

# Use of Different Geopolymeric Agents For The Stabilization/Solidification (S/S) Of A Metallurgical Waste

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## Abstract

The stabilization/solidification (S/S) of carbon steel electric arc furnace (EAF) dust containing hazardous metals such as Pb, Cd, Cr or Zn using geopolymerization technology is described in this paper. On the basis of the results obtained in other studies about the leaching behaviour of EAF dust S/S solids, it has been decided to study in greater depth the solids prepared with different geopolymeric agents, in an effort to optimize the following variables: the amounts of metakaolin (MK) and blast furnace slag (BFS) in the mixes; the grain size of the fly ash used as main silicoaluminate precursor and the amount of potassium silicate, also considering in this case that KOH has been used in one composition to increase the potassium oxide/silicon oxide molar proportion from 0.5 to 0.8 and finally, the replacement of BFS by other slag (MS) coming from a stainless steel plant. Mixtures of EAF waste with these kinds of geopolymeric materials and class F fly ash have been processed to study the potential of geopolymers as waste immobilizing agents. A compressive strength test and different leaching tests to determine the efficiency of heavy metal immobilisation have been carried out. The amounts of potassium silicate and KOH are the most important parameters to reach a higher resistance. The best results for an acid leaching were shown in samples with a high amount of potassium silicate, however, for water leaching, the blast furnace slag is the best option.

## 1. Introduction

Geopolymer technology has recently received attention in various applications. In one of them, geopolymers are being used as binders in waste stabilization/solidification (S/S) systems of heavy metal containing wastes. In immobilization of toxic metals geopolymer systems function similarly to cement binders in terms of encapsulation. They have, however, improved chemical and physical properties, such as structural integrity, low permeability, high compressive strength and durability<sup>1, 2</sup>. Low permeability is one of the properties that favour the use of these materials as immobilisation systems for hazardous metals<sup>3</sup>. The mechanisms of encapsulation are believed to be either physical or chemical where metals are taken into the geopolymer network and possibly bound into the structure for a charge balancing role or remain physically trapped by the surrounding network<sup>4</sup>.

Some ash-based geopolymer systems have been used to improve the immobilization of metals such as Cu, Pb, Cs, Sr, As Cd and Cu, in S/S solids<sup>2, 5-9</sup>. The results show that these heavy metals can be effectively immobilized into the geopolymeric matrices. We must remark that most of the previous works refer to stabilization studies carried out, not on real wastes, but on simulated wastes prepared from different metal aqueous solutions.

Other recent work<sup>10</sup> investigated the potential for the utilization of alkali-activated fly ash as a solidification binder to treat electroplating sludge. The sludge was solidified using lime, fly ash and different proportions of two alkali activators,  $\text{Na}_2\text{SiO}_3$  and  $\text{Na}_2\text{CO}_3$ . Pb, Cd, and Cu were not found in the toxicity characteristic leaching procedure (TCLP) leachates, whereas Cr, Zn, and Fe were detected and in some cases Cr exceeded U.S. EPA allowable limits.

This study focuses on the potential application of fly ash-based geopolymer systems, as S/S agents of carbon steel electric arc furnace (EAF) dust, a "real" waste that presents a challenge for both recovery, as many elements are difficult to separate, and disposal, because many of the elements are hazardous<sup>11</sup>.

The stabilization of EAF dust that results from the collecting systems of particulate material by means of geopolymerization technology is described in this study. Because of its heavy metal content, EAF dust is generally classified as hazardous waste by many regulations. Although EAF dust is a waste that is difficult to stabilize, the use of different S/S systems containing Type F coal fly ash, lime, dolomitic lime, Type I Portland cement, blast furnace slag or silica fume may be found in the literature<sup>12-14</sup>. Another alternative treatment for EAF dust is vitrification<sup>15</sup>. Some of the S/S solids obtained after treatment met some short-term regulations stated in order to evaluate the efficacy of the S/S process, but others did not.

In the course of a research carried out in the Wastewater Technology Centre (WTC) of Burlington, Ontario, Caldwell et al.<sup>16</sup> have studied different S/S formulations to stabilize EAF dust, finally choosing a formulation with blast furnace slag, lime, silica fume and sodium silicate. The authors have also compared field-cured and laboratory-cured S/S samples through time. Although contaminant concentrations in the studied leachates were generally low, Cr and Pb tended to exceed the WTC performance criteria.

In a previous work by the same authors of this paper<sup>17, 18</sup>, the stabilization of electric arc furnace dust has been studied using coal fly ash-based geopolymeric agents and has been compared with classical hydraulic (OPC) binders. In that study, compressive strength values far better than those achieved by hydraulic S/S methods were easily obtained by geopolymer solids at 28 days. Regarding leachability, the geopolymer S/S solids manifested good behaviour, in general, showing very promising results. With the exception of the aforementioned work of Caldwell et al., in which although the authors do not mention the term geopolymer some of the S/S systems used by the authors can be considered as such, the work above was the first time that a geopolymer S/S system was used to stabilize EAF dust.

