Durability of ettringite-based composite reinforced with polypropylene fibers under combined chemical and physical attack

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Contents lists available at ScienceDirect
Cement and Concrete Composites
journal homepage: www.elsevier.com/locate/cemconcomp

ARTICLE INFO
Keywords:
Ettringite
Durability
Freeze-thaw resistance
Sulfate attack
Chemical attack
By-product

ABSTRACT
High-performance fiber reinforced cementitious composites from ettringite-based binders require much understanding of durability before its real-life applications in construction industry. A strain-hardening fiber reinforced ettringite-based composite from the hydration between ladle slag and gypsum with polypropylene (PP) fibers was the object in this study. To investigate the durability of the developed composite under aggressive conditions in cold regions (e.g., the Northern Europe), the material was subjected to a combined sodium sulfate-chloride solution along with freeze-thaw cycling process, which represented the marine environment of cold regions. The experimental study reports the vital role of PP fibers in control crack propagation and, hence, greatly enhanced the durability of the composite. In addition, the developed composite attained good mechanical performance with deflection-hardening behavior and multiple crack even after aging processes. Materials, aged in water, was mainly destructed by volume expansion from water uptake in structural pores, while those, cured in Na₂SO₄–NaCl solution, was mainly spoiled by volume increase from both physical and chemical attacks.

1. Introduction

Inorganic cementitious binders from steel and ironmaking side streams are a promising alternative to partially replace ordinary Portland cement (OPC) [1,2]. Slag-cement concretes are able to attain comparable mechanical properties to conventional OPC concrete [3,4]. As reported in Refs. [5–7], the compressive strength of alkali activated slag-cements could range approximately 60–100 MPa depending on curing conditions and alkali activator sources. In addition, the industrial by-products can form ettringite-based binders due to their Al-rich phases in the chemical composition [8,9]. Recently, the ettringite-based binders are of increased interest due to good mechanical properties [9,10], high chemical resistance [11], and the ability to stabilize heavy metals in its structure [12].

In previous work, a strain-hardening ettringite-based composite reinforced with polypropylene (PP) fibers (PP-LSG) was produced from the hydration of ladle slag (LS) and gypsum. The composite attained strain-hardening behavior under bending and uniaxial tensile tests, respectively, with 2% PP fiber reinforcement [9]. Moreover, PP-LSG showed much lower CO₂ footprint compared to other traditional OPC-based engineered cementitious composite (ECC) or engineered geopolymer composite (EGC) [13,14]. Also, the manufacturing cost was optimized along with mechanical properties and CO₂ emission to obtain the best mixture as in Ref. [14]. Additionally, compared to alkali-activated materials, the developed ettringite-based binder (LSG) minimized the need for virgin chemicals that are needed to activate the LS. Therefore, LSG is easy to handle and cost efficiency due to the low-pH reaction between water and non-hazardous industrial by-products.

The durability of ettringite-based binder from industrial side streams is still an open question. Similarly to the conventional OPC concrete [15], there is a need for more understanding of the durability of alternative cement-based composites in different aspects, namely freeze-thaw resistance, corrosion, carbonation, chemical attacks [1,16–18]. In many cases, the durability of ettringite-based materials is investigated considering one single factor, e.g., corrosion or chemical attacks (e.g., chloride or sulfate) [18–20]. However, the service environmental conditions are often more complicated; the materials can be exposed to multiple factors simultaneously and, hence, lead to detriment by combined effects in aggressive environments. Özbay et al. [21] investigated the dual effects of freeze-thaw cycling and sodium sulfate solution on the properties of OPC-based ECC. Sahmaran and colleagues [22], on the other hand, studied on the mechanical behavior.
of ECC exposed to chloride solution. However, the mentioned work did not consider the combined effects of chloride and sulfate attack, which is more representative of marine conditions. Furthermore, there is no study in the literature reported on the durability of ettringite-based composite material under such harsh environments that mimic the combined load from multiple chemicals and environmental stresses.

