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1            **Behavior of calcined clay based geopolymers under sulfuric acid attack: Meta-illite and**  
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4  
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8            **Abstract**

9            Durability of geopolymers in aggressive environments are encouraging but deeper investigations are  
10            needed to understand the acid resistance of calcined clay geopolymers. This paper compares the behavior  
11            of four different calcined clay-based geopolymers under sulfuric acid attack and gives insights into the  
12            degradation mechanisms of meta-illite based geopolymers, which had not been addressed in the literature  
13            until now. Paste samples were cast using metakaolin and meta-illite as the precursors and were activated  
14            by either sodium silicate or potassium silicate solutions. After curing, geopolymers pastes were  
15            submerged in sulfuric acid solution at pH 1 for 30 days. Mineralogical, microscopic, and chemical  
16            analyses indicated that geopolymer pastes were affected by leaching of alkali cations into the immersion  
17            solution, and thus by a disequilibrium of the geopolymer network. Among all materials, meta-illite based  
18            geopolymers activated by sodium silicate presented the least damage and hold promise for improving the  
19            durability of materials under sulfuric acid attack.

20  
21            **Keywords:** geopolymerization, durability, alkali activated material, sulfuric acid attack, calcined clay,  
22            sodium silicate, potassium silicate

## 24 1. Introduction

25 Concrete structures may be susceptible to bio-deterioration in wastewater networks and other  
26 fermentation or methanogenesis environments due to complex mechanisms of sulfate/acid attacks. For  
27 instance, the so-called Microbially Induced Corrosion of Concrete (MICC) in sewer environments is a  
28 multi-step process occurring in the presence of anaerobic bacteria that reduce sulfate ions ( $\text{SO}_4^{2-}$ ) into  
29 hydrogen sulfide ( $\text{H}_2\text{S}$ ) [1–3]. Solutions containing  $\text{H}_2\text{S}$  present very low pH values (e.g., pH 1 and pH 3),  
30 which, on conventional concrete, lead to a decrease in pH of the material surface (around 9) [4–9]. This  
31 condition and the presence of sulfur develop a suitable environment for sulfur-oxidizing bacteria, which  
32 oxidize the reduced sulfur into  $\text{H}^+$  and  $\text{SO}_4^{2-}$  [10,11]. Ordinary Portland Cement (OPC) has shown poor  
33 performance under sulfuric acid attack due to the leaching of Ca-rich phases and the formation of  
34 expansive products such as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) leading to material loss [3,12]. Therefore, it is  
35 necessary to improve the durability of construction materials under sulfuric acid environments.  
36 Preliminary investigations carried out on geopolymers (Ca-poor materials) in aggressive environments are  
37 encouraging, especially for fly-ash based geopolymers [13–18]. However, deeper investigations are  
38 needed to understand the acid resistance of calcined clay geopolymers.

39 Geopolymers are alternative materials to OPC and are made by mixing solid powders that are sources  
40 (precursors) of aluminosilicates (e.g., calcined clays, fly ashes) with alkaline activating solutions (alkali  
41 silicate-based or alkali hydroxide-based such as sodium (Na) or potassium (K) based activators, for  
42 example) [19–21]. The reaction produced between the precursors and the alkaline solution is referred to  
43 as “geopolymerization”. Clay minerals (phyllosilicates) are natural aluminosilicate resources, in which  
44 silicon (Si) is in 4-fold coordination, while aluminum (Al) is in 4-, 5- or 6-fold coordination [22–24].  
45 After calcination, Al coordination changes from 6-fold to 4-fold and the precursor becomes amorphous  
46 (loss of crystallinity), which enables its dissolution in the alkaline solution [23]. After geopolymerization,  
47 a three-dimensional synthetic material is obtained and is referred to as “Si-O-Al-O network”, where Si  
48 and Al are both in 4-fold coordination [19,25]. The charge in the geopolymer network is balanced by the

49 alkali cations ( $K^+$  and  $Na^+$ ) [25]. In these materials, water is found in several states: slightly confined  
50 water in the porosity, physically bound water at the pore surface, and water in the hydration sphere of  
51 alkali cations [26].

52 Among the different clay minerals studied in the literature, kaolinite has been very popular for its  
53 potential as a precursor in alkali activated materials [24]. Gao et al., 2013 [27] studied a metakaolin (MK)  
54 geopolymer activated by K-silicate under hydrochloric acid (HCl) at pH 2 and showed that the  
55 geopolymer network was relatively stable during the first 28 days of testing. Up to this point, little  
56 damage was attributed to the exchange of  $K^+$  with  $H^+$  ions in the solution, which increased the number of  
57 Si-OH and Al-OH groups in the geopolymer. Similarly, Bouguermouh et al., 2017 [28] reported that MK-  
58 based geopolymers activated either by K-silicate or by Na-silicate showed good resistance to HCl.  
59 Conversely, Vogt et al., 2020 [29] showed that MK-based geopolymer activated by K-silicate presented  
60 degradation after sulfuric acid attack, due to the release of  $K^+$  into solution, followed by the  
61 dealumination and depolymerization of the geopolymer. Similarly, Grengg et al., 2021 [30] studied a low-  
62 Ca MK-based geopolymer (CaO = 2.5 wt.%) activated by K-silicate with addition of Cu under sulfuric  
63 acid attack at pH 2. The authors indicated that, after 35 days of exposure, the material presented complete  
64 dissolution of the geopolymer framework and the precipitation of expansive sulfate phases.

65 As previously exposed, the literature about acid resistance of calcined clay geopolymers mainly focuses  
66 on metakaolin (calcined kaolinite) based systems [27,29,31] and data on the acid resistance of other  
67 calcined clay based geopolymers is practically inexistent. Nonetheless, other common calcined clays (i.e.,  
68 meta-illite) have been studied in the literature as Portland cement replacements due to their potential  
69 pozzolanic activity, low cost, abundant availability, and low  $CO_2$  emission in addition to their good  
70 mechanical performance [32]. Therefore, the present publication focuses on the study of two calcined  
71 clays: metakaolin (MK) and meta-illite (MI) used as precursors for the fabrication of geopolymers. These  
72 two calcined clays belong to the two main groups of clay minerals, referred to as 1:1 and 2:1 minerals,  
73 respectively [22,33]. These ratios refer to the crystallographic structures of the clay minerals, which

74 consist of regular repetition of tetrahedral and octahedral sheets. Tetrahedral sheets are usually  $\text{Si}^{4+}$  or  
75  $\text{Al}^{3+}$  (each cation surrounded by four oxygens) and octahedral sheets are either divalent cations ( $\text{Mg}^{2+}$ ,  
76  $\text{Fe}^{2+}$ ) or trivalent cations ( $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ) [22,24,33]. This paper aims to (i) compare the resistance of MK and  
77 MI based geopolymers under sulfuric acid ( $\text{H}_2\text{SO}_4$ ) attack, and (ii) gain insights into their degradation  
78 mechanisms. Four different geopolymer pastes were cast using MK and MI precursors and were activated  
79 by two different alkaline solutions (Na-silicate and K-silicate). Sulfuric acid attack of geopolymers was  
80 performed under highly aggressive conditions by submerging 28 day cured paste samples in an  $\text{H}_2\text{SO}_4$   
81 solution at pH 1 for 30 days. The resistance of the geopolymers to sulfuric acid was assessed by direct  
82 observations and by measuring the mass change of samples over time. To understand the degradation  
83 mechanisms, the chemical composition of the immersion solutions was determined, and mineralogical  
84 and microscopic characterizations were performed on the geopolymers before and after sulfuric acid  
85 attack.

## 86 **2. Materials and Methods**

### 87 **2.1. Materials**

#### 88 **2.1.1. Binders/precursors**

89 The chemical compositions of the calcined clays (precursors) and the reference binder (ordinary Portland  
90 cement) were obtained by X-ray fluorescence and are presented in Table 1. The precursors/binders tested  
91 were:

- 92 - Ordinary Portland cement (CEM I), CEM I 52.5 N CE CP2 NF, from LAFARGE. This cement has  
93 a specific gravity of  $3.15 \text{ g/cm}^3$  and a Blaine specific surface of  $4160 \text{ cm}^2/\text{g}$ . It was used as the  
94 reference binder.
- 95 - Metakaolin (MK) manufactured at Fumel by ARGECO, with a specific gravity of  $2.59 \text{ g/cm}^3$  and a  
96 BET specific surface area of  $17 \text{ m}^2/\text{g}$ .

97 - Meta-illite (MI) manufactured by VICAT, with a specific gravity of 2.59 g/cm<sup>3</sup> and a BET specific  
 98 surface area of 20 m<sup>2</sup>/g.

99 **Table 1** Chemical compositions of the binder/precursors, obtained by X-ray fluorescence (% by weight).

	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	MnO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	TiO <sub>2</sub>	LOI*
CEM I	65.5	20.6	4.3	2.4	0.7	0.1	0.1	0.2	3.1	0.2	2.7
MK	0.7	68.2	23.4	3.6	1.2	0.0	0.2	0.2	0.0	1.2	1.2
MI	4.4	52.7	25.5	7.0	3.5	0.1	0.3	2.9	0.0	1.0	2.6

100 \*Loss on ignition, T= 1000°C

101  
 102 The mineralogical compositions of MK and MI precursors are presented in Table 2 and were obtained by  
 103 XRD Rietveld analyses following the parameters described in Trincal et al., 2014 [34] and previously  
 104 published in Lahalle et al., 2021 [35].

105 **Table 2** Mineralogical composition of the metakaolin (MK) and meta-illite (MI) estimated by XRD Rietveld  
 106 analyses (% by weight).

	Amorphous	Quartz	Illite	Mullite	Anatase	Calcite	Hematite	Rutile
MK	47.1±2.5	42.3±1.6	3.5±0.5	3.1±0.4	1.5±0.1	1±0.1	0.9±0.1	0.3±0.1
MI	61.3±7.9	13.5±2.3	19.0±6.7	-	-	2.6±1.6	2.0±1.4	1.7±1.7

### 107 2.1.2. Activators

108 MK and MI were activated by two different commercial products:

109 - Na-silicate solution with an SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio of 1.7, specific gravity of 1.55 g/cm<sup>3</sup> at 20 °C  
 110 (Betol<sup>®</sup> 47T: 27.5% SiO<sub>2</sub>, 16.9% Na<sub>2</sub>O and 55.6% H<sub>2</sub>O, % by weight).

111 - K-silicate solution with an SiO<sub>2</sub>/K<sub>2</sub>O molar ratio of 1.7, specific gravity of 1.5 g/cm<sup>3</sup> at 20 °C  
 112 (Geosil<sup>®</sup> 14517: 24% SiO<sub>2</sub>, 21% K<sub>2</sub>O and 55% H<sub>2</sub>O, % by weight).

### 113 2.1.3. Sample preparation and curing

114 MK-based geopolymer pastes activated either by Na-silicate or by K-silicate are referred to as “MK\_Na”  
 115 and “MK\_K”, respectively. MI-based geopolymer pastes activated either by Na-silicate or by K-silicate  
 116 are referred to as “MI\_Na” and “MI\_K”, respectively. For all the geopolymer pastes, the water content of  
 117 the commercial solutions was adjusted to obtain a water to solid (w/s) ratio of 0.4. “Solid” consisted of  
 118 the total amount of calcined clay and the dry part of the activating solution (SiO<sub>2</sub>, Na<sub>2</sub>O and K<sub>2</sub>O).

- 119 • MK\_Na and MI\_Na: MK and MI precursors were activated by adding Na-silicate solution at  
 120 77 wt. % and 78.9 wt. %, respectively (% by weight of precursor).
- 121 • MK\_K and MI\_K geopolymers: MK and MI precursors were activated by adding K-silicate  
 122 solution at 78 wt. % and 78.2 wt. %, respectively.

123 The amorphous and quartz contents were different in the two precursors (MK and MI). Thus, the amount  
 124 of reactive binder varied since only the amorphous part of calcined clays is considered to react during the  
 125 alkali activation process. To avoid misleading conclusions, CEM I and MI geopolymer pastes were  
 126 prepared using the same quartz content as in MK precursor. Therefore, a content of 50 wt. % quartz was  
 127 targeted for all the formulations (crushed sand < 120 μm). It should be noted that samples prepared in this  
 128 study were all pastes containing equivalent quartz amounts and they should not be confused with mortars.

129 All pastes were prepared following the recommendations of European Standard NF EN 196-3 and using a  
 130 hand held electric mixer as described in Lahalle et al., 2021 [35]. Pastes were cast into hermetic,  
 131 cylindrical PVC molds 6 cm in length and 3 cm in diameter and stored for 28 days in a room at T=20 °C,  
 132 RH=50% until characterization and acid immersion. The mix design of all the geopolymer pastes is  
 133 presented in Table 3.

134 **Table 3** Mix design of all the geopolymer pastes.

