Immobilization of a metallurgical waste using fly ash-based geopolymers

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Abstract

The stabilization/solidification (S/S) of electric arc furnace (EAF) dust containing hazardous metals such as Pb, Cd, Cr or Zn by means of geopolymerization technology is described in this paper. Firstly, different samples of geopolymeric material has been prepared using a class F coal fly ash and different reagents as sodium hydroxide, potassium hydroxide, sodium silicate and kaolinite. After that, mixtures of EAF waste and the geopolymeric material have been processed, for studying the potential of geopolymers as waste stabilizing agents. To this aim, the effects of curing conditions, composition and waste content have been tested. S/S solids are submitted to different physical and chemical tests to evaluate the results obtained and to ascertain the efficiency of the process. Compressive strength values in the range 12-25 MPa were easily obtained at 28 days. S/S solids have been submitted to different leaching tests. As conclusion of the leaching study we can say that the concentrations of the metals leached from S/S products were strongly pH dependent, showing that the final leachate pH was one of the most important variables for the immobilization of metals. Comparison of fly ash-based geopolymer systems with classical Portland cement stabilization methods has also been accomplished.

1. Introduction

Geopolymer technology is a relatively new technology based on an old concept that has recently received attention in various applications. These applications are grouped into two categories. Firstly, they could be used in the building sector as concrete replacements, and secondly as binder in waste stabilization/solidification (S/S) systems of heavy metal containing wastes. In immobilization of hazardous metals geopolymer systems function similarly to

cement binders in terms of encapsulation, however have improved chemical and physical properties, such as acid attack resistance, structural integrity, low permeability, high compressive strength and durability[1-2]. Low permeability is one of the properties that favors the use of these materials as immobilization systems for metals[3]. 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 charge balancing roles or remain physically trapped by surrounding network[4].

The term "geopolymer" was first used by Davidovits[1,3] to describe a family of mineral binders closely related to artificial zeolites. These structures consist of a polymeric Si–O–Al framework, similar to that found in zeolites. The main difference to zeolitic structures is observed through X-ray diffraction techniques, which reveal an amorphous microstructure. Geopolymers are sometimes also referred to as alkali-activated aluminosilicate binders.

The mechanism by which geopolymerization is thought to occur involves the dissolution, migration and polymerization of Al and Si precursor species as well as surface reaction on the remaining surface area of undissolved waste particles[2, 5]. The concentration of dissolved silicon can be artificially increased by addition of soluble silicates if dissolution does not proceed fast enough. The presence of cations (Na^+, K^+ and Ca^{2+}) is important due to charge balancing and catalytic properties. It has been proven that apart from pure materials such as kaolinite, other raw materials can be used to synthesize geopolymers such as coal fly ash (FA).

Most of the fly ash-based geopolymerization systems described in the literature mention a mixture of coal fly ash (generally an ASTM class F flyash) with NaOH or KOH and/or a soluble silicate (NaSil or KSil)[6-9], submitted to different curing processes at temperatures below 100ºC. Van Jaarsveld et al.[5,10] and Swanepoel and Strydom[11] also have tested different combinations of the same system often containing kaolinite or metakaolinite. According to Deventer[12] the reaction mechanisms involved in the geopolimerization of metakaolin and fly ash are believed to be similar.

Van Deventer et al. also have tested BFS as additive in a FA + Soluble silicate + MOH (M: Na or K) system[13]. Other authors use a calcium enriched system composed of a FA + Blast furnace slag (BFS) + alkaline activating solution[14] or FA + BFS + NaOH (10 M)[15].

Some S/S processes use different ash-based geopolymer systems to improve the immobilization of metals in the S/S solids. Two interesting articles[2, 5] describe the technology of geopolymerization[1] for the stabilization and solidification of waste materials. In one of the papers fly ash is used as a reactant in creating a geopolymeric matrix for the immobilization of process water containing large amounts of Cu and Pb.

Ash-based geopolymer systems have also been described in the literature for the S/S of simulated radioactive wastes. In most cases the stabilization of Cs and Sr was studied using metakaolin-based and also fly ash-containing

geopolymers. According to some authors most of the Cs was incorporated into the amorphous geopolymer matrix, whereas Sr was shared in crystalline and amorphous phases[16,17].

