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Journal of Hazardous Materials B109 (2004) 45–52

Journal of Hazardous Materials

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Environmental behavior of cement-based stabilized foundry sludge products incorporating additives

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Received 10 June 2003; received in revised form 23 December 2003; accepted 23 December 2003

Abstract

A series of experiments were conducted to stabilize the inorganic and organic pollutants in a foundry sludge from a cast iron activity using Portland cement as binder and three different types of additives, organophilic bentonite, lime and coal fly ash. Ecotoxicological and chemical behavior of stabilized mixes of foundry sludge were analyzed to assess the feasibility to immobilize both types of contaminants, all determined on the basis of compliance leaching tests. The incorporation of lime reduces the ecotoxicity of stabilized mixes and enhances stabilization of organic pollutants obtaining better results when a 50% of cement is replaced by lime. However, the alkalinity of lime increases slightly the leached zinc up to concentrations above the limit set under neutral conditions by the European regulations. The addition of organophilic bentonite and coal fly ash can immobilize the phenolic compounds but are inefficient to reduce the ecotoxicity and mobility of zinc of final products.

Keywords: Cement-foundry sludge products; Additives; Ecotoxicity; Pollutants leaching

1. Introduction

Stabilization and solidification (S/S) is known as one of the major technologies for treating and disposing of hazardous wastes. This S/S technologies incorporating cementitious materials have been used for decades as a final treatment step prior to the disposal of both radioactive and chemically hazardous wastes [1]. Despite its wide application to inorganic wastes, including metallic wastes, its applicability to organic wastes has been controversial [2]. From the research developed so far it has been found that organic wastes often interfere with hydration of cement, and that interactions between cement and organic wastes vary according to the characteristics of the organic wastes, thereby compromising the effectiveness of the process and the technological properties of the stabilized product [3–5]. Since organics are present to some extent in almost every waste material, their stabilization may lead to introduce additives that can be effectively used along with the binder to specifically bind the organics and render them less harmful [6–8].

The waste to study in this work is a foundry sludge from a cast iron activity previously characterized and treated by S/S technology. The characterization led to hazardous behavior due to the leaching of metals, mainly zinc, and phenolic species [9]. In order to treat this waste and considering the major content of zinc, the cement-based solidification/stabilization technology was studied and the environmental assessment of the cement-foundry sludge products was carried out [10]. In this previous work, the feasibility to immobilize both types of contaminants was studied using Portland cement as binder at different cement/waste ratios. Four batches were prepared at different cement/waste ratios in the range 1/1 to 1/4. The parameters of environmental control were the ecotoxicity and mobilization of zinc and phenolic compounds, all determined on the basis of compliance leaching tests, TCLP [11] and DIN 38414-S4 [12].

The ecotoxicity and mobility of zinc met the environmental requirements, established by the Spanish regulation [13] and the US EPA and EU Standards for landfilling [14,15],

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doi:10.1016/j.jhazmat.2003.12.011

respectively, when a minimum amount of 15% of cement was used in the mixtures, concentration given at the lowest cement/waste ratio of 1/4. However, the results of phenolic compounds obtained on the aqueous leachates showed that no retention of phenols in the cementitious matrices took place and the dilution of the phenolic compounds was the main effect. The results also evidenced a significant influence of the organic matter on the hydration reactions of cement. Therefore, setting did not take place, obtaining the cement–waste products as granular materials.

After these findings, it was carried out the present work to investigate the viability of using additives to stabilize the phenolic compounds in hazardous foundry waste prior to conventional cement-based S/S in order to inhibit the leachability of phenols and improve the physical and chemical characteristics of final products. In the first phase of this work the choice of additives to include in the S/S process was based on the research done to treat inorganic and organic industrial wastes, trying to prioritize the successful use of residual and cheaper materials. Piñeiro et al. [16] applied residual flash ashes to the S/S process of solid and sludges from iron and steel industry, obtaining satisfactory results on the physical and chemical characteristics of final products. The application of hydraulic binder as additive to treat a scarified road material immobilized especially effectively the soluble phenols and polycyclic aromatic hydrocarbon that the waste contained [17]. The use of organophilic clay as a presolidification adsorbent gave a successful S/S process in the treatment of phenol-contaminated soils [18].

