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Effect of Fiber Dosage On Mechanical Properties Of Geopolymer Mortar Under The Coupling Of Sulfate Erosion And Dry-Wet Alternation

Yan Zhang, Xianyue Hu

School of Urban Construction, Yangtze University, 1 Nanhuan Road, Jingzhou, Hubei, China

Abstract: Coastal buildings are susceptible to long-term sulfate erosion and alternating wet-dry cycles, leading to rapid degradation in mechanical properties and durability. Therefore, there is an urgent need to find a construction material that is superior to ordinary silicate concrete. Geopolymer concrete, an innovative environmentally-friendly material, offers advantages like early strength, fire resistance, and durability. Research reveals that even after sulfate erosion, geopolymer concrete outperforms regular silicate concrete in terms of mechanical properties and durability. However, geopolymer concrete suffers from high brittleness. A remedy is found in the incorporation of fibers, which substantially enhances its mechanical properties and durability. This study investigates the influence of carbon fibers and polypropylene fibers on the mechanical traits of metakaolin-geopolymer mortar, exposed to sulfate action and wet-dry cycles for 60 repetitions. Results indicate that the addition of 0.6% carbon fibers yields the highest compressive strength, while a 1:1 combination of carbon and polypropylene fibers produces peak flexural strength. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) confirm uniform fiber distribution within the mortar, reinforcing material bonds and retarding crack propagation. Consequently, mechanical properties and durability are improved.

Keywords: Metakaolin-fly ash geopolymer mortar, Sulfate erosion, Dry-wet alternation, Fiber incorporation, Mechanical properties.

1. Introduction

China's vast expanse and large population make housing an indispensable aspect of human life. In China's Northwest, North China, and coastal regions, where the soil and water contain abundant sulfates, the impact is twofold: local agriculture is affected, and concrete structures are subjected to long-term erosion by aggressive ions such as SO42- and Cl- present in water. The resulting chemical reactions with hydration products generate expansive substances like calcium alumina and salt crystals, leading to expansion, cracking, and compromised internal structure integrity[1,2]. In areas with fluctuating water levels, concrete buildings experience cyclic dry-wet conditions, causing elevated SO_4^{2-} concentration due to water evaporation, resulting in salt crystal formation and alteration of concrete pore size[3]. These processes substantially impact the mechanical properties and durability of the structures.

Geopolymer, an innovative aluminum silicate material, was first studied and discovered by J. Davidovits. It forms through the reaction of inorganic silica-aluminates and other mineral materials with alkaline-containing agents, producing a three-dimensional reticulated gel[4]. Concrete produced with aggregates not only exhibits high early compressive strength, but also excellent fire resistance and durability. particularly in sulfate-rich environments[5]. This environmentally-friendly material is well-suited for regions under prolonged chemical attack, as its production process reduces CO_2 emissions by approximately 45%[6]. Despite geopolymer concrete's elevated initial strength, brittleness remains a challenge, rendering it susceptible to cracking and accelerated deterioration due to long-term sulfate exposure and wet-dry cycles. Extensive testing has demonstrated that incorporating fibers is an effective approach to mitigating brittleness and crack susceptibility[7]. Commonly used materials for reinforcement include polyvinyl alcohol fibers, steel fibers, polypropylene fibers, and carbon fibers, however, the degree of improvement depends on the amount of fiber added[8].

This study examines the impact of fiber type and dosage on the mechanical properties of metakaolin-fly ash polymer mortar under the combined effects of sulfate erosion and wet-dry cycles. Furthermore, Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) are employed to analyze the influence of fiber addition on mortar performance from a microstructural perspective. The findings offer novel insights for enhancing building materials' resilience in regions enduring long-term sulfate erosion.

2. Experimental Materials and Methods

2.1. Experimental materials

Metakaolin was sourced from Henan Chenyi Wear-resistant Material Industry Company, while class F low-calcium fly ash was obtained from Henan Borun Refractory Material Industry Company. Table 1 presents the chemical compositions of these two materials.

