Journal of Hazardous Materials B109 (2004) 95–104

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Environmental behaviour of stabilised foundry sludge

Alberto Coz*, Ana Andrés, Sonia Soriano, Ángel Irabien

Departmento de Ingeniería Química y Química Inorgánica, Universidad de Cantabria, Avda. de los Castros s/n, 39005 Santander, Spain

Received 8 September 2003; accepted 9 March 2004

Available online 5 May 2004

Abstract

Environmental characterisation of foundry sludge (FS) and the stabilised/solidified (S/S) derived products has been performed according to the leaching behaviour. Portland cement and lime have been used as binders and foundry sand fines, activated carbon and black carbon have been used as additives in the S/S processes. The results of the characterisation show that the behaviour of the waste in acid media is mainly influenced by the inorganic components of the waste, while the organic matter only has an influence in the redox potential of the leachates. Due to the complexity of the waste, a computer modelling of equilibrium (MINTEQ) has been used in order to compare the experimental extractability with the simulated curves of the metallic species. The zinc content in the leachate is close related to the theoretical curves in the waste and all S/S products, while the rest of the metals do not show a coherent behaviour with the hydroxides evolution. The results of compliance testing allow to obtain the best S/S formulations using activated and black carbon as sorbents. The comparison between different leaching procedures leads to equivalent results depending only on the pH.

Keywords: Foundry sludge; Stabilisation/solidification; Landfill disposal; Leaching tests; Metals

1. Introduction

Management of industrial waste containing inorganic pollutants and organic matter is a very complex task. The range of industrial waste containing mixtures of pollutants is extensive, and foundry sludge is an interesting example. It is an important waste from foundry activities, which is generated after wet cleaning of gases. It is listed as hazardous waste in the European waste catalogue, identified with the code 100213* [1]. Furthermore, in previous works, and taking into account Spanish regulations [2–4] the foundry sludge shows ecotoxicity, due to some organic pollutants such as phenol, and inorganic elements such as lead, chromium and cadmium as well as important amounts of zinc.

Immobilisation processes are applied to handle the waste before land disposal, due to the properties of the sludge. The aim of immobilisation is to minimise the rate of contaminant migration into the environment and/or to reduce the pollutant toxicity level, in order to change or improve the characteristics of the waste, thereby making its disposal possible [5].

Immobilisation refers to processes retaining substances absorbed or trapped within a solid matrix. Stabilisation refers to those techniques that reduce the hazardous behaviour of a waste by means of chemical reactions and solidification refers to techniques that generate a monolithic solid of high structural integrity (S/S) [6,7].

There is a wide range of sorbents and binders available for stabilisation. Some of the most common sorbents and binders are: cement, pozzolans, lime, soluble silicates, modified clays, modified lime, humic substances, activated carbon, thermosetting organic polymers and thermoplastic materials [5].

These S/S technologies are basically being applied to inorganic waste. However, in the case of hazardous organic pollutants their management, from a technical and regulatory point of view, may be quite different. Organic pollutants in solid waste and aqueous waste with high a concentration of organic compounds are usually recycled or incinerated [6,7]. However, at low organic pollutant levels, these technologies are not feasible from the economic point of view, or reveal operational difficulties or severe environmental impacts. In

* Corresponding author. Tel.: +34-942-202027/1359; fax: +34-942-201591.
E-mail address: coza@unican.es (A. Coz).

0304-3894/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2004.03.002

this case S/S provide a useful alternative due to the low cost of maintenance and operation [8–24]. Reagents used in S/S processes for organic pollutants are usually based on different additives to the cement matrix [17,18,20,21,24–27]. The best sorbent in the S/S of organic pollutants seems to be activated carbon [28]. It is, however, an expensive additive and, therefore, other residual additives like black carbon may be used.

In this work, a study into the environmental behaviour of foundry sludge and S/S derived products has been carried out. The electric arc furnace dust (EAFD) was used for comparison as it is a well known waste, but it has no significant organic matter in its composition. A synthetic waste was used as reference, it having the same proportion of metals as foundry sludge. A comparison has been performed to establish the influence of organic matter on metal mobility. The S/S formulations have been prepared with lime and cement as binders, and with foundry sand fines, activated carbon and black carbon as additives. Lime and cement have been used as binders due to their low cost, easy handling, a previous knowledge of them in the S/S process and, in the case of cement, the ability to obtain monolithic products [26,27]. The partial substitution of the binder by residual and commercial additives has been performed in order to decrease the cost of the process, to manage two waste materials simultaneously, to absorb the organic pollutants of the foundry sludge and/or to incorporate new properties to the stabilized/solidified products.

Regulatory procedures based on equilibrium leaching tests allow the characterisation of the environmental behaviour of waste and S/S products using the solubility and/or availability of pollutants as limits. US-EPA-TCLP, DIN 38414-S4 and EN 12457 are very common tests in USA [29] and Europe [30], respectively. In the TCLP, acetic acid is used as a leachant to simulate the organic acid generation in municipal solid waste landfills, while in the DIN S-4 and EN 12457 procedures, distilled water is used to evaluate the extractability of the pollutants.

The council decision 2003/33/EC [30] establishes criteria and leaching procedures for the acceptance of waste at landfill sites. This decision will come into effect as of 16 July 2004 and establishes three classes of landfills: landfill for inert waste, landfill for non-hazardous waste and landfill for hazardous waste. The criteria and procedures for the acceptance of waste are given in an annex according to three types of procedures: basic characterisation, compliance testing and on site verification; and it establishes the criteria and limits for each landfill according to the EN 12457 leaching test or prEN 14405 percolation test.

In this work, a characterisation of foundry sludge and stabilised/solidified derived products is performed in order to study the behaviour of the waste at landfill sites. The basic characterisation of the waste and S/S products has been carried out following an acid equilibrium test (WTC) [31], because both the integrity of monolithic matrix and the solubility of pollutants depend strongly on the pH. Other important variables of the WTC test are the conductivity and the redox potential. The conductivity may be related to the mobility of ionic species and this has been considered by many authors, but the suitable range for safe disposal remains open [32–34]. In many cases, the extractability of hazardous metals in the leachate is influenced by the redox potential. In the case of metals such as chromium, with more than one oxidation state, oxidated species such as Cr(VI) can originate from Cr(III) when the conditions are appropriate [35,36]. The EN 12457 leaching test has been used to study the migration in water of organic pollutants because the main organic pollutants in the foundry sludge are totally soluble in a water solution [15,23,37].