In this article, a more complete study than that previously mentioned on the possibilities of the ash-based S/S geopolymer systems has been accomplished, trying to improve and optimize the degree of immobilization of the hazardous metals contained in EAF dust.

## 2. Experimental

### 2.1. Materials

Low calcium fly ash (ASTM class F) from the combustion of high quality pulverized coal in one the biggest coal power plants in the south of Spain, Los Barrios (550 MW) was used as the main silicoaluminate agent. Blast furnace slag (BFS) and other metallurgical slag (MS) as a lime and silicon source and kaolinite as a secondary silicoaluminate source were also used. Ordinary Portland Cement (OPC, type II) was used in order to compare geopolymer stabilization/solidification (S/S) process with conventional S/S process. The main elements of the four S/S agents are detailed in Table 1.

**Table 1.**

Main elements of Fly ash (FA), Kaolinite, Slag (BFS, MS), OPC and Electric arc furnace (EAF)

	Moisture 105 °C	LOI 750 °C	Main Elements (wt %)						
			Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O
FA	0.05	3.32	5.86	3.94	1.84	63.91	21.51	0.68	1.67
Kaolinite	1.16	12.17	0.51	<0.03	0.17	65.23	31.97	0.05	1.28
BFS	0.24	0.31	0.41	43.49	7.6	41.08	10.7	0.26	0.32
MS	0.45	1.9	1.53	53.8	9.52	31.6	4.41	0.6	0.07
OPC	0.15	-	2.15	61.7	2.76	21.2	5	0.13	0.16
EAF	0.42	12.77	36.32	8.60	3.05	6.21	2.00	1.13	0.48

The potassium silicate solution used in the samples was named as KSil 0,65 ( $K_2O/SiO_2$  weight ratio = 0.649), and was supplied by Industrias Químicas del Ebro (Zaragoza, Spain). The soluble silicates product specifications are listed in Table 2.

**Table 2.**  
Specifications of potassium silicate solutions

	SiO <sub>2</sub> , wt %	K <sub>2</sub> O, wt %	Density 25 °C, g·cm <sup>-3</sup>
KSil 0,65	23	14.9	1.38
KSil 0,46	23.1	10.6	1.31

The main elements content of EAF are shown in Table 1 and the heavy metals content of the waste are shown in Table 3.

**Table 3.**  
Heavy metal content in Electric Arc Furnace (EAF) dust

	Metal content g·kg <sup>-1</sup>			
	Zn	Cd	Cr	Pb
EAF	342.9	0.29	2.108	2.29

## 2.2. Preparation of S/S solids

Different samples were prepared maintaining constant the fly ash and EAF dust proportions and varying the proportions of the rest of components using the same methodology of previous studies<sup>17, 18</sup>. 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, samples were vibrated for 5 minutes in order to release bubbles. During curing, some samples were placed in a stove at 60 °C while others were stored at room temperature. On the other hand, hydraulic binders such as, ordinary Portland cement (OPC, type II) and lime have also been used in order to compare geopolymer S/S solids with conventional S/S solids. After 28 days, the samples were crushed and sieved to 9 mm, and were extracted using leaching tests.

Compositions of geopolymeric matrices are shown in Table 4. As can be seen, the variables studied have been: the amounts of metakaolin (MK) and slag in the mixes; the grain size of the fly ash and the amount of potassium silicate, also considering in this case that KOH has been used in one composition in order to increase the potassium oxide/silicon oxide molar proportion from 0.5 to 0.8. Finally, the replacement of BFS by other slag (MS) coming from a stainless steel plant, has also been carried out for comparative purposes. The main elements of both slags are detailed in Table 1. Compositions of cement matrices are shown in Table 5.

**Table 4.**  
Composition of S/S matrices using geopolymers

	(wt %)								
	EAf	FA	KSil	KOH	MK	BFS	MS	Water	
KSil (0,65) 0.8 BFS 0.3	0.5	1.4	0.8			0.3		0.308	
KSil (0,65) 1.2 BFS 0.3	0.5	1.4	1.2			0.3		0	
KSil (0,65) 0.8 BFS 0.6	0.5	1.4	0.8			0.6		0.233	
KSil (0,65) 0.8 BFS 1	0.5	1.4	0.8			1		0.504	
KSil (0,65) 0.8 KOH BFS 0.3	0.5	1.4	0.8	0.42		0.3		0	
KSil (0,65) 0.8 BFS 0.3 Fine	0.5	1.4	0.8			0.3		0.257	
KSil (0,65) 0.8 MS 0.3	0.5	1.4	0.8				0.3	0.233	
KSil (0,65) 0.8 MK 0.3	0.5	1.4	0.8		0.22			0.3	
KSil (0,65) 0.8 MK 0.6	0.5	1.4	0.4	0.08	0.6			0.47	