Table 1. Chemical composition of metakaolin and fly ash (%)

makings	Na_2O	MgO	Al_2O_3	SiO_2	SO_2	Fe_2O_3	CaO	KO_2	heat loss
metakaolin	0.03	0.04	13.00	54.00	0.04	0.40	0.09	0.30	2.10
fla ash	0.43	0.87	24.20	45.10	2.10	5.34	5.60	0.84	13.70

The alkali activator employed in the experiment consisted of a blend of Na_2SiO_2 and NaOH. Na_2SiO_3 is SP38 water glass sodium silicate solution produced by Jiashan Yourui Refractories Co, and NaOH, acquired as flake solid from Xinjiang Zhongtai Chemical Co., Ltd., boasting a purity exceeding 96%. The compositions of these two chemicals are detailed in Table 2. Conforming to prior research, the alkali activator's modulus ($M=n(SiO_2)/n(Na_2O)$) was established at 1.3. Fine aggregate was sourced from Xiamen Aisio standard sand. Additionally, carbon fibers (CF), 10 mm in length from Jilin Carbon Industry Co., Ltd., and 6 mm-long polypropylene fibers (PP) from Changsha Limexiang Building Materials Co. were utilized. A sulfate environment was emulated using a Na_2SO_4 solution, prepared by blending anhydrous Na_2SO_4 with tap water.

Table 2. Chemical composition of sodium hydroxide and water glass

chemical composition(%)	Na_2O	H_2O	SiO_2
Na_2SiO_3	60.25	39.75	0
NaOH	27.30	64.16	8.54

2.2. Specimen preparation

For this experiment, 33.3% of class F fly ash was chosen to replace metakaolin, a measure aimed at enhancing compatibility. Following a series of tests, a water-cement ratio of 0.5 was determined. As of now, there is no established specification for the dosage of carbon fiber and polypropylene fiber. To address this, we drew from existing experimental references and established three distinct combinations involving carbon fiber, polypropylene fiber, and an even blend of both, each applied in ratios of 0.3%, 0.6%, and 0.9%. The specific combinations are outlined in Table 3.

Table 3. Metakaolin-Fly Ash geopolymer mortar mixing ratio

samples	metakaolin (kg/cm^3)	fly ash (kg/cm^3)	standard sand (kg/cm^3)	water (kg/cm^3)	Na_2SiO_3 (kg/cm^3)	NaOH (kg/cm^{3})	Fiber (%)	
							carbon fiber	Polypropylene fiber
GM-0	333.4	166.7	1254.4	71.9	277.56	57.4	0	-
PP-0.3	333.4	166.7	1254.4	71.9	277.56	57.4	-	0.30
PP-0.6	333.4	166.7	1254.4	71.9	277.56	57.4	-	0.60
PP-0.9	333.4	166.7	1254.4	71.9	277.56	57.4	-	0.90
CF-0.3	333.4	166.7	1254.4	71.9	277.56	57.4	0.3	-
CF-0.6	333.4	166.7	1254.4	71.9	277.56	57.4	0.6	-
CF-0.9	333.4	166.7	1254.4	71.9	277.56	57.4	0.9	-
P:C-0.3	333.4	166.7	1254.4	71.9	277.56	57.4	0.15	0.15
P:C-0.6	333.4	166.7	1254.4	71.9	277.56	57.4	0.30	0.30
P:C-0.9	333.4	166.7	1254.4	71.9	277.56	57.4	0.45	0.45

Note: GM-0 stands for unadded fiber, CF stands for carbon fiber, PP stands for polypropylene fiber, P:C stands for carbon fiber and Polypropylene fibers were blended in a 1:1 volume ratio.

Specimen Preparation Process: The preparation procedure involved pre-mixing NaOH and Na_2SiO_3 solutions in accordance with the alkaline activator's proportions, a step carried out 24 hours prior. The weighed gelatinous material and alkaline activator were then combined in a mixing vessel, followed by the addition of an appropriate quantity of water. During the mixing phase, the fibrous material was gradually incorporated. After thorough mixing, the resulting slurry was poured into molds measuring 160mm × 40mm × 40mm and subjected to vibration. Post-mixing, the mortar was transferred to a curing chamber. Following a 24-hour duration, the specimens were demolded and continued their curing process until reaching 28 days. The curing environment maintained a temperature of 20±1°C and a relative humidity exceeding 95%.

2.3. Test methods

Sulfate Attack and Erosion Testing: Sulfate attack, a gradual process, was assessed in line with recommendations from U.S. ASTM C1012-18a[9] and ASTM C452-15[10] standards, as well as the "Standard for Long-Term Properties and Durability Test Methods for Ordinary Concrete" (GB/T 50082-2009)[11]. The protocol involved the geopolymer specimens were first immersed in a 5 wt% $Na2_{S}O_4$ solution at 25°C for 15 h, followed by air-drying for 1 h, drying at 75°C for 6 h, and finally air-cooling for 1 h, and refrigeration at 25°C for 1 h. Each cycle lasted 24 h until the target number of cycles was reached.

