

Iron Mineral Admixtures Improve the Sulfuric Acid Resistance of Low-Calcium Alkali-Activated Cements

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Abstract

We investigated the sulfuric acid resistance of low-calcium alkali-activated materials (*i.e.*, geopolymers) supplemented with an iron mineral admixture (*i.e.*, hematite). Geopolymers without and with 5% hematite were produced at two alkali contents (Na:Al = 0.86 and 1.39). Acid degradation reactions were comprehensively studied through three replenishes of acid. Results demonstrate that hematite is chemically active upon acid exposure yielding a short-term increase in acid neutralization capacity. Prolonged acid resistance was enhanced in high alkali content formulations with hematite. Acid exposure revealed minimal changes to mineralogy, molecular structure, and micro-scale porosity in these samples, resulting in less dealumination and silicon leaching. Thus, results indicate that the acid buffering capacity of geopolymers, specifically at higher alkali content formulations, increases due to the addition of hematite. The increased buffering capacity leads to lower degrees of dealumination of the N-A-S-H cementitious binder. These results are important to explain the increased acid durability of alkali-activated materials synthesized from industrial aluminosilicate precursors (*e.g.*, slag, fly ash, lateritic clays) that may contain iron minerals.

Keywords: Sulfuric Acid, Alkali-Activated Cements, Geopolymers, Microbial-Induced Concrete Corrosion

1.0 Introduction

A global need to improve the resilience and sustainability of civil infrastructure has prompted a recent interest in developing durable, low-CO₂ concrete technology. Microbial-induced concrete corrosion (MICC) in subterranean infrastructure is a major durability challenge. In the United States alone, local governments spend approximately \$50 billion annually to mitigate the effects of microbially-produced sulfuric acid in more than 800,000 miles of sewers [1], [2]. MICC consists of three main stages, namely: (1) carbonation of the surface ($9 < \text{pH} < 10$); (2) establishment of a microbial biofilm ($4 < \text{pH} < 5$); and, (3) severe corrosion due to sulfuric acid ($\text{pH} < 2$) [3]. Hence, concrete materials that can withstand such aggressive acidic environments are of interest. Toward this aim, alkali-activated cements (AACs) have been proposed as a possible material solution to this pervasive durability challenge. AACs are a class of low-CO₂, acid-resistant alternatives to portland cement-based materials. The lower environmental impact of AACs compared to portland cement-based materials has been previously reported in [4]–[6]. Similarly, the superior acid resistance of AACs has been discussed extensively in previous research [7]–[9]

The acid resistance of AACs is primarily dependent on both the chemical composition of the microstructure (*i.e.*, Ca:Si, Al:Si) and the permeability of the porous network [10], [11]. A recent comparison between two different AACs, slag activated vs. fly ash activated materials, revealed that slag-activated mortars, which contain higher calcium contents, could better withstand the MICC aggressive environment due to their low gas permeability when compared to fly ash activated materials. More specifically, activated slag mortars with a lower permeability were found to have lower rates of carbonation and H₂S acidification in aggressive sewer conditions during the initial stages of MICC [12]. The lower

45 permeability in AACs has also been shown to contribute to lower microbial respiration rates, which limit
46 the establishment of microbial biofilms in the second stage of MICC [13]. However, much research
47 considers the third stage of MICC and is simulated as sulfuric acid exposures [14]. Results from these
48 sulfuric solution experiments have revealed decreases in overall degradation correlated with lower calcium
49 content [15], suggesting that low-calcium AACs from metakaolin or low-calcium fly ashes are more acid
50 resistant than calcium-rich AACs produced from ground-granulated blast furnace slags (GBFS). However,
51 as noted earlier, these rates of degradation, especially in calcium-rich AACs, can be attenuated by a slow
52 diffusion process that is facilitated by complex porous networks. Pore-filling and macropore structures
53 (>100 nm) help reduce mesoporous structure (2-50 nm) and, as a result, decreases the rate of degradation
54 [16].

55 The authors have recently proposed a new theory of acid degradation in AACs. Acid degradation of
56 low-calcium AACs (*i.e.*, geopolymers) involves an ion-exchange reaction between the charge-stabilizing
57 cations (*e.g.*, sodium, Na⁺) of the aluminosilicate cementitious binder (Si-O-Al) and hydronium (H₃O⁺).
58 Association of the hydronium with the localized negative charge in aluminosilicate cementitious binders
59 results in an electrophilic attack, which ejects tetrahedral aluminum (Al) in a process named dealumination
60 [10]. Dealumination is concurrent with incorporation of silicon (Si) species, which, depending on chemical
61 composition of the pore solution (*e.g.*, internal pH), precursor chemistry (*i.e.*, CaO content) and degree of
62 Al-crosslinking (*e.g.*, SiO₂:Al₂O₃ ratio) can enable the formation of a silica gel network, as reported by
63 [17]. The formed gel network is suggested to play an important role in the durability of these materials, as
64 it may inhibit further diffusion of aggressive agents [18].

65 Recently, the authors showed experimentally that Cu⁺² and Co⁺², as well as other cations,
66 incorporated in AACs exhibited mobility during acid exposure, accumulated at the reaction front, and aided
67 in increasing the acid resistance through a process termed *polyvalent cationic stabilization* of the
68 aluminosilicate binder [19]. However, initial experimental results were observed in slag-based AACs that
69 contained a variety of mineral phases that became chemically active during acid exposure. Such complexity
70 can confound mechanistic understanding due to simultaneous inter-ionic interactions. Hence, direct
71 evidence on the role of Cu⁺², Co⁺², and other metallic cations, like iron (Fe), in pure aluminosilicate systems
72 is essential to isolate specific ionic interactions to elucidate mechanistic understanding of their fundamental
73 behavior related to acid degradation.

