Stabilization/solidification of a municipal solid waste incineration residue using fly ash-based geopolymers

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ABSTRACT

The stabilization/solidification (S/S) of a municipal solid waste incineration (MSWI) fly ash containing hazardous metals such as Pb, Cd, Cr, Zn or Ba by means of geopolymerization technology is described in this paper. Different reagents such as sodium hydroxide, potassium hydroxide, sodium silicate, potassium silicate, kaolin, metakaolin and ground blast furnace slag have been used. Mixtures of MSWI waste with these kinds of geopolymeric materials and class F coal fly ash used as silica and alumina source have been processed to study the potential of geopolymers as waste immobilizing agents. To this end, the effects of curing conditions and composition have been tested. S/S solids are submitted to compressive strength and leaching tests to assess the results obtained and to evaluate the efficiency of the treatment. Compressive strength values in the range 1–9 MPa were easily obtained at 7 and 28 days. Concentrations of the metals leached from S/S products were strongly pH dependent, showing that the leachate pH was the most important variable for the immobilization of metals. Comparison of fly ash-based geopolymer systems with classical Portland cement stabilization methods has also been accomplished.

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1. Introduction

Incineration is an effective procedure for the treatment of municipal solid waste producing recovery of energy and reducing the volume and weight of the waste. One of the inconveniences of incineration is that this process produces great amounts of residues such as fly ash and bottom ash. Municipal solid waste incinerators generate around 1.2×10^6 t/year of fly ash in Western Europe [1]. This fly ash is classified as hazardous waste due to its high heavy metals content, and the finesse of their particles. Because of the problems that the management of this residue generates, the treatment using stabilization/solidification (S/S) technology before its landfill disposal is common practice.

Many authors have studied the stabilization/solidification of municipal solid waste incineration (MSWI) fly ashes using hydraulic binders: ordinary Portland cement (OPC), lime, coal fly ash (FA) or blast furnace slag (BFS) [2–10]. Other special agents have been used such as polyester resin [1], soluble phosphate [11–13] or ferrous sulphate [14,15].

In this paper, geopolymerization technology has been proposed to stabilize and solidify a MSWI waste. Geopolymers are obtained by the reaction between a solid aluminosilicate and a highly concentrated aqueous alkali hydroxide or silicate solution [16]. The general mechanism by which geopolymerization is thought to occur involves the dissolution, migration, gelation, reorganization and polymerization and hardening [16] of Al and Si precursor species as well as surface reaction on the remaining surface area of undissolved solid particles of the source aluminosilicate [17,18]. The raw materials mainly used in geopolymerization are clays or pozzolanic materials such as kaolin, calcined kaolin (metakaolin), fly ashes and blast furnace slag that partially dissolve in the alkali solution and are therefore a source of geopolymeric precursors [19,20]. The alkali solution not only dissolves alumina and silica precursors but also hydrolyses the surface of particles allowing reactions to occur between already dissolved silicate species and the particle surface [19]. The presence of cations (Na^+, K^+ and Ca^{2+}) is important due to charge balancing and catalytic properties.

Geopolymers have received attention in various applications. These applications are divided into two categories. First, they can be used as building material such as concrete replacements, but also related to this, they find application as a binder in waste S/S systems. Applications of geopolymers in the S/S field often refer to laboratory studies carried out in most cases on simulated metal containing wastes. When geopolymers are used in S/S systems to immobilize toxic metals they function similarly to cement binders in terms of encapsulation, however, they can manifest the improved chemical and physical properties shown by geopolymers in construction, such as acid attack resistance, fire

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Table 1
Major elements present in the S/S agents and MSWI waste.

	Moisture 105 °C	LOI 750 °C	Major elements (wt%)						
			Fe_2O_3	CaO	MgO	SiO_2	Al_2O_3	Na_2O	K_2O
FA	0.05	3.32	5.86	3.94	1.84	63.9	21.5	0.68	1.67
Kaolin	1.16	12.17	0.51	<0.03	0.17	65.2	32.0	0.05	1.28
BFS	0.24	0.31	0.41	43.5	7.60	41.1	10.7	0.26	0.32
OPC	0.15		2.15	61.7	2.76	21.2	5.0	0.13	0.16
MSWI waste	1.26	24.18	2.18	44.7	3.49	26.8	12.0	3.37	0.93

resistance, structural integrity, low permeability, high compressive strength and durability, low shrinkage, fast or slow setting and low thermal conductivity, all these properties depending on the source material and the processing conditions [16,17,21]. The mechanism of heavy metals immobilization is believed to be either physical or chemical so that metals are fixed in the geopolymer network, possibly bound into the structure for charge balancing roles or remain physically trapped by the surrounding network [19]. Recently, we have studied for the first time the use of some geopolymeric agents in the S/S of electric arc furnace dust (EAFD), a difficult waste to stabilize [22]. Mixtures of EAFD waste with different geopolymeric materials and class F fly ash were processed for studying the potential of geopolymers as waste immobilizing agents. After that, we decided to apply this technology to other different industrial waste, MSWI fly ash, since this residue has a lower content of hazardous metals than EAFD.

Very scarce information can be found in the literature about the S/S of MSWI fly ash using geopolymers. Very recently a study has been published in which incinerator fly ashes have been introduced into a geopolymeric matrix and the chemical stability of geopolymers has been assessed through the heavy metals release [23]. The paper focuses on the evaluation of the possibility of using MSWI fly ash as partial replacement for metakaolin in a geopolymer matrix.

The stabilization of a MSWI fly ash containing hazardous metals such as Pb, Cd, Cr, Zn and Ba using coal fly ash-based geopolymerization technology is described in this study. The study includes a relatively complete set of leaching data of the S/S solids obtained to better understand the mechanism by which heavy metal immobilisation occurs.

The research described in this paper has been carried out in the framework of the European Union financed project "Understanding and mastering coal fired-ash geopolymerization process in order to turn potential into profit", also known by the acronym GEOASH (2004–2007) [24,25].