Many elements and species are involved in a heterogeneous waste, and the leaching process will cover a wide range of pH in the acid neutralisation capacity tests. Due to the complexity of waste the prediction of the content of pollutants in the leachate is not an easy task. Computer modelling of equilibrium is one of the approaches to give a first insight into the pollutants' extractability under different conditions [38]. In this work, the experimental behaviour of metallic pollutants' extractability has been compared with the simulation as a function of pH, using the geochemical equilibrium modelling applying the VISUAL MINTEQ 1.0 software. The MINTEQ software has been reported in [22,39–42] to study the metal speciation in aqueous solutions.

Results from the compliance tests of the waste and derived products through the EN 12457 leaching test have been compared with the limits established for the European regulation for the three classes of landfills [30]. The critical parameter in an acidic medium (WTC) is the amount of metallic pollutants, and the critical parameters in distilled water (EN 12457) are the inorganic (Zn, Pb, Cr and Cd) and organic pollutants (DOC and phenols) coming from the foundry sludge.

2. Materials and methods

2.1. Materials

Foundry sludge (FS) and electric arc furnace dust (EAFD) from Spanish factories located in Cantabria were used in the experimental study. The chemical characterisation has been determined in previous studies [2,43] and it is shown in Table 1. A synthetic reference (SR) with ZnO and Fe_2O_3 in the proportion of the foundry sludge was prepared in the laboratory. Portland cement type I 42,5R (CM) and commercial lime (LM) were used as binders. Foundry sand fines (FSF), by-product of the foundry activities; activated carbon reagent grade (AC), commercial sorbent and black carbon from the carbon industry (BC), were studied as additives.

Based on previous experiments S/S products were formulated using 70% foundry sludge and different amounts of binder and additives. The quantities of binder and addi-

Table 1
Chemical composition of the foundry sludge (FS) and electric arc furnace dust (EAFD)

Element	FS (% d.w.)	EAFD (% d.w.)
Fe	8.70	15.00
Zn	43.94	21.53
Cr	0.01	0.50
Pb	0.5	1.67
Ni	0.03	n.d.[a]
Cd	0.003	n.d.
Al	0.16	0.05
Ca	0.98	3.93
Cu	0.08	0.23
K	1.00	0.44
Mg	0.40	2.23
Mn	1.66	5.27
TOC	9.68	n.d.
LOI[b] (550 °C)	9.13	–
LOI (1000 °C)	12.44	5.11
Water content	62.43	–

[a] n.d.: not detected.
[b] LOI: loss of ignition.

tives were established in previous studies [44,45] in order to fulfil the limits of the US EPA [29] regulations. The studied mixtures are given in Table 2.

2.2. Experimental methods and analytical procedures

Waste, binders and additives were mixed in a CEMEX W-20, X-02-G laboratory scale solid mixer prototype [46]. Each mixture was transferred to a plastic bag at room temperature for 28 days of curing time. The samples were characterised using the leaching test EN 12457 [30] and WTC–ANC [47]. The pollutants measured in the water leachate were dissolved organic carbon (DOC), phenol index and metals, Zn, Pb, Cr and Cd. In the acidic leachate, the evaluated parameters were pH, conductivity, redox potential and metals concentration, Zn, Pb, Cr and Cd [30].

EN 12457/1–4 test for leaching of granular waste materials and sludge has been carried out in all samples, waste and stabilised/solidified products, in order to apply the test recommended by the EU council decision. The EN leaching test was performed after 28 days of curing. The distilled water, to solid ratio was 10 l/kg, dry weight, which was slowly agitated by tumbling at 0.5 rpm for 24 h. After extraction and filtering, chemical analysis of the leachate was carried out.

Table 2
Components of stabilised/solidified products

Product	FS (%)	CM (%)	LM (%)	FSF (%)	Additive (%)
S/S LM	70	–	30	–	–
S/S CM	70	30	–	–	–
S/S CM–AC	70	29	–	–	AC:1
S/S CM–BC	70	29	–	–	BC:1
S/S CM–FSF	70	20	–	10	–
S/S CM–AC–FSF	70	19	–	10	AC:1
S/S CM–BC–FSF	70	19	–	10	BC:1

Table 3
Total metal concentration in all samples used in the Minteq simulation

Solids	Quantity in foundry sludge	Quantity in S/S products
Zinc oxide, ZnO (mol/l)	1.12	0.784
Lead oxide, PbO (mol/l)	0.00426	0.00298
Chromium(III) hydroxide, $Cr(OH)_3$ (mmol/l)	0.162	0.113
Cadmium hydroxide, $Cd(OH)_2$ (mmol/l)	0.0342	0.0239

The results have been compared with the limits established by the European Directive [30] in order to classify the waste as hazardous, non-hazardous or inert. The critical parameters in the foundry sludge are the inorganic elements: Zn, Pb, Cr and Cd and the organic parameters: DOC and phenol index.

A procedure for the acid neutralisation capacity has been standardised by the Wastewater Technology Centre, Canada (WTC) [47]. It consists on a multiple step single-extraction batch leaching, which uses a series of dried samples at 60 °C for 3 days extracted with a nitric acid solution of increasing acidity. The liquid to solid ratio is 6 ml/g, the results are similar to a titration of a base with a strong acid, nitric acid. The values of pH of the different leachates were recorded as a function of the mequiv. acid/g of dry waste.