Erosion testing centered on geopolymer mortar specimens with 0.60% fiber doping. Following specifications, a specimen-to-Na_2SO_4 solution volume ratio of about 0.5 was maintained to stabilize the erosion solution's pH within the 7-

8 range. The solution was renewed every 30 days, with pH levels monitored using a pH meter. The testing apparatus was hermetically sealed throughout the process to prevent erosion solution evaporation during immersion. This assessment focused on the micro-morphology, composition, and mechanical properties of the geopolymer mortar after 60 cycles of wet and dry conditions.

For assessing erosion in geopolymer mortar specimens with fiber dosages of 0%, 0.30%, 0.60%, and 0.90%, pH levels were periodically measured during the immersion period without solution replacement. After 60 days of erosion, the evaluation encompassed microscopic morphology, composition, and mechanical properties.

Flexural and compressive strength tests were conducted referencing the "Test Method for Strength of Cementitious Sand" (JTG E30-2005) (ISO method).

3. Test Results and Analysis

3.1. Mechanical properties

The strengths of the experimentally measured metakaolin-fly ash geopolymer mortar are shown in Table 4.

Table 4. Mechanical properties of geopolymer mortar after 60 cycles of alternating sulfate attack-dry and wet cycles

Specimen number	Compressive strength (MPa)	Flexural strength (MPa)
GM-0-S-60	45.10	9.03
PP-0.3-S-60	42.00	9.85
PP-0.6-S-60	57.10	10.50
PP-0.9-S-60	55.00	9.50
CF-0.3-S-60	64.50	10.19
CF-0.6-S-60	73.40	10.85
CF-0.9-S-60	69.10	10.30
P:C-0.3-S-60	61.50	11.10
P:C-0.6-S-60	65.60	11.60
P:C-0.9-S-60	59.80	10.80

3.1.1. Compressive strength

Compressive Strength Analysis: Figure 1 presents the measured compressive strength. The obtained data clearly illustrates that the incorporation of fibers enhances the compressive strength of the geopolymer mortar, compared to the ordinary kaolin-fly ash geopolymer specimens. However, the diverse fiber additions yield distinct trends in compressive strength for the mortar. Overall, the mortar's compressive strength with carbon fibers surpasses that of specimens with polypropylene fibers or a 1:1 mix of polypropylene and carbon fibers. Notably, for fiber dosages under 0.3%, any type of fiber addition significantly enhances the mortar's compressive strength. Between 0.3% and 0.6% fiber dosage, specimens with 30% polypropylene fibers peak at 62 MPa, a 37.47% increase compared to fiberless mortar. A diminishing trend follows as fiber dosages increase. At 0.6% dosage, the highest compressive strengths are 73.4 MPa and 65.6 MPa for carbon fiber and 1:1 carbon-polypropylene fiber-added mortar, marking a 62.75% and 45.45% rise respectively, while compressive strength increases are less pronounced for polypropylene fiber. The addition of polypropylene fibers alone results in a 0.3% strength reduction compared to 0.3% polypropylene fiber-added mortar. In the 0.6%-0.9% fiber dosage range, all three fiber types diminish mortar compressive strength. At 0.9% polypropylene fiber dosage, compressive strength drops to its lowest but remains higher than fiberless mortar, showing a 21.95% improvement. Mortar with only 0.9% carbon fiber added or a 1:1 carbon-polypropylene fiber mix increases by 53.22% and 32.59%,respectively, compared to fiberless mortar.

