






## Article

# Durability of Glass Fiber Reinforced Cement (GRC) Containing a High Proportion of Pozzolans

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**Abstract:** Glass fiber reinforced cement (GRC) is an excellent composite for architects and engineers because it can be molded to produce laminar panels or to create complicated designs. GRC is a fine concrete reinforced with alkali-resistant glass fibers at 3–5% per mass. However, fiber durability is limited because of the aggressiveness of the alkaline medium produced during Portland cement hydration (effect of portlandite). The objective of this study is to assess GRC with high Portland cement replacement with pozzolans (ground fly ash or a mixture of ground fly ash and sonicated silica fume) in order to reduce the corrosion of the fibers. The selected high-content pozzolan (60% replacement) composites were tested under different conditions: aging, drying–wetting, freezing–thawing, and chemical attack (ammonium chloride and sulfuric acid). The modulus of rupture and toughness were determined. Composite behavior showed that the samples with pozzolans not only better resisted aging, but also physical and chemical attacks, and specimens presented a better modulus of rupture and toughness than the samples prepared with 100% Portland cement (control specimens). Due to the good behavior in durability terms, the high pozzolan content GRC products are suitable in potential corrosive environments for sunscreens, drainage channels, cable trays, sound barriers, or pavements.

**Keywords:** GRC; composite; aging; durability; pozzolan; drying–wetting; freezing–thawing; chemical attack



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## 1. Introduction

Portland cement mortars reinforced with fiberglass (known by the abbreviation GRC: glass fiber reinforced cement) contain alkali-resistant (AR) and non-dispersible (ND) glass fibers, and their stability in the cementing matrix is good [1]. Using AR glass fibers rich in zirconium oxide is recommended because they resist the alkaline pH generated during cement hydration. However, due to high temperatures and humidity, and depending on the medium, the composites made with these fibers can be affected. GRC deterioration is manifested by diminished mechanical behavior, specifically modulus of rupture (bending test) and toughness.

Several authors have reflected on the degradation of GRC composite properties. Purnell et al. indicated [2] that a highly alkaline medium and calcium hydroxide crystals (portlandite) accumulating in spaces between fibers are factors that can explain GRC deterioration. AR fibers are theoretically alkali-resistant, but are not completely inert. When an aqueous solution is formed by cement, the dissolution of sodium ions from the fiber begins. Next, the silicon network of glass is attacked by the hydroxyl ions to generate the subsequent dissolution of silicon ions, which deteriorates the fiber. Yilmaz et al. described [3] how portlandite crystals interact with fibers by accelerating corrosion and generating local

notches that cause the cutting of filaments. A mass attack begins when the hydroxylation and dissolution of glass occur, and leave voids surrounding the by-products of the reaction between cement and glass. Using scanning electron microscopy, Zhang et al. [4] demonstrated the appearance of small structural defects in fiber which, with their growth, degrade fiber and decrease its resistance. Marikunte et al. [5] identified the existence of two degradation fronts in GRC composite properties: the first is related to the type of fiber used and the chemical attack that it must withstand as a consequence of the pH exceeding 13 and the subsequent silica network hydroxylation; the second is related to the fiber physically interacting with the cementing matrix due to the growth of crystalline or amorphous hydration products on the fiber surface and between its filaments. In composites with AR fibers, localized corrosion is seen in the form of pits that deepen due to the nucleation of the portlandite around them. Similarly, it has been observed that AR fiber is attacked by the products generated during cement hydration, and calcium hydroxide crystals are embedded in the fiber and alter its physical properties [6,7]. Furthermore, a chemical reaction is generated at the interface between the fiber and the cementitious matrix, which leads to mass loss in the fiber (hydroxylation). Both factors are largely responsible for the loss of GRC composite properties, such as reduced toughness and flexural strength.

Chemical attack [7] on the surface of filaments is the first to affect the fiber because it alters the polymers of sizing, leading to fiber body corrosion. Alkaline attack leads to silicon dioxide extraction and zirconium dioxide hydration, which can form a protective layer for a subsequent attack when combined with alkali and alkaline earth ions. With the inclusion of pozzolanic materials, the pH can be lowered and minor losses in the thickness of sizing occur over time [5]. Pozzolans are used to replace one part of Portland cement in the mortar formulation so that they can react with the calcium hydroxide produced by cement hydration. In this way, the nature and microstructure of the cement matrix are modified, and a larger quantity of hydrated products, such as calcium silicate, aluminate, and silicoaluminate hydrates, develop. Hence, the mechanical properties improve and GRC durability generally increases [4]. By partially replacing Portland cement with pozzolanic materials, e.g., fly ash and silica fume, improved mechanical GRC behavior is achieved for materials with a big specific surface area, even when they are subjected to controlled aging processes [8,9]. The cementitious matrix is modified by reducing the calcium hydroxide that is present because the reaction of pozzolans with the portlandite released during cement hydration generates hydration products that do not affect fiber integrity. This represents an increase in both mechanical properties and durability by composite aging.

On the one hand, fly ashes are characterized by medium-rate pozzolanic reactivity, and the most important changes in the microstructure and phases in Portland cement replaced with the fly ash system are observed at mid- and long-term ages (more than 60 curing days). Fly ash reactivity can increase by grinding particles [10,11]. In this case, the role of the pozzolanic effect is enhanced and its contribution is observed at earlier curing ages.

On the other hand, silica fume offers higher reactivity and its effect on Portland cement systems is observed within the first 28 curing days [12]. Commercial densified silica fume (DSF) is an agglomerated material with micrometric and submicrometric particles. To increase its reactivity, it can be disaggregated by an effective process known as sonication, which consists of applying an ultrasound with a probe to an aqueous medium containing DSF particles. The resultant material (sonicated silica fume, SSF) after upgrading shows high pozzolanic reactivity and, consequently, a significant improvement in mechanical strength that presents a notably finer particle size distribution than DSF [13].

Some authors have shared advances in composites with high pozzolan addition/substitution percentage. Enfedaque et al. [14] described the behavior of GRC with low percentages of metakaolin and silica fume, and they concluded that low percentages of pozzolan do not avoid the fiber degradation in the cementing matrix. The use of these pozzolans in high proportions is not commercially suitable because of the cost of these mineral additions. Melgarejo [15] described the good behavior of GRC containing metakaolin and acrylic resin when samples were aged in a climatic chamber and immersed in hot water. Enfedaque et al. [16] studied

the natural aging (5 years) of GRC containing metakaolin (metaver) or a commercial pozzolan (Powerpozz) in a 20% addition compared to Portland cement. They found that metakaolin showed better performance in terms of fracture energy terms. Cheng et al. [17] reported how GRC composites without additions are notably affected by their mechanical behavior with aging due to fiber deterioration in the conventional Portland cement matrix, even at values close to those of mortars without AR fibers. They studied the behavior of GRC in which 20 and 40% of Portland cement was replaced with fly ash or ground granulated blast furnace slag. They concluded that at these replacing percentages, toughness was reduced with aging and long-term curing. Otherwise, GRC composites with up to 40% fly ash substitution confirm the benefit for composite strength due to the modification of the matrix. Genovés et al. [18] assessed pozzolanic activity in GRC with high fly ash content, and reported that cementing matrices have lower calcium hydroxide contents, which confer the fibers greater chemical stability. Butler et al. [19] studied matrices with supplementary cementing materials (blast furnace slag, fly ash, and silica fume) to reduce both matrix alkalinity and calcium hydroxide content by identifying reductions in pH from 12.4 to 11.8 after 360 aging days. Ayadi et al. [20] observed that fibers remain unchanged in composites with silica fume substitution, tensile strength improves, and damage by cutting fibers diminishes due to calcium hydroxide crystals, but flexural strength reduces with aging. Zhang et al. [4] studied GRC composites by replacing Portland cement with 40–60% fly ash. They obtained lower flexural strengths than the control for short curing times. For longer curing ages, flexural strength increased and calcium hydroxide content decreased with curing age. The higher substitution percentage and the greater fly ash fineness, the lower the calcium hydroxide content and the greater the strength are. Finally, the fibers are not attacked in the presence of ash.

According to the application of the different elements manufactured with GRC and the environment in which they are used, they can be affected by external and internal physical or chemical agents, which can produce erosions, cracks, and expansions that can harm composite properties. When composites are exposed to the environment, physical agents such as drying processes and freeze–thaw actions can generate surface wear. Chemically aggressive environments (sulfates, chlorides, acids) affect the cementitious matrix by causing mass loss or swelling and fissuration.