A Crison Model 2002-pH meter and a Crison basic 30-conductimeter were used. The metals concentrations,

Table 4
Hydroxide species used in the Minteq simulation

Metal	Specie	Equilibrium constant, log *k*	Enthalpy (kJ/mol)
Zn	$ZnOH^+$	−8.997	55.81
	$Zn(OH)_2$ aq	−17.79	0
	$Zn(OH)_3^-$	−28.09	0
	$Zn(OH)_4^{2-}$	−40.49	0
	Zn^{2+}	12.2	0
	ZnO (s)	11.19	−88.76
	Zincate (s)	11.33	−89.62
Pb	$PbOH^+$	−7.597	0
	$Pb(OH)_2$ aq	−17.09	0
	$Pb(OH)_3^-$	−28.09	0
	$Pb(OH)_4^{2-}$	−39.70	0
	Pb^{2+}	8.15	−58.53
	PbO (s)	12.98	0
	$Pb_2O(OH)_2$	26.19	0
Cr	Cr^{3+}	9.569	−129.6
	$CrOH^{2+}$	−5.912	−77.91
	$Cr(OH)_3$ aq	−8.422	0
	$Cr(OH)_4^-$	−17.82	0
	CrO_2^-	−17.75	0
	Cr^{3+}	1.336	−29.77
	Cr_2O_3 (s)	−2.358	−50.73
Cd	$CdOH^+$	−10.10	54.81
	$Cd(OH)_2$ aq	−20.29	0
	$Cd(OH)_3^-$	−32.51	0
	$Cd(OH)_4^{2-}$	−47.29	0
	Cd_2OH^{3+}	−9.397	45.81
	Cd^{2+}	13.644	−94.62

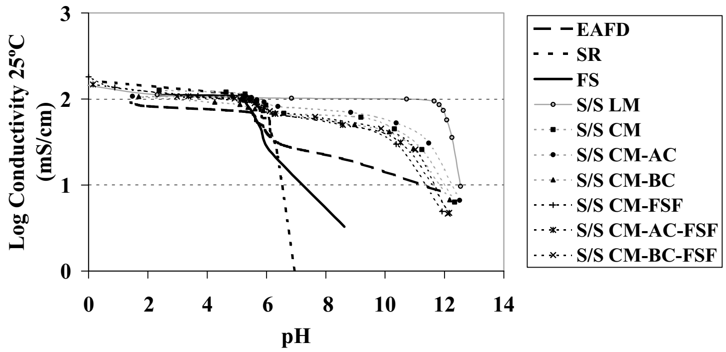

Fig. 1. Conductivity evolution from WTC–ANC test of waste and derived products.

Zn, Pb, Cr and Cd, in the leachates were measured using an atomic emission spectrometer inductively coupled plasma (ICP) [48], Model Perkin-Elmer 400. To determine dissolved organic carbon an Euroglas TOC 1200 was employed. Phenol index was determined according to the norm ISO 6439 "Determination of phenol index 4-aminoantipyrine spectrometric method after distillation" [30,49]. The equipment was the Spectrophotometer Perkin-Elmer, Lambda 2UV-Vis.

2.3. Modelling of leaching behaviour

In order to model the leaching behaviour, VISUAL MINTEQ 1.0 software has been applied to simulate the metal amount in the leachates as a function of pH. The software calculates the concentration of the different ionic species of a metal (basically hydroxides) in relation to the equilibrium constant, the enthalpy, the pH and the total concentration of this metal in the products. The total metal concentrations in all products are shown in Table 3. The ionic epecies of the metals (hydroxides) are shown in Table 4.

3. Results and discussion

3.1. Basic characterisation

The experimental results of WTC tests are shown in Fig. 1 as conductivities (logarithmic plot) versus pH, the waste and derived products show very similar results in the pH range 0–7, thus, revealing the acid addition as main influence in the acidic range. However, the results are widespread in the basic range, EAFD has the higher conductivities and the foundry sludge higher ion concentrations than the synthetic reference due to other inorganic and organic compounds in the basic range. Derived products show the same results below pH 6. Therefore, the total ion mobility in the acidic range does not depend on the binder agents and/or additives used during the treatment. However, in basic medium ($pH > 7$), the products S/S with lime as binder have higher conductivities in the leachates than the untreated waste, although, cement based S/S products show very similar results.

Fig. 2 shows the potential redox of the waste and derived products versus pH, the complex waste (FS) has a lower oxidation potential than inorganic waste (EAFD and SR) in the range of pH. The organic matter increases the redox potential of the leachates. For acid pH values ($pH < 6$), all S/S products have a much greater oxidation potential than the untreated waste. This is due to the influence of organic compounds, as mentioned above. Nevertheless, for basic pH, the values of the oxidation potential show very similar trends in all S/S products.

The acid neutralisation capacity, Fig. 3, shows the leachate pH as a function of the added equivalents of nitric acid per kilogram of dry sample and it is related to the acid-base behaviour of the waste. These figures are known as titration curves. The more equivalents a sample neutralise,

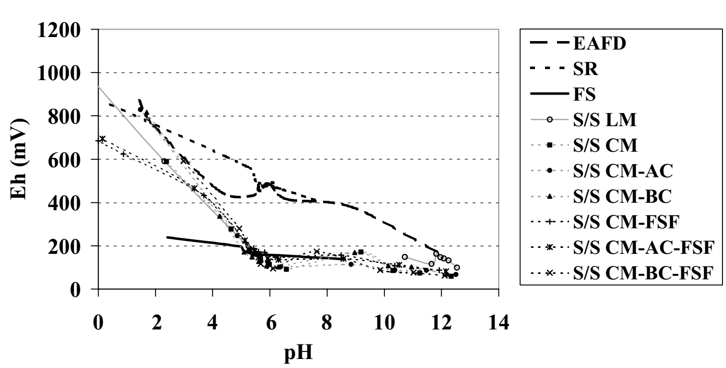

Fig. 2. Redox potential evolution from WTC–ANC test of waste and derived products.

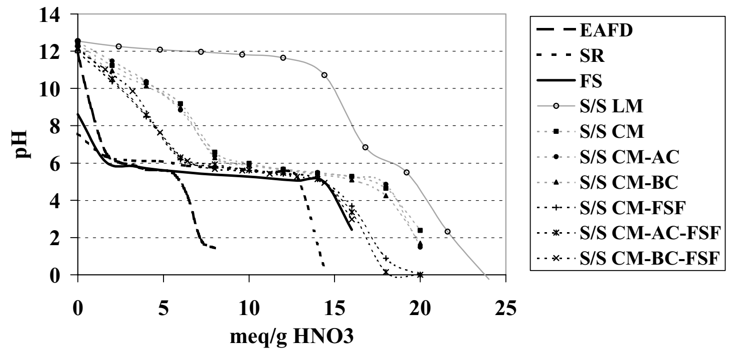

Fig. 3. pH values evolution from WTC–ANC test of waste and derived products.