CEM I (g)	MK (g)	MI (g)	Quartz <sup>a</sup> (g)	Activator <sup>b</sup> (g)	Water activator <sup>c</sup> (g)	Dry activator <sup>d</sup> (g)	Added water <sup>e</sup> (g)	w/s <sup>f</sup>
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CEM I	250	-	-	250	-	-	-	400	0.4
MK_Na	-	500	-	-	385 <sup>g</sup>	213	171	51	0.4
MK_K	-	500	-	-	390 <sup>h</sup>	216	174	55	0.4
MI_Na	-	-	289	211	228 <sup>g</sup>	127	101	114	0.4
MI_K	-	-	289	211	226 <sup>h</sup>	125	100	116	0.4

135 <sup>a</sup> Total amount of quartz added to the mixture, which is equivalent to the quartz content present in the MK  
136 precursor.

137 <sup>b</sup> Total amount of the activator.

138 <sup>c</sup> Water coming from the activator.

139 <sup>d</sup> Dry part coming from the activator.

140 <sup>e</sup> Supplementary added water.

141 <sup>f</sup> Effective water content to solid ratio (solid: anhydrous binder + sand + dry activator).

142 <sup>f</sup> Na-silicate

143 <sup>g</sup> K-silicate

## 144 2.2. Methods

### 145 2.2.1. Sulfuric acid attack test

146 After curing, all paste samples were kept into the original plastic molds for the sulfuric acid tests. In order  
147 to cause unidirectional attack, only the top of the samples was exposed. The top borders of the plastic  
148 molds (i.e., edges) were protected/sealed with a commercial epoxy resin (Resoltech 3030 BLANC) to  
149 avoid penetration of the solution into the recipient. Twenty-four hours after application of the resin, five  
150 samples per formulation were taken for sulfuric acid tests. First, all samples were weighed and then,  
151 submerged in a sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) solution prepared with distilled water and having a pH of 1±0.3.  
152 Paste samples were not previously saturated before sulfuric acid attack to avoid disequilibrium in the pore  
153 solution of geopolymers and thus, to avoid misleading conclusions [36]. The H<sub>2</sub>SO<sub>4</sub> solution was stored  
154 in closed individual plastic buckets keeping a liquid to solid (L/S) ratio of 20 (i.e., 3.7 litres of solution  
155 per bucket and per formulation) and stored in a room at T=20 °C. Direct observations and mass change  
156 measurements were made over time for a total of 30 days (results are presented for 1, 5, 12, 20 and 30  
157 days). Values are presented as the arithmetic mean of all results, with a confidence interval of 95%.

158 Moreover, the pH of the solutions was manually monitored over time using a digital pH meter. Since pH  
159 was stable at 1±0.3, solutions were not renewed during the test. Major element concentrations were  
160 determined in the immersion solutions by Inductively Coupled Plasma Atomic Emission Spectrometry



161 (ICP-AES using a Perkin Elmer Optima 7000 DV) after 4 hours of immersion (referred to as 0.17 d) and  
162 at 2, 5, 20, and 30 days of testing. All solution samples were diluted by a factor of 25 using ultrapure  
163 water (18.2 MΩ.cm) at 2 % nitric acid (HNO<sub>3</sub>) (v/v). Sulfate concentrations were determined by ion  
164 chromatography (Dionex Ion Chromatography System ICS-3000) and solutions were diluted by a factor  
165 of 250 using ultrapure water (18.2 MΩ.cm). Two solution samples were analyzed per formulation and  
166 arithmetic mean values were calculated with a confidence interval of 95%.

### 167 **2.2.2. SEM/EDS analyses**

168 Scanning electron microscope (SEM) observations were performed on carbon-coated calcined clays and  
169 polished sections of geopolymer pastes previously mounted in resin. Two different scanning electron  
170 microscopes were used, a JEOL JSM-6380LV and a JEOL JSM 7800, equipped with  
171 Rontec XFLASH 3001 and SDD X-Max 80 mm<sup>2</sup> electron dispersive spectroscopy (EDS) detectors,  
172 respectively. A series of 10 images and about 300 EDS points were taken per sample during the analyses.  
173 Images were obtained in both secondary electron (SE) and backscattered electron (BSE) configuration,  
174 applying magnifications between 25x and 100,000x. EDS mappings were obtained over a relatively large  
175 area (5000 x 3000 μm) by applying a low magnification of 25x and covering the transition zones between  
176 the unaltered and altered zones of geopolymers after sulfuric acid attack.

### 177 **2.2.3. XRD, FT-IR and MAS NMR analyses**

178 All samples, geopolymer pastes before and after (altered layer of the geopolymers) sulfuric acid attack,  
179 were crushed manually in an agate mortar to a particle size below 80 μm (sieve control) and dried in an  
180 oven at 40 °C to remove the free water. Then, all samples were investigated by X-ray diffraction (XRD),  
181 Fourier-Transform Infrared Spectroscopy (FT-IR) and solid-state magic-angle spinning nuclear magnetic  
182 resonance (MAS NMR) analyses.

183 XRD analyses were performed by using a Bruker D8 diffractometer in Bragg-Brentano configuration  
184 with a copper radiation source (Cu K $\alpha$ ,  $\lambda=1.54 \text{ \AA}$ ). The diffractometer was equipped with a vertical theta /  
185 theta goniometer, a LynxEye XE-TTM high-speed linear detector and a motorized anti-scattering knife.  
186 The anticathode voltage was 40 kV, and the electric current intensity was 40 mA.  $2\theta$  angles from  $5^\circ$  to  
187  $70^\circ$  were scanned with a  $2\theta$  step size of  $0.02^\circ$  and a total scan duration of 2.5 hours. Minerals were  
188 identified using the Bruker-AXS DIFFRACplus Eva v4 software and the 2015 ICDD PDF database.

189 FT-IR analyses were performed to detect structural modifications on absorption bands present in the  
190 geopolymers. Analyses were performed using a Perkin Elmer UATR1 device with a diamond crystal.  
191 Data were collected over the wavenumber range of  $4000\text{-}600 \text{ cm}^{-1}$ . Finally, environmental changes in Al  
192 and Si geopolymer networks were studied by solid state MAS NMR.  $^{27}\text{Al}$  spectra were acquired on a  
193 Bruker AVANCE III spectrometer operating at 221 MHz ( $B_0 = 20 \text{ T}$ ) with a spinning speed of 30 kHz  
194 (2.5 mm zirconia rotors). 1D MAS spectra were acquired after a single short pulse ( $\pi/10$ ) ensuring a  
195 quantitative excitation and quantification of  $^{27}\text{Al}$  central transition and 3072 scans were accumulated with  
196 a recycling delay of 1 s.  $^{29}\text{Si}$  spectra were acquired on a Bruker AVANCE I spectrometer operating at  
197 79 MHz ( $B_0 = 9.4 \text{ T}$ ) with a spinning speed of 6 kHz (7 mm zirconia rotors). Around 2000 scans were  
198 accumulated with a recycling delay of 60 s ensuring the complete relaxation of the signal except for those  
199 of quartz. Chemical shifts were referenced to  $(\text{Al}(\text{NO}_3)_3)$  and (TMS) for  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR  
200 analyses, respectively. For  $^{27}\text{Al}$  MAS NMR analyses, results are presented in terms of Al(IV), Al(V) and  
201 Al(VI), which refer to the coordination numbers. For  $^{29}\text{Si}$  NMR results, coordination numbers are referred  
202 to as  $Q_n$ , where the subscript number indicates the number of bonding oxygens.  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR  
203 spectra were processed using the Dmfit program developed at CEMHTI [37].

#### 204 **2.2.4. Mercury intrusion porosimetry (MIP)**

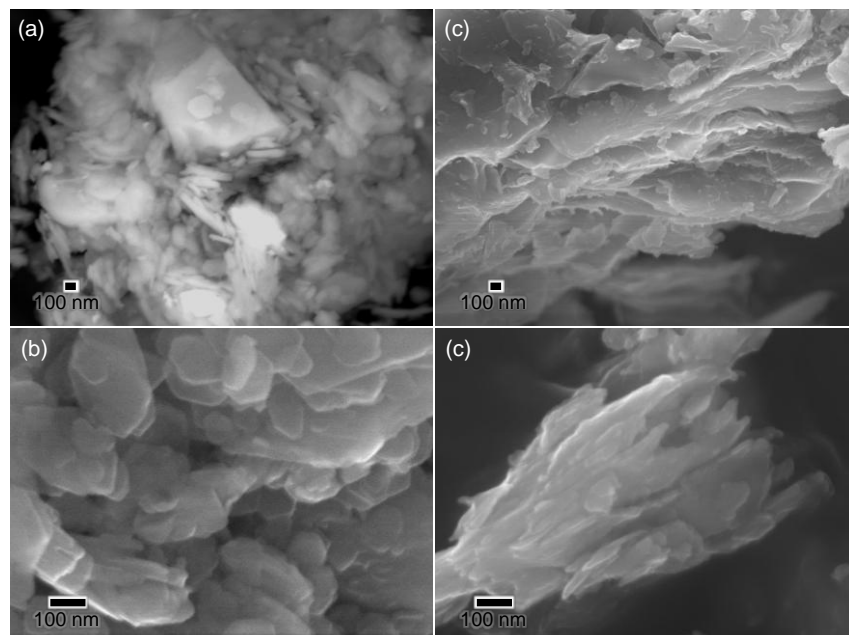
205 Geopolymers pastes, before sulfuric acid attack, were investigated by MIP (AutoPore IV 9500  
206 Porosimeter from Micromeritics according to the standard ISO 15901-1 2005) in order to obtain

207 information on their total porosity accessible to mercury and their pore size distribution. The mercury  
208 pressure used varied from 0.0007 MPa to 400 MPa and information was obtained on pore access  
209 diameters greater than 3 nm. Geopolymer pastes of about 1 g to 3 g were analyzed per formulation and  
210 were not dried before the test but put directly into the penetrometer, which allowed to the dehydration of  
211 samples during the evacuation process in the porosimeter as described by Trincal et al., 2022 [38]. Only  
212 one test was carried out per type of material.

### 213 3. Results

#### 214 3.1. Characterization of samples before sulfuric acid attack

215 The morphology of calcined clays was characterized by SEM observations before geopolymerization. Fig.  
216 1 shows SE images obtained from MK and MI precursors, revealing that microstructures of the two  
217 calcined clays were different. MK presented massive hexagonal flat platelets with lengths of the order of  
218 100-200 nm (cf. Fig. 1a and b). In contrast, MI grain particles displayed an agglomerate of numerous  
219 layers with variable, irregular shapes (cf. Fig. 1c and d).



220

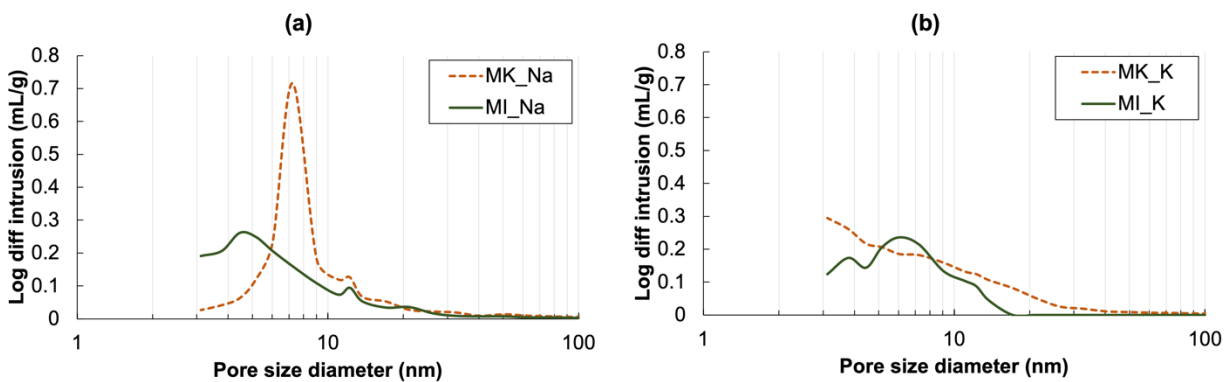
221 **Fig. 1.** SE images obtained from particles of calcined clays (a), (b) metakaolin (MK), and (c), (d) meta-illite (MI).

222 Table 4 gives information on the total volume of mercury intruded for estimation of the total accessible  
 223 porosity, and Fig. 2 presents the pore size distribution determined in unaltered geopolymers at 28 days of  
 224 curing.

225 **Table 4** Total intruded volume of mercury in unaltered pastes, determined by MIP.

