Chemical stabilization of air pollution control residues from municipal solid waste incineration

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ABSTRACT

The by-products of the municipal solid waste incineration (MSWI) generally contain hazardous pollutants, with particular relevance to air pollution control (APC) residues. This waste may be harmful to health and detrimental to the environmental condition, mainly due to soluble salts, toxic heavy metals and trace organic compounds. Solidification/stabilization (S/S) with binders is a common industrial technology for treating such residues, involving however, a significant increase in the final mass that is landfilled. In our work, the chemical stabilization of APC residues by using $NaHS \cdot xH_2O$, H_3PO_4, Na_2CO_3, $C_5H_{10}NNaS_2 \cdot 3H_2O$, $Na_2O \cdot SiO_2$ was investigated, and it was possible to conclude that all these additives lead to an improvement of the stabilization process of the most problematic heavy metals. Indeed, compliance leaching tests showed that after the stabilization treatment the waste becomes non-hazardous with respect to heavy metals. Chromium revealed to be a problematic metal, mainly when H_3PO_4, Na_2CO_3 and $Na_2O \cdot SiO_2$ were used for stabilization. Nevertheless, soluble phosphates are the most efficient additives for stabilizing the overall metals. The effect of the additives tested on the elements associated with soluble salts (K, Na, Cl^-) is almost negligible, and therefore, the soluble fraction is hardly reduced without further treatment, such as pre-washing.

1. Introduction

The municipal solid waste incineration (MSWI) has a number of advantages in the solid waste management systems, mainly because of the energy recovery from the waste, the high volume reduction of material for disposal (about 90% in volume and 70% in weight), allowing also the destruction of pathogens and other organic toxic compounds. The main disadvantages are related to the production of both gaseous emissions (with some toxic substances) and hazardous solid wastes. However, incineration with energy recovery has become a popular method in many developed countries and in Portugal as well. Nowadays, there are three mass burning incinerators in our country that burn nearly 25% of the total MSW produced in the region of Lisbon (Valorsul $\sim 600 \times 10^3$ ton/year), Oporto (Lipor $\sim 400 \times 10^3$ ton/year) and Madeira Island (Valor Ambiente $\sim 120 \times 10^3$ ton/year). Thus, considering that in general 3% of the incinerated amount corresponds to air pollution control (APC) residues, the quantity of waste generated in flue gas cleaning is about 34×10^3 ton/year. In all cases, APC residues enclose fly ashes produced during the incineration process and are carried over into the gaseous emissions plus the additives used for controlling the atmospheric emissions (lime slurry and activated carbon used in semi-dry scrubbers). This fine particulate material is mainly composed of minerals such as SiO_2, $CaCO_3$, $CaSO_4$, $Ca(OH)_2$, Fe_2O_3, Al_2O_3, $CaOHCl$, $NaCl$, KCl, and several heavy metals such as Pb, Cd, Zn, Cu, Cr, Ni, Hg [1–3]. The appropriate treatments for APC residues can be in general grouped into three classes: (i) separation processes; (ii) solidification/stabilization (S/S); and (iii) thermal methods [2,4,5]. Among these options, the S/S method has been adopted and usually involves the addition of a hydraulic binder (e.g. Portland cement) and water. The large quantity of cement required to endeavour enough mechanical strength to the final monolith is the foremost disadvantage of this technology. In this context, previous chemical stabilization of the residues may be an interesting alternative, having as main goal to convert pollutants into less soluble or less toxic forms. This can be achieved by using specific chemicals such as hydroxides, sulphides, silicates, carbonates, phosphates and chelating agents. In the end, the stabilized pollutants stay bounded within the solid matrix as part of its structure. This method entails mechanisms of microencapsulation, precipitation, adsorption and detoxification [6]. Microencapsulation allows entrapping the pollutants within the structure of the solidified matrix at a microscopic level, whereas precipitation of toxic elements, as for

Table 1
Chemical additives tested for stabilization of APC residues.

Additive/supplier and purity	Molecular formula	Notation	Physical state	Tested quantities/25 g APC residues
Ortho-phosphoric acid	H_3PO_4 (85%)	PO_4	Liquid	0.5; 1.0; 1.5; 2.0 mL
Panreac, p.a.	14.7M		1.70 kg/L	
Soluble sodium silicate	$Na_2O \cdot SiO_2$ (37%, w/w)	SSi	Liquid	1.0; 2.0; 3.0; 3.8 mL
Merck, extra pure	$SiO_2/Na_2O = 3.2$		1.35 kg/L	
Sodium carbonate anhydrous	Na_2CO_3	CO_3	Solid	2.0; 3.0; 4.0 g
Riedel-de Haen, p.a.	MW = 105.99 g/mol			
Sodium diethyldithiocarbamate trihydrate	$C_5H_{10}NNaS_2 \cdot 3H_2O$ MW = 225.31 g/mol	DDC	Solid	0.2; 0.3; 0.4; 0.5 g
Acros organics, p.a.				
Sodium hydrosulphide hydrate	$NaHS \cdot xH_2O$	HS	Solid	1.0; 2.0; 3.0 g
Acros organics, p.a.	(68–72%, w/w) MW = 56.06 g/mol			

example hydroxides, sulphides and phosphates, may form more stable compounds. The adsorption mechanism corresponds to surface phenomena involving van der Waals and hydrogen bonding, which promote electrochemical bonds between pollutants and the solid matrix. Detoxification may occur during the stabilization process whenever toxic chemicals are converted into other less toxic compounds. In the literature, several studies concerning chemical stabilization of different incineration residues can be found [7–24], with some works investigating the effect of chemicals in combination with solidification [15,22,25], and soluble phosphates are the mostly tested additives [7–11,14,16,21,26]. However, chelating agents [11,15,17,27], ferrite and/or ferrous sulphate [12,18,19,23], colloidal aluminate oxide [20], sodium sulphide [15] and soluble silicates [22,28,29] have also been used.