74 Previous work on acid-attacked fly-ash AACs with high Fe contents (>48%) demonstrated high mass
75 loss when compared to portland cement paste [20]. The content of Fe (as Fe₂O₃) in slag and fly ash has
76 been reported to be 0.4-1.8 wt.% and 3.2-18.1 wt.%, respectively [21]–[24]. Traditional mass loss
77 measurements, however, have been shown by [25] to not necessarily correlate with chemical acid
78 degradation. In addition to the limits in measurements, the presence of mineral phases in AACs obfuscates
79 the explicit role of chemically active phases during acid attack. For example, recent research by [26] found
80 that alkali-activated impure metakaolin containing iron minerals demonstrated improved acid resistance to
81 similar formulations utilizing pure metakaolin. Similar results have been reported for slag-based AACs
82 with Fe-rich additions [27]. Hence, these recent results elucidate critical gap in knowledge in the
83 understanding of the explicit role that mineral impurities have on the acid attack of AACs. To this aim this
84 study investigates the role of Fe in the acid degradation of low-calcium metakaolin-based AACs.

85 **2. Materials and Experimental Methods**

86 **2.1 Materials**

87 High purity metakaolin (MK) (MetaMax) was supplied by BASF Chemical Corporation (Georgia, USA).
88 The MK had a Si:Al ratio of unity (1.0), determined *via* ICP-OES, and an average particle size of 1.3 μm.
89 Hematite (Fe₂O₃) average particle diameter of 0.18 μm was supplied by Strem Chemicals Inc. with a
90 chemical purity of 99.8%. Alkali-activating solutions were prepared using sodium hydroxide (Sigma-
91 Aldrich, NaOH ≥ 97%) and sodium silicate (NaSi, Sigma-Aldrich, SiO₂ = 27 wt. %, Na₂O = 11 wt. %).
92 More specifically, high-density polyethylene (HDPE) 500ml bottles were used to mix NaSi, NaOH, and

93 H₂O proportions in **Table 1**. Sulfuric acid solution with a pH of 2.0 ± 0.07 was prepared by adding sulfuric
 94 acid (Sigma-Aldrich, H₂SO₄ $\geq 95\%$) to deionized water.
 95

96 **2.2 Experimental Methods**

97 *2.2.1 AAC Sample Preparation*

98 Geopolymer samples were produced with two alkaline activators to achieve Na:Al atomic ratios of 0.86
 99 and 1.39 with a uniform Si:Al atomic ratio of 1.15 (see **Table 1**). Alkali-activating solutions were prepared
 100 in high-density polyethylene bottles, which were sealed and cooled for one hour at 4 °C to enable the NaOH
 101 exothermic reaction to subside. The effect of iron mineral admixtures was explored with the addition of 5
 102 wt.% of hematite [28]. MK was alkali-activated with the respective alkaline solutions and mixed for three
 103 minutes with one minute of manual mixing, one minute of mechanical mixing, followed by one final minute
 104 of manual mixing. Mixtures achieved a homogenous consistency after the mixture procedure and were
 105 placed in Vaseline-lubricated molds (diameter: 13mm, height: 25mm). Subsequently, mixtures were
 106 tamped for 30 seconds and vibrated for 30 seconds until visible entrapped air was removed. Paste samples
 107 were then cured in sealed containers (99% RH) in a Quincy forced air laboratory oven for 48 hours at 40°C.
 108 After initial curing, samples were dried at 40°C for an additional 24 hours.

109 **Table 1.** Mixture proportions for MK-based AAC control and iron supplemented samples.

Sample Name	Constituent Materials					Important Parameters		
	MK (g)	Fe ₂ O ₃ (g)	NaSi (g)	NaOH (g)	H ₂ O (g)	Fe (%)	Si:Al	Na:Al
Control Low	50	0	13	9.4	33	0	1.15	0.86
Control Low + Fe	50	2.6	13	9.4	33	5	1.15	0.86
Control High	50	0	13	15.8	33	0	1.15	1.39
Control High + Fe	50	2.6	13	15.8	33	5	1.15	1.39

110 *2.2.2 Acid Exposure and Leaching*

111 Samples (diameter: 13mm, height: 20mm) were exposed three times to a sulfuric acid solution with a pH
 112 of 2.0 ± 0.07 until pH equilibrium was attained (< 0.0025 pH/hour). Following a modified ASTM C1308
 113 methodology, samples were suspended using a 46 mm Savillex support screen (730-0046) and constantly
 114 stirred in the acid solution. The volume-to-surface-area ratio of the solution and AAC sample was held
 115 constant at 10. A magnetic stirrer was used to ensure homogenous solution mixing. pH equilibrium was
 116 defined as the time in which the recorded change in pH was < 0.0025 per hour. pH values were obtained
 117 using a Mettler Toledo benchtop F20 pH/mV meter. The pH probe was calibrated using a three-point curve
 118 with proper bracketing with reference solutions of pH values 2.0, 7.0, 10.1, and 12.01. After equilibrium
 119 was reached, the acid solutions were replaced, and samples of the leachate media were analyzed *via* ICP-
 120 MS. Leachate media contained silica suspensions. To ensure proper analysis, samples were first acid
 121 digested to dissolve any colloidal or aggregated particles or gels and subsequently run against blank. Three
 122 separate standards were made to test the accuracy of the results by diluting certified standards. Triplicates
 123 of each sample were exposed to acid and aliquots were taken at each equilibrium point.