Unaltered geopolymer	CEM I	MK_Na	MK_K	MI_Na	MI_K
Total intruded volume (%)	35.2	29.8	30.5	26.5	30.8

226



227

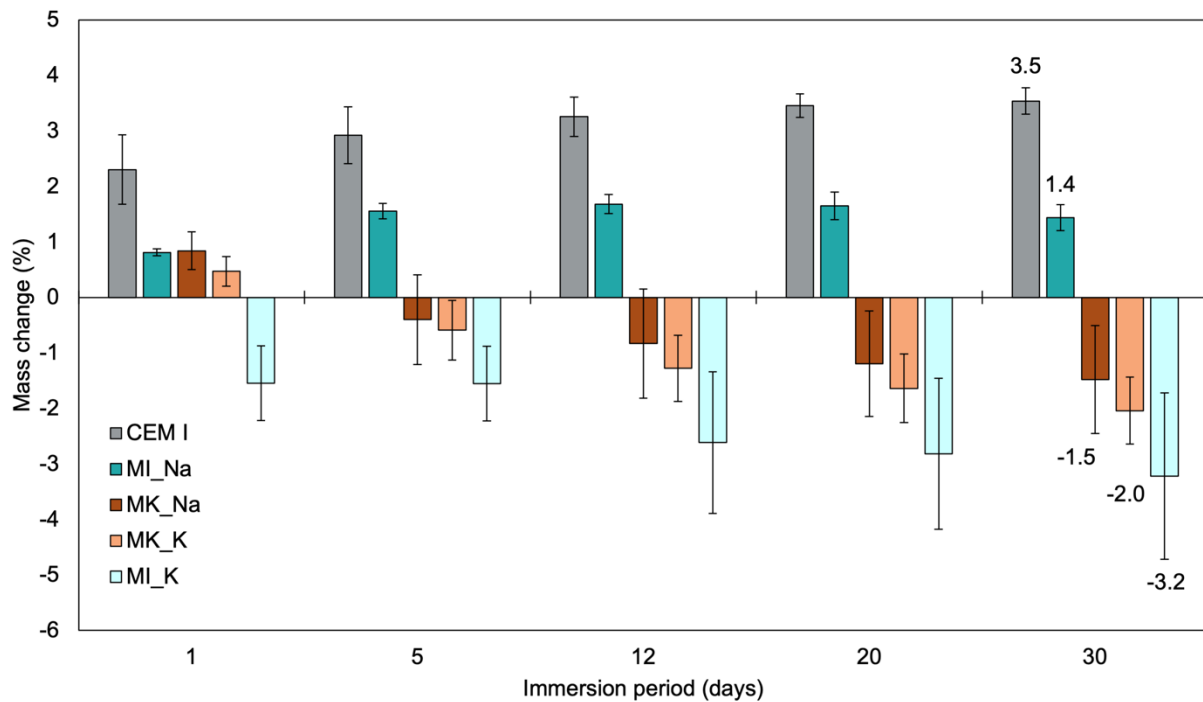
228 **Fig. 2.** Pore size distribution obtained by MIP for unaltered geopolymers. (a) MK\_Na and MI\_Na, (b) MK\_K and  
 229 MI\_K.

230 The results presented in Table 4 and Fig. 2 indicate that geopolymers activated by K-silicate seemed to  
 231 present higher values of total accessible porosity than those activated by Na-silicate. MI\_Na geopolymer  
 232 presented the least total accessible porosity among all geopolymers. Moreover, geopolymers activated by  
 233 Na-silicate exhibited a pore mode, which is in line with observations found in the literature [39,40].  
 234 MK\_Na and MI\_Na geopolymers presented one main population of pore sizes, placed at 7.2 nm and  
 235 4.5 nm, respectively. In contrast, MK\_K geopolymers presented a large range of pore sizes mainly

236 smaller than 20 nm, and MI\_K presented a main population of pore size at 6 nm. Results indicate the  
 237 existence of pore sizes smaller than 3 nm, which were not measured by this method.

238 **3.2. Mass change and direct observations during sulfuric acid attack**

239 Fig. 3 presents the mass change measured over time for CEM I and geopolymer pastes exposed to sulfuric  
 240 acid attack. Table 5 presents the pH evolution measured in the immersion solution over time and Fig. 4  
 241 presents the images obtained from the cross-sectional view of all geopolymers, using an optical  
 242 microscope to evaluate the appearance of the exposed surfaces after sulfuric acid attack.



243

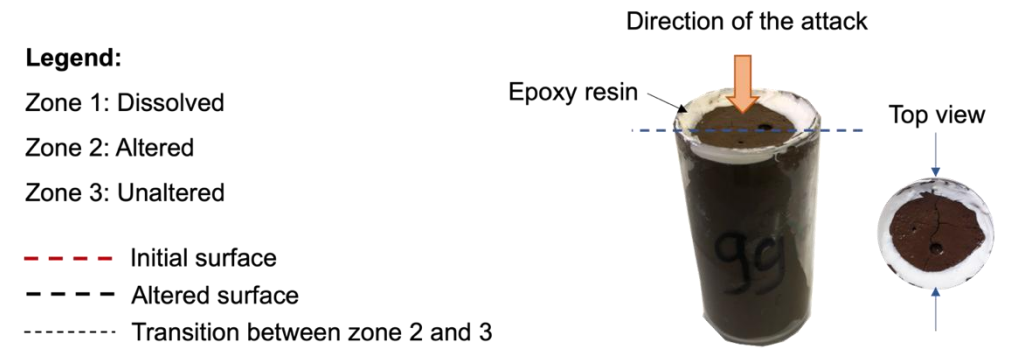
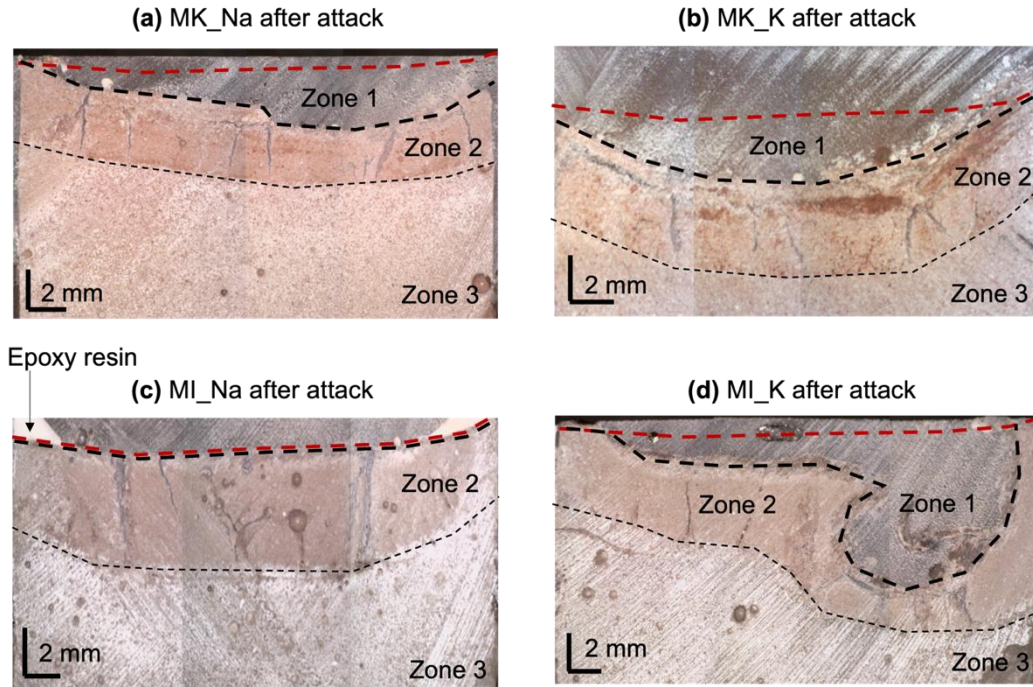
244 **Fig. 3.** Mass change given in percentage, versus immersion period in days for pastes under sulfuric acid attack at pH  
 245 1. Values are presented as the average of five results, with a confidence interval of 95%.

246 **Table 5** Evolution of pH in the sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) immersion solutions of pastes. The pH of the solutions was  
 247 manually monitored over time using a digital pH meter. pH was considered stable at 1±0.3.

Immersion solution/Time (d)	0	1	5	12	20	30
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CEM I	1.21	1.08	1.09	1.11	1.18	1.08
MI_Na	1.20	1.16	1.12	1.13	1.21	1.16
MK_Na	1.14	1.13	1.13	1.21	1.30	1.27
MK_K	1.20	1.10	1.17	1.24	1.27	1.16
MI_K	1.16	1.08	1.13	1.19	1.21	1.24

Optical microscope images – Cross section view

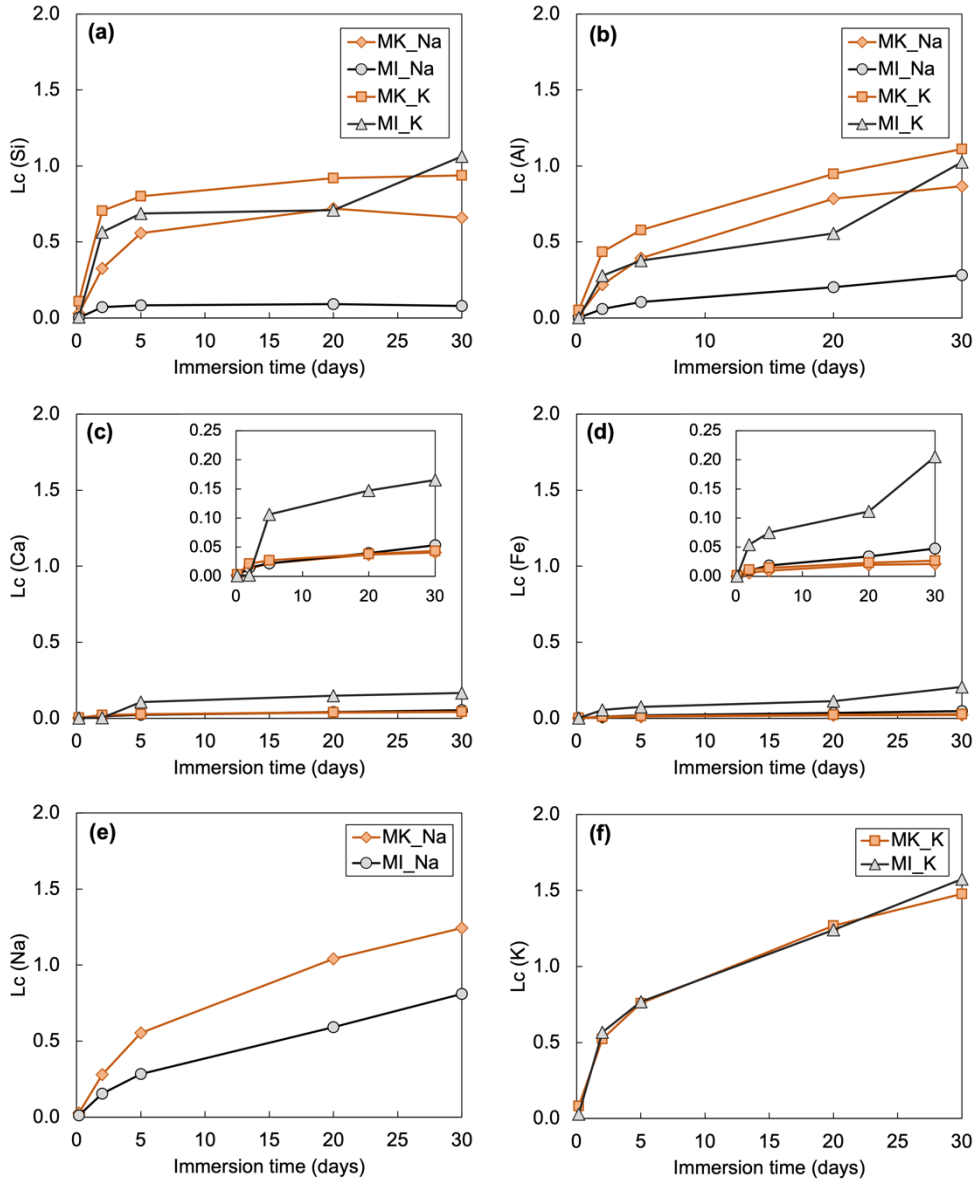


250 **Fig. 4.** Optical microscope images (cross sectional view) of attacked geopolymers. Zone 1: dissolved material, zone  
 251 2: altered geopolymer, and zone 3: unaltered geopolymer. (a) MK\_Na, (b) MK\_K, (c) MI\_Na, and (d) MI\_K.

