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Influence of commercial and residual sorbents and silicates as additives on the stabilisation/solidification of organic and inorganic industrial waste

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ABSTRACT

An environmental problem of the foundry activities is the management of industrial waste generated in different processes. The foundry sludge from gas wet cleaning treatment that contains organic and inorganic compounds and a high content of water is an interesting example. Due to their characteristics, they can be managed using different stabilisation/solidification (S/S) technologies prior to land disposal. The purpose of this work is to study S/S formulations in order to improve the control of the mobility of the pollutants and the ecotoxicity of the samples. Different mixtures of cement or lime as binders and additives (foundry sand, silica fume, sodium silicate, silicic acid, activated carbon and black carbon) have been used in order to reduce the mobility of the chemical and ecotoxicological regulated parameters and to compare the results for commercial and residual additives. The best results have been obtained with sorbents (activated carbon and black carbon) or sodium silicate. The results of the foundry sand ash as additive can conclude that it can be used as replacement in the cement products. However, silica fume in the samples with lime and siliceous resin sand as additives gives products that do not fulfil the regulated limits. Finally, some linear expressions between the chemical parameters and the quantity of material used in the samples have been obtained.

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1. Introduction

The foundry activities generate a great volume of industrial waste in the production of ferrous and steel products. One of the most important waste materials is the foundry sludge, which is obtained from gas wet cleaning treatment. It is characterised as hazardous waste by the European Waste Catalogue [1], that assigns it the code 10 02 13*. The European Waste Catalogue Draft [2] considers it as hazardous using the criteria H05 (harmful) and H14 (ecotoxic). Furthermore, in previous works [3–5], taking into account the Spanish regulation [6], the foundry sludge was found to be ecotoxic waste due to organic compounds such as phenol and organic carbon, and inorganic compounds such as Zn and other metallic elements.

Among the different treatment technologies, stabilisation/solidification (S/S) processes are the most suitable ones to manage the foundry sludge prior to land disposal, because of its characteristics [7]. The environmental availability of the S/S products can be studied through leaching tests. Among these leaching tests, the EN 12457-2 test for leaching of granular waste materials (EN) and the toxic characteristic leaching procedure (TCLP) are typically compliance tests (aimed at a direct comparison with regulatory thresholds). EN and TCLP tests are very useful to establish the interactions between countries with different regulatory requirements (US EPA and European Union) and to consider several relevant aspects of leaching behaviour. The TCLP is not relevant for many utilisation or disposal scenarios, whereas the solubility controlled conditions as obtained in the neutral to mildly alkaline pH domain are relevant for field conditions. In previous works [4,5,8], cement and lime have been used as binding materials in the S/S of foundry sludge. The results obtained for the TCLP test were satisfactory, working with a 70 wt% of waste material and 30 wt% of cement or lime; U.S. EPA limits [9] were not exceeded and the value of EC_{50} obtained was below 3000 mg L^{-1}, limit given by the Spanish regulation [6]. On the other hand, Zn and total organic carbon (TOC) concentrations on the leachate of the EN test did not comply with the limits given by EU regulation [10].

In this work, different additives (foundry sand, silica fume, sodium silicate, silicic acid, activated carbon and black carbon) have been used in order to fulfil the regulated limits and compare the behaviour of the commercial and residual additives in the process. The commercial siliceous additives (silica fume, sodium silicate and silicic acid) have been used due to their acid character and the formation of metallic silicates instead of the corresponding hydroxides [11–13]. By acidifying the mixtures, a value of pH between 9

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Nomenclature

AC	S/S products with activated carbon as additive
BC	S/S products with black carbon as additive
CM	S/S products with cement as binder
EN	EN 12457-2 test for leaching of granular waste materials
FA	S/S products with foundry sand ash as additive
FS	foundry sludge
LM	S/S products with lime as binder
OP	organic parameter
OP_{FS}	value of organic parameter in the foundry sludge
$OP_{S/S}$	value of organic parameter in the S/S product
SA	S/S products with silicic acid as additive
SF	S/S products with silica fume as additive
SR	S/S products with siliceous resin sand as additive
SS	S/S products with sodium silicate as additive
TCLP	toxic characteristic leaching procedure for waste materials

and 10 on the leachate of the EN test is expected. In this range of pH, hydroxides from amphoteric metals exhibit minimum solubility [14]. Furthermore, the solubility of silicate species is minimum in a wide range of pH [15,16]. Foundry sand (siliceous resin sand and foundry sand ash) from the foundry industry have been used as residual siliceous additives to improve the sustainable management of the steel and ferrous activities. Residual black carbon and commercial activated carbon have been used as sorbents in order to immobilise the organic content on the leachate [17–19].