2. Experimental

2.1. Materials

Low calcium fly ash (ASTM class F) from the combustion of high quality pulverized coal in one of the biggest coal power plants in the south of Spain, Los Barrios (550 MW) was used as the main aluminosilicate agent and as geopolymer precursor. Ground (granulated) blast furnace slag, as lime and silicon source, and kaolin (K) and metakaolin (MK), as secondary aluminosilicate source, were also used. Metakaolin is obtained after kaolin heating for 24 h at 750 °C. Type II ordinary Portland cement was used in order to compare with conventional stabilization/solidification processes. The waste used in this study is a fly ash generated in a European Municipal Solid Waste Incinerator (electrofilter fly ash) and was used without any pre-treatment. Hazardous metals normally found in this type of fly ash include: Zn. Pb, Cd, Cu, Ni, Sb and Cr. The major elements analyzed in all the S/S agents used and in the waste to stabilize are detailed in Table 1. The heavy metal content of the MSWI waste is shown in Table 2. The chloride weight proportion of MSWI fly ash has been determined using the UNE-EN 83492 [26] standard and the result is 9.4%.

The potassium silicate solutions used in the geopolymer samples was named KSil (0.46) (K_2O/SiO_2 molar ratio = 0.459) and KSil (0.65) (K_2O/SiO_2 = 0.649), and were supplied by Industrias Químicas del Ebro. The sodium silicate solution was supplied by Merck. Product specifications of both alkaline silicates are listed in Table 3.

The objective of S/S technology is to obtain solids that reduce the overall environmental impact of waste disposal. To achieve this goal, the US Environmental Protection Agency (USEPA) criteria, the limits stated for landfill leachate in European Regulations (European Landfill Directive, EULFD) and the leachate limits included in the decree on soil quality (DSQ, the successor of the Dutch Building Material Decree) were followed to establish quality criteria on metal concentration limits in leachates from S/S solids after the usual curing time.

Table 2
Trace metal content in the MSWI waste.

	Total metal content (mg/kg)														
	As	Mo	Zn	Pb	Co	Cr	Ni	Cu	Ba	Cd	Sn	Hg	Sb	Se	V
MSWI waste	≤60	46	15900	398	94	790	90	156	1270	≤6	1790	≤60	5110	≤80	≤40

Table 3
Specifications of sodium and potassium silicate solutions.

	SiO_2, wt%	K_2O, wt%	Dry material, wt%	SiO_2/K_2O (SiO_2/Na_2O)*	Density 25 °C, g/cm³
KSil (0.65)	23.0	14.9	37.9	1.54	1.38
KSil (0.46)	23.1	10.6	33.7	2.18	1.31
NaSil*	25.5–28.5	7.5–8.5		3.04–3.8	1.296–1.396

Table 4
Composition of matrices.

| | Proportion by weight | | | | | | | | | |
	MSWI waste	FA	NaSil	KSil	NaOH	KOH	Kaolin	Metakaolin	BFS	Water
NaSil NaOH K	0.5	1.4	0.4		0.08		0.22			0.56
NaSil NaOH MK	0.5	1.4	0.4		0.08			0.22		0.52
NaSil KOH	0.5	1.4	0.4			0.08				0.58
KSil (0.46) KOH	0.5	1.4		0.4		0.08				0.55
KSil (0.65) KOH	0.5	1.4		0.4		0.08				0.51
KSil (0.65) KOH K	0.5	1.4		0.4		0.08	0.22			0.6
KSil (0.65) KOH MK	0.5	1.4		0.4		0.08		0.22		0.6
KSil (0.65) BFS	0.5	1.4		0.5					0.3	0.68

|	MSWI waste	FA	OPC	Lime	Water
OPC LIME	1.0	1.4	0.2	0.2	0.8
OPC	1.0		0.3		0.25

2.2. Preparation of S/S solids

Various samples were prepared maintaining constant the composition of the coal fly ash and the MSWI waste and varying the rest of the components. Distilled water was used throughout. The water content was adjusted to achieve the same workability in all the mixtures. With the mass obtained, cylindrical plastic moulds (30 mm diameter and 41 mm height) were filled and compacted. Finally, the pastes were vibrated for 5 min in order to release bubbles. In addition, hydraulic binders such as, OPC and lime have been used to prepare other S/S solids in order to compare geopolymeric and conventional S/S methods. During curing, some samples were placed in a stove at 60 °C while others were maintained at room temperature. After 7 and 28 days of curing, the samples were crushed and sieved to 9 mm, and were extracted using leaching tests. Compositions of matrices studied are shown in Table 4.

2.3. Compressive strength

A compressive strength test was performed as per ASTM D-1633-84 using two cylinders of each sample and averaging the experimental values obtained. All samples were tested after 7 and 28 days. A Suzpecar, mod. MEM-102/50 t, compressive strength testing apparatus was used.