**Table 5.**

Composition of S/S matrices using hydraulic binders

	(wt %)			
	EAf	FA	CaO	OPC
OPC CaO	1	1.4	0.2	0.2

### 2.3. Compressive strength

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 28 days. A Suzpecar, 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 using four leaching tests: UNE-EN 12457-4<sup>19</sup>, USEPA TCLP<sup>20</sup>, NEN 7341<sup>21</sup>, NEN 7345 test<sup>22</sup> and GANC test<sup>23</sup>. The US Environmental Protection Agency (EPA) TCLP (Toxicity Characteristic Leaching Procedure) Method No. 1311 test consists of stirring the granular material (< 9mm), using an acetic acid solution at pH = 2.88 ± 0.02 or an acetic acid plus NaOH solution at pH = 4.93 ± 0.02 with a liquid/solid ratio (L/S) of 20 for 18 h. The UNE-EN 12457-4 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 availability test described in NEN 7341 is aimed to indicate the maximum amount of contaminant which can be leached from the material under extreme conditions, in other words, the fraction of the total contaminant potentially available for leaching. The test is performed on finely ground material (< 125 µm) at a high dilution (Liquid/Solid 100/1) by controlling the pH at 7 for 3 hours and subsequently at pH 4 for another 3 hours using HNO<sub>3</sub> 1M. The NEN 7345 test (tank leaching test) is a monolith-type leaching test that can be used to assess the leaching potential 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 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 is determined in the

leachates. The GANC (Generalized Acid Neutralization Capacity) test is, as 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<sup>24</sup>. From the data recorded, we obtain the acetic acid consumption for pH values ranging from approximately 12.5 to 5.5 and the corresponding GANC curves.

After the tests, samples were filtered through Whatman membrane filters (pore size 0.45 µm). When the procedures were completed, the metal contents in the solution were determined using Atomic Absorption Spectrometry.

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 landfill leachate regulations (European Landfill Directive, EULFD)<sup>25</sup> and the Dutch Building Materials Decree (DBMD)<sup>26</sup> were followed to establish quality criteria on metal concentrations limits in leachate from S/S solids after the usual curing time (28 days). The quality criteria applied to the metal leachate concentrations are shown in Table 6.

**Table 6.**  
Quality criteria

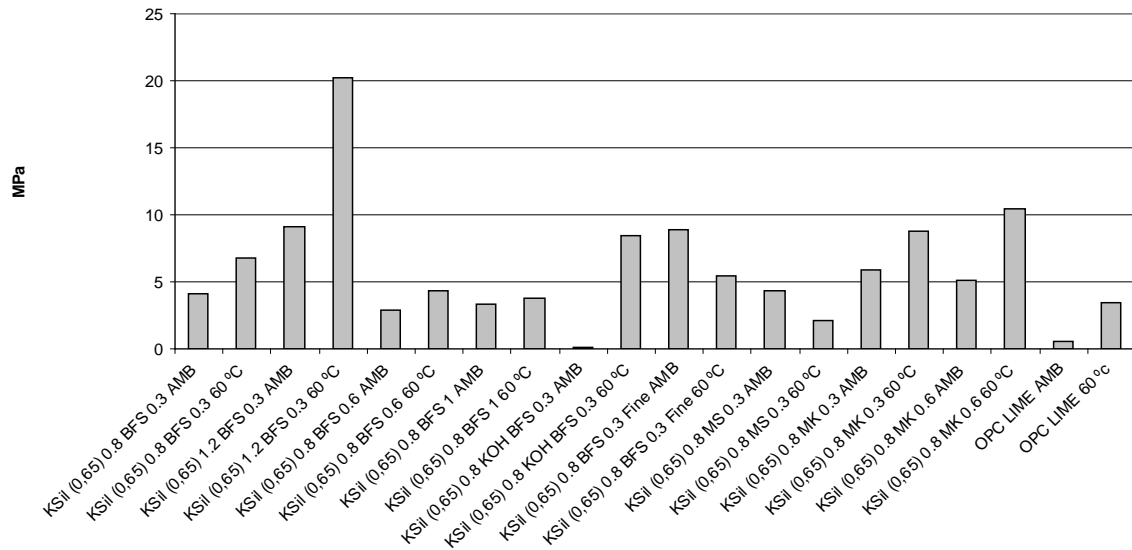
Parameter	Range/Value			
pH	2 – 12.5			
	Cd	Cr total	Pb	Zn
USEPA metal concentrations in TCLP leachate (mg·L <sup>-1</sup> )	0.5	5	5	300
Inert Waste (mg·kg <sup>-1</sup> ) EULFD	0.04	0.5	0.5	4
Non Hazardous Waste (mg·kg <sup>-1</sup> ) EULFD	1	10	10	50
Hazardous Waste (mg·kg <sup>-1</sup> ) EULFD	5	70	50	200
U1 (mg·m <sup>-2</sup> ) DBMD	1	150	100	200

### 3. Results and discussion

#### 3.1. Compressive strength (CS)

Compressive resistance of all samples at 28 days is shown in Figure 1.