The stabilization process with soluble phosphates (e.g. phosphoric acid) allows the precipitation of several calcium phosphates such as $Ca_3(PO_4)_2$, $CaHPO_4 \cdot 2H_2O$, $Ca_4H(PO_4)_3 \cdot 2.5H_2O$, $Ca_5(PO_4)_3(OH,Cl,F)$, Cu_2PO_4OH, and other very insoluble minerals containing divalent metals as Pb and Zn: $Pb_5(PO_4)_3Br$; $KNaPb_8(PO_4)_6$; β-$Pb_9(PO_4)_6$; $Pb_5(PO_4)_3Cl$; $KPb_4(PO_4)_3$; $PbHPO_4 \cdot H_2O$; $KZn_2H(PO_4)_2 \cdot 2H_2O$; α-$CaZn_2(PO_4)_2$; $Zn_3(PO_4)_2 \cdot 4H_2O$; $Zn_3(PO_4)_2$; $Zn_6(PO_4)_2(OH)_6 \cdot H_2O$ [16]. The high efficiency of phosphates for stabilizing lead, zinc and copper is pointed out in various studies [8,9,11,16,21], due to their ability to form very stable and insoluble minerals even when submitted to aggressive conditions. The main disadvantage associated to phosphates is the possibility of their consumption by flora. The soluble phosphates sources may be H_3PO_4, Na_2HPO_4, NaH_2PO_4, $NaH_2PO_4 \cdot 2H_2O$, $MgHPO_4$, $CaHPO_4$, $Ca(H_2PO_4)_2$ and $(NH_4)_2HPO_4$. H_3PO_4 with a global negative enthalpy of the reactions carried over stabilization treatments (exothermic process) is used most often [26]. The amount of soluble phosphates usually required is based on 10% wt/wt [30]. The stabilization with chelating agents may involve pyrrolidines, imines, carbamates and thiols [30]. The carbamates are often used for transition metals, and their action is based on the complexation of metals with the organic sulphide group [11,27], with satisfactory efficiencies [11,17,27]. In fact, Sakanakura [27] denoted that in Japan a number of municipalities prefer dithiocarbamic salts because no additional pre-treatment (such as pH control) is required due to the high alkalinity of the APC residues. The amounts of chelating agents required are generally around 2–5% (wt/wt) of APC residues [30]. The heavy metal affinity for dithiocarbamates is Hg > Cu > Ni > Pb > Zn > Cd and may be understandable by taking into account the reactivity of divalent metals to sulphur electron provider [27]. The stabilization involving ferrous sulphate is based on the well-established geochemical information that many iron oxides are able to bind significant amounts of trace metals [19]. The treatment with sodium sulphide is based on the very low solubility of all metal sulphides [15]. According to some literature there are some industrial plants in Japan that employ NaHS as stabilization agent [31]. This method has the shortcoming of forming toxic gases and the potential oxidation/dissolution of the sulphides in acidic conditions [15].

Another method involves the APC residues carbonation by using CO_2 [32–35], which proved to be ineffective to stabilize chlorides and sulphides [33], but satisfactory for Pb and Zn stabilization [32].

In this work, the effect of H_3PO_4, $Na_2O \cdot SiO_2$, Na_2CO_3, NaHS, $NaS_2CN(C_2H_5)_2$ was studied in order to prevent the release of the heavy metals from APC residues into the environment. Studies concerning the S/S improvement with cement by using some of these additives are ongoing, in order to avoid the leaching out of pollutants even if the blocks of cement collapse.

2. Materials and experimental procedures

The materials and experimental procedures that were used to test the chemical additives are indicated in this section. Different samples of APC residues from MSWI were collected during more than two years in a Portuguese industrial plant, and their extensive characterization was carried out in previous studies [3,36]. The present work is mainly related with samples further referred to as A2, A3 and A4. The APC residues under analysis involve fly ashes from economizer unit as well as solids produced in semi-dry scrubbers (including $Ca(OH)_2$ and activated carbon) and fabric filters.

2.1. Materials and methods for testing the different additives

For stabilizing the APC residues five different additives were tested, whose main characteristics are indicated in Table 1 (the notation referred in this table will be further used in the next sections). The quantities were selected taking into account preliminary tests, as well as the ranges indicated in the literature [8,10,11,16,21,27,30]. Depending on the fact that additives may be liquids or solids, the methodology summarized in the diagram of Fig. 1 was adopted to perform the stabilization treatment experiments for a mass of 25 g of APC residues.

2.2. Leaching tests and methods

To select the most effective additive, DIN 38414-S4 was the main leaching test performed, whereas to evaluate the final stabilization products for the treatment with soluble phosphate and silicate, besides DIN 38414-S4, NEN 7341, prEN 14429 and NEN 7343 were also used. The total dissolved solids (TDS) were determined according to NF T 90-029, pH and conductivity were measured by potentiometry, metals (Pb, Cd, Zn, Cr, Ni, Cu, K, Na) were quantified using flame atomic absorption spectrometry, Perkin Elmer 3000, and chlorides by silver nitrate titration.

The method DIN 38414-S4 is a regulatory test method (compliance test), often used to assess the leaching behaviour of residues with particle size less than 10 mm extracted in batch conditions at a liquid to solid ratio (L/S) of 10 L kg^{-1}. The suspension is agitated upside down during 24 h at room temperature and the liquid phase is separated with a 0.45 μm pore size filter. The test NEN 7341 was planned to assess the total availability (TA) of inorganic components from solid building (earthy and stony) and waste materials,
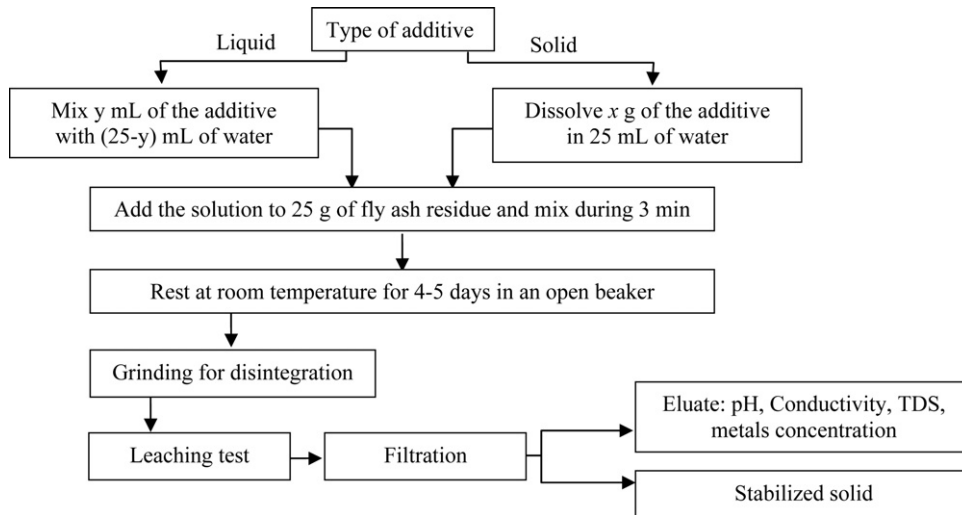
Fig. 1. Experimental methodology for testing liquid or solid additives.

when the solid was exposed to extreme conditions (very long term, disintegration, full oxidation). This method requires two consecutive extractions with a liquid to solid ratio (L/S) of $50 \, L \, kg^{-1}$ at pH 7 and at pH 4. A feedback pH controller was used for maintaining pH constant, by adding a solution of HNO_3. In our case, some previous milling was necessary to comply with the condition that 95% of the material must have dimensions under $125 \, \mu m$. The acid neutralization capacity (ANC) at pH 7 and pH 4 can be estimated from these test data. The NEN 7343 is a Dutch standard column test, often used for regulatory purposes, which intends to simulate leaching in short to medium term (less than 50 years) [37]. Seven aliquots samples of liquid are collected at the column outlet, during 21 days in order to observe the leaching that occurs in equilibrium conditions at L/S = 0.1–10 $L \, kg^{-1}$. The leachant solution is demineralized water with an initial pH of 4 (adjusted with HNO_3), but during the

test no further pH control is forced. The column has 20 cm height and 5 cm diameter, and the solid being milled up to 4 mm. When the test is used for compliance, L/S = 1 is the reference value.

For studying the pH influence, the prEN 14429 was selected, which examines the leaching behaviour of granular materials under certain pH conditions. This test consists in a set of parallel batch extractions at L/S = 10 ($L \, kg^{-1}$) in closed flasks, where sub-samples of material (25 g) are in contact with aqueous solutions with increasing quantities of HNO_3 for 48 h under agitation. The leachant volume (V) was separated in three equal volumes and added at t_0, $t_0 + 30$ min, $t_0 + 2$ h. The suspensions were agitated between each leachant addition, and the final pH should be in the range 4–12.

