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Interface bonding properties of polyvinyl alcohol (PVA) fiber in alkali-activated slag/fly ash

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Keywords: bonding; interface; fiber pullout; PVA; alkali-activation; slag; fly ash

Abstract

This paper presents an experimental study on the interface bonding properties of polyvinyl alcohol (PVA) fiber in alkali-activated slag/fly ash (AASF) pastes. Three interface bonding properties (i.e., the chemical bonding energy G_d , the initial frictional bond strength τ_0 , and slip-hardening behavior β) were determined using single-fiber pullout tests. The microstructure and chemical composition of the reaction products in the fiber/matrix interfacial transition zone (ITZ) and the nearby matrix were also characterized to reveal the influence of PVA fiber to its surrounding matrix. It is found that G_d increases primarily with increasing Ca/(Si+Al) ratio of C-(N)-A-S-H gel. Unlike that in cementitious materials, the inclusion of PVA fiber in AASF pastes promotes the formation of a high-Ca C-(N)-A-S-H phase rather than crystalline portlandite near the fiber surface. This study provides useful guidance for tailoring the interface bonding properties of AASF and also the development of high-performance composites such as strain-hardening geopolymer composites.

1. Introduction

Alkali-activation is one of the few technologies that can transform wastes and industrial by-products into cement-free building materials. Alkali-activated materials (AAMs) including those classified as geopolymer are derived by the reaction of an alkali metal source (solid or dissolved) with a solid alumino-silicate powder [1, 2]. With proper mixture design, they can provide significant environmental benefits, particularly regarding the reduction of CO₂ emissions and energy consumption [3-5].

32 Furthermore, AAMs as binder material for concrete could maintain comparable mechanical properties
33 and even better durability under certain exposure conditions [6-9]. Among all AAMs, the ones based
34 on blast furnace slag, class F fly ash, and their blends are the most intensively studied [10]. This is
35 mainly due to the large quantity of annual production as well as the relatively stable chemical
36 compositions of these two solid precursors [1, 2, 11, 12]. Previous studies on the slag/fly ash-based
37 AAMs, namely alkali-activated slag/fly ash (AASF), have focused on microstructure development,
38 nature of reaction products as well as mechanical properties [13-18]. The application of AASF for
39 engineering practices has also been greatly promoted.

40 Like conventional cementitious binders, AAMs are also inherently (quasi-)brittle and thereby
41 susceptible to cracking [19-22]. As one of the classic approaches to control brittleness, fiber
42 reinforcement has been researched in AAMs and was found to hold promise in achieving advanced
43 fracture and tensile performances [23-26]. Polymeric micro-fibers were used to effectively obtain a
44 composite with extraordinary tensile performance, among which, polyvinyl alcohol (PVA) fiber with
45 good bonding to hydration products and sound mechanical properties has been widely used [23-26].
46 Particularly, it is applied for the development of high-performance composites such as strain-
47 hardening cementitious composite (SHCC) [27] and strain-hardening geopolymer composite (SHGC)
48 [23-25].

49 For the development of PVA fiber-reinforced cementitious and/or alkali-activated composites, the
50 fiber/matrix interface bonding properties are crucial. Many previous studies thereby focused on the
51 characterization and modification of the PVA fiber/matrix interface by performing single-fiber pullout
52 tests [28-30]. However, the interface bonding properties of PVA fiber within AAMs are not sufficiently
53 investigated. Only a few experimental studies could be found. For instance, Ohno and Li [23]
54 researched the interface properties of PVA fiber in a fly ash-based geopolymer matrix. They found
55 that, in comparison to those in conventional SHCC materials, the chemical bonding G_d is almost 5
56 times stronger while the frictional bond and tendency for slip-hardening behavior is considerably
57 weaker. Nematollahi et al. [24] tested the interface properties of PVA fiber/matrix properties in alkali-
58 activated fly ash mixtures. The influence of using both sodium and potassium silicate-based activators
59 and the surface oiling treatment on the interface properties were addressed. Compared to the sodium-
60 based activator, the potassium silicate-based ones significantly enhance the chemical bond while
61 weakening the frictional bond and slip-hardening. Similar findings have also been confirmed by
62 Trindade et al. in the study of PVA fiber in metakaolin-based systems [31]. Additionally, Nematollahi
63 et al. [26] concluded that the strong chemical bonding of PVA fiber within a one-part AASF matrix
64 could effectively enhance the fiber-bridging strength of the composite. Zhang et al. [25] tested the
65 interface bonding properties of PVA fiber in AASF matrices and reported that the chemical bonding
66 could be effectively modified by changing the silicate modulus of the alkaline activator. Furthermore,
67 with the help of molecular dynamics (MD) simulation, they also found that adhesion between PVA

68 fiber surface and the reaction products in AASF is mainly due to electrostatic interactions rather than
69 van der Waals force [32].

70 The scope of most of these previous studies is limited to the experimental determination of interface
71 bonding properties and their impact on the tensile behavior of composites. Since the main reaction
72 products in a cementitious matrix and an alkali-activated matrix are not the same, the influence of
73 reaction product chemistry on the interface bonding properties of PVA fiber, as well as its interaction
74 mechanism with the AASF system, is worth to be studied in more depth. This can help understand the
75 microscale interface bonding properties and mechanisms, which are of primary importance for the
76 development of PVA fiber-reinforced alkali-activated composites (such as SHGC). In the existing
77 studies, however, the influence of the reaction product chemistry on the interface bonding properties
78 are usually neglected. Furthermore, studies on the interfacial transition zone (ITZ) between the PVA
79 fiber and AASF matrix have been rarely reported.

80 The goal of this experimental study is to characterize the interface bonding properties of PVA fiber in
81 AASF matrices and to further clarify the effects of PVA fiber on the reaction products chemistry in the
82 PVA fiber/matrix ITZ in AASF matrices. To this end, the chemical bonding energy G_d , initial frictional
83 bond τ_0 , and slip-hardening coefficient of PVA fiber to the AASF matrix were systematically
84 investigated using single-fiber pullout tests. The influence of PVA fiber on the microstructure of the
85 ITZ and the chemical composition of the reaction products within the ITZ were characterized using
86 multiple techniques. Based on the experimental results, the relationship between G_d and the chemical
87 composition of the reaction products was further explored. The origin of the initial frictional bond and
88 slip-hardening behavior of PVA fiber in AASF pastes were also discussed.

89 **2. Materials and methods**

90 **2.1 Materials**

91 The solid precursors were ground granulated blast furnace slag and Class F fly ash produced locally
92 in the Netherlands. The physical properties, chemical compositions, mineralogical composition, and
93 reactivity of both raw materials have been reported in our previous studies [17, 25]. The polyvinyl
94 alcohol (PVA) fiber (RECS 15, Kuraray) with 1.2% oiling treatment on the surface was used. The
95 chemical structure of the PVA fiber is shown in Figure 1. The PVA polymer is primarily composed of
96 the vinyl group (C-OH) with a minor content of the acetate group (C-OCOCH₃). According to the
97 supplier, the acetate group is introduced by the synthesis process, although it is the vinyl group that
98 determines the surface property of the fiber.

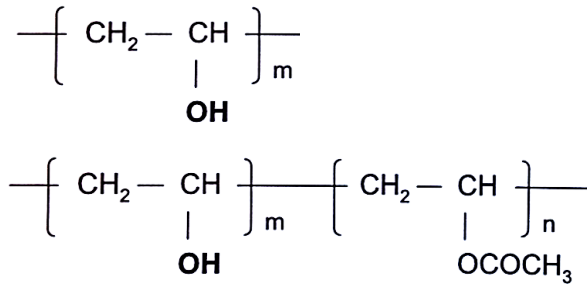


Figure 1 Structure of PVA polymer according to the fiber supplier [33]

The physical and mechanical properties of PVA fiber are presented in Table 1. A filament-type PVA fiber with a diameter of 40 μm was adopted for the characterization of the mechanical properties of the fiber/matrix interface. The study of the ITZ, whereas, adopted PVA fiber with a diameter of 300 μm in order to facilitate the characterization of ITZ by means of ESEM and EDX. The alkaline activator was a sodium-based silicate solution prepared by dissolving NaOH pellets (analytical grade, purity $\geq 98\%$) and sodium silicate (Na_2O : 8.25 wt.%, SiO_2 : 27.50 wt.%) in distilled water. The activator solution was cooled down to room temperature before mixture preparation.

Table 1 Physical and mechanical properties of PVA fiber

Fiber	Diameter (μm)	Density (g/cm^3)	Length (mm)	Strength (MPa)	Elastic modulus (GPa)
PVA	40, 300	1.30	filament	1640	41.1

2.2 Mixture design and preparation

The mixture design originates from AASF pastes that exhibit a good combination of fresh properties and mechanical properties [18]. Since the microstructure and reaction product of AASF pastes is significantly influenced by the contents of Si from the activator [13, 17, 34], the silicate modulus M_s (M_s being the $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratios) of the activator was selected as the main variables in this study. The mixture design of AASF paste matrices is shown in Table 2, in which the binder composition with different activator silicate modulus M_s (0 to 1.5) are given. The AASF matrices were named M0 to M1.5 accordingly. In each mixture, the w/b ratio and Na_2O content (in activator with respect to total binder mass) were kept constant to be 0.32 and 4%, respectively. The w/b ratio was chosen in a way that adequate workability for all paste mixtures was maintained.