In order to check the formation of metallic silicates, an acid neutralisation capacity test, standardised by the Wastewater Technology Centre (WTC-ANC), was carried out. Thanks to this test, it is possible to represent the metal concentration on the leachate vs. pH [20]. From the solubility curves obtained, it will be possible to know if the silicate formation predominates.

Many papers have studied cement or lime as binders and siliceous and sorbents as additives in S/S technologies [11–13,18,19,21–35]. Siliceous additives have been used in order to improve the physical and textural properties [12,24,29], to immobilise the heavy metals [23,25,26,28–30,32,34] and some organic compounds [21,24] and to resist physico-chemical attacks [11]. Sorbents have been used in order to immobilise the organic pollutants [18,19,21,33,35] and some heavy metals [22,27,31]. Although many papers have reported these S/S treatment, few results have been obtained on waste materials of mixed character [17,36–38] and the comparison of the different siliceous additives and different sorbents (commercial and residual) has not been reported. The purpose of the present work is to develop new S/S formulations based on the use of mixtures of cement (or lime) and several additives in a real waste of mixed character and to study the behaviour of the residual and commercial additives in the process.

2. Methods and materials

2.1. Materials

Foundry sludge (FS) has been used as waste. It is a hazardous waste of mixed character derived from foundry activities, which is generated after wet cleaning of gases with a production of 500 tonnes/year. Portland cement type I (CM) was the main binding material used. In some cases it was replaced by standard lime (LM). The siliceous additives incorporated to the mixtures were silica fume (SF), which is basically SiO_2, sodium silicate Na_2SiO_3 (SS) in a 40% solution, silicic acid (SA) and foundry sand ash (FA) and siliceous resin sand (SR), which are by-products from foundry activities. Foundry sand ash and resin sand are generated from casting and coremaking processes and their production are 6000 and 4000 tonnes/year, respectively. Activated carbon (AC) reagent grade and black carbon (BC) from the carbon industry have been studied as sorbents.

Based on previous studies [4,5,8], S/S products have been formulated using 70 wt% foundry sludge and different amounts of binder and additives. The formulations of the S/S products are shown in Table 1. The samples with cement as binder have been formulated according to the literature: sodium silicate have been used in other studies until 30% in relation to the binder and additives percentage [15,39], in this work, samples with 5–75 wt% have been formulated due to the percentage of sodium silicate in the solution (40%); silica fume and activated carbon have been widely used in cement stabilisation [13,18,21,35], in this work, 3.33–15 wt% of silica fume, activated carbon and black carbon have been used in order to optimise the minimum quantity of additive that is necessary to fulfil the regulated limits. We will compare both additives (activated carbon as sorbent and silica fume as siliceous additive) and study the possibility of using residual waste (black carbon) as sorbent material. Foundry sand ash and siliceous resin sand have been used as waste residuals from the foundry industry. The quantity of foundry sand ash has been optimised in previous studies [5]. A minor quantity of resin sand has been used due to the organic pollutants in their composition. The quantities of binder and additives used in lime products are shown in Table 1. 3.33–15 wt% silica fume has been used in order to compare the results of two binders (cement and

Table 1
Stabilisation/solidification formulations (% wt) with 70% waste material

Foundry sludge (70%)[a]						
Cement (CM)[b]						
None[c]	Silica fume (SF)[c]	Sodium silicate (SS)[c]	Siliceous resin sand (SR)[c]	Foundry sand ash (FA)[c]	Activated carbon (AC)[c]	Black carbon (BC)[c]
0	3.33, 15	5, 25, 50, 75	10, 20	33.3	3.33, 15	3.33, 15

Foundry sludge (70%)[a]		
Lime LM[b]		
None[c]	Silica fume (SF)[c]	Silicic acid (SA)[c]
0	3.33, 15, 90, 95, 100	15

The quantity of the additive in the mixture is shown. The quantity of the binder (cement or lime) is obtained as 30%—Additive%.

[a] Waste.

[b] Binder.

[c] Additive.