The stabilization of electric arc furnace (EAF) dust containing hazardous metals such as Pb, Cd, Cr and Zn by means of geopolymerization technology is described in this study. Compressive strength test and different leaching tests for determining the efficiency of heavy metal stabilization have been carried out. EAF dust has been chosen because is a waste with a high concentration of various hazardous components, which is considered in the S/S field as a waste difficult to stabilize.

2. Experimental

2.1. Materials

Low calcium fly ash (ASTM class F) from the combustion of high quality pulverized coal in the biggest coal power plant in the south of Spain, Los Barrios (550 MW) was used as the main silicoaluminate agent. Blast furnace slag (Slag) as a lime and silicon source, kaolinite and other local clay as a secondary silicoaluminate source were also used. Ordinary Portland Cement (OPC) was used for comparative purposes. The sodium silicate solution used was supplied by Merck. Product specifications are listed in Table 1.

2.2 Characterization of EAF

EAF is a dust that results from the collecting systems of particulate material in a carbon-steel electric arc furnace. The hazardous metals normally found in electric arc furnace dust are: Pb, Cd, and Cr. The main elements of the four S/S agents and EAF dust are detailed in Table 2. The heavy metal content of the EAF waste is shown in Table 3.

The speciation of the several metals contained in the EAFD, has been determined through micro-mineralogy analysis. The methods used are the scanning electronic microscopy (SEM) and the transmission electronic microscopy (TEM), both coupled with an EDS micro-analyzer. Practically, a preliminary identification of heavy metals bearing phases has been performed using a "K.E. Development" Back Scattered Electron Imaging device, then refined using a Hitachi S-2500 SEM, equipped with a "superquantum DELTA" EDS micro-analyzer. The SEM analysis have been performed on carbon vaporized, polished sections. TEM characterization has been carried out with a Philips SM20 apparatus, fitted with EDS micro-analyzer. The observations and microanalyses were made on powders spread from alcohol suspension on a carbon film supported by a copper grid.

The S/S waste objective was to obtain solids that reduce the overall environmental impact of waste disposal. To achieve this goal, the EPA criteria and the landfill leachate regulations (European Landfill Directive, EULFD[18])

were followed to establish quality criteria on metal concentrations limits in leachates from S/S solids after the usual curing time (28 days).

2.3 Preparation of geopolymers

A methodology for obtaining solids was established that includes the following steps:

1. Firstly, NaOH or KOH were dissolved in the sodium silicate solution. After that, fly ash was added to the solution. Then, kaolinite or clay was incorporated, depending of the samples. Enough water was added to the mixture to make the paste castable. Finally, the resulting mixture is agitated in a planetary mixer.

2. With the mass obtained, cylindrical plastic moulds are filled and compacted. During curing time, some samples obtained were placed in room temperature and the rest in a stove at 60 ºC.

3. After 7, 14 and 28 days, the samples were submitted to the compressive strength test.

The composition of the blends is shown in Table 4.

2.4. Preparation of S/S solids

Various samples maintaining constant the composition of fly ash and EAF dust and varying the rest of components were prepared. 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 ºC while others were stored at room temperature. On the other hand, hydraulic binders such as, ordinary Portland cement and lime have been used to prepare other samples using conventional S/S methods. During curing these samples were placed in a bag to get saturated humidity conditions, at room temperature (BAG samples). After 7 days and 28 days, the samples were crushed and sieved to 9 mm, and were extracted using leaching tests. Compositions of matrixes are shown in Table 5.

2.5. 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 7 and 28 days. A Suzpecar, mod. MEM-102 / 50 t, compressive strength testing apparatus was used.

2.6. Leaching tests

The stabilization/solidification efficacy was assessed from the chemical point of view according to three leaching tests: USEPA TCLP[19], UNE-EN 12457[20] and NEN 7341[21] tests. 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 other 3 hours using HNO_3 1M. 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 quality criteria applied to the metal leachate concentrations are shown in Table 6.