2.4. Leaching tests

The stabilization/solidification efficacy was assessed from the chemical point of view according to four leaching tests: USEPA TCLP, UNE EN 12457-4, NEN 7345 and GANC test. The USEPA TCLP (toxicity characteristic leaching procedure) [27] method no. 1311 test consists of stirring the granular material (< 9 mm), using in our case an acetic acid solution at pH 4.93 ± 0.05 (fluid no. 2) with a liquid/solid ratio (L/S) of 20 for 18 h. The UNE EN 12457-4 test [28] is an extraction method similar to the TCLP, but the extraction fluid is distilled water, in a liquid to solid ratio of 10 for 24 h. The NEN 7345 test (tank leaching test) [29] is a monolith-type leaching test which can be used to assess the potential and leaching rate of stabilized/solidified wastes over the long term. The leaching agent is distilled water acidified at pH 4 with nitric acid. The liquid to solid ratio used is between 2 and 5 and the extraction fluid is renewed in 8 extractions at 0.25, 1, 2.25, 4, 9, 16, 36 and 64 days from the test start. After each stage, pH and conductivity are determined in leachates. The GANC (generalized acid neutralization capacity) [30] test is, like the ANC, a single-batch procedure that uses from 0 to 6 equivalents of acid (in this case acetic acid, the same acid used in the TCLP test) per kilogram of solids. The GANC test was adapted as described by Vale Parapar [31]. From the data recorded, we obtained the acetic acid consumption for pH values ranging from approximately 12.5–5.5 and the corresponding GANC curves. After the tests, samples were filtered through
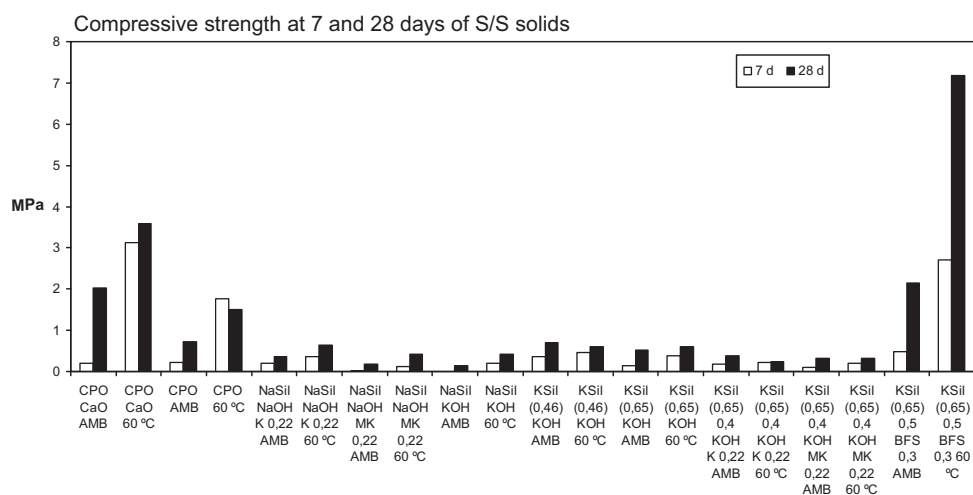
Fig. 1. Compressive strength at 7 and 28 days of S/S solids.

Whatman membrane filters (pore size 0.45 μm). When the procedures were completed, the metal contents in the solutions were determined using atomic absorption spectrometry and inductively coupled plasma techniques.

The aim of S/S technology is to obtain solids that reduce the overall environmental impact of waste disposal. To achieve this goal, the USEPA criteria, the EU Landfill regulations (European Landfill Directive, EULFD) (1999) [32], and the decree on soil quality) (2007) [33] were followed to establish quality criteria on metal concentrations limits in leachate from S/S solids after the usual curing time (28 days).

3. Results and discussion

3.1. Compressive strength

As can be observed in Fig. 1, compressive strength increased with time for practically all the samples. The largest increments with time were observed at room temperature in all the cases. Increments of 90%, 93% and 78% were reached for samples prepared with OPC and lime, sodium silicate and potassium silicate and BFS slag respectively.

The use of OPC and lime led to high resistances. Samples prepared using OPC and lime showed better results than samples prepared with OPC alone. The use of BFS slag in the geopolymer mixtures produced a significant increase in the resistance especially at 60 °C, yielding 7.2 MPa at 28 days.

The use of kaolin and metakaolin did not give significant results in compressive strength. Besides, it can be observed that samples prepared with kaolin reached higher compressive strength than metakaolin, which is corroborated by the literature [34,35].

Generally, samples cured at 60 °C showed larger resistances than those cured at room temperature. Some studies [34,36] indicated that an increase of the curing temperature leads to an increment of the extent and rate of geopolymerization reaction which produces an accelerated setting time, and finally an increase in the compressive strength. Increasing the curing temperature from 25 to 60 °C led to the highest strength increments in OPC and lime (94%), sodium silicate (95%) and potassium silicate and BFS slag samples (83%). Besides, it must be taken into account that in waste S/S processes the lowest required compressive resistance for the final S/S solids is 0.35 MPa [37], so all the tested samples met this value.

3.2. Leaching tests

3.2.1. UNE EN 12457-4

Table 5 shows the pH and the metal content (mg/kg) values in the UNE EN 12457-4 leachates of the S/S solids cured for 28 days at ambient temperature and at 60 °C.

As can be seen, the UNE-EN leachates were always alkaline (pH 11.5–12.7). Moreover, in all the cases, leachates related to samples cured at room temperature showed a higher leachate pH than those cured at 60 °C, which seem to lose their initial alkalinity quickly after 28 days.

The leached fractions have been calculated for most metals. Zn, Co, Ni, Cu and Sn showed the lowest extraction percentages. Low leached amounts were observed for Zn in all compositions. Thus, the average percentage of Zn leached was about 10^{-4}%. Bearing in mind the high Zn content in the residue (15,900 mg/kg) it is worth noting that Zn was excellently immobilized in the S/S solids.

Elements often found as oxyanions such as Mo, V and Cr showed the worst results in most mixtures, independently of the immobilization method used, whether using OPC and lime or geopolymeric

Table 5
pH and metal concentrations in the UNE EN 12457-4 leachates at 28 days and EULFD limits (≤ means under detection limit).