252 As observed in Fig. 3, all samples (except MI\_K) presented a gain in mass on the first day of immersion,  
253 which was attributed to the uptake of water. At the end of the test (at 30 days), CEM I pastes presented a  
254 gain in mass of  $3.5\% \pm 0.2\%$ , followed by the MI\_Na geopolymer, in which a gain in mass of  $1.4\% \pm 0.2\%$   
255 was obtained. In contrast, MK\_Na, MK\_K and MI\_K geopolymers presented mass losses of  $1.5\% \pm 0.9\%$ ,  
256  $2.0\% \pm 0.6\%$  and  $3.2\% \pm 1.5\%$ , respectively. Furthermore, direct observations of the geopolymer cross-  
257 sections (cf. Fig. 4) allowed the altered (or corrosion) depth layer to be estimated in all the samples. Three  
258 distinct zones were identified: (i) dissolved material, (ii) altered geopolymer (characterized by a layer  
259 about 4-5 mm deep, with microcracks), and (iii) unaltered or non-attacked geopolymer. Fig. 4a and b  
260 show that exposed surfaces of MK\_Na and MK\_K geopolymers were altered and about 2-4 mm of  
261 material had been dissolved at the end of the test. In the case of MI-based geopolymers, MI\_K seemed to  
262 be the most altered material, exhibiting a considerable loss of material (cf. Fig. 4d). Meanwhile, MI\_Na  
263 geopolymer presented an exposed surface that was not visibly dissolved even though several vertical  
264 microcracks were identified (cf. Fig. 4c).

### 265 **3.3. Chemical evolution of the immersion solution**

266 Fig. 5 presents the evolution of the leaching coefficient (Lc) according to time. Fig. 5 allows to compare  
267 the degree of leaching of the geopolymer pastes (MK\_Na, MK\_K, MI\_Na and MI\_K). In the present  
268 paper, the leaching coefficients were calculated according to [41,42] and considering the total volume of  
269 samples submerged in the sulfuric acid solution and thus, the initial molar concentrations of Si, Al, Ca,  
270 Fe, Na, K, Mg and Ti present in the solid fraction of the geopolymers (cf. Table 1) as well as the  
271 additional Si, K, and Na amount coming from the activators (cf. Table 3). A Lc equal to 0 means that the  
272 element was not leached from the geopolymers, and a Lc equal to 100 indicates that the element was  
273 completely leached.



274

275 **Fig. 5.** Evolution of the leaching coefficients (Lc) determined according to time for MK\_Na, MK\_Na, MI\_K and  
 276 MI\_K geopolymers during the sulfuric acid attack. **(a)** Silicon, **(b)** Aluminum, **(c)** Calcium, **(d)** Iron, **(e)** Sodium,  
 277 and **(f)** Potassium.

278 As observed in Fig. 5, the degree of leaching increased over time for all the samples. Overall, the rate of  
 279 Si release into the immersion solution was characterized by an accelerated rate during the first five days.  
 280 After this point, Si concentrations were relatively stable, except for the immersion solution of MI\_K  
 281 geopolymer, in which the concentration of Si increased at the end of the test (cf. Fig. 5a). Regarding the



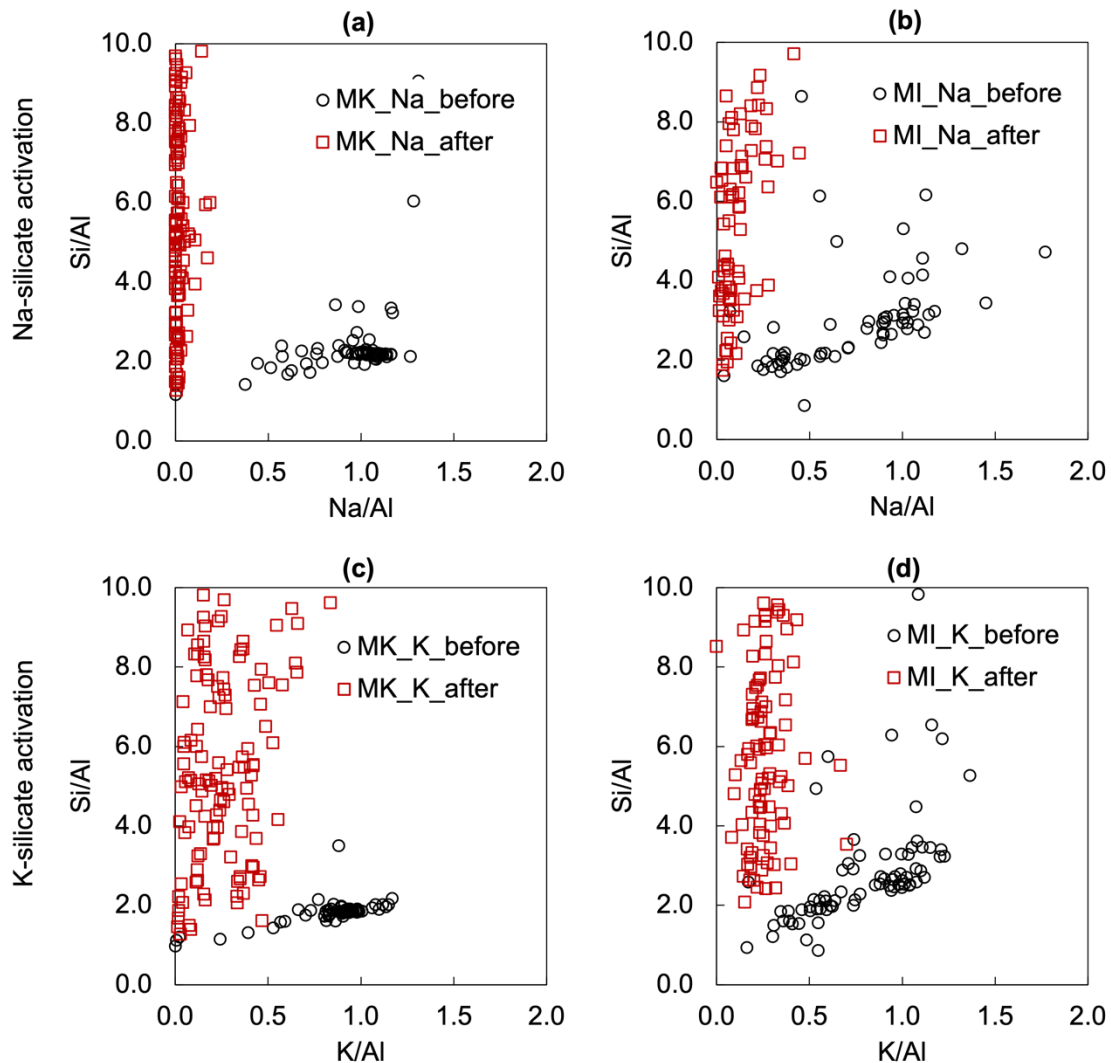
282 behavior of Al, concentrations increased with time for all the geopolymers (cf. Fig. 5b). In either case,  
283 immersion solution of MI\_Na geopolymer exhibited much lower Si and Al concentrations, especially for  
284 the Si concentration, which was relatively stable during the test. In the case of the MI\_K immersion  
285 solution, Al and Si elements exhibited a rapid increase in concentration at the end of the test. Nonetheless,  
286 Al concentrations were slightly higher in the MK\_K immersion solution.

287 On the other hand, the trend of Ca leaching was similar for MK\_Na, MK\_K and MI\_Na geopolymers  
288 increasing linearly over time (cf. Fig. 5c). Among these three geopolymers, MI\_Na presented a higher Ca  
289 concentration in the immersion solution, which is explained by the greater initial concentration of Ca in  
290 the meta-illite (cf. Table 1). On the contrary, the immersion solution of the MI\_K geopolymer presented  
291 very high Ca concentration at the beginning of the test and then leaching kinetics were less rapid.  
292 Similarly, immersion solution of MK\_Na, MK\_K and MI\_Na geopolymers exhibited a low release of Fe  
293 into the solutions, with slightly higher concentrations of Fe for the MI\_Na due to the composition of the  
294 MI, which contains higher amounts of Fe. As for the Ca concentration in the MI\_K immersion solution,  
295 Fe concentrations were higher than those measured for the other geopolymers, and leaching kinetics were  
296 very rapid (cf. Fig. 5d).

297 Finally, Fig. 5e and Fig. 5f present the degree of leaching of Na and K separately. Fig. 5e presents the  
298 results obtained for geopolymers activated by Na-silicate, and Fig. 5f presents the results obtained for  
299 geopolymers activated by K-silicate. Fig. 5e illustrates that Na release into the immersion solution  
300 followed a similar trend in both immersion solutions, in which Na concentrations increased with time.  
301 Nonetheless, the leaching coefficient ( $L_c$ ) of Na was higher in the immersion solution of the MK\_Na  
302 geopolymer. Likewise, the release of K into the immersion solutions of MK\_K and MI\_K geopolymers  
303 presented similar behavior (i.e., K concentration increased with the time of immersion). However, the  
304 immersion solution of the MI\_K geopolymer showed higher K concentrations than those measured for the  
305 MK\_K.

306 **3.4. SEM/EDS characterization**

307 Si/Al and R/Al (R=Na or K) molar ratios were determined by performing EDS pointing analyses in all the  
308 geopolymers before attack (at 28 days of curing) and in the altered zones of geopolymers exposed to  
309 sulfuric acid attack. Fig. 6 presents EDS pointing analyses in the form of mixing diagrams, where R/Al  
310 molar ratios are plotted versus Si/Al molar ratios (x-axis and y-axis, respectively).



311

312 **Fig. 6.** EDS diagrams of Si/Al vs. R/Al molar ratios (R = Na or K) for all geopolymers before (black circles) and  
313 after (red squares) sulfuric acid attack. After sulfuric acid attack, analyses were carried out on the altered zones (cf.

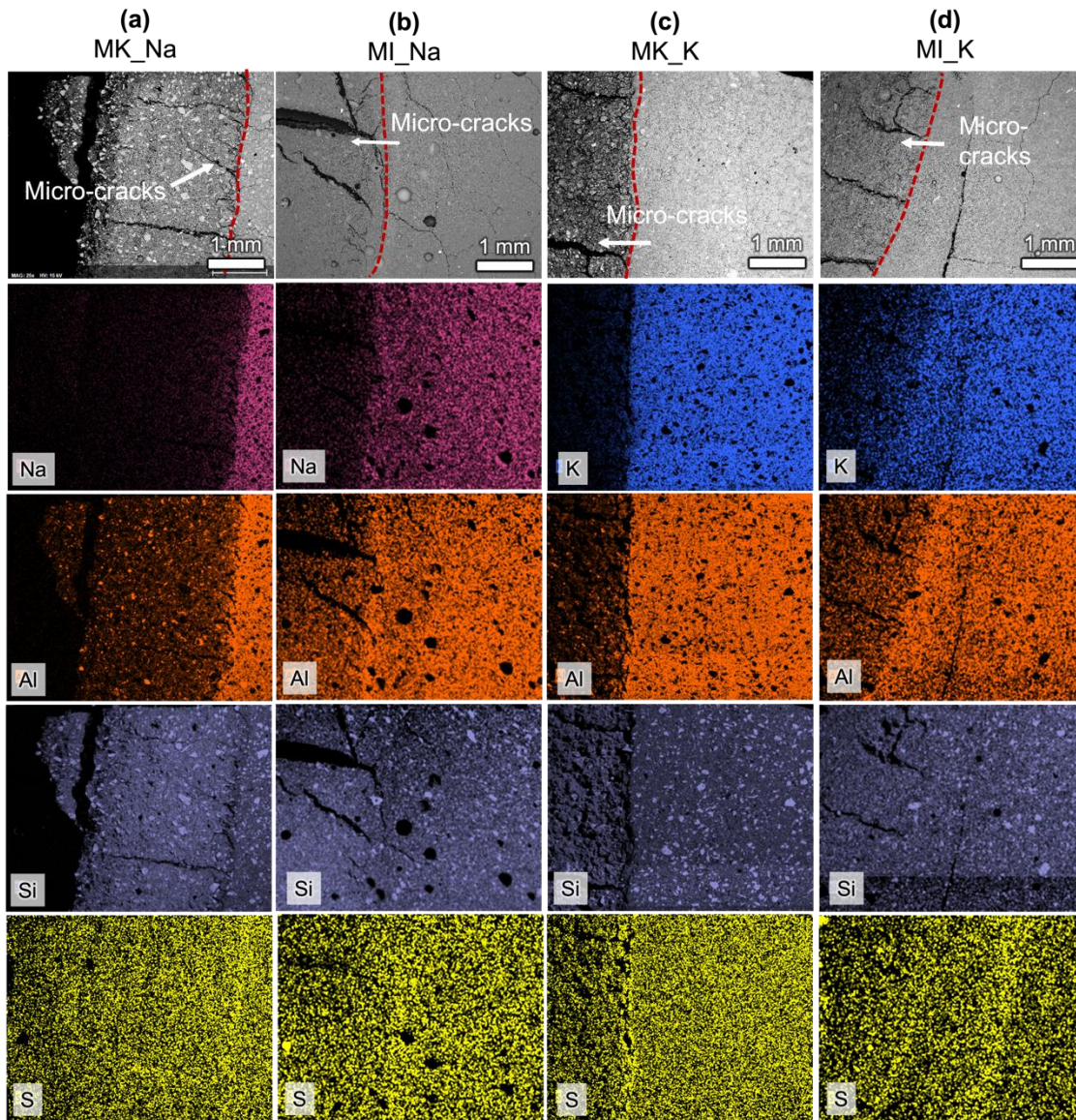
314 Fig. 4). (a) MK\_Na, (b) MI\_Na, (c) MK\_K, and (d) MI\_K.