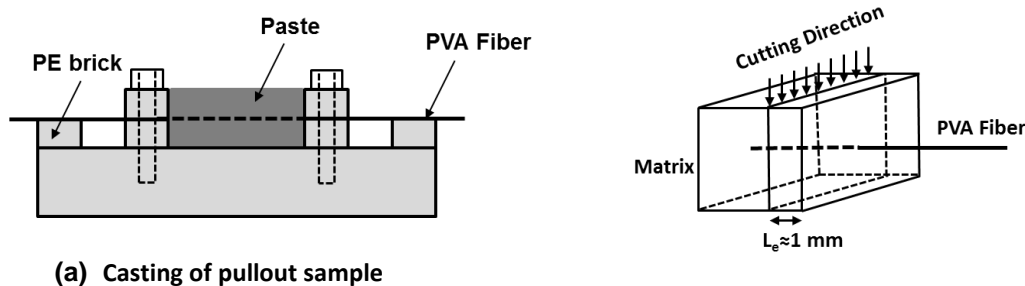
Table 2 Mixture proportions of alkali-activated slag/fly ash matrices

Mixture	Solid precursor (wt.%)			Alkaline activator (wt.%)		
	Slag	Fly ash	Water	Na ₂ O	SiO ₂	Silicate Modulus M_s
M0					0	0
M0.5					1.94	0.50
M0.8	50	50	32	4.0	3.10	0.80
M1.0					3.88	1.00
M1.2					4.65	1.20
M1.5					5.82	1.50

122

123 2.3 Determination of interface bonding properties

124 The interface bonding properties of PVA fiber AASF matrices were tested experimentally by single-
 125 fiber pullout tests with the set-up following Redon et al. [28]. The set-up is shown in Figure 2 (a). A
 126 mold equipped with two-layer polyethylene (PE) bricks developed by Katz and Li [35] was used. The
 127 PVA fiber was cut, aligned, and fixed onto the PE brick using double-sided tape. The fresh AASF
 128 paste was then poured into the mould around the fibers. The specimens were put on a vibration table
 129 to remove entrapped air before sealing them with plastic wrap. After 24 hours, the specimens were
 130 demolded and transferred to a climate room (20°C and 95% RH) until 28 days. At 28 days, the
 131 hardened specimens were cut into very thin sliced samples using a low-speed saw (Minitom, Struers).
 132 As shown in Figure 2 (b), the cutting leaves the fiber on one side of the sample. The thickness of the
 133 sample, i.e., the embedded length (L_e) of PVA fiber, was approximately 1 mm, which was short enough
 134 to avoid fiber rupture during the fiber pullout process.

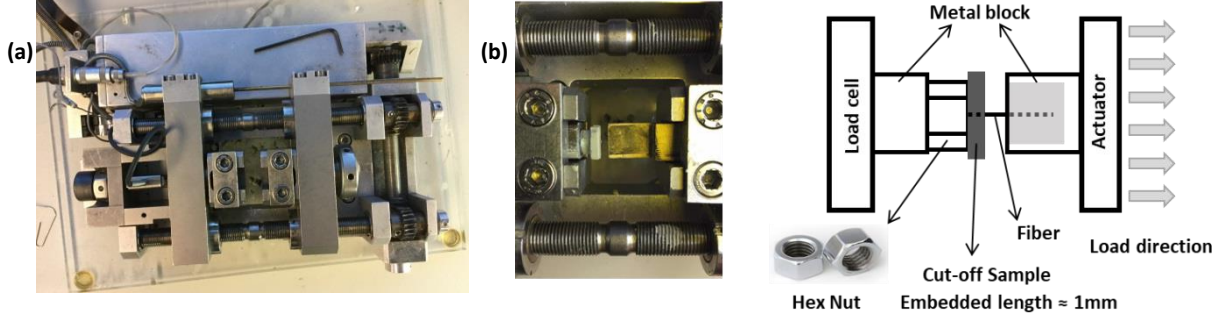


135

136 Figure 2 Pullout sample preparation methods: (a) casting and (b) precise cutting [25].

137 For the single-fiber pullout tests, a micro tension-compression testing device (Kammrath & Weiss)
 138 was used as shown in Figure 3 (a). The schematic pullout test set-up is shown in Figure 3 (b). The
 139 surface of the thin-sliced sample and the free end of the PVA fibers were glued to two small metal
 140 blocks. The fiber was then aligned vertically to the matrix surface to avoid the influence of matrix
 141 spalling on the testing result. A hex nut was applied in between the cut surface and the metal block to
 142 avoid gluing the fiber ends. Then, the two metal blocks with the pullout sample were carefully mounted
 143 onto the testing device and were further fixed to an actuator and a load cell. Notably, a fiber segment

144 with a length of approximately 1 mm was kept free of loading between the actuator and the pullout
 145 sample. A 10 lb (44.48 N) load cell was used to measure the pullout load with an accuracy of 0.1%.
 146 The pullout tests were conducted using displacement control with a constant displacement rate of
 147 0.01 mm/s. At least 20 tests were conducted for each fiber/matrix combination.



148

149 Figure 3 Single-fiber pullout test: (a) micro tension-compression device, (b) schematic tests set-up [25].

150 To quantitatively determine the interface properties, the chemical bonding energy G_d , initial frictional
 151 bond τ_0 , and slip-hardening coefficient β were derived from the single fiber pullout curves (see Figure
 152 4) with Equations (1) to (3). All these equations were derived from a fiber debonding/pullout model by
 153 Lin et al. [36]. In formula form:

$$G_d = \frac{2(P_a - P_b)^2}{\pi^2 E_f d_f^3} \quad (1)$$

$$\tau_0 = \frac{P_b}{\pi d_f L_e} \quad (2)$$

$$\beta = \frac{d_f}{L_e} \left(\frac{(\Delta P / \Delta S |_{\Delta S \rightarrow 0})}{\pi \tau_0 d_f} + 1 \right) \quad (3)$$

154 where E_f , d_f , and L_e are the elastic modulus [GPa], diameter [mm], and embedded length [mm] of PVA
 155 fiber, respectively. $\Delta P / \Delta S$ is the initial slope of the pullout load P [N] vs displacement S [mm]. P_a is the
 156 load at the moment when the fiber is fully debonded (debonded length $L_d =$ embedded length L_e) and
 157 P_b is the load when the fiber starts to slip.

158

159 2.4 Microstructural characterizations

160 The microstructure and the chemical compositions of reaction products in AASF bulk matrices and
 161 the (possible) ITZ around PVA fiber were characterized using environmental scanning electron
 162 microscopy (ESEM) and energy dispersive X-ray (EDX) analysis. In this study, the area of interest
 163 extends to as far as 30 μm away from the fiber. Such range is considered appropriate to study the
 164 influence of PVA fiber on the reaction product formation at the fiber/matrix interface (see also [37]).
 165 Mixtures including M0 to M1.5 were used to characterize the reaction product composition in AASF
 166 bulk matrices. Only the M1.0 sample as a representative was studied to determine the distribution of

167 element/reaction products near the PVA fiber. All samples were prepared following the method for
168 single fiber pullout tests as described in Section 2.3.

169 Before the ESEM/EDX tests, the chemical reaction in hardening pastes was stopped by the solvent
170 exchange method using isopropanol. After vacuum drying, the samples were impregnated using low-
171 viscosity epoxy resin. After the hardening of the epoxy resin, the samples were polished until reaching
172 a surface roughness of 0.25 μm . Backscattered electron (BSE) images and secondary electron (SE)
173 images were taken at an accelerating voltage of 15 kV and 5 kV, respectively. The polished samples
174 were coated with carbon and then the EDX measurements were conducted at an accelerating voltage
175 of 15 kV in high vacuum mode.

176 Furthermore, ESEM/EDX-based spectral imaging (SI) was performed to study the chemical
177 compositions of the reaction products. The points for EDX spot analysis were carefully selected within
178 the binder region, keeping sufficient distance from the unreacted slag and fly ash particles [38]. In
179 each EDX measurement, corrections on the characteristic X-ray intensity were made by taking into
180 account the atomic number, absorption, and fluorescence excitation (ZAF) effect. These corrections
181 convert apparent concentrations (raw intensities) into corrected concentrations to eliminate inter-
182 element matrix effects.

183 Finally, automated phase mapping was used to study the phases formed in AASF pastes under the
184 influence of PVA fiber. For this purpose, the COMPASSTM as a built-in function in the Pathfinder
185 software (ThermoFisher Scientific) was applied. The phase mapping was based on the analysis of
186 spectral imaging (SI) data using principal component analysis (PCA). With a multivariate statistical
187 approach, COMPASS could analyze the spectrum at each pixel location and groups the pixels with
188 similar spectra together into principal components [39]. These principal component maps were
189 translated into phase maps using the same types of intensity threshold algorithms used for traditional
190 element-based phase mapping. The phase spectrum was thus the summation of the spectra from
191 each pixel within the phase [39, 40]. The final results were a list of chemically unique phase spectra
192 and phase maps. In this way, the hidden phases could be also revealed, regardless of the inevitable
193 intermixing of the phases and the noise signals from unreacted precursor particles [41]. For one
194 automated phase mapping analysis, at least 300 frames of EDX element mapping were taken on the
195 selected area covering the PVA fiber, the ITZ, and the matrix. The presence of the phases was further
196 examined by the density plots using the channel intensity correlations (net counts) from each pixel of
197 the EDX phase mapping.

