 1, 2, 3 % w/w in addition in specimens containing 0, 5, 10, 15 % w/w EAFD			
2nd Group of specimens			
H_3PO_4 1, 2, 3 % w/w in addition in specimens containing 0, 5, 10, 15 % w/w EAFD			
3d Group of specimens			
H_3PO_4 1 % w/w + $FeSO_4.7H_2O$ 0.25 % w/w,			
in addition in specimens containing 0, 5, 10, 15 % w/w EAFD			

[1] Chemical characteristics in Table 2

2.2. Methods of Analyses and Testing

The concentrations of the metals in the EAFD as well as in the specimens' leachates were determined by using a Perkin Elmer AAnalyst 800 atomic absorption spectrophotometer either with flame or graphite furnace. Carbonate and hydroxide content of leachates were determined by titration according to Standard Methods 2320 B. (Alpha AWWA WEF, 1992). Leaching tests on EAFD and specimens were performed in compliance to EN 12457.1 (2002) and EN 12457.4 (2002) according to the particle size of the material. The method followed for the study of influence of pH on leachability is described by Mitrakas *et al.*, (2007). The testing methods and the accepted values for Modulus of rupture (MOR) and water absorption for the prepared products are given by Sikalidis and Mitrakas (2006).

3. RESULTS AND DISCUSSION

3.1. Chemical and technical characteristics.

The Pb concentrations in the EAFD leachate (Table 2) were found to be far above the MAL (EN 12457, 2002) suggesting the necessity of measures to be taken in order to be disposed in landfills.
In addition, the experimental results of Table 2 show that significant quantity of Cr(VI) was leached from cement, which contribute to the total chromium leached from the concrete based specimens. In order to stabilize the leached Pb, the EAFD was incorporated in concrete building products.

Table 2. Chemical characteristics of EAFD, its leachate* and of cement leachate**

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
EAFD, wt%	0.06	0.31	0.24	27.8	2.6	0.03	2.2	2.1
EAFD Leachate, mg kg^{-1}	0.83	0.23	4.8	ND	ND	ND	873	13.7
MAL, mg kg^{-1}	3	25	50	-	-	20	25	90

	EAFD Leachate	Cement Leachate
Conductivity	52 mS cm^{-1}	12540 μS cm^{-1}
pH	12.45	12.55
Hardness	769 ^{0}F	662 ^{0}F
CO_3^{2-}	1560 mg kg^{-1}	
OH^-	1462 mg kg^{-1}	
UV_{254}	0.92 dm^{-1}	
Pb		0.5 mg kg^{-1}
Cr(VI)		9.6 mg kg^{-1}

*L/S = 2 ** L/S = 10, (Liquid to Solid concentration according to EN-12457, 2002).
ND = Non Detected.

Table 3. MOR* and WA of the concrete based specimens prepared by the addition of EAFD and of successive over and above addition of each one of NaH_2PO_4, of H_3PO_4 and of H_3PO_4 plus $FeSO_4.7H_2O$

EAFD	NaH_2PO_4			H_3PO_4			H_3PO_4 (1 wt%) plus $FeSO_4.7H_2O$ (0.25 wt%)		
wt%	wt%	MOR kgf cm^{-2}	WA wt%	wt%	MOR kgf cm^{-2}	WA wt%	wt%	MOR kgf cm^{-2}	WA wt%
0	0	43	7.6	0	43	7.6	0	43	7.6
5	0	44	7.6						
»	1	43	8.1	1	41	3.7	1.25	36	4.2
»	2	42	8.3						
»	3	42	8.6						
10	0	48	7.8						
»	1	36	8.4	1	36	3.9	1.25	31	4.5
»	2	35	8.5						
»	3	33	9.7						
15	0	46	7.6						
»	1	30	8.6	1	30	4.4	1.25	26	4.7
»	2	28	9.0						
»	3	20	9.3						

