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1 Resistance of alkali-activated grouts to acid leaching

2

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7 **Abstract**

8 At very low pH values materials based on hydraulic binders cannot be directly exposed to
9 acid solutions due to leaching, hence the need for additional coatings. As these are generally
10 characterized by relatively high cost and environmental impact, new solutions are being
11 developed. In this study, **grouts based on** alkali-activated materials (activated slag and
12 activated metakaolin with and without fly ash) have been considered as an alternative to be
13 directly exposed to acid solutions at pH = 3.5, and compared with slag cement grout. The
14 direct monitoring of mass and volumes was combined with the chemical analysis of the
15 leachate and the observations of cross sections through SEM/EDS and X-ray tomography in
16 order to understand the mechanisms involved in the leaching of studied materials. The
17 cumulated amount of leached ions was converted into an equivalent mortar volume loss and
18 compared with the direct measurement of the volume loss. A good correlation was found for
19 slag cement and activated metakaolin, as leaching mainly affected the binding phase. For
20 activated slag the volume loss was lower than expected due to the formation of new phases
21 **such as silica-rich gel. The higher volume loss of metakaolin-fly ash grout was attributed to**
22 the influence of partially reacted fly ash particles.

23 **Keywords:** Leaching, acid attack, **alkali-activated materials**, slag, metakaolin

24 **1. Introduction**

25 Leaching consists in the progressive dissolution of a solid material through the action of a
26 percolating liquid. Its consequences depend on multiple chemical and environmental
27 parameters such as pH, temperature, liquid/material ratio and the mobility of the leaching
28 medium (still or flowing) [1, 2]. The loss of leached elements is likely to weaken the binding
29 phase, which affects its mechanical properties [3] and eventually leads to the complete failure
30 of the material [4]. In severe environmental conditions, the resistance to leaching is a decisive
31 parameter in the choice of the material to be used.

32 In Portland cement-based materials, leaching mainly affects the behavior of calcium-rich
33 hydration products [5]. Portlandite ($\text{Ca}(\text{OH})_2$) is usually the first phase to be dissolved in the
34 process [6,7]. This releases calcium cations as well as hydroxides. Since leaching is a
35 diffusion-dissolution phenomenon [8], the dissolution of portlandite causes an increase in
36 porosity which favors the penetration of the environmental water into the material [9]. Once
37 portlandite is exhausted, the decalcification of the calcium silicate hydrates (C-S-H) can
38 occur. As the C-S-H are the main contributor to mechanical strength, their decalcification
39 weakens the material and causes irreversible damage to its microstructure [10]. Other phases
40 are then dissolved as the front of attack goes further.

41 The process is significantly accelerated in acid waters, since the added H_3O^+ ions actively
42 participate in the attack through a faster destruction of the chemical bounds [11].

43 Consequently, the pH of the interstitial water can be a limiting factor to the use of traditional
44 cement-based materials, especially in soil reinforcement and underground structures. The EN
45 206 European Standard allows implementing performance-based tests and specifications for
46 the durability of concrete. The French standard P18-011 is referred to in NF EN 206-1
47 standard. According to P18-011, cement-based materials cannot be directly exposed to

48 environments of pH lower than 4 without any coating [12]. However, near contaminated and
49 industrial sites, as well as in specific exposures, the acidity of the underground water can be
50 even more aggressive. Additional coatings need to be installed [13]. This dramatically
51 increases the cost and complexity of such projects.

52 Extractive industries are likely to cause some situations where huge volumes of soils need to
53 be contained to avoid the pollution of water resources and the loss of biodiversity. For
54 instance, acid mining drainage consists in the drainage of acid water containing dissolved
55 metals as a result of natural oxidization of sulphides found in waste rock, ore and tailings
56 exposed to air and water [14]. Cement grouts can be used to improve the mechanical and
57 physical properties of soils and rocks. They allow reducing their permeability for containment
58 purposes. They are directly exposed to aggressive waters [15]. In this context, grouts based on
59 alkali-activated materials (AAM) have been considered as a possible alternative to traditional
60 solutions. Sometimes highlighted for their environmental advantages, the main interest of
61 alkali-activated materials remains their better durability in multiple aggressive situations [16,
62 17]. Their acid resistance has been studied by several authors for different applications.

63 At the macroscopic level, the main indicators of the resistance to acid leaching are weight
64 loss, decrease in compressive strength, and damaged depth. These consequences are not
65 specific of acid attack, thus most of studies include a characterization of the microstructure
66 and nanostructure of corroded and corroded samples [18]. The weight loss and the strength
67 decrease are both due to the degradation of binding phases. The main phases produced by
68 alkali-activation are the sodium aluminosilicate hydrate (N-A-S-H) gel, and the aluminum-
69 modified calcium silicate hydrate (C-A-S-H) gel with different Ca/Si ratios, depending on the
70 calcium content of aluminosilicate precursors [19]; $\text{Ca}(\text{OH})_2$ and AFm can also be observed at
71 higher calcium contents. The resistance to acid leaching was found to depend closely on
72 microstructure and nanostructure. Denser matrices are characterized by lower diffusivity,

73 which delays the detrimental effects of leaching [20]. The effect of acid attack also depends
74 on the chemical structure of the matrix. Calcium-rich phases are vulnerable to leaching due to
75 their possible decalcification [21]. As a consequence, the replacement of Portland cement by
76 mineral additions such as slag and fly ash generally results in better resistance to acid leaching
77 due to a denser microstructure as well as a lower calcium content [22]. N-A-S-H gel can be
78 affected by the exchange reaction of sodium and hydronium ions [23], and the loss of
79 aluminate from the aluminosilicate network (“geopolymer” gel) or the amorphous phase of
80 high-alumina fly ash [24]. Zhang et al. [18] actually observed that the Al/Si ratio was lower in
81 the corroded layer after acid attack, and this reduction increased with fly ash/slag ratio. The
82 alkali-activation of metakaolin and fly ash mainly results in N-A-S-H gel, whereas activated
83 slag mainly consists of C-A-S-H gel [25, 26]. Even if cement-based and alkali-activated
84 materials are both eventually affected by acid leaching, most of studies mention that alkali-
85 activated materials with low-calcium content show better resistance. Sodium ions are easily
86 leached from the nanostructure of N-A-S-H gel, where they balance the Al negative charges,
87 but this does not affect much the strength of the material [18, 27], as the negative charge can
88 be compensated by the H_3O^+ ions provided by the acid solution. Koenig et al. [28] studied
89 several materials over a wide range of calcium contents. They actually observed that N-A-S-H
90 (low-calcium AAM and geopolymer) had better resistance than C-A-S-H (calcium-rich single
91 or multicomponent AAM), and C-S-H (Portland cement). They suggested a CaO limiting
92 value of 10% in mass to distinguish low-calcium and high-calcium alkali-activated binders.