The total dissolved solids (TDS) were evaluated by gravimetric analysis according to NF T 90-029, by evaporating a specific volume of eluate in a crucible, and drying at $105 \, ^\circ C$ until constant weight.
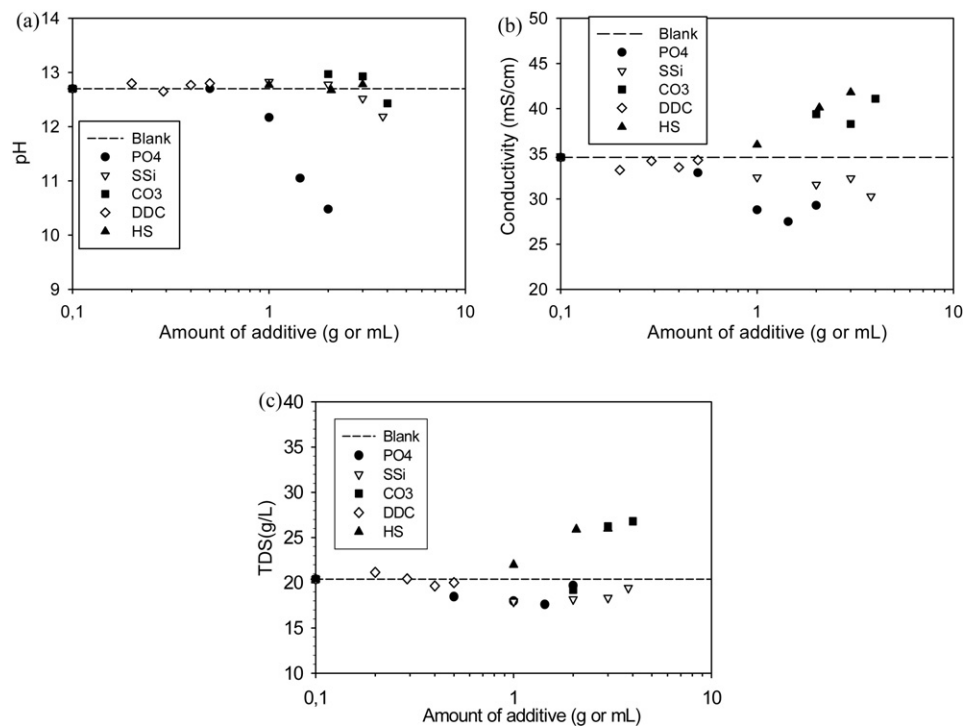

Fig. 2. Results in eluates after stabilization of sample A2 with several additives (a) pH; (b) conductivity and (c) TDS. Amount of additive in mL for PO_4 and SSi and in g for CO_3, DDC and HS.
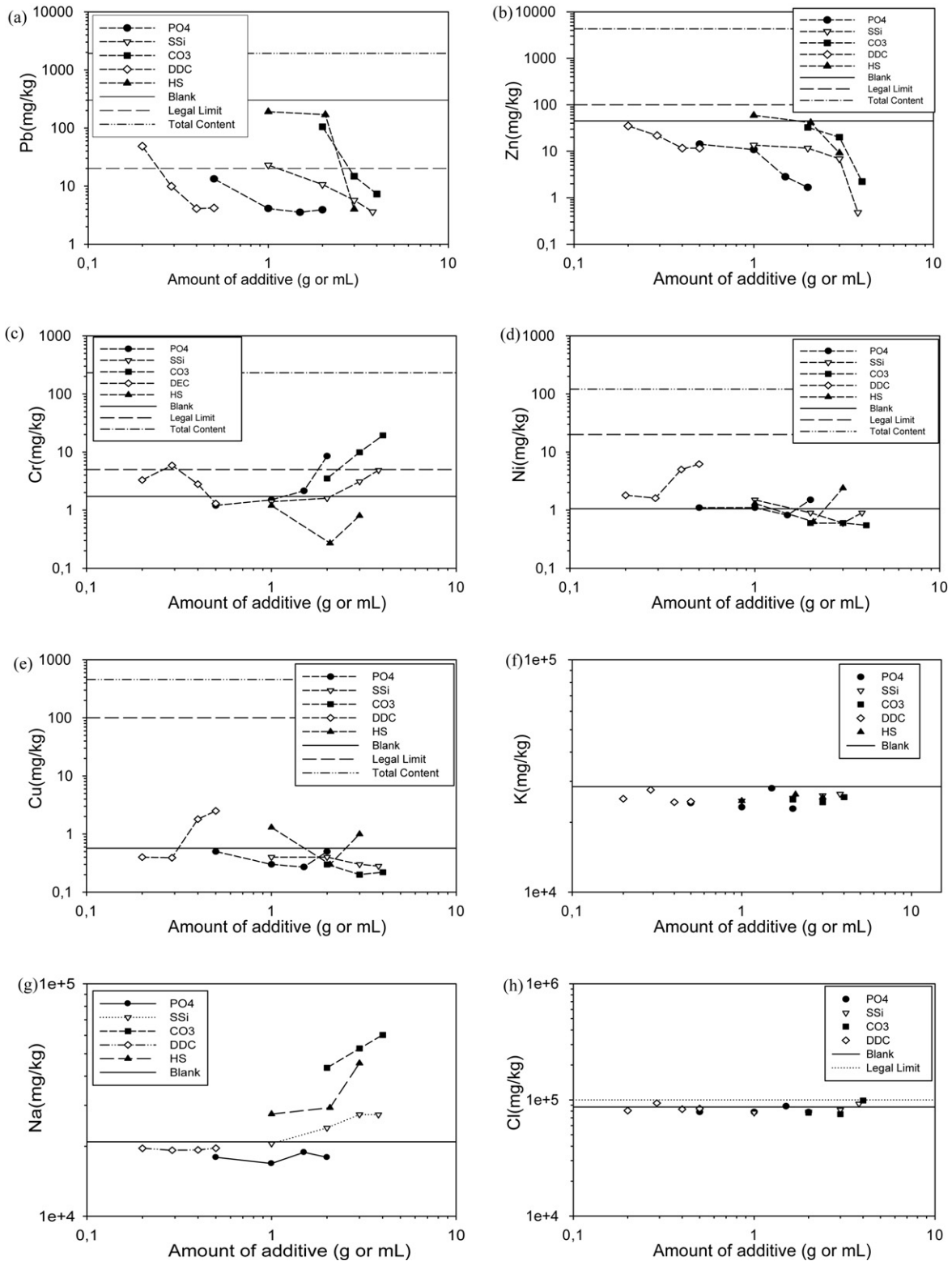
Fig. 3. Release of (a) Pb; (b) Zn; (c) Cr; (d) Ni; (e) Cu; (f) Na; (g) K and (h) Cl$^-$ as a function of additives amount.

3. Results and discussion

In this section the results concerning the assessment of five different additives in order to stabilize the inorganic species in the APC residues from MSWI are presented and discussed. After the screening phase, soluble phosphates and soluble silicates were selected and studied in particular. To complete the evaluation of the stabi-

lization process, the influence of pH and the liquid to solid ratio (L/S) was investigated.