Table 2
Results of characterisation of foundry sludge

	Total composition			
	Water content (%)[a]	ZnO (% d.w.)[a]	TOC (% d.w.)[a]	Phenol index (mg kg^{-1} d.w.)[a]
Waste FS	47.49–62.43	50–54.69	9.68	290.2

	Test						
	EN leaching test				TCLP		
	pH[a]	Zn (mg kg^{-1})[a]	Phenol index (mg L^{-1})[a]	TOC (mg L^{-1})[a]	pH[a]	Zn (mg kg^{-1})[a]	EC_{50} (mg L^{-1})[a]
Waste FS	9.07–9.65	18.4–29	1.23–45.3	9.95–254.2	5.79–6.59	1826–2133	769–1026
Non hazardous limit	>6 [10]	50 [10]	Not reg. limit	80 [10]	Not reg. limit	Not reg. limit	<3000 [6]

[a] Parameter.

lime). The rest of samples with lime have been formulated in order to obtain the value of pH with minimum solubility of heavy metals, according to the literature [15,16].

2.2. Methods

Waste samples were mixed in a CEMEX W-20, X-02-G laboratory-scale solid mixer prototype. Each mixture was transferred to a plastic bag at room temperature for 7 days. The samples were characterised using the TCLP [40] and EN 12457-2 [10] leaching tests. The parameters measured on the TCLP leachate were pH, ecotoxicity (EC_{50}) and Zn concentration, while on the EN leachate were pH, TOC, phenol index and Zn concentration. The WTC-ANC test [20] was carried out in order to check the pH influence on the Zn mobility of the S/S products.

2.2.1. Ecotoxicity evaluation

The parameter EC_{50} was determined using the luminescence bioassay with marine bacterium *Photobacterium phosphoreum* in a Microtox toxicity analyser. The standard method is based on the light diminution of bioluminiscent bacterial cells, when mixed with toxic substances. Ecotoxicity results were compared to the value $EC_{50} < 3000$ mg L^{-1} given by Spanish regulation (H14) [6].

2.2.2. Analytical evaluation

The Zn concentration on the leachate was measured using a Spectrometer of Atomic Emission by Inductive Coupled Plasma, ICP PERKINELMER 400. To determine the TOC the system EUROGLAS TOC 1200 was employed. Phenol index was determined according to DIN 38409-H16 “Determination of phenol index 4-aminoantipyrine spectrometric methods after distillation”, using a PERKINELMER LAMBDA 2UV/VIS spectrophotometer [41].

3. Results and discussion

Seven samples of waste material, foundry sludge (FS), have been characterised. The results can be observed in Table 2. The foundry sludge is an ecotoxic waste due to organic parameters (phenol index and TOC on the EN leaching test) and inorganic parameters (zinc on EN and TCLP leaching tests). The non-regulated parameters (phenol index on the EN test and zinc on the TCLP test) have been studied because they have an influence on the ecotoxicity of the waste [42].

As can be observed in Table 2, the results of inorganic parameters are very similar in all samples. However, the results of organic parameters are very heterogeneous, due to their accumulation in the wet process of cleaning gases from the shaft furnace [4].

Figs. 1 and 2 show the results of the value of pH and zinc concentration, respectively, in all the S/S products versus the quantity of the studied additives in the binder–additive mixture. In all cases, a 70% waste material has been used. To control the mobility of amphoteric metal (zinc as hydroxide speciation) on the leaching tests, a value of pH on the leachate of 9–10 should be achieved [15,43]. If only cement or lime is used as binder, pH values rises to approximately 12. With the use of additives in the samples, if the quantity of additive is smaller than 80%, in spite of the fact that the pH value on the EN leachate is in the range of 12–12.5, the zinc concentration is in the wide range of 10–100 mg kg^{-1}. Only the product with 25% cement and 75% sodium silicate (SS) does not fulfil the limit for non hazardous waste. When a mixture of lime and silica fume is used, if an EN test is carried out with only silica fume, the pH value of the leachate is 8.15, but when mixed with lime it can be observed that lime neutralises the acid effects of the silica fume, obtaining zinc concentrations smaller than 10 mg kg^{-1} (Fig. 2).