In order to improve the efficiency of S/S technology by means of additives incorporation, the experiments were planned in this study at the lowest cement/waste ratio of 1/4 at which the cement-based products were obtained in the previous work [10]. A series of experiments were conducted to stabilize the inorganic and organic pollutants in foundry sludge using three different types of additives, organophilic bentonite, lime and coal fly ash. Ecotoxicity and leachability of stabilized mixes of foundry sludges were analyzed to assess their feasibility in disposal facilities.

The results suggested that the incorporation of lime as additive produced a higher reduction of the ecotoxicological character and leachability of phenolic compounds respect to the results given by organophilic bentonite and coal fly ash. Besides, ecotoxicological character was reduced respect to the cement-based sludge products and soluble phenols retained up to a maximum of 72%. However, the alkalinity of lime increased slightly the leached zinc under neutral conditions up to values above the European regulated limit for landfilling of inert waste (Zn concentration $= 0.5\,\mathrm{mg\,l^{-1}}$) [15]. The organophilic bentonite-stabilized mixes rendered the leachate quality unpredictable. Ecotoxicological behavior and zinc mobility of final products increased with the augment of organophilic bentonite/cement ratio and respect to the cement-based sludge products. However, with the incorporation of this additive, a retention of 60% of soluble phenols was attained. Finally, the fly ash-stabilized mixes led to worsen the ecotoxicological character, mobility of zinc and phenolic compounds respect to lime and even organophilic clay-stabilized mixes, although a retention of phenols up to 15% was reached.

The general conclusion is that the substitution of cement by lime improved the treatment of foundry sludges, but mobility of zinc under neutral conditions should be mainly considered to asses the efficiency of the stabilization process. Taking into account the legal framework of European Union in which the regulations established for landfilling of wastes are becoming stricter, more research on additional additives should be provided to assure the stabilization process of both inorganic and organic pollutants.

2. Materials and methods

2.1. Materials

The waste is a foundry sludge from wastewater treatment, previously characterized. This industrial waste shows a high water content (62.4%) and hazardous behavior given by the ecotoxicity characteristic, $EC_{50} < 3000\,\mathrm{mg\,l^{-1}}$, as prescribed by the Spanish regulation [13]. The toxicity is due to its metallic content, mainly Zn (16.5%), together with a low fraction of organic pollutants, mainly phenolic compounds (0.01%). Table 1 shows the physical and chemical characterization of the foundry sludge.

The mixing process was carried out between the waste and Portland cement I-42.5 R and the additives of organophilic bentonite, lime and coal fly ash. Table 2 shows the chemical characterization of Portland cement I-42.5 R and the additives.

2.2. Experiments

Two batches were prepared at the additive/binder ratios of 1/1 and 1/2. Each batch was composed of four mixtures in which water content was increasing. The (binder + additive)/waste ratio was kept constant and equal to 1/4, the minimum ratio at which the cement-based products assessed in the previous work [10] accomplished the ecotoxicity criteria established by the Spanish regulation ($EC_{50} < 3000\,\mathrm{mg\,l^{-1}}$) [13], and mobility of zinc in accordance with the US EPA Universal Treatment

Table 1
Physical and chemical characterization of the foundry sludge

Elemental composition of the foundry sludge, % wet weight
Pb: 0.20; Cr: 0.004; Cd: 0.001; Zn: 16.51; Cu: 0.03; Ni: 0.01; Fe: 3.27; Ca: 0.37; Mn: 0.36; Al: 0.06; Si: 2.79; water content (%): 62.43; LOI (%): 4.07; TOC (%): 3.64; TC (%): 4.99; phenolic compounds (%): 0.01