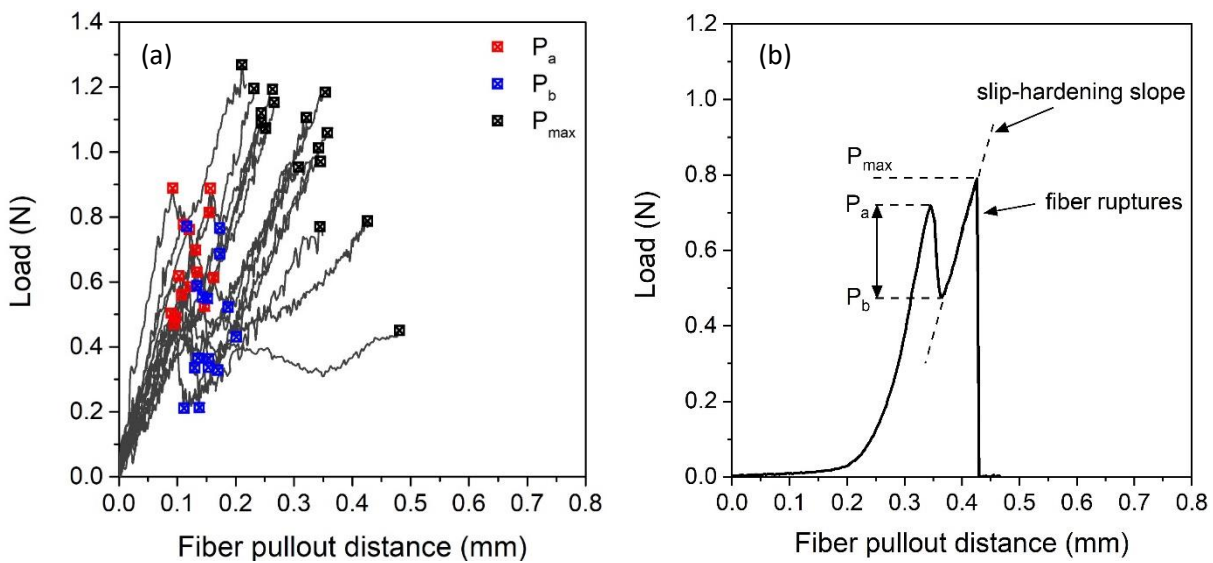
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3. Results and discussions

3.1 PVA fiber/matrix interface bonding properties characterization

3.1.1 Single-fiber pullout behavior

The single-fiber pullout behavior, i.e., the load-displacement relationship of PVA fibers embedded in the AASF matrix, is shown in Figure 4 (a). The PVA fiber debonding and pullout behavior in the AASF matrix is similar to that of PVA fiber in the cementitious matrix [28, 42]. As illustrated in Figure 4 (b), the general profile of a single-fiber pullout curve can be decomposed into three main regimes [28]: (1) the stable debonding stage in which the load increases up to P_a until the moment when the debonded length equals the embedded length of the fiber, (2) the slippage stage in which the fiber starts to slide from load P_b and the pullout is resisted by frictional forces only, and finally (3) the slip-hardening stage in which the friction force increases linearly with increasing pullout distance up to the maximum load P_{max} before the fiber ruptures. The increasing pullout resistance is referred to as the slip-hardening effect and is characterized by the slip-hardening coefficient β ($\beta > 0$) [43].



212

Figure 4 (a) Representative pullout curve of PVA fiber in AASF matrix; and (b) schematic illustration of fiber pullout process.

214

The results of all interface bonding properties including chemical bonding energy G_d , initial frictional bond τ_0 , and slip-hardening coefficient β are given in Table 3. Their standard deviations (STDs) generally fall between 25% to 40% of the mean values. The clustering of the data around the mean value thereby implies the trend in the data set could be determined using the mean values.

219

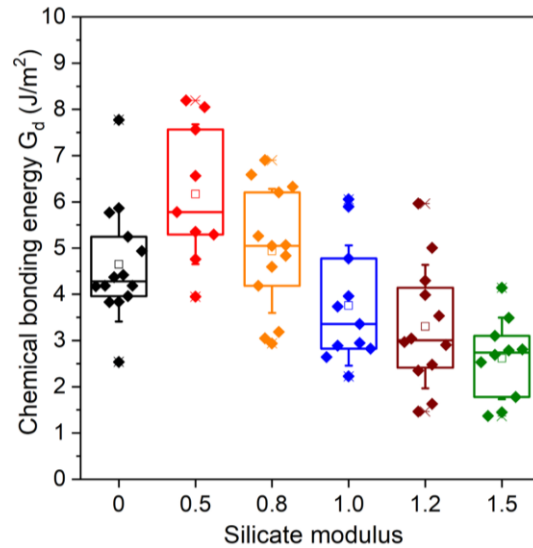
Table 3 PVA fiber/matrix interface bonding properties

Mixture	Chemical bonding energy G_d (J/m ²)	Initial frictional bond τ_0 (MPa)	Slip-hardening coefficient β
M0	4.61±1.21	2.29±0.56	0.34±0.05
M0.5	6.15±1.49	4.09±1.14	0.43±0.08
M0.8	4.92±1.27	3.22±0.81	0.47±0.13
M1.0	3.74±1.31	3.41±0.84	0.44±0.10
M1.2	3.29±1.34	3.21±0.82	0.40±0.08
M1.5	2.62±0.88	2.96±0.97	0.35±0.09

221

222 3.1.2 Chemical bonding energy G_d

223 Most previous studies assume that the debonding process in the fiber pullout test is a tunnel crack
 224 propagation and the pullout of the fiber is thereby resisted by the debonding fracture energy of the
 225 tunnel-shaped crack [36]. This fracture energy is also known as the chemical bonding energy G_d and
 226 can be calculated by Equations (1) [28]. The G_d of PVA in AASF matrices is presented in Figure 5, in
 227 which the average values of G_d versus the activator silicate modulus (M_s) show a clear trend. The
 228 values of G_d vary from 2.6 to 6.2 J/m² with the M_s ranging from 0 to 1.5. Knowing that the G_d normally
 229 ranges from 1 to 2 J/m² [29] in conventional strain-hardening cementitious composite (SHCC) and
 230 from 0.5 to 1.5 J/m² in high-volume fly ash SHCC [30], the chemical bonding of PVA fiber (with 1.2%
 231 oiling) in AASF matrices is significantly stronger than those reported in the above cementitious
 232 systems. In fact, the average values of G_d in SHGC matrices are generally 1.5 to 2.5 times higher than
 233 those in conventional SHCC [27, 29, 30]. Notably, the SHCC matrices in these studies have a limited
 234 amount of fine quartz sand with a maximum particle size of 250 μ m. However, due to the limited sand
 235 content (lower than 30 wt.%) and fineness (average particle size 110 μ m), a reasonable comparison
 236 of the interface bonding properties between two systems can be made. Furthermore, with increasing
 237 M_s , G_d first increases, peaks at M_s of 0.5, and then gradually decreases. This trend is somehow well
 238 correlated with the chemical composition change of the reaction product with increasing M_s . Further
 239 discussions are given later in Section 3.3.1.



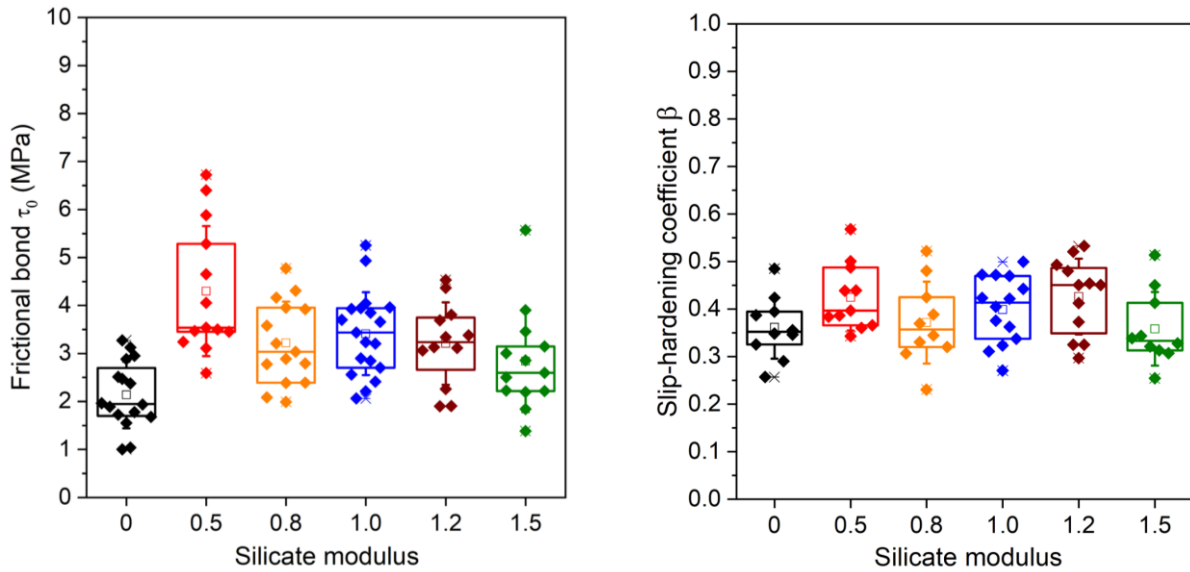
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241 Figure 5 Box plot of chemical bonding energy (G_d) of PVA fiber in AASF matrices with different activator
 242 silicate modulus. The box plot illustrates the median value (-), the mean (\square), the values at 25% and 75%
 243 (box edges), and the standard deviation (Whiskers).

