SULFURIC ACID RESISTANCE OF STRAIN HARDENING FIBER REINFORCED GEOPOLYMER COMPOSITE

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Abstract

This paper reports on sulfuric acid resistance of a strain-hardening fibre-reinforced geopolymer composite, named Engineered Geopolymer Composite (EGC). EGC is a promising material for durable and resilient wastewater infrastructure applications due to its acid-resistant geopolymer matrix and high tensile ductility along with self-controlled microcracking. In the present study, the weight loss, residual compressive and flexural strengths, and deflection capacity of acid-exposed EGC specimens are experimentally investigated. In comparison with normal cement concrete and Engineered Cementitious Composite (ECC), EGC exhibited a three times slower rate of weight loss and no significant degradation in mechanical performances.

Keywords: Fiber-reinforced composite, Geopolymer, Strain hardening, Sulfuric acid.

1. INTRODUCTION

Geopolymer is a potential alternative to cement materials for sewer infrastructure applications. It is a family of alkali-activated binders that form alumino-silicate polymeric structure in the matrix formation. Previous studies reported the high sulfuric acid resistance of geopolymer concrete, especially in terms of weight loss caused by acid exposure [1-4]. Since the biogenic sulfuric acid attack is one of the main deterioration mechanisms of concrete wastewater facilities [5-8], the high acid resistance of geopolymer concrete seems promising for improving durability of wastewater infrastructure.

Recently, a new family of strain-hardening fibre-reinforced geopolymer composites – named Engineered Geopolymer Composite (EGC) – has been developed to improve durability of geopolymer concrete [9]. EGC shows strain-hardening and multiple cracking characteristics in uniaxial tension, with high tensile ductility of over 4%, which is comparable to Engineered Cementitious Composite (ECC) [10]. The multiple microcracks are self-controlled to be smaller than 50 μm on average, even under a high imposed tensile strain. The tight cracks and high tensile ductility are expected to enhance durability properties of EGC, including penetration resistance of aggressive agents such as water and acidic media. Due to the unique characteristics, various research efforts have been recently made in EGC development and characterization of their mechanical properties [11-13]. However, the high sulfuric resistance of EGC has not been experimentally demonstrated yet.

This paper reports an experimental investigation on sulfuric acid resistance of EGC in comparison with normal cement concrete and ECC; the latter two materials serve as controls. Weight loss and residual compressive strength of cylinder specimens subjected to sulfuric acid exposure are presented. In addition, to study combined effects of cracking and acid attack on mechanical property degradation, residual flexural strength and deflection capacity are measured for beam specimens that are preloaded to create cracks before acid exposure.

2. MATERIALS AND METHODS

2.1 Ingredients and Mix Designs

Table 1 lists the ingredients and their mix proportions of Portland Cement concrete, ECC and EGC used in this study. Type I Portland Cement and ASTM class F fly ash (labeled Fly ash A) were used as the binder materials for the concrete and ECC. For EGC, class F fly ash from a different power plant (labeled Fly ash B) was blended with the Fly ash A. Chemical compositions and physical properties of the two types of fly ash are presented in Table 2. Crushed limestone with a maximum size of 25 mm and silica sand with a fineness modulus of 2.43 were used as coarse and fine aggregates of the cement concrete, respectively. F-75 Ottawa fine silica sand and short polyvinyl alcohol (PVA) fibre with 1.2% oil coating were used for both ECC and EGC. Fiber properties are listed in Table 3. To obtain adequate workability, polycarboxylate-based superplasticizer was added to the concrete and ECC mixtures. The alkali activator of EGC consists of laboratory-grade sodium hydroxide (NaOH) pellets, sodium silicate solution (Na_2SiO_3 with 8.9 wt% Na_2O, 28.7 wt%

SiO_2, and 62.5 wt% H_2O) and tap water (labeled Pre-mix water), which were mixed together at least 24 hours before its use. Additional water was added to the fresh EGC mixture to achieve desired rheology.