Oxide composition of the foundry sludge, % dry weight (1000 °C)
PbO: 0.72; K_2O: 1.44; SO_3: 1.33; SnO_2: 1.22; MgO: 0.54; Fe_2O_3: 14.8; CaO: 1.57; MnO: 2.17; Al_2O_3: 0.57; SiO_2: 18.2

Table 2
Chemical characterization of the binder and the additives

	Oxide composition (%)									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	CO_2	H_2O
Portland cement	20–20.5	6–7	2–2.5	65–67	1.5	1.0	–	–	–	–
Organophilic clay	65	19.5	2.9	2.3	1.3	–	2.3	0.5	–	–
Lime	–	0.2	0.2	96	0.5	–	–	–	2.5	0.3
Fly ash	87.90		2.67	0.84	0.24	–	–	–	–	

Standard for landfilling restrictions (Zn concentration $= 4.3\,mg\,l^{-1}$) [14], and the EU for landfilling of inert waste (Zn concentration $= 0.4\,mg\,l^{-1}$) [15].

Primarily, the additive was added to the waste and were mixed for about 2 min and then Portland cement binder was included and postmixing was continued for 5 min more until its becoming homogeneous. The total weight of each prepared sample was about 500 g. The mixing was done with a high-speed mixer which provided a high homogeneity of mixtures and enhanced the handle of little amount of materials. Table 3 shows the composition of the cement-stabilized foundry sludge products incorporating additives.

Table 3
Composition of cement-based stabilized foundry sludge products incorporating additives

Sample	Water, w (%)	Cement, c (%)	Dry sludge, s (%)	Additive, a (%)	$w/(a+c)$
Organophilic bentonite					
$a/c = 1/1$					
OB111	22.19	7.78	62.26	7.78	1.43
OB112	30.55	6.94	55.55	6.96	2.20
OB113	36.51	6.35	50.80	6.35	2.87
OB114	52.38	4.76	38.10	4.76	5.50
$a/c = 1/2$					
OB121	20.25	10.63	63.79	5.32	1.27
OB122	29.08	9.46	56.74	4.72	2.05
OB123	35.48	8.60	51.61	4.30	2.75
OB124	52.42	6.34	38.07	3.17	5.51
Lime					
$a/c = 1/1$					
L111	16.11	8.39	67.12	8.39	0.96
L112	25.76	7.42	59.39	7.42	1.73
L113	32.53	6.75	53.98	6.75	2.11
L114	52.38	4.76	38.10	4.76	5.50
$a/c = 1/2$					
L121	17.58	10.99	65.94	5.49	1.07
L122	25.82	9.89	59.35	4.95	1.74
L123	32.79	8.96	53.76	4.48	2.44
L124	52.39	6.35	38.10	3.18	5.50
Coal fly ash					
$a/c = 1/1$					
FA111	16.11	8.39	67.12	8.39	0.96
FA112	25.93	7.41	59.26	7.41	1.75
FA113	33.33	6.67	53.33	6.66	2.50
FA114	52.38	4.76	38.10	4.76	5.50
$a/c = 1/2$					
FA121	16.11	11.19	67.12	5.59	0.96
FA122	25.96	9.87	59.23	4.94	1.75
FA123	33.33	8.88	53.33	4.46	2.50
FA124	52.42	6.33	38.08	3.17	5.52

2.3. *Characterization methods*

Subsamples of each mixture were cast into cubic moulds of 50 mm side and sealed into polyethylene bags. Samples were taken out from their moulds after 28 and 56 days of curing. The environmental assessment was performed according to the ecotoxicity and the chemical composition of leachates.

Leaching of samples was performed according to the compliance TCLP [11] and DIN 38414-S4 [12] leaching tests. The leachant used in TCLP test is a buffer solution of acetic acid at a liquid to solid ratio of 20:1 while the leachant used in the DIN 38414-S4 test is demonized water at a liquid to solid ratio of 10:1.