The present investigation reports, for the first time, the properties of deflection-hardening ettringite-based composite under freeze-thaw cycling with combined chloride and sulfate attacks. The work aims to present full understanding of the durability of the developed ettringite-based composite subjected to the aggressive environment that represent the marine conditions of regions close to the Arctic Circle. The freeze-thaw cycle was designed based on the climate of Oulu (Finland), which is typical for the Northern Europe. The sodium chloride and sulfate was artificially prepared according to Ref. [23] with 5 wt% Na₂SO₄ and 3 wt% NaCl solution. The composite exposed to the solution for roughly 2 months with up to 180 freeze-thaw cycles. The phase composition and mechanical properties (4-point bending and compressive strength) of ettringite-based composite was evaluated to give better understanding of the combined effects of sulfate-chloride attack along with freeze-thaw cycles. Finally, the mechanisms of destruction were discussed and compared between different environments.

2. Materials and methods

2.1. Materials

The LS was collected at the slag cooling pit of SSAB Europe Oy (Finland) in which the raw slag was exposed to natural weathering. Moreover, the as-received LS was sieved with a 2-mm sieve to remove all the leftover steel flakes before milled by a ball mill (TPR-D-950-V~FU-EH by Germatec, Germany) to reach a d₅₀ value of less than 10 μm as suggested in Ref. [6]. The free CaO of LS was zero. In addition, fine sand (FS) with d₅₀ under 100 μm was employed as fine aggregate; Sahmaran et al. [24] suggested using micro silica sand (particle size roughly 200 μm) for better deflection-hardening behavior and uniform dispersion of fibers.

A commercial gypsum (CaSO₄·2H₂O supplied by VWR Finland, product code 22451.360) was used as a calcium sulfate source in this study. According to the heat evolution of LSG binder, reported in Ref. [30], there is no significant hydration after 1–2 h due to the retardant effects of citric acid. Hence, the effects of mixing time on hydration products are negligible. Mortar samples were cast into molds and vibrated for 3 min at a frequency of 1 Hz. Samples were cured in plastic bags at room temperature for 24 h before demolding. Then samples were cured in a water bath for 28 days before starting artificial aging by freeze-thaw cycling. The samples were tested to measure mechanical properties and phase composition (detailed in Section 2.3) after 0, 90, and 180 cycles. The volume fraction of PP fibers and recipe of the LSG and PP-LSG are shown in Table 3.

2.2. Fiber reinforced mortar preparation

The preparation of mortar specimens proceeded as follows: citric acid solution was prepared with a concentration of 1.8%, and the solution then was kept at room temperature (roughly 23 °C). LS, gypsum, FS, and the superplasticizer were then weighted and mixed in a 5-L Kenwood mixer at low and high speed (70 rpm and 150 rpm, respectively) for 1 min at each level. The citric acid solution was well-mixed with the fiber dispersing agent and then added gradually to the dry mixture. The mortar was mixed at low speed for 3 min before adding the fibers into the mixture. The fibers were added gradually to the mortar to obtain uniform fiber distribution and to prevent fiber clustering during mixing. During the process, the mixing speed was kept at low level and the mortar was checked periodically to ensure a uniform fiber dispersion in the mortar. After adding the fibers, mixing was continued for 10 min at high speed. It took 20–25 min to complete the mixing process as suggested in Ref. [29]. According to the heat evolution of LSG binder, reported in Ref. [30], there is no significant hydration after 1–2 h due to the retardant effects of citric acid. Hence, the effects of mixing time on hydration products are negligible. Mortar samples were cast into molds and vibrated for 3 min at a frequency of 1 Hz. Samples were cured in plastic bags at room temperature for 24 h before demolding. Then samples were cured in a water bath for 28 days before starting artificial aging by freeze-thaw cycling. The samples were tested to measure mechanical properties and phase composition (detailed in Section 2.3) after 0, 90, and 180 cycles. The volume fraction of PP fibers and recipe of the LSG and PP-LSG are shown in Table 3.

