

Stabilization of Cr in fly ash using magnesia

E. Ntinoudi¹, H. Yiannoulakis², Th. Zampetakis², A.I. Zouboulis¹ and E. Pantazopoulou¹

¹Department of Chemistry, Aristotle University, Thessaloniki, GR 54124, Greece

²Grecian Magnesite Research & Development Centre, Thessaloniki, GR 57006, Greece

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Presenting author email: evaggeliantinou@gmail.com

Abstract

Lignite thermal power plants are the main source for electricity generation in Greece resulting in large amounts of fly ash (FA), reaching about 12 million tonnes per year. The reuse of fly ash is rather limited and a relatively small amount is used in cement or in other construction materials. Characterization of the FA leachates showed high amounts of hexavalent chromium which exceeded the acceptable level for disposal in non-hazardous waste landfills according to EU Decision 2003/33/EC. In this study, the stabilization of Cr (VI) in FA was examined by the addition of magnesia (MgO). FA was mixed with MgO in different ratios and the stabilized mixtures were subjected to the standard leaching test EN 12457-2 after 7 and 42 days, in order to check long term stability of the stabilized mixtures. Mixing FA with MgO resulted in a stabilized waste accepted for disposal in landfills for non-hazardous wastes with the addition of only 5% MgO. MgO might be used as an alternative amendment material for Cr stabilization, presenting additional benefits, such as the reduced purchasing cost.

1. Introduction

Lignite is the main source for electricity generation in thermal power plants in Greece, producing around 50% of the country's power requirements and resulting in large amounts of FA, reaching about 12 million tonnes per year. FA is produced as a by-product during the combustion of lignite in boilers of electrical power stations, collected from off-gas combustion in electrostatic precipitators and deposited on the soil around the power plant [1, 2].

FA particles are spherical and are composed primarily of amorphous ferro-aluminosilicates. The aluminosilicate matrix of FA may contain calcium oxides and various trace elements [3]. Ptolemais FA is produced in North Greece. The CaO content is always higher than 20% and thus it is characterized as cementitious. It is classified as Type C FA, as the sum of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ is between 50% and 70% [1].

FA is mainly used in the cement industry replacing cement clinker and aiming to the production of special types of Portland cements (CEM II type), according to EN 197-1 standard. FA has predominantly been used as a raw material in the construction industry for the production of several mortars, pavement blocks, as structural fill, in embankments and for the production of fly ash-cement grouts [4, 5]. However, only about 10% of the total FA volume is used, while the rest is disposed of in exhausted lignite mines, exposed to weathering [1].

Stabilization/solidification aims to convert hazardous substances to more stable chemical forms, which are much less soluble, mobile and toxic, using various additives, therefore stabilized wastes can be safely disposed to the environment with minimal risk of leaching toxic substances and polluting surface water or groundwater resources [6]. Various stabilizing agents (amendments), such as cement, hydrated lime, phosphoric compounds, as well as pozzolanic materials, have been used in stabilization/solidification processes [6, 7].

The current global trend towards increasingly stringent environmental standards, favor the use of more cost-effective and less disruptive sorbent materials for the treatment of heavy metal-contaminated solid wastes. Heavy metal stabilization in highly contaminated soils and in electric arc furnace slag (EAFD) using MgO has been proposed by Garcia et al. and Cubukcuoglu et al., respectively [8, 9]. Specifically, in this study, MgO was examined for the treatment of FA, in order to stabilize Cr (VI). Cr (VI) concentration of FA leachate exceeds the limit value for disposal at landfills for non-hazardous wastes, according to the EU Decision 2003/33/EC [10].

2. Materials and Methods

In this study FA, which is produced as a by-product in the thermal power plant of Ptolemais in Northwest Greece, was used. The MgO was a Grecian Magnesite S.A. microcrystalline caustic calcined magnesia (grade 83 CG) of 83.41% nominal purity, specific surface area of 32 m²/g, milled below 75 μm.

FA was mixed with MgO in different ratios (40:60, 50:50, 60:40, 70:30, 80:20, 90:10, and 95:5) and deionized water was added, according to the absorption capacity of the solid mixture. Formulations were left to age for 7 days (short-term study of stabilization) and 42 days for long-term study of stabilization. Leaching tests were conducted with deionized water at L/S 10 L/Kg, following EN 12457-2 standard leaching test. Classification of the examined wastes was based on the EU Decision 2003/33/EC, regarding the acceptance of wastes at landfills [10]. Heavy metals, which exceed non-hazardous limit values, were determined using atomic absorption spectrometer (AAS Analyst 400). In order to determine the amounts of Cr(VI) present, the samples were analysed with the diphenylcarbazide colorimetric method [11]. According to this method, Cr(VI) reacts with 1,5-diphenylcarbohydrazide in an acidic medium (H₂SO₄) to produce a reddish-purple colour, which is measured photometrically at a wavelength of 540 nm.