The samples remolded after 28 days of curing were crashed to reduce the particle size up to the values set by the standard procedures, TCLP and DIN 38414-S4, and submitted to both tests and further toxicological and chemical characterization. The toxicological analysis was done in the TCLP leachate by means of the luminescence bioassay [19] as prescribed by the Spanish regulation [13]. According to this guideline, a waste is considered hazardous when the ecotoxicity value is attained at an $EC_{50} < 3000\,mg\,l^{-1}$. The zinc concentration was measured in TCLP and DIN-38414 S4 leachates, and the results were compared to the limits for landfilling prescribed by US EPA regulation [14] and EU regulation [15], respectively. Chemical analysis was performed using a Perkin-Elmer 1100 B Atomic Absorption Spectrometer. The phenolic index was determined in the aqueous DIN-38414 S4 leachate using a colorimetric method and UV-Vis spectrophotometer detection [20].

3. Results and discussion

3.1. *Ecotoxicity of leachates*

The results of ecotoxicity were obtained from the leachates after 28 days of curing. For all stabilized products, the values of ecotoxicity were above the ecotoxicity of the foundry sludge ($EC_{50} = 1015\,mg\,l^{-1}$) as well as the standard limit of the Spanish regulation ($EC_{50} = 3000\,mg\,l^{-1}$). Figs. 1–3 present the results obtained by incorporation of additives to the cement matrices along with the old results

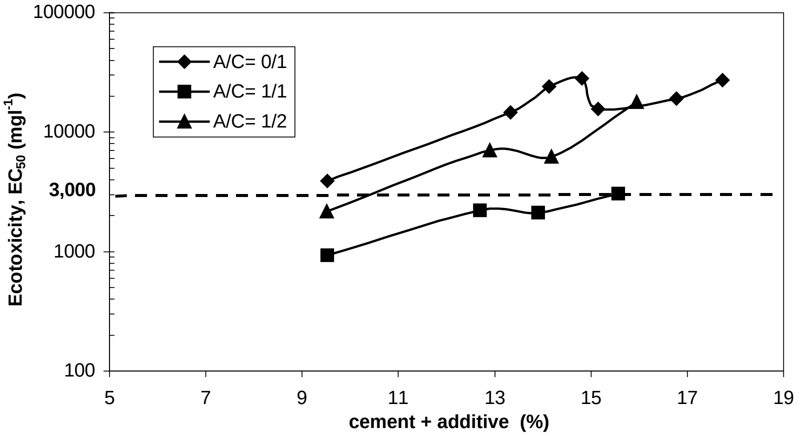

Fig. 1. Results of ecotoxicity incorporating organophilic bentonite.

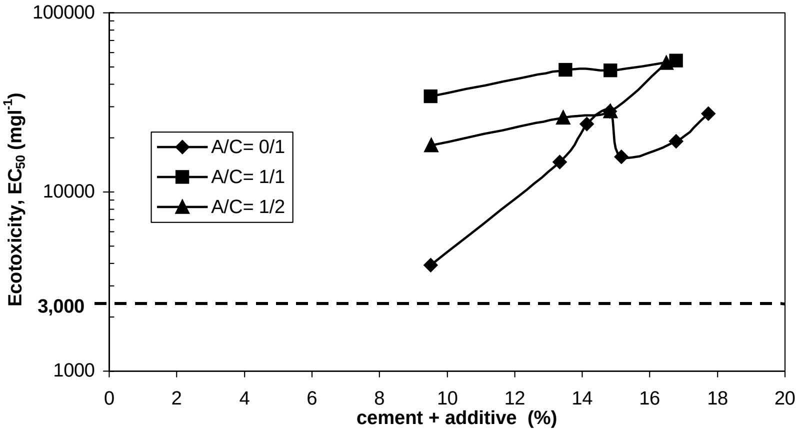

Fig. 2. Results of ecotoxicity incorporating lime.