124 *2.2.3 Fourier-Transform Infrared Spectroscopy (FTIR)*

125 Unexposed and exposed samples were ground in a slurry of ethanol using a McCrone micronizing mill with
 126 yttrium-stabilized zirconium (American Elements) grinding beads for five minutes to achieve particle sizes
 127 $< 5\mu\text{m}$. Collected slurries were dried overnight at 60°C. Next, 0.02 ± 0.005 grams of each sample were
 128 mixed with 2.00 ± 0.050 grams of potassium bromide (KBr) powder and dried at 70 °C. Then, the powder
 129 mixtures were homogenized in a Spex Grinder mill and pressed into KBr disk pellets for analysis in a
 130 Thermo Scientific Nicolet iS10 FTIR Spectrometer. As a result, KBr disks with sample concentrations of

131 1% (by weight) were produced. Disks were analyzed against a blank background to remove the absorption
132 spectra from the chamber purged with nitrogen.

133 2.2.4 Energy Dispersive Spectroscopy (EDS)

134 The silicon (Si:Fe) and iron (Fe:Al) content of each unexposed and exposed sample were quantified by
135 analyzing the Si K α , Al K α , and Fe K α , which were obtained using a JEOL-8230 electron microprobe with
136 a ThermoScientific energy dispersive spectrometer (EDS). An acceleration voltage of 15 keV and beam
137 current of 20 nA was used for all acquisitions. EDS acquisition was standardless using a spectral acquisition
138 of 15 seconds, which was sufficient to accumulate counts over 4000. A ZAF correction for the elemental
139 matrix was performed in all acquisitions. Twenty randomized points were collected for five different
140 locations in all samples (top, bottom, center, left, and right), totaling an acquisition of 100 EDS points per
141 sample. These points were collected at random to provide an unbiased selection of points and elucidate any
142 general trends of the elemental chemistry and mobility before and after acid exposure. Atomic percentages
143 were quantified and used to discern the central tendencies of bulk Si:Fe and Fe:Al ratios.

144 2.2.5 X-Ray Diffraction (XRD)

145 Mineralogy was determined *via* semi-quantitative X-ray diffraction (XRD) using Cu K α radiation (Siemens
146 D500 X-ray diffractometer). In this methodology, corundum (American Elements) was used as an internal
147 standard to normalize peak heights between samples and align diffraction patterns. AAC samples were
148 powdered and homogenized using a micronizing mill with well-packed yttrium-stabilized zirconium
149 grinding beads. After samples were ground, samples were homogenized in plastic scintillation vials with
150 three Delrin balls. 500 μ L of Vertrel cleaning agent (Miller-Stephenson) were added to vials in order to
151 generate aggregates with random particle orientation. Subsequently, samples were sieved through a 250 μ m
152 mesh and packed into XRD analysis plates. Samples were then analyzed from 5 to 65 degrees 2 θ using Cu
153 K α X-ray radiation with a step size of 0.02 degrees and a dwell time of 2 seconds per step. Mineralogy was
154 identified using Jade software (MDI, Version 9) and the International Centre for Diffraction Data (ICDD)
155 2003 database.

156 2.2.6 Micro-Computerized Tomography (μ -CT)

157 AAC samples before and after acid exposure were analyzed in a Zeiss Xradia 520 X-ray microscope. Acid-
158 exposed samples were dried in a laboratory oven for at least 12 hours at 40 °C prior to imaging. A micro-
159 computerized tomograph was produced using the 0.4x objective with X-ray source parameters of 60 kV
160 acceleration voltage and 5 Watts. A LE2 filter was utilized to reduce the transmission values between 26%
161 and 40% and maintain intensity counts above 5000. A pixel size resolution of $6.143 \pm 0.38 \mu$ m was achieved
162 utilizing a pixel averaging of bin one during the acquisition. The tomography images (size: 1.2 cm x 1.1
163 cm) were reconstructed using a Zeiss reconstruction software to adjust for center-shift and beam hardening
164 artifacts. In addition, ring artifacts from the images were removed using a high-contrast removal operation
165 as well as a despeckling operation to remove pixel defects in the images. Prior to pore-structure
166 segmentation, performed using Dragonfly 3.5, the 32-bit tomography images were pre-processed to correct
167 for noise and uneven grey values within the image. First, a local entropy minimization (node: 9, count: 2)
168 was performed to correct for non-uniform illumination and counteract noise by reducing randomness.
169 Second, an open mathematical morphology operation was performed with a cross structuring element
170 (kernel size: 9) to smooth images and remove isolated pixels. Finally, a median-based smoothing operation
171 was performed to equalize the grey-levels of the image and remove salt-and-pepper noise. Prior to
172 quantification, features of $< 1 \mu$ m were removed, as these could not be resolved given the pixel-size
173 resolution.