**Figure 1.**  
Compressive strength at 28 days



In general, the resistance is higher when geopolymeric agents are used. In relation to the effect of the slag amount, it can be observed that the greater the blast furnace slag amount, the lower the compressive strength, possibly caused by some kind of saturation effect. Samples with a slag proportion of 0.3 (Slag 0.3) or less are enough to achieve good mechanical properties.

Regarding the type of slag, the best results have been obtained with the blast furnace slag (BFS) both at ambient temperature and 60 °C, possibly due to the lower proportions of  $Al_2O_3$ ,  $SiO_2$  and  $K_2O$  in the MS slag.

As can be seen, a positive relationship between the potassium silicate amount and the CS of the S/S solids may be observed: the higher the potassium silicate proportion, the higher the compressive strength. If KOH is used to increase the  $K_2O/SiO_2$  ratio, the compressive strength is slightly higher, but this increment is lower than expected. With regard to the CS it seems that the KSil proportion in the mix is more important than the previous ratio.

In relation to the effect of the metakaolin proportion, the resistance values are similar in all the cases studied. It should be necessary to test a wider range of MK amounts to check the influence of this parameter.

The fly ash grain size influences the mechanical properties of the S/S solids. As evidenced in the graph, the compressive strength varies with the ash grain size and also with the curing temperature. The fine fraction fly ash has a positive effect on the resistance at room temperature, however, at 60°C, its influence is the opposite.

## 3.2. Leaching tests

### 3.2.1. UNE-EN 12457-4 leaching test

Table 7 shows the pH and the Zn, Pb, Cr and Cd contents of the EN 12457-4 leachates at 28 days.

**Table 7.**

pH and metal concentrations in UNE-EN 12457-4 leachates at 28 days and EULFD limits

	pH	Metal concentration (mg·kg <sup>-1</sup> )			
		Zn	Pb	Cr	Cd
KSil (0,65) 0.8 BFS 0.3 AMB	11.43	0.9	<2	3.6	≤0.2
KSil (0,65) 0.8 BFS 0.3 60 °C	11.23	5.7	8	6.5	≤0.2
KSil (0,65) 1.2 BFS 0.3 AMB	11.78	2.8	6.4	14.4	≤0.2
KSil (0,65) 1.2 BFS 0.3 60 °C	11.86	5	4.8	5	≤0.2
KSil (0,65) 0.8 BFS 0.6 AMB	11.56	2.1	≤0.2	13.4	≤0.2
KSil (0,65) 0.8 BFS 0.6 60 °C	11.18	8.5	9.4	8.4	≤0.2
KSil (0,65) 0.8 BFS 1 AMB	11.84	1	<2	4	≤0.2
KSil (0,65) 0.8 BFS 1 60 °C	11.29	2.9	3.9	8.5	≤0.2
KSil (0,65) 0.8 KOH BFS 0.3 AMB	12.68	17.5	17	8	≤0.2
KSil (0,65)0.8 KOH BFS 0.3 60 °C	12.8	41.2	16.1	6.4	≤0.2
KSil (0,65) 0.8 BFS 0.3 Fine AMB	11.5	6.4	10.6	13.2	0.2
KSil (0,65) 0.8 BFS 0.3 Fine 60 °C	11.3	6.2	6.2	7.8	0.2
KSil (0,65) 0.8 MS 0.3 AMB	11.4	2.3	3.3	14.4	≤0.2
KSil (0,65) 0.8 MS 0.3 60 °C	11.13	5.6	8.2	12.4	0.2
KSil (0,65) 0.8 MK 0.3 AMB	10.9	1.4	2.1	15.2	≤0.2
KSil (0,65) 0.8 MK 0.3 60 °C	11	5.5	8	8.3	0.2
KSil (0,65) 0.8 MK 0.6 AMB	11.27	1.2	<2	14.7	≤0.2
KSil (0,65) 0.8 MK 0.6 60 °C	11.64	1	<2	13.8	≤0.2
OPC CaO AMB	12.21	12.6	3760	≤0.5	≤0.2
OPC CaO 60 °C	12.17	14.7	950	2	≤0.2
Inert Waste		4	0.5	0.5	0.04
Non Hazardous Waste		50	10	10	1
Hazardous Waste		200	50	70	5

Both for OPC and lime and for geopolymer systems, the pH values in EN 12457-4 leachates at 28 days were between 11 and 13. In general, the lowest leached amounts for the metals studied were obtained for EAF stabilized with geopolymeric activators. Large amounts of Pb (and in some instances Cr) are leached from samples prepared with OPC and lime, probably because of a high leachate pH (12.2-12.3). Therefore, the low Pb leachabilities found in geopolymer samples in many cases at the same (high) pHs evidence a higher degree of Pb immobilization in geopolymer matrices and must be emphasized.