3.1. Assessment of chemical additives for stabilizing APC residues

In our previous studies [3] the results showed that the APC residues under analysis are hazardous wastes, lead (Pb) being the
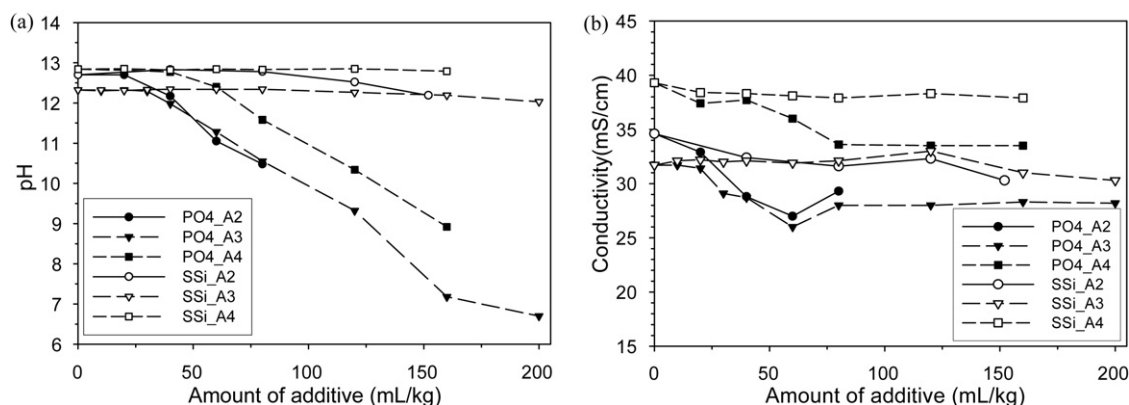
Fig. 4. Results in the eluates after stabilization of samples A2–A4 with soluble phosphates and silicates (a) pH and (b) conductivity.

most problematic heavy metal. In fact, if the residue is in contact with water, Pb can leach out more than 20 times the legal limit (20 ppm) established by the Portuguese legislation (in accordance with EU) for disposal of a material (tested through DIN 38414-S4) in a hazardous waste landfill site. The metals Zn, Cd, Cr, Ni and Cu may also become critical metals if the residue is submitted to severe conditions, when in contact with strong acidic solutions. The TDS is usually another crucial parameter particularly due to the high amount of chlorides that is released.

At present, industrial treatment of APC residues usually involves the addition of Portland cement (S/S treatment) followed by land-filling. The major drawback of this S/S treatment is that the final mass may be increased more than twice. An alternative method is its stabilization with chemical additives, so forth in this work the chemicals tested and the corresponding quantities used for the first screening were previously indicated in Table 1. The experimental procedure for stabilizing the waste with soluble H_3PO_4, $Na_2O \cdot SiO_2$, Na_2CO_3, $C_5H_{10}NNaS_2 \cdot 3H_2O$ and NaHS, slightly differs if the additive is in liquid or solid state, since in the first case the amounts were considered in volume and for solid chemicals in mass (Fig. 1). This preliminary evaluation of the stabilized APC residues involved sample A2 in respect to the behaviour observed for pH, conductivity, TDS and amount released of several pollutants measured in the eluates of DIN 38414-S4 tests. Fig. 2(a) shows pH measured at the end of the experiments as a function of the quantity of the different additives. The dashed horizontal line indicates the results for the blank test (without any additive), where it is evident that the APC residues are characterized by very high natural pH values (pH > 12.5). The final solution pH tends to be independent of the added amount of sodium diethyldithiocarbamate trihydrate (DDC) and sodium hydrosulphide hydrate (HS), decreases slightly for soluble sodium silicate (SSi) and sodium carbonate (CO_3), while an effective decrease is observed for phosphoric acid (PO_4). These trends are dominated by basic, neutral or acidic characteristics of the different additives. In fact, DDC has neutral characteristics (pH 7 for 20 g/L of H_2O, 20 °C), three of them have basic properties (HS: pH 11 for 10 g/L of H_2O, 20 °C; CO_3: pH 11.5 for 50 g/L of H_2O, 25 °C; SSi:

pH 11.0–11.5 for 50 g/L of H_2O, 20 °C), and PO_4 has acidic properties (PO_4: pH 1.08 for 1 M of H_3PO_4, 25 °C). After waste stabilization with these additives, depending on the characteristics and amounts used in each case, partial acid neutralization occurred, and thus the pH values at the end of the leaching tests were affected. The outcome of solution pH variation may be extremely important in leaching processes, since the amount of the leached metals is, in general, strongly dependent on this parameter [36]. The conductivity (Fig. 2(b)) provides a measurement of the quantity of ions in solution, giving indirect information about the TDS (Fig. 2(c)). This parameter may be critical in the management of these materials, and the results show that only phosphates (PO_4) and silicates (SSi) slightly reduce TDS.

Fig. 3(a)–(e) shows the leaching results obtained for Pb, Zn, Cr, Ni and Cu, after stabilization of APC residues according to the methodology indicated in Fig. 1. Some straight horizontal lines were included in order to identify the total elemental content (determined by acid digestion), the amount released in the blank test (without additive), and the legal limit (established to classify a waste as hazardous with respect to the standard DIN 38414). The released Pb (Fig. 3(a)) in the blank test largely exceeds the legal limit (20 ppm). However, all the additives potentially decrease the level of Pb below the legal limit. For example, in the case of quantities equal to or higher than 0.3 g DDC, the concentration of Pb in the eluate is lower than 20 ppm. As indicated in Table 2, 12 g of DDC will be required for the treatment of 1 kg of APC residues, which corresponds to a cost of 3.5 €/kg of APC residues. The results summarized in this table show that the most economical solution for stabilizing Pb corresponds to soluble phosphates and silicates. For the case of Zn (Fig. 3(b)), all the experimental data are lower than the legal limit (100 ppm). Nevertheless, all additives have a positive effect, and it is possible to decrease the quantities released for levels close to or lower than 10 ppm.

In what concerns chromium, Fig. 3(c) shows that this metal may be a problematic one, since after stabilization its solubility can increase. In fact, H_3PO_4, Na_2CO_3 and $Na_2O \cdot SiO_2$ may lead to an increase in the amount of Cr that can be leached out. For NaHS,

Table 2
Minimum quantity of chemical additive for stabilizing Pb and costs involved.