174 2.2.7 Compressive Strength

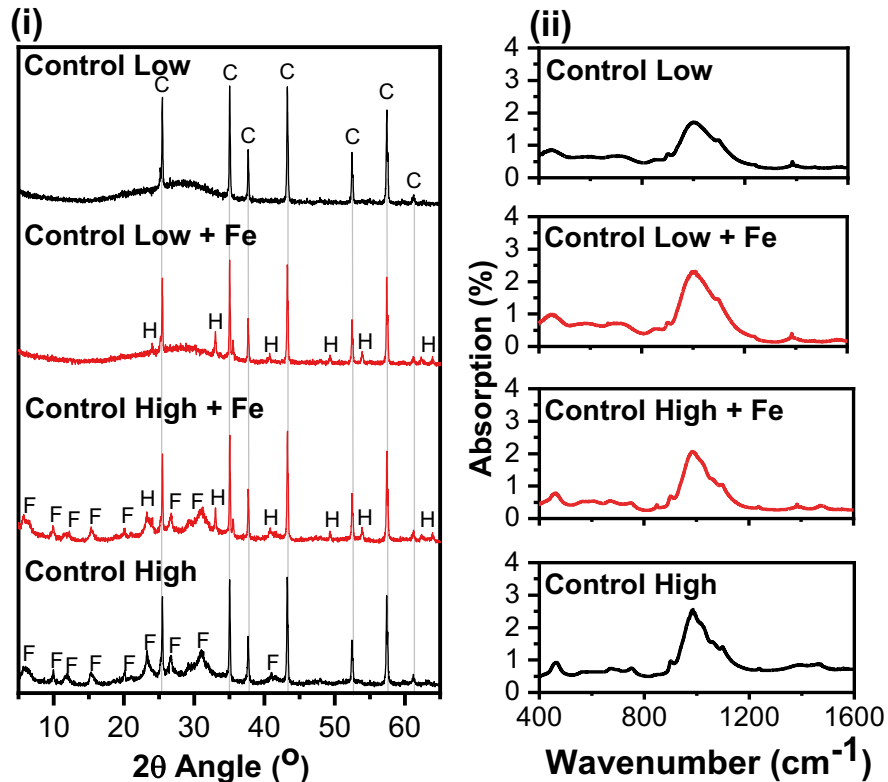
175 An Instron 5869 universal and an MTS Exceed E43-504 (Tension/Compression) testing machine with a
176 10,000 lbs load cell was employed to test the compressive strength of AAC samples (diameter: 13 mm,
177 height: 20 mm). In order to ensure proper flat testing surfaces, both top and bottom surfaces of AAC samples
178 were smoothed employing 1200 and 2000 abrasive grit sheets. Acid-exposed samples were also tested after
179 two acid exposure cycles. KimWipes™ were used to ensure a saturated surface-dry testing condition.
180 Surface smoothing of these samples was not employed to ensure minimal sample damage. As a result, the
181 compressive strength reported here is likely conservative measurements of the mechanical properties.
182 Moreover, the significance of the compressive strength here is to provide a relative indication of the sample
183 damage due to acid attack in comparison to an unexposed sample of the same dimension and composition.
184 All samples were dimensioned before testing in the load cells and compressed *via* displacement-controlled
185 loading. Between six and eight samples were tested for all samples with the exception of Control High prior
186 to acid exposure which had four samples tested. A higher number of specimens, in comparison to generally
187 accepted triplicates, were tested to provide robust statistical analysis.

188 3. Results and Discussion

189 3.1 Mineralogy and Molecular Structure Prior to Sulfuric Acid Exposure

190 Regardless of Fe content, Control High samples form faujasite (**Figure 1(i)**), while Control Low samples
191 do not exhibit mineral formation, as expected [29]. The presence of faujasite in geopolymer materials,
192 which is well documented [29]–[33], is known to depend on silica availability, alkali content, processing,
193 and curing conditions (*i.e.*, temperature, humidity). The elevated temperature and humidity during curing,
194 along with high concentration of Na⁺ cations in the Control High samples, thermodynamically favor
195 formation of faujasite minerals. The authors have previously shown that the mineralization process depends
196 mainly on hydrothermal curing conditions, time, and Na⁺ content, which impacts silica availability during
197 geopolymerization. The mineralization of silica-rich zeolites, such as faujasite, in the aluminosilicate
198 binders is important for acid resistance, as it can lower porosity and increase strength in comparison to
199 unmineralized formulations of equal stoichiometry [29], [30].

200 Control High samples without and with Fe have a higher degree of N-A-S-H crosslinking compared
201 to lower Na:Al counterparts as a consequence of higher alkalinity. Also observed by others, higher
202 precursor dissolution is to be expected, due to a higher concentration of Na⁺ cations [34]. Consequently, in
203 Control High samples, there is an increase in Al content and formation of a highly crosslinked geopolymer
204 binder (*i.e.*, N-A-S-H) [34]–[36]. This is evidenced in **Figure 1(ii)** by shifts to lower wavenumbers of both
205 the main Si-O-Al band (1002–1005 cm⁻¹) and the Si-O-Al symmetric-stretching band (720 cm⁻¹) to 984 cm⁻¹
206 and 670 cm⁻¹, respectively [37]. This observation is further supported by strong peaks for in-plane
207 stretching and bending of Si-O and Al-O (460 cm⁻¹), symmetric vibrations of Si-O-Al and Si-O-Si bonds
208 (750 cm⁻¹), and stretching vibrations of Al-O and Si-O tetrahedral (900 cm⁻¹). Control Low samples yield
209 lower absorption intensities for these peaks, signifying lower degrees of reactivity and N-A-S-H
210 crosslinking. Lastly, the presence of carbonates is confirmed for all samples by peaks at 1384 cm⁻¹ and 1560
211 cm⁻¹, which correspond to O-C-O asymmetric stretching.