93 Several studies focused on the evolution of the mechanical and macroscopic properties when
94 exposed to different types of acid attacks, such as nitric acid [23, 29, 30] and sulfuric acid [31
95 32]. Organic acids, such as acetic acid [31, 33], cause a more severe damage compared to so
96 called “strong” acids, such as sulphuric or hydrochloric acid, because of the acid buffer
97 action and the high solubility of the reaction products [34, 35]. Alkali-activated slag

98 performed better than Portland cement-based material, even in acetic acid [34]. Damage
99 mechanisms are strongly dependent on the applied acid solution. Several experiments actually
100 induce couplings between acid attack and other degradation mechanisms, such as sulfate
101 attack and chloride ingress. Even if there are correlations between the resistance to leaching
102 and chemical stability [22], each mechanism implies different chemical reactions thus
103 different phases are formed with different consequences on microstructural and engineering
104 properties. Organic acids are relevant for biogenic acid attack in sewage or agricultural
105 concrete applications [36]. Sulfuric acid is also often used to represent sewer conditions.
106 Sulfate-rich phases such as gypsum have been observed in alkali-activated materials exposed
107 to sulfuric acid [18, 20, 37]; Gu et al. [38] also mentioned the development of a barrier of
108 expansive products. Vafaei et al. [39] studied several materials including AAM; H₂SO₄ attack
109 caused more deterioration than HCl attack due to the accelerating effect of gypsum formation.
110 The sulfate resistance of AAM was also generally found to be better than Portland cement
111 systems [40], but sulfuric acid does not seem appropriate to study only acid leaching.

112 A better understanding of the damage mechanism of alkali-activated materials has also been
113 achieved through chemical analyses of the leachate and damaged samples [41]. Keulen et al.
114 [42] used nitric acid and controlled pH to determine element release as a function of leachate
115 pH. The analysis of the leachate actually allows investigating the leaching of metals [42, 43]
116 or naturally occurring radionuclides [44] from alkali-activated slag. The links between the
117 chemical evolutions and macroscopic indicators have not been sufficiently discussed.

118 The specifications on fresh cement grouts include low viscosity as they are meant to be
119 injected in soils [45]. Low viscosity implies relatively high water-to-binder ratios. In the case
120 of cement-based materials, the rheological performances can be enhanced through chemical
121 admixtures [46, 47]. This allows finding compromises between low viscosity and low
122 permeability. The increase of water-to-cement ratio actually has a detrimental effect on the

123 permeability and the resistance to leaching [20, 48]. Cement grouts used for the containment
124 of acid waters had higher w/c; Sephton et al. [15] studied grouts with w/c between 0.8 and
125 1.2. Moreover, the rheological properties of fresh alkali-activated grouts cannot be improved
126 through the same strategy based on chemical admixtures due to the higher alkaline content of
127 the grouts [49-51]. Existing studies mainly focus on alkali-activated materials with relatively
128 low water-to-solid ratios. However, the use of grouts for soil improvement and containment of
129 aggressive waters leads to consider the behavior of alkali-activated materials with relatively
130 high water-to-solid ratios.

131 This paper presents a comprehensive study of the resistance of alkali-activated grouts to
132 leaching in acid conditions. First the experimental program is presented. The specimens were
133 immersed in regularly renewed solutions of demineralized water at a constant pH of 3.5
134 controlled by automatically adding nitric acid. The testing procedure was designed to achieve
135 well-defined exposure conditions, in order to better understand the basic phenomena involved
136 in the degradation mechanism. Through the coupling of multiple characterization techniques
137 (SEM/EDS, X-Ray tomography, chemical analyses) with macroscopic monitoring of mass
138 and volume, a multi-parameter comparison of different mixes has been performed.
139 Metakaolin, metakaolin-fly ash and slag mixtures are studied, compared to a reference
140 Portland-Slag cement grout. Then the results are presented, first macroscopic indicators, then
141 the direct observation of cross-section, and chemical analyses. Finally the correlations
142 between macroscopic indicators and chemical parameters are plotted and discussed.

143 **2. Materials and methods**

144 **2.1 Materials, mixing, and curing**

145 The physical and chemical properties of the materials are given in Table 1. The analysis of
146 specific surface of slag, metakaolin and fly ash was performed from Brunauer, Emmett et

147 Teller (BET) theory. The packing density of powders was determined from their water
 148 demand using the flow spread test. Commercially available products were used to design the
 149 studied mixtures. Slag cement CEM III/C with high slag content (85 %) was chosen here as it
 150 is often recommended to design grout mixtures for chemically aggressive environments.
 151 Binders with high slag content actually show relatively good behavior in pure or acid water
 152 [52]. Metakaolin was obtained from flash calcination of clay from Fumel, France. Low-
 153 calcium fly ash was produced from thermal power plant in Hornaing, France. Sodium silicate
 154 had a SiO₂/Na₂O molar ratio of 1.7, a dry matter content of 44% and a density of 1.57.

155 **Table 1.** Chemical composition and physical properties of materials

	Slag cement	Slag	Metakaolin	Fly ash
(Mass, %)				
Total SiO ₂	31.7	37.2	67.1	50.0
Total Al ₂ O ₃	9.5	10.5	26.8	20.0
CaO	44.8	43.2	1.1	1.0
Fe ₂ O ₃	0.8	0.6	2.6	8.5
MgO	6.6	7.0	0.1	3.0
SO ₃	3.1	0.1	-	0.6
TiO ₂	0.5	0.5	1.3	1.0
Na ₂ O	0.2	0.6	0.0	0.6
Slag content (%)	85	100	0	0
Density (10 ³ kg/m ³)	2.92	2.89	2.63	2.24
Median diameter (μm)	-	10	18	38
BET (m ² /g)	-	0.45	16.50	1.24
Packing density (Vol., %)	-	44.4	43.9	62.6

156

157 The compositions of the studied mixtures are given in Table 2. The grouts were designed
 158 keeping a constant water-to-solid mass ratio of 0.75. As revealed by specific surface BET
 159 (Table 1), the internal porosity of metakaolin was high, thus relatively high water-to-cement
 160 ratio was needed to achieve required flowability. The replacement of metakaolin by fly ash
 161 improves the rheological properties [53]. The study has been carried on mortars made with

162 these grouts and 0/2 mm quartz sand from Palvadeau, France. The volume fraction of sand
 163 was kept constant at 47%. The grouts were prepared in a high-shear mixer, by dissolving the
 164 powders to the activating solution and water in the case of cement. This solution was prepared
 165 by diluting a commercial sodium silicate solution in demineralized water, and adding sodium
 166 hydroxide in pellet form. The grouts were then mixed with the sand in a mortar mixer. For
 167 each mixture, five 20x20x160 mm³ specimens were prepared and stored under plastic film for
 168 7 days at 20 ±1°C. Then, one centimeter of each extremity was coated with resin to avoid
 169 damage near the measurement inserts. The specimens were stored under water until testing.