Table 1: Mixture proportions of cement concrete, ECC, and EGC (in kg/m^3)

	CEMENT CONCRETE	ECC M45	EGC (V_f –1.5%)
Type I cement	292	581	
Fly ash A	103	697	463
Fly ash B			694
Coarse aggregate	873		
Fine aggregate	956		
Fine silica sand		464	463
PVA fibre		26	19.5
Super plasticizer	2.1	4.4	
Water	174	337	116
NaOH (pellet)			60.1
Na_2SiO_3			260
Pre-mix water			26.6

Table 2: Chemical compositions and physical properties of fly ash

	FLY ASH A	FLY ASH B
SiO_2	42.20	46.09
Al_2O_3	22.51	23.15
Fe_2O_3	9.20	19.48
CaO	15.66	5.08
SO_3	1.85	0.77
MgO	3.20	1.12
Na_2O	0.98	0.58
K_2O	1.53	1.73
Moisture	0.12	0.16
Loss on ignition	1.34	1.99
density	2.53	2.58
Fineness (% retained on 45 μm sieve)	16.58	22.24

Table 3: Properties of PVA fibre

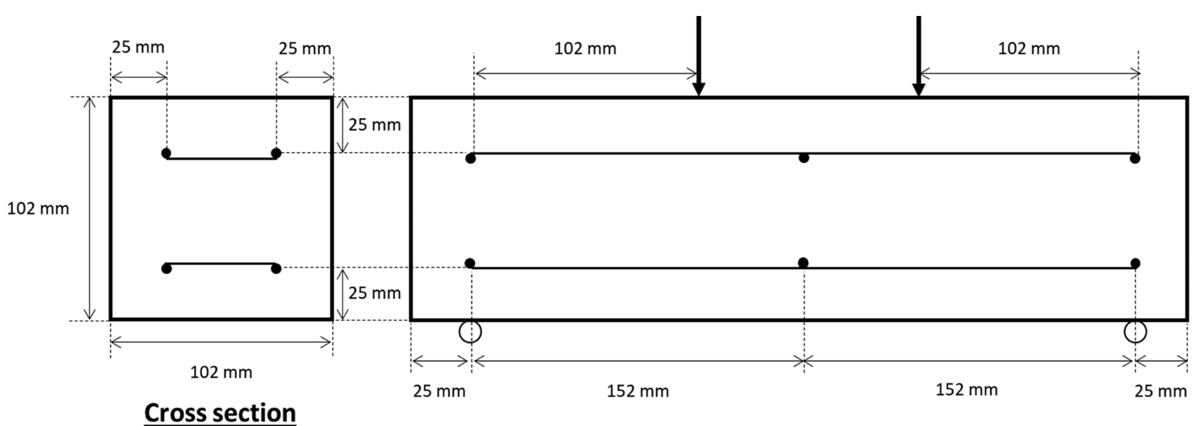
NOMINAL STRENGTH (MPa)	DIAMETER (μm)	LENGTH (mm)	YOUNG'S MODULUS (GPa)	ELONGATION (%)
1620	39	12	42.8	6.0

The mix proportion of the cement concrete follows the mixture design used in a study by Peyvandi et al. [14], which is commonly used in dry-mixed concrete pipe production. ECC used in this research is the most-studied standard version, called M45 [15], with a fibre volume fraction of 2%. The EGC design with 1.5% fibre content is the one developed in a previous study [16].

2.2 Specimen Preparation

In all series, powder materials and sand were first dry-mixed. Water and superplasticizer were mixed with the solid materials to prepare cement and ECC mortars, while the alkaline activator and mixing water were employed in the case of EGC mortar. Coarse aggregate was then added for concrete mixing, while PVA fibres were added to both ECC and EGC mortars. The mixture of each series was cast into 76 x 152 mm cylinder and 102 x 102 x 356 mm beam molds.

Steel wire reinforcement was placed for the concrete beam specimens, as shown in Figure 1. W 1.4 (gage 10) steel wire mesh that meets ASTM 1064 [17] was used for both the longitudinal and transverse reinforcement. The reinforcement ratio satisfies requirements of Class IV, Wall C reinforced concrete (RC) pipe, specified in ASTM C76 [18], which has a wall thickness of 102 mm and an internal diameter of 686 mm. It should be noted that, while the transverse reinforcements were placed to represent



* W-1.4 (gage 10) welded wire mesh for both transverse and longitudinal reinforcement

Figure 1: RC beam design and testing setup of four-point bending.

the inner and outer circular cages in ASTM-specified pipes, they would not effectively carry the load in the flexural strength test.

