STRAIN-HARDENING ETTRINGITE-BASED COMPOSITE WITH POLYPROPYLENE FIBER REINFORCED LADLE SLAG: DURABILITY UNDER COMBINED CHLORIDE AND SULFATE ATTACK

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Abstract

Ladle slag, an industrial waste from steel manufacturing processes, is an interesting raw material for sustainable inorganic binders. In earlier work, we have developed an ettringite-based binder (LSG) from the hydration between ladle slag and gypsum. In addition, polypropylene (PP) fiber was employed to attain a strain-hardening cementitious composite from LSG. To investigate the durability of PP fiber reinforced LSG, the composite was exposed to a combined chloride and sulfate environment under freeze-thaw cycling. The compressive and flexural behavior of PP fiber reinforced LSG after up to 180 freeze-thaw cycles was experimentally characterized. The experimental results confirm the durability of LSG under Na_2SO_4-NaCl environment. Furthermore, the PP fibers generally enhance the mechanical properties and durability of the reinforced composite. Since there is a lack of study on the durability of ettringite-based binders from industrial wastes under harsh environments, this experimental study reveals the feasibility of using fiber reinforced ettringite-based composite as an alternative construction material.

Keywords: Ladle slag cement; Durability; Recycling; Mechanical properties; Sulfate attack

1. INTRODUCTION

Ettringite-based binder is a promising alternative cementitious material. The binder can attain considerable mechanical properties [1,2], good chemical resistance [3], and has the potential to immobilize heavy metals [4]. In previous work, ladle slag (LS) and gypsum were combined together to give an ettringite-based binder (LSG) via hydration by water [2]. In addition, a fiber reinforced cementitious composite from this binder (PP-LSG) was produced.

The developed composite exhibited strain-hardening behavior when subjected to bending and uniaxial tensile load with 2% v/v polypropylene (PP) fiber as reinforcement [2]. Therefore, LSG and its composite PP-LSG are of particular interest being the hydration between water and non-hazardous industrial by-products at low pH, while still obtaining high mechanical performance.

The knowledge of the durability of ettringite-based binder is limited, as reported in the literature. In many cases, the durability of the binder is studied assuming one single factor, e.g., carbonation or chemical attacks (e.g., chloride or sulfate) [5–7]. However, the real-life conditions present a combination of different factors. The material can be subjected to the synergetic effect of multiple factors in aggressive environment. Furthermore, studies are not available in the literature considering the durability of ettringite-based composite material under harsh environments that mimic the combination of chemical and environmental stresses. As for engineered cementitious composite (ECC), the effects of freeze-thaw process and Na_2SO_4 solution on the mechanical properties of Portland cement-based ECC are of particular interest [8], as well as the chloride attack [9]. However, the mentioned work did not consider the combined effects of multiple factor (e.g., combined sulfate and chloride attack).

This experimental research is an attempt to investigate the mechanical properties of deflection-hardening ettringite-based composite under freeze-thaw and combined chloride and sulfate environment. The aim of the work is to present understanding on the durability of the developed ettringite-based composite under such aggressive conditions.

2. MATERIALS AND METHODS

2.1. Materials

LS was provided by SSAB Europe Oy (Finland). The as-received slag was removed all the leftover steel flakes and then milled by a ball mill (TPR-D-950-V-FU-EH by Germatec, Germany) to attain a d_{50} of roughly 10 µm. Additionally, fine sand (FS) (d_{50} < 100 µm) was used as fine aggregate as suggested in Ref. [10].

Pure gypsum ($CaSO_4.2H_2O$ supplied by VWR Finland**,** product code 22451.360) was employed in this study. The chemical composition of the LS and gypsum was analyzed by X-ray fluorescence (XRF) (PANalytical Omnian Axiosmax) and detailed in Table 1. The hydration mechanism to form ettringite was reported in Ref. [2].