*MOR tests were performed 27 days after the specimens' preparation day

MOR and WA were tested since these properties are essential for the specimens' technical characterization. They were measured according to EU standard methods of testing of EN 772-01 (2000). The addition of EAFD found to have a positive effect on MOR values being in agreement to Sikalidis and Mitrakas (2006). The addition of stabilizing materials found to have a noticeable negative effect especially in the case of higher EAFD concentrations (Table 3). The presence of these materials might affect negatively the formation of other compounds that assist setting and strength, which needs further investigation. Low WA values observed in the case of H_3PO_4 and of $H_3PO_4/FeSO_4.7H_2O$, were connected to relatively higher MOR values compared to NaH_2PO_4 addition. This also could be attributed to the effect of stabilizing materials on the formation of various compounds during setting, which needs also further investigation. Concerning the MOR and WA values, from the added stabilizing materials, the a) 1 wt% NaH_2PO_4, b) 1 wt% H_3PO_4 and c) 1.25 wt% [H_3PO_4 (1 wt%) plus$FeSO_4.7H_2O$ (0.25 wt%)] additions over and above the 5 wt% EAFD appears to be the most promising (Table 3). The MOR and WA values could be improved by more intense vibration of the moulds and relatively higher powder pressing.

3.2. Leaching tests

The European Counsel Directive 33/16-1-2003, is establishing MAL for the elements under consideration for disposal of the wastes in landfills. The addition of EAFD alone in concrete-based specimens might result to products which are close to the limit in order to be characterized as environmentally accepted. The quantities leached in mg kg^{-1} according to the EU directive 33 (2003), for the most of the chemical parameters are lower from the accepted limits i.e.: As<0.02, Ba<1, Cd<0.002, Cu<0.2, Fe<0.5, Hg<0.002, Mn<0.2, Ni<0.2, Sb<0.02, Sn<0.2, F^- 1-3, Cl^- 2-4x10^3, PO_4^{3-} 0.2-0.6. This low leachability of the toxic parameters could be attributed in both; the fixation of the wastes particles in the concrete solid matrix and the immobilization due to chemical binding of the elements.

However, EAFD addition of 10 and 15 wt% resulted in leached Pb quantities 5.1 and 5.5 mg kg^{-1}(Table 4), respectively, over passing the MAL (5 mg kg^{-1}) for non dangerous wastes disposal.

Table 4. Influence of NaH_2PO_4, H_3PO_4 and of H_3PO_4 / $FeSO_4.7H_2O$ additions on Pb and Cr(VI) leachability from concrete based specimens prepared by EAFD addition

EAFD	NaH_2PO_4	Leachate Pb	Leachate Cr(VI)	H_3PO_4	Leachate Pb	Leachate Cr(VI)	1wt%H_3PO_4 plus 0.25wt% $FeSO_4.7H_2O$	Leachate Pb	Leachate Cr(VI)
wt%	wt%	mg kg^{-1}		wt%	mg kg^{-1}			mg kg^{-1}	
5	0	1.0	2.7		1.0	2.7		1.0	2.7
»	1	0.8	2.7	1	0.8	0.6	1.25	0.7	0.4
»	2	0.5	4.3						
»	3	0.2	6.4						
10	0	5.1	4.0						
»	1	1.8	4.1	1	2.3	1.4	1.25	2.3	0.5
»	2	1.5	5.4						
»	3	1.4	7.2						
15	0	5.5	4.3						
»	1	2.6	5.1	1	4.3	1.5	1.25	3.3	0.8
»	2	2.2	6.3						
»	3	2.0	8.4						

MAL in mg kg^{-1} (Liquid/Solid ratio, L/S=2) for Pb and Zn for inert, non dangerous and dangerous wastes for landfill disposal (EN 12457-1, 2002)

	Inert wastes	Non Dangerous	Dangerous wastes
Pb	0.2	5	25
Cr	0.2	4	25

This high leachability of Pb could be attributed to high pH value of the leachate (Table 5), since from pH 12 to 13, Pb appears in the extremely soluble form $Pb(OH)_4^{2-}$ according to the reaction 1:

$$Pb^{2+} + 4H_2O \leftrightarrow Pb(OH)_4^{2-} + 4H^+ \qquad \log K = -39.699 \qquad (1)$$