Additive	Minimum quantity of additive/kg of APC residues		Commercial reagents price[a]		Treatment costs (€/kg APC residue)
H_3PO_4 (85%)	0.02	L/kg	10.5 €/L	6176 €/t	0.2
$Na_2O \cdot SiO_2$ (37%,w/w)	0.08	L/kg	5 €/L	3703 €/t	0.4
Na_2CO_3	0.12	kg/kg	16 €/kg	16000 €/t	1.9
$C_4H_{10}CNNaS_2 \cdot 3H_2O$	0.012	kg/kg	290 €/kg	290000 €/t	3.5
$NaHS \cdot xH_2O$ (68–72%, w/w)	0.12	kg/kg	22.5 €/kg	22500 €/t	2.7

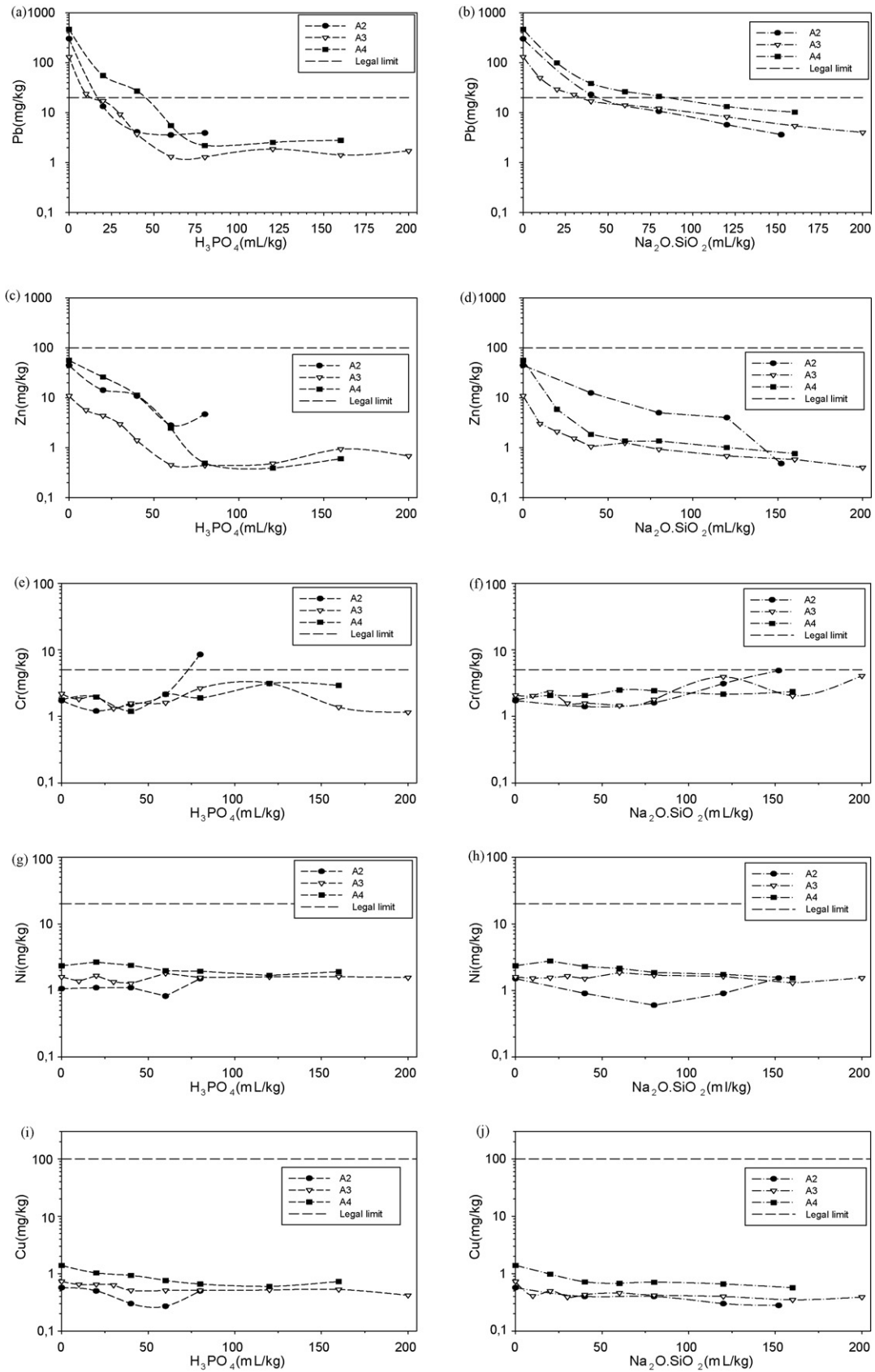[a] The prices correspond to the reagents used in laboratorial studies.

Fig. 5. Released amounts of Pb, Zn, Cr, Ni and Cu after treatment with soluble phosphate (a), (c), (e), (g), (i) and with silicates (b), (d), (f), (h) and (j), for samples A2–A4.

DDC more experimental tests should be performed in order to conclude about their effect on the Cr behaviour. It is important to stress that sulphides of metals are stable under reducing conditions, and in these circumstances Cr(III) is predominant (less soluble). It is important to note that the value of the legal limit included in Fig. 3(c) corresponds to Cr(VI), and the experimental points correspond to Cr-total, since the quantification was obtained by flame atomic absorption spectrometry. For oxidizing conditions and high pH (as in the case of APC residues) Cr is likely to form CrO_4^- (oxyanions), becoming somewhat mobile because sorption to hydrous iron (hyd)oxides and aluminium (hydr)oxides is not significant, and in this case a set of complex solubility controlling minerals are generally referred to justify the observed concentrations [38]. In the case of Ni and Cu the compliance with regulatory thresholds of 20 ppm and 100 ppm, respectively, was observed for all tests. Indeed, the blank test shows that the residue without treatment easily complies with those limits (Fig. 3(d)–(e)) and the chemical additives do not significantly change this situation.

Fig. 3(f)–(h) illustrates the results for soluble species such as Na, K and Cl⁻. The releasing behaviour of Na is in agreement with the fact that some additives were added as sodium salts (SSi, CO_3, DDC and HS). Thus, the released quantity should rise as the amount of additive was increased. For the case of DDC this is not observed as a consequence of the low amount used. The behaviour of K (Fig. 3(g)) and Cl⁻ (Fig. 3(h)) is independent of the type and mass of the additive. For the case of using NaHS, the quantification of Cl⁻ was not possible since sulphides also react with silver nitrate [39]. It should be noted that the amounts of Cl⁻ leached easily exceed the regulatory threshold. In conclusion, the high soluble fraction of the APC residues produced during the MSW incineration cannot be reduced through stabilization strategies.

3.2. Stabilization with soluble phosphates and silicates

The analysis presented in the previous section allows the selection of phosphates and silicates as the most reliable and economical chemicals for stabilizing the APC residues. In addition, these chemicals are used at industrial level [8,29]. On other hand, during the treatment, no toxic gases are produced, and the phosphates and silicates of metals are very stable in the environment. Thus, in this section a more thorough analysis is presented only for these liquid additives, based also on the methodology indicated in Fig. 1. In this section, three industrial samples of APC residues (A2, A3, A4) were tested. Fig. 4(a)–(b) shows the results obtained for pH and electrical conductivity (correlated with TDS), respectively. The results illustrate that when the samples of APC residues were treated with more than 40 mL/kg (0.59 mol/kg) of soluble phosphates the pH of the solution in contact with the residue decreased significantly, which is related to the fact that the acid neutralizes the strong alkaline characteristics of the APC residues (high acid neutralization capacity – ANC). The addition of soluble silicates does not change the alkalinity of the material. The conductivity presented in Fig. 4(b) shows that silicates have little effect on the soluble salts and the phosphates may slightly reduce this parameter.

