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Geopolymerisation of fly ashes with waste aluminium anodising etching solutions

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Abstract

Combined management of coal combustion fly ash and waste aluminium anodising etching solutions using geopolymerisation presents economic and environmental benefits. The possibility of using waste aluminium anodising etching solution (AES) as activator to produce fly ash geopolymers in place of the commonly used silicate solutions was explored in this study. Geopolymerisation capacities of five European fly ashes with AES and the leaching of elements from their corresponding geopolymers were studied. Conventional commercial potassium silicate activator-based geopolymers were used as a reference. The geopolymers produced were subjected to physical, mechanical and leaching tests. The leaching of elements was tested on 28 days cured and crushed geopolymers using NEN 12457-4, NEN 7375, SPLP and TCLP leaching tests. After 28 days ambient curing, the geopolymers based on the etching solution activator showed compressive strength values between 51 and 84 MPa, whereas the commercial potassium silicate based geopolymers gave compressive strength values between 89 and 115 MPa. Based on the regulatory limits currently associated with the used leaching tests, all except one of the produced geopolymers (with above threshold leaching of As and Se) passed the recommended limits. The AES-geopolymer geopolymers demonstrated excellent compressive strength, although less than geopolymers made from commercial activators. Additionally, they

demonstrated low element leaching potentials and therefore can be suitable for use in construction works.

Key words: Recycling, Geopolymer, Waste aluminium etching solution, Fly ash, Leaching

1. Introduction

Electricity generation by pulverised coal facilities produces worldwide huge quantities of coal combustion fly ashes (PFA: Pulverised Fuel Ash). These ashes constitute one of the most important industrial residues, as illustrated by the annual production of some countries (Basu et al., 2009): India (112 Mt), China (100 Mt), USA (75 Mt), Germany (40 Mt) and the UK (15 Mt). The global annual production of PFA is estimated at 750 Mt (Izquierdo et al., 2012). These volumes of PFA, together with its content of potentially hazardous leachable trace elements make it practically impossible to be disposed of in landfills. Almost all naturally occurring elements are present in PFA, and among those As, Cd, Cr, Hg, Mo, Se, Sb and V have been detected as the most hazardous (Izquierdo et al., 2012; Moreno et al., 2005; Bingol and Akcay, 2005; Vassilev and Vassileva, 2007; Pandey et al., 2011). As a consequence, disposal of PFA is not sustainable, and environmentally sound management of these residues is required.

Aluminium is the second most used metal apart from iron (Chen et al., 2010). Moors (2007) reported global annual production of primary aluminium in 2003 to be 21.9 Mt. The demand for aluminium is predicted to double by 2050 (Milford et al., 2011). Some aluminium products, mainly those used for building, transportation, manufacturing machines and household utensils, are subjected to anodisation to make them decorative and protected from corrosion (Alvarez-Ayuso, 2009). During anodisation, a protective anodic oxide layer is formed on the aluminium products in an electrochemical process with sulphuric acid as the electrolyte. Prior to anodisation, the surface of the aluminium material is thoroughly cleaned by etching in a sodium hydroxide (NaOH) solution. During etching some aluminium is dissolved as sodium aluminate according to:

$$2\ Al\ (s) + 2\ NaOH\ (aq) + 2\ H_2O \rightarrow 2\ NaAlO_2\ (Sodium\ aluminate) + 3\ H_2$$

The aluminium items are rinsed and the rinsing solution together with the spent alkaline etching solutions form a waste stream with up to 150 $g.kg^{-1}$ of Al (as Na-aluminate) and up to 50 $g.kg^{-1}$ of free NaOH. Because alloy metals and trace elements (Fe, Cu, Zn, As, Mo, Sb, Se and V) are dissolved as well, these effluents require proper treatment before disposal (Alvarez-

Ayuso, 2009). The aluminium waste etching solutions (AES) are sometimes used for dephosphatising sewage water, but mostly treated by neutralisation with acid wastes from the same anodising process to form anodising mud (aluminium hydroxide and calcium sulfate), which is sent to landfill (Alvarez-Ayuso, 2009).