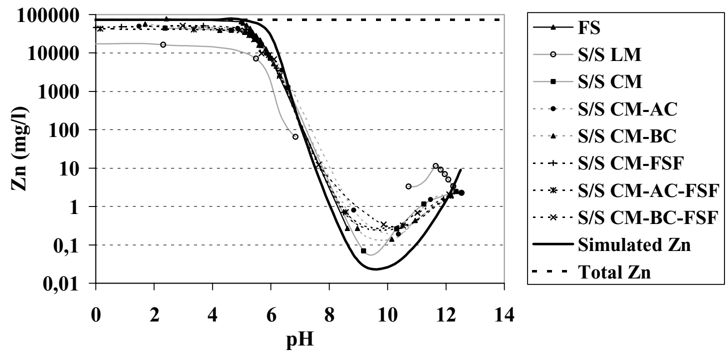

Fig. 4. Zinc extractable amount following the WTC leaching test.

the greater buffering capacity it has, taking into account the influence of pH in the mobility of the different heavy metal species. This variable depends on the acid attack and buffer capacity of the waste, a plateau at a defined pH describes the waste buffer capacity [50]. The titration curves show buffer capacities between 2 and 15 mequiv. HNO_3/g, being the plateau at a pH between 5 and 6, therefore, it can be concluded that the mentioned buffer capacities are only influenced by the inorganic species of the waste, the metals Zn and Fe. The buffer capacity of the electric arc furnace dust is lower due to its lower zinc oxide content. Contents of Zn in both samples are already shown in Table 1.

The results of pH versus added equivalents of nitric acid in the S/S products is based on the alkaline reagents of the formulation, which are lime and Portland cement. Consequently, its neutralisation capacity of S/S products is very high [26,41,50–55] depending on the amount of alkaline reagents.

The acid neutralisation capacities (ANC) of the S/S products and waste are obtained from the titration curves. ANC is defined as the equivalents of nitric acid for kilogram of dry solid product needed to reduce the value of the leachate pH to 9 in the WTC test [47]. The values of ANC of waste and S/S products have been obtained. The best results of ANC are obtained in the mixture with calcium oxide, 15.46 mequiv./g of nitric acid. Black carbon and activated carbon have a negligible influence on the acid neutralisation curves due to their neutral behaviour and to the fact that they are present in very small amounts. From 5.79 to 3.82 mequiv./g of nitric acid are necessary to get a final pH of 9 in samples with cement and these adsorbents. However, the substitution of 10% cement for foundry sand fines originates a reduction of the buffering capacity, 3.46–3.82 mequiv./g of nitric acid are necessary in all samples with FSF. In the literature it has been shown that pozzolanic agents of the cement have a negative effect on the acid neutralisation capacity with nitric acid due to the substitution of basic reagents by acidic oxides [56], in good agreement with these results. The pozzolanic behaviour of foundry sand fines has been tested in previous studies [37].

3.2. Metals results

The zinc extractable amounts from WTC test of S/S products and untreated waste is shown in Fig. 4. The results show

Table 5
Availability of metals from foundry sludge

Metal	Available concentration[a]	Available amount[b] (%)
Zn	466 (g/kg dry sludge)	100
Pb	117 (mg/kg dry sludge)	2.20
Cr	10.4 (mg/kg dry sludge)	20.5
Cd	20.2 (mg/kg dry sludge)	87.8

[a] Total metal content, obtained from Table 1.
[b] Percentage accessible on WTC test with regard to total concentration.

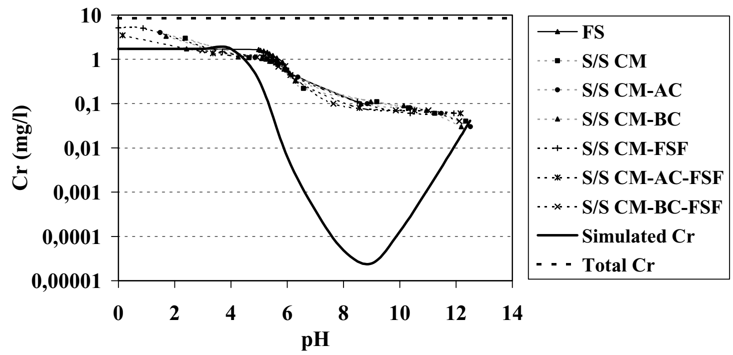

Fig. 5. Chromium extractable amount following the WTC leaching test.

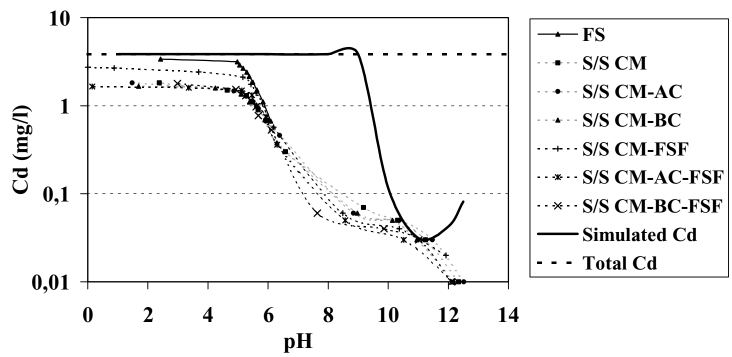

Fig. 6. Cadmium extractable amount following the WTC leaching test.

very similar trends in S/S products with Portland cement as binder, while lime stabilisation shows a lower mobility of this metal at the same pH.

The maximum available amount of metal has been considered the metal concentration at pH equal to 2 from WTC test, and it is shown in Table 5. The maximum available lead and chromium concentration is very different to the total concentration identified in the waste after acid digestion analysis. The availability indicated an available amount of 2.20 and 20.5% of lead and chromium, respectively. Zinc and cadmium are very available ranging for 100–87.8%, respectively.