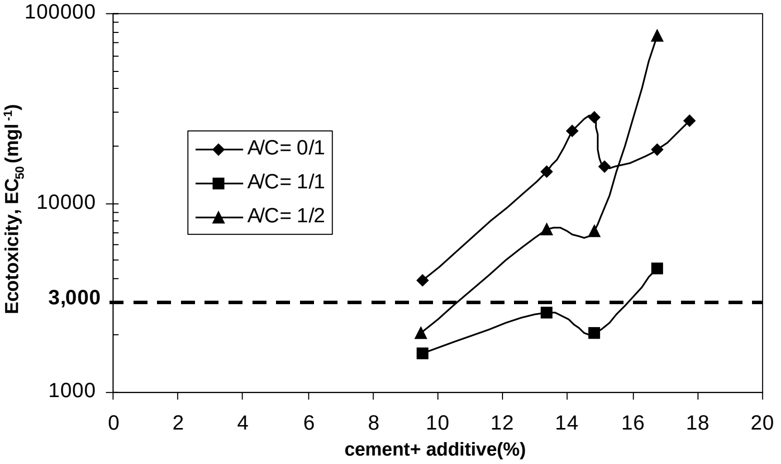

Fig. 3. Results of ecotoxicity incorporating fly ash.

obtained without additives in the previous work [10]. The ecotoxicity results were higher for the leachates of products in which cement was substituted by lime, which means a lower ecotoxicological character in comparison with the cement-foundry sludge products. Besides, results improved when the lime/cement ratio increased. On the other hand, the incorporation of organophilic bentonite and coal fly ash reduced the ecotoxicity values in comparison with the cement-foundry sludge products, which means a higher ecotoxicological character.

These results may be explained by the different acidity of final TCLP leachates on which ecotoxicity was deter-

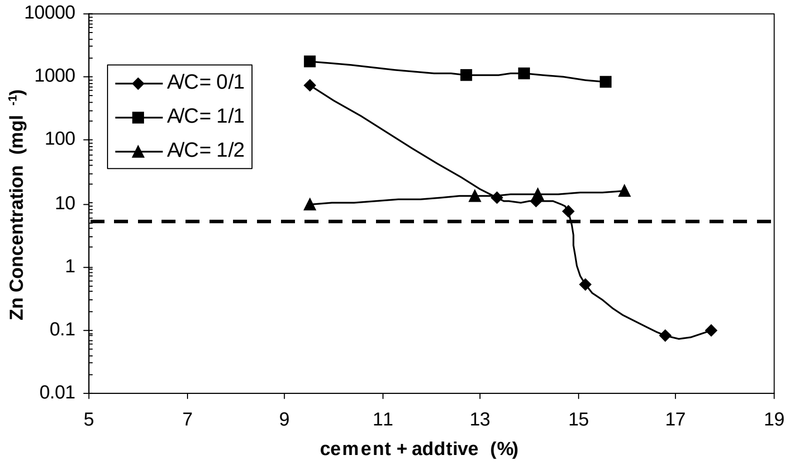

Fig. 4. Zinc mobilization into TCLP leachate incorporating organophilic bentonite.

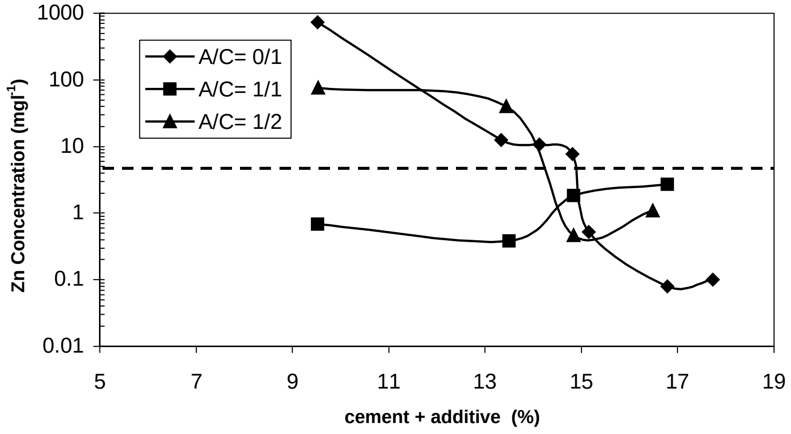

Fig. 5. Zinc mobilization into TCLP leachate incorporating lime.