3. Results and discussion

3.1 Mineralogical status of the main heavy metals

The SEM and TEM analysis of AFDW are illustrated in Figure 1.

The analysis reveals that several elements are associated, typically Si, Mg, Al, Ca, Mn, Zn, Fe, Cr, Pb and Cl. The main identified minerals may be listed as follow:
- spinels. $(Zn, Fe)Fe_2O_4$;
- spinels $(Mg, Fe)Fe_2O_4$;
- zincite $(Zn, Fe, Mn, Mg)O$;
- wustite $(Fe, Zn, Mn, Mg,)O$;
- Pb-oxy-chlorides;
- (Pb, Zn)-glass.

Most of the spinels and oxides display several cationic substitutions, a situation very common for these compounds. Furthermore, considering the high stability of spinel-like structure, one may predict that the elements included in these compounds are immobilized at long term, independently of the AFWD S/S conditions.

On the contrary, the stability of zincite and Pb-oxy-chlorides *s.l.* are rather restricted depending of the pH. Practically, these minerals are highly soluble at high pH (~12) and low pH (~5)[22]. Considering that the pH of geopolymer systems are generally alkaline (around 12), these mineral phases are probably dissolved, partly or totally, during the S/S process. Thus, a potential immobilization of these metals through the S/S process requires either a physical encapsulation inside the pores of the final solid matrix or chemical trapping in the atomic framework of the geopolymer-like cement of this solid matrix.

3.2. Compressive strength

Ash-based geopolymers

The results of the compressive strength tests are shown in Table 7. As can be seen, the compressive strength increases with time, so that at 28 days, the strength reaches the maximum values in all cases. Regarding the effect of the curing temperature, we can see that the compressive strength of samples cured

at 60ºC were higher than those cured at room temperature (AMB samples). At room temperature the best results were obtained in samples prepared with clay, but they are not as good as those found in the case of the KOH 60ºC samples.

S/S geopolymers

As can be seen in Figure 2, the compressive strength increases along the time for most of the S/S solids (the largest increments were observed at room temperature). Exceptions were found in those samples cured at 60 ºC using kaolinite and metakaolinite. In these cases, curing for longer periods of time at elevated temperature appears to weaken the structure, suggesting that small amounts of structural water need to be retained in order to reduce cracking and maintain structural integrity. This reduction in compressive strength at longer curing times is also supported by other researchers[23,24].

The use of OPC and lime leads to poor resistances in the S/S solids. The greatest compressive strength was obtained by samples prepared with NaSil + KOH at 60 ºC, reaching 15 and 25 MPa at 7 and 28 days respectively. Besides, it can be observed that those samples prepared with KOH generally exhibited much higher compressive strength than those using NaOH. So, it seems that the content of potassium in the S/S mixtures plays an important role in strength development.

The use of kaolinite and metakaolinite produced similar results in compressive strength, about 5 MPa at 7 days at room temperature. However, it can be observed that samples prepared with kaolinite gave at 28 days (AMB) slightly higher compressive strength than metakaolinite, a result also corroborated by the literature[14].

In relation to the effect of curing temperature, generally, samples cured at 60 ºC showed greater resistances than those samples cured at room temperature. The only exception was observed in NaSil NaOH Kaolinite samples at 28 days.

3.3. Leaching tests

3.3.1. Analysis of UNE-EN 12457 leachates

Table 8 shows the value of the pH and the metal content (mg/kg) in the UNE-EN 12457 leachates of all samples 28 days. Samples cured at 60ºC always gave a lower pH in the EN 12457 leachate.

Both for OPC and lime and for geopolymer systems, the pH in EN 12457 leachates at 28 days was between 11 and 13. In general, the lowest leached amounts were obtained for many metals in EAF stabilized with geopolymeric activators. Large amounts of Zn, Pb and Cr are leached from samples prepared with OPC and lime (17, 300 and 35 mg/kg respectively). S/S solids prepared with NaSil KOH showed the best results for these metals. Cd concentrations in EN 12457 leachates were very low and in most cases below the detection limit of analytical technique.