170 **Table 2.** Compositions of the studied grouts and origins of the materials (g/L)

	Type	C3	AS	AM	AMF
Cement	CEM III/C 32.5	923.1	-	-	-
Slag	GGBFS	-	739.8	-	-
Metakaolin	Flash calcination	-	-	670.9	402.5
Fly ash	Type F	-	-	-	228.6
Sodium silicate	Commercial	-	454.2	583.0	583.0
Sodium hydroxide	Pellets, 98.5%	-	3.0	3.0	3.0
Water	Demineralized water	692.3	450.0	366.7	366.7

171

172 2.2 Experimental procedures

173 28 days after mixing, two samples were immersed in demineralized water for acid exposure,
 174 under permanent magnetic stirring and controlled temperature of 20°C, and the three other
 175 specimens were stored in water as control samples. The pH of each cell was individually
 176 controlled at 3.5 using 0.5M nitric acid [52, 54]. The added volume of acid was periodically
 177 monitored, at least once daily, and samples of the solutions were extracted after every
 178 renewal. The solution was renewed at fixed intervals of added volume of acid (every 40 ml
 179 during the first testing week, 20 ml later) in order to maintain the gradient of concentrations
 180 between the acid solution and the pore solution. Samples of the demineralized water were also

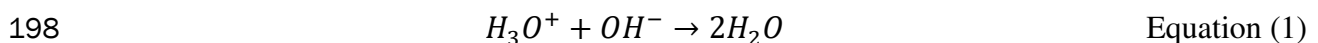
181 taken before the immersion of mortar samples to establish a baseline for the chemical
182 analysis. With each renewal, the saturated surface dry mass of the samples was measured,
183 along with their volume variation via hydrostatic weighing. The same measurements were
184 carried on control samples kept in demineralized water in order to assess relative variations of
185 monitored parameters. The leachate solutions as well as the water samples were analyzed in a
186 certified lab for the quantification of six ions: silicon, aluminum, calcium, sodium,
187 magnesium, and iron.

188 The mass and volume of control and tested specimens, and added acid volume, were
189 monitored for 120 days. Then the central part specimens exposed to acid attack was sawn to
190 extract two prismatic samples for SEM-EDS and X-ray microtomography. The detailed
191 conditions of these observations and analyses are given in [55].

192 **3. Results and discussion**

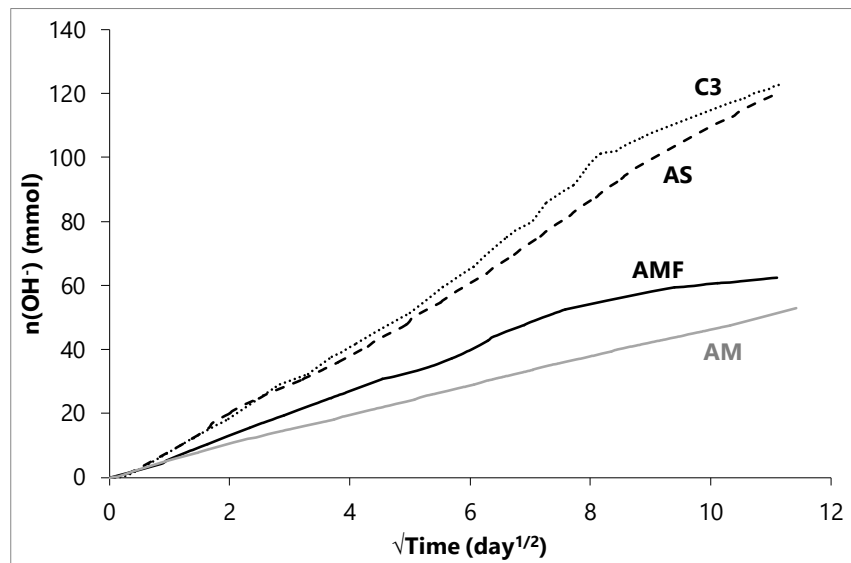
193 **3.1 Macroscopic evolutions**

194 As the studied mortars were exposed to acid attack in four different cells, the control of pH
195 directly provides the first indication of the degradation of the materials through the cumulated
196 amount of added acid. The H_3O^+ cations provided by the nitric acid actually neutralize the
197 OH^- ions leached from the pore solution of samples (equation 1).



199 The average quantity of leached OH^- ions can be deduced from the cumulated volume of acid.
200 In Fig. 1, this quantity is plotted against the square root of time. The curves are quasi-linear,
201 showing that the mechanism of degradation is based on diffusion and dissolution [10, 52].
202 The slope of each curve is an indicator of the leaching kinetics, [which provides](#) a first

203 classification of the studied samples. AM and AMF samples underwent a slower leaching
204 process (4.6 and 7.0 mmol/ $\sqrt{\text{day}}$) than C3 and AS (12.7 and 11.2 mmol/ $\sqrt{\text{day}}$).



205

206

Fig. 1. Leached OH^- ions as a function of the square root of time

207 The mass and volume losses calculated from measurements after 120 days are presented in
208 Table 3. The ranking is the same as the leaching kinetics. The significant mass loss of the C3
209 samples (8 % in 4 months) can be associated to the weakened binding phases and the
210 subsequent loss of sand particles. In the AM samples, the mass loss was very low (less than 1
211 %), confirming the good stability of metakaolin geopolymers in these conditions [56]. The
212 mass loss of AMF samples was higher, which could be explained by the presence of
213 unreacted FA particles that lower the effective binder content and add more inclusions to the
214 material [57]. The average volume loss of the samples after 120 days partly confirms the
215 trends given by the mass losses. The volume decrease of C3 samples was significant. AM
216 showed good volume stability, which is consistent with the quasi absence of degradation
217 observed on the surface of the samples. The results given in Table 3 also indicate a
218 discrepancy between mass and volume variations of AS and AMF specimens. Their volume
219 loss was lower than their mass loss, and their behavior was different from C3 and AMF