244 3.1.3 Initial frictional bond τ_0 and slip-hardening coefficient β

245 The initial friction bond τ_0 for AASF mixtures with M_s from 0 to 1.5 As shown in Figure 6 (a). Despite
 246 the relatively large STDs, the mean value of τ_0 follows a somewhat similar trend when comparing to
 247 G_d . It also reaches a maximum value at M_s 0.5 and then in general decreases with increasing M_s .
 248 Notably, the mean τ_0 is found to be about 2 to 3 times higher than those in cementitious systems [27,
 249 30]. The slip-hardening coefficients β of the AASF mixtures are shown in Figure 6 (b). The mean
 250 values of β are in a range of 0.26 to 0.42, which are much lower than those found in conventional
 251 SHCC (1.15) [29] and high-volume fly ash-based SHCC (0.58-0.63) [44]. No clear trend of β could be
 252 identified with increasing M_s .

253 The above findings, in line with several previous studies of SHGC [23-25], thus demonstrate significant
 254 differences in interface bonding properties in SHGC. Further discussions on the origin of the frictional
 255 bond and the mechanism of slip-hardening are given in Section 3.3.3.



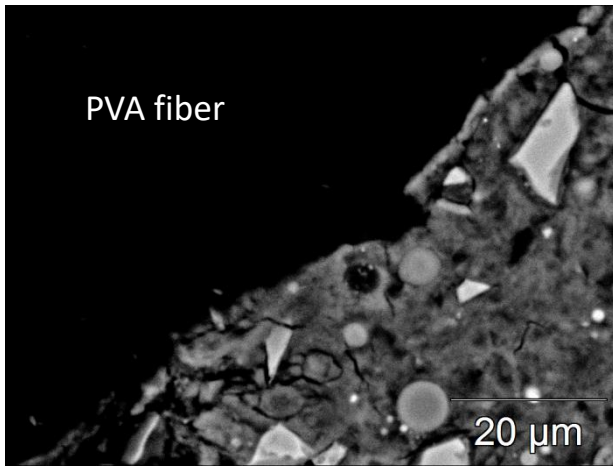
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257 Figure 6 Box plot of (a) initial frictional bond (τ_0) and (b) slip-hardening coefficient β of PVA fiber in AASF
 258 matrices with different activator silicate modulus. The box plot illustrates the median value (-), the mean
 259 (\square), the values at 25% and 75% (box edges), and the standard deviation (Whiskers).

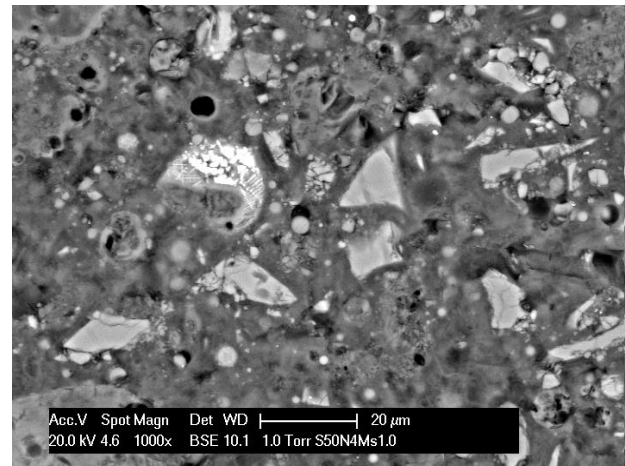
260 3.2 Microstructural characterization of ITZ

261 3.2.1 Morphology of PVA fiber/matrix interface

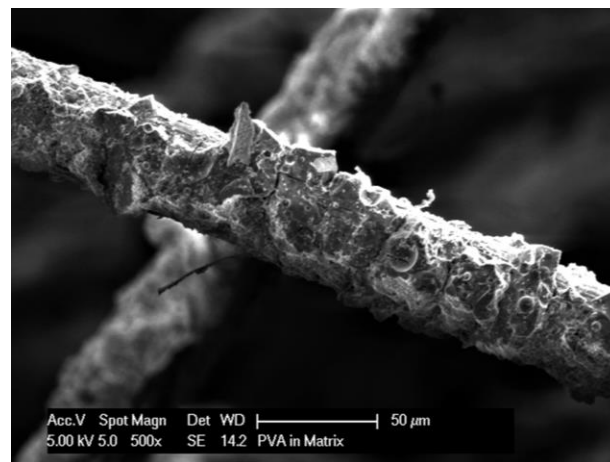
262 The morphology of the PVA fiber/matrix interface was firstly observed using backscattered electron
 263 imaging on polished sections. Figure 7 (a) and (b) show typical BSE micrographs of the cross-section
 264 of both the PVA fiber and the ITZ in AASF (M1.0). The grey level contrast in both BSE micrographs
 265 distinguishes among different constituents, i.e., the PVA fiber, reaction products, the remnant slag and
 266 fly ash particles, as well as the micro-cracks and pores.



(a) the ITZ of PVA fiber in AASF matrix M1.0



(b) the AASF matrix M1.0



(c) PVA fiber surface after single-fiber pullout

267

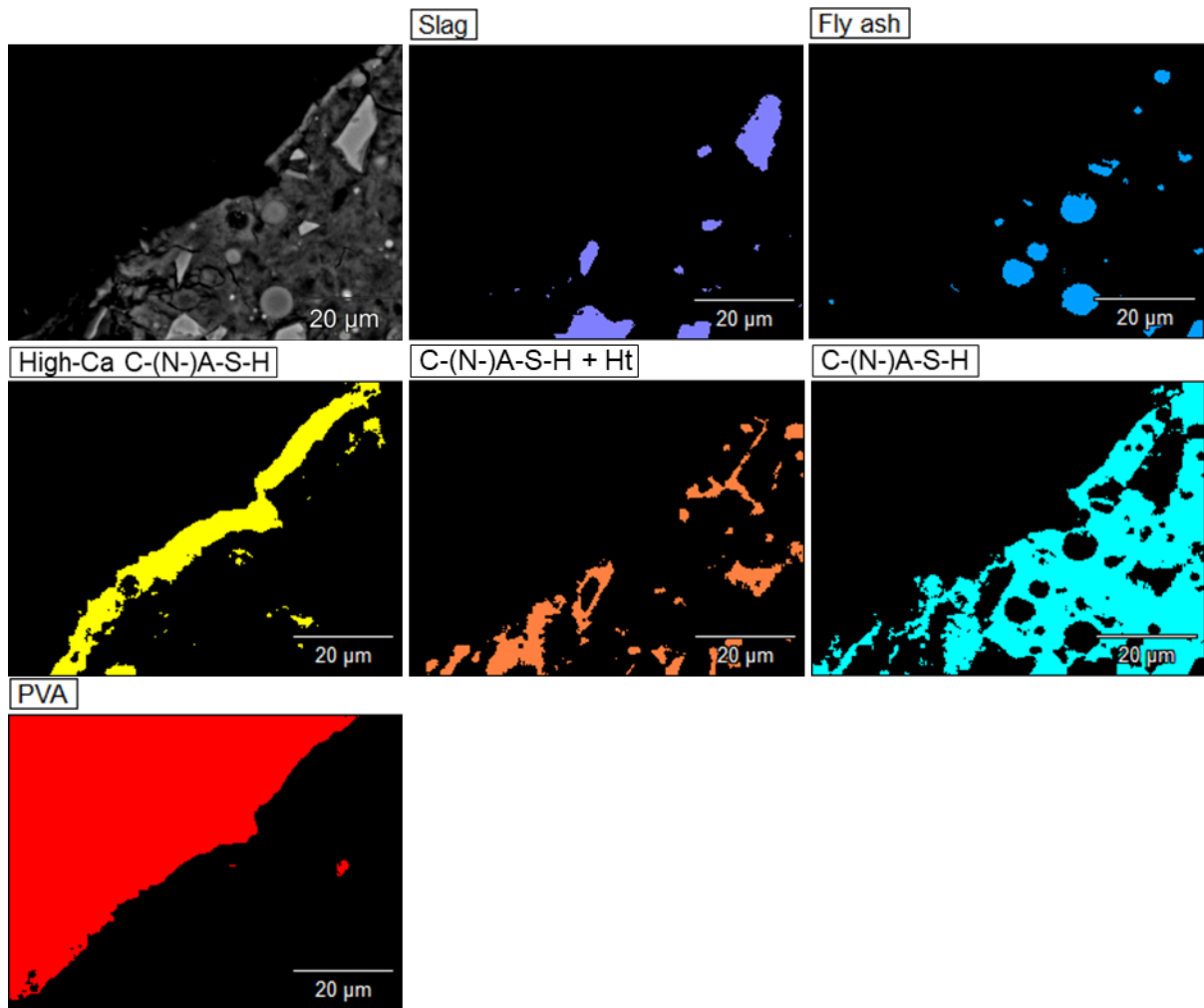
268 Figure 7 Comparison of typical SEM micrographs of (a) the ITZ of the AASF M1.0 at 28 days and (b) AASF
269 matrix M1.0 at 28 days.