S/S solids prepared with kaolinite showed slightly higher Zn and Pb leachabilities than metakaolinite samples. Therefore, although kaolinite S/S solids had relatively higher resistances than metakaolinite mixtures, their leaching behavior was worst.

NaSil slag samples gave a low pH when are compared with other geopolymer samples and maybe for this reason, their Cr concentrations are higher.

The EN-12457 leachate results have been compared with the limits of European Union Landfill Directive (EULFD) to Inert Waste, Non Hazardous Waste and Hazardous Waste. The main conclusions being that all the samples could be disposed in a hazardous waste landfill because none of metals were above the leachate limit. The hazardous waste limit for Pb was exceeded in samples prepared with OPC and lime. The non-hazardous limit for Pb was exceeded by some of the geopolymer samples, but the hazardous limit was not exceeded by any samples prepared with geopolymeric activators.

3.3.2. Analysis of TCLP leachates

Table 9 shows the value of the pH and the metal content (mg/L) in the leachate TCLP of all samples at 28 days:

The leachates of all the samples prepared with OPC and lime were alkaline, with pH around 11.5. However, samples prepared with geopolymeric activators showed a neutral pH between 5.1 and 6.7.

The leachability of Zn, Pb and Cd varies enormously when the waste is stabilized with OPC and lime or when geopolymeric activators are used: leached amounts in OPC systems are negligible in comparison with the amounts leached in geopolymeric systems, possibly due to the leachate pH, consequence of a higher alkalinity in OPC samples. Cr leachate concentrations showed the opposite behavior. The great differences found in leachate metal concentrations when the extraction fluid (acetic acid in TCLP and water in EN-12457) changes must be emphasized.

TCLP metal concentrations and USEPA limits have been compared. Thus, while OPC systems met the limits for Zn, Pb and Cd, geopolymeric systems worked better for Cr. It also can be observed that slag S/S solids (especially KSil Slag 60ºC) gave the best result of all the geopolymeric systems.

3.3.3. Results of the NEN 7341 test

The results of the NEN 7341 test for some stabilized/solidified solids are shown in Table 10. As can be seen the availability levels of the heavy metals analyzed in all mixtures were found to be lower than the total content in EAF dust. Therefore under the worse conditions only a fraction of the total content is released. The leached fractions, the percentage ratio between the measured leachate metal concentration and the total concentration of the same metal in EAF dust (Table 3), have been calculated.

Low extraction percentages were found for Zn and Cr, so these two metals were quite well immobilized in almost all mixtures. Zn, which is the main metal in EAF, is present in the EAF batch studied at a very high level (34.29%, a figure that seems more adequate for recycling Zn than for immobilizing it). However, although its immobilization is not total, it ranges between 90-97 %. Practically 100 % of the EAF Cr was immobilized using geopolymeric systems. On the contrary, Pb and Cd showed the highest availability in all samples. Pb and Cd immobilized fractions in geopolymer samples ranged from 30 to 87 % and from 60 to 82 %, respectively, the results being in general better with geopolymeric activators than with conventional hydraulic binders.

4. Conclusions

Regarding to compressive strength developed by the S/S solids, the use of OPC and lime leads to poor resistances, when comparison is made with the ash-based geopolymer S/S solids. The highest value with geopolymeric mixtures was obtained using sodium silicate plus KOH. Samples prepared with kaolinite gave slightly higher compressive strength than metakaolinite. In relation to the effect of curing temperature, generally, samples cured at 60 ºC showed larger resistance than those samples cured at room temperature.

It is difficult to find a relationship between metal leachability and compressive strength of the S/S solids. It rather seems that both physical and chemical properties of the final product are independent.

In relation to the environmental assessment carried out, depending on the leaching test used, the behavior of samples is different. The strongly alkaline pH obtained in the UNE-EN 12457 test showed that the best results were obtained in samples stabilized with geopolymeric materials, but classical hydraulic S/S solids better resist the acid conditions of the TCLP test.