To date, very few studies on GRC durability in aggressive environments have been carried out. In this work, the role of ground fly ash (GFA) and sonicated silica fume (SSF), dosed at high proportions to replace Portland cement (60%), in GRC durability terms is presented, specifically on drying–wetting and freezing–thawing processes, as well as acid attacks (ammonium chloride and sulfuric acid).

## 2. Materials and Methods

### 2.1. Materials

The raw materials used to manufacture composites were: siliceous aggregate with a fineness modulus of 3.1; Alkali-resistant (AR) glass fibers, which were 12 mm long (see Table 1 for its chemical composition); chemical admixture: superplasticizer Melment L240; cement: a mixture of CEM I/52.5R Portland cement and filler limestone (75%/25% per mass) was prepared (this mixture is the equivalent to a CEM II-B L 42.5 R cement); Type F fly ash (FA) according to the ASTM C-618 classification was ground for 40 min (ground fly ash GFA); Densified silica fume (DSF) was sonicated for particle deagglomeration and yielded sonicated silica fume (SSF). Table 2 summarizes the chemical composition of the employed pozzolans.

**Table 1.** Chemical composition of alkali-resistant (AR) fibers (%). \* Alkali oxides, \*\* Alkaline earth oxides.

SiO <sub>2</sub>	ZrO <sub>2</sub>	(Na <sub>2</sub> O, K <sub>2</sub> O) *	(CaO, MgO) **	B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	F <sub>2</sub>
55–75	15–20	11–21	0–6	0–2	0–5	0–3	0–2

**Table 2.** Chemical composition of Portland cement and pozzolanic materials (%). FA= fly ash; DSF: densified silica fume. \* indicates loss on ignition.

Oxide	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	LOI *
CEM I/52.5R	22.05	5.44	3.64	62.53	2.43	3.75	1.42	-	1.6
FA	40.94	24.65	13.59	9.83	1.59	1.60	1.40	0.34	2.44
DSF	90.77	0.46	4.53	0.78	0.23	0.02	0.37	0.21	3.43

## 2.2. Conditioning of Pozzolans

The silica fume activation process: to deagglomerate the DSF particles and reduce particle size, a Sonicator3000 ultrasound probe (MISONIX, Vernon Hills, IL, USA) was used. A water suspension process of sonication was proposed (constant power of 10 min, power level 10 (120 watts)) for a suspension of DSF and water, with a solid/liquid ratio of 0.29 [21]. Fly ash activation was achieved by milling with a planetary ball mill using a 1-L alumina jar with 98 alumina balls (20 mm in diameter) for 60 min to grind 450 g of fly ash [22]. Fly ash before (FA) and after (GFA) grinding, and silica fume in a densified state (DSF), and after being subjected to a sonication process (SSF), were characterized by laser diffraction analysis (LDA) using a MASTERSIZER2000 (Malvern Panalytical, Malvern, UK) in the water medium. The granulometric results are summarized in Table 3.

**Table 3.** Particle size parameters of fly ash before (FA) and after milling (GFA), and silica fume before (DSF) and after the sonication process (SSF).

	Mean Particle Diameter (μm)	d (0.1) μm	d (0.5) μm	d (0.9) μm
FA	29.92	2.30	18.55	74.32
GFA	10.38	1.46	8.19	22.25
DSF	76.67	7.95	34.82	199.55
SSF	23.47	2.45	18.36	52.57

## 2.3. Preparation of GRC Specimens

Premixed GRC composites were manufactured (size: 10 × 50 × 225 mm specimens, obtained by cutting from 400 × 400 × 10 mm plates) following the procedure described in Standard UNE-EN 1170-5 [23]. The parameters taken into account for composite dose were: the aggregate/cementitious material ratio = 0.67; the water/cementing material ratio = 0.35; fiber content: 3% of the total mortar weight.

Table 4 shows the dose for the manufactured GRC mortars. The control sample was prepared without pozzolans; in GFA60, 60% of cementing material was replaced with GFA; in GFA50+SSF10 the replacement levels were 50% with GFA and 10% with SSF.

**Table 4.** Dose of the manufactured GRC mortars (values in g).

Sample	CEM I 52.5R	Limestone Filler	Pozzolan	Siliceous Sand	AR Fiber	Superplastizicer	Mixing Water
C	1153.7	384.6	0	1025.5	93	15.4	529.8
GFA60	461.5	153.8	923	1025.5	93	12.3	531.6
GFA50+SSF10	461.5	153.8	769.1 + 153.8	1025.5	93	20	527.0

## 2.4. Curing and Aging Methods

Composites were subjected to different processes:

- (1) Curing composites. For the physical and chemical attack tests, specimens were subjected to two different curing processes: a) standard curing (SC) for 28 days in a humid chamber at 20 ± 1 °C and 90% relative humidity; b) to accelerate pozzolanic reactions, accelerated curing (Acc) was carried out (7 days at 20 °C and 21 days of immersion in water at 55 °C);



- (2) Accelerated aging. Specimens were previously cured under standard conditions and placed in a thermostatic water bath at 55 °C for 28 days (SC+Ag). The equivalence in predictive durability terms is, according to Purnell et al. [24], 100 days at 20 °C and in a humid environment (UK conditions) for each aging day, which would amount to about 8 aging years under standard conditions.

### 2.5. Testing Procedures

The 10 × 50 × 225 mm plates were assayed in all the tests carried out, except for thermogravimetry (pastes) and SEM (small pieces of plates or AR-attacked fibers).

- (1) Water absorption and dry density. To determine the percentage of water absorption by immersion and dry density, the procedure described in Standard UNE-EN 1170-6: 1998 [25] was followed. Six specimens were measured for each GRC type and treatment;
- (2) A four-point bending test (10 × 50 × 225 mm specimens, load rate 0.03 ± 0.003 mm/s) was performed in accordance with European Standard EN 1170-5 [23] to calculate the composites' modulus of rupture (see Equation (1)) and toughness (computed as the area under the load-displacement curve until the load drops to 10% of  $F_{MOR}$ ).

$$\text{Modulus of rupture (in MPa)} = \frac{F_{MOR} \times L}{b \times d^2} \quad (1)$$

where  $F_{MOR}$  the maximum load (in N),  $L$  is the major span (in mm, 200 mm in our test),  $b$  is the width (in mm, 50 mm in our test), and  $d$  is the thickness (in mm, 10 mm in our test);

- (3) Electronic scanning microscopy (SEM, JEOL JSM6300), equipped with energy dispersive X-ray (EDS: Link-Isis, Oxford Instruments, Oxford, UK) for microanalyses, was used to observe fiber deterioration. The acceleration voltage was 20 kV and the samples were covered with carbon. AR glass fibers were subjected to different aggressive reagents and heat treatment in aqueous medium between 28 and 70 days at 55 °C by immersion in saturated Ca(OH)<sub>2</sub> and 5% NaOH solutions. After exposure, fiber deterioration was analyzed by SEM.
- (4) Wetting–drying cycles. Specimens were subjected to wetting–drying cycles according to Standard UNE-ENV 1170-8:1997 [26], and were immersed for 24 h in either deionized water or a solution with 3.5% NaCl. Next, they were dried in a ventilated oven at 60 °C for 23 h. When removed from the oven, they were allowed to cool for 1 h. This cycle was repeated 10, 25, and 50 times for both the specimens saturated with water and those saturated with the NaCl solution to monitor the mass of each specimen at the end of every cycle. Six specimens were measured for each GRC type and treatment;
- (5) A thermogravimetric analysis (TGA 850 Mettler-Toledo, Greifensee, Switzerland) was carried out on pastes to assess the calcium hydroxide content and combined water in the cementing products. Samples were subjected to a heating ramp of 10 °C/min from 35 °C to 600 °C using a sealed aluminum crucible with a pinhole. The test atmosphere was nitrogen, fed at a rate of 75 mL/min;
- (6) Freeze–thaw cycles. Specimens were subjected to freezing–thawing according to ASTM C 1185-03, Section 12, “Freeze-Thaw-Cladding Products” [27]. Next, specimens were frozen at –20 °C for 2 h before being submitted to the thawing process at 20 °C for 2 h immersed in water. This cycle was repeated 50 and 100 times. A visual record and monitoring the mass of each specimen were carried out at the end of every cycle. Six specimens were measured for each GRC type and treatment;
- (7) Exposure to chemically aggressive agents. After specimens underwent the curing and aging processes, they were immersed in different aggressive solutions: 1 M solution of ammonium chloride (NH<sub>4</sub>Cl) at 20 °C and 0.5 M of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) at 20 °C. A visual record was made and the mass evolution of each specimen was recorded periodically by controlling the changes in the pH of each solution, which

varied constantly as an effect of the interaction between acid solutions and alkaline composites. The  $\text{NH}_4\text{Cl}$  solution was changed when pH reached 9, as was the  $\text{H}_2\text{SO}_4$  solution when it reached 1.5. Six specimens were measured for each GRC type and treatment.