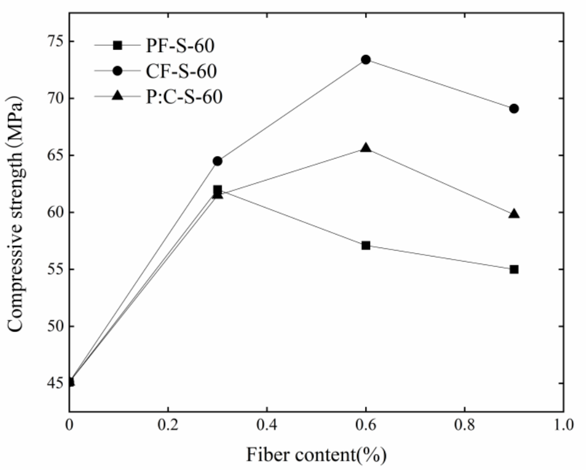


Figure 1. Compressive strength of geopolymer mortar

3.1.2. Flexural strength

Flexural Strength Assessment: Figure 3-2 illustrates notable enhancements in flexural strength for the three mortar compositions, particularly evident when fiber dosage remained under 0.3%. Among these, the specimen with a 1:1 combination of carbon fiber and polypropylene fiber exhibited the most substantial increase, registering at 11.1 MPa. Notably, the flexural strength improved by 22.92% compared to the unfibered counterpart. When fiber dosages reached 0.6%, the flexural strength peaked for all three types of mortar: carbon fiber and polypropylene fiber added 1:1, carbon fiber-only, and polypropylene fiber-only, with respective values of 11.6 MPa, 10.85 MPa, and 10.5 MPa. This represented a 28.46%, 20.16%, and 16.28% increase over fiberless mortar, with the 1:1 carbon-polypropylene fiber addition imparting the most significant enhancement. Upon exceeding 0.6% fiber dosage, all three specimens exhibited a noticeable decrease in flexural strength. The lowest point occurred at 0.9% fiber dosage, where the polypropylene fiber-added mortar experienced a 9.52% decline compared to the 0.6% dosage. Nonetheless, this value still surpassed the flexural strength of unfibered mortar, manifesting a 5.20% increase.

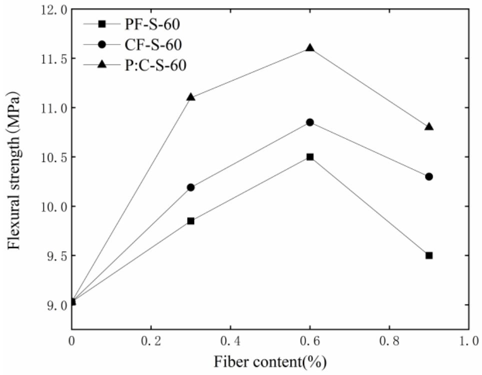


Figure 2. Flexural strength of geopolymer mortar

3.2. Micro-analysis

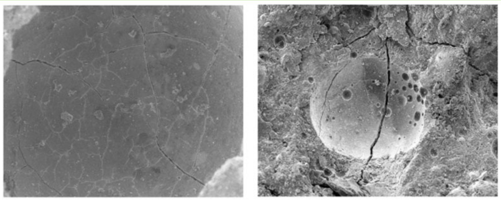
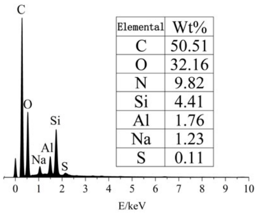
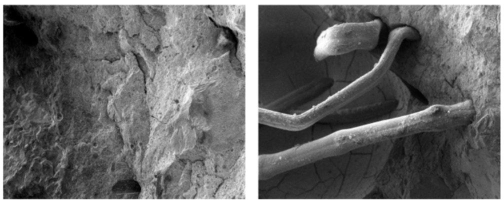
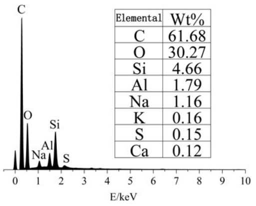
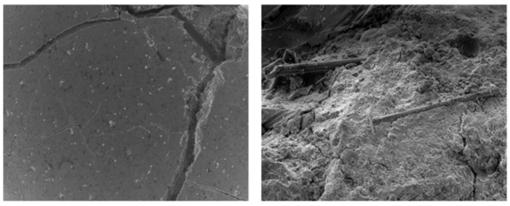
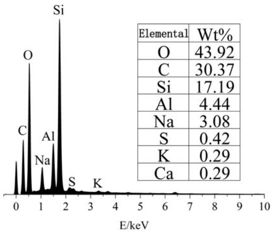
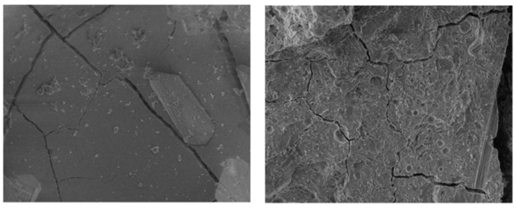
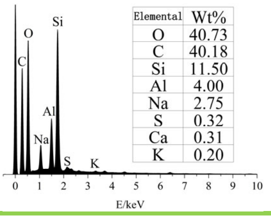
Mechanical Analysis and Microscopic Observation: The preceding examination of geopolymer mortar's mechanical attributes under dual influences of sulfate erosion and dry-wet alternation reveals that, when fiber doping reaches 0.6%, irrespective of fiber type, both compressive and flexural strengths exhibit varying degrees of decline. Hence, microscopic analysis in this study concentrates on scrutinizing the morphological shifts within the mortar subjected to 60 cycles of sulfate erosion-dry and wet conditions with 0.6% fiber doping. As depicted in table 5, the distribution of fibers within the specimen with added polypropylene fibers and carbon fibers is readily discernible. In contrast to unfibered specimens, fiber distribution is both longitudinal and transverse, thereby reinforcing the bond between fibers and cementitious materials. This augmentation confers a reinforcing function, enhancing the geopolymer mortar's mechanical properties.

