Dissertation Title: “Degradation of Basalt Fiber Reinforced Polymer Bars under Aggressive Environmental Conditions”

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ABSTRACT

Coastal bridges are continually subjected to chloride-rich exposure, where seawater contact drives chloride penetration into concrete and speed up corrosion and degradation in steel and prestressed composites. Basalt fiber reinforced polymer (BFRP) reinforcement is increasingly gaining interest because of its potential to replace steel in infrastructures and compete with other corrosion-resistant FRP systems. This dissertation has two main objectives: (1) to determine how basalt-fiber sizing influences corrosion resistance by evaluating sizing stability and transport at the fiber-environment interface, directly comparing sized and unsized fibers, quantifying ion exchange and leaching across 16 controlled pH-salinity exposure conditions, and using SEM-EDX (scanning electron microscopy and energy-dispersive X-ray spectroscopy) analysis to identify the dominant physicochemical degradation mechanisms; and (2) to define the role of resin matrix in BFRP rebar durability by testing three rebar types under the same 16 environments, comparing chemical leaching across rebar-resin systems, assessing the effect of epoxy versus vinyl ester on degradation resistance, characterizing microstructural damage in both rebars and neat resins using SEM, and correlating solution chemistry with microscopy to establish the governing mechanisms.

Sizing effects and basalt-fiber corrosion mechanisms were evaluated by comparing sized and unsized fibers across 16 environments spanning pH 4-13, 0-20,000 ppm Cl^-, and synthetic versus natural seawater, using up to 600 days of conditioning at 60ºC with SEM-EDX analysis and solution-phase ion-exchange/chemical-release analysis. Degradation increased systematically with alkalinity and salinity, with natural seawater consistently producing more severe attack than compositionally similar synthetic media, indicating that sulfate and other seawater constituents intensify disruption of the silica-based network (also reflected by larger diameter loss, for unsized fibers). Sizing acted as an initial transport barrier and unsized fibers showed thicker corrosion layers in SEM. However, this protection was limited; in aggressive matrices the coating degraded,

resulting in elevated TOC and precipitation behavior that marked the end of the early protective stage. High pH drove OH^- to rupture of Si–O–Si network, chloride primarily contributed by forming [Fe-Cl] complexes and ultimately rust-like product formation. Sulfate depletion in seawater was consistent with precipitation/adsorption with leached metals (e.g., gypsum formation and association with Fe/Al hydroxides). Overall, basalt fibers remained comparatively stable up to ~pH 10, while pH 13 produced rapid breakdown, defining an approximate stability window of pH 4-10 and supporting basalt reinforcement performance under typical marine pH conditions.

Resin chemistry strongly controlled the long-term durability of BFRP rebars. Three rebar systems (Type A, B, C; Lots 1–2) produced with epoxy (Types A and C) and vinyl ester (Type B) were conditioned for 600 days at 60ºC in the same 16 exposure environments, combining exposure-solution chemistry with SEM damage characterization of both rebars and resin specimens. Across the matrix, the resin governed solution uptake, microcrack development, and the degree of fiber-matrix interphase exposure, thereby dictating transport pathways and damage progression. The greatest deterioration occurred in pH 13 with seawater, consistent with the added aggressiveness of seawater multivalent ions (e.g., Mg^{2+}, Ca^{2+}) that promoted thicker reaction layers and salt–hydroxide crust formation. SEM supported a clear resin-dependent ranking: epoxy-based rebars (Types A and C) exhibited greater surface roughening, matrix stripping, fiber exposure, microcracking, and interfacial debonding with increasing severity. In contrast, vinyl-ester rebars (Type B) retained a more continuous surface with predominantly localized damage and indicated smaller salinity shifts in chloride-seawater exposures, indicating reduced ion exchange/leaching and a more stable barrier. TOC trends were consistent with this behavior: vinyl ester systems (rebar and neat resin) apparently released less TOC than epoxy-based systems, indicating lower polymer degradation. Finally, anions (Cl^-, SO_4^{2-}) did not directly reacted with the epoxy or vinyl-ester backbones like OH^-, but they strongly influenced degradation indirectly by enabling [Fe–Cl] associated rust formation and by forming soluble precipitates with leached metals (e.g., sulfate-bearing deposits such as gypsum and association with Fe/Al hydroxides), which intensified surface crusting and crack development.

Overall, this dissertation provides an exposure-based durability framework for BFRP systems by identifying when sizing offers meaningful protection and when it fails under aggressive coupled chemistry and demonstrating that resin chemistry (vinyl ester vs. epoxy) can dominate long-term durability by controlling transport, microcracking, and interphase stability under alkaline–saline attack. These findings directly support practical material selection for marine and concrete infrastructure and establish quantitative directions for future research (e.g., improving barrier/coating systems, and linking chemical release to interfacial fracture and mechanical retention thresholds) to accelerate reliable field applications.