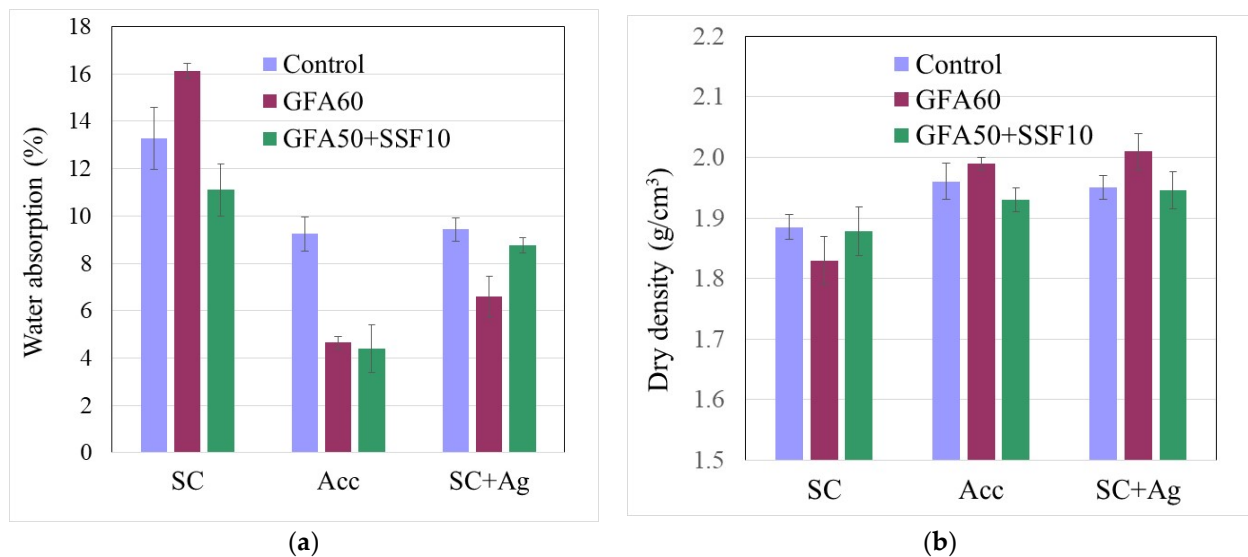
### 3. Results and Discussion

The first part of this section describes composite properties before and after aging. The second part presents the behavior of the composites subjected to physical attacks: wetting–drying and freeze–thaw. In the third part, the results obtained regarding the behavior of the composites subjected to acid attacks are analyzed: ammonium chloride and sulfuric acid aggressive solutions.

#### 3.1. Characterization of Composites and Their Evolution by Aging

##### 3.1.1. Water Absorption and Dry Density

The water absorption values found ranged between 4–16%, which is in agreement with typical GRC values [28,29]; dry density fell within the range of 1.8–2.0  $\text{g}/\text{cm}^3$ , with similar values being found in the literature [29]. Figure 1 shows the water absorption and density values of the studied composites. The aging and accelerating processes decreased water absorption and increased dry density. This behavior was attributed to the cementing matrix developing with rising temperature. Composite GFA60 had a higher water absorption percentage than composite C and GFA50+SSF10 after SC curing given the low pozzolanic reactivity of GFA at early ages. Absorption significantly decreased with the aging (SC+Ag) or acceleration (Acc) processes, and was below the other samples. This behavior was repeated, albeit to a lesser extent, for the GFA50+SSF10 system. The rise in curing temperature activated the pozzolanic reaction for the GFAs, and their contribution to cementing matrix development became very intense.

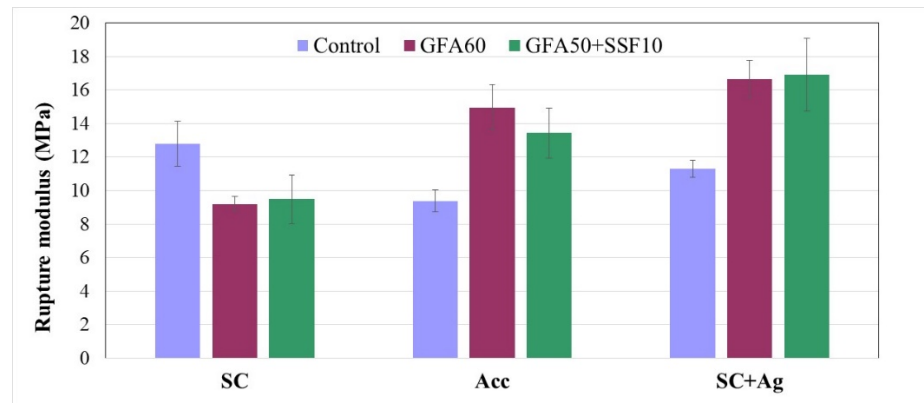


**Figure 1.** Water absorption (a) and dry density (b) of the GRC composites. (SC, standard curing for 28 d at 20 °C; SC+Ag, 28 d SC plus aging for 28 d at 55 °C; Acc, short curing for 7 d at 20 °C plus Acc for 21 d at 55 °C).

##### 3.1.2. Mechanical Behavior of the Aged GRC Composites

The modulus of rupture (bending strength) values of the composites and their evolution with aging time are depicted in Figure 2. The values found ranged in 8–16 MPa, which are typical values found in the literature [29]. During SC, composite C obtained the highest value (12.79 MPa) and the pozzolan-containing composites values were below 10 MPa (9.20 MPa for GFA60 and 9.48 MPa for GFA50+SSF10). However, the behavior

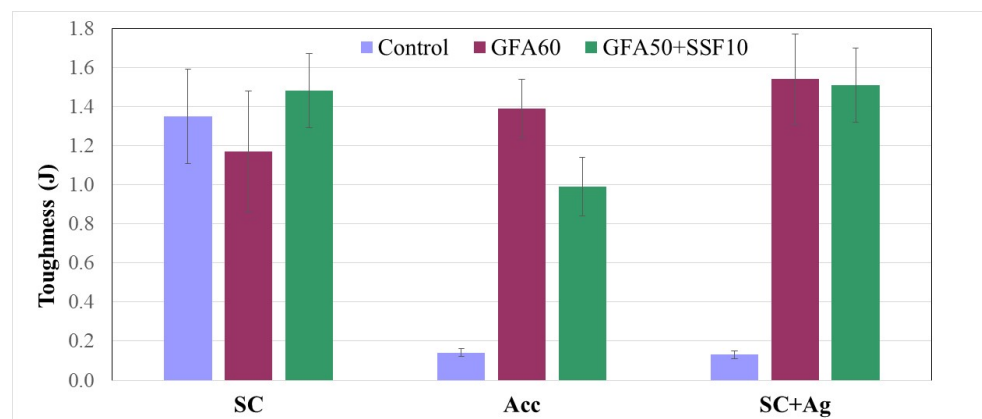
was very different for the composites that underwent Acc. Composite C had values under 10 MPa due to fiber deterioration (see the following subsections), whereas the composites containing pozzolans developed a very good cementing matrix and had significantly increased bending strength [17]: GFA60 with 14.95 MPa and GFA50+SSF10 with 13.44 MPa. This behavior demonstrated that the most important contribution of the pozzolanic reaction was achieved by increasing curing temperature. For the aging process (SC+Ag), the contribution of pozzolans was much more significant because the cementing matrix development was more intense during the ageing process: GFA60 with 16.67 MPa and GFA50+SSF10 with 16.92 MPa.



**Figure 2.** Modulus of rupture (bending strength) of the GRC composites. (SC, standard curing for 28 d at 20 °C; CS+Ag, 28 d SC plus aging for 28 d at 55 °C; Acc, short curing for 7 d at 20 °C plus Acc for 21 d at 55 °C).