In Fig. 5(a)–(j) the behaviour of Pb, Zn, Cr, Ni and Cu is indicated for three different samples (A2–A4) that were previously stabilized with phosphates and silicates. The results point out that the main problem concerning the leaching of Pb may be solved with this type of additives, independently of the initial amount of lead in the APC residues. In fact, release quantities as low as 1 mg/kg may be reached for Pb, the phosphates being a valuable additive until amounts of 60 mL/kg (or 0.88 mol/kg). For example, for sample A4, the total elemental content of Pb is 2143 ppm and without treatment 465 mg/kg is released during the DIN 38414-S4. In this case (the worst case), to comply with the legal limit of 20 mg/kg more than 60 mL/kg will be required, and the cost
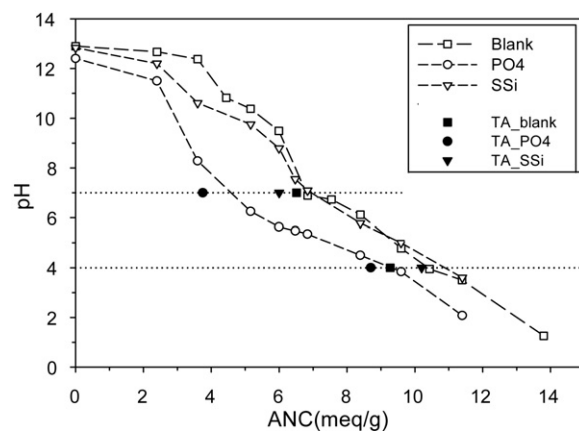

Fig. 6. Comparison of the ANC for sample A4 without treatment and after stabilization with soluble phosphates (PO_4) and silicates (SSi).

of the treatment with phosphates may increase to 0.63 €/kg of APC residues (for analytical grade reagent). The results for soluble silicates (Fig. 5(b) indicate that as the quantities of additive increase the released amounts decrease, and the greater variation is observed until 40 mL/kg. In order to guarantee that all samples comply with the legal limit, 40 mL/kg of silicates are required to stabilize sample A2, but 80 mL/kg must be used for sample A4. Concerning Zn both phosphates and silicates (Fig. 5(c) and (d)) revealed a positive stabilization effect, and releasing amount as low as 1 mg/kg of APC residues was attained.

For chromium (Fig. 5(e) and (f)), the stabilization treatment with phosphates or silicates does not have a marked positive effect, and the stabilized waste does not comply with the legal limit of 5 mg/kg for Cr(VI). It should be noted that for alkaline pH a prevalence of Cr(VI) over Cr(III) probably occurs and since Cr(VI) is more toxic than Cr(III) this could be adverse for the environment. Nickel and copper (Fig. 5(g)–(j)) are both in low concentrations for all samples, and the stabilization treatment with phosphates and silicates have a slight positive effect on the leaching quantities. However, for these metals the regulatory limits are always complied. Concerning Na, K, Cl⁻, which are elements associated with soluble salts, the results obtained in these set of experiments confirm the ones indicated before in Fig. 3(f)–(h), for all the three samples tested (A2–A4).

3.2.1. Total availability

The TA is an important parameter for evaluating the stabilization process, since the worst leaching environmental scenario is simulated through this test, pointing out the potential upper leaching limit. Thus, after the stabilization of the sample A4 (sample with higher amount of toxic heavy metals) with 60 mL/kg of H_3PO_4 and 80 mL/kg of $Na_2O·SiO_2$ (according to the results shown in the previous section) the availability test (NEN 7341) was performed and the results are indicated in Table 3. The quantities for each element (mg/kg) correspond to mean values obtained in at least three experiments. The results referred as TA_{red} mean the percentage of reduction after treatment with phosphates (TA_{red,PO_4}) or silicates ($TA_{red,SSi}$) when compared with the reference values (without treatment). For the phosphate treatment, the main feature is the significant stabilization for all metals (mainly for Pb), and the shortcoming is the ANC reduction. Similar conclusions are referred in the literature [11]. The stabilization with silicates reveals some apparent ambiguous results, mainly with respect to Pb. Indeed, the amount of Pb increases when compared with the reference case (without treatment). Neither our experiments nor literature (as far as we know) allows a satisfactory explanation for these results.

Table 3
The total availability for sample A4 without treatment, and stabilized with phosphates and silicates.

Treatment	Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	ANC_ pH 7 (meq/g)	ANC_ pH 4 (meq/g)
Without treatment	216	86	4360	28	26	288	6.5	9.3
Phosphates (PO$_4$)	39	43	2705	27	24	76	3.8	8.7
Silicates (SSi)	428	78	4118	30	26	240	6.2	10.2
TA$_{red,PO_4}$	82%	50%	38%	3.6%	7.7%	74%		
TA$_{red,SSi}$	−98%	9.3%	5.6%	−7.1%	0.0%	17%		

3.2.2. Influence of pH

The stabilized APC residues were tested according to prEN 14429, for evaluating the influence of pH on the leaching behaviour of the different components. Other studies stressed that this test may be valuable for testing stabilized wastes [17]. In practice, it is very important that the treated waste be stable not only for its natural pH (12–13) but also when the material is exposed to extreme conditions, such as acidic solutions. Fig. 6 shows that sta-

bilization with phosphates significantly reduces the ANC, which is the major drawback of this treatment. In this figure, the results referred as blank correspond to the ones obtained without stabilization treatment. The ANC values estimated at pH 7 and pH 4 during the NEN 7341 (Table 3) were also included (filled points marked with TA), and it is possible to conclude that those values are underestimated. The importance of ANC was indicated in our previous study [3].
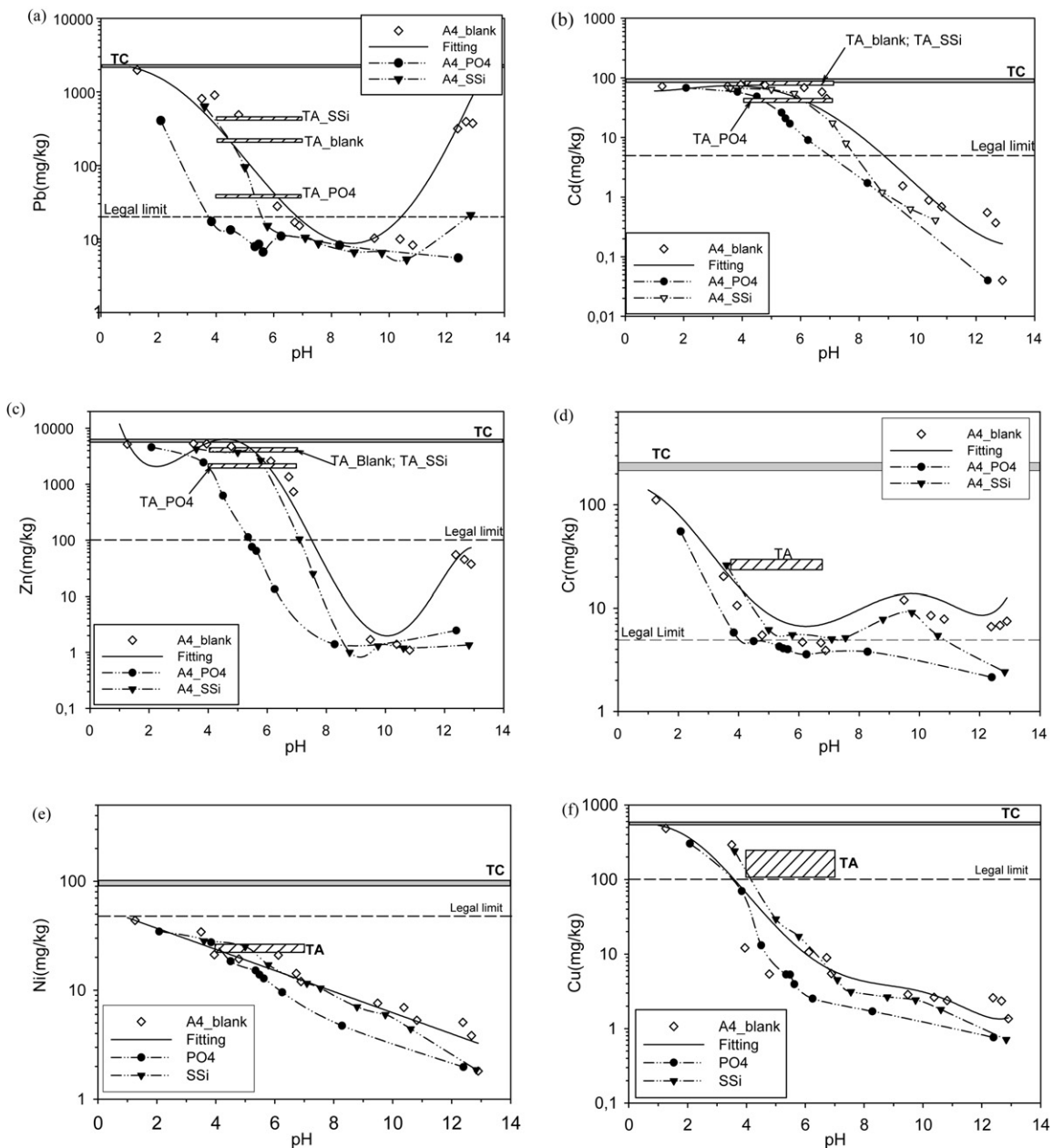