3. Results and Discussion

Table 1 shows the chemical composition in the form of oxides of Ptolemais FA, which is used in this study. Ptolemais FA, a typical Type C FA, contains 20.2% wt. CaO and 65.8% wt. $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$. XRD analysis of FA is presented in Figure 1 and reveals the presence, among others, of quartz, anorthite, anhydrite, calcite and lime.

Table 1 Typical analysis of FA

% wt.								
Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	SiO_2	TiO_2	SO_3
16.3	20.2	7.0	1.65	3.6	0.75	42.5	1.0	7.0

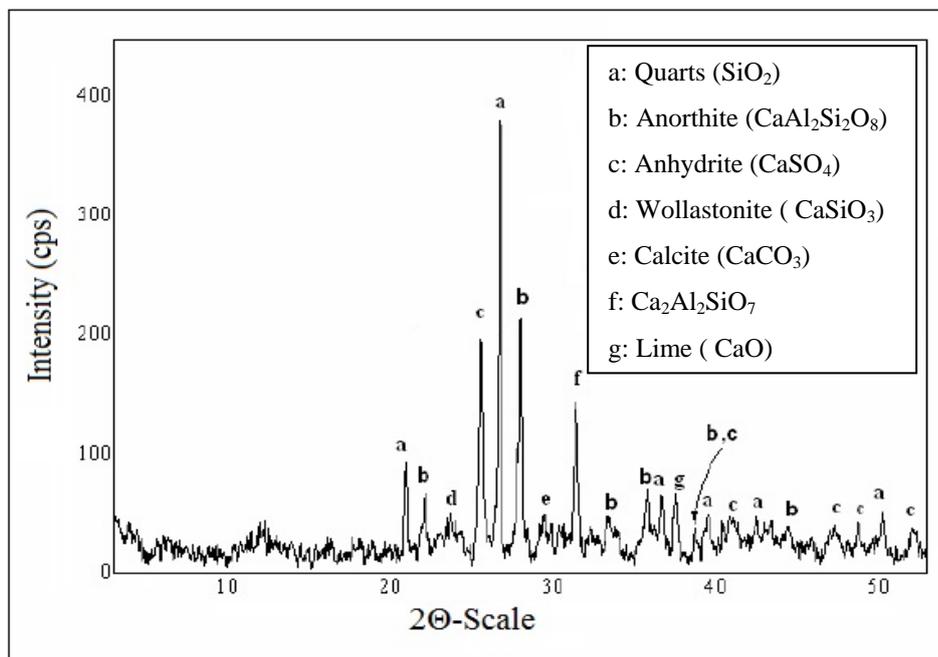


Figure 1 XRD diagram of FA

Characterization of FA is presented in Table 2. As shown in the table, the leached Cr concentration, i.e. 16.5 mg Cr/kg, exceeds the limit value for disposal in non-hazardous waste landfills (10 mg Cr/kg), according to EU Decision 2003/33/EC. According to the colorimetric method, the existed Cr is in the hexavalent form. Consequently, FA cannot be accepted in landfills for non-hazardous wastes, which in turn indicates the need for its stabilization.

Table 2 FA leaching characteristics determined using the EN 12457-2 standard leaching test

	FA	Detection limit	Regulation limits		
			Inert waste	Non-hazardous waste	Hazardous waste
pH	12.7	-	-	-	-
EC mS/cm)	10.6	-	-	-	-
Redox (mV)	-13.5	-	-	-	-
mg/Kg					
As	1.87	0.01	0.5	2	25
Cd	0.04	0.001	0.04	1	5
Cr	16.5*	0.01	0.5	10	70
Cu	0.37	0.01	2	50	100
Ni	ND	0.01	0.4	10	40
Pb	2.55	0.01	0.5	10	50
Sb	0.07	0.01	0.06	0.7	5
Se	0.18	0.01	0.1	0.5	7
Zn	ND	0.1	4	50	200
Chloride	315	50	800	15,000	25,000
Fluoride	ND	0.1	10	150	500
Sulphate	720	100	1,000	20,000	50,000
DOC	43	5	500	800	1,000

ND: Not Detected

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

Figures 2 and 3 present the leached Cr concentrations for different proportions of FA with MgO after 7 and 42 days, respectively. Mixing FA with MgO in 95:5 ratio resulted in the production of a stabilized waste acceptable in non-hazardous waste landfills according to the EU regulation limit for Cr total (Cr 10 mg/kg), i.e. Cr 5,8 mg/kg for 7 days and 2,4 mg/kg for 42 days. More specifically, Cr leaching potential decreased 65% after 7 days and 85% after 42 days, beyond the expected reduction of the dilution of the mixing. Wildt et al. also observed that the decrease of leached Cr, when using MgO at Cr-contaminated sediment, reached 60%, while Garcia et al. noticed that 10% of low grade MgO is needed to stabilize Cr, while a ratio over 10% contributes to long-term stabilization.