A sustainable method of waste management that has gained worldwide acceptance is conversion of waste into resources. Alkali activation of PFA is used to produce alumino-silicate binders, known as geopolymers (Xua and Van Deventer, 2000; Andini et al., 2008; Nugteren et al., 2009; Rickard et al., 2011). Geopolymers may replace cement and concrete in construction Xua and Van Deventer, 2000; Davidovits, 1994; Van Deventer et al., 2012) and can immobilise hazardous materials (Ogundiran et al., 2013; Davidovits, 1994; Van Jaarsveld et al., 1997). Sodium and potassium hydroxide, as well as sodium and potassium silicate solutions have been used as activators for the synthesis of geopolymers. However, so far aluminate solutions have only been considered in a fundamental study (Phair and van Deventer, 2002) and the use of waste solutions as activators has been applied for just one particular case in combination with heavy metal immobilisation by the present authors (Ogundiran et al., 2013). Therefore, the use of waste solutions as activator for geopolymerisation in a broader sense for different fly ashes including comparison with conventional activators was investigated in this study.

In this investigation five coal combustion fly ashes (FA) of different origin, fuel feedstock and combustion conditions were used as the main precursor and a waste aluminate solution (AES) serves as the activator solution. By utilising these geopolymers in the construction sector, savings will be made both in the cost of disposal of these materials as wastes, as well as avoiding the manufacturing of the high CO_2 binder Portland cement.

2. Materials and methods

2.1. Materials for synthesis

Five coal combustion fly ashes were collected from coal-fired power plants in the Netherlands (TUD-1 and TUD-5), Spain (CSIC-1 and AICIA-2) and Belgium (ISEEP-1). Table 1 provides the basic information on origin, feedstock and combustion conditions for the selected ashes. Note that the first four ashes are PFA type, whereas the last one is a fluidised bed ash, therefore, FA will subsequently be referred to rather than PFA. Further information on TUD-5, CSIC-1 and AICIA-2 is also given in Moreno et al. (2005).

Table 1

Origin, feedstock and combustion conditions for the selected fly ashes.

Fly ash sample identification	Origin of samples	Fuel blends	Combustion conditions
TUD-1	The Netherlands Amer Power Plant	Coal + 14% biomass (11% wood chips and 3% palm stones)	Pulverised fuel combustion (T = 1500 ^{o}C)
TUD-5	The Netherlands EPZ Power Plant	Coal (giving acid fly ash)	Pulverised fuel combustion (T = 1500 °C)
CSIC-1	Spain Narcea Power Plant	Coal	Pulverised fuel combustion (T = > 1500 ^{o}C)
AICIA-2	Spain Los Barrios Power Plant	Coal	Pulverised fuel combustion (T = 1250 ^{o}C).
ISEEP-1	Belgium	55 % Coal tailing + 45% biomass (wood pellets)	Fluidised bed (T = 850 ^{o}C)

Blast furnace slag (BFS) was used as a silicate source. The chemical compositions of FA and BFS are given in Table 2. Except ISEEP-1, the fly ashes can be classified as class F according to ASTM C618.

Table 2

Chemical composition (wt. %) of European FAs and BFS (Source: GEOASH Report, 2007; n.a.

= not analysed).

Composition	TUD-1	TUD-5	CSIC-1	ISEEP-1	AICIA-2	BFS
SiO_2	48.9	51.9	54.1	51.9	58.1	37.2
Al_2O_3	27.8	28.8	23.3	23.0	22.7	11.8
Fe_2O_3	7.90	8.30	8.50	4.70	6.10	n.a.
TiO_2	2.44	1.50	0.90	0.90	1.10	0.58
MnO	0.04	0.03	0.04	0.10	0.10	n.a.
CaO	6.03	1.70	3.50	3.50	3.50	42.0
MgO	1.77	1.00	2.00	1.70	1.80	7.48
K_2O	0.84	2.30	3.20	3.30	1.60	n.a.
Na_2O	0.58	0.50	0.90	0.50	0.60	0.24
P_2O_5	1.11	0.20	0.80	0.30	0.50	n.a.
LOI	2.39	3.10	2.00	9.10	3.50	n.a.
SiO_2/Al_2O_3	1.76	1.80	2.30	2.30	2.60	3.15
$SiO_2+Al_2O_3+ Fe_2O_3$	84.6	89.0	85.9	79.6	86.9	49.0