	pH	As	Mo	Zn	Pb	Co	Cr	Ni	Cu	Ba	Cd	Sn	Hg	Sb	Se	V
		UNE EN 12457-4 (mg/kg)														
OPC LIME AMB	12.7	≤0.3	2.0	0.18	5.0	≤0.02	≤0.02	≤0.1	≤0.03	86.1	≤0.03	≤0.2	0.4	≤0.2	≤0.4	≤0.2
OPC LIME 60 °C	11.5	≤0.3	1.9	0.04	≤0.3	≤0.02	≤0.02	≤0.1	≤0.03	8.18	≤0.03	≤0.2	≤0.3	≤0.2	≤0.4	≤0.2
OPC AMB	12.5	≤0.3	5.0	1.49	46.3	≤0.02	2.63	≤0.1	≤0.03	7.16	≤0.03	≤0.2	≤0.3	≤0.2	≤0.4	≤0.2
OPC 60 °C	12.1	≤0.3	7.7	≤0.01	≤0.3	≤0.02	3.31	≤0.1	≤0.03	2.79	≤0.03	≤0.2	≤0.3	≤0.2	≤0.4	≤0.2
NaSil NaOH K AMB	12.7	4.1	8.0	0.43	≤0.3	≤0.02	5.33	≤0.1	≤0.03	0.18	≤0.03	≤0.2	≤0.3	11.2	2.5	15.7
NaSil NaOH K 60 °C	12.2	≤0.3	6.2	≤0.01	≤0.3	≤0.02	5.46	≤0.1	≤0.03	0.27	≤0.03	≤0.2	≤0.3	1.7	≤0.4	6.1
NaSil NaOH MK AMB	12.4	≤0.3	6.4	0.07	≤0.3	≤0.02	6.21	≤0.1	≤0.03	0.38	≤0.03	≤0.2	≤0.3	7.3	≤0.4	11.0
NaSil NaOH MK 60 °C	12.1	≤0.3	5.3	0.20	≤0.3	≤0.02	4.87	≤0.1	≤0.03	0.09	≤0.03	≤0.2	≤0.3	≤0.2	≤0.4	2.7
NaSil KOH AMB	12.4	2.7	5.3	0.35	≤0.3	≤0.02	3.83	≤0.1	≤0.03	≤0.01	≤0.03	≤0.2	≤0.3	4.9	≤0.4	6.5
NaSil KOH 60 °C	11.9	≤0.3	5.1	≤0.01	≤0.3	≤0.02	2.98	≤0.1	≤0.03	0.44	≤0.03	≤0.2	≤0.3	≤0.2	≤0.4	1.2
KSil (0.46) KOH AMB	12.7	≤0.3	9.0	0.23	≤0.3	≤0.02	10.8	≤0.1	≤0.03	0.55	≤0.03	≤0.2	≤0.3	8.6	1.8	11.0
KSil (0.46) KOH 60 °C	12.0	2.2	7.5	≤0.01	≤0.3	≤0.02	8.90	≤0.1	≤0.03	0.82	≤0.03	≤0.2	≤0.3	0.7	≤0.4	1.5
KSil (0.65) KOH AMB	12.5	2.2	9.7	0.88	≤0.3	≤0.02	5.44	≤0.1	≤0.03	0.16	≤0.03	≤0.2	≤0.3	8.3	2.4	10.4
KSil (0.65) KOH 60 °C	12.5	≤0.3	4.4	0.10	≤0.3	≤0.02	5.29	≤0.1	≤0.03	0.61	≤0.03	≤0.2	≤0.3	2.3	≤0.4	3.5
KSil (0.65) KOH K AMB	12.5	2.5	8.5	0.70	≤0.3	≤0.02	7.01	≤0.1	≤0.03	0.39	≤0.03	≤0.2	≤0.3	8.5	2.4	13.2
KSil (0.65) KOH K 60 °C	11.8	≤0.3	7.3	≤0.01	≤0.3	≤0.02	6.24	≤0.1	≤0.03	0.29	≤0.03	≤0.2	≤0.3	5.2	≤0.4	7.4
KSil (0.65) KOH MK AMB	12.6	≤0.3	7.6	0.16	≤0.3	≤0.02	5.04	≤0.1	≤0.03	0.30	≤0.03	≤0.2	≤0.3	3.8	≤0.4	6.4
KSil (0.65) KOH MK 60 °C	12.1	≤0.3	8.0	≤0.01	≤0.3	≤0.02	4.71	≤0.1	≤0.03	0.32	≤0.03	≤0.2	≤0.3	≤0.2	≤0.4	1.1
KSil (0.65) BFS AMB	12.3	≤0.3	6.4	≤0.01	≤0.3	≤0.02	≤0.02	≤0.1	≤0.03	1.45	≤0.03	≤0.2	≤0.3	1.3	≤0.4	3.1
KSil (0.65) BFS 60 °C	12.2	≤0.3	4.4	≤0.01	≤0.3	≤0.02	≤0.02	≤0.1	≤0.03	1.46	≤0.03	≤0.2	≤0.3	0.9	≤0.4	0.9
Inert Waste		0.5	0.5	4	0.5		0.5	0.4	2	20	0.04		0.01	0.06	0.1	
Non-hazardous Waste		2	10	50	10		10	10	50	100	1		0.2	0.7	0.5	
Hazardous Waste		25	30	200	50		70	40	100	300	5		2	5	7	

Table 6
pH and metal concentrations in the TCLP leachates at 28 days and USEPA limits (≤ means under detection limit).