270 The presence of a 300 μm PVA fiber in the matrix could disturb the packing of slag particles. This is
271 known as the wall effect, which could increase the local liquid-to-solid ratio near the PVA fiber [45].
272 However, the ITZ around the 300 μm PVA fiber in the 28-day bulk AASF matrix was found to be not
273 significantly more porous compared to the bulk matrix. This observation is consistent with previous
274 studies on the ITZ around the fine sand particle (300 μm) in alkali-activated slag (AAS) mortar, which
275 was found to be dense with very low porosity [46, 47]. As a result, Figure 7 thus suggests that the wall
276 effect around a 300 μm PVA fiber in the AASF matrix is not significant. Based on this evidence, it is
277 conceivable that the wall effect of a 40 μm PVA fiber in the AASF matrix is even less significant.

278 Furthermore, the reaction products in the ITZ appeared to be firmly attached to the surface of the PVA
279 fiber. This observation is also confirmed by the SE micrograph in Figure 7 (c) of the pulled-out fiber
280 after the single-fiber pullout tests. However, unlike the finding of the portlandite phase formed around
281 PVA fiber in the cementitious system [48], no newly-formed crystalline phases (with distinct
282 morphological characteristics) could be observed.

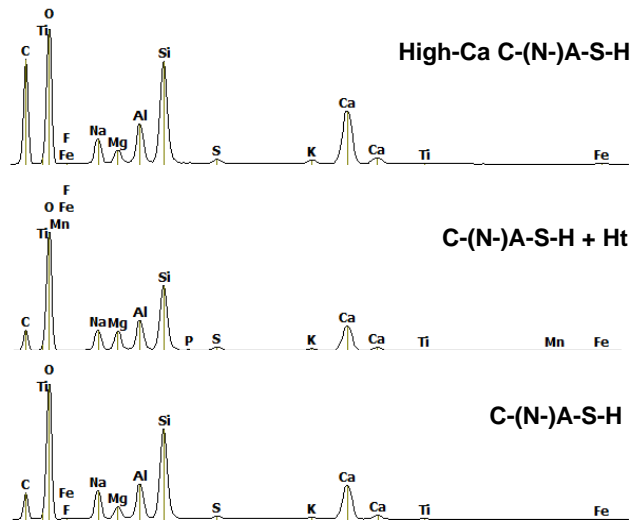
283 **3.2.2 Phase mapping based on the chemical composition**

284 To further assess the reaction product formed in the ITZ, the automated phase mapping based on the
285 chemical composition of different phases was applied using a principal component analysis (PCA)
286 approach. The results of PVA fiber in the M1.0 matrix are illustrated in Figure 8. The unreacted slag
287 particles, unreacted fly ash particles, and PVA fiber can be clearly identified. Furthermore, phase
288 mapping also helps to identify at least three types of chemically distinct reaction products. Their
289 representative EDX spectra are given in Figure 9 and the chemical compositions of these phases
290 (atomic ratios) are given in Table 3.4. Based on their chemical compositions, the three phases are
291 labeled as (1) high-Ca C-(N-)A-S-H, a C-(N-)A-S-H gel with very high Ca content; (2) C-(N-)A-S-H +
292 Ht, a C-(N-)A-S-H gel intermixed with Mg-rich hydrotalcite (Ht), and (3) a C-(N-)A-S-H gel, the major
293 reaction product formed in the matrix. The latter two phases are commonly found in AAS and AASF
294 with high slag content (>50 wt. %) [13].



295

296 Figure 8 Phases mapping using principal component analysis based on the chemical composition of
297 reaction products (in atomic %) in the ITZ of M1.0



298

299 Figure 9 EDX spectra for three C-(N-)A-S-H phases identified by automated COMPASS phases mapping:
 300 High-Ca C-(N-)A-S-H, C-(N-)A-S-H + Ht, and C-(N-)A-S-H phases

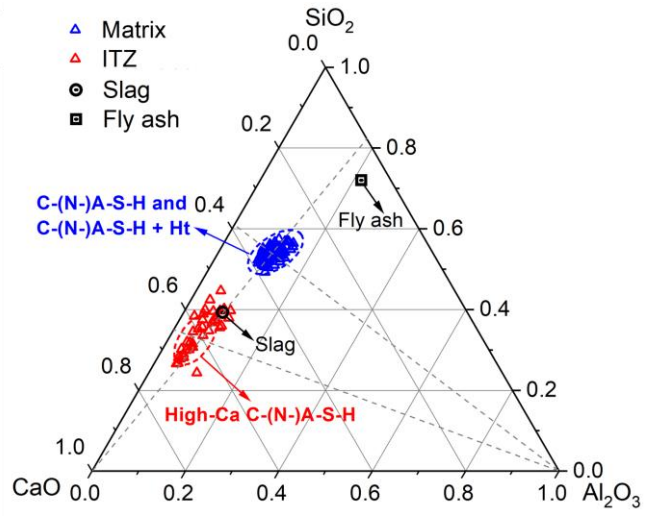
301 Table 3.4 Atomic ratios of the reaction products determined by EDX spot analysis

Reaction product	Ca/Si	Ca/(Si+Al)	Al/Si	Mg/Ca	Mg/Si
High-Ca C-(N-)A-S-H	1.82±0.53	1.44±0.30	0.34±0.06	0.12±0.03	0.13±0.03
C-(N-)A-S-H + Ht	0.61±0.03	0.43±0.05	0.42±0.05	0.50±0.11	0.31±0.11
C-(N-)A-S-H	0.61±0.04	0.43±0.05	0.40±0.05	0.24±0.11	0.15±0.11

302 Note: Hydrotalcite (Ht) phases as secondary reaction products are intermixed with the main reaction product C-(N-)A-S-H
 303 gel, although the amount of hydrotalcite differs according to the region for EDX testing as can be reflected by the Mg/Ca and
 304 Mg/Si ratio.

305 High-Ca C-(N-)A-S-H phase

306 The most important finding is the Ca-rich reaction product formed in the ITZ, namely the high-Ca C-
 307 (N-)A-S-H (Table 3.4). The location of this phase matches perfectly the location of the Ca-rich rim
 308 around PVA fiber in the EDX element mapping reported in our previous study [32]. Further EDX spot
 309 analysis in the area of the Ca-rich reaction product and the rest areas in the matrix are presented in a
 310 CaO-SiO₂-Al₂O₃ ternary diagram in Figure 10. The result shows that the high-Ca C-(N-)A-S-H phase
 311 has a significantly higher Ca/Si (1.82) and Ca/(Si+Al) ratio (1.44) than both C-(N-)A-S-H and C-(N-)A-
 312 S-H+Ht phases (see also Table 3.4.). On the other hand, the high-Ca C-(N-)A-S-H phase has at least
 313 a similar Al/Si ratio as the reaction products formed elsewhere. In fact, despite its high Ca content,
 314 Figure 9 shows the high-Ca C-(N-)A-S-H phase has the characteristic EDX spectrum of C-(N-)A-S-H
 315 gel, which has been confirmed by our previous study as the main reaction product formed in identical
 316 AASF systems [18]. All the above evidence indicates the high-Ca C-(N-)A-S-H formed near the PVA
 317 fiber surface is a kind of C-(N-)A-S-H gel with a high Ca/Si ratio and Ca/(Si+Al) ratio.



318

319 Figure 10 Ternary diagram of CaO-SiO₂-Al₂O₃ of EDX spot analysis for reaction product in the matrix and
 320 the Ca-rich region in the ITZ

321 The formation of the high-Ca C-(N-)A-S-H is due to the hydroxyl group on the PVA fiber surface. Our
 322 previous study within identical AASF matrices using MD simulation indicates the polarity of the PVA
 323 molecule induced by the hydroxyl functional group and its interaction with C-(N-)A-S-H gel presents a
 324 high affinity of Ca and Na cations to the PVA molecule, leading to a higher coordination number of Ca
 325 to O_{PVA} in comparison to Si and Al [32]. At an early age, the strong polarity induced by the hydroxyl
 326 group effectively attracts the free-moving Ca²⁺ cation in the pore solution to accumulate near the PVA
 327 fiber surface. This effect leads to the formation of Ca-rich C-(N-)A-S-H gel that later will have
 328 considerable influence on the chemical bonding energy of PVA fiber in the AASF matrix.

329 Interestingly, this finding is somewhat different than what has been reported in cementitious systems.
 330 There, the Ca-rich reaction product around the PVA fiber is a layer of crystalline portlandite (CH) [30,
 331 48, 49] and it plays a dominant role in determining the interface bonding properties in PVA-based
 332 SHCC [50]. In the AASF system, however, the formation of CH as a crystalline phase is highly unlikely
 333 because CH has a much higher solubility product K_{sp} than C-(N-)A-S-H gel [51]. In this case, the
 334 formation of the amorphous C-(N-)A-S-H gel is more preferential as predicted by thermodynamics
 335 modeling [52, 53]. In fact, the main reaction products of sodium silicate-based AASF are reported to
 336 be amorphous [13, 34, 54] and seldom have new crystalline phases except for hydrotalcite has been
 337 reported. The above evidence thus precludes the possibility that the Ca-rich reaction product is due
 338 to the intermixing of C-(N-)A-S-H gel with CH.