LOI= Loss on ignition

The KS activator had a K_2O/SiO_2 molar ratio of 0.8, which was obtained by adding KOH to a commercial grade KS solution (PQ Holland). The AES was collected from an aluminium anodising company in the Netherlands. The solution sampled contained 85 $g.L^{-1}$ Al as sodium aluminate and 30 $g.L^{-1}$ free NaOH. The measured pH of this solution was 14.0. The solution contained 1.3 wt% of very fine dispersed particles of precipitated sodium aluminate containing metal sulfides (mainly Zn and Cu). Inductively coupled plasma-optical emission spectrophotometry (ICP-OES) analysis of the filtered AES showed the presence of trace elements such as As, Cu, Fe, Mo, Sb, Se, V and Zn (Ogundiran et al., 2013).

2.2. Synthesis of geopolymers

Geopolymers synthesis and measurements were performed as reported previously (Ogundiran et al., 2013). The AES- and KS-based geopolymers were produced by adding fly ash to mixtures of 15 g BFS / 3 g NaOH / 17 g AES and 15 g BFS / 10 g KS / 10 g H_2O respectively. To these mixtures, amounts of fly ashes were adjusted to make workable pastes. In this way the ratios of BFS and liquid components were kept constant, whereas the amounts of fly ashes varied depending on the fly ash properties. The quantities were recalculated on a wt % basis, as shown in Table 3.

Table 3

Mix compositions used to produce geopolymers (wt.%). FA: coal fly ash; BFS: blast furnace slag; AES: aluminium etching solution; KS: potassium silicate solution with $K_2O/SiO_2 = 0.8$.

European FAs	AES Solution				KS solution			
	FA	BFS	10 M NaOH	AES	FA	BFS	H_2O	Ksilicate
TUD-1	46	23	5	26	46	23	15	15
TUD-5	50	21	4	24	53	20	13	13
CSIC-1	59	18	4	20	64	16	10	10
ISEEP-1	34	28	6	32	39	26	18	18
AICIA-2	46	23	5	26	50	25	13	13

The solid starting materials were dry mixed in a mixer for 3 minutes to homogenise the samples. The liquid components were mixed separately and then added to the solid mixture in the mixer and again mixed for 5 minutes for AES-based geopolymer pastes, and 1 minute for KS-based geopolymer pastes. This difference in mixing time was necessary because KS-geopolymers set faster. The thixotropic pastes were cast into cylinders of 29 mm diameter to a height of about 30 mm and vibrated on a sieve shaker for 5 minutes for compaction and reduction of entrapped air. Ten cylinder moulds were filled for each experiment. The curing was performed at room temperature in closed moulds to prevent evaporation and shrinkage of the

geopolymers. After one week, the geopolymer samples were de-moulded and kept in sealed plastic bags.

Setting time was measured as the time elapsed between the moulding and the onset of hardening. Compressive strength was measured after 7, 14 and 28 days curing at room temperature. Dry densities of geopolymer binders were measured after 28 days according to NEN 1170-6.

For each curing time, compressive strength tests were conducted on two moulds using the compression test machine MATEST C 98 version 10.0.

2.3. Leaching tests

Two European (NEN 12457-4 Dutch Compliance Test and NEN 7345 Dutch Tank Leaching Test and two United States environmental standard leaching tests {Toxicity Characteristics Leaching Procedure (EPA Method 1311, 1990) and Synthetic Precipitation Leaching Procedure (EPA Method 1312, 1994) were employed to determine the leaching behaviour of inorganic elements from the starting solid materials and from the geopolymer products in order to assess their potential environmental impacts. The details of the procedures as applied in this study were presented earlier (Ogundiran et al., 2013). The elemental concentrations were determined using Inductively Coupled Plasma-Optical Emission Spectroscopy (Spectro Arcos ICP-OES). The linearity, repeatability and reproducibility of the ICP-OES were tested using duplicate, standard solutions and blank analyses. Accuracy and precision of the analyses were good for all the elements. In all the duplicate samples the elemental concentrations had relative percent difference (RPD) less than 10% which fall within EPA acceptable limit of 20% RPD (USEPA, 2002).