	pH	TCLP (mg/L)														
		As	Mo	Zn	Pb	Co	Cr	Cu	Ni	Ba	Cd	Sn	Hg	Sb	Se	V
OPC LIME AMB	10.78	≤0.03	0.288	≤0.001	≤0.03	≤0.002	0.214	≤0.003	≤0.01	0.343	≤0.003	≤0.02	≤0.03	0.39	≤0.04	0.07
OPC LIME 60 °C	7.50	≤0.03	0.183	7.67	≤0.03	0.152	0.222	≤0.003	0.15	0.420	≤0.003	≤0.02	≤0.03	0.43	≤0.04	0.10
OPC AMB	11.59	≤0.03	0.407	≤0.001	≤0.03	≤0.002	0.520	≤0.003	≤0.01	0.584	≤0.003	≤0.02	≤0.03	0.02	≤0.04	0.02
OPC 60 °C	10.87	≤0.03	0.427	≤0.001	≤0.03	≤0.002	0.454	≤0.003	≤0.01	0.244	≤0.003	≤0.02	≤0.03	0.18	≤0.04	0.04
NaSil NaOH K AMB	7.69	≤0.03	0.399	1.05	≤0.03	≤0.002	0.572	≤0.003	0.06	0.439	≤0.003	≤0.02	≤0.03	1.08	≤0.04	0.26
NaSil NaOH K 60 °C	6.72	≤0.03	0.295	0.428	≤0.03	0.115	0.527	0.028	0.13	0.258	≤0.003	≤0.02	≤0.03	0.66	≤0.04	0.30
NaSil NaOH MK AMB	8.37	≤0.03	0.294	0.101	≤0.03	≤0.002	0.642	≤0.003	≤0.01	0.480	≤0.003	≤0.02	≤0.03	1.41	≤0.04	0.23
NaSil NaOH MK 60 °C	7.03	≤0.03	0.245	6.64	≤0.03	0.068	0.623	≤0.003	0.11	0.120	0.468	≤0.02	≤0.03	0.64	≤0.04	0.22
NaSil KOH AMB	7.36	≤0.03	0.279	3.77	≤0.03	0.055	0.511	≤0.003	0.07	0.276	0.326	≤0.02	≤0.03	1.06	≤0.04	0.17
NaSil KOH 60 °C	7.33	≤0.03	0.262	0.868	≤0.03	≤0.002	0.515	≤0.003	0.09	0.281	0.184	≤0.02	≤0.03	0.92	≤0.04	0.16
KSil (0.46) KOH AMB	7.44	≤0.03	0.290	8.67	≤0.03	0.102	0.732	≤0.003	0.11	0.466	≤0.003	≤0.02	≤0.03	0.50	≤0.04	0.17
KSil (0.46) KOH 60 °C	6.84	≤0.03	0.337	3.98	≤0.03	≤0.002	0.719	≤0.003	0.08	0.395	≤0.003	≤0.02	≤0.03	0.71	≤0.04	0.19
KSil (0.65) KOH AMB	7.72	≤0.03	0.336	2.35	≤0.03	≤0.002	0.560	≤0.003	0.04	0.531	≤0.003	≤0.02	≤0.03	0.54	≤0.04	0.17
KSil (0.65) KOH 60 °C	7.54	≤0.03	0.251	1.29	≤0.03	≤0.002	0.694	≤0.003	0.10	0.606	≤0.003	≤0.02	≤0.03	0.53	≤0.04	0.23
KSil (0.65) KOH K AMB	7.56	≤0.03	0.357	3.53	≤0.03	≤0.002	0.649	≤0.003	0.06	0.604	≤0.003	≤0.02	≤0.03	0.69	≤0.04	0.18
KSil (0.65) KOH K 60 °C	7.12	≤0.03	0.326	3.54	≤0.03	0.133	0.661	≤0.003	0.18	0.575	≤0.003	≤0.02	≤0.03	0.59	≤0.04	0.26
KSil (0.65) KOH MK AMB	7.06	≤0.03	0.219	9.78	≤0.03	0.113	0.539	≤0.003	0.10	0.478	≤0.003	≤0.02	≤0.03	0.18	≤0.04	0.13
KSil (0.65) KOH MK 60 °C	6.83	≤0.03	0.300	0.673	≤0.03	0.096	0.593	≤0.003	0.12	0.504	≤0.003	≤0.02	≤0.03	0.28	≤0.04	0.17
KSil (0.65) BFS AMB	8.53	≤0.03	0.291	0.037	≤0.03	≤0.002	≤0.002	≤0.003	≤0.01	0.396	≤0.003	≤0.02	≤0.03	0.41	≤0.04	0.15
KSil (0.65) BFS 60 °C	6.78	≤0.03	0.229	3.87	≤0.03	≤0.002	≤0.002	≤0.003	0.07	0.423	≤0.003	≤0.02	≤0.03	0.39	≤0.04	0.13
USEPA limits		5		300	5		5			100	1		0.2		1	

activators. For Ba and Pb, the worst results were obtained in those mixtures prepared with hydraulic (OPC) materials, whereas, the worst results for Sb were obtained in the geopolymeric mixtures. In general, the most problematic element in geopolymeric samples is Sb, for which a few S/S solids exceeded the Hazardous Waste limit, but most of the geopolymeric mixtures exceeded the Non Hazardous Waste limit. However, none of the cement S/S solids exceeded the Non Hazardous Waste limit for Sb. With the exception of Sb, almost all the geopolymeric systems met the non-hazardous waste limit for metals. Mixtures prepared with potassium silicate and BFS slag and some OPC and lime samples showed the best results.

3.2.2. Toxicity characteristic leaching procedure (TCLP)

Table 6 shows the pH and metal content (mg/L) values in the TCLP leachates of the S/S solids cured for 28 days at ambient temperature and at 60 °C.

The TCLP leachates of samples prepared with OPC and mixtures of OPC and lime were alkaline, with pHs between 10.8 and 12.7. However, geopolymer leachates showed a neutral pH between 6.8 and 8.5. Metal contents in TCLP leachates (mg/L) have been compared with the limits defined by USEPA for As, Cr, Cu, Zn, Pb, Ba, Cd, Hg and Se, and the metal concentrations were lower than the respective limits.

A comparison between the TCLP and EN-12457 leachabilities of the MSWI waste S/S solids stabilized with OPC and lime and those stabilized with geopolymers has been made. Some metals such as Zn, Ni and Cr showed higher concentrations in TCLP leachates than in EN 12457-4 leachates. Conversely, other metals such as Sb and V (though they are not regulated by USEPA) presented lower concentration values in TCLP leachates, possibly due to their more acidic pHs.

With regard to geopolymer S/S solids, the best results were obtained in samples prepared with potassium silicate and metakaolin. These, however, were the mixtures with the least compressive strength. S/S solids prepared with BFS slag (which showed the highest compressive strength) showed in general good results in TCLP test (as occurred in the EN-12457 test), although they release appreciable amounts of Mo, V, Sb and Ba.

3.2.3. NEN 7345

After 28 days of curing, solids were subjected to the tank leaching test. The NEN 7345 leaching test accumulative results (mg/m²) of certain heavy metals are shown in Table 7 and have been compared with the decree on soil quality limits.