Leaching tests performed on concrete-based specimens containing various percentages of EAFD (5, 10, 15 %) showed that after the additions of even 1% of NaH_2PO_4 or H_3PO_4 or of H_3PO_4 / $FeSO_4.7H_2O$ mixture, the Pb concentrations in the leachate decreases significantly below MAL for landfill disposal of non-dangerous materials (Table 4). This low Pb solubility could be attributed to the formation of pyromorphite type minerals (Yang *et al.*, 2001) favored from the presence of relatively high Cl^- (2-4 g kg^{-1}) concentration (reaction 2). These results are in agreement with previous work of Mitrakas *et al.*, (2007).

$$5Pb^{2+} + 3H_2PO_4^- + Cl^- \leftrightarrow Pb_5(PO_4)_3Cl_{(s)} + 6H^+ \qquad \log K = -25.05 \qquad (2)$$

The relatively high quantities, in comparison to above mentioned metals, of Cr in Cr(VI) form that leached from concrete-based specimens was attributed to cement (Table 4), since no Cr(VI) detected in EAFD leachates. However, the quantity of Cr(VI) was increased as the addition of NaH_2PO_4 increased (Table 4), either due to the increase of hydroxyl concentration, or probably due to the higher amount –as expressed by the conductivity - of soluble salts leached (Table 5).

Addition of NaH_2PO_4 results in precipitation of metals in the most insoluble form of phosphate salts instead of hydroxides increasing hydroxyl and other soluble ions (e.g. chromate) concentration and in the leachate. For this reason the experiments with additions of H_3PO_4 and of H_3PO_4 / $FeSO_4.7H_2O$ mixture were performed. These additions were successfully reduced the concentration of Cr(VI) in the leachate below the MAL (Table 4). Experimental data of Table 4 showed also significant influence of Fe^{2+} to Cr(VI) leached, due to Cr(VI) reduction to most insoluble form of Cr(III) hydroxide.

Table 5. Influence of NaH_2PO_4, H_3PO_4 and of H_3PO_4 / $FeSO_4.7H_2O$ additions on the leaching characteristics of concrete based specimens prepared by EAFD addition

EAFD (wt%)	NaH_2PO_4 (wt%)	pH	Conductivity (mS cm^{-1})	Hardness (^0F)	OH^- (mg kg^{-1})	CO_3^{2-} (mg kg^{-1})
0	0	12.45	7.5	573	2,217	192
5	0	11.85	7.5	610	1,496	288
»	1	12.00	10.5	274	2,462	240
»	2	12.00	12.9	285	2,829	288
»	3	12.00	15.9	291	2,843	480
10	0	11.75	10.4	587	1,333	240
»	1	11.85	11.5	276	2,189	240
»	2	12.00	14.8	287	2,842	240
»	3	12.10	21.3	302	3,305	336
15	0	11.70	10.5	613	1,210	144
»	1	11.85	12.6	347	1,700	192
»	2	12.15	17.4	353	2,955	238
»	3	12.15	17.5	385	2,992	240
0	1% H_3PO_4	12.45	7.5	573	2,217	192
5	>>	11.95	8.4	693	999	96
10	>>	12.05	10.1	740	1,020	96
15	>>	12.05	13.5	756	1,129	120
0	1wt% H_3PO_4 plus 0.25wt%$FeSO_47H_2O$	12.45	7.5	573	2,217	192
5	>>	12	8.7	724	755	120
10	>>	12	10.3	740	939	120
15	>>	12.05	12.5	771	755	120

4. CONCLUSIONS

The main problem for the environmental disposal of the EAFD is the high leachability of the various toxic metals that contains and mainly of Pb. Technological tests support the utilization of EAFD as raw material in the production of concrete-based building products like bricks, tiles etc, if the Pb leachability problem could be solved. The Pb stabilization within the structure of these products was achieved with the addition of small percentages of each one NaH_2PO_4, H_3PO_4 and $H_3PO_4/FeSO_4.7H_2O$ mixture. Furthermore H_3PO_4 and $H_3PO_4/FeSO_4.7H_2O$ mixture additions were successfully reduced both, the concentration of Cr(VI) and of Pb in the leachate, significantly below the MAL for non dangerous wastes for landfill disposal. The products obtained found to be technically and environmentally accepted, resulting also to profitable economics.

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