2.3. Experimental features and procedures

Artificial aging was conducted by using a Weiss WK3-180/40 climatic chamber (Germany) for 180 freeze-thaw cycles. The duration of aging process was approximately 2 months in which the cycles was divided into 90 ‘cold’ and 90 ‘warm’ cycles. Fig. 1a shows the weather recorded in Oulu, Finland in 8 consecutive years from 2010 to 2018. Consequently, the adopted artificial cycles (see Fig. 1b) intend to simulate the extreme weather conditions characterized by a cold/wet winter and a hot/wet summer. In the ‘cold’ cycle, the temperature ranges from 5 °C to −20 °C, while in the ‘warm’ cycle, the temperature

<table>
<thead>
<tr>
<th>ID</th>
<th>Type</th>
<th>Young’s modulus (GPa)</th>
<th>Elongation at break (%)</th>
<th>Tensile strength (MPa)</th>
<th>Length (mm)</th>
<th>Diameter (μm)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>Multi-fiber</td>
<td>9</td>
<td>22</td>
<td>910</td>
<td>10</td>
<td>12</td>
<td>0.91</td>
</tr>
</tbody>
</table>
is from 10°C to 30°C. One single cycle lasts for 8 h, and the ‘cold’ and ‘warm’ cycles were alternated every 45 cycles (roughly 2 weeks). Temperature was controlled automatically by thermal sensors within the climatic chamber. As for relative humidity, specimens were fully immersed into curing solutions (detailed below), hence the humidity was not controlled and recorded by the climatic chamber.

The unreinforced LSG and PP-LSG was artificially aged in 2 solutions, namely tap water (W) and combined sodium chloride and sulfate.

### Table 3
Mix proportions (by mass) of the LSG reinforced with PP fiber.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Slag</th>
<th>Gypsum</th>
<th>Sand</th>
<th>Citric acid</th>
<th>W/B</th>
<th>PP fiber</th>
<th>Fiber volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSG</td>
<td>0.7</td>
<td>0.3</td>
<td>0.5</td>
<td>1.8%</td>
<td>0.45</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PP-LSG</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>High tenacity PP</td>
<td>2%</td>
</tr>
</tbody>
</table>

* Citric acid mixed with water to produce solution with 1.8 wt% concentration.

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

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**Fig. 1.** (a) Average temperature recorded in Oulu, Finland in 8 years from 2010 to 2018; (b) proposed aging cycles namely cold (left) and warm (right) cycle representing winter and summer time in cold regions; the temperature rate depends on the temperature limits and the duration of the cycle (i.e., 8 h).
solution (SL). The former was used to simulate a non-coastal environment, while the latter represented to aggressive marine conditions. The SL was prepared based on the previous study reported in the literature [23]: 5 wt% Na₂SO₄ (product code 1.06649.0500 by Merck KGaA, Germany) and 3 wt% NaCl (product code 7647-14-5 by J. T. Baker, the Netherlands). After 28 days curing in water bath, specimens of LSG and PP-LSG were immersed separately into W and SL and aged by freeze-thaw cycles in the climatic chamber. The solutions fully cover all faces of samples and were changed after every 90 cycles.

To assess the mechanical performance of the LSG and PP-LSG the following loading conditions were considered: flexural, compressive. After 0, 90, and 180 aging cycles, the 4-point bending for un-notched specimens and compressive tests were conducted by a Zwick test device (load cell of 100 kN). Fig. 2 shows the scheme of the bending setup and the geometry of specimen. It is worth noting that the testing setup and sample size may affect the mechanical response of material. Hence, the 4-point bending test and geometry of sample in this study were based on recommendations in Ref. [31] for strain-hardening cementitious composites. At least three specimens for each material were tested to determine the flexural characteristics of the PP-LSG composition. The 4-point bending test was controlled by displacement with a speed rate of 0.4 mm/min. The flexural strength and flexural modulus of elasticity were calculated according to ASTM and ISO standards [32,33]:

\[
\sigma_f = \frac{FL}{bh^2} \quad (1)
\]

\[
E_f = \frac{0.21L^3}{bh^3} \left( \frac{\Delta F}{\Delta s} \right) \quad (2)
\]

where: \(\sigma_f\) and \(E_f\) is flexural strength and flexural modulus, respectively; \(F\) is maximum load; \(L\) is span; \(b\) and \(h\) are width and high of the specimen, respectively; \(\Delta F\) and \(\Delta s\) are the difference in load and the corresponding deflection at the two levels of flexural stress as suggested in the adopted standards. The compressive strength was measured by loading halves of the prismatic bending specimens and calculated according to EN 196-1 [34]. At least four specimens were tested for each material, setting a displacement speed of 1 mm/min.