315 Before attack, MI-based geopolymers exhibited the presence of two populations of points in the Si/Al vs.  
316 R/Al charts, probably due to the presence of non-reactive illite content (about 19 wt. %), which may have  
317 modified the R/Al (R = Na or K) molar ratios (cf. Fig. 6). This would partially explain why arithmetic  
318 average values of Si/Al molar ratios obtained from MI-based geopolymers were slightly higher than those  
319 determined in MK-based geopolymers ( $2.5\% \pm 0.2\%$ ,  $2.4\% \pm 0.2\%$ ,  $2.2\% \pm 0.1\%$ ,  $1.8\% \pm 0.1\%$  for MI\_Na,  
320 MI\_K, MK\_Na and MK\_K, respectively) in addition to a higher amorphous content in the MI precursor  
321 (cf. Table 2). Moreover, Si/Al molar ratios were higher in Na-silicate activated geopolymers (MK\_Na and  
322 MI\_Na) than in K-silicate activated geopolymers (MK\_K and MI\_K). This is explained by the higher Si  
323 concentration in the Na-silicate solution: 27.5% SiO<sub>2</sub> versus 24% SiO<sub>2</sub> in the K-silicate solution (cf.  
324 section 2.1.2).

325 After attack, altered zones of geopolymers displayed higher dispersion of data than before attack.  
326 Moreover, R/Al molar ratios decreased, while Si/Al molar ratios increased compared to the samples  
327 before sulfuric acid attack, which suggests that Al and the alkali content (Na or K) decreased in the  
328 altered zones of geopolymers exposed to sulfuric acid attack. These results are in line with the evolutions  
329 of element concentrations determined in the immersion solutions (cf. Fig. 5) and further details will be  
330 presented in the discussion section.

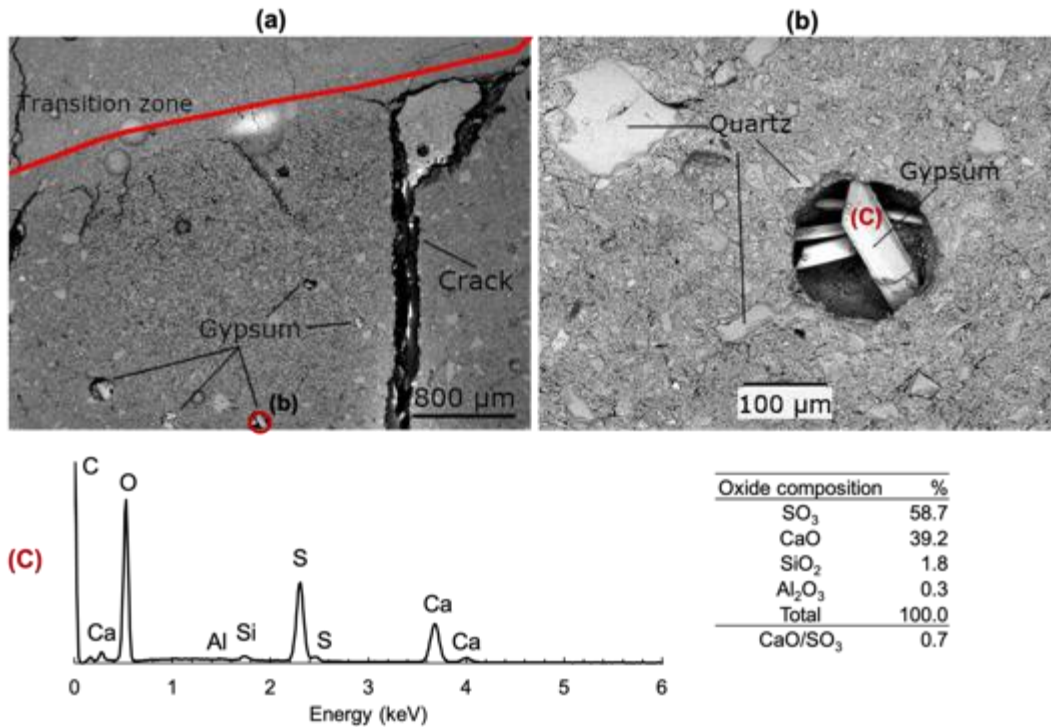
331 EDS mapping was performed on geopolymers after sulfuric acid attack to corroborate the leaching  
332 behavior of elements in the altered zones. Fig. 7 displays EDS mapping for Al, Na, K, Si and S elements.  
333 All geopolymers were characterized by the presence of two distinct zones referred to as altered and  
334 unaltered zones. The transition between these two zones is marked by a red dotted line. Scans of Al, Na  
335 and K elements showed that these elements dropped in concentration in the altered zones. Si and S scans  
336 were difficult to interpret, possibly because Si concentrations were similar in altered and unaltered zones  
337 (further information is presented in section 3.6, in which <sup>29</sup>Si NMR analyses are showed). Moreover, EDS  
338 scans showed that S was not chemically bonded in the geopolymers except in the layer of the altered zone  
339 of the MI\_Na geopolymer, in which gypsum was identified. Fig. 8 presents images obtained from

340 SEM/EDS observations carried out on the altered layer of MI\_Na geopolymers, showing the presence of  
341 gypsum, which precipitated in the pore space, which may modify further ingress of sulfuric acid into the  
342 matrix. Further discussion will be addressed in the discussion section 4.1.



343

344 **Fig. 7.** EDS mapping obtained from the scan of Na, K, Al, Si and S elements in polished surfaces of geopolymer  
345 pastes after sulfuric acid attack. The red dashed line marks the border between altered (left) and unaltered zones  
346 (right) (a) MK\_Na, (b) MI\_Na, (c) MK\_K, and (d) MI\_K.

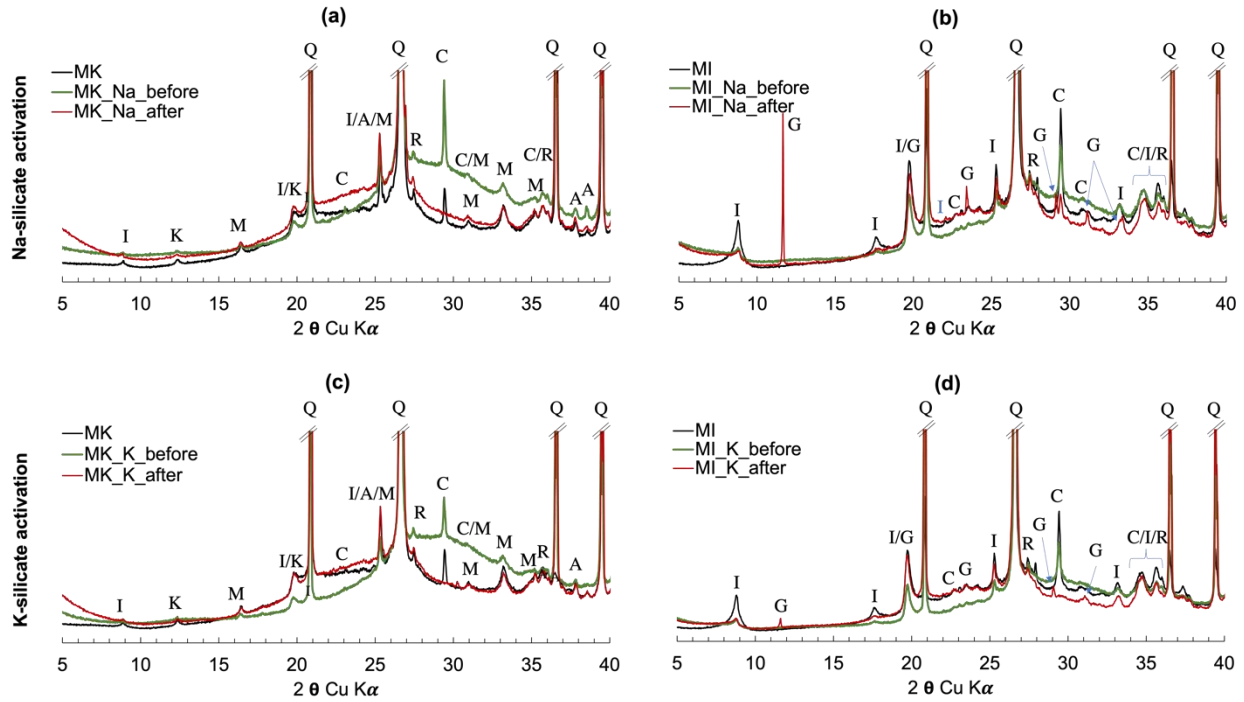


347

348 **Fig. 8.** SEM images of MI\_Na geopolymer after sulfuric acid attack and EDS spectrum of gypsum. (a) Transition  
 349 between altered (bottom) and unaltered zones, (b) zoom on one pore containing gypsum and located in image (a),  
 350 and (c) EDS spectrum and oxide composition of gypsum found in a pore of the altered material.

### 351 3.5. XRD characterization

352 Fig. 9 presents XRD analyses performed on crushed samples taken from geopolymers before acid attack  
 353 and from the altered layer of geopolymers exposed to sulfuric acid. All XRD patterns were plotted in the  
 354 selected range of  $2\theta$  from  $5^\circ$  to  $40^\circ$  to zoom in on the main differences. XRD patterns from the precursors  
 355 (MK and MI) are also plotted for comparison.



A: Anatase, C: Calcite, G: Gypsum, I: Illite, K: Kaolinite, M: Mullite, Q: Quartz, R: Rutile

356

357 **Fig. 9.** XRD patterns obtained from crushed geopolymers activated by Na-silicate (top) and by K-silicate (bottom),  
 358 plotted in the selected range of  $2\theta$  from  $5^\circ$  to  $40^\circ$  to zoom in on the main differences. (a) MK\_Na, (b) MI\_Na, (c)  
 359 MK\_K, and (d) MI\_K. **Black lines:** precursors (MK or MI). **Green lines:** geopolymers before attack. **Red lines:**  
 360 altered layer of geopolymers after sulfuric acid attack.

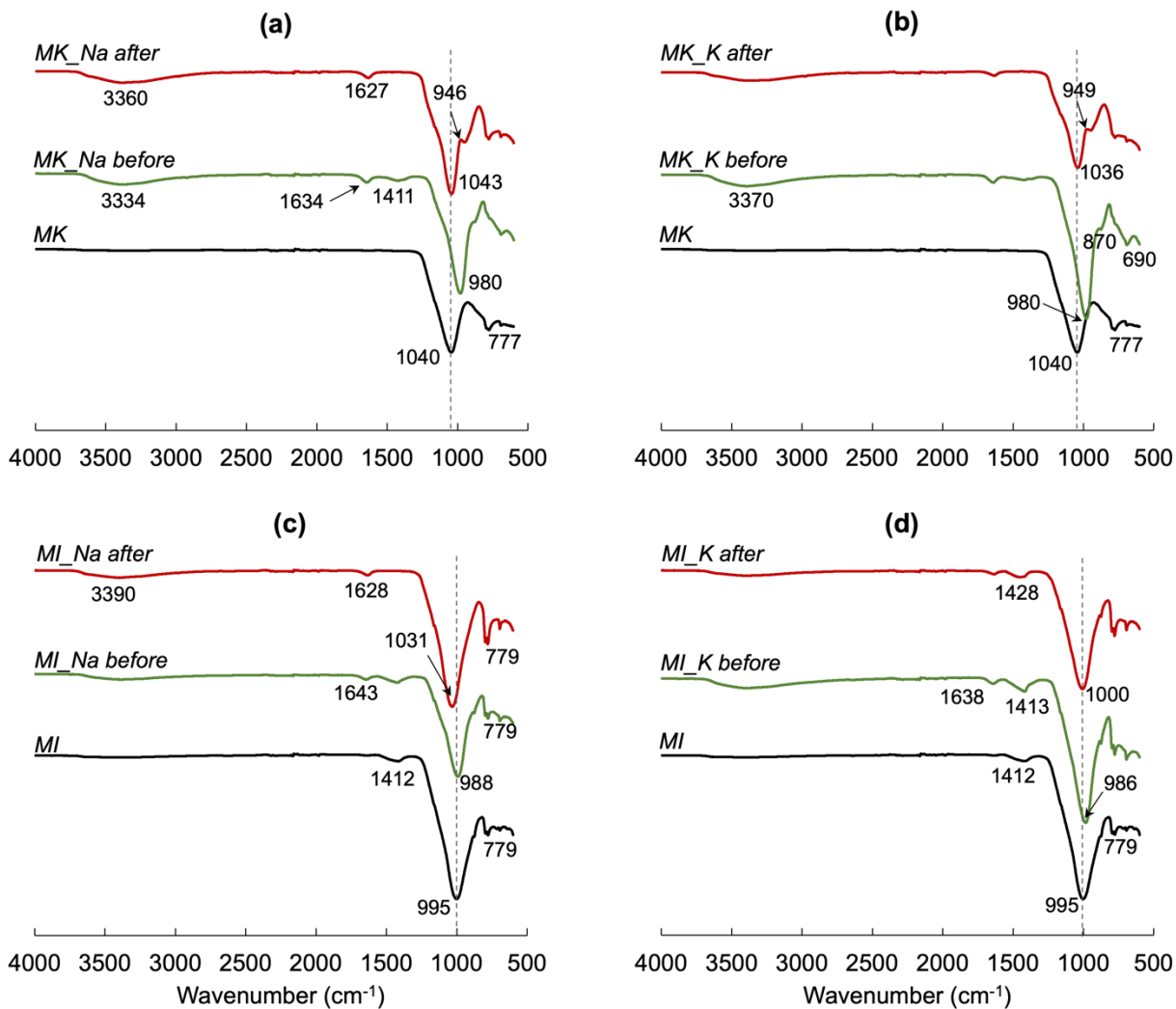
361 XRD patterns obtained from the precursors showed a semi-crystalline structure, in which several main  
 362 common crystallized phases were identified as illite, kaolinite, calcite, rutile and quartz. MK precursor  
 363 also displayed the presence of mullite and anatase. Patterns for both calcined clays presented a hump  
 364 mainly centered at  $2\theta$   $26^\circ$ - $27^\circ$ , which was attributed to amorphous phases [22,43]. After the alkali  
 365 activation process and before the sulfuric acid attack, these humps were broader and shifted toward higher  
 366 degrees ( $2\theta$   $29^\circ$ - $30^\circ$ ) because of the activation, which was accompanied by an increase of the relative  
 367 intensity of amorphous content. The relative intensity of these humps seemed higher in MK-based  
 368 geopolymers than in MI-based geopolymers. Furthermore, peaks originally identified in the precursors  
 369 remained in geopolymer patterns but with reduced relative intensity. This was mainly observed for illite