In spite of this, under the worse conditions simulated by the NEN 7341 test only a fraction of the total metal content in EAF dust is released. Cr and Zn were well immobilized in all the mixtures. However, the leached fractions of Pb and Cd are relatively high. In general, the results obtained in the availability test were better in the case of the ash-based geopolymer S/S solids than in solids stabilized with Portland cement. Thus, although further research is still necessary to elucidate the stabilization mechanisms and to optimize mixtures, ash-based geopolymer methods seem to have great potential in the waste stabilization/solidification field.

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Table 1.
Specifications of sodium silicate solution

	SiO_2. %	K_2O. %	SiO_2/K_2O	Density 25 ºC. $g \cdot cm^{-3}$
NaSil	25.5-28.5	7.5-8.5	3.04-3.8	1.296-1.396

Table 2.
Main elements of geopolymer binders, Portland cement and Electric arc furnace dust

	Moisture 105 ºC	LOI 750 ºC	Main Elements (% w/w)						
			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	63.91	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
Slag	0.24	0.31	0.41	43.49	7.6	41.08	10.7	0.26	0.32
OPC	0.15		2.15	61.7	2.76	21.2	5.00	0.13	0.16
EAF	0.42	12.77	36.32	8.60	3.05	6.21	2.00	1.13	0.48

Table 3.
Total metal content in Electric Arc Furnace dust

	Metal content g/kg			
	Zn	Cd	Cr	Pb
EAF	342.9	0.29	2.108	2.29

Table 4. Composition of ash-based geopolymers

SAMPLE	FA (g)	NaSil (mL)	NaOH (g)	KOH (g)	Clay (g)	Kaolinite (g)	Water (mL)
NaSil NaOH	600	126	28				70
NaSil Clay	520	126	28		80		46
NaSil K	520	126	28			80	41
NaSil KOH	600	126		39.2			50

Table 5.
Composition of S/S matrixes

	Composition. Proportions by weight									
	EAF	FA	NaSil	KSil	NaOH	KOH	Kaolinite (K)	Metakaolinite (MK)	Slag	Water
NaSil NaOH	0.50	1.4	0.4		0.07					0.21
NaSil NaOH K	0.46	1.4	0.46		0.08		0.22			0.11
NaSil NaOH MK	0.46	1.4	0.46		0.08			0.22		0.13
NaSil KOH	0.50	1.4	0.4			0.09				0.19
NaSil Slag	0.5	1.4	0.8						0.3	0.53

Table 6.
S/S Quality criteria

Parameter	Range/Value			
pH	2 – 12.5			
	Cd	Cr total	Pb	Zn
Metal concentrations in TCLP leachates (mg/L)	0.5	5	5	300
Inert Waste (mg/kg) EULFD	0.04	0.5	0.5	4
Non Hazardous Waste (mg/kg) EULFD	1	10	10	50
Hazardous Waste (mg/kg) EULFD	5	70	50	200

Table 7.
Compressive strength of ash-based geopolymers (MPa)

	1 week	2 weeks	4 weeks
NaSil NaOH AMB	3.8	10.3	20.6
NaSil NaOH 60 ºC	19.9	12.0	28.9
NaSil Clay AMB	8.5	14.8	24.3
NaSil Clay 60 ºC	20.9	19.6	27.6
NaSil K AMB	5.4		21.2
NaSil K 60 ºC	25.0	19.0	27.6
NaSil KOH AMB	3.5	11.8	13.8
NaSil KOH NaSil 60 ºC	26.3	23.4	39.5

Table 8.
pH and metal concentration in UNE-EN 12457 leachates at 28 days and the EULFD limits

	pH	DIN (mg/kg)			
		Zn	Pb	Cr	Cd
OPC Lime AMB	12.4	17.0	300	35	0.3
OPC Lime BAG	12.3	23.0	390	27	0.3
NaSil NaOH AMB	13.2	12.2	4.53	2.28	<0.05
NaSil NaOH 60 ºC	12.6	38.7	20.35	1.41	<0.05
NaSil NaOH K AMB	12.4	30.6	11.92	2.25	<0.05
NaSil NaOH K 60 ºC	12.1	10.0	5.09	1.15	<0.05
NaSil NaOH MK AMB	12.3	15.0	11.00	3	0.3
NaSil NaOH MK 60 ºC	12.0	2.6	2.00	0.9	0.2
NaSil KOH AMB	13.1	3.7	0.50	3.69	<0.05
NaSil KOH 60 ºC	12.4	19.2	9.88	1.12	<0.05
NaSil Slag AMB	11.6	8.90	12.50	7.7	<0.2
NaSil Slag 60 ºC	11.3	10.50	6.50	10.6	<0.2
Inert Waste		4	0.5	0.5	0.04
Non Hazardous Waste		50	10	10	1
Hazardous Waste		200	50	70	5