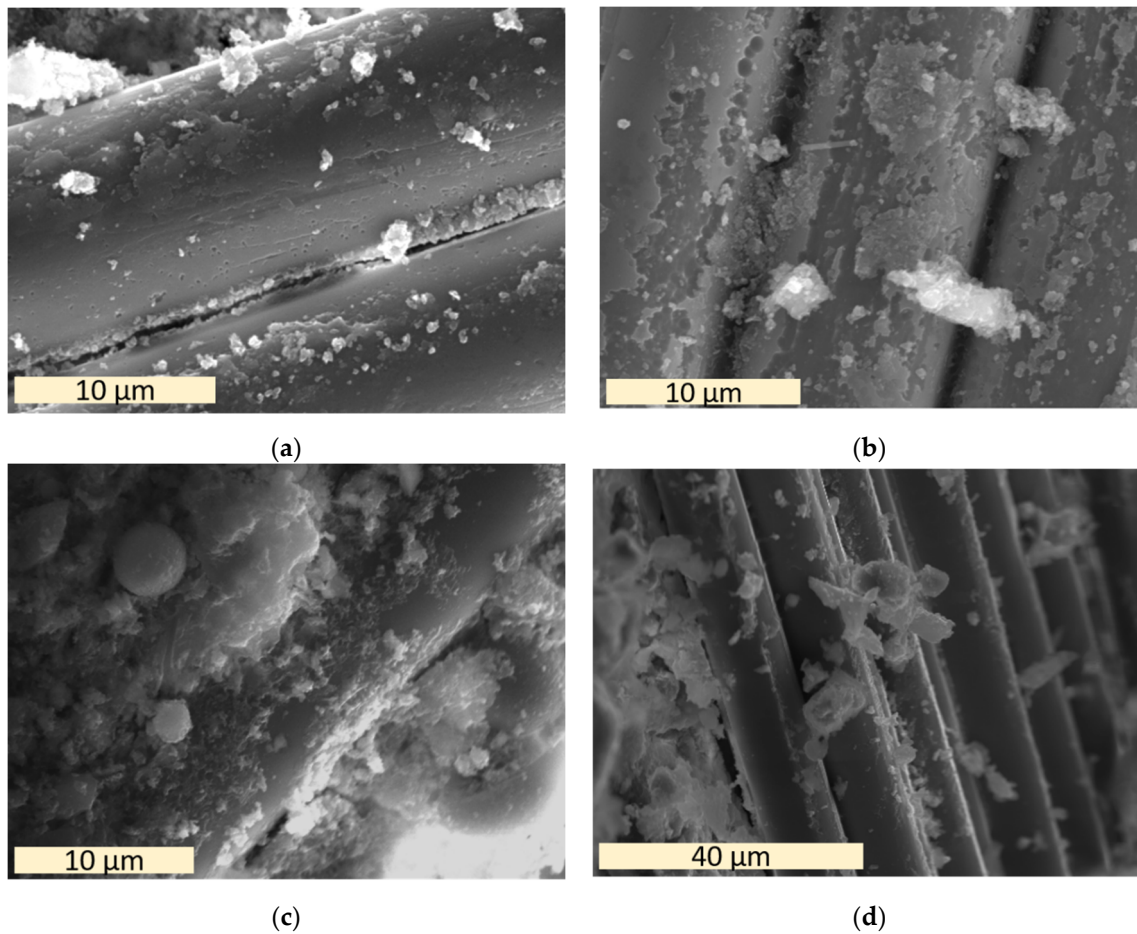
The density of composite C increased with aging (Figure 1), but its modulus of rupture did not (Figure 2). For the pozzolanic composites, an increase in both density and strength took place with aging. This means that increasing density was not the key to strength development for the C composite because fiber deterioration occurred. For the pozzolan composites, fiber integrity was maintained, and increasing density favored an increase in mechanical properties.

Figure 3 shows the toughness of the studied composites. For SC (28 days at 20 °C), composite C obtained a significant toughness value (1.35 J), which was only exceeded by pozzolanic composite GFA50+SSF10 (1.48 J). During the acceleration and aging processes, the toughness for C drastically dropped, but toughness was maintained for the pozzolanic composites.



**Figure 3.** Toughness of the GRC composites. (SC, standard curing for 28 d at 20 °C; CS+Ag, 28 d SC plus aging for 28 d at 55 °C; Acc, short curing for 7 d at 20 °C plus Acc for 21 d at 55 °C).

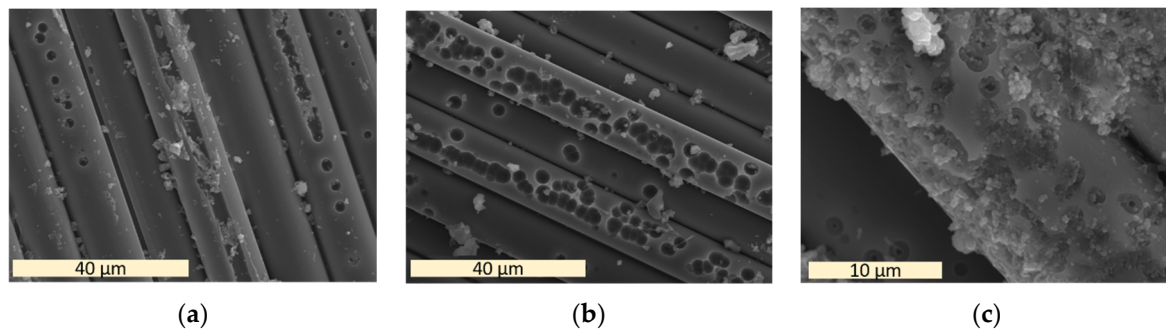
The micrographs in Figure 4 show the state of the AR fibers in the different composites and for various curing/aging conditions. The fiber surface deterioration in the C composite after curing is evident, with deterioration corresponding to sizing loss (Figure 4a). This behavior was previously reported by Nourredine et al. [30]. Fiber deterioration increases with the aging process (pitting on the fiber surface) and the mass loss of filaments is quite evident (Figure 4b). Figure 4c,d show the state of the fibers in the pozzolan-containing composites after aging: good fiber condition is observed. There is no evidence for pitting and the accumulation of cementing hydration products on the filament surface appears in the pozzolan composites [8].



**Figure 4.** AR fibers extracted from the GRC composites: control composite (C) after standard curing (SC, (a)) and after aging (SC+Ag, (b)); the GFA60 composite after SC+Ag (c); and the GFA50+SSF10 composite after SC+Ag (d).

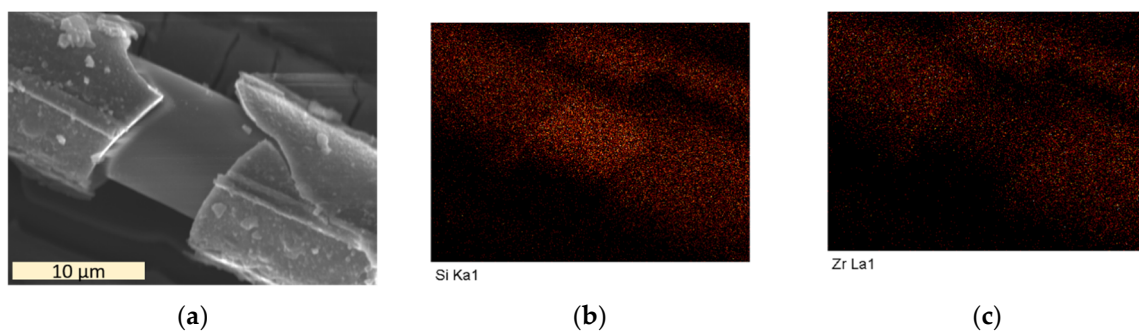
### 3.1.3. Exposing AR Fibers to Different Aggressive Environments

Figure 5 shows the micrographs of the fibers immersed in the saturated  $\text{Ca}(\text{OH})_2$  solution at  $55^\circ\text{C}$  for different treatment days. The attack generated by the alkaline solution is observed in the form of pitting on the surface of some filaments after 28 treatment days (Figure 5a); the effect of attack increases with aging at 56 and 70 days (Figure 5b,c), where the grouping of the affected areas and their increasing depth are observed.



**Figure 5.** AR fibers immersed in the saturated  $\text{Ca}(\text{OH})_2$  solution: (a) 28 d at  $55\text{ }^\circ\text{C}$ ; (b) for 56 d at  $55\text{ }^\circ\text{C}$ ; and (c) for 70 d at  $5\text{ }^\circ\text{C}$ .