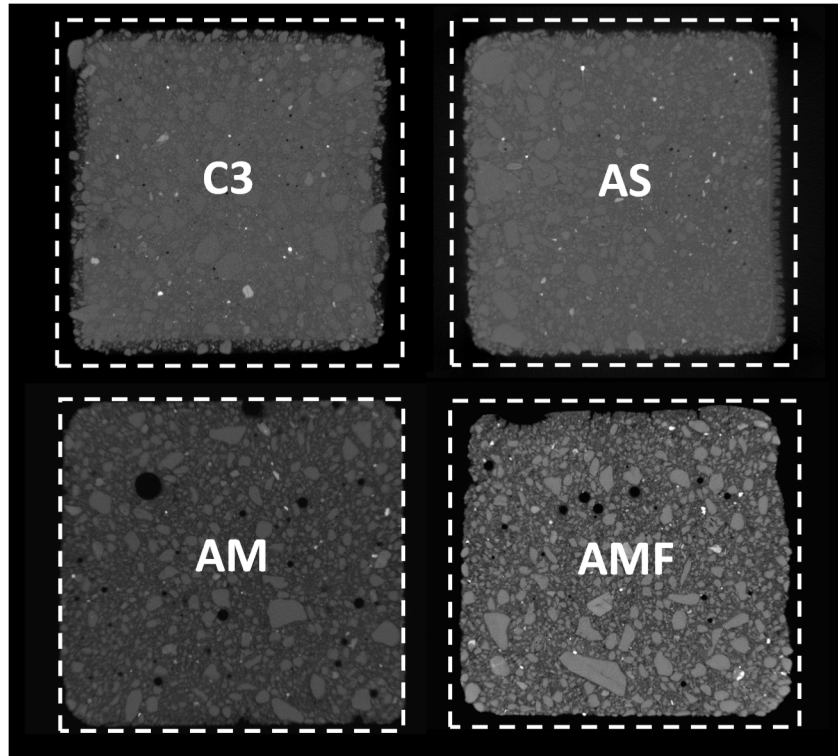
220 specimens. AMF showed approximately the same volume variation as AS, in spite of much
221 lower leaching kinetics. AS showed relatively lower volume variation, or conversely C3
222 showed high volume variation. The “mass” variations refer to the mass of specimens at SSD
223 state (saturated, dried surface); this volume includes porosity. The “volume” variations refer
224 to the volume of solid phases determined from buoyancy method. The relatively low volume
225 loss of AS implies that new phases had formed in the porosity of the specimens. One can also
226 consider that the mass decrease of C3 specimens was higher than expected from volume
227 variations, which allows assuming that the porosity of the sample increased. The same
228 phenomena could have occurred in AMF and AM respectively. The discrepancies between
229 mass and volume variations could also originate from the density of dissolved or lost phase,
230 which can significantly differ from the average density of the material. Thus it is not possible
231 to conclude from mass and volume data to explain the behavior of studied materials. Further
232 analyses were needed to check these hypotheses.

233 **Table 3.** Mass and volume losses after 120 days of leaching

Mixes	C3	AS	AM	AMF
Mass loss (%)	8.0	4.4	0.9	3.6
Volume loss (%)	8.6	2.4	0.3	2.2

234

235 X-ray microtomography can be used to assess the extent of damage within the samples. Cross
236 sections of the specimens are presented in Fig. 2.



237

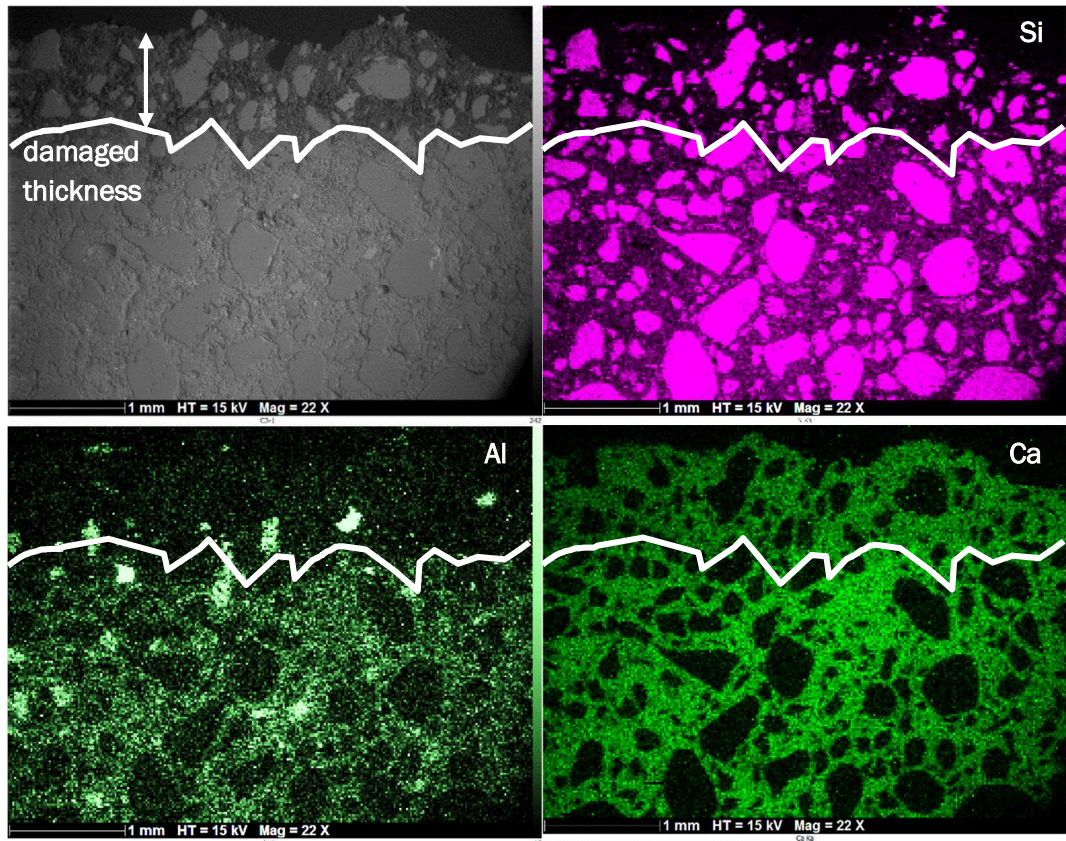
238 **Fig. 2.** X-ray micro-tomography scans of the samples and initial section (dashed lines)

239 As the ends of prismatic specimens were protected by an acid resistant resin, leaching was
240 mainly two-dimensional. The degradations observed on cross-sections can be used to
241 understand the mass and volume variations. In the AM and AMF samples, the binding matrix
242 remained homogeneous with no signs of cracking or increased porosity. The AMF picture
243 shows a seriously altered outer surface attributable to the significant loss of sand and FA
244 particles. The damaged zone in the outer part of C3 sample reveals an increase in porosity. A
245 significant proportion of the matrix has been dissolved, accompanied by the loss of sand
246 particles. The AS sample shows a similar aspect but the reduction of cross section and the
247 depth of damaged zone are lower. The information provided by microtomography is
248 consistent with mass and volume variations provided by direct measurements. AM showed
249 good stability, C3 showed the highest volume and cross-sections losses, and AS and AMF
250 intermediate behaviors.