AMB: Cured at ambient conditions (room temperature)

Table 9.
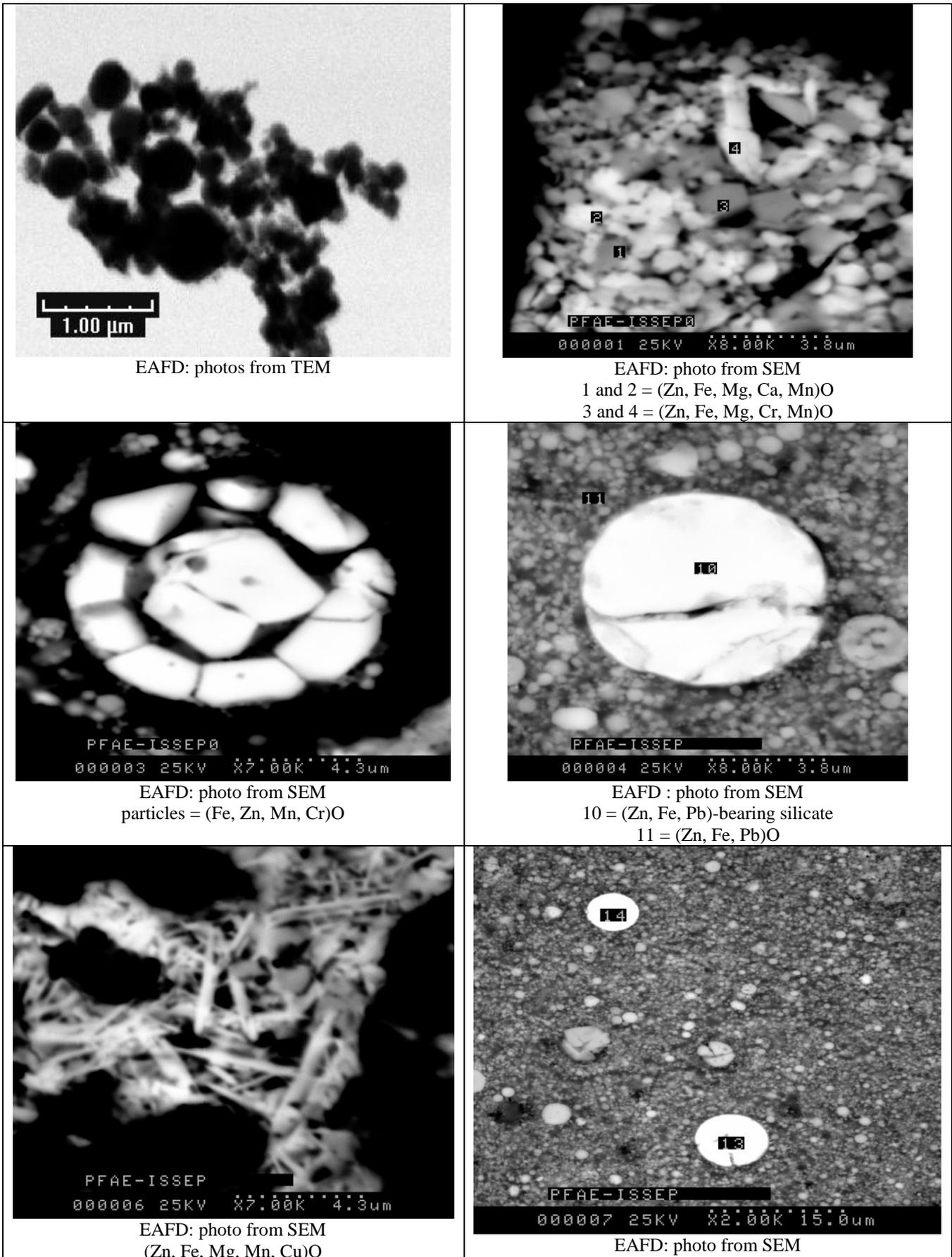pH and metal concentration in TCLP leachates at 28 days and the USEPA limits