212

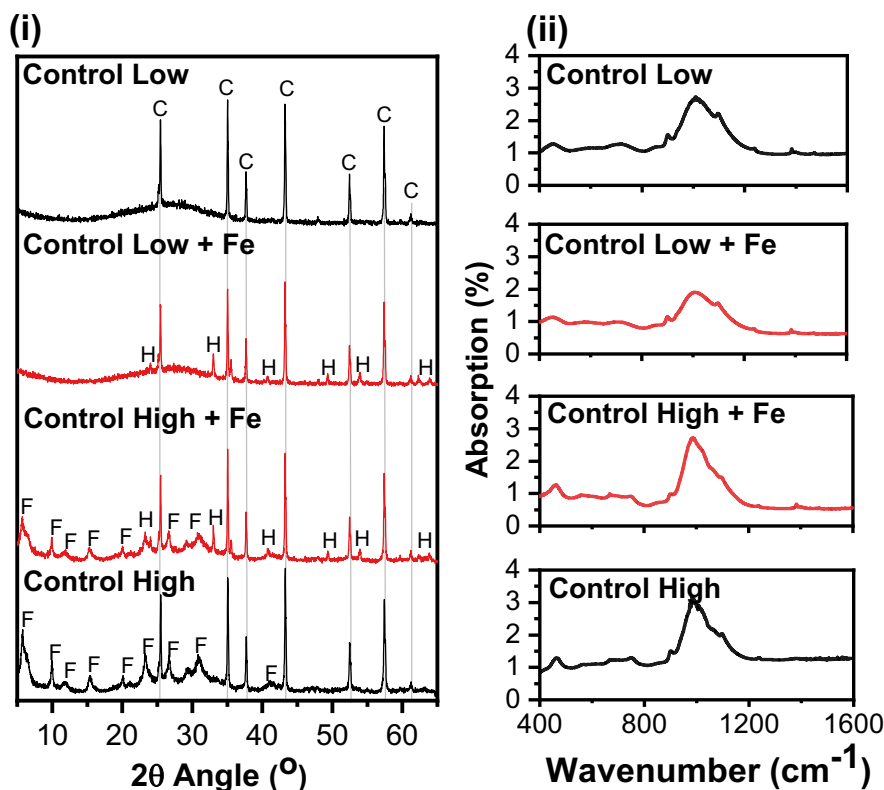
213 **Figure 1.** Mineralogy (i) and Fourier-transform infrared (FTIR) spectroscopy (ii) of all samples. In panel
 214 (i), F = faujasite ($\text{Na}_{2.06}\text{Al}_2\text{Si}_{3.8}\text{O}_{11.63}\cdot 8\text{H}_2\text{O}$); H = hematite (Fe_2O_3); and, C = Corundum (Al_2O_3). Main Si-
 215 O-T band assignments for Control Low, Control Low + Fe, Control High, and Control High + Fe were 1005
 216 cm^{-1} , 1006 cm^{-1} , 985 cm^{-1} , and 982 cm^{-1} , respectively.

217 No evidence was observed herein to indicate presence of a Fe-modified N-A-S-H cementitious
 218 binder (*i.e.*, Fe-O-Si bonds). Previous research has produced high-Fe alkali-activated materials from Fe-
 219 rich aluminosilicate precursors, such as laterite clays, Bayer red mud waste, and fayalitic slags. Contentious
 220 evidence has suggested, however, that high Fe content can result in (1) Si-O-Fe incorporation into the
 221 geopolymer network or (2) segregated formation of Fe octahedral phases [38]–[41]. Research has suggested
 222 that the consumption of Fe mineral phases leads to isomorphic substitution of Al by Fe ions, which possibly
 223 occurs in extremely distorted sites of gel-like phases. However, these results vary depending on precursor
 224 chemistry and dissolution kinetics associated with activating conditions [42]–[44]. Further research in
 225 similar metakaolin-based AACs as those studied here found no significant structural changes induced by
 226 hematite in similar metakaolin-based AACs [43], [45]. As a result, the FTIR data presented in **Figure 1(ii)**
 227 reveals no further structural evidence of Fe-O-Si bond formation.

228 3.2 Mineralogical and Structural Effects of Sulfuric Acid Exposure

229 After acid exposure, the mineral composition of all geopolymer samples remains largely identical to
 230 unexposed samples. Increases in faujasite formation were observed in samples with high alkali contents
 231 (**Figure 2(i)**). As expected, a loss of carbonates, Si, and Al was evidenced by FTIR band intensities (**Figure**
 232 **2(ii)**). Carbonates are expected phases in N-A-S-H binders, due to the carbonation of alkalis (*e.g.*, Na^+) that
 233 remain after NaOH activation. In all geopolymer samples, carbonates exhibit some dissolution due to the
 234 low pH induced by sulfuric acid. This dissolution is evidenced in **Figure 2(ii)**, as a peak intensity decrease
 235 or absence in the 1384 cm^{-1} and 1560 cm^{-1} regions which correspond to O-C-O asymmetric stretching in
 236 carbonates [46], [47]. Notably absence of these peaks was observed in Control High samples, while Control