251 This is consistent with the works stating a better resistance of activated slag than Portland
252 cement to acid environments [33, 58]. Shi and Stegemann [59] attributed the difference to the
253 nature of reaction products present in each material. The main products in activated slag are
254 calcium silicate hydrates (C-S-H) with a low Ca/Si ratio, while cement paste contains higher
255 Ca/Si C-S-H accompanied by $\text{Ca}(\text{OH})_2$. Since decalcification is the main degradation
256 mechanism, hydrated cement is more vulnerable to acid exposition and displays stronger
257 effects. Mellado et al. [30] reported that the alkali-activated materials with the lowest calcium
258 content lead the best performance.

259 **3.2 Chemical analyses and microstructural characterization**

260 The increase in porosity of C3 sample could explain its relatively high volume loss (Table 3).
261 However, this variation needs to be quantified thus chemical data were used to identify the
262 leached or precipitated species. The damaged zone in C3 has been examined via SEM/EDS
263 (Fig. 3).



264

265

Fig. 3. SEM/EDS scan of the C3 sample showing the damaged zone

266

Keeping in mind that the outer edge has been eroded to some degree, the remaining interfacial

267

zone shows a distinct discoloration. Confirming the microtomography observations, signs of

268

increased porosity and loss of binder are visible. This weaker part of the sample also shows a

269

lower concentration of structural elements such as silicon, aluminum and calcium. In cement-

270

based materials, these elements are actually the main constituents of hydration products such

271

as C(A)SH, Ca(OH)₂, AFm, and calcium aluminate hydrates. These products have different

272

solubility thus different dissolution fronts should theoretically be observed [60]. Here a

273

common front can be distinguished between the damaged and the sound parts of the C3

274

sample, indicating the extent reached by the acid attack after 4 months. In the damaged zone,

275

the loss of binding phases is likely to accelerate the degradation of the material in the case of

276

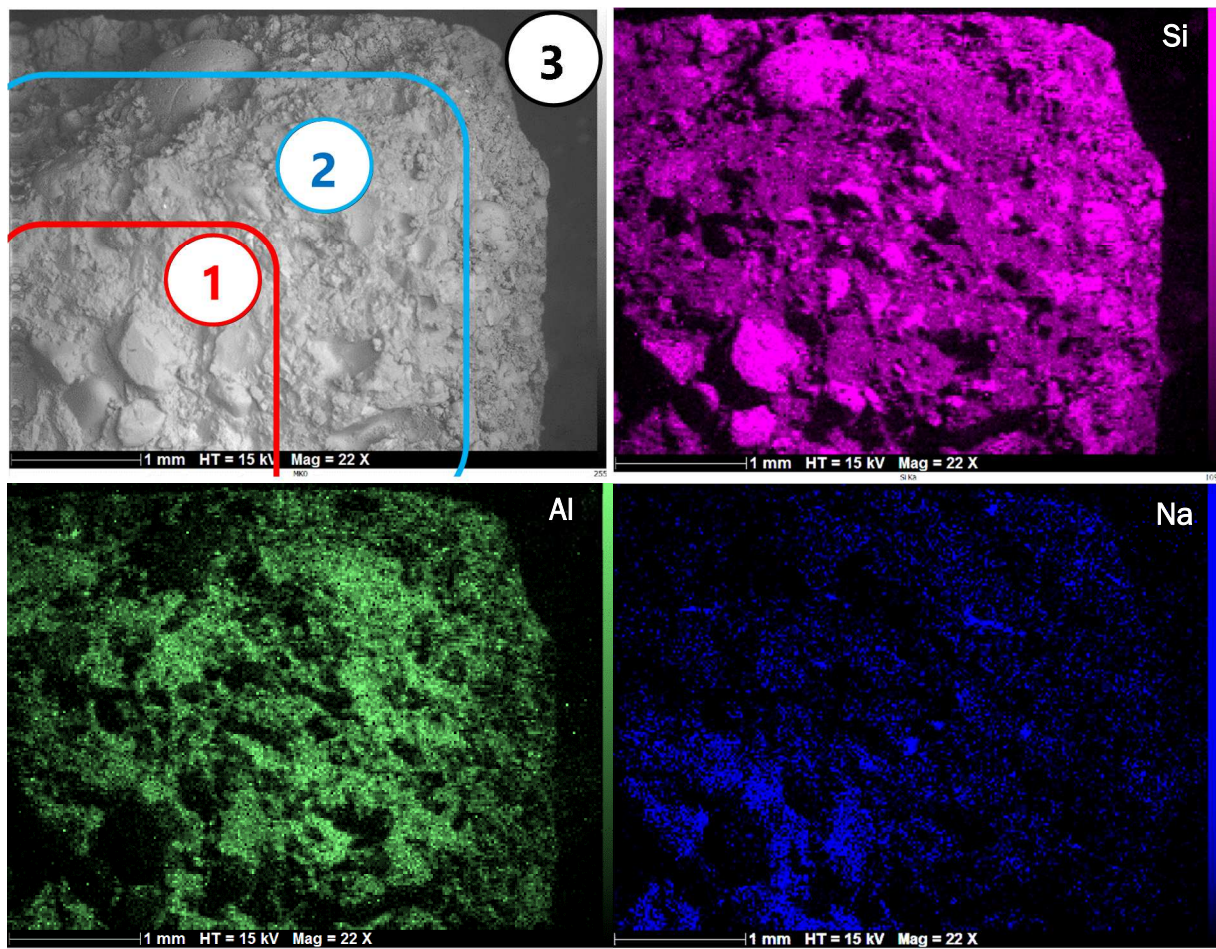
coupled phenomena such as carbonation, chloride or sulfate ingress [22]. Weakened binding

277

phases and an increase in porosity seem to be the main factors behind this alteration, as stated

278 by Beddoe and Dorner [11]. In our study, the higher water/cement ratio (0.75) leads to a
279 relatively high porosity and weaker hydrates, causing favorable conditions for the diffusion
280 and ions exchange between the pore solution and acid environment.

281 The SEM/EDS analysis of AM also reveals the leaching of each element with some
282 differences in the extent (Fig. 4). While Si seems barely affected by the acid attack, other
283 elements such as Al and especially Na show a significant variation in their concentration
284 between the edge and the core of the sample. Sodium appears to be the most mobile species,
285 as it is mostly present in the pore solution [61] and it is not covalently bonded to the
286 aluminosilicate network [62]. Aluminum is less present in the outermost part of the sample.



287

288

Fig. 4. SEM/EDS scans of the AM sample

289 The three elements have different leaching kinetics and they have been shown to follow the
290 same pattern in different pH and temperature conditions by Aly et al. [63]. The sample can
291 thus be separated into three distinct areas as shown on the picture in Fig. 4. In the zone (3),
292 lower aluminum and sodium contents are observed, showing a partial modification of the
293 chemical components of the aluminosilicate network. Zone (2) displays initial concentration
294 of aluminum, whereas sodium content has significantly decreased. The limit between zones
295 (1) and (2) can be considered as the diffusion front of acid into the material. While not
296 presented in this paper, the AMF sample analysis did not show a similar pattern. This is likely
297 due to the erosion that affected the damaged thickness as soon as the network lost its
298 aluminum ions.