Table 1: Chemical composition (wt %) of LS and gypsum measured by XRF

Oxide	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Others	Loss on ignition
LS	51.0	8.3	27.9	1.1	6.3	0.8	3.6	1
Gypsum	41.4	1.0	0.1	0.1	0.5	53.8	3.1	-

Citric acid (product code C1949 by Tokyo Chemical Industry Co., Ltd., Japan) was employed as a retarder for the reaction between LS and gypsum. As reported in Ref. [11], citric acid prevents nucleation and the subsequent crystal formation process of ettringite. Based on previous work [2], 1.8 wt.% citric acid solution was prepared to attain an initial setting time of 1.2 hours for LSG mortar. A melamine-based chemical specified for calcium sulfate cements (commercial name: Melment F10 provided by BASF, Germany) was used as superplasticizer.

As fiber dispersing agent, a sodium polymethacrylate agent named Darvan 7-N (supplied by Vanderbilt, USA) was employed. The dose of Melment F10 and Darvan 7-N were 0.5% and 1%, respectively, by weight of total binder mass.

PP fibers were employed as fibrous reinforcement to produce a deflection-hardening ettringite-based composite. The mechanical and physical properties of fibers was reported in Ref. [2,12]. The minimum fiber volume fraction of 2% was chosen to yield pseudo strain hardening (PSH) behavior with adequate workability as reported in Ref. [2,12]. Table 2 shows the recipe of the mixtures for LSG and PP-LSG

Table 2. Mix proportions of the LSG and PP-LSG

Sample ID	Slag	Gypsum	Sand	Citric acid	W/B*	Fiber volume fraction
LSG	0.7	0.3	0.5	1.8 wt.%	0.45	-
PP-LSG						2% v/v

*W/B (water-to-binder ratio) with total binder mass by the sum of the mass of slag and gypsum

2.2. Methods

The preparation of mortar specimens was detailed in [2]. It is worth noting that it usually took 20–25 minutes to complete the mixing process for one batch of mortar.

Artificial aging was conducted in a climatic chamber Weiss WK3-180/40 (Germany). The duration of aging process was approximately 2 months with approximately 180 cycles. The cycles were divided into 90 ‘cold’ and 90 ‘warm’ cycles, and changed every 45 cycles (almost 2 weeks). The adopted artificial cycles were designed based on the weather record in Oulu (Finland) during 2010–2018. The aim was to simulate the extreme weather conditions of Northern area. In the ‘cold’ cycle, the temperature ranged from 5° to -20°C, while in the ‘warm’ cycle, the temperature varied from 10° to 30°C. One single cycle lasted for 8 h. Specimens were fully covered by curing solution, hence the climatic chamber did not control the humidity during the aging scheme.

The LSG and PP-LSG were aged by combined sodium chloride and sulfate solution (SL). The SL was prepared based on Ref. [13]: 5% wt. Na_2SO_4 (product code 1.06649.0500 by Merck KGaA, Germany) and 3% wt. NaCl (product code 7647-14-5 by J. T. Baker, the Netherlands) to represent harsh marine conditions. After 28 days curing in water, specimens of LSG and PP-LSG fully immersed in SL, were submitted to freeze-thaw cycles in the climatic chamber. The mechanical performance of LSG and PP-LSG samples were assessed after 0, 90, and 180 aging cycles by 4-point bending and uniaxial compressive loading, conducted by a Zwick device (load cell of maximum 100 kN). The dimensions of 4-point bending sample were: length 280 mm, width 40 mm, height 30 mm, span 240 mm, and the distance between loading points 80 mm. The flexural tests were displacement controlled (0.4 mm/min) according to ASTM C1609 [14]. The compressive strength was measured by loading halves of the prismatic bending specimens (loading speed 1 mm/min) according to EN 196-1 [15].

3. RESULTS AND DISCUSSIONS

3.1 Flexural strength

PP-LSG attained deflection-hardening behavior regardless the aging periods. Figure 1a illustrates the stress *vs.* crack opening displacement (COD) curves of PP-LSG in different aging periods and in comparison with the reference LSG. LSG showed typical brittle behavior with sudden failure at very small COD. On the other hand, PP-LSG showed deflection-hardening behavior with very high ductility (large COD at the peak load). The COD at peak load of PP-LSG after 180 cycles was roughly 2.7 mm. As discussed in Ref. [12], PP fiber offered a better load transferring capacity than PVA fiber reinforced composites cured in the same conditions.