In relation to the zinc behaviour, it is possible to observe that in all pH range, the zinc concentration is very similar to the solubility curves of the hydroxide ions. The zinc contents show an amphoteric behaviour in the waste and all derived products. The zinc behaviour indicates that it is necessary an acidic medium with pH lower than 8 in the leachates of the mixtures with cement Portland to leach a high zinc concentration. The lower zinc concentrations are obtained at pH between 8 and 11. This behaviour has been reported for different waste in [57]. In the mixtures with lime, the high content of zinc is also found at very alkaline pH. It is possible to assume that zinc concentration is mainly related to the leachate pH and it is important to remark a negligible influence on the use of additives.

The chromium concentration of the leachates is shown in Fig. 5. The chromium extractable amount is below 10 mg/l

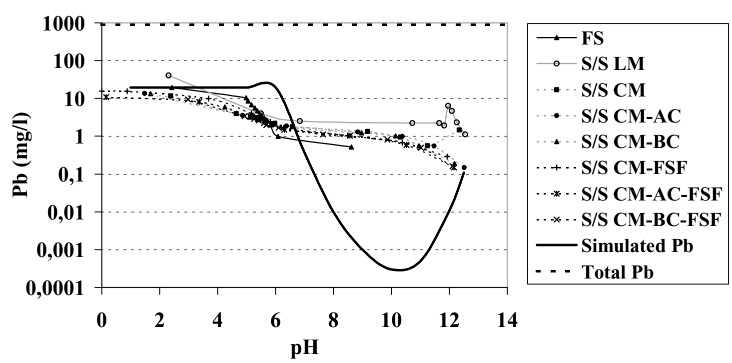

Fig. 7. Lead extractable amount following the WTC leaching test.

in all the range of pH and is lower at higher values of pH in acidic medium (pH < 7) and lower than 0.1 mg/l in basic medium (pH > 7). The experimental curves do not show the behaviour of hydroxide species, since the experimental results are above the simulated curve in the waste and S/S derived products. In all cases, the chromium content does not show any amphoteric behaviour.

The cadmium results are indicated in Fig. 6. In the waste and all S/S products, similar trends are found. The cadmium extractability is lower than the simulated at high range of pH in acidic medium and lower than 0.1 mg/l in basic medium. In all range of pH, the experimental concentration of cadmium is completely displaced towards the left in comparison with hydroxide species. Tamás et al. [58] obtain similar results from chromium and cadmium leaching in the acid neutralisation capacity tests using cement and cement with activated carbon as additive in S/S processes of electroplating waste.

The lead contents following the WTC test are shown in Fig. 7. The results with lime as binder show a higher concentration of lead than cement products. Cement stabilisation shows very similar trends. The studied additives (foundry sand fines, activated carbon and black carbon) have a negligible influence in the lead extractability. The pH should be lower than 9 in the products with Portland cement in order to reach a lead content higher than 1 mg/l. However, in the case of mixtures with lime, this concentration is lower than the results in all interval of pH. These results are

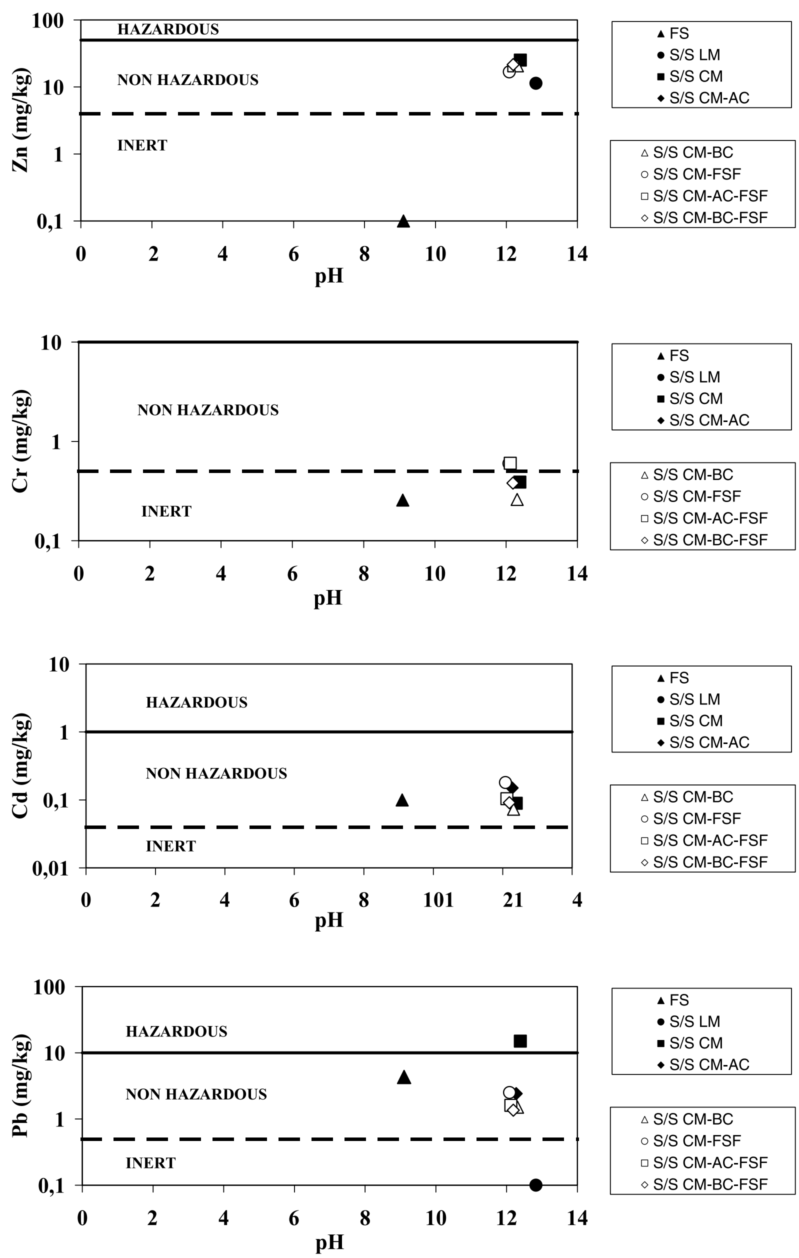

Fig. 8. Obtained results for inorganic pollutants following the EN12457 leaching test.

