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1 **Geopolymerisation of fly ashes with waste aluminium anodising etching solutions**

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13

14 **Abstract**

15 Combined management of coal combustion fly ash and waste aluminium anodising etching
16 solutions using geopolymerisation presents economic and environmental benefits. The possibility
17 of using waste aluminium anodising etching solution (AES) as activator to produce fly ash
18 geopolymers in place of the commonly used silicate solutions was explored in this study.

19 Geopolymerisation capacities of five European fly ashes with AES and the leaching of elements
20 from their corresponding geopolymers were studied. Conventional commercial potassium silicate
21 activator-based geopolymers were used as a reference. The geopolymers produced were
22 subjected to physical, mechanical and leaching tests. The leaching of elements was tested on 28
23 days cured and crushed geopolymers using NEN 12457-4, NEN 7375, SPLP and TCLP leaching
24 tests. After 28 days ambient curing, the geopolymers based on the etching solution activator
25 showed compressive strength values between 51 and 84 MPa, whereas the commercial
26 potassium silicate based geopolymers gave compressive strength values between 89 and 115
27 MPa. Based on the regulatory limits currently associated with the used leaching tests, all except
28 one of the produced geopolymers (with above threshold leaching of As and Se) passed the
29 recommended limits. The AES-geopolymer geopolymers demonstrated excellent compressive
30 strength, although less than geopolymers made from commercial activators. Additionally, they

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

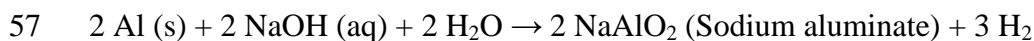
33 **Key words:** Recycling, Geopolymer, Waste aluminium etching solution, Fly ash, Leaching

34

35 **1. Introduction**

36 Electricity generation by pulverised coal facilities produces worldwide huge quantities of
37 coal combustion fly ashes (PFA: Pulverised Fuel Ash). These ashes constitute one of the most
38 important industrial residues, as illustrated by the annual production of some countries (Basu et
39 al., 2009): India (112 Mt), China (100 Mt), USA (75 Mt), Germany (40 Mt) and the UK (15 Mt).
40 The global annual production of PFA is estimated at 750 Mt (Izquierdo et al., 2012). These
41 volumes of PFA, together with its content of potentially hazardous leachable trace elements
42 make it practically impossible to be disposed of in landfills. Almost all naturally occurring
43 elements are present in PFA, and among those As, Cd, Cr, Hg, Mo, Se, Sb and V have been
44 detected as the most hazardous (Izquierdo et al., 2012; Moreno et al., 2005; Bingol and Akcay,
45 2005; Vassilev and Vassileva, 2007; Pandey et al., 2011). As a consequence, disposal of PFA is
46 not sustainable, and environmentally sound management of these residues is required.

47 Aluminium is the second most used metal apart from iron (Chen et al., 2010). Moors
48 (2007) reported global annual production of primary aluminium in 2003 to be 21.9 Mt. The
49 demand for aluminium is predicted to double by 2050 (Milford et al., 2011). Some aluminium
50 products, mainly those used for building, transportation, manufacturing machines and household
51 utensils, are subjected to anodisation to make them decorative and protected from corrosion
52 (Alvarez-Ayuso, 2009). During anodisation, a protective anodic oxide layer is formed on the
53 aluminium products in an electrochemical process with sulphuric acid as the electrolyte. Prior to
54 anodisation, the surface of the aluminium material is thoroughly cleaned by etching in a sodium
55 hydroxide (NaOH) solution. During etching some aluminium is dissolved as sodium aluminate
56 according to:



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

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

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

79 In this investigation five coal combustion fly ashes (FA) of different origin, fuel
80 feedstock and combustion conditions were used as the main precursor and a waste aluminate
81 solution (AES) serves as the activator solution. By utilising these geopolymers in the
82 construction sector, savings will be made both in the cost of disposal of these materials as
83 wastes, as well as avoiding the manufacturing of the high CO₂ binder Portland cement.

84

85 **2. Materials and methods**

86 *2.1. Materials for synthesis*

87 Five coal combustion fly ashes were collected from coal-fired power plants in the
88 Netherlands (TUD-1 and TUD-5), Spain (CSIC-1 and AICIA-2) and Belgium (ISEEP-1). Table
89 1 provides the basic information on origin, feedstock and combustion conditions for the selected
90 ashes. Note that the first four ashes are PFA type, whereas the last one is a fluidised bed ash,
91 therefore, FA will subsequently be referred to rather than PFA. Further information on TUD-5,
92 CSIC-1 and AICIA-2 is also given in Moreno et al. (2005).