	pH	TCLP (mg/L)			
		Zn	Pb	Cr	Cd
OPC Lime AMB	11.2	0.1	0.6	2.7	0.03
OPC Lime BAG	11.8	0.3	8.8	5.1	0.04
NaSil NaOH AMB	5.70	1143	31.67	≤0.005	3.90
NaSil NaOH 60 ºC	5.70	1296	21.20	≤0.005	4.52
NaSil NaOH K AMB	5.53	701	19.76	≤0.005	2.16
NaSil NaOH K 60 ºC	5.10	842	24.60	≤0.005	1.90
NaSil NaOH MK AMB	5.43	672	16.7	0.05	1.9
NaSil NaOH MK 60 ºC	5.67	726	9.9	0.05	2.1
NaSil KOH AMB	5.84	862	21.98	≤0.005	2.46
NaSil KOH 60 ºC	5.48	508	17.21	≤0.005	2.45
NaSil Slag AMB	6.68	528	10.7	<0.05	2.6
NaSil Slag 60 ºC	6.55	590	7.3	<0.05	1.2
USEPA Limits		200	5	5	0.5

Table 10.
Leached fractions in availability test leachates

	Leached fraction (%)			
	Zn	Pb	Cr	Cd
OPC LIME AMB	5.2	12.3	2.5	39.7
OPC LIME BAG	7.0	99.9	2.6	52.4
NaSil NaOH AMB	9.2	45.9	0.3	37.0
NaSil KOH AMB	10.1	69.3	0.3	40.1
NaSil KOH 60 ºC	9.7	13.1	0.3	36.4
NaSil NaOH K AMB	8.3	45.9	0.3	33.1
NaSil NaOH MK AMB	5.5	24.2	0.3	18.0

Figure 1. TEM and SEM analysis of EAF dust

EAFD: photos from TEM

EAFD: photo from SEM
1 and 2 = (Zn, Fe, Mg, Ca, Mn)O
3 and 4 = (Zn, Fe, Mg, Cr, Mn)O

EAFD: photo from SEM
particles = (Fe, Zn, Mn, Cr)O

EAFD : photo from SEM
10 = (Zn, Fe, Pb)-bearing silicate
11 = (Zn, Fe, Pb)O

EAFD: photo from SEM
(Zn, Fe, Mg, Mn, Cu)O

EAFD: photo from SEM

13 and 14 = (Pb, Zn)-glass
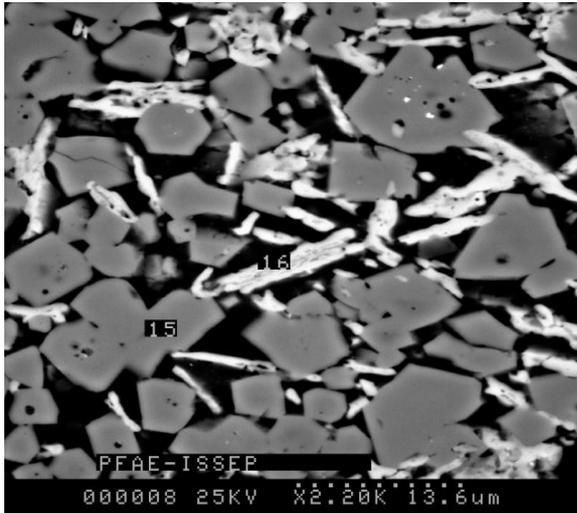
EAFD: photo from SEM
15 = (Fe, Zn, Mn)O
16 = franklinite

Figure2. Compressive strength of ash-based geopolymer S/S solids after 7 and 28 days (MPa)