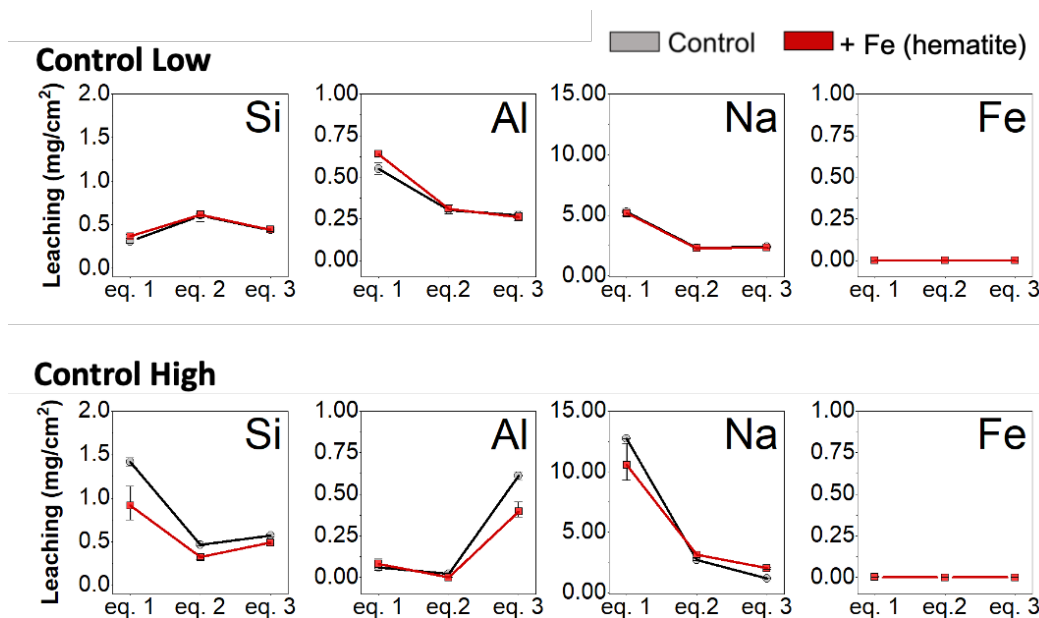
237 High + Fe samples retained the carbonate peak at 1384 cm^{-1} . This results indicate that these samples can
 238 conserve carbonates after sulfuric acid exposure. Further comparison between these spectra is presented in
 239 supplementary information, **Figure S.1**. This is important as the consumption of carbonates is expected to
 240 aid in arresting the protic dissolution of the Si-O-Al binder by serving as a pH buffering agent. For all
 241 Control Low formulations, regardless of Fe supplementation, structural modifications to the N-A-S-H
 242 binder, from a loss of Al (dealumination) and Na, is represented by a shift to higher wavenumbers, mainly
 243 from 999 cm^{-1} to $\sim 1010\text{ cm}^{-1}$, in the main Si-O-T band (1002 cm^{-1}) [48]–[51]. The relative peak intensity
 244 decrease renders other Si-O-Al symmetric stretching vibrations (670 cm^{-1} , 600 cm^{-1} , and, to a lesser extent,
 245 590 cm^{-1}) peaks negligible indicating the loss of these Si-O-Al bonds most likely due to the dealumination
 246 of the material (**Figure S.1**). Control High samples with hematite addition remain largely unchanged after
 247 acid exposure, as evidenced by an increase in the main Si-O-T band (1002 cm^{-1}) intensity. However, a loss
 248 of a sharp peak at 850 cm^{-1} was observed after acid exposure indicating the deprotonation of silanols (Si-
 249 OH) bonds after acid attack [52]–[54]. The loss of silanols bonds may reflect a binder reorganization after
 250 acidic exposure, which could correlate with formation of faujasite as also shown in the XRD data due to an
 251 increase in the relative diffraction peak intensity (**Figure 2(i)**).



252
 253 **Figure 2.** Acid exposed mineralogy (i) and Fourier-transform infrared (FTIR) spectroscopy (ii) of all
 254 samples. In panel (i) the “F” indicates the presence of faujasite ($\text{Na}_{2.06}\text{Al}_2\text{Si}_{3.8}\text{O}_{11.63}\cdot 8\text{H}_2\text{O}$); “H” indicates
 255 the presence of hematite (Fe_2O_3); and, “C” indicates the presence of corundum (Al_2O_3).

256 Ion leaching profiles collected after three repeated sulfuric acid exposures are shown in **Figure 3**.
 257 Control Low samples without and with hematite addition bear no significant differences in Si, Na, and Fe
 258 leaching. However, slightly lower dealumination in the Control Low samples without hematite addition
 259 was observed. This result was supported by evidence obtained *via* FTIR (**Figure 2(ii)**). Contrastingly,
 260 Control High samples supplemented with hematite demonstrate up to 50% and 33% reductions in Si and
 261 Al leaching during acid exposure, respectively, confirming that hematite addition improves the acid
 262 resistance of these samples. The retention of these framework metals further substantiates the preservation

263 of the Si-O-Al bonds in the N-A-S-H cementitious binder and possible formation of Si-O-(Si) gels—a result
 264 also substantiated by FTIR data [49]. Na leaching in these samples is observed to be slightly higher at the
 265 third acid exposure. This result may indicate that Fe species could displace Na from local negative moieties
 266 (Al) in the N-A-S-H binder due to a higher chemical affinity. However, more research is necessitated to
 267 confirm this hypothesis.



268

269 **Figure 3.** Normalized elemental leaching upon acid exposure for all sample formulations. Maximum and
 270 minimum leaching values are presented as lines, while average values are presented as squares.