Other results found are the following:

- S/S solids prepared using the fly ash fine fraction showed worse behaviour than those containing the bulk fly ash (as received).



- The addition of an excess of KOH to increase the  $K_2O/SiO_2$  ratio of the potassium silicate geopolymer samples lead to an increment of the pH and a decrease of the retention capacity of metals specially of Pb and Zn.
- The replacement of BFS by MS worsens the Cr leachability.

The lowest leached amounts were found for samples prepared with KSil 0,65 and BFS at room temperature. In general, lower S/S solid leachabilities are observed at room temperature instead of 60°C, except for Cr that almost always has lower concentrations in the 60°C-cured samples. Heating could have to do with a possible Cr(VI) reduction reaction to Cr(III) causing a decrease of the Cr leachability.

The EN-12457-4 results have been compared with the limits of the EULFD and the main conclusion is that it is difficult to obtain a S/S solid classified as inert waste on the basis of the Directive. Besides, the detection limit of the analytical method used for Cd is above the EULFD limit, so it is impossible in most cases to take a decision on the accomplishment of the inert waste limit for Cd. The hazardous waste limit for Pb was exceeded by samples prepared with OPC and lime. In general, and with some exceptions, the S/S solids based on geopolymeric agents meet the limits for non-hazardous waste landfills.

### 3.2.2. TCLP leaching test

Table 8 shows the pH and the concentrations of the metals studied in the TCLP leachates at 28 days.

**Table 8.**

pH and metal concentrations in TCLP leachates at 28 days and USEPA limits

	pH	Metal concentration (mg·L <sup>-1</sup> )			
		Zn	Pb	Cr	Cd
KSil (0,65) 0,8 BFS 0,3 AMB	6.87	318	4.16	<0.05	1.38
KSil (0,65) 0,8 BFS 0,3 60 °C	6.68	500	10.3	<0.05	1.49
KSil (0,65) 1,2 BFS 0,3 AMB	7.05	188	1.82	<0.05	0.95
KSil (0,65) 1,2 BFS 0,3 60 °C	6.1	404	14.1	<0.05	1.04
KSil (0,65) 0,8 BFS 0,6 AMB	6.86	373	4.11	<0.05	1.37
KSil (0,65) 0,8 BFS 0,6 60 °C	6.46	514	14.7	<0.05	1.6
KSil (0,65) 0,8 BFS 1 AMB	7.27	163	0.32	<0.05	0.27
KSil (0,65) 0,8 BFS 1 60 °C	7.07	371	3.99	<0.05	0.55
KSil (0,65) 0,8 KOH BFS 0,3 AMB	8.49	137	<0.2	<0.05	0.03
KSil (0,65) 0,8 KOH BFS 0,3 60 °C	5.84	105	0.99	<0.05	0.22
KSil (0,65) 0,8 BFS 0,3 Fine AMB	6.5	399	8.41	<0.05	1.08
KSil (0,65) 0,8 BFS 0,3 Fine 60 °C	6.4	516	9.1	<0.05	1.36
KSil (0,65) 0,8 MS 0,3 AMB	6.9	196	2.07	<0.05	1.23
KSil (0,65) 0,8 MS 0,3 60 °C	6.8	271	2.57	<0.05	1.4
KSil (0,65) 0,8 MK 0,3 AMB	2.94	1544	3.38	2.24	4.51
KSil (0,65) 0,8 MK 0,3 60 °C	3.07	1640	3.69	2	4.58

KSil (0,65) 0,8 MK 0,6 AMB	5.2	732	38.5	0.11	2.38
KSil (0,65) 0,8 MK 0,6 60 °C	5.14	708	21.5	0.18	2.22
OPC CaO AMB	10.97	0.05	0.9	0.31	<0.2
OPC CaO 60 °C	11.24	0.09	0.3	0.48	<0.2
USEPA limits		300	5	5	0.5

The leachates of all the samples prepared with OPC and lime were alkaline, with pH values around 11. However, samples prepared with geopolymeric activators showed a neutral or slightly acidic pH (slightly alkaline in a few cases).

The leaching of Zn, Cd and Pb in the S/S solids is clearly dependent on pH and on the acid neutralization capacity (ANC) of the solid matrix. The leachabilities of Zn, Cd and Pb can be significant in EAF dust, as large fractions of these contaminants are found as chlorides and oxides<sup>16</sup> that are easily soluble in a near neutral medium. For this reason, most of the results in the Table 7 may be interpreted in the light of the TCLP leachate pH.