Figure 6a shows the fibers immersed in 5% NaOH solution for 28 days at  $55\text{ }^\circ\text{C}$ . A different deterioration to that observed in the previous case is seen. In this case, the fiber underwent a more aggressive attack due to mass loss by the rings along its length detaching (shelling). Figure 6b,c show the mapping corresponding to Si and Zr, respectively. In the former, a higher Si concentration appears more in the central zone than on fiber filament ends. Conversely, for the second one, a higher Zr concentration is seen on filament ends (corresponding to the outer layer) than in its center. A higher Zr concentration is present in the outer filament perimeter, which provides an alkaline environment with greater resistance capacity. The most important fact is related to fiber deterioration, which depends on the nature of the cation present in the solution: the presence of  $\text{Ca}^{+2}$  produces pitting, whereas the presence of  $\text{Na}^+$  leads to shelling. This is why pitting is observed in the GRC composites prepared with Portland cement (the control sample, C), where the concentration of  $\text{Ca}^{+2}$  and  $\text{OH}^-$  ions is higher. However, this deterioration is inappreciable for the GRC pozzolan-containing samples. The reason for this is attributed to the low concentration of these ions because most are combined with pozzolans to form insoluble cementing products.



**Figure 6.** AR fibers submerged in 5% NaOH solution: (a) 28 d at  $55\text{ }^\circ\text{C}$ ; (b) Silicon EDS mapping (Si); and (c) Zirconium EDS mapping (Zr).

The absence of portlandite,  $\text{Ca}(\text{OH})_2$ , was critical for avoiding the deterioration of the fibers surrounding the cementing matrix. TGAs were carried out on the pastes prepared with Portland cement/GFA using proportions of 100/0 and 50/50. After 28 SC days, the portlandite contents were 9.69% and 1.98%, respectively. After aging (28 days at  $55\text{ }^\circ\text{C}$ ), the contents were 10.19% and 0.23%, respectively. This demonstrates the role of GFA in lowering the  $\text{Ca}^{+2}$  and  $\text{OH}^-$  contents in the cementing matrix, which preserved the fibers.

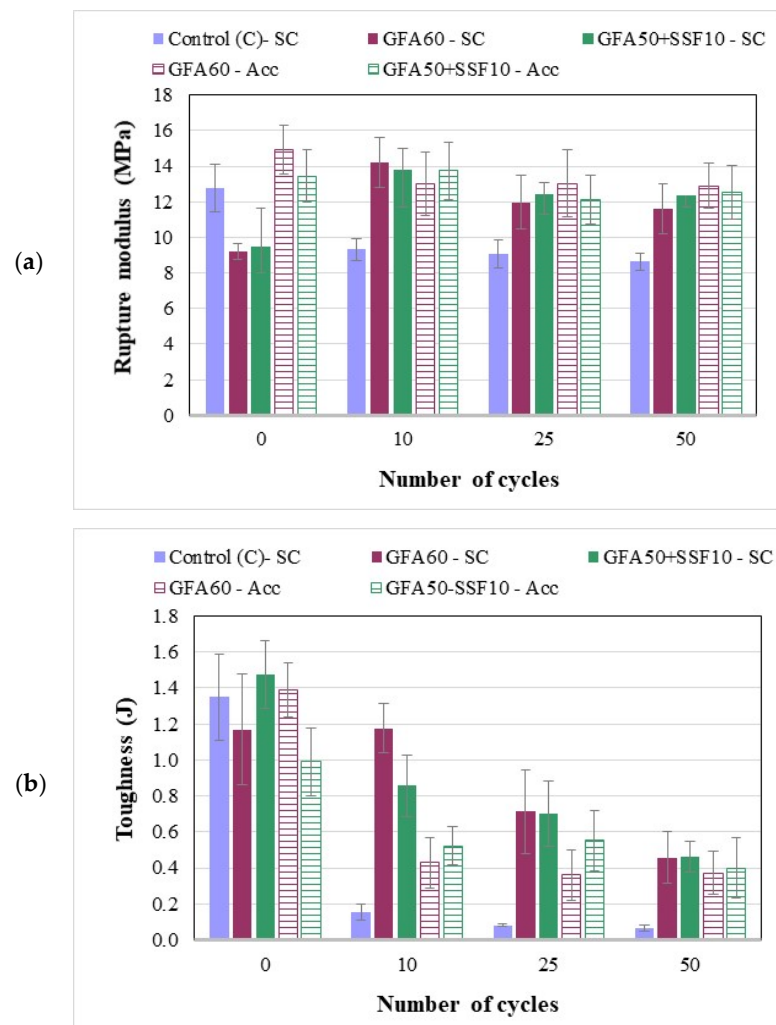
### 3.2. Evaluation of the Composites' Behavior Subjected to Physical Attacks

The standard cured (SC) and accelerated cured (Acc) specimens were tested in wetting–drying and freeze–thaw processes.



### 3.2.1. Wetting–Drying in Water

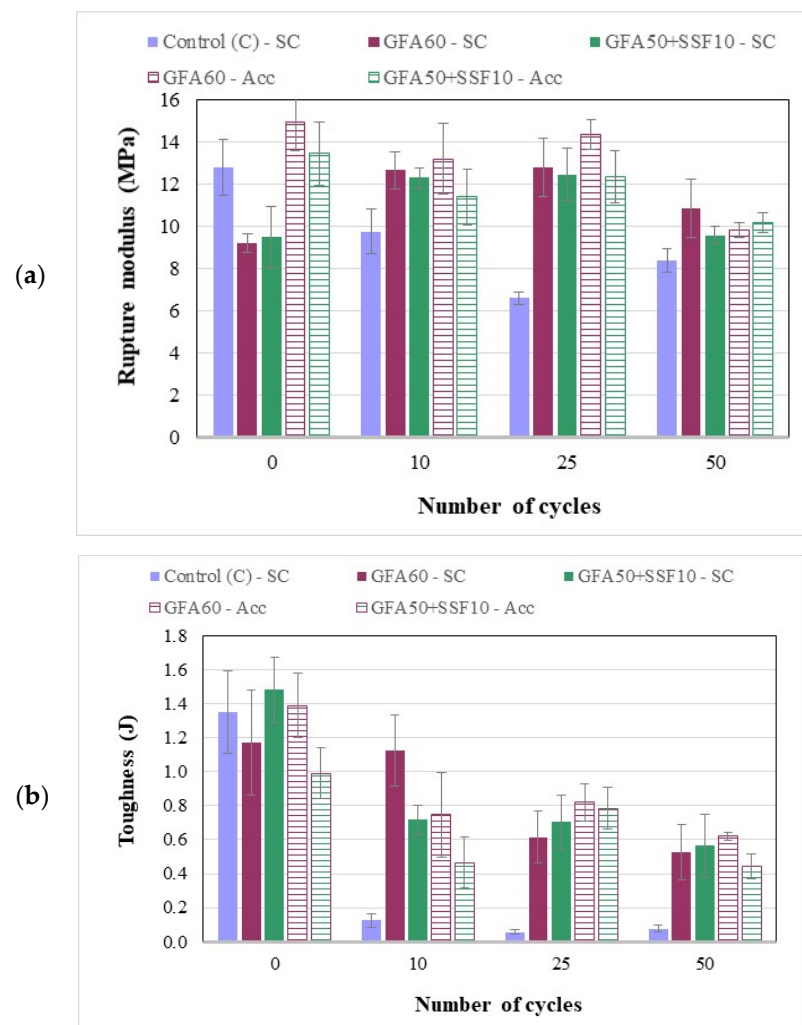
Figure 7a shows the modulus of rupture for composites before (0 cycles, the samples with SC) the wetting–drying process and after 10, 25, and 50 cycles. After SC (0 cycles), the composites with the pozzolanic substitution had lower strength values than the control (12.79 MPa). The pozzolanic composites with Acc had slightly higher strength values than the control. This was because the pozzolanic reaction better progressed with the acceleration process. This allowed a larger quantity of hydration products to form. After 10 cycles, a significant drop in the mechanical behavior of composite C was noted (9.32 MPa), but its value remained after 50 cycles. Similar behavior has been reported [14] for the control GRC: after 50 cycles, the modulus of rupture lowered from 17 MPa to 13 MPa. On the other hand, the pozzolan-containing composites had similar or higher values than 12 MPa after cycles, and greatly exceeded composite C’s behavior. A large toughness difference (Figure 7b) was observed between composite C and the other composites with pozzolans. In the presence of pozzolans, toughness progressively decreased with the number of cycles, and very significant embrittlement was observed for C after 10 cycles. After all the cycles, it was noteworthy that the toughness for the pozzolanic composites with SC was always greater than it was for the composites with the accelerated pozzolanic reaction (Acc). This behavior means that previous curing strongly influenced the development of composite properties in this physical attack type.