93

94

95 Table 1

96 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 °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 °C)
AICIA-2	Spain Los Barrios Power Plant	Coal	Pulverised fuel combustion (T = 1250 °C).
ISEEP-1	Belgium	55 % Coal tailing + 45% biomass (wood pellets)	Fluidised bed (T = 850 °C)

97

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

101

102 Table 2

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

104 = 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 ₂ O ₃	27.8	28.8	23.3	23.0	22.7	11.8
Fe ₂ O 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 ₂ O	0.84	2.30	3.20	3.30	1.60	n.a.
Na ₂ O	0.58	0.50	0.90	0.50	0.60	0.24
P ₂ O 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 ₂ O ₃	1.76	1.80	2.30	2.30	2.60	3.15
SiO ₂ +Al ₂ O ₃ + Fe ₂ O ₃	84.6	89.0	85.9	79.6	86.9	49.0

105 LOI= Loss on ignition

106

107

108 The KS activator had a K₂O/SiO₂ molar ratio of 0.8, which was obtained by adding KOH
109 to a commercial grade KS solution (PQ Holland). The AES was collected from an aluminium
110 anodising company in the Netherlands. The solution sampled contained 85 g.L⁻¹ Al as sodium
111 aluminate and 30 g.L⁻¹ free NaOH. The measured pH of this solution was 14.0. The solution
112 contained 1.3 wt% of very fine dispersed particles of precipitated sodium aluminate containing
113 metal sulfides (mainly Zn and Cu). Inductively coupled plasma-optical emission
114 spectrophotometry (ICP-OES) analysis of the filtered AES showed the presence of trace
115 elements such as As, Cu, Fe, Mo, Sb, Se, V and Zn (Ogundiran et al., 2013).

115

116 2.2. *Synthesis of geopolymers*

117 Geopolymers synthesis and measurements were performed as reported previously
 118 (Ogundiran et al., 2013). The AES- and KS-based geopolymers were produced by adding fly ash
 119 to mixtures of 15 g BFS / 3 g NaOH / 17 g AES and 15 g BFS / 10 g KS / 10 g H₂O respectively.
 120 To these mixtures, amounts of fly ashes were adjusted to make workable pastes. In this way the
 121 ratios of BFS and liquid components were kept constant, whereas the amounts of fly ashes varied
 122 depending on the fly ash properties. The quantities were recalculated on a wt % basis, as shown
 123 in Table 3.

124

125 Table 3

126 Mix compositions used to produce geopolymers (wt.%). FA: coal fly ash; BFS: blast furnace
 127 slag; AES: aluminium etching solution; KS: potassium silicate solution with K₂O/SiO₂ = 0.8.

European FAs	AES Solution				KS solution			
	FA	BFS	10 M NaOH	AES	FA	BFS	H ₂ O	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

128

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

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

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

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

145

146 *2.3. Leaching tests*

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

160

161 **3. Results and discussion**

162 *3.1. Setting time of the geopolymers*

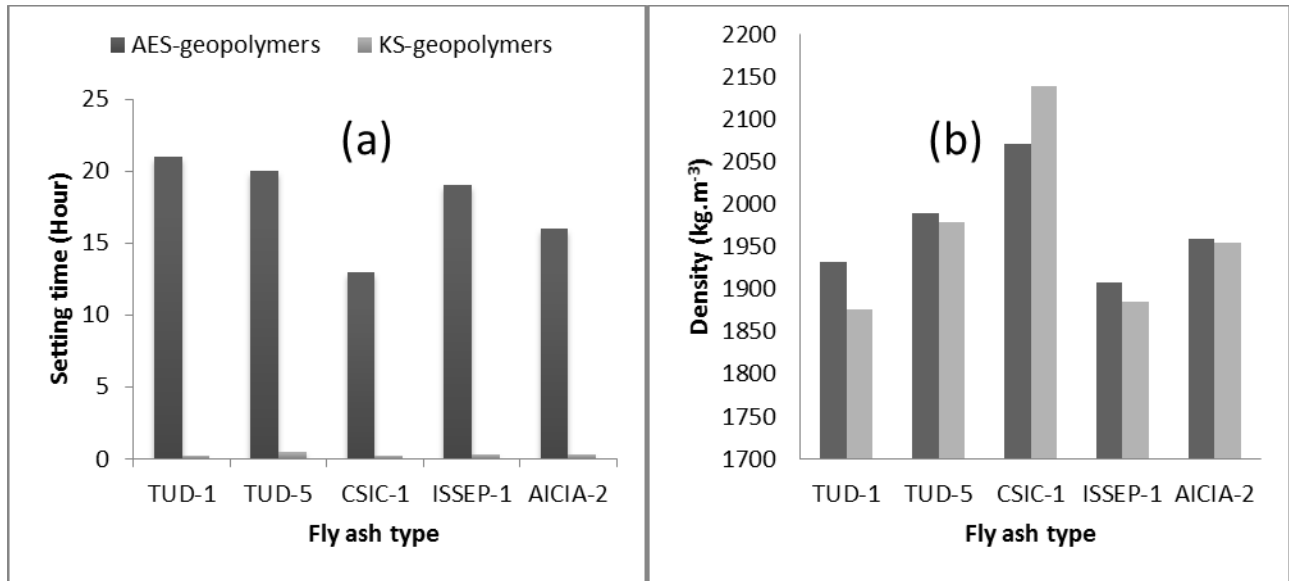
163 The results of final setting times for both AES- and the reference KS-geopolymers are
164 presented in Fig. 1 (a). The replacement of KS by AES as activator retarded the
165 geopolymerisation reaction. The KS-geopolymers hardened in 30 minutes or less, whereas the
166 AES-geopolymers did set in the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