370 peaks at  $2\theta$   $8^\circ$ - $10^\circ$  and  $2\theta$   $17^\circ$ - $18^\circ$  in the XRD patterns of the MI\_Na geopolymer. These minerals do not  
371 normally participate in the geopolymerization process but present lower intensities due to a dilution effect  
372 [22,28].

373 After sulfuric acid attack, XRD patterns from the altered zones presented the main crystallized phases  
374 originally identified in calcined clays and in geopolymers before attack, except for calcite (main peak  
375 situated at  $2\theta$   $29^\circ$ ), which disappeared from all geopolymer patterns after attack. Moreover, all patterns  
376 exhibited a decrease in the relative intensity of the amorphous hump initially centered at  $2\theta$   $29^\circ$ - $30^\circ$ ,  
377 which also shifted toward lower angles ( $2\theta$   $22^\circ$ - $26^\circ$ ). Altered zones of MI-based geopolymers displayed  
378 the presence of gypsum (main peak at  $2\theta$   $11^\circ$ - $12^\circ$ ). The relative intensity of the main peak of gypsum was  
379 much lower in MI\_K than in MI\_Na.

### 380 **3.6. FT-IR and solid-state NMR characterization**

381 FT-IR spectra obtained from samples before sulfuric acid attack and from altered geopolymers were  
382 plotted for wavenumbers ranging from  $4000\text{ cm}^{-1}$  to  $500\text{ cm}^{-1}$  and are presented in Fig. 10. Fig. 11  
383 presents the  $^{27}\text{Al}$  NMR spectra obtained from the precursors and from the geopolymers before and after  
384 (altered layer) sulfuric acid attack. Finally, Fig. 12 shows the  $^{29}\text{Si}$  NMR spectra of geopolymers before  
385 and after (altered layer) acid attack for the MI\_Na and MK\_Na geopolymers.

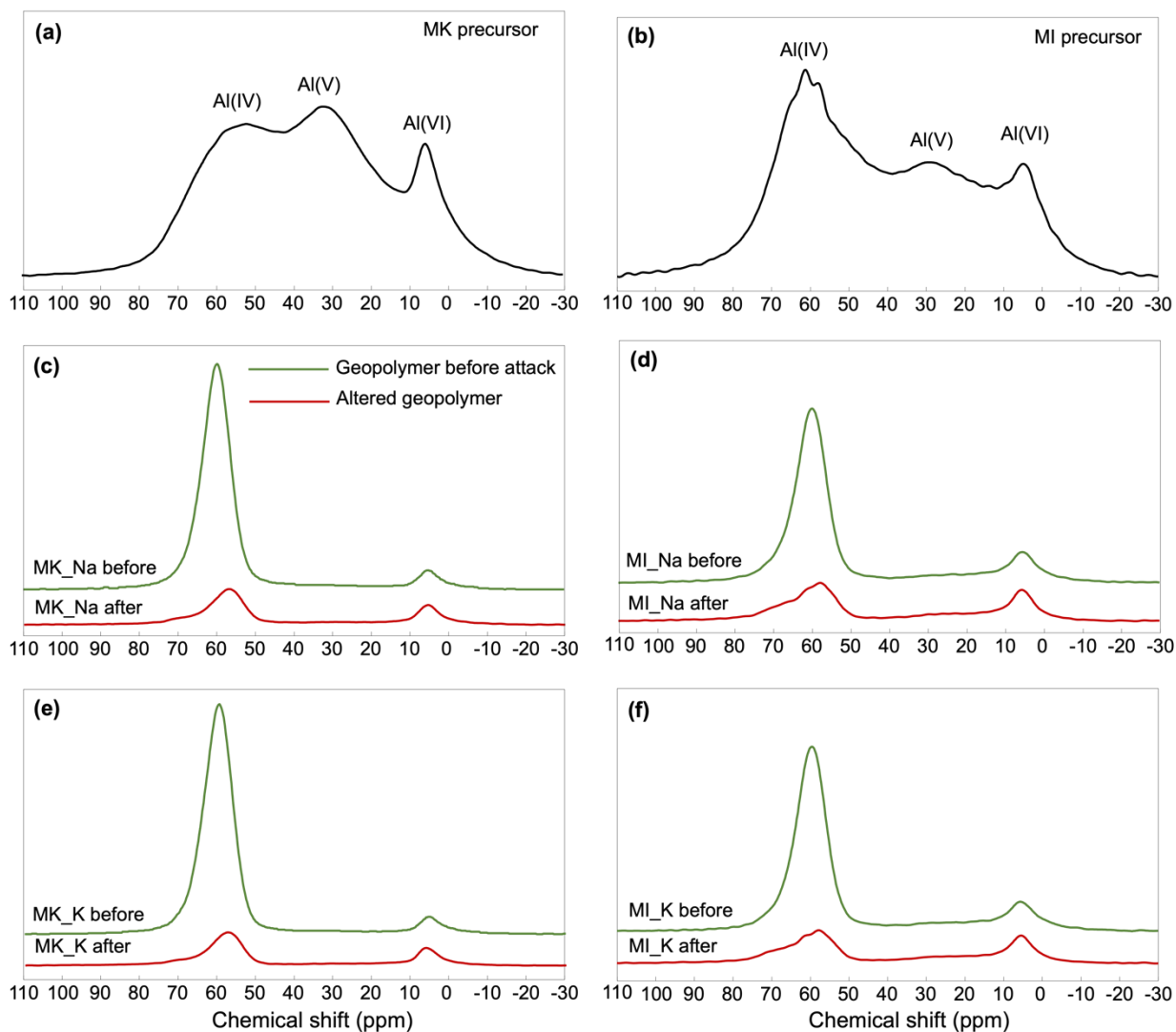


386

387 **Fig. 10.** FT-IR spectra obtained from crushed geopolymers before (green lines) and after (altered layer) sulfuric acid  
 388 attack. (a) MK\_Na, (b) MK\_K, (c) MI\_Na, and (d) MI\_K. **Black lines:** precursors (MK or MI).

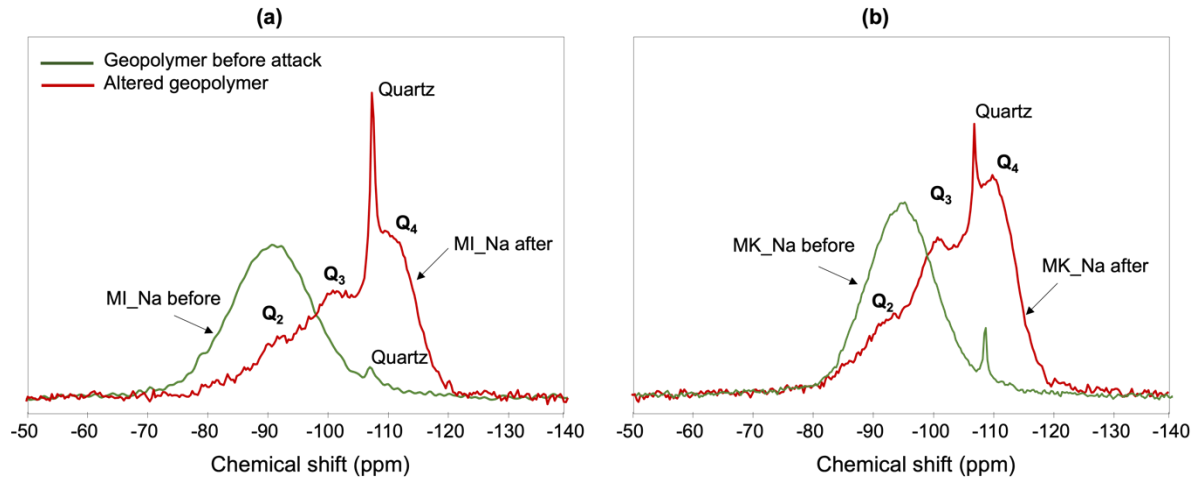
389





390

391 **Fig. 11.**  $^{27}\text{Al}$  MAS NMR spectra (a) MK precursor, (b) MI precursor, (c) MK\_Na, (d) MI\_Na, (e) MK\_K, and (f)  
 392 MI\_K. **Black lines:** precursors. **Green lines:** crushed geopolymers before sulfuric acid attack. **Red lines:** crushed  
 393 altered layer from geopolymers after sulfuric acid attack. The relative intensities of Al(VI) were normalized before  
 394 and after sulfuric acid attack for comparison.



395

396 **Fig. 12.**  $^{29}\text{Si}$  MAS NMR spectra obtained from geopolymers activated by Na-silicate before and after sulfuric acid  
 397 attack (a) MI\_Na, and (b) MK\_Na. After attack, spectra correspond to the altered layer identified in the  
 398 geopolymers.

399 In FT-IR spectra, the main absorption bands and corresponding assignments identified in Fig. 10 were:  
 400  $3600\text{-}3100\text{ cm}^{-1}$  (O-H stretching bands), O-H stretching bands of Si-OH and Al-OH groups appearing in  
 401  $3700\text{-}3200\text{ cm}^{-1}$  (Si-OH and Al-OH stretching),  $1500\text{-}1400\text{ cm}^{-1}$  (O-H deformation),  $1130\text{-}900\text{ cm}^{-1}$   
 402 (asymmetrical Si-O-T stretching vibrations, T = Al, Si),  $900\text{-}850\text{ cm}^{-1}$  (asymmetric Si-OH and Al-OH  
 403 stretching vibrations), and  $795\text{ cm}^{-1}$  (symmetric stretching vibrations of Si-O-T, T = Al, Si) [16,44].  
 404 Spectra obtained from the precursors showed that asymmetrical Si-O-T (T= Al, Si) stretching vibration  
 405 bands were located at  $1040\text{ cm}^{-1}$  and  $995\text{ cm}^{-1}$ , respectively. After alkali activation and before sulfuric  
 406 acid attack (green spectra), O-H stretching bands were identified at  $3600\text{-}3100\text{ cm}^{-1}$  due to hydrogen  
 407 bonding. Moreover, asymmetrical Si-O-T stretching bands (initially placed between  $1040\text{ cm}^{-1}$  and  
 408  $995\text{ cm}^{-1}$ ) shifted toward lower wavenumber values (about  $980\text{ cm}^{-1}$ ), which indicates that the degree of  
 409 polymerization increased after alkali activation. According to the literature, substitution of Si by  
 410 tetrahedral Al in the Si-O-Si network results in a shift of the Si-O-T asymmetric stretching band toward  
 411 lower wavenumbers [45]. On the contrary, FT-IR spectra obtained from altered zones of geopolymers

412 exposed to sulfuric acid (red spectra) showed that asymmetrical Si-O-T stretching vibration bands shifted  
413 toward higher wavenumber values and were narrower than those obtained before attack. FT-IR results are  
414 consistent with XRD analyses, which may imply a modification of both the geopolymerization degree and  
415 the structure of Si-O-T bonds after sulfuric acid exposure.