299 The results presented above show different leaching kinetics of the chemical elements. To
300 study this aspect, a sample of the leachate was extracted at every renewal of the solution and
301 analyzed for six elements: Aluminum, Silicon, Calcium, Sodium, Magnesium and Iron. As the
302 initial content depends on the studied mixture, a representative quantity has been used to
303 compare the leaching kinetics of different materials for a given element. The equivalent
304 damaged thickness (EDT) represents the ratio of leached material to the initial quantity,
305 normalized by the area exposed to the attack. It is individually calculated for each of the six
306 elements following equation (2)

$$307 \quad EDT(m) = \frac{\frac{n_{leached}(mol)}{A_{exp}(m^2)}}{C_{ini}(mol/m^3)}}{\quad} \quad \text{Equation (2)}$$

308 where $n_{leached}$ is the leached ion content, A_{exp} is the exposed area of the sample and C_{ini} is the
309 initial content in the mixture. The values of the EDT after 120 days are summarized in Table
310 4. By comparing the different values, it is noticeable that almost [all the leached ions](#) followed
311 the same tendency, with some variations in the ranking of the mixtures. [Again, C3 presents](#)
312 [the highest leaching rates. The samples mainly lose calcium, which is tightly linked to the](#)

313 dissolution of portlandite and the decalcification of C-S-H in cement-based materials [11, 52],
 314 but also considerable amounts of silicon and aluminum. This indicates damaged calcium
 315 aluminosilicate (C-A-S-H) gel phase and partly dissolved secondary phases [6]. The leaching
 316 of iron was significantly higher than in any other mixture. It can be an indicator of the
 317 stability of metallic oxides in aggressive conditions when incorporated in alkali-activated
 318 matrices. This application has already been investigated by other authors [64-66], but further
 319 work needs to be carried out to confirm the results in acid/aggressive environments. Although
 320 the pictures obtained from SEM analyses (Figure 3) showed a common leaching front, the
 321 EDT values are different (Table 4). As shown by the SEM mapping, the remaining aluminum,
 322 silicon, and calcium contents in the damaged zone are still significant in the outer part of the
 323 remaining section.

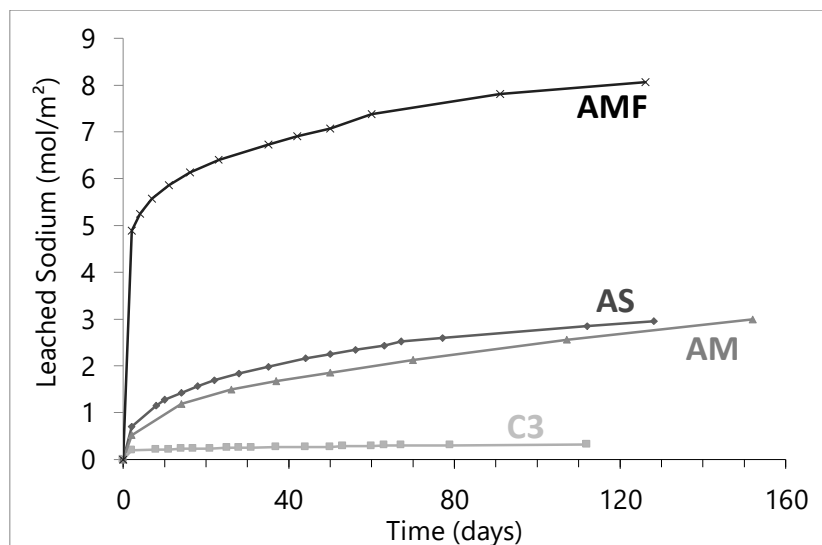
324 **Table 4.** Equivalent Damaged Thickness after 120 days for each element

<i>EDT (μm)</i>	C3	AS	AM	AMF
<i>Sodium</i>	7058	1419	1118	3021
<i>Magnesium</i>	496	293	0	0
<i>Aluminium</i>	412	251	145	307
<i>Silicon</i>	300	266	118	191
<i>Calcium</i>	707	737	110	627
<i>Iron</i>	260	200	12	13

325

326 A significant loss of aluminum took place in the AMF samples, which confirms the
 327 weakening of the binder as the main damage mechanism. Compared to AM, the AMF mortar
 328 appears to be more sensitive to the attack, with a possible contribution coming from partially
 329 reacted fly ash particles that are subsequently dissolved in the acid solution. Previous studies
 330 actually showed that significantly acid concentration promotes the extraction of aluminum
 331 ions in the amorphous phase of high-alumina fly ash, and that Calcium and Sodium are
 332 efficiently removed from fly ash [24]. Another particularity of the AMF samples is the high

333 amount of sodium that is released in the solution at the time of the first exposure (Fig. 5). This
334 behavior can be explained by significant content of free sodium cations that migrate easily to
335 the surface of the samples before being transferred to the solution. This can be associated with
336 the substitution of metakaolin with fly ash, a less reactive material with lower aluminum
337 content, **which results** in an excess of sodium. The Al/Na ratio has been reported to have a
338 significant influence on the mechanical properties of **alkali-activated** metakaolin, such as
339 compressive strength and elastic modulus [67]. Moreover the specimens have been exposed to
340 acid solution at relatively early age of 28 days, while the reactivity of fly ash is much slower
341 than metakaolin. This results in significantly lower strength at 28 days, even if this material
342 finally reaches equivalent strength at long-term [26]. The sodium cations are then more
343 numerous than necessary for the electric equilibrium and thus more mobile.



344

345

Fig. 5. Evolution of the leached sodium content

346

3.3 Correlations between chemical data and macroscopic behavior

347

The leaching behaviors of the samples characterized by the different elements globally agree

348

with the previously described evolutions of the mass loss and volume variations. The main

349

degradation mechanism seems to be the dissolution of the binding phases, i.e. calcium-

350 sodium-aluminosilicate (C-(A)-S-H) hydrates in the case of C3 and AS, and the
351 aluminosilicate network present in AM and AMF. C-A-S-H and N-A-S-H gel are actually the
352 main products of reactions in studied materials, depending on the calcium content and pH
353 [19]. The nanostructure of studied alkali-activated metakaolin actually consists in
354 polymerized 3D network where SiO_4 and AlO_4 tetrahedra are connected to 4 bridging
355 oxygens linking it to silicon or aluminum atoms, as shown by solid-state nuclear magnetic
356 resonance (NMR) spectra in another study [26]. Sodium silicate-activated slag can be
357 described as a C-(A)-S-H gel with tobermorite of various levels of crosslinking [25]. Recent
358 works have reported a decrease in the level of cross-linking at longer term, with higher
359 structural organization of the C-A-S-H phase which suggests a later stage of aluminum
360 incorporation in this phase [26]. Moreover C-A-S-H phase can coexist with polymerized N-A-
361 S-(H) gel due to the structural limitations on Al substitution within the C-(N)-A-S-H gel and
362 absence of Ca-rich phases [68].