Flexural tests for un-notched beams were assisted by 2D digital image correlation (DIC) technique to monitor the cracks pattern evolution. Images were captured and analyzed by LaVision StrainMaster [35]. The area of interest (AOI) of DIC is indicated in Fig. 2. The image acquisition frequency was set at 1 Hz, and the speckle pattern region of the sample was illuminated by a LED light source. The aperture and the shutter speed of camera were set to f/4.0 and 2000 μs, respectively. Post processing of images allows to measure crack opening displacement (COD) from the full-field observation of DIC on the white-painted surface with randomly-distributed black acrylic paint dots. Some of the adopted parameters for correlation were subset size 37 and step size 3.

After the mechanical testing, LSG and PP-LSG in W and SL after aging periods were characterized by XRD and SEM to distinguish the mineralogy of the materials. XRD analysis was performed using Rigaku SmartLab 9 kW. The analysis employed Co Kα radiation (Kα1 = 1.78892 Å; Kα2 = 1.79278 Å; Kα1/Kα2 = 0.5), at a scan rate of 3°/min in the range 5°–90° (2θ), and 0.02°/step. Quantitative XRD was employed to determine the fraction of amorphous and crystalline phases in LSG and PP-LSG using TiO₂ (10–12 wt%) as an internal standard. As for XRD patterns reported in this study, samples were analyzed without the internal standard for better visualization of crystals in the materials. Phase identification was done using “Xpert HighScore Plus” (PANalytical software). SEM observation was done on Zeiss Sigma using a secondary electron detector with a voltage of 5–15 kV to observe the fracture surface of samples, which were coated with a 70 nm Pt layer prior to the observation, after bending tests.

3. Results and discussions

The mechanical properties and phase characterization of the developed composites under freeze-thaw cycles in W and SL are detailed in this section. The comparisons are based on three main aspects: the differences among materials in W and SL, the effect of PP fiber reinforcement, and the mechanical response at different aging periods.

3.1. Mechanical properties

3.1.1. Weight variation

The effects of water/moisture absorption during aging period is one of root causes in deterioration of mechanical properties. Under freeze-thaw cycling, the moisture uptake is considered as a factor of the possible damage imparted due to the volume expansion of freezing water in pores that causes cracks in matrix and debonding at the interface between fibers and matrix [36,37]. Therefore, the weight variation of samples during aging processes can be a preliminary evaluation of the effects of the aging solutions and freeze-thaw cycles after each month of artificial aging. Specimens were dried out in laboratory conditions for roughly 5 days and carefully removed any superficial condensation and residual dust. The weight variation was calculated as in Ref. [37]:

\[
\Delta m = 100 \times \frac{m_t - m_0}{m_0} \quad (3)
\]

where \(m_0\) and \(m_t\) are the mass of specimen at the initial state and at the time \(t\), respectively.

PP-LSG varied its mass just slightly during the aging period, while LSG suffered from water uptake. Fig. 3a shows the average weight change of 3 samples at the initial state and after 90 and 180 aging cycles. The reinforced composite has kept the mass stable; just a slight change of 3 samples at the initial state and after 90 and 180 aging cycles. The reinforced composite has kept the mass stable; just a slight change (i.e., approximately 2% mass loss) after 180 freeze-thaw cycles was observed in both W and SL. In contrast, LSG in W had a mass change of roughly 15% after 180 cycles, although there was not such significant change observed after 90 cycles (i.e., around 1.5%). It is worth mentioning that the scatter bar of LSG in W after 2-month aging was large because the material had a considerable degradation. On the other hand, LSG in SL was decomposed completely after 1 month in climatic chamber under the combination of sulfate and chloride attacks. These results highlight the role of PP fibers in terms of resisting the expansion caused by freeze-thaw process and also the chemical attacks in SL.
The positive effects of the fibrous reinforcement on LSG in both W and SL environments is confirmed by visual inspection (Fig. 4). There was no macrocracks observed on PP-LSG samples in W and SL after 90 and 180 cycles. However, some micro cracks were found on the PP-LSG aged in SL after 2 months (Fig. 4B). The samples showed good appearance (i.e., no significant damage observed by the naked eye) even after aging in as harsh environment as SL. The ability of fibers to manipulate crack propagation is the main contributing factor to this phenomenon as reported in Ref. [23]. In contrast, the unreinforced material exhibited very poor freeze-thaw resistance (i.e., in W) and sulfate-chloride resistance (i.e., in SL). Macro cracks appeared on LSG in W after 90 freeze-thaw cycles, and until 180 cycles, the material was significantly damaged by the volume expansion of absorbed water in pores. Regarding LSG in SL, the matrix reacted significantly with the environment and formed a layered structure (Fig. 4A); more details and information about the reaction and phase composition will be provided in Section 3.2.