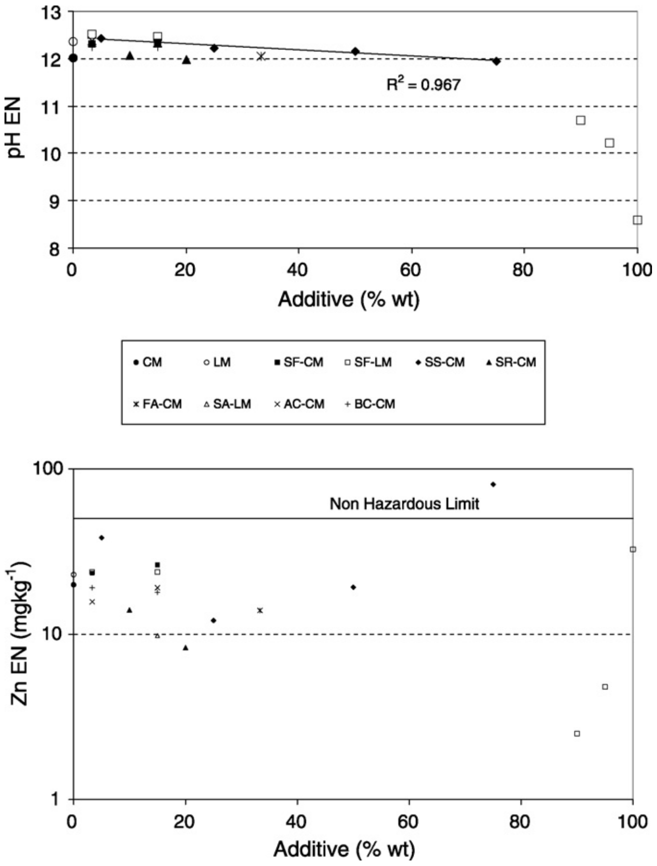


Fig. 1. Results of pH value and zinc concentration from the EN leaching test.

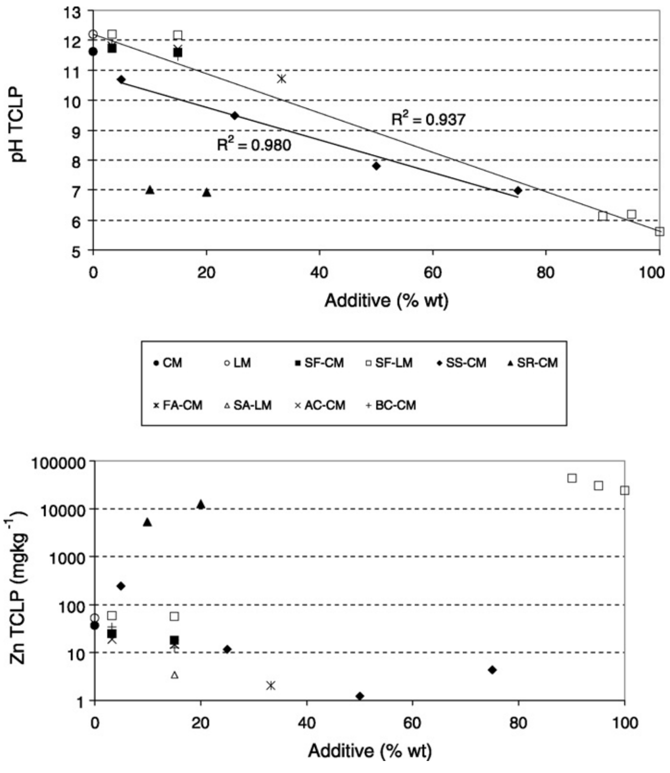


Fig. 2. Results of pH value and zinc concentration from the TCLP leaching test.

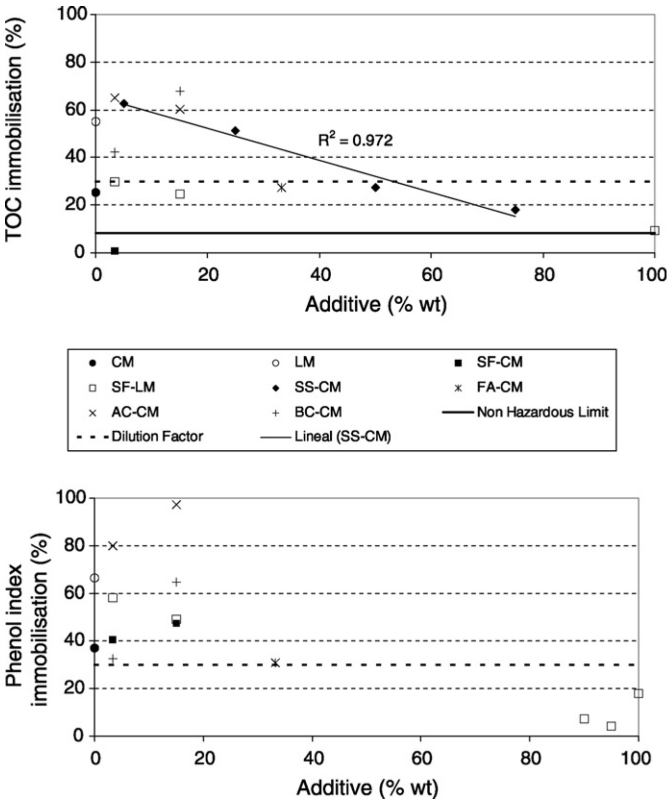


Fig. 3. Results of organic parameters from the EN leaching test.