3. Results and discussion

3.1. Setting time of the geopolymers

The results of final setting times for both AES- and the reference KS-geopolymers are presented in Fig. 1 (a). The replacement of KS by AES as activator retarded the geopolymerisation reaction. The KS-geopolymers hardened in 30 minutes or less, whereas the AES-geopolymers did set in the order of 15 to 20 hours. With both activators, CSIC-1 set faster than the others while TUD-1 took longer times to harden. The delayed setting time and

consequently the low early strength gain of AES-geopolymers may be advantageous for construction materials such as concretes which are not put to usage immediately after they are produced. It will give more time for processing of other geopolymer products on the building site.

3.2. Density of the geopolymers

The dry densities of the synthesised geopolymer binders for the different FAs and the activators are reported in Fig. 1 (b). The densities of AES-geopolymers which ranged from 1908-2071 kg.m^{-3} were comparable with the densities of KS-geopolymers (1876– 2139 kg.m^{-3}). The highest density was achieved with CSIC-1 for both activators. The values are within those

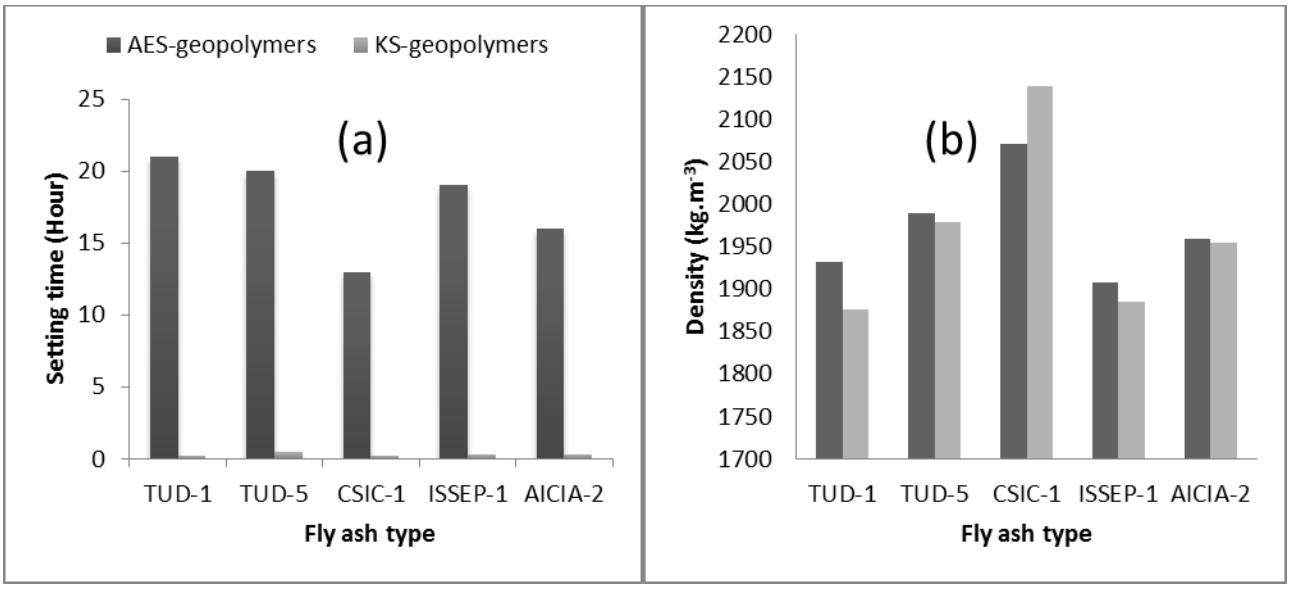

Fig. 1. Effects of fly ash type on Setting time (a) and density (b) of AES- and KS-geopolymer pastes.

reported in literature (Andini et al., 2008; Sofi et al., 2007). Nevertheless only the CSIC-1 geopolymer met the condition for normal OPC-based materials, for which the apparent densities fall within the range of 2000-2600 kg.m^{-3}. High density binders will have low water absorption capacity upon application as construction materials, a characteristic property of high density concrete (Kearsley and Wainwright, 2001).