All the samples studied showed Ba, Zn, Pb, Cr and Cd concentrations under the DSQ limits. In general, the results obtained are similar for both S/S systems. However, in relation to Zn and Cr cumulative releases at 64 days, the lowest values were obtained in S/S solids prepared with OPC and lime and those geopolymeric S/S solids prepared with blast furnace slag.

On the other hand, the cumulative release of Ba showed the worst value in the hydraulic (OPC) system. This difference could

Table 7
Results of the NEN 7345 tank leaching test in MSWI waste S/S solids at 64 days.

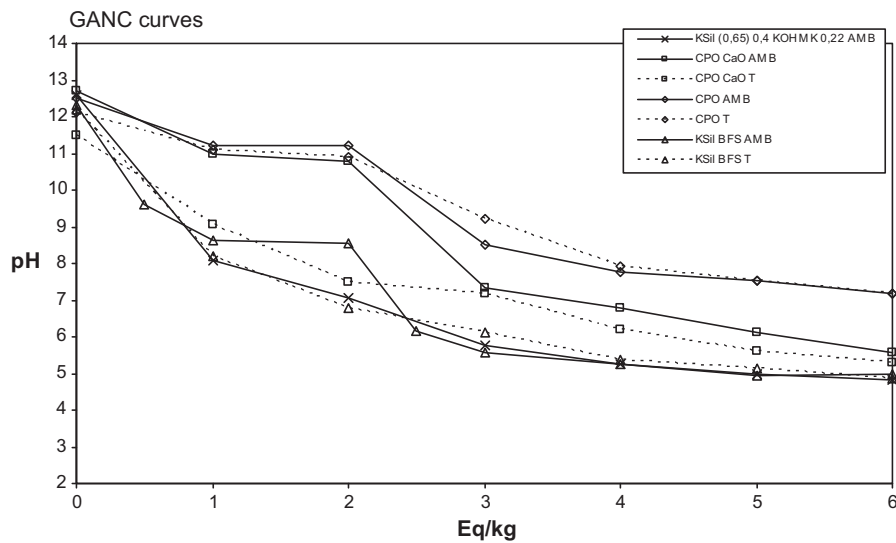|	Cumulative releases (mg/m²)				
	Ba	Zn	Pb	Cr	Cd
OPC LIME	219	4	<31	4	<3.1
KSil (0.65) KOH	20	15	<28	28	<2.9
KSil (0.65) K	21	11	<29	43	<3
KSil (0.65) MK	20	7	<30	39	<3
KSil (0.65) BFS	29	3	<29	4	<2.9
DSQ limits	1500	800	400	120	3.8

GANC curves

Fig. 2. GANC curves.

be due to a better Ba immobilization in the geopolymer matrix, by physical encapsulation (entrapment) of this metal or by chemical interaction with the aluminosilicate network. Notwithstanding, the difference could also be due to the presence of a different sulphate content in the two S/S matrices.

As can be seen, all samples met the DSQ limits for all studied metals.

The evolutions of the leachate pH and conductivity values were also studied during the test. pH values indicated an alkaline system, decreasing slightly from the first to the final extraction. The conductivity values also decreased with time. OPC and lime systems and those geopolymer S/S solids prepared with BFS showed conductivity values lower than other geopolymeric samples which indicated the presence of less dissolved species in these leachates.

3.2.4. Acid neutralization capacity test (GANC)

After 28 days of curing, some of the S/S solids were also subjected to the GANC leaching test. To study the Acid Neutralization Capacity (ANC) of the S/S solids, pH versus equivalents of acid (acetic) per kilogram of S/S solid is drawn in Fig. 2. As can be seen, the curves for all ambient cured S/S solids have the same shape. At 0 eq/kg, the pH is alkaline (between 12 and 13), and curves begin to fall around 1 eq/kg. Between 1 and 2 eq/kg a plateau appears, again followed by a steep drop until neutral pH. The pH plateau in BFS samples is found at pH 8.5 and the final pH (at 6 eq/kg) is around 5, whereas the OPC systems have the plateau at pH 11 and the final pH depends on the use of lime in the mixtures (if lime is used the final pH is 6, but if lime is not used, the final pH is 8). Metakaolin samples do not show a plateau.

The GANC curves of 60 °C-cured S/S solids are different from the ambient-cured S/S solids curves especially in the range of 1–2 eq/kg (the range corresponding to the TCLP leaching test) and for OPC and lime S/S solids. However, differences are not very significant for the OPC S/S solids. The presence of lime in the OPC CaO samples seems to produce a quicker response to the acid attack at 60 °C.

Fig. 3 shows the Zn leachate concentrations versus pH values of the MSWI waste and some of its S/S solids stabilized by means of OPC systems and BFS and MK geopolymer systems.

Zn solubility in MSWI waste is strongly dependent on pH and exhibits characteristic hydroxide amphoteric behavior, that is, solubility minimum at pH value of 9–10, increasing the concentration

rapidly when pH decreases, reaching nearly constant concentration at pH less than 6, and also increasing though more slowly when pH increases above 10. The behavior of MSWI waste S/S solids is similar to that of the waste itself, although the pH of minimum solubility is shown in a wide pH range (8–12) depending on the S/S method and curing conditions.