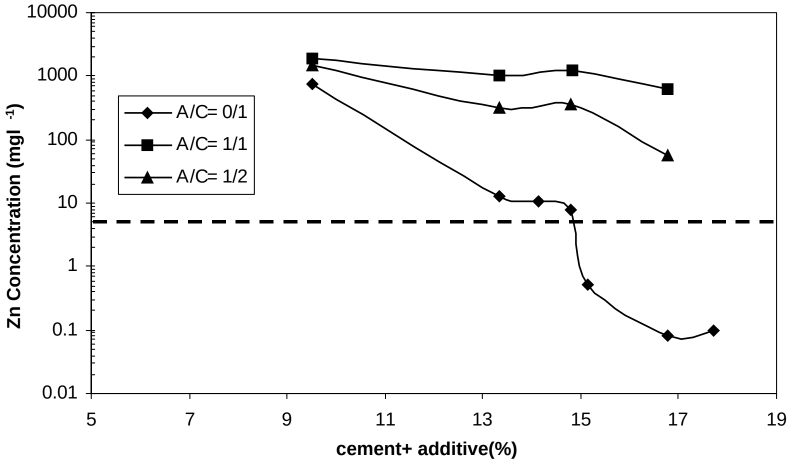

Fig. 6. Zinc mobilization into TCLP leachate incorporating fly ash.

mined. The addition of organophilic bentonite and lime augmented the acidity of final solutions and therefore solubility of zinc increased. However, the addition of lime neutralized the acidity of TCLP leachates and reduced the solubility of the metal.

3.2. Chemical characterization of leachates

3.2.1. Zinc mobility

The mobility of zinc from the products was determined in the leachates from the standard TCLP and DIN 38414-S4

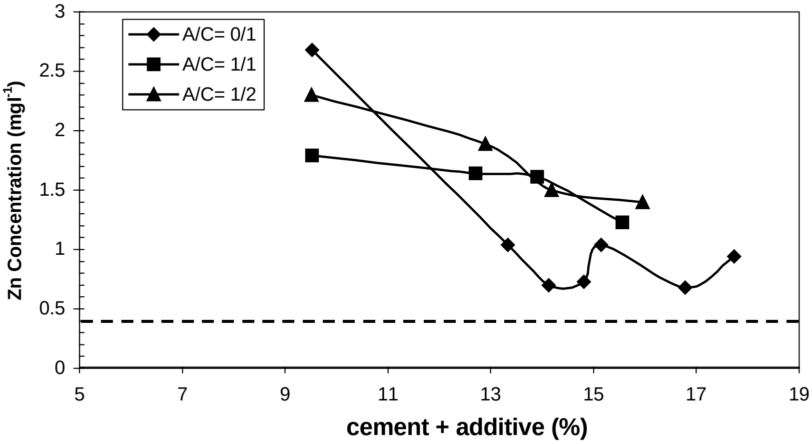

Fig. 7. Zinc mobilization into DIN 38414-S4 leachate incorporating organophilic bentonite.

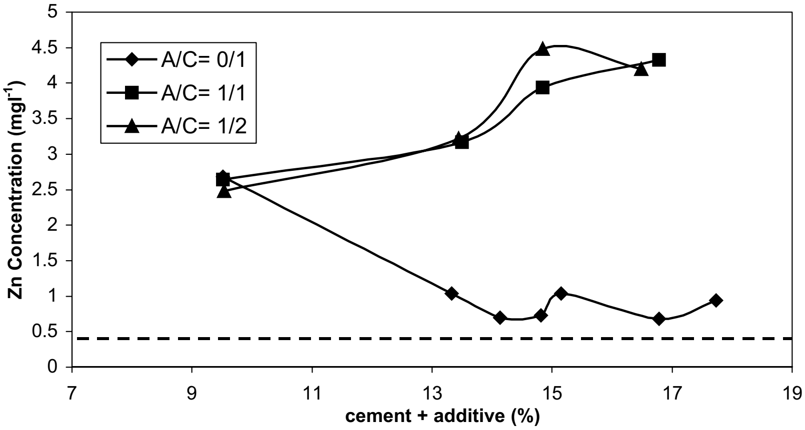

Fig. 8. Zinc mobilization into DIN 38414-S4 leachate incorporating lime.