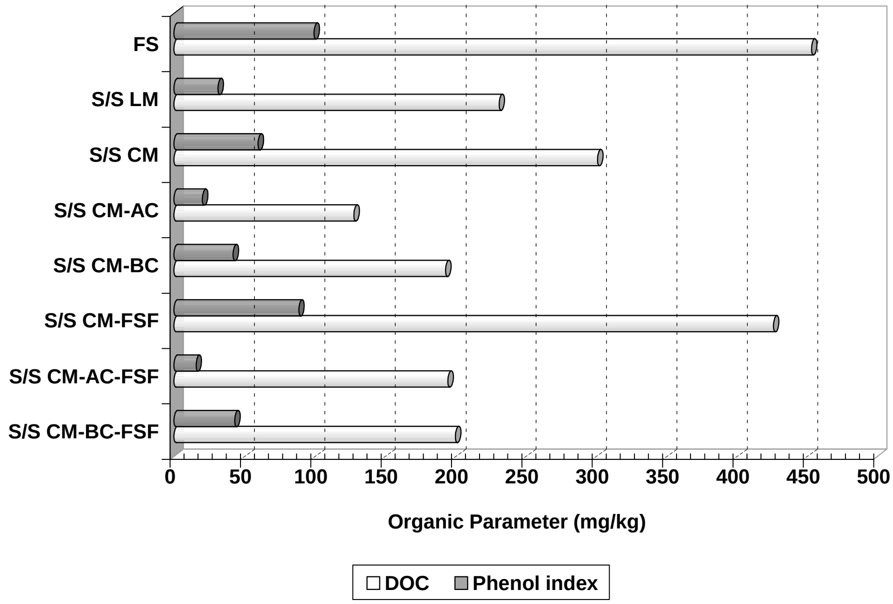

Fig. 9. Obtained results for organic pollutants following the EN12457 leaching test.

in good agreement with the amphoteric behaviour of lead hydroxide.

On the other hand, the lead results do not seem to respond to the behaviour of hydroxide compounds, since the curve is completely displaced to the left in acid medium or to the right in the basic range. Furthermore, only the S/S product that has been stabilised with calcium oxide has a higher availability than the simulated solubility curve.

3.3. Compliance tests

The limit of the pollutants related to landfilling has to be referred to the 2003/33 EU council decision [30]. Three landfills have been established: landfills for inert waste, non-hazardous waste and hazardous waste.

The results of metallic pollutants are based on the European Norm 12457, shown in Fig. 8. All stabilised/solidified products can be disposed of in a non-hazardous waste landfill, with the exception of the product stabilised with cement, which may be disposed of in a landfill for hazardous waste due to the lead limit. Lead hydroxides have an amphotheric behaviour and it is very sensitive to the amounts of binder and additives to obtain the pH of the leachate in the range of lead limit. The binders and additives used in the immobilisation process have a small influence on the compliance testing of metallic compounds.

The dissolved organic carbon and the phenol index in the EN leachate are shown in Fig. 9. The foundry sludge contains a phenol concentration of 99.5 mg/kg. However, in the literature it has been found that the initial phenol concentration in this type of waste have not any influence on the phenol fixation in the S/S process [15,23,27]. All S/S products fulfil the limit of 500 mg/kg for hazardous and inert waste according to the European Decision [30] for DOC. However, S/S products do not fulfil the limit of phenol index (1 mg/kg) for inert waste. Therefore, all samples can be disposed of in landfill for non-hazardous waste. The S/S products with lime have a lower quantity of organic compounds in the leachate than products with cement. This may be due to the exothermal reaction of lime hydration and the adsorption of these compounds on the solid surface [9]. Derived products with black carbon or active carbon as additives show the best results. The samples with foundry sand fines show similar results when it compares with cement.

It is very important to note that the conclusions of both EN and WTC leaching tests, are very similar in spite of their different procedure, therefore, it is possible to conclude that the metals extractability mainly depends on pH of the leachate. The amphoteric behaviour of zinc leads to lower concentrations at pH between 8 and 10 and higher concentrations when pH increases. However, chromium and cadmium concentrations are very similar in the basic range (pH 8–14).

4. Conclusions

The acid neutralisation capacity tests applied to the waste and the stabilised/solidified products leads to results of environmental interest, conductivity, redox potential and metal extractability, as a function of the pH in the liquid phase. The results show that the pH as well as the conductivity and the contents of the pollutants depend on its inorganic composition (mainly the content of Zn and Fe), specially in the acid range. The organic compounds, however, affect the redox potential of the waste.

The evolution of metals, Zn, Pb, Cr and Cd, in the S/S products is very similar, being the leachate pH (and not the additives and binders used) the most important factor on the stabilisation process. Computer modelling of equilibrium has been performed in order to compare the experimental amounts curves as a function of pH with the theoretical curves. The zinc extractable amounts are very similar to the simulated curves, while the lead and chromium behaviours do not agree well with hydroxide solubility curves in S/S products. Cadmium does not behave as the hydroxide showing lower solubilities. The available lead in the leachate is also lower than that simulated one in all range of pH.

The binders lime and cement, allow to fit the buffer capacity and the best results of neutralisation capacity have been obtained using lime as binder and the worse using foundry sand fines as additive due to their pozzolanic behaviour. Black carbon and activated carbon have a negligible influence on the neutralisation processes due to their neutral behaviour and to the fact that they are present in a very small amounts.

All stabilised/solidified products may not be disposed of in a landfill for inert waste, the immobilisation process contributes only to increase the neutralisation capacity of the derived products. The additives used in the process contribute to the retention of organic pollutants. The samples with black carbon or active carbon as additive show the best results in the organic matter, giving a higher grade of fixation in the matrix.