416 <sup>27</sup>Al NMR spectra obtained from the precursors showed the presence of Al in three different coordination  
417 states: Al(IV), Al(V) and Al(VI) (cf. Fig. 11a and b). Moreover, the shape of the MI spectrum suggested  
418 the coexistence of at least two different environments for Al(IV). After alkali activation, <sup>27</sup>Al NMR  
419 spectra exhibited the presence of Al mainly in 4-fold coordination with small amounts of Al in 6-fold  
420 coordination (around 6% for MK\_Na and MK\_K and 15% for MI\_Na and MI\_K). For MI-based  
421 geopolymers, a small resonance of Al(V) can still be observed. These results are in line with the literature  
422 showing that, after alkaline activation, Al in 5- and 6-fold coordination is mainly converted to 4-fold  
423 coordination [19,25]. After sulfuric acid attack, <sup>27</sup>Al NMR of altered zones were more complex to  
424 interpret. Spectra exhibited an increase in the proportion of Al(VI) and Al(V) and the existence of at least  
425 two tetrahedral Al environments in both MK and MI geopolymers. Surface areas of all <sup>27</sup>Al NMR spectra  
426 were calculated and compared to the spectra of geopolymers before attack to estimate the amount of Al  
427 released from the altered zones. Table 6 summarizes the proportions of Al calculated to remain in the  
428 altered layer of the geopolymers after sulfuric acid attack. Overall, calculations indicated that about 40-  
429 60% of Al was released from the altered layers of the MI- and MK-based geopolymers.

430 Regarding the <sup>29</sup>Si NMR analyses, spectra obtained from MI or MK-based geopolymers activated by Na-  
431 silicate showed the presence of Si in the form of silicate tetrahedra in three different environments (Q<sub>2</sub>, Q<sub>3</sub>  
432 and Q<sub>4</sub>). Before sulfuric acid, the main resonances were found at -90 ppm (Q<sub>2</sub>) and at -110 ppm (Q<sub>4</sub>), the  
433 latter corresponding to quartz. In the altered zones, spectra shifted toward lower chemical shifts, and  
434 tetrahedral silicate was mainly present in Q<sub>3</sub> and Q<sub>4</sub> environments. These results suggested that the  
435 polymerization degree of Si increased after sulfuric acid attack. Further details will be presented in the  
436 discussion section 4.3.

437 **Table 6** Calculated percentage (%) of total aluminum remaining in the altered layer of geopolymers after sulfuric  
438 acid attack. Values were obtained with  $^{27}\text{Al}$  NMR spectra taking the initial mass of each sample into account.

Geopolymer	MK_Na	MK_K	MI_Na	MI_K
Before attack	100	100	100	100
Altered layer	37	52	60	53

439

## 440 **4. Discussion**

### 441 **4.1. Behavior of geopolymers under sulfuric acid attack**

442 In this study, the resistance of four calcined clay-based geopolymers to sulfuric acid attack has been  
443 investigated. To this end, geopolymers were exposed to aggressive conditions by the immersion of paste  
444 samples in an  $\text{H}_2\text{SO}_4$  solution at pH 1 for 30 days. The resistance of samples to sulfuric acid was assessed  
445 by following the mass evolution and by direct observations. Results indicated that all geopolymers were  
446 susceptible to sulfuric acid attack, but degradation degrees were slightly different. Overall, geopolymers  
447 activated by Na-silicate were less likely to be damaged than those activated by K-silicate. In fact, MI\_Na  
448 geopolymer showed minor degradation compared to all the other geopolymers; its exposed surface  
449 seemed to present the least damage (lower dissolution than the other geopolymers) even though some  
450 vertical cracks were identified (cf. Fig. 4).

451 After 30 days of acid exposure, MI\_Na geopolymer showed a gain in mass of about 1.4%. Meanwhile,  
452 MK\_Na, MK\_K and MI\_K geopolymers presented losses in mass of 1.5%, 2.0%, and 3.2%, respectively  
453 (cf. Fig. 3). The initial gain in mass observed in all the materials (except for MI\_K) may correspond to the  
454 initial uptake of water at the beginning of the test. At the end of the test, the gain in mass in MI\_Na  
455 geopolymers could be partially explained by the precipitation of gypsum in the pore space of the altered  
456 layer as determined by SEM/EDS (cf. Fig. 8) and verified by XRD analyses (cf. Fig. 9). The precipitation

457 of gypsum was explained by the reaction between Ca ions present in MI precursor ( $\text{CaO} = 4.4 \text{ wt. } \%$ ) and  
458 the sulfate ions present in the immersion solution. Altered zones of MI\_K geopolymers also displayed the  
459 presence of gypsum (cf. Fig. 9), but with a relative intensity much lower than that observed in altered  
460 MI\_Na. This may be due to the amount of material that was dissolved in the MI\_K geopolymer during the  
461 test. In contrast, gypsum did not precipitate in the altered zones of MK-based geopolymers, due to the  
462 unavailability or very low concentration of Ca ( $\text{CaO} = 0.7 \text{ wt. } \%$ ). Since the deterioration was very slight  
463 in the surface of MI\_Na geopolymers, it was assumed that the amount of gypsum was not deleterious to  
464 the material. Instead, the formation of gypsum could help to fill pores and block further acid ingress into  
465 the material. This phenomenon has also been reported in the literature for different low-Ca geopolymer  
466 systems. Allahverdi and Škvára, 2005 [46] studied the resistance of a geopolymer (made by a  
467 combination of fly ash and slag, activated by NaOH and a Na-silicate solution) to sulfuric acid (pH 1).  
468 These authors explain that, during the acid attack, Ca ions exchanged with  $\text{H}^+$  or  $\text{H}_3\text{O}^+$  ions present in the  
469 immersion solution and, during this process, Ca and sulfate reacted. This reaction led to the formation and  
470 deposition of non-deleterious gypsum precipitates in the altered material.

471 Other investigations carried out on alternative binders under sulfuric acid attack have also shown that  
472 such systems present mass loss over time. Bakharev, 2005 [16] studied the behavior of class F fly ash  
473 geopolymer systems (activated by NaOH, KOH or Na-silicate) under 5% sulfuric acid solution. These  
474 authors showed that all the geopolymers presented mass losses ranging from 2 to 12%. Similarly, Sata et  
475 al., 2012b [47] studied the resistance of fly ash and lignite bottom ash geopolymers immersed in a  
476 solution containing 3% sulfuric acid. They showed that geopolymer mortars presented mass losses  
477 varying from 1.4 to 3.6%, which were much lower than those in OPC systems after 120 days of  
478 immersion. In the present study, CEM I-based samples showed a gain in mass of 3.5% after 30 days of  
479 immersion, probably due to the initial saturation of pores and the precipitation of gypsum. Since the  
480 immersion solution was not renewed, the layer of altered materials remained in the material and, unlike  
481 the situation in MK\_Na, MK\_K and MI\_K geopolymers, no dissolution of the material was observed.

482 Longer examination of CEM I and MI\_Na materials will need to be carried out to compare the  
483 performance of materials when exposed to sulfuric acid.

484 **4.2. Methodology for the evaluation of sulfuric acid resistance: immersion procedure and**  
485 **monitoring of elemental concentrations**

486 Sulfuric acid resistance was assessed by static immersion of geopolymer paste samples in sulfuric acid  
487 solution at pH 1. This chemical test is not a bio-chemical investigation and therefore, it may present some  
488 bias, such as the precipitation of products due to the equilibrium occurring with time between the material  
489 and the non-renewed solutions. However, this static immersion test is a good way to select cementitious  
490 binders to be used when acid attack is probable and in future bio-chemical applications (e.g., wastewater  
491 networks, fermentation or methanogenesis environments).

492 The evolution of the leaching coefficients of the leached elements determined in the immersion solutions  
493 (cf. Fig. 5) were well in line with the mass variation results (cf. Fig. 3). To compare the leaching degree  
494 of geopolymers, total leaching coefficients (Lc) were calculated according to [41,42] and presented in  
495 Table 7. Lc values are relative to the initial volume of samples, which was about 0.21 L per formulation,  
496 which explains the low values of the coefficients determined per leached element and per formulation.  
497 Moreover, the order of magnitude of the Lc values are in line with the low values of mass variations  
498 obtained from the geopolymers during the sulfuric acid attack (cf. Fig. 3). As presented in Fig. 4,  
499 geopolymer samples exhibited layers of dissolved material varying from 2 mm to 8 mm deep, which  
500 represent a proportion of 3 to 10% of dissolved material compared to the initial volume of the geopolymer  
501 pastes.

502 **Table 7** Total leaching coefficients (Lc) calculated for all the paste samples over time.

Time (d)	0.17	2	5	20	30	Total Lc
CEM I	0.03	0.06	0.08	0.19	0.25	0.61
MK_Na	0.08	0.85	1.54	2.60	2.83	7.90

MI_Na	0.02	0.33	0.53	0.99	1.32	3.19
MK_K	0.25	1.70	2.18	3.20	3.59	10.91
MI_K	0.04	1.47	2.02	2.77	4.03	10.34

503

504 Leaching coefficients (Lc) indicated that geopolymer pastes activated by K-silicate presented the highest  
505 release of elements into the immersion solutions. Furthermore, Lc results corroborated that MI\_Na  
506 geopolymer was the material that presented the lowest deterioration among all geopolymers under  
507 sulfuric acid attack, since the degree of leaching was about 3.5 times lower than the one calculated for  
508 geopolymers activated by K-silicate (MK\_K and MI\_K) and about 2.5 times lower than that in the  
509 MK\_Na geopolymer. Nonetheless, total Lc in MI\_Na was higher than the one calculated for the reference  
510 material (CEM I), in which the total leaching coefficient was of about 0.61. This may be explained by a  
511 different degradation mechanism that consisted in the leaching of Ca into the immersion solution due to  
512 the decalcification of Ca-rich phases (e.g., portlandite and calcium silicate hydrates). In fact, the total  
513 leaching coefficient of Ca calculated in the immersion solution of CEM I corresponded to about 72% of  
514 its total leaching coefficient. Therefore, the swelling observed in CEM I samples (gain in mass of 3.5%)  
515 can be attributed to the precipitation of sulfate-rich phases (e.g., gypsum) in the solid material, which has  
516 already been demonstrated in the literature for Ca-rich materials [12,48]. The precipitation of expansive  
517 phases due to the high amount of Ca in the cement may eventually lead to cracking and thus, the loss of  
518 material and mechanical resistance.

519 On the other hand, the trend of Na<sup>+</sup> or K<sup>+</sup> release into the immersion solutions was similar for all the  
520 geopolymers. This means that the kinetics of Na<sup>+</sup> or K<sup>+</sup> release into the immersion solution was rapid, and  
521 concentrations increased with increasing exposure time (cf. Fig. 5). However, Na concentration was about  
522 1.6 times higher in the MK\_Na immersion solution than that measured in the MI\_Na immersion solution  
523 (cf. Fig. 5e). This suggests that the release of Na into the solution was more rapid in the MK\_Na  
524 geopolymer than in the MI\_Na samples, which may dissolve the material in a much rapid rate, which

525 could be partially explained by the higher total porosity in the MK-based geopolymers, increasing the  
526 diffusion rates. The EDS mapping results confirm that the relative concentration of Na and K dropped in  
527 all the altered zones of geopolymers exposed to sulfuric acid (cf. Fig. 7). These results are in line with the  
528 EDS pointing analyses, which showed that Si/Al and R/Al (R=Na or K) molar ratios were modified in the  
529 altered zones of the geopolymers (cf. Fig. 6). Si/Al molar ratios increased in all the geopolymers,  
530 suggesting that Al content decreased after attack. R/Al molar ratios dropped after sulfuric exposure, due  
531 to a decrease in both Al and alkali content (Na or K).

### 532 **4.3. Degradation mechanisms of geopolymers under sulfuric acid attack**

533 According to the results previously discussed, the main hypothesis explaining the degradation  
534 mechanisms of geopolymers is that the release of alkali cations ( $\text{Na}^+$  or  $\text{K}^+$ ) into the acid solution leads to  
535 disequilibrium of the aluminosilicate geopolymer network (Si-O-Al). Al in 4-fold coordination needs  
536 counter ions to respect electroneutrality, so the mechanism of degradation should be the breaking of the  
537 Si-O-Al bonds and the depletion of Al in the material (cf. Table 6).