The pH value on the TCLP leachate diminishes when increasing the quantity of additive in the mixture without the dependence of the binder used. The results of pH value on the TCLP leachate with cement and sodium silicate as additive (SS–CM) follow a linear law whose regression coefficient is 0.980. The rest of the samples, except for the additions of 10 and 20% of siliceous resin sand additive (SR), follows also a linear law whose regression coefficient (R^2) is 0.937. Regarding the resin sand samples (SR), the acid character of this residual additive gives more acid pH values obtaining a high mobility of zinc (>1000 mg kg^{-1}) on the TCLP leachate.

The results of organic parameters (TOC and phenol index) in the S/S products have been obtained as immobilised percentage due to their heterogeneous composition. The immobilisation percentage is defined as follow: OP immobilised (%) = $100(\mathrm{OP}_{\mathrm{FS}} - \mathrm{OP}_{\mathrm{S/S}})/\mathrm{OP}_{\mathrm{FS}}$, where OP is the organic parameter, $\mathrm{OP}_{\mathrm{S/S}}$ is the value of leachable organic parameter in the S/S product and $\mathrm{OP}_{\mathrm{FS}}$ is the value of leachable organic parameter in the foundry sludge used in the S/S process.

The results of organic parameters on the EN leachate are given in Fig. 3. The best results of organic immobilisation are obtained in the samples with sorbent materials (activated carbon as commercial additive and black carbon as residual material). Furthermore, the higher quantity of sorbent is, the higher organic immobilisation results are obtained. Other satisfactory results of organic parameters are obtained in the products with lime as binder and low quantities of silica fume (SF–LM 0–15%) and the mixtures with 5–25% of sodium silicate and cement (SS–CM). The results of total organic parameter in the samples with sodium silicate show a lineal law versus the quantity of the additive in the sample. The regression coefficient is 0.972. The immobilisation of the TOC and phenol index on the EN leaching test has been smaller than the dilution factor (30% immobilisation) in the mixtures with sodium silicate percentages between 50 and 75% in the binder and all the rest of samples with cement and siliceous additives. The results of phenol index in the products with siliceous resin sand are not satisfactory due to some phenolic compounds in the sand. The immobilisation results in that case are below 0% and have not been represented in the figure.

Ecotoxicity results are shown in Fig. 4. If the value of the ecotoxicity is greater than 3000 mg L^{-1}, then the sample is not ecotoxic in relation to Spanish regulation [6]. The best results are obtained with sorbent materials; foundry sand ash (FA) and silica fume (SF) as additives in the samples with cement (CM) as binder. Satisfactory results appear in the mixtures with sodium silicate and cement (SS–CM). However, results close to the regulated limit are obtained in the mixtures with siliceous resin sand (SR) and the samples with