Fig. 7. Influence of pH after treatment with H$_3$PO$_4$ and Na$_2$O·SiO$_2$ for sample A4. (a) Pb; (b) Cd; (c)Zn; (d) Cr; (e) Ni and (f) Cu.
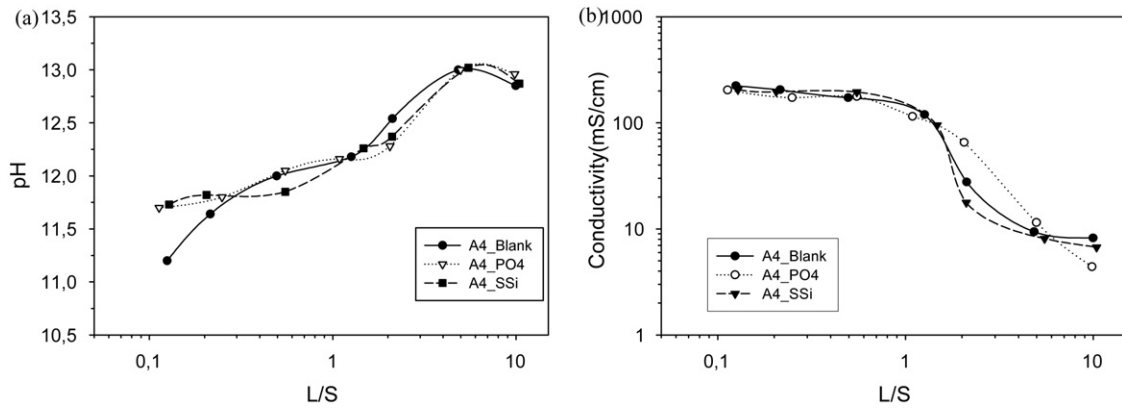
Fig. 8. (a) pH and (b) conductivity measured in the eluates from column tests for sample A4 without treatment (blank) and after treatment with soluble phosphates and silicates.
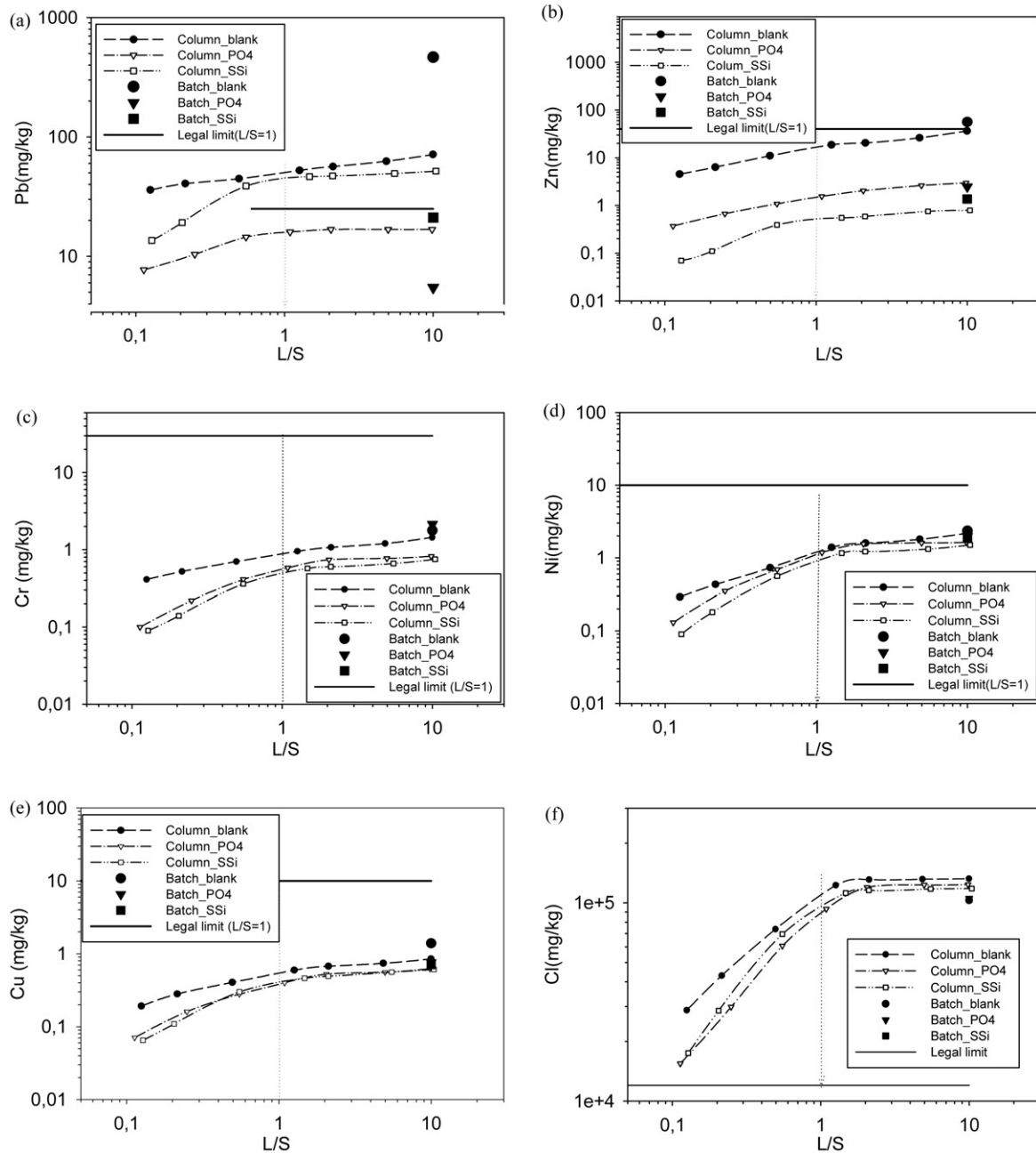

Fig. 9. Released amount observed in column experiments (NEN 7343) and in batch tests (DIN 38414) for (a) Pb; (b) Zn; (c) Cr; (d) Ni; (e) Cu and (f) Cl^-.