Inspection of the specimen devoid of fibers unveils minor cracks post-compression, likely attributable to sulfate erosion and wet-dry cycles. These cycles induce free water seepage, elevating capillary pressure. In contrast, specimens with a 1:1 mix of carbon and polypropylene fibers exhibit a capacity to disperse external forces, enabling the mortar to endure higher loads while preserving structural integrity.

Notably, during sulfate erosion and wet-dry cycles, the geopolymer mortar exhibits minimal material crystallization and expansion internally. This suggests that, compared to ordinary silicate mortar, geopolymer mortar better resists sulfate infiltration, safeguarding component performance. Elevated fiber dosages compromise slurry fluidity, engendering non-uniform fiber dispersion, reducing internal mortar structure density, and ultimately compromising mechanical properties.

Meanwhile, the relative Na content in EDS spectroscopy analysis reveals that mortars with solely polypropylene fibers maintain near-identical Na levels to unfibered mortar (1.23%). In contrast, specimens with carbon-polypropylene fibers and carbon-polypropylene fibers in a 1:1 ratio display Na content increments to 3.08% and 2.75% each. This outcome likely stems from the presence of fibers impeding unreacted alkaline exciters' dissolution in sodium sulfate solution, fostering subsequent polymerization reactions and bolstering mortar mechanical attributes.

Table 5. SEM image and EDS spectroscopy of geopolymer mortar

Specimen number	SEM figure	EDS spectroscopy
GM-0-S-60		 Elemental Wt% C 50.51 O 32.16 N 9.82 Si 4.41 Al 1.76 Na 1.23 S 0.11
PP-0.6-S-60		 Elemental Wt% C 61.68 O 30.27 Si 4.66 Al 1.79 Na 1.16 K 0.16 S 0.15 Ca 0.12
CF-0.6-S-60		 Elemental Wt% O 43.92 C 30.37 Si 17.19 Al 4.44 Na 3.08 S 0.42 K 0.29 Ca 0.29
P:C-0.6-S-60		 Elemental Wt% O 40.73 C 40.18 Si 11.50 Al 4.00 Na 2.75 S 0.32 Ca 0.31 K 0.20

4. Conclusion

(1) Enhancement of Mechanical Properties: The controlled incorporation of fibers yields improved mechanical attributes in metakaolin-fly ash geopolymer mortar following 60 cycles of sulfate erosion and alternating wet-dry coupling. Notably, specimens with a 0.6% carbon fiber doping exhibit the most substantial increase in compressive strength. Conversely, specimens with polypropylene fiber doping exceeding 0.3% demonstrate a tendency for decreased compressive strength. Furthermore, the most noticeable elevation in flexural strength is observed in specimens with a 1:1 ratio of carbon fiber and polypropylene fiber doping at 0.6%. However, beyond a fiber dosage of 0.6%, mechanical properties exhibit a decline.

(2) Microscopic Analysis: SEM microscopic morphology and EDS energy spectrum analyses were conducted on 0.60% fiber-doped kaolin-fly ash geopolymer mortar following 60 cycles of sulfate erosion and dry-wet alternation. Comparison with specimens lacking fiber doping revealed that the introduction of fibers and subsequent anchoring effects within the mortar forestalled extensive cracking upon destruction. Moreover, the inhibitory influence on alkaline excitants' dissolution in sodium sulfate solution underpins polymerization reactions, reinforcing the mortar's strength.

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