271 The acid neutralization capacity of geopolymers samples after the first and second acid exposure is
 272 temporarily improved by an increase in hematite and alkali content (see **Table 2**). The acid neutralization
 273 capacity of samples is an important material property, as it demonstrates the ability of a material to buffer
 274 the pH of an acidic medium. The first acid exposure reveals that alkali content solely increases the acid
 275 neutralization capacity with higher final pH values for Control High formulations (12.43, 12.36) when
 276 compared to Control Low formulations (10.23, 10.59). As expected from earlier work on acid degradation
 277 of cementitious materials [48], [55]–[58]. After the second exposure, the addition of hematite increased the
 278 final pH from 4.10, as achieved by the Control High samples, to 5.27. This increase is likely due to the
 279 dissolution of hematite since lower Si leaching and minimal differences in dealumination are observed.
 280 However, by the third exposure, the acid neutralization capacity imparted by hematite is negligible.
 281 Minimal changes to the final pH were observed between samples without and with hematite (*i.e.*, 3.81 vs.
 282 3.99). These data show that the acid resistance benefits of the Control High samples supplemented with Fe
 283 described by the mineralogy, molecular structure, and leaching data cannot be solely due to the acid
 284 buffering capacity of hematite-containing samples.

285

286 **Table 2.** Final pH value at each equilibrium exposure for all sample formulations.

Sample Name	Acid Exposure Cycle	Final pH
Control Low	1	10.23
	2	3.96
	3	3.96

Control Low + Fe	1	10.59
	2	3.95
	3	4.09
Control High	1	12.43
	2	4.10
	3	3.81
Control High + Fe	1	12.36
	2	5.27
	3	3.99

287

288 3.3 Physico-Mechanical Changes after Sulfuric Acid Exposure

289 **Table 3** summarizes the observable ($> 6 \mu\text{m}$) segmented porosity of geopolymer samples before and after
 290 sulfuric acid exposure. The porosity of Control Low samples without and with Fe approximately doubled
 291 upon exposure to acid, thus confirming previous FTIR, XRD, and leaching results that, at low alkali
 292 contents, hematite addition reveals a negligible benefit to acid resistance. Increasing alkali content of
 293 geopolymer formulations, regardless of hematite addition, yields an increase in the original observable
 294 porosity. Upon sulfuric acid exposure, however, Control High samples with hematite additions do not reveal
 295 a significant change in porosity (1.11%). Hence, the changes to the molecular structure (*i.e.*, Si-rich gel
 296 formation and Si-O-Al preservation) minimally affect the porosity of Control High with hematite samples.
 297 Control High samples without hematite, however, structurally cracked excessively (structural failure) after
 298 acid exposure, probably due to the small sample size required for μ -CT analysis. The sample geometry may
 299 have increased the rate of deleterious sample desiccation and produce destructive diffusion-driven hydro-
 300 mechanical forces [59], [60].

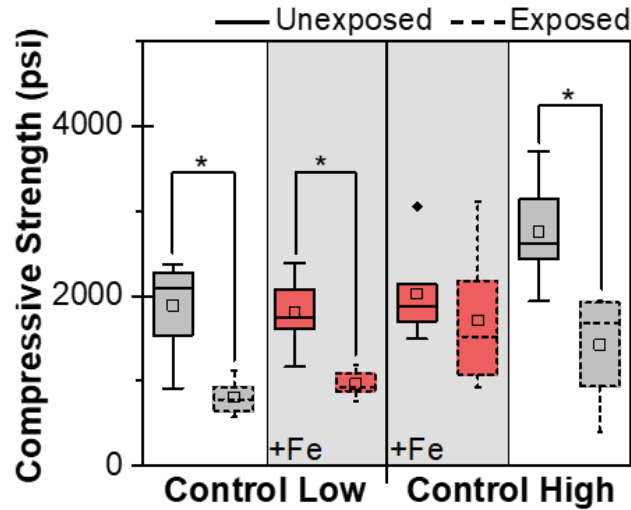
301 **Table 3.** Cumulative visible porosity ($> 6 \mu\text{m}$) as determined by μ -CT scans of unexposed and acid
 302 exposed geopolymer samples. * Sample structurally failed with excessive cracking due to acid exposure.

Sample Name	Unexposed	S.D.	Exposed	S.D.
Control Low	0.73%	0.01%	1.30%	0.13%
Control Low + Fe	0.62%	0.01%	1.29%	0.09%
Control High	1.09%	0.02%	NA*	NA*
Control High + Fe	1.11%	0.03%	1.11%	0.03%

303 The compressive strength of all geopolymer samples before and after acid exposure is shown in
 304 **Figure 4**. For low Na:Al ratio samples, similar compressive strengths are observed prior to and upon acid
 305 exposure. Thus, no significant effect on the acid resistance was found for hematite supplements at low
 306 Na:Al formulations. This result corroborates previous experimental results obtained for low Na:Al samples.
 307 Aside from the slightly higher dealumination of Control Low with hematite samples, the Control Low
 308 samples with and without hematite do not differ significantly in molecular structure, mineralogy, observable
 309 porosity or, as evidenced in **Figure 4**, compressive strength.

310 Increasing the Na:Al content yields increased compressive strengths for geopolymer samples, as
 311 expected higher degrees of binder crosslinking (**Figure 1(ii)**). Hematite addition, however, reduced the
 312 unexposed compressive strength by $\sim 29\%$ in Control High samples. Recent research has demonstrated
 313 similar effects on mechanical performance, attributing iron phases with the formation of weak interfacial
 314 planes between the mineral and cementitious matrix [61]. Once acid-exposed, the compressive strength is

315 not significantly affected for Control High samples with hematite, indicating improved acid resistance.
 316 These results reveal the synergistic acid resistance benefits of higher alkali contents (Na:Al = 1.39) and
 317 hematite (5 wt.%). Contrastingly, compressive strength decreased by ~36% in the Control High samples
 318 without hematite upon exposure to acid.