3.2. Flexural strength and modulus of elasticity

The flexural strength of PP-LSG in W kept stable, while the strength of the composite reduced gradually under the combined sulfate-chloride attack. Fig. 3b shows the flexural strength of the developed composite in W and SL after different aging periods in comparison to the plain material. After 180 freeze-thaw cycles in W, the composite attained approximately 10.5 MPa in flexural strength; no strength reduction was recorded compared to the samples before aging. In contrast, the plain LSG dropped flexural strength by around 35% after 90 cycles in W. As reported in the literature [38,39], freeze-thaw cycles may cause physical damages via volume expansion and eventually cracks in material structure. In addition, sulfate and chloride ions induce chemical volume changes through a reaction between these ions with cementitious materials [38]. Therefore, micro fibers were proposed as a solution to resist the frost and chemical attacks by preventing crack propagation [39,40]. In this study, PP fiber played a critical role in terms of controlling the crack development and eventually preventing degradation of the mechanical properties under freeze-thaw and chemical attacks. It is worth noting that PP-LSG in SL still obtained very good flexural strength (i.e., roughly 6.5 MPa after 2-month aging) and much better than the unreinforced LSG (i.e., destroyed after 90 freeze-thaw cycles) under such aggressive conditions.

PP fibers also played an important role in the reduction of the flexural modulus of elasticity of the composite under the aging scheme, but seem have no clear effects on the modulus at initial state (Fig. 3c). It can be seen that the PP fibers helped avoid drastic reduction of the flexural modulus of elasticity via the fiber bridging action that transfers the loads caused by both physical and chemical effects. In W, the modulus of PP-LSG slightly decreased by approximately 4% and 8% after 1 and 2 months of aging, respectively. As for PP-LSG in SL, the harsh environment led to a reduction of 53% after the 2-month period. The effects of combined chemical and physical attacks in SL was distinguishable from the physical attack in W; after 180 freeze-thaw cycles, the modulus of PP-LSG in W was roughly 48% higher than that of the composite in SL. However, the flexural modulus of elasticity of the developed composite was much better than that of the plain LSG. PP-LSG in W and SL attained a flexural modulus of about 4.9 and 2.5 GPa, respectively, after 2 months of aging; in contrast, LSG in those environments was completely degraded within the same aging scheme. This result is comparable with other high-performance fiber reinforced cementitious composites reported in Refs. [21,41,42] with approximately 35% reduction in relative elastic modulus after 300 cycles.

Fig. 3. Mechanical properties of LSG (left) vs. PP-LSG (right): (a) Weight variation, (b) flexural strength, (c) flexural modulus of elasticity, and (d) compressive strength in W and SL after different aging periods.
However, it is worth noting that the mentioned studies complied with ASTM C 666 [43], which proposes a different cycling scheme than the one used in this investigation. Consequently, further investigation is recommended to obtain consistent comparison with other data in the literature. Regarding the flexural modulus of elasticity at the unconditioned state, fibrous reinforcement had no clear improvement with roughly 6.2 GPa for both PP-LSG and LSG.