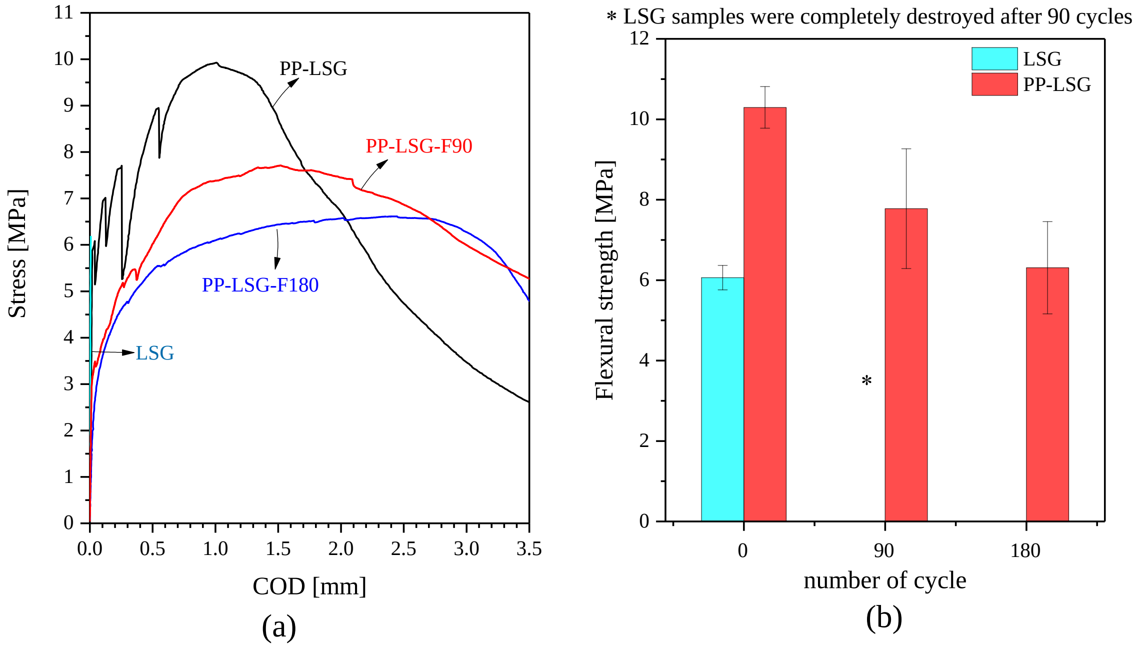


Figure 1: Flexural tests: (a) flexural strength from 4-point bending test and (b) average flexural strength of LSG and PP-LSG after different number of freeze-thaw cycles

PP-LSG had good flexural strength under the combined SO_4^{2-} and Cl^- attack. Figure 1b shows the flexural strength of the developed composite SL after different aging periods in comparison to the plain LSG. After 180 cycles, PP-LSG still retained roughly 6.2 MPa in flexural strength (almost 60% of the unaged material).

Sulfate and chloride ions were the main factors influencing the mechanical properties degradation. A reaction between these ions with cementitious materials generates a chemical volume change [16]. On the other hand, the freeze-thaw cycles contributed to the physical modification due to the expansion of water in structure pores. Therefore, the fibrous reinforcement played a vital role in controlling the cracks development and eventually preventing degradation of the mechanical properties. On the contrary, unreinforced LSG was completely destructed after 90 freeze-thaw cycles.

3.2 Compressive strength

PP-LSG in SL gradually decreased the compressive strength, while the reference LSG was completely spoiled after the aging. Figure 2 shows the compressive strength of LSG and PP-LSG after different aging periods in SL. The composite slightly reduced the compressive strength by roughly 11% after 180 freeze-thaw cycles. PP fibers seemed delayed the crack propagation under the attacks and led a slow diffusion of sulfate and chloride ions [13,16]. As consequence, only a slight decrease in the compressive strength of PP-LSG in SL was recorded. In contrast, the unreinforced LSG suffered the combined physical and chemical attacks getting a negligible strength after only 90 freeze-thaw cycles. This result highlighted the important role of PP fibers in retaining the mechanical properties and leading to a good durability under such harsh conditions.