3.3. Compressive strength

All the five fly ashes showed geopolymerisation with both activators, demonstrating continuous strength gain, although at different rates. The average values of the compressive strengths development with time for both AES- and KS-geopolymers for the different fly ashes are presented in Fig. 2. At 28 days AES-geopolymers indicated compressive strength values which varied from 51.3 to 84.3 MPa and those of KS-geopolymers ranged between 89.5 and 119 MPa. The AES-geopolymer binders demonstrated excellent compressive strength, although less than geopolymers made from commercial activators. However, they demonstrated low element leaching potentials which is an added advantage. It can be observed from Fig. 2 that samples TUD-1, TUD-5 and CSIC-1 exhibited higher compressive strengths than geopolymers AICIA-2 and ISSEP-1 with AES activator whereas geopolymers CSIC-1, AICIA-2 and TUD-1 exhibited higher compressive strengths than geopolymers TUD-5 and ISEEP-1 with KS activator at 28 days curing. Factors that may account for the differences in strength are discussed below and include differences in activator to fly ash ratio, the nature of the activators and chemical composition of the fly ashes.

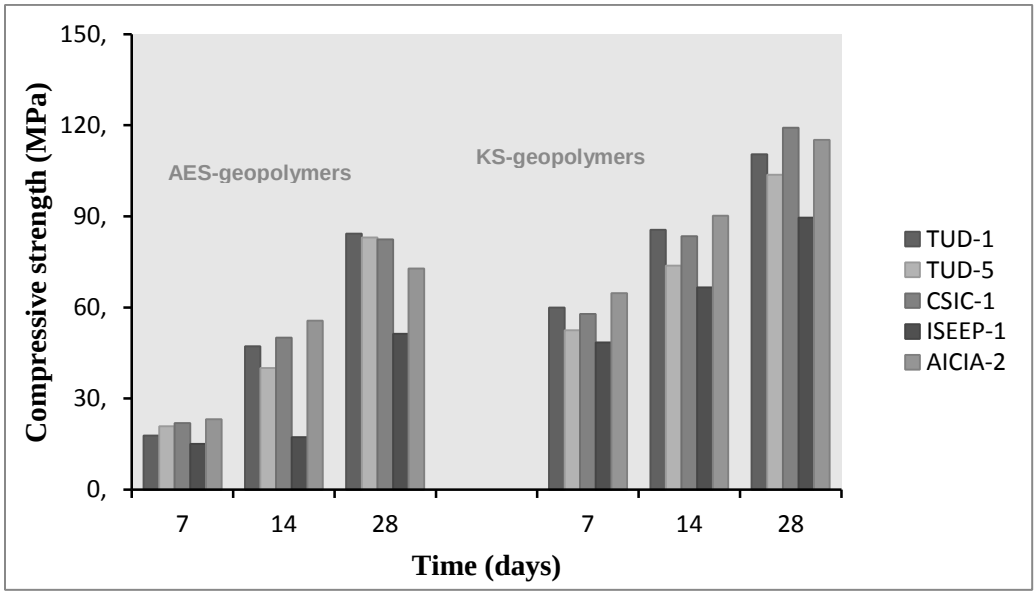

Fig. 2. Compressive strength of AES- and KS-geopolymers at 7, 14 and 28 days curing.

3.3.1. Activator to fly ash ratio

The difference in the compressive strength between AES- and KS-geopolymers may be associated with the difference in the amount of fly ash utilised to achieve a workable paste. As

shown in Table 3, KS-silicate-geopolymers allowed higher fly ash contents. The amount of fly ash required to form a workable paste follows the order CSIC-1> TUD-5> AICIA-2> TUD-1> ISEEP-1, and obviously this depends on the nature of the fly ash. Both trends suggest that the more the fly ash that can be accommodated in the mixture, the stronger the geopolymers will be.

3.3.2. The nature of the activators

It is observed that the strength of the geopolymers depends on the nature of the activators. The KS-geopolymers were stronger than the AES-geopolymers from the same fly ashes. Addition of KS to fly ash increases the importance of the stronger Si-O-Si and Si-O-Al bonds in geopolymers (Duxson et al., 2005). Conversely, addition of AES to fly ash possibly enhances the amount of Al-O-Al bonds which are weaker, leading to lower compressive strength. Furthermore, for both activators, the degree of strength gained varied with fly ash type. In both cases the lowest compressive strength was observed with ISEEP-1 geopolymers whereas the highest strength was observed with TUD-1 and CSIC-1 for AES- and KS-geopolymers respectively.