**Figure 7.** Modulus of rupture (a) and toughness (b) of the GRC composites subjected to wetting–drying tests in water.

### 3.2.2. Wetting–Drying in 3.5% NaCl Solution

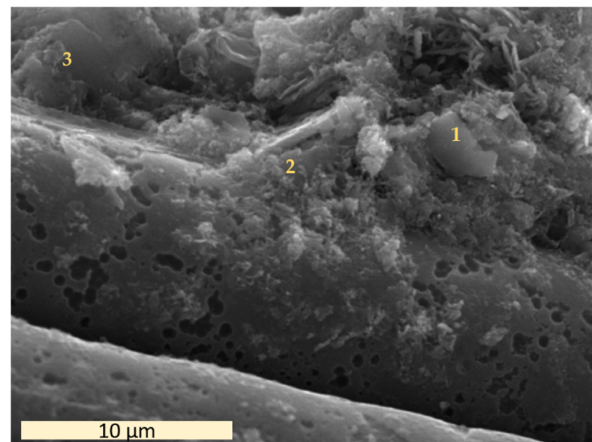
The generally observed behavior was similar to that for wetting–drying in water at both the strength and toughness levels. Evidently, the attack decisively affected the stability of composite C (Figure 8a), with a progressive drop in mechanical behavior close to 8 MPa after 50 cycles being observed. The composites with pozzolans that underwent SC displayed improved properties, which were favored by heat treatment (drying step) during cycles. Such behavior obtained a maximum value after 10 cycles, slightly decreased up to 50 cycles, and values remained close to 10 MPa. For the Acc samples, a slight decrease took place with the cycles, although a similar or higher strength than 10 MPa was recorded. With the pozzolan-containing composites, toughness (Figure 8b) progressively decreased with the number of cycles, whereas very significant embrittlement was observed for the control composite and, once again, after 10 cycles. These results imply that the presence of NaCl did not significantly affect the stability of the fibers in the cementing matrix.



**Figure 8.** Modulus of rupture (a) and toughness (b) for the GRC composites subjected to wetting–drying tests in 3.5% NaCl solution.

Significant fiber deterioration was observed for the control composite (C) after 50 cycles (Figure 9). Craters appeared on the surface of fiber filaments and hydration products were seen, especially calcium hydroxide crystals, which were embedded in the surface. When evaluating the chemical composition (Table 5) at the points of interest marked in the micrograph, the presence of hydrated calcium silicoaluminates was seen in spots 1 and 2

(at this point, the sodium and chlorine percentages were significant), and portlandite was mostly observed in spot 3.



**Figure 9.** SEM micrographs of the fibers in the control GRC composite subjected to wetting–drying test with 3.5% NaCl.

**Table 5.** Chemical analysis (energy dispersion spectroscopy, K and L EDS lines) of hydrated cement paste for control GRC subjected to a wetting–drying test with 3.5% NaCl (see spot numbering in Figure 9).

Element	Spot 1	Spot 2	Spot 3
	Atomic%	Atomic%	Atomic%
O <sub>K</sub>	77.36	65.23	76.39
Na <sub>K</sub>	0.68	3.00	0.00
Mg <sub>K</sub>	0.26	0.62	0.96
Al <sub>K</sub>	2.74	2.68	0.29
Si <sub>K</sub>	4.37	9.18	3.93
S <sub>K</sub>	0.25	2.11	0.46
Cl <sub>K</sub>	0.44	2.74	0.76
K <sub>K</sub>	0.53	0.10	0.00
Ca <sub>K</sub>	13.28	13.31	17.02
Fe <sub>K</sub>	0.10	0.24	0.07
Zr <sub>L</sub>	0.00	0.80	0.10

The TGA information presented in Table 6 shows the changes in the cementing matrix evolution. We can see that the percentage of combined water of the hydrates for the systems with pozzolanic substitution is lower after SC, but increases after 50 cycles. This fact confirms the improved composite properties and progressive cementing hydrate production. After curing 28 days, only calcium hydroxide remains in the control composite, whose value lowers when applying cycles because part of the portlandite dissolves when reacting with the chlorides present in solution and Friedel’s salt originates [31] (identified on the TGA curve, with mass loss centering at 300–400 °C).

**Table 6.** Thermogravimetry results on the composites subjected to wetting–drying tests with 3.5% NaCl solution.

Composite	% Combined Water from Hydrates		%Ca(OH) <sub>2</sub>	
	Standard Curing 28 Days at 20 °C	After 50 Cycles	Standard Curing 28 Days at 20 °C	After 50 Cycles
C	10.27	12.17	7.98	4.67
GFA60	7.39	12.26	0.00	0.00
GFA50+SSF10	9.50	12.03	0.00	0.00

### 3.2.3. Freeze–Thaw Attack

Figure 10 shows the modulus of rupture and toughness for the GRC composites subjected to freeze–thaw cycles. After 10 cycles, a significant drop in the modulus of rupture values for the C composite (Enfedaque et al. [14] reported this behavior after 30–50 cycles) and the pozzolan-containing composites is highlighted. This drop is much more marked for the specimens with pozzolan and SC because they have a lower modulus of rupture for all the tested cycles. These samples drastically lost their properties after 50 cycles. For 100 cycles, they yield around 8 MPa for the GFA50+SSF10 composite, and the GFA60 composite yielded around 6 MPa. This is evidenced because the matrix with pozzolan is not fully developed, a weakening that occurs due to the effect of the freezing water present in pores. For the specimens with an accelerated pozzolanic reaction (the Acc series), the drop after 50 cycles is marked, but the modulus of rupture continues to be higher than that for the control composite, C, under the same conditions. All this indicates that the accelerated pozzolanic reaction is a positive factor for freeze–thaw durability. Figure 10b shows the composites’ toughness results after exposure to cycles. The toughness value of the control composite C is lower, with values close to zero (brittle fracture). This implies significant damage to fiber integrity due to the physical attack. The pozzolan composites generally present values close to the control by the end of the curing process, and their toughness lowers much less after 50 and 100 cycles. This result suggests that the freeze–thaw process damages the matrix, but a certain fiber integrity remains. The decrease in mechanical properties is generally due to the effect of the water present in composite pores freezing which, given its increasing volume, initiates a progressive cementing matrix deterioration process. This effect is much more noticeable for the composites with pozzolan and standard curing because they present greater water absorption (see Figure 1).