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

172

173 *3.2. Density of the geopolymers*

174 The dry densities of the synthesised geopolymer binders for the different FAs and the
 175 activators are reported in Fig. 1 (b). The densities of AES-geopolymers which ranged from 1908-
 176 2071 kg.m⁻³ were comparable with the densities of KS-geopolymers (1876– 2139 kg.m⁻³). The
 177 highest density was achieved with CSIC-1 for both activators. The values are within those



178

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

181

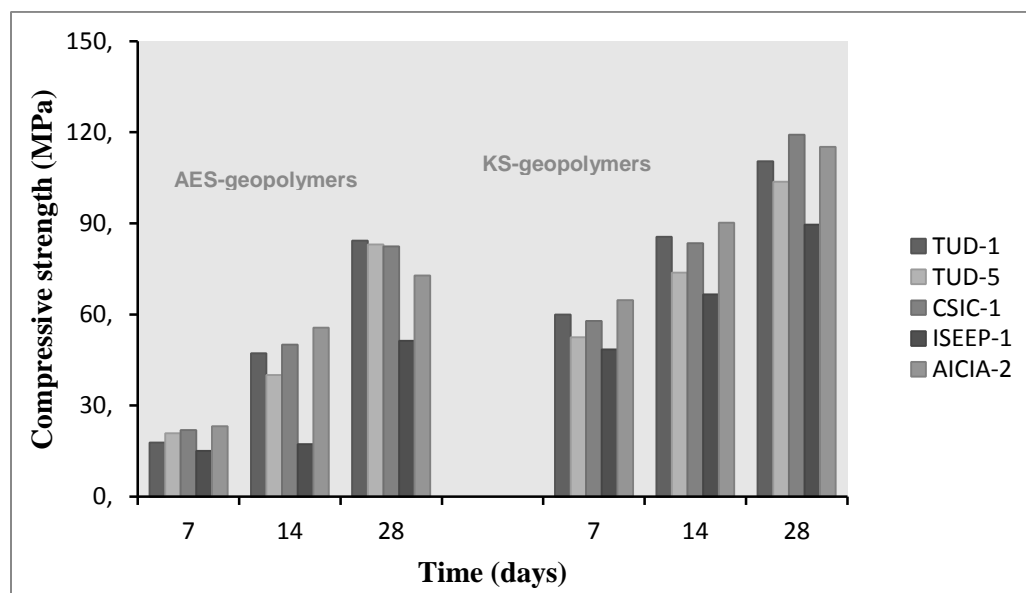
182 reported in literature (Andini et al., 2008; Sofi et al., 2007). Nevertheless only the CSIC-1
 183 geopolymer met the condition for normal OPC-based materials, for which the apparent densities
 184 fall within the range of 2000-2600 kg.m⁻³. High density binders will have low water absorption
 185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

187

188 *3.3. Compressive strength*

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

203



204

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

206

207 *3.3.1. Activator to fly ash ratio*

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

210 shown in Table 3, KS-silicate-geopolymers allowed higher fly ash contents. The amount of fly
211 ash required to form a workable paste follows the order CSIC-1> TUD-5> AICIA-2> TUD-1>
212 ISEEP-1, and obviously this depends on the nature of the fly ash. Both trends suggest that the
213 more the fly ash that can be accommodated in the mixture, the stronger the geopolymers will be.
214