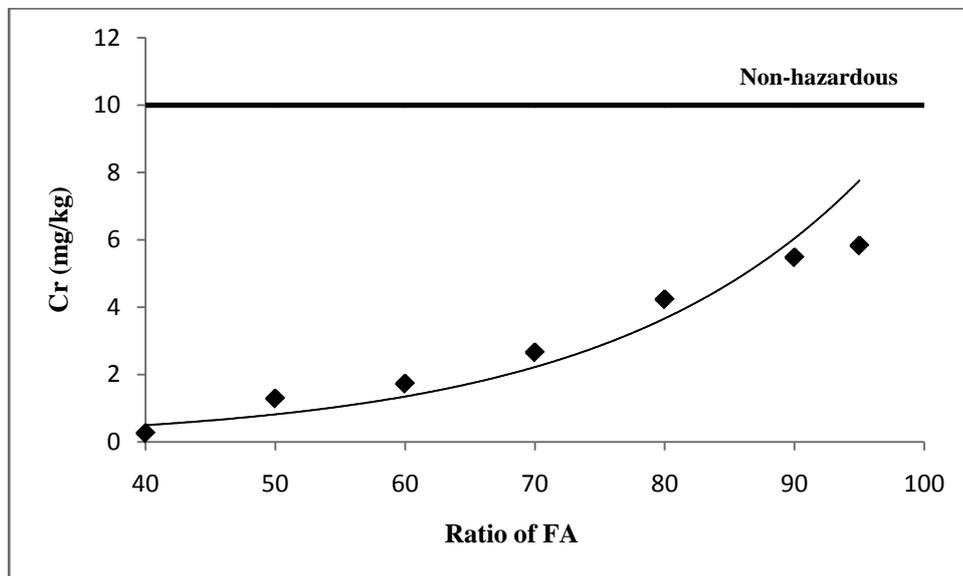


Figure 2 Effect of MgO addition on Cr leaching after 7 days of stabilization

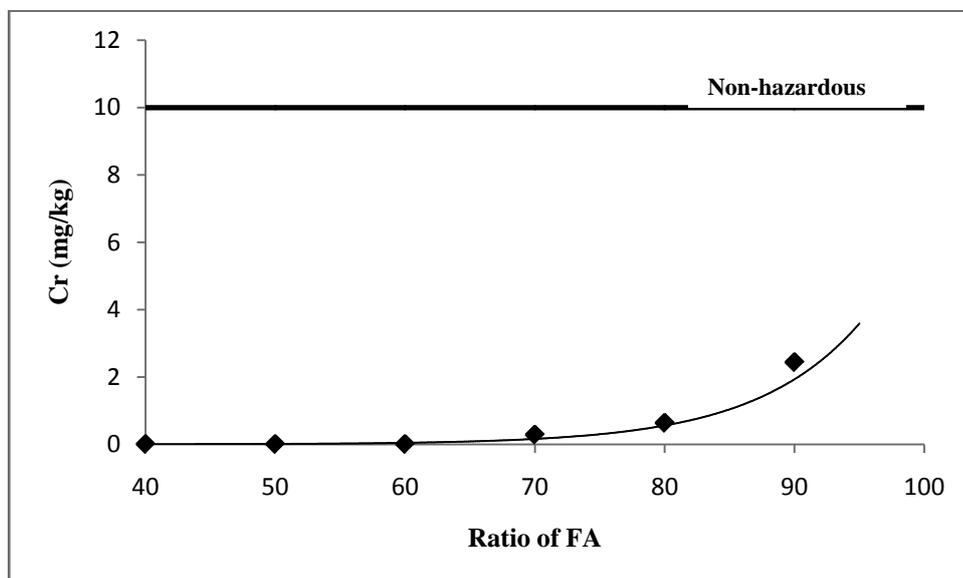
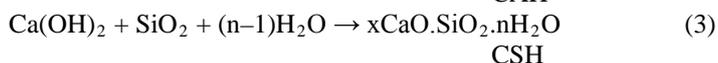
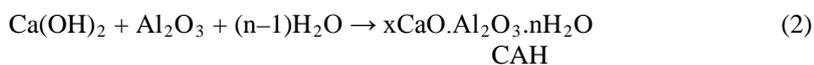


Figure 3 Effect of MgO addition on Cr leaching after 42 days of stabilization

MgO has very good bonding behavior and decreases significantly the leaching of heavy metals [8, 9]. It seems that the addition of MgO in FA gives good resistance at FA. Additionally, silica and alumina, present in FA, react with free calcium, originating from FA and MgO; therefore, the cementitious hydrates CAH and CSH compounds are formed according to the following equations:



It is likely that Cr is transformed to calcium–chromium minerals, or immobilized in the stable calcium silicate hydrate phase (CSH) by the applied stabilization treatment [13].

3. Conclusions

Large quantities of FA are disposed of annually in exhausted lignite mines, causing environmental problems. In the proposed process, MgO was investigated for Cr stabilization in FA to achieve an integrated management presenting additional benefits, such as the reduced treatment cost and high resistance during time. Using MgO in only 5% on ash weight basis was enough to stabilize chromium below the non-hazardous limit, according to the European Decision 2003/33/EC.

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