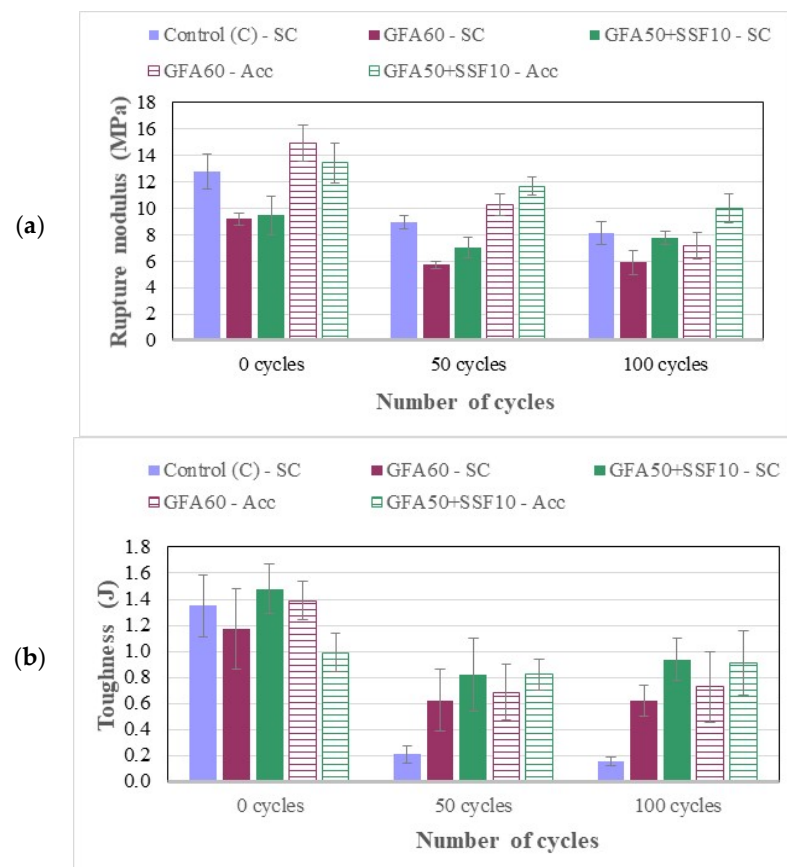


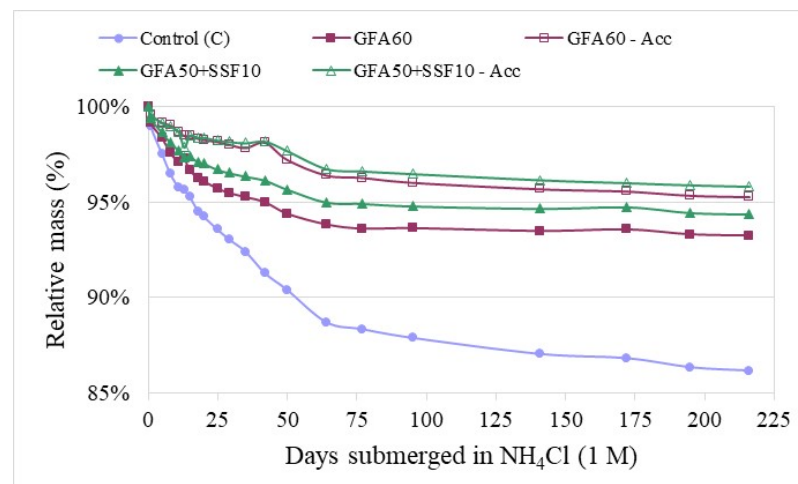
Figure 10. Modulus of rupture (a) and toughness (b) of the GRC composites subjected to freeze–thaw tests.

### 3.3. Assessment of the Behavior of the GRC Composites Subjected to Chemical Attacks

This subsection presents the behavior of the control composite C, standard cured composites GFA60 and GFA50+10SSF, and the accelerated cured (Acc) GFA60-Acc and GFA50+10SSF-Acc composites. The performed chemical attacks were acid attacks with ammonium chloride and sulfuric acid solutions.

#### 3.3.1. Exposing the GRC Composites to a $\text{NH}_4\text{Cl}$ Solution

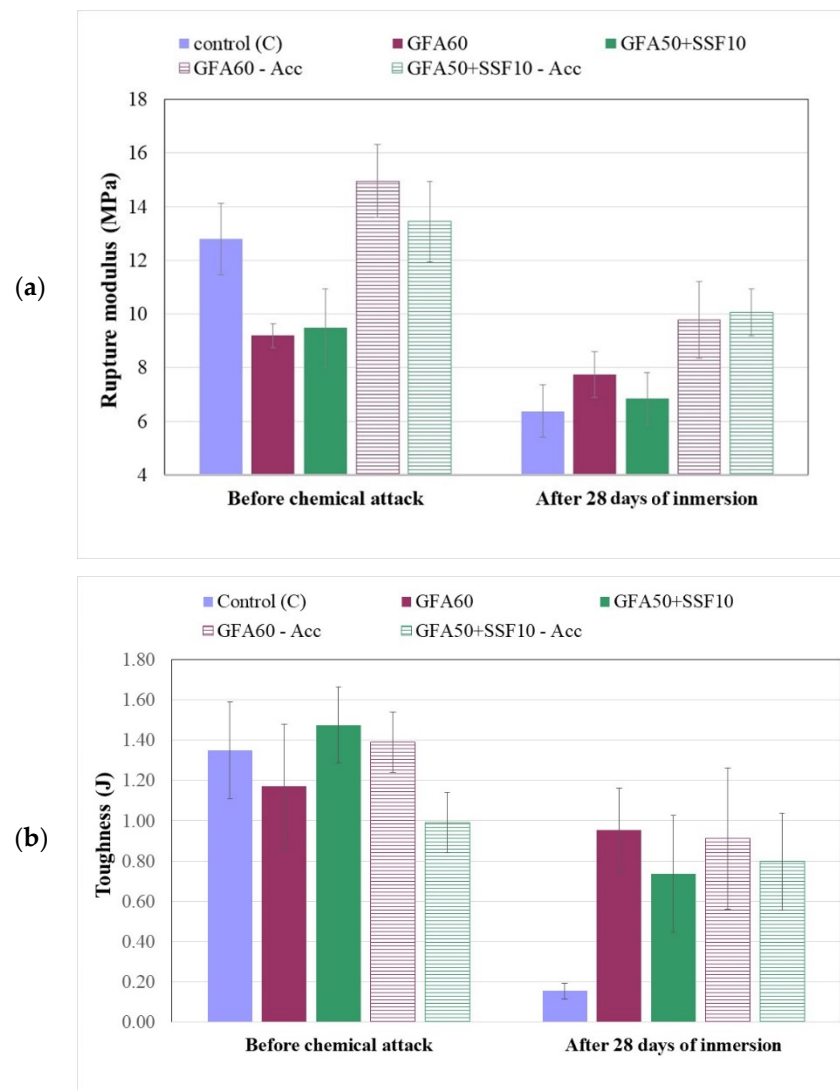
Figure 11 shows the variation in mass that specimens underwent when exposed to the aggressive medium. The initial mass was reduced in all cases. Greater loss occurred for the control specimen, C, because of the decalcification of the matrix, specifically dissolution of portlandite, and decomposition of C-S-H [32]. After 216 exposure days, this loss was close to 14%. For the specimens with pozzolans and SC, much less mass loss took place compared to the control, given the mass loss values of between 5% and 7% after 216 days. The pozzolanic composites with Acc were those with the least loss (4–5%). This behavior was directly related to the increase in density and the lowering degree of water absorption. For these cementing matrices, portlandite content was measured (0%  $\text{Ca}(\text{OH})_2$ ) by the TGA test, which means less leaching of the matrix by acid–base reactions. Lun et al. [33] demonstrated the effect of pozzolans on the leaching reduction of calcium in cement-based materials.



**Figure 11.** Mass variation for the GRC composites immersed in a 1 molar (1 M)  $\text{NH}_4\text{Cl}$  solution.

Figure 12 shows mechanical composite behavior before and 28 days after the  $\text{NH}_4\text{Cl}$  attack. When evaluating the modulus of rupture (Figure 12a), and after being immersed in the solution for 28 days, the strength of all the mortars decreased. One very important fact was that the GRC composites with Acc were clearly maintained over the control GRC. The hydrated products from the pozzolanic reaction were much more resistant to the ammonium chloride attack, and the reaction to portlandite was not possible. When assessing toughness (Figure 12b), the pozzolan-containing composites better responded to the aggressive agent than composite C. For 28 curing days, all the composites obtained high toughness values. After being exposed to the aggressive environment, the control composite's toughness decreased with values close to zero (brittle fracture). Although the toughness of the GRC with pozzolans decreased after being exposed to the aggressive agent, their behavior was notably superior than the control, C.





**Figure 12.** Modulus of rupture (a) and toughness (b) for the GRC composites immersed in a 1 M  $\text{NH}_4\text{Cl}$  solution.

Table 7 shows that calcium hydroxide was present only in composite C after 28 curing days, a value that lowered when the attack was applied because portlandite dissolves when it reacts with the ammonium cation ( $\text{NH}_4^+$ ) present in the aggressive solution. When analyzing the combined water of hydrates, 0.13% corresponded to Friedel’s salt, produced by the reaction among calcium aluminate hydrate, calcium hydroxide, and the chloride anion [34]. In the systems with pozzolan, all the portlandite was consumed by the high proportion of pozzolan by modifying the aggressive environment for fibers and reducing acid attack leaching.