The leachability of Zn, Pb and Cd varies enormously when the waste is stabilized with OPC and lime or when geopolymeric activators are used. In general, leached amounts in OPC systems are negligible in comparison with the amounts leached in geopolymeric systems, especially for Cd and Zn, possibly due to the leachate pH, alkaline in the first system and neutral in the latter. Cr leachate concentrations showed the opposite behaviour. Among the geopolymer samples, the best results are accomplished by KSil BFS 0.3 KOH and KSil BFS 1 (the sample with a high blast furnace slag amount), which have a higher pH than the rest of geopolymer samples.

Heating at 60°C during geopolymer preparation lowers the pH and worsens leachability practically in all the cases. Heating could provoke some alkalinity consuming reactions that negatively affect the metal immobilization.

Other TCLP results are as follows:

- S/S solids prepared using the fly ash fine fraction and the fly ash as received showed similar behaviour.
- The addition of an excess of KSil improved the TCLP leachability.
- The MS samples showed a better Pb leachability than BFS samples.
- MK geopolymers have very low ANC (the leachate pHs were the lowest). Thus, MK S/S solids showed the worst leaching behaviour of all the samples studied.

The concentration values were compared with the USEPA limits. In relation to this, the hydraulic binders showed better behaviour as they met the Cr, Zn, Pb and Cd limits; however, the geopolymeric agents better stabilized Cr than lime and OPC.

### 3.2.3. NEN 7341 leaching test. Availability test

The Dutch NEN 7341 leaching test (Determination of the availability for leaching from granular and monolithic construction materials and waste materials) aims to determine the maximum leaching of inorganic material from stony and earth-like construction material and waste. The purpose of the availability test is to indicate what quantity of a particular component may leach out from a material exposed to extreme conditions, in an aerobic environment, that is supposedly in the worst possible scenario. Therefore, this test is especially relevant to describe the degree of fixation of a metal in a matrix.

The leached fractions, that is, the percentage ratio between the measured leachate metal concentration and the total concentration of the same metal in EAF dust have been calculated and detailed in Table 9.

**Table 9.**

Leached fractions in availability test leachates (NEN 7341)

	Leached fraction (%)			
	Zn	Pb	Cr	Cd
KSil (0,65) 0.8 BFS 0.3 AMB	7.89	10.2	0.25	24.4
KSil (0,65) 0.8 BFS 0.3 60 °C	8.56	18.78	0.25	25
KSil (0,65) 1.2 BFS 0.3 AMB	6.57	1.02	0.25	17.6
KSil (0,65) 1.2 BFS 0.3 60 °C	6.1	2.33	0.25	16.6
KSil (0,65) 0.8 BFS 0.6 AMB	7.11	2.43	0.25	17.3
KSil (0,65) 0.8 BFS 0.6 60 °C	7.71	12.32	0.25	20.3
KSil (0,65) 0.8 BFS 1 AMB	5.59	2.89	0.31	1.9
KSil (0,65) 0.8 BFS 1 60 °C	5.16	3.32	0.3	1.8
KSil (0,65) 0.8 KOH BFS 0.3 AMB	0.47	0.98	0.59	5.8
KSil (0,65) 0.8 KOH BFS 0.3 60 °C	1.3	0.94	0.26	4.8
KSil (0,65) 0.8 BFS 0.3 Fine AMB	7.78	2.72	0.26	18.9
KSil (0,65) 0.8 BFS 0.3 Fine 60 °C	8.19	6.06	0.25	15.6
KSil (0,65) 0.8 MS 0.3 AMB	5.72	1.02	0.81	24.3
KSil (0,65) 0.8 MS 0.3 60 °C	7.4	6.86	0.25	29.8
KSil (0,65) 0.8 MK 0.3 AMB	7.11	0.91	0.74	28.4
KSil (0,65) 0.8 MK 0.3 60 °C	8.94	0.9	0.39	35.1
KSil (0,65) 0.8 MK 0.6 AMB	7.7	62.47	0.25	31.2
KSil (0,65) 0.8 MK 0.6 60 °C	6.83	40.54	0.24	25.3
OPC CaO AMB	9.79	100	0.25	43.7
OPC CaO 60 °C	15.46	100	0.25	64.1

Low extraction percentages were found for Zn and Cr, so these two metals were quite well immobilized in almost all mixtures. Zn, usually the main metal in EAF dust, is present in the batch studied at a very high level (34.29%). However, although its immobilization is not total, it ranges between 92-99.9 % using geopolymeric binders and between 84.5-90.2 % using conventional methods. Almost 100 % of Cr is immobilized using both geopolymeric and hydraulic binders. Conversely, Pb and Cd

showed the highest availabilities in all samples, although they were always lower with geopolymeric agents (immobilization percentages: 37.5-99.1 % and 64.9-98.2% respectively). Samples stabilized by means of hydraulic binders cured at ambient temperature and at 60°C gave a Pb leached fraction of 100%, that is, practically all the Pb is leached. For Cd, the immobilization percentages were between 35.9-56.3 %. We need to emphasize that the good behaviour observed by the OPC S/S solids in the TCLP test, better than that shown by the geopolymer S/S solids in the same test, is inverted in this more complete leaching test.