The leaching behaviour (solubility curves) of Pb, Cd, Zn, Cr, Ni and Cu as a function of pH in the leaching solution is indicated in Fig. 7(a)–(f) for sample A4 without treatment (blank), and after stabilization with phosphates (PO_4) and silicates (SSi). In this figure additional information is included: total elemental content (TC), TA indicated in Table 3, and the legal limit established for DIN 38414-S4 (a compliance test). The curves labelled with "fitting" were obtained by non-linear fitting for five samples (A1–A5) of APC residues [36]. The influence of pH on the behaviour of each metal is largely analysed in literature, in particular for APC residues [2,36,37]. Nevertheless, in the present study the leaching behaviour without treatment (blank) is compared with the results observed after stabilization. Fig. 7(a) shows that the treatment with soluble phosphate has advantages in all the range of pH, since the solubility of Pb was reduced. In fact, even for the natural pH of the waste (near to 12.5) the stabilized residue complies with the regulatory threshold of 20 ppm. As shown in a previous study [3] the released amount of Pb may exceed that limit more than 20 times. An overall analysis of the behaviour of the different metals (Cd, Zn, Cr, Ni and Cu) also confirms that the treatment with phosphates is positive for all the cases. A similar conclusion is valid when soluble silicates were used, but the advantages are not so pronounced.

3.2.3. Influence of liquid to solid ratio

Besides the influence of pH on the leaching behaviour, the L/S ratio may be an important parameter for assessing the risk of some pollutants released from waste materials exposed to environmental conditions [40–42]. The variable L/S may be evaluated through column leaching tests (percolation tests), such as Dutch column test (NEN 7343) used in this study, being defined as litters of leachant in contact with kilograms of dry material. Indeed, percolation tests have been progressively considered as one of the few powerful tools indispensable to characterize the leaching behaviour of wastes, both in the short and the long terms [40]. Based on column data, six release patterns may be identified, the most relevant being the "fast release or washout" and "slow release or solubility/dissolution control" [37]. Fig. 8(a) and (b) shows that no significant differences were observed for pH and conductivity without and with treatment with phosphates and silicates. These experimental values correspond to direct measurements in seven eluates collected at the column outlet. In Fig. 8(b), it is possible to detect that the conductivity strongly decreases for L/S higher than 1. Indeed, as expected, the concentrations of Na, K and Cl⁻, expressed as mg/L, revealed similar trends (results not shown in this work for Na and K). These results confirm that after 1 L of leachant is in contact with 1 kg of dry waste, almost all soluble salts are washed out from the residue.

As referred before, the leaching behaviour of heavy metals may be characterized for very different patterns, since in these cases a complex network of chemical reactions may occur among the huge amount of species that can be present in the leaching solutions. In Fig. 9(a)–(e) cumulative quantities of Pb, Zn, Cr, Ni, Cu and Cl⁻, in mg per kg dry APC residue, were represented as a function of cumulative L/S ratio. In this figure additional information is also included: the legal limit (solid horizontal lines) for considering the residue hazardous according to Dutch regulations, and the results obtained in batch experiments with L/S = 10 L/kg (DIN 38414-S4). Regarding Pb, the most important outcome from column experiment is the fact that a classification of non-hazardous is only obtained for stabilization with phosphate, because in Fig. 9(a) the threshold of 25 mg/kg is complied in this case. For this problematic element, although the stabilization with soluble silicates has a positive effect, the improvement is not sufficient to change classification. For Pb, the results observed in batch experiments with L/S = 10, and the column data for a cumulative L/S = 10 do not match [42]. Indeed, without treatment (blank) the batch experiments overestimate the quantity observed in column analysis. Contrarily, after stabiliza-

tion, the batch data seem to underestimate the release in batch tests. These findings are the consequence of complex phenomena (precipitation, dissolution, sorption, aging reactions, complexation reactions, etc.) occurring in the leaching system. On the other hand, variables such as pH, redox conditions, aging reactions, precipitation and dissolution of mineral phases may contribute to the referred results. According to Fig. 9(b)–(f), for Zn, Cr, Ni, Cu and Cl⁻ the batch experiments may be used for estimating released quantities for L/S = 10. This feature is very important regarding laboratory work, since batch results may be obtained in 24 h, and for column tests 21 days are required. Fig. 9(f) clearly shows an important drawback of the stabilization treatments, due to the fact that the legal limit of 12,000 mg/kg is largely exceeded by the stabilized material. In fact, the problem of the high concentration of chlorides cannot be solved through chemical stabilization, since these ions hardly interact with other chemical compounds. Almost all chloride salts are soluble (a singular exception is silver chloride). At the technological level, the problem of the high amounts of soluble salts may be solved by washing treatments [43].

4. Conclusions

In this work, the chemical stabilization treatment of fly ash and APC residues produced in the MSW incineration is addressed. In order to reduce the amount of heavy metals that can be leached out to the environment, several chemical additives were tested: sodium hydrosulphide hydrate (NaHS), phosphoric acid (H_3PO_4), sodium carbonate (Na_2CO_3), sodium diethyldithiocarbamate trihydrate ($C_5H_{10}NNaS_2 \cdot 3H_2O$) and soluble sodium silicate ($Na_2O \cdot SiO_2$). All these additives have a positive effect for stabilizing Pb and Zn. In the case of Cr, the addition of H_3PO_4, Na_2CO_3 and $Na_2O \cdot SiO_2$ led to an increase of the leached quantity. For K, no reduction was detected when the different additives were used. The soluble fraction is only slightly reduced through H_3PO_4 and $Na_2O \cdot SiO_2$, and hence different strategies will be required to solve this problem. The screening of these five additives allowed the selection of phosphates and silicates as the most reliable and economical chemicals for stabilizing the APC residues. In the worst case, to comply with the legal limit of 20 mg/kg more than 60 mL/kg of H_3PO_4 will be required, and the cost of the treatment is 0.63 €/kg of APC residues (for analytical grade reagent). Both phosphates and silicates revealed a positive stabilization effect for Zn, and releasing amounts as low as 1 mg/kg of APC residues was observed. For chromium, it is possible that the stabilized waste does not comply with the legal limit of 5 mg/kg for Cr(VI). Nickel and copper are both in low concentrations for all samples of APC residues, and the stabilization treatment with phosphates and silicates have a slight positive effect on the leaching quantities.

The stabilization with phosphates significantly reduces the ANC of APC residues, which is a disadvantage of this treatment. Nonetheless, the treatment with phosphates reduces the solubility of Pb in all the range of pH. In fact, the analysis of the influence of pH showed that the stabilization with phosphates is positive for all the different metals considered (Pb, Cd, Zn, Cr, Ni and Cu). Also the analysis of the influence of L/S ratio revealed that with respect to heavy metals a classification of non-hazardous is obtained for stabilization with phosphate only, and thus this is considered to be the best additive tested.

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