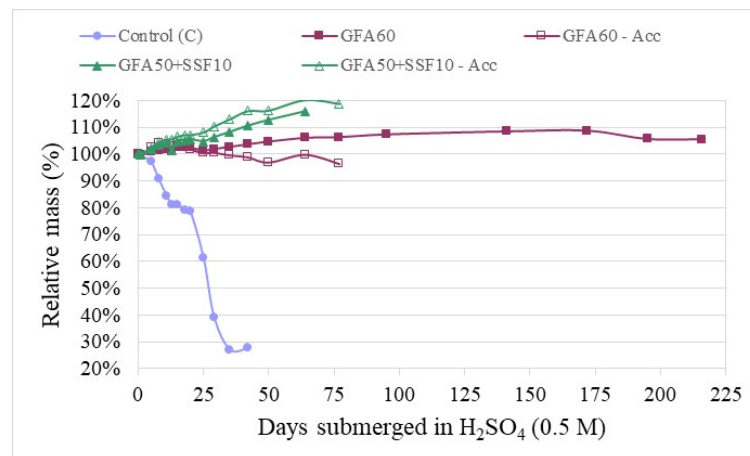
**Table 7.** Thermogravimetry results for the composites immersed in a 1 M  $\text{NH}_4\text{Cl}$  solution.

Composite	% Combined Water from Hydrates		%Ca(OH) <sub>2</sub>	
	Standard Curing 28 Days at 20 °C	Immersed for 28 Days in $\text{NH}_4\text{Cl}$	Standard Curing 28 Days at 20 °C	Immersed for 28 Days in $\text{NH}_4\text{Cl}$
C	10.27	13.76 *	7.98	0.00
GFA60	7.40	9.10	0.00	0.00
GFA50+SSF10	9.50	8.30	0.00	0.00

\* 0.13% of water corresponds to Friedel’s salt.

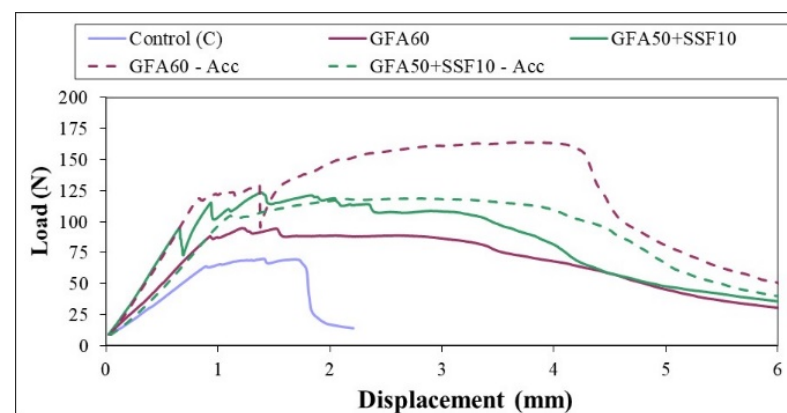
### 3.3.2. Exposing the GRC Composites to a $H_2SO_4$ Solution

Figure 13 shows the mass loss of the composites immersed in a 0.5 M  $H_2SO_4$  solution. When exposed to the aggressive solution, the control specimens underwent significant mass loss (close to 60%) after 40 exposure days. On the other hand, very stable behavior was noted for the specimens with pozzolanic materials on the first exposure days. Wanna et al. [35] found similar behavior for low water/cement Portland cement concrete. Subsequently, a significant increase in mass was recorded after 28 exposure days, especially for the composites with Acc (close to 15% mass gain). This can be attributed to sulfate salts forming in the cementing matrix by the reaction of the calcium-aluminate-based hydrates and  $SO_4^{2-}$  to form gypsum ( $CaSO_4 \cdot 2H_2O$ ) or ettringite [35].



**Figure 13.** Mass variation for the GRC composites immersed in a 0.5 molar (0.5 M)  $H_2SO_4$  solution.

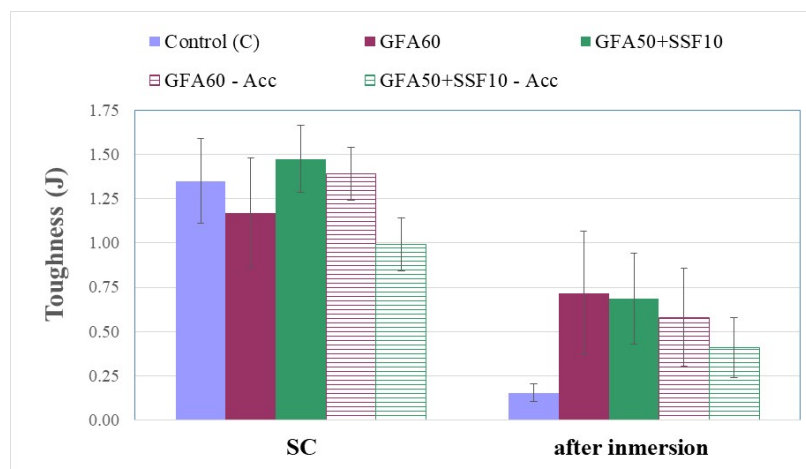
Figure 14 shows the load vs. displacement curves from the bending tests for the attacked samples. After immersion in the acid solution for 28 days, the control composite showed less mechanical behavior than the pozzolanic composites. A brittle fracture occurred after maximum loading. On the other hand, for the pozzolan GRC-containing samples, significantly higher loads and toughness values were obtained. The composites prepared with an accelerated pozzolanic reaction (the Acc series) showed better mechanical behavior after exposure to the aggressive agent than the GRC mortars cured under normal conditions.



**Figure 14.** Load–displacement curves (load rate  $0.03 \pm 0.003$  mm/s) for the GRC composites immersed for 28 days in a 0.5 M  $H_2SO_4$  solution.

For the calculated toughness (Figure 15), the samples with pozzolans yielded higher values because they had hydrated products (generated by the portlandite reaction with

pozzolans), which were much more resistant to the acid attack. After exposure to the acid solution, the toughness of the control reduced to values close to zero (brittle fracture).



**Figure 15.** Toughness of the GRC composites before (SC series) and after immersion (28 days) in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

#### 4. Conclusions

GRC composites with a high replacement (60%) of Portland cement with pozzolanic admixtures showed that the aging process lowered the water absorption percentage and increased density to values similar to the control values. The aging process activated the pozzolanic reaction, which caused cementing matrix densification. The improvement and increase in the hydrated products led to greater composite resistance due to the higher cohesion force at the paste–aggregate and matrix–fiber interfaces.

The AR fiber degradation phenomenon was confirmed by directly exposing the fiber to high alkalinity solutions: when fibers are exposed to a saturated Ca(OH)<sub>2</sub> solution, the attack generated craters or pitting on the surface, and the effect of the attack increased with aging by connecting the affected areas and increasing their depth. The AR fiber attack by exposure to a NaOH solution showed a different deterioration mechanism (shelling). This demonstrates the important role that Ca<sup>+2</sup> plays, which was why marked damage was observed on the fibers in the Portland cement matrix that had a high percentage of portlandite.

The wetting–drying process decisively affected the control composite’s stability with a significant drop in mechanical behavior after 10 cycles because of fiber integrity damage or loss. The 60% replacement of cement with pozzolan (GFA, or a mixture of GFA and SSF) improved composite behavior to the wetting–drying processes. The behavior observed for composites after the wetting–drying cycles with NaCl slightly affected the advantages offered from using a high percentage of pozzolans.

In general, the decrease in mechanical properties due to the effect of freezing the water present in pores took place in all the GRC composites. However, this effect was much less relevant for the composites with pozzolan and an accelerated pozzolanic reaction. Initial cementing matrix development notably influenced composite behavior against the freeze–thaw process.

Exposing GRC mortars to a 1M NH<sub>4</sub>Cl solution diminished their mechanical behavior due to mass loss through leaching. One notorious fact was that the composites with the accelerated pozzolanic reaction displayed more resistance. This was due to: (a) increasing density; (b) lowered degree of water absorption; and (c) the chemical stability of the pozzolanic reaction products in an ammonium medium.

Exposing GRC samples to a 0.5M H<sub>2</sub>SO<sub>4</sub> solution led to a marked difference in the mass loss between the control composite and pozzolan-containing composites, which implies the good stability of the cementing matrix when pozzolans are present at the 60%

replacement level. The differences in mass loss evolution were much larger for the control composite than for the composites with pozzolans, which reflected better mechanical behavior for the pozzolanic composites.

In short, it can be stated that substituting Portland cement for 60% pozzolan, or GFA, or for GFA + SSF, provides much more resistant and durable GRC composites. Generally speaking, these new proposed composites would be interesting in the architectural and civil engineering fields for developing products, such as claddings, permanent formworks, cornices, and canopies, among others. Given their good behavior in durability terms, they are specifically indicated for suitable products in potential corrosive environments (industrial, agro-industrial, and urban areas with high traffic density), such as sunscreens, drainage channels, cable trays, sound barriers, or pavements.

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