Regarding the use of blast furnace slag, an increase of the amount of BFS is beneficial for the immobilization, reducing the leachability of Zn, Cd and Pb (this effect being more important for Cd and Pb). The addition of an excess of soluble silicate (KSil) is beneficial too, with a similar effect to that observed in the case of BFS.

Other comments to the NEN 7341 results are:

- The amount of KOH added improves the retention of Cd, Zn and Pb
- The use of metakaolin instead of blast furnace slag negatively affects the immobilization of Cr
- The substitution of coarse fly ash by a finer grain size fly ash produces an increment of the retention of Pb and Cd

### 3.2.4. NEN 7345 leaching test

Table 10 shows the cumulative concentration at 64 days of tank leaching test leachates.

**Table 10.**

Results of the NEN 7345 tank leaching test in S/S solids at 64 days and U1 limits according to Dutch Building Materials Decree (DBMD)

	Accumulated concentration (mg·m <sup>-2</sup> )			
	Zn	Pb	Cr	Cd
KSil (0,65) 0.8 BFS 0.3 AMB	11.54	36.92	33	<3.69
KSil (0,65) 0.8 BFS 0.3 60 °C	18.27	39.94	55.87	<3.4
KSil (0,65) 1.2 BFS 0.3 AMB	70.11	100.24	139.38	<4.39
KSil (0,65) 0.8 BFS 0.6 AMB	20.35	47.33	118.55	<3.54
KSil (0,65) 0.8 BFS 1 AMB	5.98	34.09	44.66	<3.19
KSil (0,65) 0.8 KOH BFS 0.3 60 °C	49.5	82.54	72.87	<3.77
KSil (0,65) 0.8 BFS 0.3 Fine AMB	72.33	144	134	<4.62
KSil (0,65) 0.8 MS 0.3 AMB	41.75	74.93	141.06	<3.61
KSil (0,65) 0.8 MK 0.3 AMB	49.85	73.26	143	<3.47
KSil (0,65) 0.8 MK 0.3 60 °C	26.32	41.94	70.39	<3.42
KSil (0,65) 0.8 MK 0.6 AMB	18.59	49.28	125	<3.72
OPC CaO AMB	109	15503	8.98	<3.59
OPC CaO 60 °C	85.18	3970	17.35	<3.56

DBMD U <sub>1</sub>	200	100	150	1
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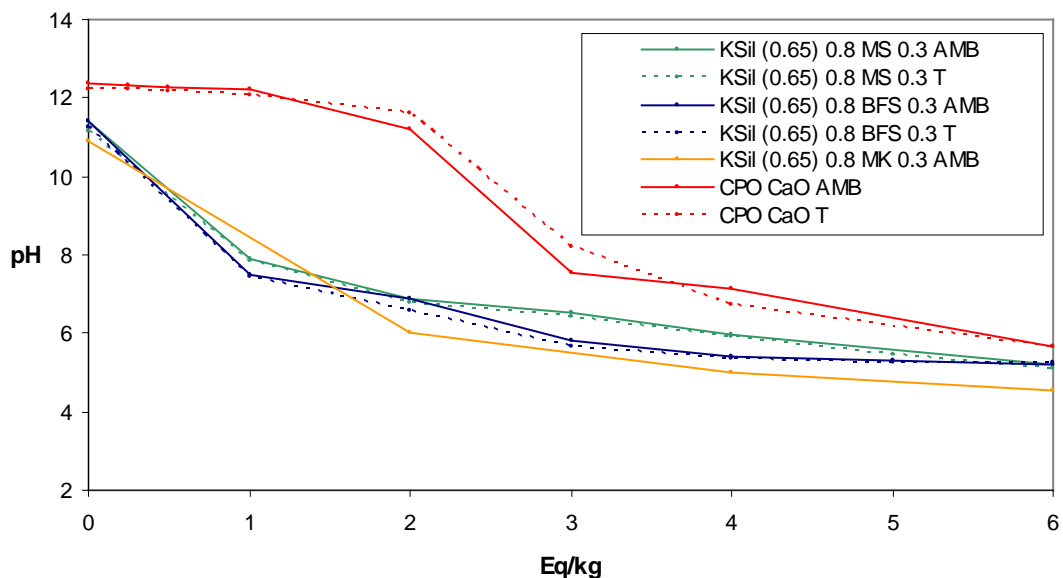
The metal releases in geopolymer based S/S solids were very low in general according to the NEN 7345 tank leaching test at 64 days. Thus, in all the cases, the measured Cd concentrations (and in some samples also Pb) in NEN 7345 leachates in geopolymer samples were under detection limits. Comparing geopolymer and OPC S/S solids, in general, the leaching benefit of geopolymeric techniques is clear, especially for Pb and Zn. On the contrary, Cr leachability is less when conventional OPC methods are used.