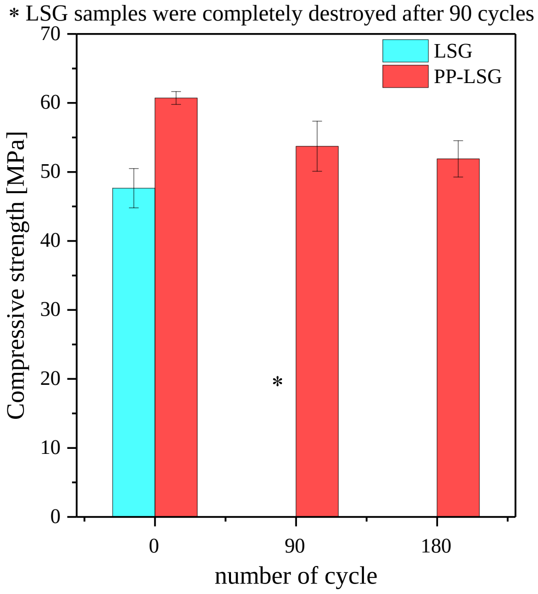
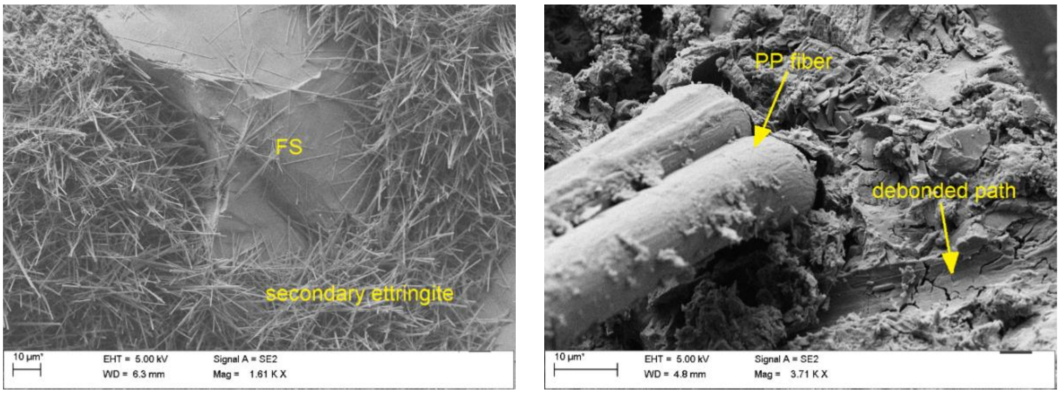


Figure 2: Compressive strength of LSG and PP-LSG after different number of freeze-thaw cycles

3.3 Phase characterization

SEM observations confirm the role played by PP fibers in slowing down the chemical attack in SL. Figure 3 shows SEM images of LSG and PP-LSG aged in SL after 180 freeze-thaw cycles. LSG reacted with SO_4^{2-} and formed visible crystal called secondary ettringite, as shown in Figure 3a. In contrast, the matrix of PP-LSG remained unreacted and structurally stable under the combined chemical attack of SO_4^{2-} and Cl^- (Figure 3b). The PP fibers showed good bonding with LSG matrix after the aging period. In addition, some micro cracks were observed on the fracture surface, which could be attributed to both the freeze-thaw and combined chemical attack. The morphology from SEM images reflects the good mechanical properties of PP-LSG, as detailed in Section 3.1 and 3.2, compared to the plain LSG.



(a) (b)

Figure 3: SEM images of (a) LSG and (b) PP-LSG after 180 freeze-thaw cycles in SL

4. CONCLUSIONS

- PP-LSG exhibited deflection-hardening behavior under flexural load after 180 freeze-thaw cycles in the combined sulfate-chloride solution.
- The mechanical properties of PP-LSG slightly decreased after the aging scheme, while the reference LSG was destructed just after 90 freeze-thaw cycles.
- The main damage mechanism in SL with freeze-thaw aging was the combined of physical attack from water uptake in structural pores and chemical attack led to volume expansion from the reaction between LSG matrix with the environment.

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