All specimens were demolded 24 hours after casting. Concrete specimens were then moist-cured with a relative humidity of over 95% at a room temperature (23 ± 3°C) until the age of 28 days. ECC specimens were moist-cured for only 6 days and then air-cured at a room temperature until the age of 28 days. EGC specimens are dry-cured at 60°C for 24 hours right after demolding, followed by air curing at a room temperature until the age of 28 days.

2.3 Sulfuric Acid Exposure

A sulfuric acid resistance test developed by Kaempfer and Berndt [19] was adopted in this study. At the age of 28 days, specimens were fully immersed in tap water. After 2 days, the specimens were removed from the water bath, wiped with paper towels, and weighed with a precision of 0.01 g. Subsequently, specimens were immersed in diluted sulfuric acid solution with a pH value of 2. The pH value of the acid bath was checked daily and kept constant by adding extra sulfuric acid solution, if needed. After 6 days of the acid exposure, specimens were gently brushed under running water to remove loose particles on their surface, and then immersed in a water bath for 24 hours. The weight measurement, 6-day acid exposure, and 1-day water bath, which constitutes one cycle of the acid resistance test, were then repeated. The sulfuric acid bath was replaced every cycle. Kaempfer and Bernd suggested that 5 cycles of the testing (i.e. 35-day acid and water exposure) represent the 20-year corrosion stress of ordinary concrete sewer pipes in the field [19].

2.4 Compressive Strength Test

Uniaxial compression testing was first conducted on three cylinder specimens of each material for their 28-day compressive strength. Specimens were capped with sulfur capping compounds at least one day prior to testing. The loading rate was 0.25 ± 0.05 MPa/s.

Nine intact cylinders for each material were subjected to the acid exposure. Out of these, three randomly selected specimens were tested for residual compressive strength after every 5 cycles (i.e. 35-day exposure). Namely, the average weight change was determined for 9 specimens for 1-5 cycles, 6 specimens for 6-10 cycles, and 3 specimens for 11-15 cycles. To evaluate the effects of continuous hydration of cementitious materials, another set of 9 cylinders for concrete and ECC were prepared as control specimens and subjected to water bath for the same exposure periods as those of acid-exposed specimens. The control specimens were then tested for reference compressive strength. For EGC specimens, no significant strength increase after 28 days was observed in preliminary studies. Control specimens for EGC were therefore not prepared in this study.

2.5 Flexural Strength Test

A four-point bending test was first performed on three beam specimens of each material to measure their 28-day flexural strength – known as modulus of rupture (MOR) – and their deflection capacity (i.e. deflection at MOR). The span length was 305 mm and a constant loading rate of 0.076 mm/min was applied under displacement control of the loading head. To measure the mid-point net deflection, two potentiometers were mounted on both sides of a rectangular jig that surrounded the beam specimen and was clamped at mid-depth directly above the loading supports.

Another set of three beams for each material were preloaded at the age of 28 days. The testing configurations are identical to the above flexural strength test, except that the test was stopped at the net mid-point deflection of 0.51 mm, which is equivalent to 1/600 of the span length. Subsequently, the preloaded specimens were immersed in tap water for 2 days, and subjected to the acid exposure of 15 cycles (105 days). The acid-exposed beams were then reloaded to measure their residual MOR and deflection capacity.

3. RESULTS AND DISCUSSION

3.1 Weight Change

Figure 2 shows results of the weight change measurement. As can be seen, the weight loss is limited until about 35 days in both cement concrete and ECC. The limited weight loss might be related to weight gain of sulfuric acid-exposed cement concrete in early exposure periods, which has been reported in many other studies. Chang et al. suggested that such weight gain could be attributed to many factors, including continuous cement hydration, formation of gypsum due to acid attack, and increase in absorbed water of specimens [20]. Despite the initial weight gain, the rate of subsequent weight loss of concrete and ECC is about three times that of EGC. As a result, the weight loss of either concrete or ECC after 15 cycles (105 days) is more than double that of EGC.