All the samples showed leachate concentrations for the four metals analysed under DBMD U<sub>1</sub> limits, except the two OPC samples, although the high Cd detection limits do not strictly allow the drawing of any conclusions on the accomplishment of the U<sub>1</sub> limit. However, the behaviour shown by this element in the EN 12457-4 leaching test in an alkaline medium (a medium also observed during the NEN 7345 test) allows us to conclude that it would probably not be a problem.

### 3.2.5. GANC leaching test

Figure 2 shows the GANC curves for samples prepared by means of conventional methods with OPC and lime compared with those obtained after using geopolymeric agents.

**Figure 2.**  
GANC Curves



As can be seen, all curves have the same downward profile, except samples prepared with OPC and lime since they showed a plateau between 0 and 2 eq/kg at pH around 12. Besides, in general, no differences exist between ambient and 60 °C-cured samples.

The figure could explain the differences observed between the TCLP and NEN 7341 leaching tests. The results can be deduced in many cases after seeing the curves because the TCLP test in these samples corresponds to the addition of 2 equiv/kg (the maximum amount added in the TCLP using fluid no. 2), which implies pH values in the leachate of the OPC S/S solids, ranging in the zone of minimum solubility of the metals under consideration (pH 11-12), or a value around pH 7 in the geopolymer S/S solids, and therefore outside the optimum pH zone for Cd, Pb and Zn<sup>14, 24</sup>.

Similarly, although we should take into account the influence of the L/S ratio used, the GANC curve can also predict the leaching in distilled water (EN 12457 test); we need only check the pH values for 0 equiv/kg and see that geopolymer and hydraulic binders present now similar pH values. In the zone of the curves corresponding to 2 eq/kg is when the difference between geopolymer and hydraulic binders is maximum. Notwithstanding, when 3 or more eq/kg are consumed (NEN 7341 test) the differences between the two types of binders is again reduced and we can observe a better behaviour in the geopolymer matrices when the availability test is applied, as we appreciated using the EN 12457-4 test.

#### **4. Conclusions**

Regarding the compressive strength developed by the S/S solids, the use of OPC and lime leads to poor resistances, as compared with geopolymeric mixtures, particularly those using potassium silicate and blast furnace slag that show the highest values among the geopolymeric S/S solids. In general, the resistances are improved when samples are cured at 60 °C, and also when KSil+KOH and when the finer FA fraction are used. On the contrary, using metallurgical slag and adding a great amount of slag is damaging for the compressive strength.

In relation to the environmental assessment carried out using different leaching tests, depending on the test different behaviour is observed. Although the leachate pH is one of the most important variables for the immobilization of metals, the EN 12457-4 and NEN 7345 results showed that similar pH values gave in some cases different leachabilities.

The TCLP test is the only test in which the OPC S/S systems manifested better behaviour than the geopolymer systems. This is due to a higher acid resistance in the conditions of the test, an action that is beneficial for the retention of Zn, Cd and Pb, although it is damaging for Cr. This phenomenon is less marked in the UNE-EN 12457-4 test, except for Cr.

In general, very low extraction percentages were found for Zn and Cr according to NEN 7341, showing that these two elements are practically immobilized both in OPC

and geopolymer S/S solids. On the contrary, Pb and Cd immobilized fractions were very variable, being always lower with geopolymeric activators.

Other general conclusions are:

- In general, many of the variables studied produce an opposite effect on the mechanical and leaching properties of the geopolymer S/S solids. Thus, the resistances are improved when samples are cured at 60°C or when the mix contains a lesser amount of slag. These parameters reduce the metal retention capacity in most cases. Therefore, although compressive strength is one of the most important parameters used to assess the geopolymerization reaction, we should not pay excessive attention to it in the S/S field, provided that a minimum resistance is guaranteed.
- The ash particle size separation and the use of segregated ash fractions is not justified from the point of view of the applications of ash-based geopolymers in the S/S field
- Other slag products different from the granulated blast furnace slag can be used as geopolymer agents in the applications of ash-based geopolymers in the S/S field

The main problem of the ash-based geopolymer S/S solids compared with the solids stabilized using OPC is due to their lower acid resistance, a consequence of their lower alkalinity. However, this lower alkalinity is possibly maintained during a long period of time, while OPC S/S solids undergo a great reduction of alkalinity with time, so it would be desirable to study the long term evolution of the metals stabilized in ash-based geopolymer matrices to have a better picture of the comparison between classical and geopolymer S/S methods.

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