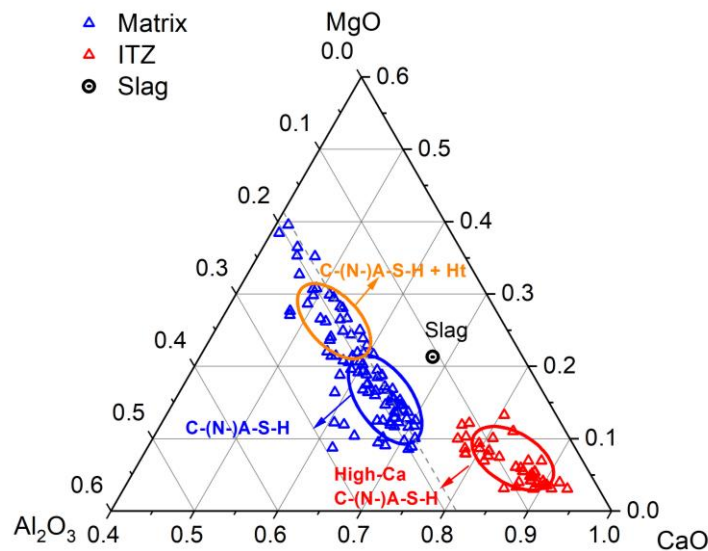
339 It is also worth noting that the reaction product around aggregate particles in previous studies on AAS
 340 mortar has a lower Ca/Si ratio than that in the bulk matrix due to the “wall effect” [47]. The higher Ca/Si
 341 ratio of the reaction product near the PVA fiber thus indicates that the physical “wall effect” is not
 342 dominating in this case. Instead, the chemical characteristics of the PVA fiber surface could play a
 343 more significant role in the formation of Ca-rich reaction products. This could also be the reason for

344 the differences between the chemical bonding energy of PVA fiber in AAMs systems and cementitious
345 systems [23-25]. Further discussions are given in Section 3.3.2.

346 C-(N-)A-S-H and C-(N-)A-S-H+Ht phase

347 The phase mapping also identified two types of C-(N-)A-S-H phase, viz., C-(N-)A-S-H and C-(N-)A-S-
348 H+Ht (see Table 3.4). The presence of these two phases could not be shown using the CaO-SiO₂-
349 Al₂O₃ ternary diagram, because their Ca, Si, and Al composition are rather similar. However, they can
350 be distinguished by their different Mg composition (Table 4.3) using the CaO-Al₂O₃-MgO ternary
351 diagram in Figure 11. It is evident that the C-(N-)A-S-H+Ht phase has a higher Mg content than the
352 C-(N-)A-S-H phase.

353 As shown in Figure 8, the C-(N-)A-S-H+Ht phase is distributed majorly around the unreacted slag
354 particles. This region matches the so-called “dark rim” around the remnant slag particles, which has
355 been detected in previous research on AAS and AASF [53-57] due to the in-situ reaction between the
356 outer layer of GGBFS and alkali [58, 59]. The Mg ions, due to their low mobility, cannot significantly
357 migrate away from the original slag grain [60]. This is also the reason for the formation of the “dark
358 rim”. Since hydrotalcite (Ht) is the only possible reaction product containing Mg, the higher Mg/Si and
359 Mg/Ca ratios in Table 3.4 thus suggest that the reaction products around the slag particles are most
360 probably a composite phase of C-(N-)A-S-H and hydrotalcite (C-(N-)A-S-H+Ht) [59, 61]. Unlike the C-
361 (N-)A-S-H+Ht phase, the C-(N-)A-S-H phase is distributed quite homogeneously in the matrix. It is
362 also the most abundant with the largest area coverage in the phase mapping (Figure 8).



363

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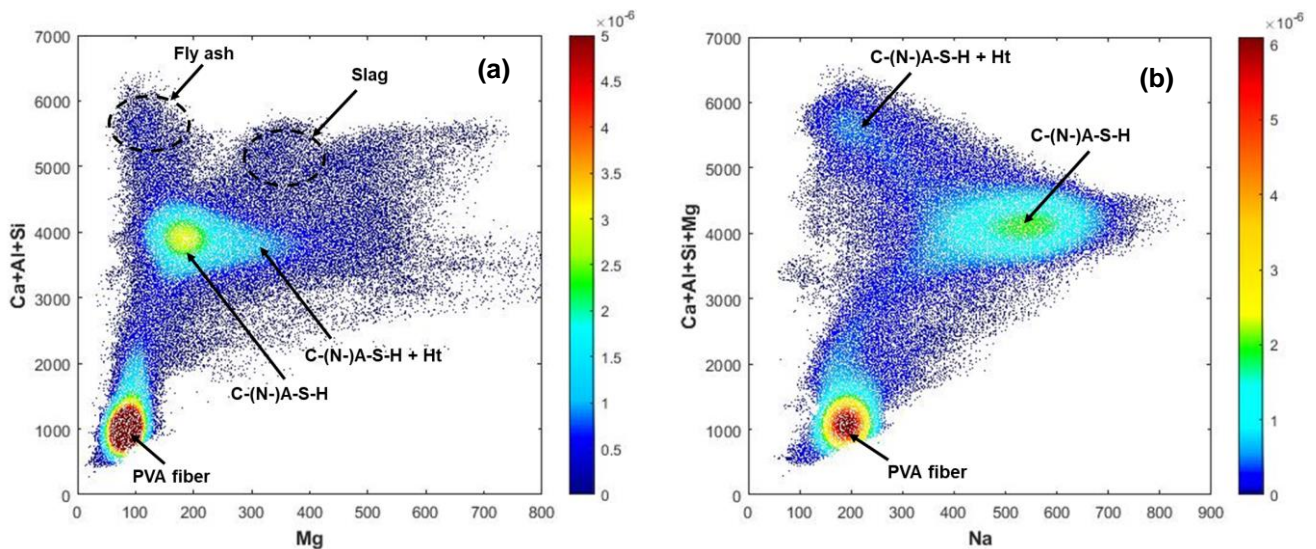
Figure 11 CaO-Al₂O₃-MgO ternary diagram of EDX spot analysis in the ITZ

365 Unfortunately, the EDX element/phase mapping cannot distinguish separately the hydrotalcite and the
366 C-(N-)A-S-H phase. Hydrotalcite is a layered double hydroxide (LDH). Its host brucite-like Mg-Al layers
367 have a strong positive charge [62]. As a result, the hydrotalcite layers are strongly attracted to the

368 negatively charged C-(N-)A-S-H layers during the alkali-activation reaction. This affinity thereby leads
369 to a highly intermixed hydrotalcite and C-(N-)A-S-H gel at the nanoscale [58]. For a clear separation
370 of intermixed phases at this scale, most X-ray based analysis techniques have reached their resolution
371 limits. As a result, the hydrotalcite phase was rarely studied individually in AASF pastes.

372 3.2.3 Density plots of phases based on EDX element mapping

373 The presence of the phases determined by the automated phase mapping is further examined by the
374 density plots using the channel intensity correlations between (1) Ca+Al+Si versus Mg and (2)
375 Ca+Al+Si+Mg versus Na. The channel intensities used here are the net counts from each pixel of the
376 EDX phase mapping. They were extracted from the spectra imaging (SI) data from the phase mapping
377 results in Figure 8. The density plots of the abovementioned two correlations were created following
378 Van Hoek et al. [63] and Nedeljković et al. [54]. The Ca+Al+Si versus Mg density plots in Figure 12
379 (a) help to distinguish the remnant slag and fly ash particles, and the PVA fiber from the reaction
380 products. The Ca+Al+Si+Mg versus Na density plots in Figure 12 (b) help to better illustrate the
381 differences between the reaction products. In all density plots, the statistically distinct phases could
382 then be distinguished by their different positions in the data cluster, with the abundance of the phases
383 reflected by the different colors.



384

385 Figure 12 Density plot of channel intensities Ca+Al+Si versus Mg, and density plot of channel intensities
386 Ca+Al+Si+Mg versus Na.

387 The clusters of PVA in all density plots show the highest abundance in red color. This is in line with
388 the phase mapping in Figure 8 where the PVA fiber occupies almost half of the areas. There are no
389 evident clusters for remnant slag and fly ash particles, indicating their limited content in the ITZ. The
390 positions of clusters for slag and fly ash particles have been marked in Figure 12 (a) and (b) with black
391 dotted circles. The C-(N-)A-S-H and C-(N-)A-S-H+Ht phases, as the main reaction products, could be
392 distinguished according to their different Mg content. In comparison to C-(N-)A-S-H, C-(N-)A-S-H+Ht

393 phase is more abundant in all density plots. These results coincide well with the ones from the phase
 394 mapping in Figure 8, in which C-(N-)A-S-H among all reaction products occupies the largest area. No
 395 sharp boundaries are observed between these two phases. Similar findings were found by Nedeljković
 396 et al. [54] using Phase Recognition and Characterization (PARC), the reaction products, namely Ca-
 397 Na-Al-Si-H gel and Ca-Mg-Na-Al-Si-H gel, which correspond to the C-(N-)A-S-H and C-(N-)A-S-H+Ht,
 398 respectively [54].