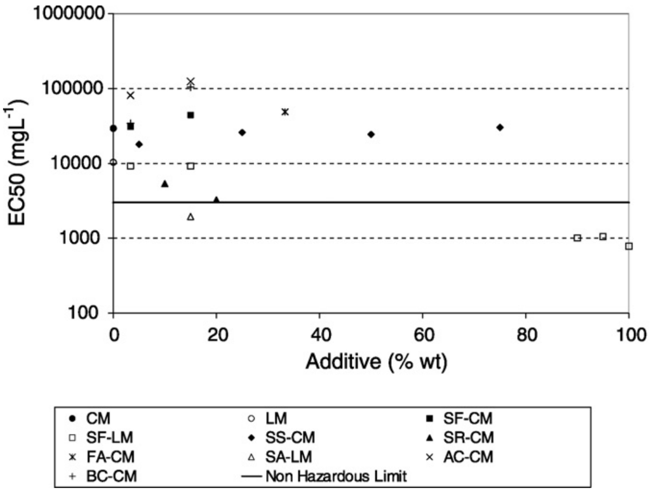
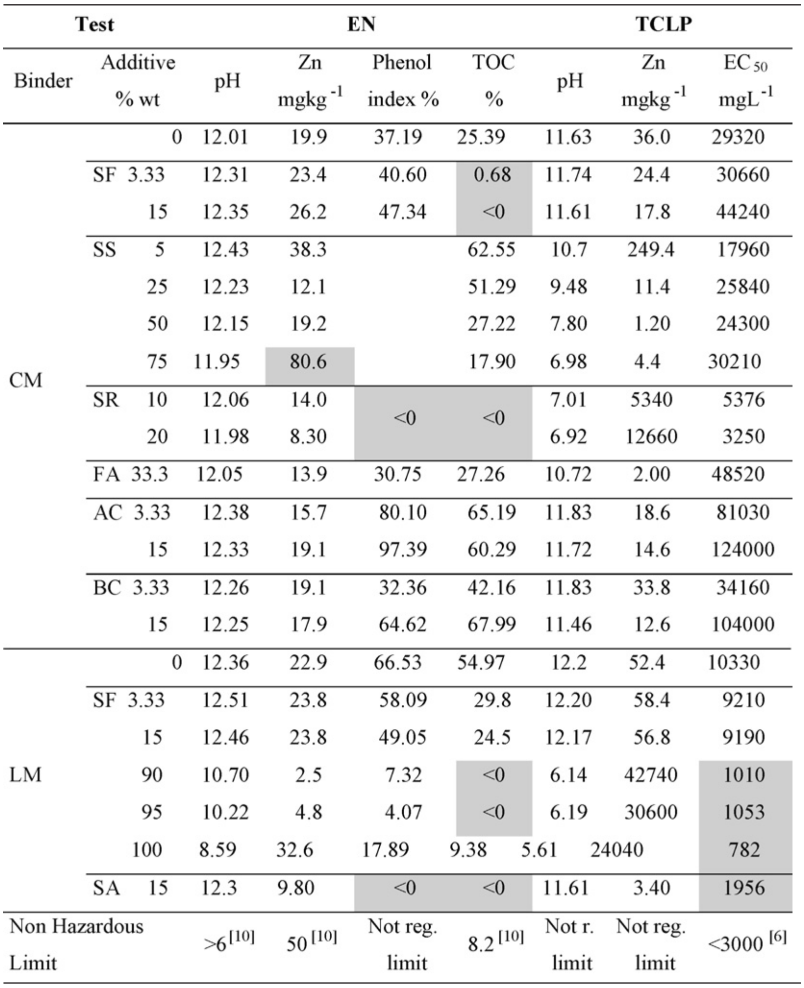


Fig. 4. Results of ecotoxicity from the TCLP leaching test.

Table 3
Results of characterisation of the S/S end-products



Test		EN				TCLP		
Binder	Additive % wt	pH	Zn mgkg^{-1}	Phenol index %	TOC %	pH	Zn mgkg^{-1}	EC$_{50}$ mgL^{-1}
CM	0	12.01	19.9	37.19	25.39	11.63	36.0	29320
	SF 3.33	12.31	23.4	40.60	0.68	11.74	24.4	30660
	15	12.35	26.2	47.34	<0	11.61	17.8	44240
	SS 5	12.43	38.3		62.55	10.7	249.4	17960
	25	12.23	12.1		51.29	9.48	11.4	25840
	50	12.15	19.2		27.22	7.80	1.20	24300
	75	11.95	80.6		17.90	6.98	4.4	30210
	SR 10	12.06	14.0	<0	<0	7.01	5340	5376
	20	11.98	8.30			6.92	12660	3250
	FA 33.3	12.05	13.9	30.75	27.26	10.72	2.00	48520
	AC 3.33	12.38	15.7	80.10	65.19	11.83	18.6	81030
	15	12.33	19.1	97.39	60.29	11.72	14.6	124000
	BC 3.33	12.26	19.1	32.36	42.16	11.83	33.8	34160
	15	12.25	17.9	64.62	67.99	11.46	12.6	104000
LM	0	12.36	22.9	66.53	54.97	12.2	52.4	10330
	SF 3.33	12.51	23.8	58.09	29.8	12.20	58.4	9210
	15	12.46	23.8	49.05	24.5	12.17	56.8	9190
	90	10.70	2.5	7.32	<0	6.14	42740	1010
	95	10.22	4.8	4.07	<0	6.19	30600	1053
	100	8.59	32.6	17.89	9.38	5.61	24040	782
	SA 15	12.3	9.80	<0	<0	11.61	3.40	1956
Non Hazardous Limit		>6 [10]	50 [10]	Not reg. limit	8.2 [10]	Not r. limit	Not reg. limit	<3000 [6]