Acknowledgements

This work has been supported by a Spanish Ministry of Education and Culture I+D Project. Programme FEDER No. 1FD97-0506-C02-01. A Project of the Spanish Environment Ministry, Programa National/No. 2000/09 is also acknowledged.

References

[1] DOCE, European Waste Catalogue, L226/3-24. 2000/532/EC, Commission Decisions 2001/118/EC, 2001/119/EC and Council Decision 2001/573/EC, 2001.

[2] A. Andrés, A. Coz, C. Ruiz, C. de Miguel, A. Irabien, Biotreatment of Foundry Sludges: Study of Feasability, Chemical Industry and Environment III, Technical University of Lódz, Lódz, 1999, pp. 491–497.

[3] C. Ruiz, A. Andrés, A. Irabien, Environmental characterization of ferrous foundry wastes, Environ. Technol. 21 (2000) 891–899.

[4] BOE, Decree Real 952/97, 20/06, that modifies the Regulation for the Execution of the Law 20/86, approved by means of Decree Real 833/88, Boletín Oficial del Estado, Spain, 160, 1997.

[5] IPPC, Draft Reference Document on Best Available Techniques for the Waste Treatments Industries, European IPPC Bureau, 2003.

[6] J.R. Conner, S.L. Hoeffner, The history of stabilization/solidification technology, Crit. Rev. Environ. Sci. Technol. 28 (4) (1998) 325–396.

[7] J.R. Conner, S.L. Hoeffner, A critical review of stabilization/solidification technology, Crit. Rev. Environ. Sci. Technol. 28 (4) (1998) 397–462.

[8] E.F. Barth, et al., Stabilization and Solidification of Hazardous Wastes, Noyes Data Corporation, New Jersey, 1990.

[9] J.R. Conner, Chemical Fixation and Solidification of Hazardous Wastes, Van Nostrand Reinhold, New York, 1990.

[10] J.E. Noakes, Solidification of Organic Waste Materials in Cement, US Patent 5 269 975, 1993. http://www.uspto.gov/patft/.

[11] M.D. LaGrega, P.L. Buckingham, J.C. Evans, Gestión de residuos tóxicos, Tratamiento, eliminación y recuperación de suelos, McGraw-Hill, Madrid, Spain, 1996.

[12] D.L. Oliver, M.S. Roberts, P. Atkinson, N.J. Calos, Stabilizing soil and aggregate mixtures and structures, US Patent 5 820 302, 1998. http://www.uspto.gov/patft/.

[13] J.-E. Chang, T.-T. Lin, M.-S. Ko, D.-S. Liaw, Stabilization/solidification of sludges containing heavy metals by using cement and waste pozzolans, J. Environ. Sci. Heal. A 34 (5) (1999) 1143–1160.

[14] J.M. Gunter, Lime/cement columnar stabilization of soil, US Patent 5 967 700, 1999. http://www.uspto.gov/patft/.

[15] V.M. Hebatpuria, H.A. Arafat, H.S. Rho, P.L. Bishop, N.G. Pinto, R.C. Buchanan, Immobilization of phenol in cement-based solidified/stabilized hazardous wastes using regenerated activated carbon, J. Hazard. Mater. B 70 (1999) 117–138.

[16] M. Kamon, J. Katsumi, K. Watanabe, Heavy-metal leaching from cement stabilized waste sludge, in: T.B. Edil, P.J. Fox (Eds.), Geotechnics of High Water Content Materials, ASTM STP 1374, West Conshohocken, PA, 2000, pp. 123–136.

[17] J. Viguri, A. Andrés, Cement-waste and clay-waste derived products from metal hydroxides wastes, in: C. Ruiz, A. Irabien, F. Castro (Eds.), Transactions of IChemE, vol. 79B (2001) pp. 38–44.

[18] N. Hytiris, I.E. Kapellakis, R. La Roij de, K.P. Tsagarakis, Resour. Conserv. Recy. 40 (2004) 129–139.

[19] M. El-Fadel, E. Bou-Zeid, W. Chahine, B. Alayli, Temporal variation of leachate quality from pre-sorted and baled municipal solid waste with high organic and moisture content, Waste Manage. 22 (2002) 269–282.

[20] S. Valls, E. Vázquez, Stabilisation and solidification of sewage sludges with Portland cement, Cement Concrete Res. 30 (2000) 1671–1678.

[21] R. Cioffi, L. Maffucci, L. Santoro, F.P. Glasser, Stabilization of chloro-organics using organophilic bentonite in a cement-blast furnace slag matrix, Waste Manage. 21 (2001) 651–660.

[22] J.D. Mckinley, H.R. Thomas, K.P. Williams, J.M. Reid, Chemical analysis of contaminated soil strengthened by the addition of lime, Eng. Geol. 60 (2001) 181–192.

[23] H. Rho, H.A. Arafat, B. Kountz, R.C. Buchanan, N.G. Pinto, P.L. Bishop, Decomposition of hazardous organic materials in the solidification/stabilization process using catalytic-activated carbon, Waste Manage. 21 (2001) 343–356.

[24] A.J. Pedersen, Evaluation of assisting agents for electrodialytic removal of Cd, Pb, Zn, Cu and Cr from MSWI fly ash, J. Hazard. Mater. B 95 (2002) 185–198.

[25] J.R. Conner, P.R. Lear, Immobilization of low-level organic compounds in hazardous waste, in: Proceedings of the Annual Meeting of Air and Waste Management Association, 84 (11), 1991, pp. 91/22.9 1–18.

[26] J.R. Conner, F.G. Smith, Immobilization of low-level hazardous organics using recycled materials, in: T.M. Gilliam, C.C. Wiles (Eds.), Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes, ASTM STP 1240, 1996, pp. 52–68.

[27] V.M. Hebatpuria, H.A. Arafat, H.S. Rho, P.L. Bishop, N.G. Pinto, R.C. Buchanan, Leaching behavior of selected aromatics in cement-based solidification/stabilization under different leaching tests, Environ. Eng. Sci. 16 (6) (1999) 451–463.

[28] J.R. Conner, Recent findings on immobilization of organics as measured by total constituent analysis, Waste Manage. 15 (5/6) (1995) 359–369.