538 Mineralogical and structural analyses carried out on the altered layer of geopolymers indicated that  
539 amorphous structures of all the samples were modified by the exposure to sulfuric acid. XRD patterns  
540 displayed a decrease in the relative intensity of the hump characteristic of the amorphous network (cf. Fig.  
541 9). Additionally, FT-IR analyses showed that the asymmetrical Si-O-T (T= Al, Si) stretching band shifted  
542 toward higher wavenumbers, which is related to a modification of the Si-O-T bonds due to the release of  
543 Al from the geopolymer network (cf. Fig. 10).  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR spectra confirmed the  
544 modification of the structural environments of Al and Si after attack (cf. Fig. 11, Fig. 12 and Table 6).  
545 Additional treatment of  $^{27}\text{Al}$  MAS NMR spectra revealed that the signals attributed to Al(IV) decreased in  
546 proportion by 72%, 62%, 57% and 62% in the altered geopolymers of MK\_Na, MK\_K, MI\_Na and  
547 MI\_K, respectively compared to the proportions obtained from unaltered geopolymers. Moreover,  $^{29}\text{Si}$   
548 MAS NMR spectra obtained from geopolymers activated by Na-silicate indicated an increase in the



549 polymerization of Si due to the transformation of tetrahedron environments from Q<sub>2</sub> to Q<sub>4</sub>. This suggests  
550 that the Si network was reorganized because of the absence of Al, leading to the formation of an  
551 amorphous silica gel. Similar results have been observed in the literature for other systems exposed to  
552 sulfuric acid attacks, in which a silica gel was likely to be formed in the altered layer of the materials as a  
553 result of the decomposition of Si-rich phases [48–50]. Moreover, FT-IR spectra of geopolymers after  
554 attack presented a slight modification in the O-H stretching bands at 3700-3100 cm<sup>-1</sup>, which indicated an  
555 increase of Si-OH and Al-OH groups due to the sulfuric acid attack. Bakharev, 2005 [16] explained that  
556 exposure of class F fly ash geopolymers to strong acidic solutions increased the number of Si-OH and Al-  
557 OH groups following the breakage of Si-O-Al bonds. This phenomenon could be confirmed by  
558 performing <sup>1</sup>H MAS NMR analyses coupled with <sup>27</sup>Al MAS NMR investigations. However, the  
559 geopolymers studied in this investigation contained amounts of Fe that led to paramagnetic perturbations  
560 and no such results were exploitable.

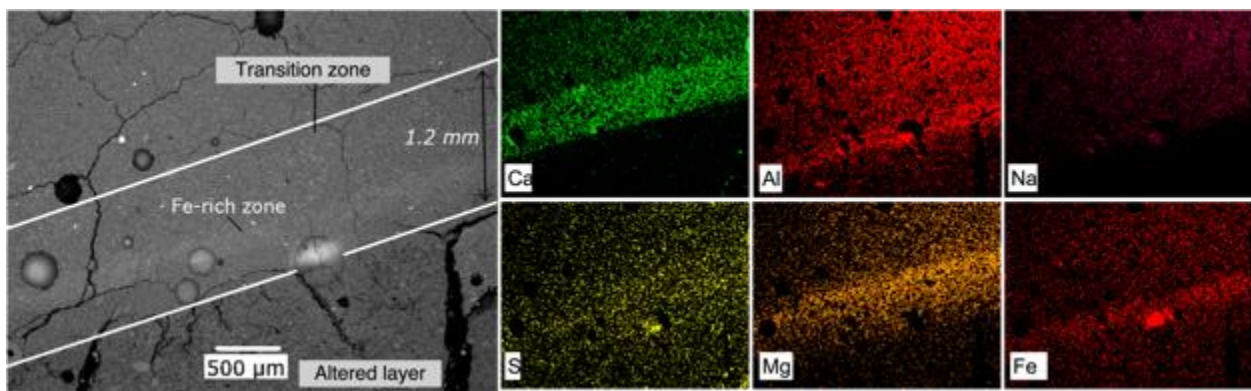
561 In addition, geopolymers activated by K-silicate exhibited highly altered surfaces (cf. Fig. 4) and high  
562 leaching coefficients of leached elements in the immersion solutions (cf. Fig. 5). The porosity of these  
563 materials may partially explain these results. In fact, the total porosities accessible to mercury of  
564 geopolymers activated by K-silicate were slightly higher than those determined in geopolymers activated  
565 by Na-silicate (cf. Table 4). According to the literature, geopolymers activated by K-activating solutions  
566 seem to present greater degradation than those activated by Na-activating solutions [5,29]. Grengg et al.,  
567 2021 [30] studied MK-based geopolymers activated by K-silicate (SiO<sub>2</sub>/K<sub>2</sub>O ratio of 0.95) under sulfuric  
568 acid attack at pH 2. These authors showed that samples presented a complete dissolution of the  
569 geopolymer structure and the formation of a silica gel in the altered materials. Vogt et al., 2020 [29] also  
570 studied an MK-based geopolymer activated by K-silicate under sulfuric acid at pH 1. They suggested that  
571 the geopolymer degradation was first due to the leaching of K<sup>+</sup> ions into the immersion solution, followed  
572 by the dealumination and depolymerization of the geopolymer.

#### 573 4.4. Performance of MI-based geopolymers under sulfuric acid attack

574 To the best of the authors' knowledge, no studies of MI-based geopolymers under sulfuric acid attack are  
575 available in the literature. This investigation showed that MI-based geopolymers activated by Na-silicate  
576 resisted sulfuric acid attack well. This was attributed to a combination of properties, such as the mineral  
577 structure of illite, the chemical composition of the MI and the transfer properties of the geopolymer  
578 pastes. The mineral structure of the illite (2:1 clay mineral) consists of repetitive tetrahedral and  
579 octahedral cation sheets [22,33] which should reduce the availability of Al cations and thus decrease the  
580 dissolution of Al when it is exposed to sulfuric acid attack. Regarding the total porosity accessible to  
581 mercury, MI\_Na pastes presented the lowest values of all the geopolymers (cf. Table 4), which may have  
582 contributed to a less rapid diffusion of the aggressive ions into the solid material.

583 Additionally, EDS mapping performed on MI\_Na geopolymers resulted in the identification of a layer  
584 about 1 mm thick occurring in the transition zone between altered and unaltered zones. This phenomenon  
585 was only identified in MI\_Na geopolymer. Fig. 13 presents SEM/EDS analyses obtained from the MI\_Na  
586 exhibiting this transition zone after attack. The zone was composed of different layers of elements  
587 (mainly Mg, Ca, and Fe). XRD analyses performed on the surface of this layer did not reveal the  
588 formation of any crystalline Mg or Fe-rich phase but an increase in calcite. These observations may  
589 suggest the formation of a protective gel layer preventing further degradation of the material. Gevaudan et  
590 al., 2021 [31] studied the influence of Fe content on the resistance of MK geopolymers to sulfuric acid  
591 (pH 2). They suggested that Fe-rich phases such as hematite could improve the acid resistance of  
592 geopolymers activated by Na activating solutions, especially at high Na/Al ratios ( $> 1.39$ ). The MI  
593 precursor used in this study contained 7 wt. %  $\text{Fe}_2\text{O}_3$ , which is twice that of the MK precursor (cf. Table  
594 1). Surprisingly, MI\_K geopolymer did not exhibit behavior similar to that of MI\_Na. For MI\_K  
595 geopolymer, the release of Fe into the immersion solution was 76% higher than that from MI\_Na. This  
596 could be explained by the higher total porosity of MI\_K (30.8%) compared to the porosity of MI\_Na  
597 (26.5%), which may have been influenced by the alkaline solution used for activation. Bakharev, 2005  
598 [16] has shown that class F fly ash geopolymers activated by KOH and exposed to 5% sulfuric acid

599 solution presented 12.43% of mass loss, against 2.56% obtained from the same material activated by Na-  
600 silicate. The authors mention that the activation of the fly ashes by KOH increased the average pore  
601 diameter and reduced the material's resistance to sulfuric acid attack. Further analyses should be carried  
602 out in calcined clay geopolymers by using techniques with much lower detection limits (e.g., MET) to  
603 better understand degradation mechanisms and to discard similar local behaviors. Moreover, MK-based  
604 geopolymers activated by Na-silicate and containing more than 7 wt. %  $\text{Fe}_2\text{O}_3$  could be tested in order to  
605 corroborate the influence of Fe present in the precursor on the sulfuric resistance of the geopolymers.



606  
607 **Fig. 13.** BSE image and EDS mapping obtained from the scan of Ca, Al, Na, S, Mg and Fe elements in MI\_Na  
608 geopolymer paste after sulfuric acid attack. White solid lines demarcate the transition between altered and unaltered  
609 zones.

610 Compared to other cementitious materials reported in the literature, calcined clay geopolymers appear to  
611 show promising performance under sulfuric acid attack, since their mass variations have been relatively  
612 low. Experimental tests should be carried out on calcined-clay geopolymers under similar and less  
613 aggressive conditions and the results compared to those of other materials such as calcium aluminate  
614 cements (CAC), which are well known for having higher resistance to a biogenic acid attack than OPC, in  
615 both *in-situ* and laboratory conditions [51–53]. Finally, the study of geopolymers in the form of paste  
616 samples allows to carry out mineralogical and microscopical characterizations of these materials and to  
617 better understand their behavior under sulfuric acid attack. The investigation of geopolymers in the form

618 of pastes also gives insights into the degradation of these materials for their use as protective coating of  
619 structures exposed to aggressive environments. However, the behavior of geopolymer pastes under  
620 sulfuric acid attack should be compared to those of mortars and concrete to verify the kinetics of  
621 degradation and to assess the influence of other parameters on the resistance to sulfuric acid attack.

## 622 **5. Conclusions**

623 Findings in this paper allowed the behavior of different calcined clay based geopolymers under sulfuric  
624 acid ( $H_2SO_4$ ) attack to be compared by using highly aggressive conditions. Moreover, this study gave  
625 insights into the degradation mechanisms of meta-illite based geopolymers exposed to sulfuric acid,  
626 which had not been addressed in the literature until now. In this study, metakaolin (MK) and meta-illite  
627 (MI) precursors were activated by two different alkaline solutions (Na-silicate and K-silicate). Thus, four  
628 different geopolymer pastes were studied: one MK-based geopolymer activated by Na-silicate (MK\_Na),  
629 one MK-based geopolymer activated by K-silicate (MK\_K), one MI-based geopolymer activated by Na-  
630 silicate (MI\_Na), and one MI-based geopolymer activated by K-silicate (MI\_K). After 28 days of curing,  
631 samples were submerged in an  $H_2SO_4$  solution at pH 1 for 30 days.

632 The main conclusions drawn from this study were:

- 633 1. All geopolymers were susceptible to degradation after sulfuric acid attack at pH 1. Overall, paste  
634 samples presented a layer of altered material after exposure to sulfuric acid.
- 635 2. MK\_Na, MK\_K and MI\_K geopolymers lost mass during the test, unlike MI\_Na geopolymer, in  
636 which the exposed surface seemed to be the least altered surface of all the geopolymers. Element  
637 concentrations determined in the immersion solution of MI\_Na were very low compared to those  
638 in the solutions of the other geopolymers.
- 639 3. Gain in mass in the MI\_Na geopolymer was explained by the saturation of pores due to the  
640 immersion process and to the precipitation of non-deleterious gypsum in the altered layer.

- 641 4. Geopolymers activated by K-silicate solution (MK\_K and MI\_K) exhibited highly dissolved  
642 surfaces leading to the mass loss of the material.
- 643 5. The general degradation mechanism in all geopolymers consisted of the release of alkalis (Na<sup>+</sup>  
644 and K<sup>+</sup>) into the solution by the exchange with H<sup>+</sup> and H<sub>3</sub>O<sup>+</sup> ions. This was followed by the  
645 disequilibrium of the geopolymer phase (Si-O-Al) and, therefore, the release of Al into the  
646 solution.
- 647 6. MI\_Na geopolymers seemed to present a better resistance to sulfuric acid attack, which was  
648 attributed to a combination of various factors: the mineral structure of illite, the transfer  
649 properties, the chemical composition of the MI as well as the small precipitation of gypsum in the  
650 altered zone, probably blocking further ingress of solution into the paste. Additionally, the  
651 formation of an Fe-rich layer deposited in the transition zone between altered and unaltered  
652 geopolymer may constitute a protective barrier inhibiting further degradation.
- 653 7. Despite degradation of geopolymers due to the highly aggressive conditions, the low mass  
654 variations determined during the tests hold promise for improving the durability of materials  
655 under sulfuric acid attack. The performance of these materials should be tested under less  
656 aggressive conditions, for longer exposure times and on mortars and concrete samples to compare  
657 degradation mechanisms.

658 **CRedit author statement**

659 **Laura Diaz Caselles:** Investigation, Formal analysis, Writing – original draft, Project administration.

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665 administration.

## 666 **Declaration of competing interest**

667 The authors declare no conflict of interest.

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