215 *3.3.2. The nature of the activators*

216 It is observed that the strength of the geopolymers depends on the nature of the
217 activators. The KS-geopolymers were stronger than the AES-geopolymers from the same fly
218 ashes. Addition of KS to fly ash increases the importance of the stronger Si-O-Si and Si-O-Al
219 bonds in geopolymers (Duxson et al., 2005). Conversely, addition of AES to fly ash possibly
220 enhances the amount of Al-O-Al bonds which are weaker, leading to lower compressive
221 strength. Furthermore, for both activators, the degree of strength gained varied with fly ash type.
222 In both cases the lowest compressive strength was observed with ISEEP-1 geopolymers whereas
223 the highest strength was observed with TUD-1 and CSIC-1 for AES- and KS-geopolymers
224 respectively.
225

226 *3.3.3. Relation between compressive strength and chemical composition of the fly ashes*

227 Looking at the relationship between the mechanical strength of the geopolymers
228 and the chemical composition of the corresponding fly ashes by combining the data from Table 2
229 and Fig. 2, there seems to be no direct and obvious correlation between compressive strength and
230 chemical composition of the fly ashes. A statistical analysis, although with a low number of
231 samples, shows no other significant correlation than a positive one for Fe_2O_3 and a negative one
232 for LOI with compressive strength.
233

234 *3.3.4. Compressive strength development with time*

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

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

243 The lowest compressive strength values of both AES- and KS-geopolymers are higher
244 than the compressive strength values of Type IV (17 MPa) and V (21 MPa) Portland cement at
245 28 days (ASTM C150, 2007). Based on this, fly ashes activated with waste aluminium anodising
246 etching solution can be applied as binder in construction and engineering works that require high
247 mechanical strength.

248

249 *3.4. Leaching status of AES- and KS-geopolymers*

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

256

257 *3.4.1. NEN 12457-4 leaching test*

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

270 Table 4

271 Leached amounts ($\text{mg}\cdot\text{kg}^{-1}$) of selected elements from AES- and KS-geopolymers, according to the NEN 12457-4 leaching procedure.

272 The maximum limits for non-hazardous waste according to the EU Landfill Directive (EU LLV= European Union leaching limit

273 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

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

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

287

288 *3.4.2. Toxicity Characteristics Leaching Procedure (TCLP)*

289 The amounts of elements in the TCLP extracts of the geopolymers are presented in Table
290 5. Silver (Ag), Cd, Cr, Hg and Pb were found below their detection limits and consequently
291 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
292 respectively. All other elements found in the extracts were below the regulatory limits. The
293 concentrations of As revealed that none of the geopolymers failed the toxicity limits.

294

295 *3.4.3. Synthetic Precipitation Leaching Procedure (SPLP)*

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

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

303

304 *3.4.4. Tank leaching test*

305 The NEN 7345 is a tank leaching test that was used to assess the leaching potentials of
306 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.

314 Table 5

315 TCLP leached concentration (mg.L^{-1}) for AES- and KS-geopolymers of the different fly ashes. The following elements were also
316 determined but found below detection limits for all samples: Ag (<0.0013); Cd (<0.0002); Cr (<0.0001); Hg (<0.0011); Pb (<0.0031)
317 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

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325 Table 6

326 NEN 7345 cumulative leaching test results ($\text{mg}\cdot\text{m}^{-2}$) for the various geopolymers and comparison with the Dutch Soil Quality
 327 Regulation emission limits. The following elements were also determined but found below detection limits for all samples, which
 328 recalculated to the following values in $\text{mg}\cdot\text{m}^{-2}$ cumulative leaching: Cd (<0.009); Cr (<0.05); Co (<0.03); Cu (<0.02); Ni (<0.02); Pb
 329 (<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

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333 **4. Conclusions**

334 Geopolymerisation of fly ashes with waste aluminium anodising etching solution resulted
335 in geopolymers of remarkable strength and densities. At 28 days ambient curing, the
336 geopolymers that were produced with the etching solution activator showed compressive
337 strength values between 51 and 84 MPa, whereas the compressive strength values of the
338 reference, i.e. potassium silicate based geopolymers, were between 89 and 115 MPa. It was
339 observed that the delayed setting time and consequently the low early strength gain of AES-
340 geopolymers may be advantageous for construction materials such as concretes which are not put
341 to usage immediately after they are produced. The densities of AES-geopolymers ranged from
342 1908- 2071 kg.m⁻³ and were comparable with the densities of KS-geopolymers (1876– 2139
343 kg.m⁻³). Based on this, fly ashes that are activated with waste aluminium etching solution can be
344 applied as binders in construction and engineering works that require high mechanical strength.

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

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