3.3.3. Relation between compressive strength and chemical composition of the fly ashes

Looking at the relationship between the mechanical strength of the geopolymers and the chemical composition of the corresponding fly ashes by combining the data from Table 2 and Fig. 2, there seems to be no direct and obvious correlation between compressive strength and chemical composition of the fly ashes. A statistical analysis, although with a low number of samples, shows no other significant correlation than a positive one for Fe_2O_3 and a negative one for LOI with compressive strength.

3.3.4. Compressive strength development with time

All geopolymers show an increase in strength with time for both activators, which is an indication of continuous chemical reactions strengthening the geopolymers. The compressive strength of the reference KS-geopolymers were higher at the same curing time than those of the AES-geopolymers. Early strength gain during the first 7 days for AES-geopolymers is much lower than for KS-geopolymers (Fig. 2). However, for longer curing times, AES-geopolymers showed a relative acceleration in strength gain compared to the KS-geopolymers.

For ISEEP-1-geopolymers, it took even more than 14 days before real strength development started.

The lowest compressive strength values of both AES- and KS-geopolymers are higher than the compressive strength values of Type IV (17 MPa) and V (21 MPa) Portland cement at 28 days (ASTM C150, 2007). Based on this, fly ashes activated with waste aluminium anodising etching solution can be applied as binder in construction and engineering works that require high mechanical strength.

3.4. Leaching status of AES- and KS-geopolymers

Assessment of the environmental quality of the geopolymers produced is required to ascertain their potential uses. For application in the construction industry, leaching of certain elements under certain leaching conditions that mimic environmental conditions, is regulated by leaching limit values (LLVs). For American leaching tests some metals were not considered of much environmental interest while they are very significant in European environmental leaching standards.

3.4.1. NEN 12457-4 leaching test

The results of the elements leached using the compliance test NEN 12457-4 and the EU Directive leaching limit values (LLV) for non-hazardous granular waste are presented in Table 4. The elements specified by the EU Landfill Directive include As, Ba, Cd, Cu, Hg, Cr, Mo, Ni, Pb, Sb, Se, Zn and Cl. The levels of all elements specified by the EU Landfill Directive were low in the geopolymers except for As in KS-TUD-5 geopolymer and Se in AES and KS-TUD-5 geopolymers. The concentrations of elements leached from the geopolymers depend on the FA type, amount of ash in the mixture and the activators used for the synthesis. For instance, geopolymers made with TUD-5 and KS activator had the highest leached As (3.5 $mg.kg^{-1}$) and Se (3.6 $mg.kg^{-1}$) concentrations which are higher than the threshold limit values. In general, the amounts leached from the raw materials for KS-geopolymers were higher than for AES-geopolymers, which matches with the higher amount of FAs used. Generally, re-mobilisation was higher with KS-based geopolymers.

Table 4

Leached amounts ($mg.kg^{-1}$) of selected elements from AES- and KS-geopolymers, according to the NEN 12457-4 leaching procedure. The maximum limits for non-hazardous waste according to the EU Landfill Directive (EU LLV= European Union leaching limit value) are given as indicative values.

Parameters measured	AES-Geopolymers					KS-Geopolymers					EU LLVs
	TUD-1	TUD-5	CSIC-1	ISEEP-1	AICIA-2	TUD-1	TUD-5	CSIC-1	ISEEP-1	AICIA-2	
As	0.50	1.20	0.40	<0.0022	<0.0022	0.29	3.50	0.80	<0.0022	<0.0022	2.00
Ba	0.10	<0.0005	<0.0005	0.10	<0.0005	0.22	0.10	0.10	0.10	0.10	100
Cd	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	1.00
Cl	42.0	32.4	26.2	130	20.5	57	36.4	52.6	267.4	39.8	15000
Cr	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.07	<0.0001	<0.0001	<0.0001	<0.0001	10.0
Cu	<0.0009	<0.0009	<0.0009	<0.0009	<0.0009	<0.0009	<0.0009	<0.0009	<0.0009	<0.0009	50.0
Hg	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	0.2
Mo	0.67	1.40	0.80	0.40	0.50	1.34	2.90	1.20	0.50	0.70	10.0
Ni	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	10.0