extraction procedures. Results were compared to the limit concentration of Zn in TCLP leachate, $\mathrm{Zn} = 4.3\,\mathrm{mg\,l^{-1}}$, established by the US EPA as Universal Treatment Standard for landfilling restrictions [14] and the limit set by EU for landfilling of inert waste, $\mathrm{Zn} = 0.4\,\mathrm{mg\,l^{-1}}$, [15]. Both try to evaluate the efficiency of stabilization of contaminants considering different scenarios of landfilling.

Results from TCLP and DIN 38414-S4 leachates are included in Figs. 4–6 and Figs. 7–9, respectively. It can be seen that results from the cement-based stabilized products, which were obtained in the previous work at cement/waste ratio equal to 1/4 and therefore additive/cement ratio equal to 0/1 [10], have also been added in the figures in order to compare them with the new results.

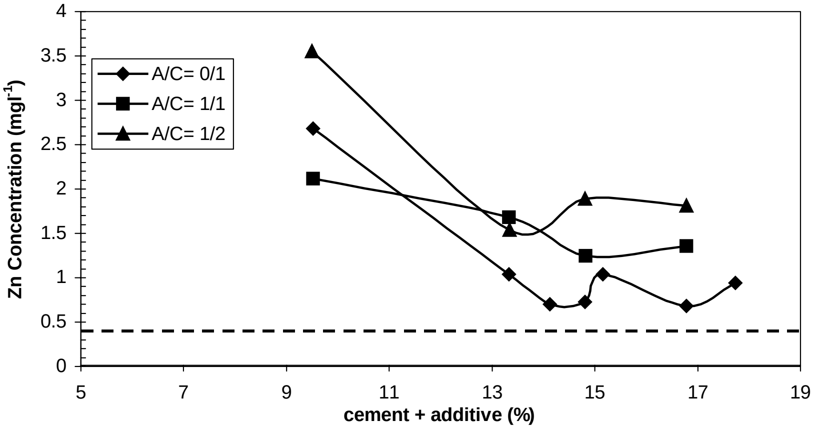

Fig. 9. Zinc mobilization into DIN 38414-S4 leachate incorporating fly ash.

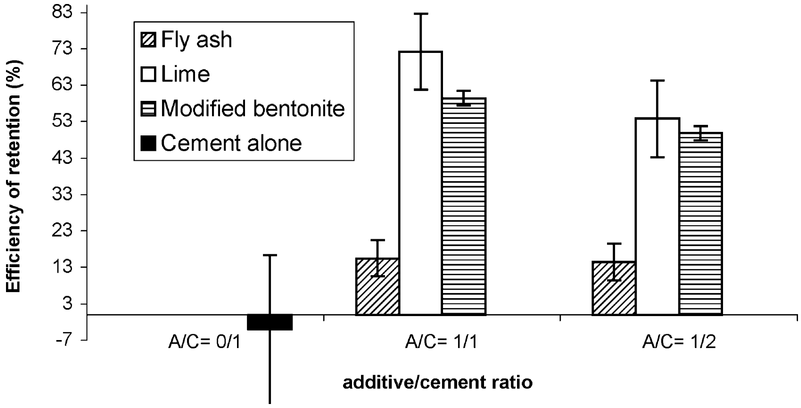

Fig. 10. Efficiency of retention of phenolic compounds incorporating additives at additive/cement ratios of 1/1 and 1/2.

When the organophilic bentonite and fly ash were added, the experiments done in the acidic conditions of TCLP leaching test showed an increment of the zinc mobility respect to the cement-based products and concentrations of zinc were above the standard limit, see Figs. 4 and 6. However, the introduction of lime decreased the zinc mobility into TCLP leachates comparing with the experiments without additive and concentrations of zinc were below the standard limit, especially when the additive/cement ratio was equal to 1/1, see Fig. 5.