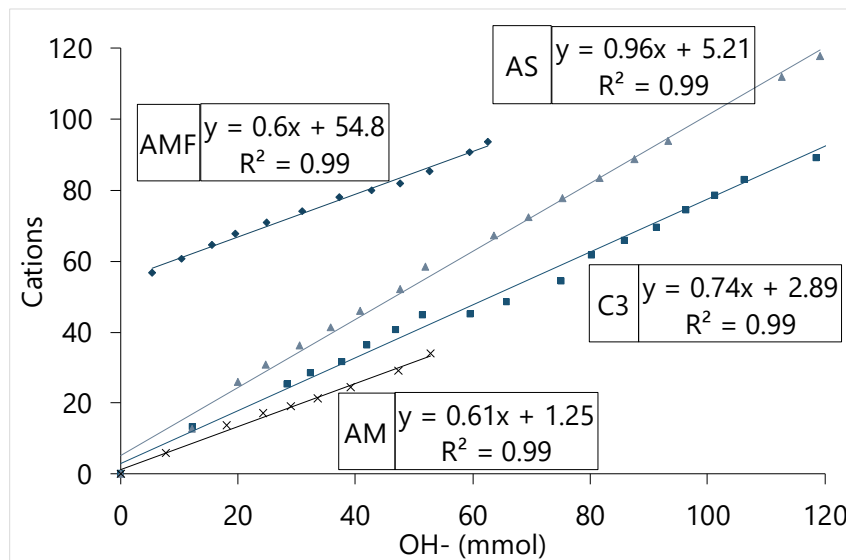
363 [This confirms that](#) aluminum, silicon and calcium are the relevant elements for the assessment
364 of the leaching kinetics and related nanostructural damage. Sodium leaching, however, does
365 not appear to have a significant effect on the integrity of the materials. The corresponding
366 EDTs were much higher than the other elements, signaling a higher diffusion rate through the
367 matrix. Sodium ions are weakly bound in the nanostructure of N-A-S-H gel, where they
368 balance the Al negative charges. Na can be leached out without affecting the strength of the
369 material [27]. In the case of acid leaching, the negative charge can be compensated by the
370 H_3O^+ ions provided by the solution.

371 In high-calcium binders, the leaching of hydroxide anions is driven by the dissolution of
372 portlandite ($\text{Ca}(\text{OH})_2$) [69]. The ratio between Ca^{2+} and OH^- concentrations in the leachate is
373 generally around 2. Based on this observation, a quantity of positive charges has been
374 calculated for the different mixtures, and correlated to the quantity of leached OH^- . The

375 cations considered are those belonging to the alkaline and alkaline earth metals groups, i.e.
 376 sodium, calcium and magnesium, each pondered by its respective charge. The quantity is then
 377 expressed in Equation 3.

378
$$\text{Cations} = n(\text{Na}^+) + 2n(\text{Ca}^{2+}) + 2n(\text{Mg}^{2+}) \quad \text{Equation (3)}$$

379 Fig. 6 displays the evolution of Cations as a function of hydroxide anions. The first
 380 observation is a good correlation ($R^2 > 0.99$) for all the mixtures, showing that both
 381 components are ruled by the same mechanism and follow similar kinetics.



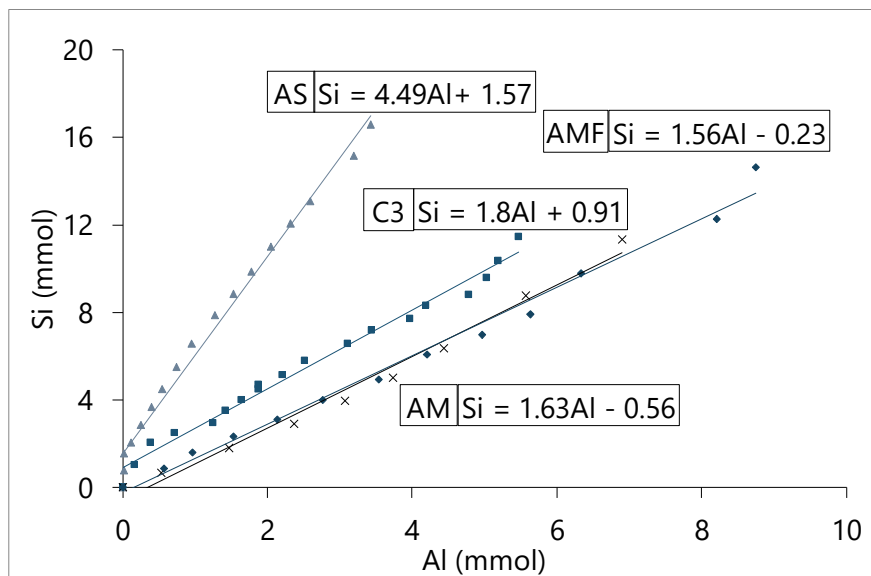
382

383 **Fig. 6.** Correlations between the leached cations and OH⁻

384 For AS the Cations-to-hydroxide ratio is relatively high (~1), the value is lower for C3 and the
 385 other mixtures. For the geopolymer mortars, this can be attributed to the nature of the alkaline
 386 pore solution, where alkaline cations are associated to hydroxide anions [61]. Another
 387 explanation could be the dissociation of the hydroxyl groups present in the aluminosilicate
 388 network [69]. These ions are present either in terminal sites in the geopolymer chains or result
 389 from the ejection of aluminum tetrahedra after the acid attack. Allahverdi and Skvara
 390 suggested the steps of this process and its consequences in [23]. In the case of C-S-H
 391 structures found in hydrated cement [70], the exposition to acid environments causes the **loss**

392 of OH⁻ ions and a deterioration of the chains due to their decalcification. The offset present in
393 the AMF curve is related to the quantity of sodium released at the start of the experiment, as
394 seen in Fig. 5, then the ratio is exactly the same as AM.

395 Among the multiple correlations that can be investigated, the silicon-to-aluminum ratios are
396 particularly interesting for the aluminosilicate materials. Fig. 7 shows a good correlation
397 between the leached quantities of these two elements for the AM and AS samples.