The fiber reinforced composite exhibited deflection-hardening behavior under 4-point bending tests regardless of aging period and conditions. Fig. 5 shows the average stress vs. COD curves of the materials divided into three blocks, namely before freeze-thaw aging (Fig. 5a) and after 90 and 180 cycles (Fig. 5b and c, respectively). LSG showed typical brittle failure under the bending test with very small COD (Fig. 5a and b); under the physical attack in W, the flexural strength of the plain material dropped by around 45% after 90 cycles. On the other hand, PP-LSG in W, in all cases, obtained deflection-hardening behavior with COD at maximum load about 1 mm. Interestingly, the post-peak branch of PP-LSG after 180 cycles in W (see Fig. 5c) seemed to be prolonged with better load carrying capacity, while the peak loads of the composite were almost the same among different aging periods. The reason was attributed to better load transfer from fibers to matrix, leading to the formation of another crack in other flaw positions in the matrix [44]. Due to the attacks under the aging schemes, some micro damages were already occurred in the matrix. Similar behavior was also observed on PP-LSG aged in SL after 180 freeze-thaw cycles; the residual load at 2 mm COD was roughly 90% of the peak load. In Ref. [21], the authors reported a significant reduction in load level in the post-peak branch of OPC-based PVA-ECC under 4-point bending tests after 300 rapid freeze-thaw cycles (according to ASTM C 666 [43]). It seems that PP fiber reinforced cementitious composite cured in water offered a better load transferring capacity than ones reinforced with PVA fibers cured in the same conditions as discovered in Ref. [45].

The developed composite showed high ductility under bending load after the aging schemes. Multiple cracks were observed on the peak load of the reinforced composite by DIC (Fig. 6) under 4-point flexural tests. Regardless of the aging times and environments, PP-LSG generated multiple cracks in the AOI of DIC observation, which is in-line with the deflection-hardening shown in Fig. 5. Furthermore, more cracks appeared on PP-LSG cured in SL after 180 cycles due to the weaker matrix fracture toughness, which improved the load transferring capacity from fibers to the matrix [44]. In contrast, LSG exhibited brittle

<table>
<thead>
<tr>
<th>Environment</th>
<th>W</th>
<th>SL</th>
<th>W</th>
<th>SL</th>
</tr>
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<tr>
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<tr>
<td>After 90 freeze-thaw cycles</td>
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<tr>
<td>After 180 freeze-thaw cycles</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Fig. 4. Sample appearance of LSG and PP-LSG after 0, 90, and 180 cycles aging in W or SL; zoomed-in surface of (A) LSG and (B) PP-LSG aged in SL after 180 cycles captured by optical microscope.
failure represented by a single sharp crack at the peak load.

3.2.1. Compressive strength

PP-LSG in W retained good compressive strength, while there was a slight reduction for samples cured in SL. Fig. 3d shows the compressive strength of materials in different aging periods and environments. The composite kept its compressive strength stable at roughly 60 MPa after 2 months in W. On the other hand, PP-LSG in SL decreased the compressive strength by around 11% after 180 freeze-thaw cycles. It is worth noting that the compressive strength of the reinforced sample after the aging period meet the requirements of many design codes, including Euro code 2 [46]. In the literature, Liu et al. [23] naturally aged OPC-based ECC samples in Na₂SO₄ + NaCl solution, and observed an increase in compressive strength after 120 days of aging due to the pozzolanic reactions between cementitious materials and the environment. In the present study, the freeze-thaw cycles might accelerate the chemical attacks, and thus the initial reaction between residual cementitious materials in LSG and ions in SL was not observed. On the other hand, PP fibers delayed the crack propagation starting on the surface of sample, which kept the diffusion rate of sulfate and chloride ions at a low level [23,38], and hence led to only gradual reduction in the compressive strength of PP-LSG in SL.

![Fig. 5. Flexural tests: average stress vs. COD curves of materials at (a) initial state, after (b) 90 and (c) 180 freeze-thaw cycles in W or SL.](image-url)
The plain LSG suffered from the physical and chemical attacks and degraded after 180 cycles. The compressive strength of LSG in W decreased by approximately 18% after 90 cycles and completely spoiled after 180 cycles. Under the harsh marine conditions of SL, the plain material degraded after 1 month of aging with major changes in its structure as observed in Fig. 4. These results confirmed the vital role of PP fiber reinforcement in terms of improving the durability of ettringite-based binder under such very aggressive conditions.