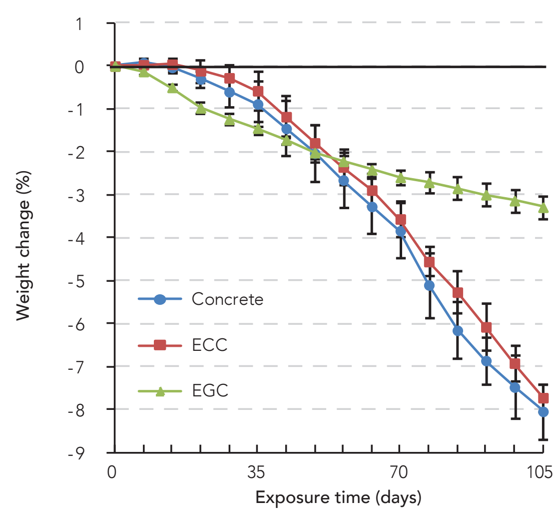


Figure 2: Weight change of cement concrete, ECC, and EGC in the sulfuric acid exposure test.

During the acid exposure test in this study, PVA fibres on the surface of ECC were loose and easily brushed off after the acid exposure. On the other hand, much less PVA fibres were brushed off from the EGC surface. This implies that the interface between the geopolymer matrix and PVA fibres is more durable against sulfuric acid attack than the cement matrix-PVA fibre interface in ECC.

3.2 Compressive Strength Degradation

Figure 3 shows normalized residual compressive strengths of each material. The raw residual strength data of EGC are normalized by its 28-day compressive strength, while those of cement concrete and ECC are normalized by strength of water-cured control specimens with the same specimen age, to extract effects of continuous hydration in cement materials. The test results indicate that no significant degradation is observed in EGC and ECC, implying negligible effects of the observed weight loss on strength degradation. Conversely, continuous degradation can be clearly seen in cement concrete.

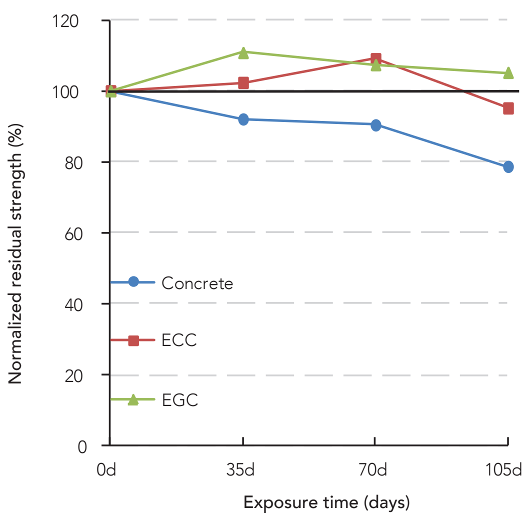


Figure 3: Normalized residual strength of cement concrete, ECC and EGC.

The insignificant strength degradation in ECC could be attributed to the limited loss of cement matrix than in cement concrete. The measured weight loss of ECC includes brushed-off PVA fibres from the surface. On the other hand, the weight loss of concrete is associated with lost hardened cement paste and aggregate. In addition, the larger amount of fly ash incorporated in ECC than cement concrete could enhance the sulfuric acid resistance of the cement matrix, as reported by Torii and Kawamura [21]. As a result, relatively large loss of cement matrix in concrete could cause significant strength degradation, while effects of the lost fibres from ECC surface are limited.

3.3 Residual Flexural Performance

Average MOR and deflection capacities of beam specimens at 28 days and after acid exposure are summarized in Table 4. Unfortunately, data of one acid-exposed RC beam was lost due to an unexpected power outage during its reloading, and the average flexural properties are therefore computed for only two specimens. In RC and EGC series, differences in either MOR or deflection capacity before and after acid exposure are found to be insignificant based on a statistical t-test with an assumption that the data are normally distributed with the equal variance. Therefore, the acid-induced weight loss observed in this study seems to cause insignificant degradation in the MOR and deflection capacity of RC and EGC.