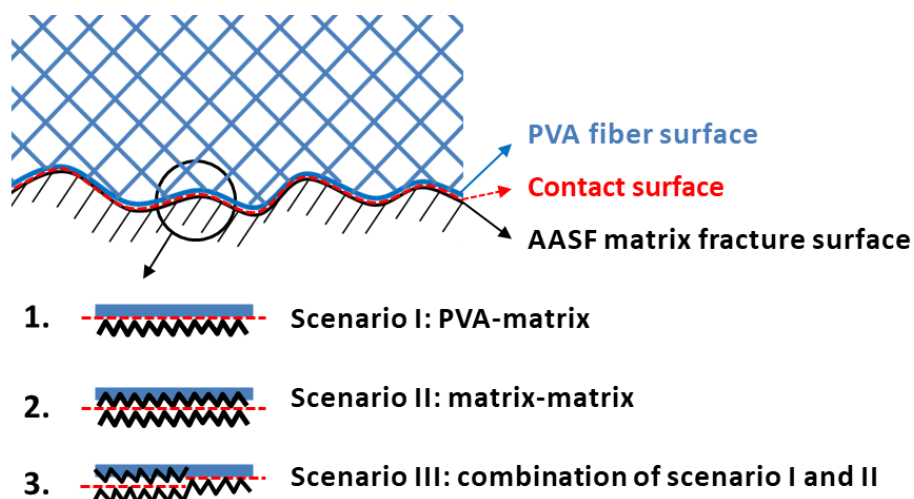
399

400 3.3 General discussions

401 3.3.1 Debonding scenarios between PVA fiber and AASF matrix

402 It is generally assumed that the debonding would happen along the weakest link among constituents
 403 in the fiber-reinforced composite, for example, along the fiber/matrix interface [64]. However,
 404 considering the strong adhesion between PVA fiber and AASF matrix (Section 3.1.2), the bond failure
 405 scenarios could be different. A schematic representation of the possible bond failure scenarios is
 406 illustrated in Figure 13, which depicts the debonded surfaces at the end of the fiber debonding process,
 407 i.e., the starting point of the slippage phase. This is also the moment when the pullout load drops from
 408 P_a to P_b in Figure 4 (b). With the completion of the debonding process, three possible debonding
 409 scenarios can be considered:

- 410 • Scenario I: the debonding due to the adhesive failure at the interface (PVA-matrix).
- 411 • Scenario II: the debonding due to the cohesive failure of the matrix in the ITZ (matrix-matrix).
- 412 • Scenario III: the debonding due to the combined adhesive-cohesive failure [65].



413

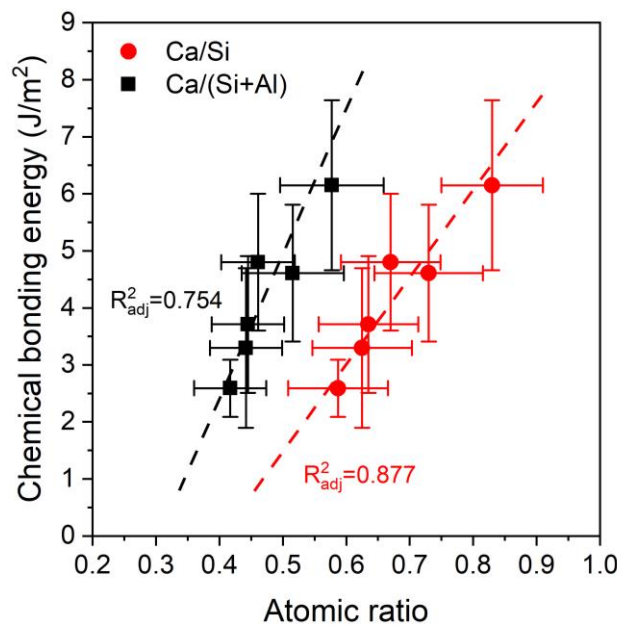
414 Figure 13 Schematic representation of the bond failure scenarios.

415 The debonding scenario I normally holds for hydrophobic polymeric fiber, which have negligible
 416 adhesion with the reaction product in the matrix [42, 66, 67]. During pullout, the tunnel crack
 417 propagates exactly along the fiber surface. The adhesive failure at the interface determines that the

418 later friction will be between the fiber surface and the matrix [68]. This is also the reason why the
 419 friction between the hydrophobic fibers and the matrix could be substantially improved by increasing
 420 the surface roughness of the fibers [66, 69, 70]. In contrast, debonding according to scenario II occurs
 421 normally when a hydrophilic fiber strongly adheres to the matrix. Under such circumstances, the
 422 adhesion between fiber and matrix is stronger than the cohesion in the matrix. As a result, the tunnel
 423 crack tends to propagate in the matrix near the PVA fiber leading to the cohesive failure of the matrix
 424 in the ITZ. Finally, debonding scenario III happens when the adhesion between fiber and matrix is
 425 about equal to the cohesion in the matrix. The tortuous tunnel crack propagates partially along the
 426 fiber surface but also in the matrix, which leads to an adhesive-cohesive failure in the ITZ [29, 71].
 427 In this study, even after the pullout, the surface of PVA fiber appears to be almost fully covered with
 428 matrix residue (see also Figure 7 (c)). Considering the very high G_d of PVA fiber in AASF matrices (2
 429 to 3 times higher than that in cementitious materials), the debonding is most probably scenario III, but
 430 dominated by scenario II [72, 73].

431 3.3.2 Chemical bonding energy G_d and chemical composition of C-(N)-A-S-H gel

432 The main reaction product in AASF pastes was characterized to be C-(N)-A-S-H gel (Section 3.2.2).
 433 By changing the activator M_s , the availability of silica species was effectively altered and thereby
 434 changed the global reaction and chemical nature of the reaction products [74-76]. Such effects lead
 435 to the formation of C-(N)-A-S-H gel with various Ca/Si and Ca/(Si+Al) ratios. A strong linear
 436 relationship was also identified between chemical bonding energy G_d and the Ca/Si and Ca/(Si+Al)
 437 ratios of the C-(N)-A-S-H gel in AASF pastes shown in Figure 14. This implies that the G_d of PVA fiber
 438 in AASF pastes is also strongly governed by the chemical composition of C-(N)-A-S-H gel.



439
 440 Figure 14 Correlation of chemical bonding energy G_d as a function of Ca/Si and Ca/(Si+Al) ratios of C-(N)-

441)A-S-H gel in AASF pastes.

442 Based on the experimental results and discussions in this study, the reason for the strong correlations
443 between the G_d and the Ca/Si and Ca/(Si+Al) ratios of the C-(N-)A-S-H gel could be due to both the
444 adhesion between fiber and matrix and the cohesion of the matrix in the ITZ (scenario III).

445 First of all, the hydroxyl group (-OH) on the surface of PVA fiber has a strong polarity due to the high
446 electronegativity of the oxygen atom. It thus serves as a favorable oxygen site provider for the
447 formation of electrostatic interactions. Similar to C-S-H gel, C-(N-)A-S-H gel with high Ca/Si or
448 Ca/(Si+Al) ratios present a high negative surface charge density [77]. Under such circumstances, the
449 formation of the electrostatic $O_{C-(N-)A-S-H}-Ca-O_{PVA}$ bonds is highly feasible [78, 79]. In fact, our previous
450 studies on PVA fiber in identical AASF matrices have confirmed that the chemical bonding (adhesion)
451 between PVA and C-(N-)A-S-H gel is mainly due to such electrostatic interactions between the
452 hydroxyl group (-OH) in PVA and the Ca^{2+} cations within C-(N-)A-S-H gel [32]. Since the C-(N-)A-S-H
453 gel with higher Ca/Si or Ca/(Si+Al) ratios have a higher charge density, it is conceivable that the
454 electrostatic interaction between the C-(N-)A-S-H gel and PVA fiber surface are enhanced. These
455 stronger interactions finally result in a stronger adhesion, thus stronger chemical bonding at higher
456 Ca/Si or Ca/(Si+Al) ratios in debonding scenarios I.

457 Secondly, our previous study on identical AASF matrices confirmed that the matrix fracture toughness
458 (K_{Ic}) and the crack tip toughness (J_{tip}), i.e., the resistance of crack initiation in the AASF matrix, are
459 also dominated by the Ca/Si and Ca/(Si+Al) ratios of the C-(N-)A-S-H gel [18]. Both K_{Ic} and J_{tip} as
460 fracture properties of the matrix are fundamentally related to the interaction between the reaction
461 product particles (i.e., cohesion). This is reasonable considering that C-(N-)A-S-H gel with high Ca/Si
462 or Ca/(Si+Al) ratios present a high negative surface charge density [77], which leads to enhanced
463 cohesion in the AASF matrix [18]. As a result, the stronger cohesion also leads to stronger chemical
464 bonding energy at higher Ca/Si or Ca/(Si+Al) ratios in debonding scenarios II.