### 3.3. Phase characterization

XRD results distinguished the attacks and mechanism of degradation in W and SL (Fig. 7). Differences in XRD patterns of LSG and PP-LSG samples after 2 months of aging in W compared to the non-aged reference LSG are indistinct (Fig. 7a). Ettringite is the main crystalline hydrated product and the strength-giving phase as reported in the LSG samples after 2 months of aging in W compared to the non-aged reference LSG and mayenite (C\textsubscript{12}A\textsubscript{7}) left over from the hydration process affecting on the durability of cementitious composite. Hence, it can be seen that physical attack (i.e., volume expansion due to water uptake) is the main factor that affected LSG after 180 freeze-thaw cycles in W. In contrast, chemical attack was the main factor degrading the materials in SL. Sulfate could produce secondary ettringite (C\textsubscript{3}A·3C\textsubscript{3}S·H\textsubscript{2}O) via reaction with Al-rich phases (e.g., C\textsubscript{12}A\textsubscript{7}) and C–S–H phase in the cementitious matrix [38,47]. The formation of this ettringite caused volume expansion; also, the secondary ettringite has reportedly poor crystallinity and stability [38]. After 180 cycles in SL, C\textsubscript{12}A\textsubscript{7} in LSG was undetectable by XRD (Fig. 7b) most likely due to probably the aforementioned reaction with sulfate. However, these crystals were seen on PP-LSG cured in the same aging scheme (see dash lines in Fig. 7b for comparison). This is because PP fibers had good crack control that delays the diffusion of sulfate ions into the matrix via cracks on the surface of specimen.

The XRD reflexes showed noticeable differences in LSG aged in W and SL after 180 cycles compared to its initial state (Fig. 7). The quantitative XRD phase analysis results (Fig. 7c left) are consistent with the following interpretation. When aged in the SL solution, the fraction of ettringite increased by roughly 50%. Secondary ettringite formation was likely enabled by sufficient SO\textsubscript{4}\textsuperscript{2-} ions provided by the SL environment. In the same time, there was a reduction in amorphous phase (i.e., C–S–H, poorly-ordered monosulfate, and aluminum hydroxide) by about 13%, and no C\textsubscript{12}A\textsubscript{7} was detected in LSG after 180 cycles in SL. In contrast, the phase composition of unaged and W-aged LSG was fairly identical, consistent with negligible chemical reaction in LSG aged in water. Interestingly, γ-C\textsubscript{2}S seemed to have very low reactivity in neither W nor SL environment. As reported previous work [30], LS contained γ-C\textsubscript{2}S approximately 22%; the phase formed C–S–H [48] as a part of amorphous phase in LSG and remained about 6% after 28 days of hydration and aging periods in W and SL. The long-term reactivity of γ-C\textsubscript{2}S under chemical loads is suggested as a future investigation.

The phase quantification of PP-LSG (Fig. 7c right) showed negligible changes in phase composition of fiber reinforced LSG in W and SL compared to the initial state. Ettringite was approximately 20 wt%, while the leftover γ-C\textsubscript{2}S and C\textsubscript{12}A\textsubscript{7} was in range 4–6 wt% and 1.5–2.5 wt%, respectively, in PP-LSG before and after aging. In SL, PP fibers delayed the diffusion of SO\textsubscript{4}\textsuperscript{2-} and Cl\textsuperscript{-} into the matrix via crack control and prevented the chemical reactions of C\textsubscript{12}A\textsubscript{7} and monosulfate with these ions. In contrast, since PP-LSG in W was mainly under physical attack, the phase composition of the developed composite remained unchanged and was identical to the unreinforced LSG (see Fig. 7c). Without significant changes in phase composition under combined chemical and physical attack, PP-LSG in both SL and W was able to retain high residual mechanical performance as discussed in Section 3.1.