In contrast, effects of the acid exposure on both the MOR and deflection capacity of ECC are statistically significant. While the residual MOR has only 8% reduction from the 28-day value, the decrease is significant when the observed small sample variances are taken into account. The degradation could be mainly attributed to brushed-off PVA fibres due to the surface erosion. Unlike compressive strength, flexural strength of ECC beams highly depends on the number of fibres that can bridge cracks. Therefore, loss of the considerable amount of PVA fibres has a direct impact on the load-carrying capacity.

Conversely, 87% increase in the deflection capacity of ECC could be associated with the degraded cement matrix; due to the acid-induced surface erosion, first cracking strength of ECC matrix could be lowered, which is beneficial for achieving a higher ductility. In fact, more multiple cracks were observed in reloading on ECC beams than the 28-day flexural strength test. Therefore, although ECC matrix is eroded by sulfuric acid attack, the damage could offer better deflection-hardening and a higher deflection capacity.

Table 4: Flexural properties of RC, ECC, and EGC at 28 days and after acid exposure.

	28-DAY PERFORMANCE		AFTER ACID EXPOSURE		f_1 / f_0	σ_1 / σ_0
	MOR, f_0 (MPa)	DEFLECTION AT MOR, σ_0 (mm)	MOR, f_1 (MPa)	DEFLECTION AT MOR, σ_1 (mm)		
RC	9.2 ± 1.4	1.25 ± 0.27	8.3 ± 0.7	1.39 ± 0.14	0.90	1.11
ECC	15.0 ± 0.4	1.23 ± 0.49	13.8 ± 0.3	2.30 ± 0.16	0.92	1.87
EGC	10.8 ± 1.0	5.39 ± 1.09	11.6 ± 1.5	5.26 ± 0.95	1.08	0.98