Pb	<0.003	<0.0031	<0.0031	<0.0031	<0.0031	<0.003	<0.003	<0.003	<0.003	<0.003	10.0
Sb	0.09	<0.0022	<0.0022	<0.0022	<0.0022	0.07	<0.0022	<0.0022	<0.0022	<0.0022	0.7
Se	0.21	1.30	0.30	0.30	0.30	0.38	3.60	0.5	0.3	0.40	0.5
Zn	0.03	<0.0002	<0.0002	<0.0002	<0.0002	0.03	<0.0002	<0.0002	<0.0002	<0.0002	50

274

275

Barium (Ba), Cr, Sb and Cl^- were immobilised in all the geopolymers but immobilisation was higher with AES-geopolymers compare to the concentrations in the unstabilised raw materials (data not shown). Molybdenum (Mo) was slightly retained in all AES-geopolymers except CSIC-1 where geopolymerisation appeared to have no influence on its leaching. The leachability of Mo from KS-geopolymers did not considerably differ from the leachability from the unreacted raw materials, but all values were well below the threshold limit values.

Generally, utilisation of AES as activator yielded the lowest release and highest retention of elements. Except for TUD-5, the concentrations of leached As, Ba, Cd, Cu, Hg, Cl, Cr, Mo, Ni, Pb, Sb and Zn from the geopolymers are below the EU Directive LLVs for non-hazardous granular waste. This implies that the geopolymers (except TUD-5) synthesised are classified as non-hazardous and can be applied as construction materials.

3.4.2. Toxicity Characteristics Leaching Procedure (TCLP)

The amounts of elements in the TCLP extracts of the geopolymers are presented in Table 5. Silver (Ag), Cd, Cr, Hg and Pb were found below their detection limits and consequently below the TCLP regulatory levels of 5 $mg.L^{-1}$ for Ag, Cr, Pb and 1 and 0.2 mgL^{-1} for Cd and Hg respectively. All other elements found in the extracts were below the regulatory limits. The concentrations of As revealed that none of the geopolymers failed the toxicity limits.

3.4.3. Synthetic Precipitation Leaching Procedure (SPLP)

The results of the SPLP (data not shown) for Cd, Cr, Cu, Hg, Tl, Pb and Sb were below their detection limits in all the SPLP geopolymer extracts. Accordingly, they were below their USEPA National primary water quality standard (NPWQS) limits of 0.005, 0.1, 1.3, 0.002, 0.002 and 0.006 $mg.L^{-1}$ (Dungan and Dees, 2009.). Concentrations of As and Se were detected, although below the NPWQS limits, except for As in TUD-5-geopolymers.

It is interesting to note that ISEEP-1-geopolymers differed largely from other FA-geopolymers in mechanical strength but are relatively safe in terms of chemical leaching.

3.4.4. Tank leaching test

The NEN 7345 is a tank leaching test that was used to assess the leaching potentials of uncrushed geopolymer binders over a long time (64 days). The results of the Dutch Monolithic

307 test in $mg.m^{-2}$ revealed that Cd, Cr, Co, Cu, Ni, Pb and Zn were found below detection limits. All
308 detected elements, except Se in TUD-5 geopolymer, were below the Dutch Soil Quality
309 Regulation emission limits for moulded building materials (Dutch Soil Quality Decree, 2007) for
310 both activators (Table 6). These results suggest that the use of waste aluminium etching solution
311 as activator to synthesise FA-geopolymers proposed to replace commercial activator does not
312 really have an increased impact on the diffusion of the elements from the geopolymers and
313 consequently environmental fitness when applied as construction materials.

Table 5

TCLP leached concentration ($mg.L^{-1}$) for AES- and KS-geopolymers of the different fly ashes. The following elements were also determined but found below detection limits for all samples: Ag (<0.0013); Cd (<0.0002); Cr (<0.0001); Hg (<0.0011); Pb (<0.0031) and Sb (<0.0022).