[29] EPA, Identification and listing of hazardous waste, 40 CFR, I-Part 261, 1999.
[30] DOCE, Council Decision 2003/33/EC establishes uniform criteria and procedures for the acceptance of waste at landfill sites, in accordance with Article 16 of Annex. II to Directive 1999/31/EC, 2003.
[31] WTC, Proposed Evaluation Protocol for Cement-based Solidified Wastes, Wastewater Technology Centre, Environment Canada, Report EPS 3/HA/9, 1991.
[32] D.E. Bleiker, G. Farquar, E. McBean, Landfill settlement and the impact on site capacity and refuse hydraulic conductivity, Waste Manage. Res. 13 (1995) 533–554.
[33] M.M.D. Coleman, T.J. Whalen, A. Landua, Investigation on the placement of lime neutralization sludge on acid generating waste rock, in: Proceedings of the Fourth International Conference on Acid Rock Drainage, Vancouver, Canada, 1997, pp. 1163–1175.
[34] C. Ludwig, F. Ziegler, C.A. Johnson, Heavy metal binding mechanisms in cement-based waste materials, in: J.J.J.W. Goumans, G.J. Senden and H.A. van der Sloot (Eds.), Waste Materials in Construction: Putting Theory into Practice, Elsevier, Amsterdam, 1997, pp. 459–468.
[35] D.C. Dusing, P.L. Bishop, T.C. Keener, Effect of redox potential on leaching from stabilized/solidified waste materials, J. Air Waste Manage. 42 (1) (1992) 52–62.
[36] R.D. Spence, Chemistry and Microstructure of Solidified Waste Forms, Lewis Publishers, 1993.
[37] A. Coz, Comportamiento ambiental de lodos de fundición estabilizados/solidificados, PhD Thesis, Departamento Química, Universidad de Cantabria, Santander, Spain, 2001.
[38] J. Yan, L. Moreno, I. Neretnieks, The long-term acid neutralizing capacity of steel slag, Waste Manage. 20 (2000) 217–223.
[39] H.K. Karapanagioti, A. Atalay, Adsorption of acid mine drainage metals on fly ash, in: Proceedings of the Annual Meeting of the American Society for Surface Mining and Reclamation, Knoxville, Tennessee, May 1996, pp. 659–670.
[40] M. Shum, L. Lavkulich, Speciation and solubility relationships of Al, Cu and Fe in solutions associated with sulfuric acid leached mine waste rock, Environ. Geol. 38 (1) (1999) 59–68.
[41] J.A. Stegemann, A. Roy, R.J. Caldwell, P.J. Schilling, R. Tittsworth, Understanding environmental leachability of electric arc furnace dust, J. Environ. Eng. 126 (2) (2000) 112–120.
[42] A.J. Pedersen, L.M. Ottosen, A. Villumsen, Electrodialytic removal of heavy metals from different fly ashes: influence of heavy metals speciation, J. Hazard. Mater. 100 (1–3) (2003) 65–78.
[43] S. Soriano, Ensayos de lixiviación para residuos industriales con elementos metálicos, PhD Thesis, Departamento de Ingeniería Química y Química Inorgánica, Universidad de Cantabria, Santander, Spain, 2002.
[44] A. Coz, A. Andrés, C. Ruiz, J. Viguri, A. Irabien, Estabilización/solidificación de residuos con cal o cemento, Medio Ambiente RETEMA 87 (2002) 24–33.
[45] A. Coz, A. Andrés, C. Ruiz, J. Viguri, A. Irabien, Procesos de estabilización/solidificación de lodos de fundición de carácter mixto (orgánico-inorgánico), Medio Ambiente RETEMA 88 (2002) 29–38.
[46] CEMEX, Commercial information, Barcelona, Spain, 1989.
[47] J. Stegemann, P.L. Côté, Investigation of test methods for solidified waste evaluation—appendix B: test methods for solidified waste evaluation, Environment Canada Manuscript Series, Document TS-15, Burlington, Ontario, Canada, 1991.
[48] US EPA, Test Methods for Evaluation Solid Waste: Physical/Chemical Methods, Inductively Coupled Plasma-Atomic Emission Spectrometry, SW 846-6010B, 1996.
[49] DIN, German Standard Determination of the Phenol Index by Water, Waste Water and Sludges, 38409-H16, 1984.
[50] C. Bäverman, The importance of the pH buffering capacity-comparison of various methods to estimate the pH properties of a waste material, in: Proceedings of the Fifth Annual North American Waste to Energy Conference, Research Triangle Park, NC, US, 22–25 April 1997, pp. 739–748.
[51] J.R. Conner, F.G. Smith, Composition and method for immobilizing organic compounds in hazardous wastes and soils, US Patent 5 536 898, 1996. http://www.uspto.gov/patft/.
[52] D.S. Kelly, E.C. Diethelm, Effects of various additives on the solidification of oily sludges: a bench-scale study, in: T.M. Gilliam, C.C. Wiles (Eds.), Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes, vol. 3, ASTM, 1996.
[53] Jones Chemicals, Solidification/stabilization of hazardous wastes, Chem. Process. October (1997) 177–178.
[54] G. Sarritzu, Inertization of waste material contaminated with heavy metals, WO Patent 9 944 688, 1999.
[55] K.W. Yost, D. Pal, Fixation and stabilization of metals in contaminated soils and materials, US Patent 5 916 123, 1999. http://www.uspto.gov/patft/.
[56] C.S. Poon, K.W. Lio, The limitation of the toxicity characteristic leaching procedure for evaluating cement-based stabilised/solidified waste forms, Waste Manage. 17 (1) (1997) 15–23.
[57] H.A. van der Sloot, Characterization of the leaching behavior of concrete mortars and of cement-stabilized wastes with different waste loading for long term environmental assessment, in: J. Méhu, G. Keck, A. Navarro (Eds.), Proceedings of the Waste Stabilisation and Environment, Société Alpine de Publications, Lyon, France, 1999, pp. 131–139.
[58] F.D. Tamás, L. Csetényi, J. Tritthart, Effect of adsorbents on the leachability of cement bonded electroplating wastes, Cement Concrete Res. 22 (1992) 399–404.