Regarding the neutral conditions of DIN 38414-S4 procedure, neither of the additives included in the present work improved the results of zinc mobility respect to the cement-foundry sludge products, Figs. 7–9. Following the limit proposed by EU for landfilling, all the concentrations were above the standard limit for landfilling of inert wastes (Zn concentration $= 0.4\,\mathrm{mg\,l^{-1}}$), but they were below the standard limit for landfilling of non hazardous wastes (Zn concentration $= 5\,\mathrm{mg\,l^{-1}}$). When lime was introduced, the increase of alkalinity and subsequent mobility of zinc was noticed which revealed the amphoteric character of the metal, see Fig. 8. The addition of some acidic materials, as silica fume or silicates, could keep the conditions at which the minimum solubility of zinc occurred and enhance the control of this parameter.

3.2.2. Phenolic compounds

The mobility of phenolic compounds was studied in the leachates obtained from the neutral conditions of DIN 38414-S4 leaching test. In the previous works it was proven that the phenolic compounds were in the liquid phase and no retention of phenols in the cementitious matrices took place [9,10]. The incorporation of additives produced the immobilization of the phenolic compounds, especially the addition of organophilic bentonite and lime. Fig. 10 shows the average of retention efficiency versus the ratio of additive/cement for the stabilized products. In all cases, it can be observed the retention improvement of soluble phenols comparing with the use of cement as only binder agent. The introduction of organophilic bentonite retained the phenols up to 60% when the cement/additive ratio was 1/1, descending up to 50% when the ratio was 1/2. The incorporation of lime improved the efficiency up to 72% when the cement/additive ratio was equal to 1/1 and 54% when the ratio was 1/2. Finally, the fly ash addition could only immobilize around 15% of phenolic compounds.

Clearly, the addition of lime gave the higher efficiency of retention but the concentration of soluble phenols analyzed on the aqueous leachates ranged between 0.6 and $2.8\,\mathrm{mg\,l^{-1}}$ when lime/cement was equal to 1/1 and between 1.0 and $5.0\,\mathrm{mg\,l^{-1}}$ when lime/cement was equal to 1/2, values that were above the standard limit for landfilling of inert waste (phenolic compounds $= 0.1\,\mathrm{mg\,l^{-1}}$) and which led to consider the products as non-hazardous wastes. This fact suggested to prove more specific additives as activated carbon to effectively immobilize the organic pollutants until the landfilling of inert waste conditions.

4. Conclusions

The cement-based S/S technique incorporating additives was studied for the treatment of foundry sludges. To improve the environmental behavior at the lowest cement/waste ratio 1/4, some additives as organophilic bentonite, lime and coal fly ash were introduced in the cement-foundry sludge mixtures. The incorporation of lime reduces the ecotoxicity of products and immobilizes the zinc and phenolic compounds into the matrices, improving the results when the lime/cement ratio is 1/1. However, environmental requirements for landfilling of inert wastes are not met for the leaching of zinc and phenolic compounds under neutral conditions. The addition of organophilic bentonite and coal fly ash makes possible to immobilize the phenolic compounds but increases the mobilization of zinc and therefore the ecotoxicity of products.

The use of lime is more efficient since immobilizes inorganic and organic pollutants at once and final products are non-hazardous. Besides, this additive is cheap and easily available. However, the stricter regulations on landfilling of wastes in the European level suggests to guarantee the stabilization until the inert level which involves the reduction of zinc and soluble phenols on aqueous leachates. The addition of some acidic materials, as silica fume or silicates, could keep the conditions at which the minimum solubility of zinc occurred and more specific additives as activated carbon to effectively immobilize the organic pollutants until the landfilling of inert waste requisites would enhance the S/S process.

Although further experiments should be planned incorporating the additives mentioned above, this work has approached to formulate the products efficiently and economically.

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