CM: cement; LM: lime; SF: silica fume; SS: sodium silicate; SR: siliceous resin sand; FA: foundry sand ash; SA: silicic acid; AC: activated carbon; BC: black carbon. The shady cell indicates the non-fulfilment of the regulated limit for non hazardous waste.

silica fume and cement (SF–CM) when a low quantity of silica fume is added. Ecotoxic products are obtained in the samples with silicic acid (SA) and silica fume (SF) with lime (LM) when a high quantity of silica fume is used.

Table 3 shows the results in all end-products. The shady cell indicates the non-fulfilment of the regulated limit for non hazardous waste. As it can be observed, the best results are obtained in the samples with sorbents as additives (AC and BC). However, all S/S products with high quantities of additives in their composition (>75 wt%), the samples with silica fume (SF) and siliceous resin sand (SR) and cement (CM) and the end-products with silicic acid and lime (SA–LM) are hazardous waste due to the organic pollutants.

It is important to analyse the values of ecotoxicity in relation to the zinc mobility and the value of pH on the leachates showed in Figs. 1 and 2 and Table 3. When siliceous resin sand (SR) or silica fume (SF) and lime (LM) with a large quantity of silica fume in the mixtures is used, even though acceptable results of pH are obtained on the EN leaching test, achieving a Zn concentration on the leachate below the limit established by the European regulation, a low value of pH and high Zn concentration on the leachate of the TCLP test drives to undesirable values of EC$_{50}$ according to the Spanish regulation.

The products containing 5–50% sodium silicate comply with the references given by the Spanish and European regulations, and also the zinc mobility on the TCLP leachate is low. It is important to notice that although the pH value around 9 was not obtained, the concentration of the amphoteric metal, Zn, on the EN leachate was below the European limit. It could have happened that not only have metal hydroxides been formed, but also metal silicates. While metallic hydroxides exhibit minimum solubility through a narrow pH range, metallic silicates have minimum solubility through a wide range of pH. If too little sodium silicate is added, metallic hydroxides will form, and at high value of pH will be leached. However, if an excess of this additive is added, unwanted leachable metal ion silica complexes might form [11–13,15,29]. The low results of zinc mobility give satisfactory results of ecotoxicity. As shown in Fig. 2, the minimum Zn concentration in the EN leachate is achieved with a sodium silicate percentage of 5–25% in the binder.

In order to study, in a different way, the mobility of zinc versus pH and the neutralisation capacity of the obtained products, a WTC-ANC test has been carried out in the optimum end-products. The results are shown in Fig. 5. The samples were formulated with the optimum quantities of the additives (15% AC, 15% BC, 15% SS and 33% FA with cement). The products with SR and SF have not been studied due to the high results of organic mobility obtained. However, the product with 15% SA and lime has been formulated in order to study the acid behaviour of the additive in the neutralisation capacity of the obtained product. Furthermore, a comparison

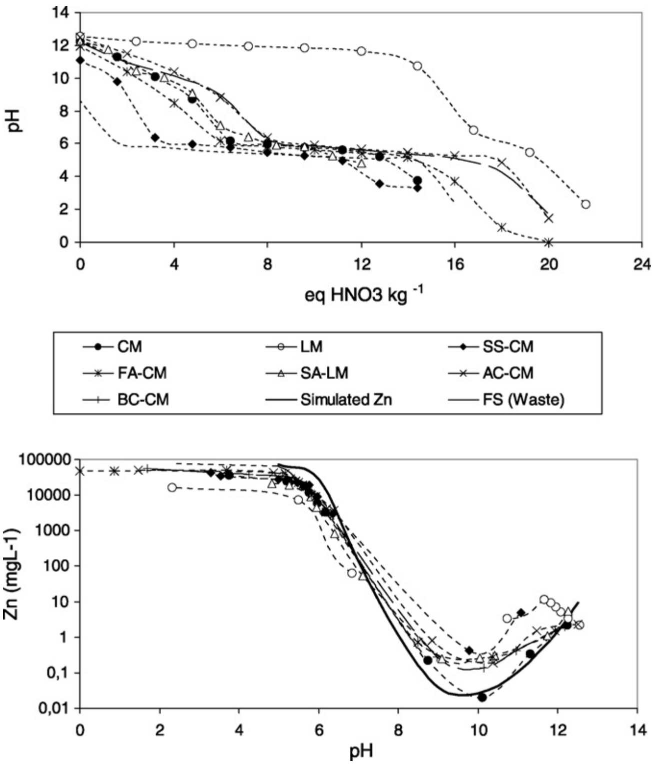


Fig. 5. Results of WTC-ANC test.

with the hydroxide curve is studied in the zinc results to check the silicate formation in mixtures containing siliceous additives. The results were compared to those (Fig. 5) obtained for the mixture containing only cement (CM) or lime (LM) as binders.