As can be seen, in general, the Zn leached amount is lower in the S/S solids than the waste itself. Mixtures prepared using KSil and BFS cured at ambient and 60 °C conditions reached the lowest
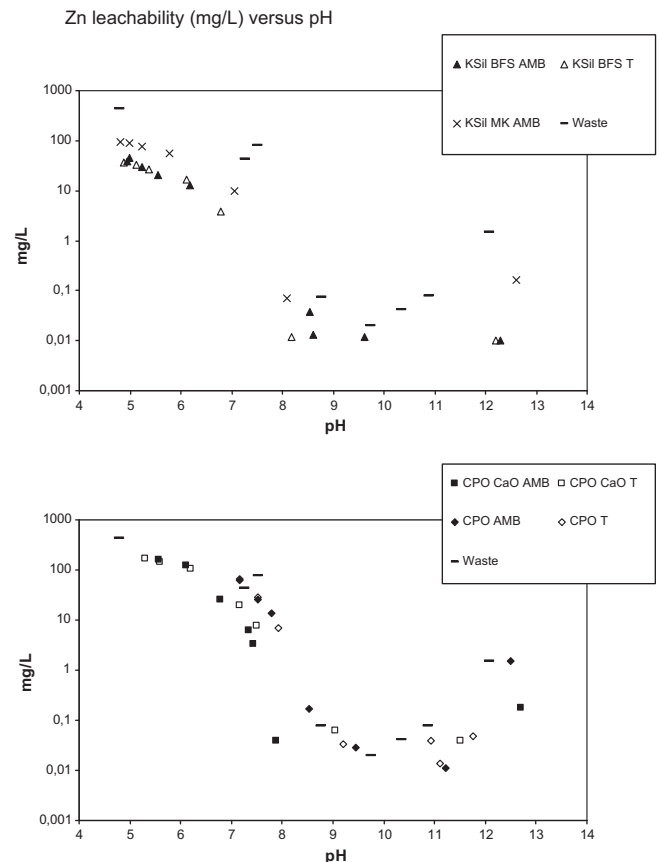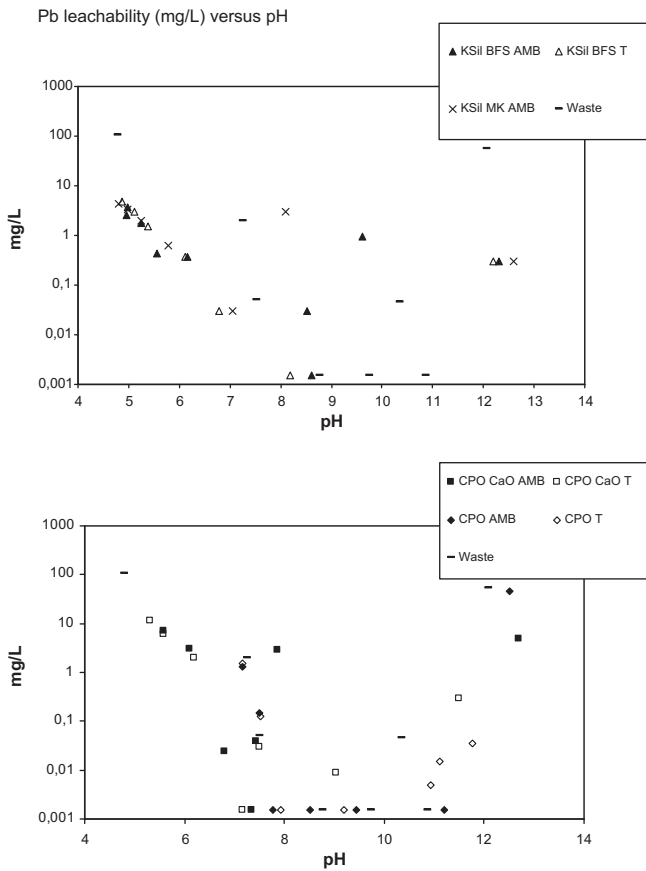
Zn leachability (mg/L) versus pH

Fig. 3. Zn leachability (mg/L) versus pH.

Fig. 4. Pb leachability (mg/L) versus pH.

Fig. 5. Cr leachability (mg/L) versus pH.

Zn concentration in the whole pH range. Geopolymeric activators exhibit, on the whole, lesser Zn concentrations than hydraulic binders in acidic or neutral pHs. In alkaline conditions (pH > 9), both systems showed the same solubilities.

Fig. 4 shows the Pb leachate concentrations versus pH values of the MSWI waste and some of its S/S solids stabilized by means of OPC systems and BFS and MK geopolymer systems.

Pb solubility in MSWI waste is strongly dependent on pH too, and exhibits hydroxide amphoteric behavior as Zn does, that is, a minimal solubility at pH values between 8.5 and 10. Lead in MSWI waste does not present a plateau at acidic pH, as happened to Zn, instead its concentration increases from pH 7 to 4.

Waste S/S solids do not show clear Pb leaching behavior. At pHs lower than 8 and higher than 12, geopolymeric mixtures exhibit a lower solubility than hydraulic binder systems. Conversely, when pH is between 8 and 12, OPC systems show best results.

Fig. 5 shows the Cr leachate concentrations versus pH values of the MSWI waste and some of its S/S solids stabilized by means of OPC systems and BFS and MK geopolymer systems.

Cr leachability is more difficult to explain because no clear relationship with pH is found. Except at a very high pH all the S/S solid samples (geopolymer or hydraulic) showed a Cr leachability lower than that of the raw waste manifesting some Cr immobilization. When the two geopolymer mixtures were compared it is evident that the BFS samples had a better Cr immobilization capacity than the MK samples. The BFS samples showed better behavior at acidic pHs in relation to the Cr leachability of all the samples analyzed. This could be related to a partial Cr speciation in the form of hexavalent Cr, coupled with a reducing effect of Cr(VI) to Cr(III) provoked by BFS. MK samples showed a constant Cr concentration along the acidic and neutral pH range increasing when the pH is alkaline. All
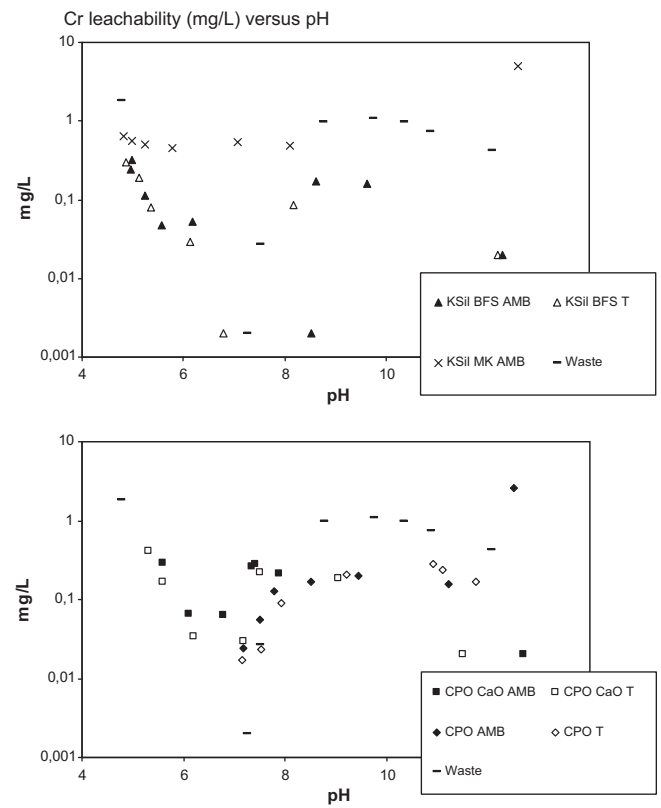
the samples analyzed seem to show their lowest Cr leachability at neutral pH.