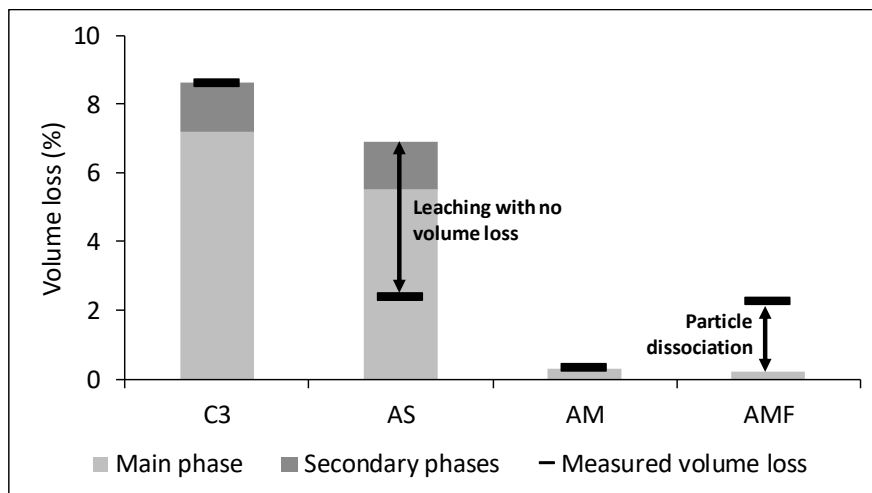
398

399 **Fig. 7.** Leached Si as a function of leached Al through time

400 Since they are generally associated in the matrix (the geopolymer network in AM [69] and the
401 C-A-S-H gel in AS [25]), this pattern is expected. By comparing the slopes of the curves to
402 the initial Si/Al ratios in both materials, some conclusions can be drawn. In AM, the initial
403 theoretic ratio is 1.83, but the leaching produces Si and Al with a growing ratio that reaches
404 1.63 after 4 months. This is most likely because Al are released first due to the lower bond
405 dissociation energy of the “Al-O-Si” bonds compared to the “Si-O-Si” bonds [71]. This
406 results in a more siliceous network, as described in [23]. For the AS mixture, the leaching
407 ratio is much closer to the initial Si/Al, which is 4.56. This shows that these two elements are
408 mainly associated in the hydrate phases and are subjected to similar effects of the acid attack.

409 The degradation of the binder is then more uniform and it is mainly driven by the dissolution
 410 of calcium which weakens the C-A-S-H structure [72]. In C3, the leached Si/Al ratio is much
 411 lower than the initial ratio of the material (1.8 versus 2.86). This indicates that the aluminum
 412 hydrates are more vulnerable to the attack and are thus more easily dissolved [73]. Combined
 413 to the loss of calcium ensuing from the dissolution of portlandite, this fact leads to more
 414 decalcified and poorly structured silicon products in the damaged zone [74].

415 Based on the initial compositions of the grouts, an equivalent volume composition can be
 416 calculated for the mortars. It can be used to determine the volume of material loss by
 417 converting the amounts of leached ions into dissolved volumes (Fig. 8). This calculation
 418 highlights the presence of an excess of leached calcium in C3 and AS for example, explained
 419 by the presence of secondary hydrated phases.



420

421 **Fig. 8.** Volume loss: calculated vs. measured

422 It also highlights the disproportionate amount of particles (sand and fly ash) that were
 423 dissociated from the AMF sample and lead to a higher volume loss than predicted by
 424 chemical calculations. The influence of curing methods on the strength development of alkali-
 425 activated bottom ash has been investigated recently [75]. The authors concluded that seal
 426 curing is more suitable, as the leaching of OH⁻ and free alkali affects the strength

427 development. The strength of AMF samples could have been lower than expected due to
428 leaching of activating solution while fly ash particles had not fully reacted. On the contrary, in
429 the AS sample, the leached quantities of matter should have corresponded to a higher volume
430 loss than the one measured. A possible modification in the density of the outer layer, with the
431 formation of a lighter gel structure could explain this difference. Shi and Stegemann [30] have
432 suggested the development of a protective gel layer that prevented the excessive corrosion of
433 the material in the case of alkali-activated slag. This was confirmed by Sturm et al. [20]; silica
434 gel precipitates at the mortar/acid interface, due to the low solubility of silica at low pH,
435 inhibiting further degradation of the mortar. Bernal et al [34] mentioned an aluminosilicate
436 type gel resulting from the decalcification of alkali-activated slag exposed to acetic acid at pH
437 4.5. In our study, there could be a similar phenomenon, with the formation of a barrier that
438 slows the degradation of the binder, while still allowing the leaching of some elements. The
439 measured volume via hydrostatic weighing would then show a lower value than predicted by
440 the loss of matter.

441 **4. Conclusion**

442 The experimental study presented in this paper focuses on the resistance of cement-based and
443 alkali-activated materials to acid leaching. A new combination of macroscopic and chemical
444 indicators was proposed in order to understand the behavior of four binders, namely: slag
445 cement, activated slag, activated metakaolin, and activated metakaolin with fly ash. The
446 evolution of the global indicators and chemical analyses were associated with the direct
447 observation of cross sections through SEM/EDS and X-ray microtomography. Based on the
448 results presented in this paper the following conclusions can be drawn:

- 449 • At relatively low pH value of 3.5, the mortar mixture based on slag cement showed
450 significant mass and volume losses, whereas activated metakaolin showed good

451 stability after 4-month exposure in controlled conditions. The performances of
452 activated slag and activated metakaolin with fly ash were intermediate.

453 • Leaching resulted in a reduction of the cross section of exposed specimens. The
454 remaining part of metakolin-based materials was physically sound, whereas slag-based
455 materials showed a leaching front and a damaged depth attributable to the dissolution
456 of calcium-rich phases.

457 • Whatever the binder composition, sodium was the most leachable element. However
458 its release from binding phase did not result in significant damage of the material. This
459 can be attributed to its replacement by H_3O^+ ions to balance the [aluminates](#) negative
460 charges.

461 • The silicium-to-aluminium ratio of the leachate provides valuable information about
462 the nature of hydration and alkali-activation products affected by leaching. Both
463 elements are actually the main constituents of the binding phases, N-A-S-H or
464 “geopolymer network” in activated metakaolin, and the C-A-S-H gel in activated slag.

465 • The amount of leached ions was converted into an equivalent mortar volume loss and
466 compared with the direct measurement of the volume loss. This highlighted different
467 behaviors of the studied materials which could not be predicted from their
468 composition. It showed an excess of leached calcium for slag cement and activated
469 slag, explained by the presence of secondary hydrated phases. Activated metakaolin
470 with fly ash was characterized by a significant loss of sand and unreacted fly ash
471 particles.

472 From the results of the study, materials based on activated metakaolin showed good
473 performance at low pH values, for which cement-based materials cannot be directly exposed
474 to acid solution. Although the replacement of metakaolin by fly ash could be valuable in
475 terms of rheology or cost, it affected the resistance to leaching. [Acid leaching should be](#)

476 combined with other ions to investigate the behavior of alkali-activated materials in real
477 exposure conditions. This performance still needs to be associated to other engineering
478 properties and volume stability in order to recommend the use of these materials in severe
479 conditions.

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