319
 320 **Figure 4.** Compressive strength of all formulations. * Denotes statistically significant difference in the
 321 sample mean (p-value < 0.05).

322 3.4 Mechanisms of Acid Degradation in Geopolymers with Iron Mineral Admixtures

323 Results from EDS chemical mapping (see **Table 4**) suggest that hematite influences the acid degradation
 324 of the N-A-S-H cementitious binder and that this influence depends on the degree of Al crosslinking of the
 325 binder, which is affected by activating conditions (i.e., Na₂O wt.%). As observed in **Table 4**, acid exposure
 326 slightly changes the mean Si:Fe ratio of Fe-supplemented Control Low and Control High samples.
 327 However, these changes are minimal and reveal no statistical significance. The slight decrease in the mean
 328 Si:Fe ratio in Control High + Fe samples can be understood due to the high leaching of Si from these
 329 samples' formulations, see **Figure 3**. Expectedly, the Si:Al ratio increases in Control Low samples (**Table**
 330 **4**) as a result of the dealumination of the material, observed in **Figure 3** and **Figure 2**. However, when
 331 hematite is present the Si:Al ratio of the microstructure is statistically similar after acid exposure. The
 332 unchanged Si and Al content in the acid-attacked microstructure was not indicative of the material's
 333 durability performance as this Fe-supplemented material revealed similar compressive strength as Control
 334 Low samples (**Figure 4**); indicating that hematite addition was likely not a contributor to the acid durability
 335 of these samples. Lastly, compressive strength benefits were observed for Control High + Fe samples
 336 (**Figure 4**) as well as both lower Si and Al leaching (**Figure 3**) and higher acid buffering capacities (**Table**
 337 **2**). These acid resistance improvements are associated with a slight increase in the Fe:Al ratio within the
 338 microstructure (**Table 4**). In order to add more confidence to this correlated finding larger datasets must be
 339 analyzed.

340 **Table 4.** Microstructural stoichiometric ratios (Si:Al, Si:Fe, and Fe:Al) of geopolymer materials before
 341 (control) and after sulfuric acid exposure (acid). ^A statistically significant mean difference calculated with
 342 One-way ANOVA (p-value = 0.059). ^B p-value = 0.171, which is higher than the *a priori* p-value (0.05,
 343 95% confidence).

Sample Name	Si:Al		Si:Fe		Fe:Al	
	Control	Acid	Control	Acid	Control	Acid

Control Low	1.27 ^A	1.30 ^A	-	-	-	-
Control Low + Fe	1.29	1.29	28.30	29.24	0.06	0.09
Control High	1.28	1.27	-	-	-	-
Control High + Fe	1.27	1.25	31.95	26.29	0.06 ^B	0.09 ^B

344

345 As discussed, the acid degradation behavior of samples was observed to vary depending on the
 346 degree of crosslinking in the cementitious binder and formation of secondary phases, such as faujasite
 347 zeolites. Chemical evidence gathered by EDS demonstrates increases of the central tendencies (*i.e.*, median,
 348 mean) for the Fe:Al ratio after sulfuric acid exposure (**Table 4**). The formation of thermodynamically
 349 favorable Fe cationic molecules (*e.g.*, FeSO₄⁺) may result in association with negatively charged moieties
 350 of the aluminosilicate network (Si-O-Al). As evidenced by leaching (**Figure 3**) and FTIR data (**Figure 2**),
 351 dealumination occurs in these samples, which creates a concomitant increase in negative moieties during
 352 protic electrophilic attack. During this process, the electrophilic attack may be arrested if released cationic
 353 species can stabilize the unstable negative moiety of the Si-O-Al network.

354 4. Conclusions

355 This study explains, for the first time, how iron mineral admixtures (*i.e.*, hematite) affect material properties
 356 prior to and after sulfuric acid exposure (pH = 2.00 ± 0.07) and how resultant microstructural effects can
 357 explain the acid resistance commonly observed in alkali-activated materials. Results indicate that iron
 358 phases, such as hematite, can improve the acid resistance in high Na:Al geopolymer formulations. Improved
 359 acid resistance resulted in lower compressive strength loss due to acid attack, lower increases in observable
 360 porosity, and an arrest of the degradation of the cementitious binder.

361 Hematite was observed to be inert during alkali activation. Prior to acid exposure, increasing the
 362 sodium content yielded expected formation of silicon-rich mineral phases (*i.e.*, faujasite) as well as an
 363 increase in the extent of N-A-S-H binder network formation. No evidence for Fe-induced modification of
 364 the geopolymer cementitious binder was observed. Instead, weak bonding between the cementitious binder
 365 and hematite particles resulted in lower initial compressive strength.

366 After acid exposure, the addition of hematite was only observed to have a beneficial effect at high
 367 alkali contents (Na:Al = 1.39). Acid resistance was observed by (1) statistically insignificant loss of
 368 compressive strength, (2) minimal changes to the molecular structure (main Si-O-Al bond), (3) statistically
 369 insignificant changes to porosity, and (4) low leaching of Al (*i.e.*, dealumination) and Si. However, these
 370 results were not found true for samples with lower alkali contents (Na:Al = 0.86), most likely due to a lesser
 371 extent of Al-crosslinked N-A-S-H and lack of secondary mineral phases forming (*i.e.*, zeolites).

372 The evidence collected and reported herein indicates that the acid buffering capacity of
 373 geopolymers, specifically at higher alkali content formulations, increases due to the addition of hematite.
 374 In turn, an increased buffering capacity leads to lower degrees of dealumination of the N-A-S-H
 375 cementitious binder.

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