Fig. 6 shows the Cd leachate concentrations versus pH values of the MSWI waste and some of its S/S solids stabilized by means of OPC systems and BFS and MK geopolymer systems.

Cd leachability in both the MSWI waste and its S/S solids is also clearly dependent on pH exhibiting typical hydroxide amphoteric behavior, with a solubility minimum at pH values between 9.5 and 11. Waste S/S solids behavior is similar to the waste itself, although the minimum solubility is found in a wider pH range (7–12) depending on the S/S method used and the curing conditions. At pHs lower than 7.5 geopolymeric mixtures exhibit lower solubilities than hydraulic binder systems. At pHs higher than 7.5 both methods showed the same Cd concentrations.

4. Conclusions

Municipal solid waste incineration fly ash containing heavy metals such as Pb, Cd, Cr or Zn may be effectively stabilized/solidified using fly ash-based geopolymerization technology. The stabilization (S/S) process studied in this paper has been assessed by means of the mechanical and leaching properties of the S/S solids obtained. Moreover, the geopolymer S/S solids were compared with similar solids obtained after the stabilization of the MSWI waste with classical hydraulic binders.

The compressive strength developed by the S/S solids increased with time for all the samples. The largest increments were observed at room temperature in all cases. The use of OPC and lime led to high resistances but the use of BFS slag in the geopolymer mixtures produced the most important increments in the compressive strength. The use of kaolin and metakaolin did not give signifi-
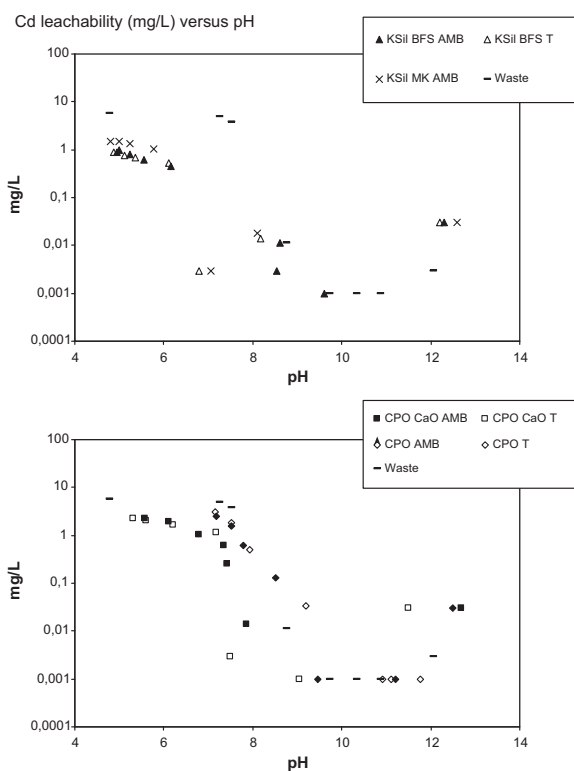
Fig. 6. Cd leachability (mg/L) versus pH.

cant results in mechanical resistance. Generally, samples cured at 60 °C showed greater resistances than those cured at room temperature.

The environmental assessment carried out evidences that, depending on the leaching test used, the S/S solid behavior is different. Zn, Co, Ni, Cu and Sn were the metals with the lowest extraction percentages in EN-12457 leachates. Zn, Sb and Sn were excellently immobilized in the S/S solids, while Mo, V and Cr (elements typically found as oxyanions) showed the worst results in most of the mixtures, independently of the immobilization method used. S/S solids prepared with potassium silicate and blast furnace slag and some OPC and lime samples showed the best results.

In relation to the TCLP test, a more aggressive test than EN-12457, the best results were obtained in samples prepared with potassium silicate and metakaolin. S/S solids containing slag, although they release appreciable amounts of Mo, V, Sb and Ba, in general showed good results in this test.

The lowest Zn and Cr leachate concentrations were obtained in the tank leaching test in samples prepared with OPC and lime and the geopolymeric samples prepared with blast furnace slag. These low values are possibly due to a higher alkalinity in the cement leachates and to the reducing power of BFS respectively. On the other hand, the cumulative release of Ba had the worst value in hydraulic OPC systems.

With regard to the speciation of metals, it can be concluded that Zn, Pb and Cd exhibit typical hydroxide-amphoteric behavior, irrespective of the S/S method (geopolymeric or hydraulic) used. The GANC test also showed that the geopolymeric S/S solids have less acid neutralization capacity, thus less alkalinity than OPC S/S solid samples. However, in general a lower metal (Cd, Cr, Pb and Zn) leachability is observed at neutral and acidic pHs for the geopolymer S/S solids. In addition, the geopolymer alkalinity might possibly be maintained during a longer period of time, while OPC S/S solids, as is well known, quickly lose their alkalinity. It would therefore be necessary to study the long term evolution of the metals stabilized in both matrices in order to take a more complete decision with regard to the comparison between classical hydraulic and geopolymer S/S methods.

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