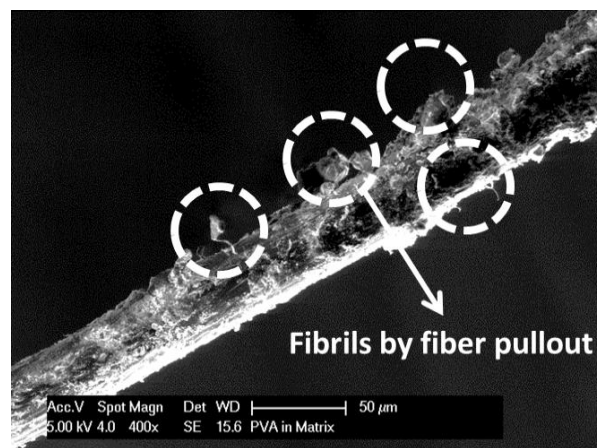
465 **3.3.3 Origin of initial frictional bond τ_0 and slip-hardening behavior**

466 The initial friction between the PVA fiber and AASF matrix can be described as “dry friction” between
467 two solid surfaces. The classic coulomb-type friction law is thereby assumed to be applicable. The
468 initial frictional bond τ_0 is then determined by (1) the surface properties of the two contact surfaces
469 (normally characterized by the friction coefficient) and (2) the residual stress of the surrounding matrix
470 onto the fiber surface [27, 80].

471 Firstly, the initial friction bond is stronger with a higher friction coefficient, which could be achieved by
472 a higher fracture surface roughness of the AASF matrix. According to Lange et al. [81], the fracture
473 surface roughness in a cementitious matrix is positively related to its fracture toughness (K_{Ic}). While
474 in our study on identical AASF matrices, we found a strong positive linear relationship between matrix
475 K_{Ic} and the Ca/Si ratio of C-(N-)A-S-H gel [18]. As a result, AASF matrices with high Ca/Si ratios are
476 expected to have a higher friction coefficient, which contributes to a stronger initial friction bond. This

477 consistency of the initial friction and K_{Ic} has also been reported previously by Nematollahi et al. [24] in
478 fly ash-based SHGC.

479 Secondly, the residual stress of the surrounding matrix onto the fiber surface also affect the initial
480 friction bond τ_0 [82]. This residual stress is caused by shrinkage of the AASF matrix, such as
481 autogenous and/or possible drying shrinkage. Naturally, it is also affected by the creep and relaxation
482 behavior of the AASF matrix. Given the fact that the shrinkage and creep are governed by various
483 factors (such as pore structure, mechanical properties, and most likely chemical composition of the
484 reaction products [83, 84]), further insight into the mechanism of shrinkage and creep in AASF
485 systems are needed to better understand the residual stress and the related friction behavior.



486

487 Figure 15 Fibrils on PVA fiber surface after single-fiber pullout test

488 The slip-hardening behavior results from the lower rigidity of the PVA fiber in comparison to the
489 surrounding AASF matrix, leading to severe abrasion between the PVA fiber and the surrounding
490 rough AASF matrix tunnel. The SEM micrograph in Figure 15 shows the surface of the pulled-out PVA
491 fiber contain a substantial amount of fibrils as well as spalled micro-debris from the matrix attached to
492 the fibrils. This is a result of the abrasion, which results in “micro-excavation” damage to the PVA fiber
493 surface and leaves the fiber debris in the form of stripped fibrils [43]. With increasing fiber pullout
494 displacement, the accumulation of these fibrils (with matrix micro-debris) promotes the formation of a
495 “locking front”, which increases the pullout resistance [85]. This effect is also referred to as the
496 “jamming effect” [29, 43]. The slip-hardening behavior may lead to a tensile load exceeding the fiber
497 tensile strength causing rupture of the fiber. This rupture happens when the pullout load reaches the
498 maximum P_{max} as shown in Figure 4 (b).

499 The slip-hardening behavior of PVA fiber is influenced by at least three factors: fiber/matrix adhesion,
500 matrix surface roughness, and shrinkage-induced residual stress. The adhesion between the PVA
501 fiber and the matrix plays a crucial role in preventing *adhesive* failure at the fiber/matrix interface
502 (Scenario I in Section 3.3.1), which in turn allows for the initiation of "micro-excavation". Additionally,
503 the higher surface roughness of the matrix, reflected by the matrix fracture toughness (K_{Ic}), can
504 promote the “micro-excavation” damage at fiber surface. This results in a higher resistance during the

505 pullout process due to a more severe fiber-matrix interaction. Finally, the shrinkage-induced residual
506 stress on the fiber surface contributes to the accumulation of fibrils and formation of a "locking front,"
507 leading to increased pullout resistance.

508 **3.3.4 Implications on the development of strain-hardening geopolymer composites (SHGC)**

509 The findings of this study have significant implications for the advancement of new strain-hardening
510 geopolymer composite (SHGC). The fiber/matrix interfacial transition zone (ITZ) observed in this study
511 is dense and has low porosity. Moreover, the stronger chemical bonding (Section 3.1.2) suggests that
512 PVA fibers embedded in an alkali-activated matrix might be more susceptible to fiber rupture during
513 the pullout process than those in cementitious matrices. As a result, special attention should be given
514 to designing suitable chemical bonding energy (G_d) to improve the fiber's bridging capacity during the
515 stages of crack initiation and propagation, and thereby the composite performance [86].

516 In cementitious system, the most convenient and effective approach to modify the chemical bonding
517 is to incorporate supplementary cementitious materials (SCMs) into the cementitious matrix [30]. The
518 modification of the fiber surface is also effective [29], yet it is considered difficult for a commercially
519 available product like PVA fibers. Furthermore, the relationships between SCM content and surface
520 characteristics (e.g., surface oiling) to the G_d is also complicated to establish. Fortunately, the chemical
521 bonding of PVA fiber in alkali-activated system can be more conveniently adjusted compared to
522 cementitious system. The strong linear correlation between G_d and Ca/Si of the C-(N-)A-S-H gel in
523 alkali-activated matrix identified in this study (Figure 14) offers useful guidance to adjust the chemical
524 bonding. In the case of AASF, this could be achieved by changing the ratio between slag/fly ash (Ca
525 content) and the silicate modulus in the alkaline activator (Si content). Considering that the Ca/Si ratio
526 of C-(N-)A-S-H gel has a wide range to be adjusted (0.3 to 0.8), the findings offer clear guidance and
527 also freedom for researchers and engineers to tailor the chemical bonding energy G_d by adjusting the
528 mixture design of alkali-activated matrix. Particularly, they are valuable for mixture development that
529 require accurate engineering of interface bonding properties for a satisfactory performance of high-
530 performance alkali-activated composite such as SHGC.

531 **4. Conclusions**

532 This paper presents a systematic experimental investigation of the PVA fiber/matrix interface bonding
533 properties in AASF pastes. The influence of PVA fiber on the microstructure and the reaction product
534 formation within the ITZ were also characterized. Based on the experimental results, the relationship
535 between chemical bonding and the chemical composition of the C-(N-)A-S-H gel as main reaction
536 product was further explored. The origin of the initial frictional bond and slip-hardening behavior of
537 PVA fiber in AASF pastes were also discussed. Based on the results and discussions, the following
538 conclusions can be drawn:

- 539 • The chemical bonding energy G_d between PVA fiber and AASF matrix increases with increasing
540 Ca/Si and Ca/(Si+Al) ratio of C-(N-)A-S-H gel, the main reaction product in AASF pastes.
- 541 • The hydrophilic nature of PVA fiber promotes the formation of a high-Ca C-(N-)A-S-H phase near
542 the PVA fiber surface. This high-Ca C-(N-)A-S-H phase has considerably higher Ca/Si and
543 Ca/(Si+Al) ratios, similar Al/Si ratios, and lower Mg/Ca ratios compared to the C-(N-)A-S-H phases
544 in the bulk matrix.
- 545 • C-(N-)A-S-H and C-(N-)A-S-H+Ht phases were formed in the bulk matrix of AASF pastes. The
546 main difference between them is their different Mg content due to the different amounts of
547 hydrotalcite intermixed within C-(N-)A-S-H phases.
- 548 • Because of the strong chemical bond between PVA fiber and AASF matrix, the debonding
549 process is dominated by the *cohesive* failure that happened within the ITZ rather than the
550 *adhesive* failure along the PVA fiber surface. As a result, the initial friction bond τ_0 is primarily
551 determined by the interaction between the fracture surfaces of the AASF matrix and not between
552 PVA fiber and the AASF matrix.
- 553 • The initial frictional bond τ_0 , unlike the chemical bonding energy G_d , is not only determined by the
554 chemical composition of the reaction products. A synergistic mechanism of the fracture surface
555 roughness of the matrix (positively related to K_{Ic}) and shrinkage-induced residual stress
556 determines the magnitude of the frictional resistance.
- 557 • The slip-hardening behavior of PVA fiber in the AASF matrix is caused by a 'jamming' effect. The
558 accumulation of the stripped fibrils (along with matrix micro-debris) identified on the fiber surface
559 increases the pullout resistance.
- 560 • The study provides important insights into the interface bonding properties of PVA fiber in AASF
561 matrix. It also provides able guidance for tailoring the interface bonding properties and thus the
562 development of high-performance alkali-activated composites such as strain-hardening
563 geopolymer composite (SHGC).

564

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