Parameters measured	AES-geopolymers					KS-geopolymers					TCLP regulatory level
	TUD-1	TUD-5	CSIC-1	ISEEP-1	AICIA-2	TUD-1	TUD-5	CSIC-1	ISEEP-1	AICIA-2	
As	0.02	0.04	0.02	0.01	0.01	0.01	0.03	0.02	<0.0022	<0.0022	5.0
Ba	1.75	1.90	1.46	0.93	1.66	2.83	1.78	1.23	0.98	2.27	100
Se	0.02	0.02	<0.007	0.01	0.01	<0.007	0.04	0.01	0.01	0.01	1.0
V	0.13	0.04	0.04	0.03	0.01	0.01	0.03	0.05	0.03	0.01	0.03
Zn	1.69	<0.0002	<0.0002	<0.0002	<0.0002	2.83	<0.0002	<0.0002	<0.0002	<0.0002	300

Table 6

NEN 7345 cumulative leaching test results ($mg.m^{-2}$) for the various geopolymers and comparison with the Dutch Soil Quality Regulation emission limits. The following elements were also determined but found below detection limits for all samples, which recalculated to the following values in $mg.m^{-2}$ cumulative leaching: Cd (<0.009); Cr (<0.05); Co (<0.03); Cu (<0.02); Ni (<0.02); Pb (<0.20) and Zn (<0.01).

Parameters	AES-geopolymers					KS-geopolymers					Emission limits
	TUD-1	TUD-5	CSIC-1	ISEEP-1	AICIA-1	TUD-1	TUD-5	CSIC-1	ISEEP-1	AICIA-1	
pH (64^{th} day)	12.1	10.2	10.1	10.7	10.4	12.3	10.3	10.1	12.4	12.2	-
As	4.80	27.6	10.4	1.00	35.0	2.90	25.9	19.9	2.0	0.001	260
Ba	0.42	0.30	0.60	1.00	1.00	1.70	1.00	1.00	1.00	0.002	1500
Mo	35.2	24.7	8.46	5.87	8.79	11.8	32.3	33.0	5.43	1.80	144
Sb	0.26	1.60	1.70	1.50	1.40	0.82	0.90	1.50	1.00	0.001	8.70
Se	0.40	7.72	0.50	1.00	0.80	0.99	8.36	2.00	0.004	<0.0002	4.80
V	32.3	64.1	25.2	38.3	38.5	22.8	75.4	9.81	6.49	5.38	320

4. Conclusions

Geopolymerisation of fly ashes with waste aluminium anodising etching solution resulted in geopolymers of remarkable strength and densities. At 28 days ambient curing, the geopolymers that were produced with the etching solution activator showed compressive strength values between 51 and 84 MPa, whereas the compressive strength values of the reference, i.e. potassium silicate based geopolymers, were between 89 and 115 MPa. It was observed that the delayed setting time and consequently the low early strength gain of AES-geopolymers may be advantageous for construction materials such as concretes which are not put to usage immediately after they are produced. The densities of AES-geopolymers ranged from 1908- 2071 $kg.m^{-3}$ and were comparable with the densities of KS-geopolymers (1876– 2139 $kg.m^{-3}$). Based on this, fly ashes that are activated with waste aluminium etching solution can be applied as binders in construction and engineering works that require high mechanical strength.

The geopolymers of four of the fly ashes (TUD-1, ISEEP-1, CSIC-1 and AICIA-2) demonstrated high potential to immobilise trace elements that are present both in the fly ashes and the waste activator. As established by the regulatory limits that are currently associated with the used leaching tests, all, except one (TUD-5-geopolymers) of the produced geopolymers (with above threshold limiting values of As and Se), passed the recommended limits. When compared with KS-geopolymers, AES-geopolymers performed better in terms of environmental quality. However, from the geopolymerisation of TUD-5- and ISEEP fly ashes with waste aluminium etching solution and the reference commercial activators, it could be deduced that not all fly ashes can be recycled into geopolymer binders that are intended for structural applications. Finally, using wastes as the source materials in geopolymer synthesis will result in green and sustainable geopolymer technology. Fly ash and waste aluminium etching solution require sound environmental management. The expensive feedstock in geopolymer synthesis is the activator. Using fly ash and waste aluminate solution as feedstock in geopolymer synthesis present both economic and environmental benefits.

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