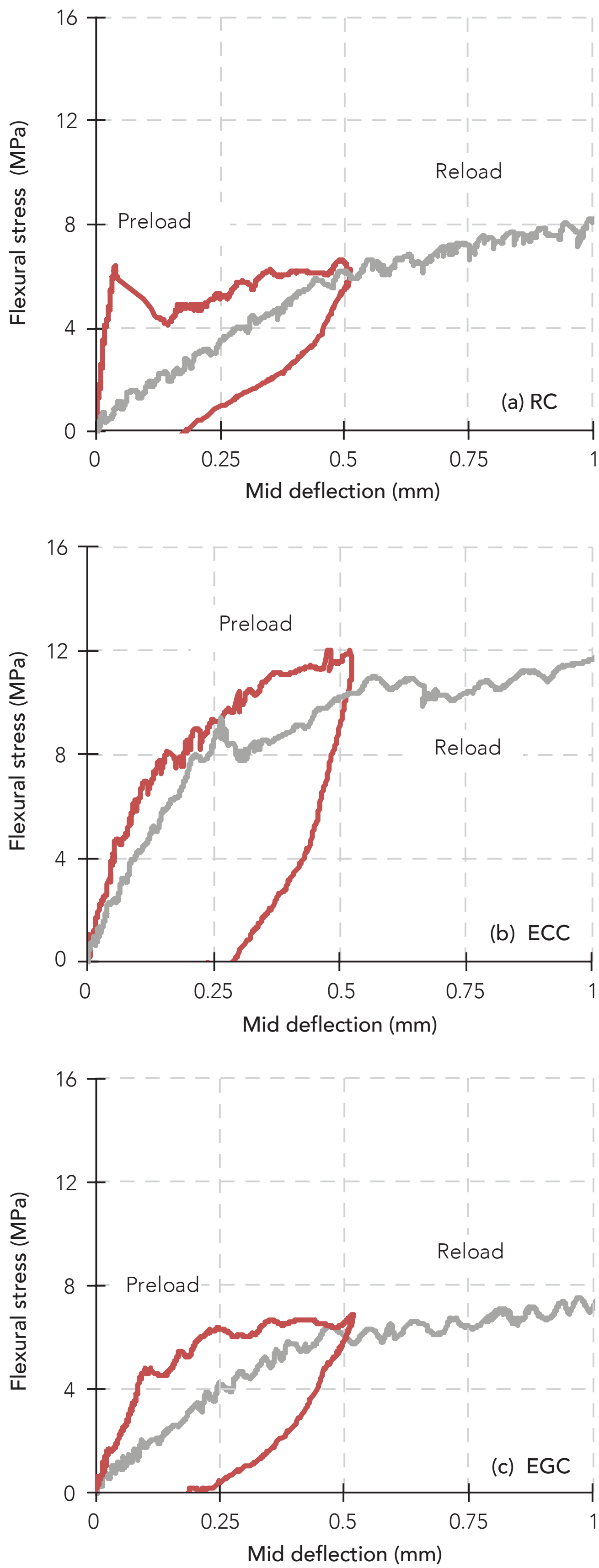


Figure 4: Typical bending curves of RC, ECC, and EGC in preloading and reloading. For easy comparison of bending stiffness, the curves are plotted up to a mid-deflection of 1 mm.

Aside from the MOR and deflection capacity, notable reduction in bending stiffness was observed for all the acid-exposed beams. Figure 4 shows typical bending curves, plotted up to a mid-deflection of 1 mm, of each material for preloading and reloading on the same specimen. For a quantitative evaluation, linear bending stiffnesses are computed for data from 0.5 to 4 MPa by linear regressions, which show high r-squared values of over 0.9 in all the series. The average residual stiffnesses of RC, ECC, and EGC are 5, 43, and 33%, respectively, of their initial stiffnesses in preloading.

It should be mentioned here that cracks in both RC and ECC beams were completely sealed during the acid exposure. Even under sulfuric acid environments, the self-healing ability of cement materials was functional. Thus, the relatively large residual stiffness of ECC might be attributed to mechanical property recovery due to the self-healing. On the contrary, cracking was completely sealed in RC beams, but not healed along with stiffness recovery. As a result, the stiffness reduction in RC beams due to combined effects of preloading and acid attack was significant. In the case of EGC, no crack sealing was observed. Instead, fine surface cracking was found as in the cylinder specimens. Nevertheless, the residual stiffness of EGC is notably higher than that of RC, when compared with the initial stiffness of each series. This implies that acid-induced damage on the fibre-matrix interface in EGC is limited compared with that on the interface between cement concrete and steel wire reinforcement in RC.

4. CONCLUSIONS

This paper experimentally demonstrated the high sulfuric acid resistance of EGC. Acid-induced surface erosion of EGC specimens was limited compared with cement concrete and ECC, especially in terms of weight loss. No significant degradation was observed for its compressive strength, MOR and deflection capacity after acid exposure. While combined effects of preloading and acid attack caused remarkable degradation in its linear bending stiffness, the degree of reduction is less than RC. Due to the considerably slower rate of weight loss in EGC than those in concrete and ECC, differences in mechanical property degradation among the materials would be more remarkable when subjected to longer acid exposure or more severe acidic environments.

The following findings were also obtained during this study;

- Compared with EGC, a larger amount of PVA fibres are brushed off in ECC due to the acid-induced surface erosion. The loss of fibre did not reduce compressive strength of ECC, but caused statistically significant degradation in its MOR.
- The deflection capacity of ECC can be increased after acid exposure. This could be attributed to the degraded cement

matrix with lower matrix tensile strength, which is beneficial for achieving better deflection-hardening and a higher ductility.

- Self-healing functionality of cement materials can be realized even under acidic environments. Cracks of preloaded RC and ECC beams were completely sealed during the acid exposure.

- Significant mechanical performance recovery due to the self-healing was observed in linear bending stiffness of the ECC beams only. Despite the sealed cracking in preloaded RC beams, their stiffness reduction was the largest among the materials.

It has been argued that the accelerated sulfuric acid resistance test does not fully represent the microbial effects on concrete in the field [8]. Therefore, further research would be required to more accurately assess the durability of EGC under sewer environments.

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