The results of pH versus the added nitric acid per kilogram of dry product are related to the acid–base behaviour of the sample. The more equivalents a sample neutralise, the greater buffering capacity it has, taking into account the influence of pH in the mobility of heavy metal species. The plateau at a defined pH describes the sample buffer capacity [44]. As it can be observed, all products show a plateau between pH 5 and 6, corresponding to the buffer capacities of the Zn and Fe [5]. The acid neutralisation capacities (ANC) of the samples 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 [20]. The bigger neutralisation capacities are obtained in the sample with lime (15.2 eq. HNO_3 kg^{-1}), followed by the samples with sorbents where similar results are obtained (6 eq. HNO_3 kg^{-1}). Other similar results are obtained in the samples with cement and the samples with silicic acid and lime (4.8 eq. HNO_3 kg^{-1}). The worst neutralisation capacities are obtained in the mixtures with foundry sand ash (3.5 eq. HNO_3 kg^{-1}) and the samples with sodium silicate (2 eq. HNO_3 kg^{-1}) in spite of their good results on the EN and TCLP leaching tests.

The results of the zinc mobility are very similar in all cases. All curves have their minimum at pH values around 10 and the zinc concentration is very similar to the solubility of the hydroxide ions. The zinc concentrations show an amphoteric behaviour in the waste and all end-products. In the mixtures with lime or cement and sodium silicate, a high content of zinc is also found at very alkaline pH. However, the results of pH when the sodium silicate is used, so that the results of mobility of zinc are very satisfactory in all leaching tests due to the acid character of this additive in the samples. Nearly the same results were achieved for the mixture containing only cement and for the mixtures containing siliceous additives or sorbent materials. It can be concluded that for the amounts of siliceous additives added, the formation of silicates is negligible.

4. Conclusions

This work has studied the influence of siliceous and sorbent materials as additives on the S/S of a real waste of mixed character, foundry sludge. The EN 12457-2 and the TCLP leaching tests were carried out to characterise the mixtures and to study the environmental availability of organic parameters (TOC and phenol index), inorganic pollutants (zinc) and ecotoxicity. The purpose of adding siliceous materials, silica fume, sodium silicate and silicic acid, was to acidify the S/S products and also to promote the formation of metallic silicates. The sorbents, activated carbon and black carbon, were used due to their organic immobilisation properties. Furthermore, foundry sand ash and siliceous resin sand from the foundry industry have been used as residual additives to improve the sustainable management of the steel and ferrous activities.

The use of sorbents in all cases has originated the best results due to their organic retention and the best neutralisation capacities, giving non-ecotoxic end-products. When siliceous additives are used, some products have a low metal mobility, however, taking into account the behaviour of the zinc concentration on the leachates, it is not possible to guarantee the formation of metallic silicates in the mixtures, at least for the percentages used in the present work.

Foundry sand ash can be used as replacement of cement due to their similar behaviour in relation to the cement product and their low cost because of their residual character. However, the results of siliceous resin sand as residual additive have not been satisfactory due to their acid character and its content of phenolic compounds.

Silica fume as additive in the mixtures with lime shows suitable results for the EN leaching test, whereas for the TCLP the great amount of leached zinc drives to undesirable EC_{50} values when a high quantity of additive is used. However, the results of silica fume in the mixtures with cement have been satisfactory.

It can be concluded that the best results of the siliceous additives are obtained using mixtures of cement and sodium silicate as binding material. In this system, a silicate content range of 5–25% (in the mixture with cement) gives optimum leachability. Both in the TCLP test and in the EN test, all the results comply with the limits proposed by the corresponding regulation. The results of zinc mobility in those cases are due to the acid capacity of this additive in the samples.

Lineal expressions have been obtained through the relationships between the value of pH on the TCLP leaching test and the total organic carbon on the EN leaching test in relation to the quantity of additive used in the process.

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