The role of chloride in the SL solution along with freeze-thaw aging needs further investigation. As reported in Refs. [23,49,50], the presence of chloride could slow down the sulfate attack because the sulfate diffusion rate is lower in SL than that of only Na\textsubscript{2}SO\textsubscript{4} solution. Moreover, the diffusion rate of chloride is much higher than that of sulfate; thus, Friedel’s salt (i.e., Ca\textsubscript{3}A\textsubscript{2}CaCl\textsubscript{2}·10H\textsubscript{2}O) might be formed from the reaction between Al-rich phases and chloride at the first stage [49]. However, the salt was not detected by XRD in this study (see Fig. 7b). This may be due to the freeze-thaw cycles that accelerate chemical diffusion and processes via the physical attack to form secondary ettringite as the final product. Another possibility can be attributed to the effects of PP fibers, resulted in a reduction of chloride diffusivity as reported in Ref. [51]. In addition, Kong et al. [52] reported the difference between natural and artificial aging process affecting on the durability of cementitious composite. Hence, further study on the effects of aging schemes and solutions on ettringite-based binders is recommended.

SEM observation confirms the role of PP fibers in slowing down the chemical attack in SL. Fig. 8 shows SEM images on fracture surface of cementitious composite.
samples after 180 freeze-thaw cycles in W and SL in comparison to the initial state of material. Both LSG and PP-LSG at initial state and after 2-month aging in W (Fig. 8a and b, respectively) exhibited stable ettringite phase and good bonding between PP fibers and the matrix. On the other hand, LSG in SL reacted with the environment and formed secondary ettringite as shown in Fig. 8c (left) as clearly visible crystals. In contrast, the matrix of PP-LSG remained unreacted and structurally sound under the combined chemical attacks (Fig. 8c, right). However, via the debonded path of PP fibers in the matrix, a number of micro cracks were observed; this was attributed to the physical and chemical attacks which eventually forced micro cracks in the material structure. Furthermore, it is worth noting that PP fibers had excellent chemical resistant [53] due to its semi-crystalline and no-polar-group structure [54]. Therefore, there was likely no degradation in the mechanical properties of PP fibers in the aggressive environment as observed in SEM images.

Overall, the damage mechanism of the studied ettringite-based materials in W and SL is consistent with reactions that are schematically presented in Fig. 9. The physical attack was the main factor spoiling the materials in W. Volume expansion occurred through freeze-thaw cycles, due to absorbed water in structural pores (Fig. 9a). Hence, this process impart internal stress \( \sigma_i \), which then led to crack formation in the matrix. On the other hand, in SL, the destructive mechanism was a combination of physical and chemical attacks. First, \( \text{Cl}^- \) and \( \text{SO}_4^{2-} \) diffused into structural pores along with water. Similarly to ones in W, the freeze-thaw process led to volume expansion from water uptake.
Additionally, sulfate ions might have some initial reactions with the matrix to form secondary ettringite, causing volume expansion from these chemical reactions (Fig. 9a). Therefore, this destructive process produced internal stress $\sigma_m$ via the volume change from both chemical and physical attacks. In addition, the role of chloride was unclear since the freeze-thaw cycling probably accelerated the diffusivity of the ion and, hence, rapidly formed Friedel's salt before reaction with sulfate ions. In both environments, PP fibers offered bridging action, which delayed crack propagation by crack deviation and bridging (Fig. 9b). Consequently, the fibers dramatically slowed down the combined destructive processes via volume expansion and also prevented further chemical reactions between SO$_4^{2-}$ and LSG matrix in SL.

4. Conclusions

This experimental investigation studied the durability of strain-hardening PP fiber reinforced ettringite-based composite under aggressive conditions, considering a combined sodium sulfate-chloride solution along with freeze-thaw cycling process, which represented the marine environment of cold regions (e.g., the Northern Europe). The PP fibers played a critical role in enhancing the durability of the developed composite under the very aggressive marine conditions of Northern Europe. The crack bridging action of the fibers delayed the diffusion of sulfate and chloride ions into the matrix, and eventually prevented the volume expansion from physical (i.e., freeze-thaw process) and chemical (i.e., artificial coastal environment with Na$_2$SO$_4$ and NaCl) attacks. On the contrary, the unreinforced material exhibited very poor durability under such harsh conditions and completely destructed under the aging schemes in W and SL.

PP-LSG exhibited deflection-hardening behavior along with multiple cracks under 4-point bending tests regardless aging periods and environments. The composite showed excellent resistance to the physical attack from freeze-thaw cycles. The mechanical performance remained stable with no clear changes in micro structure observed via SEM and XRD in comparison to the initial state of the material. As for PP-LSG in SL, the mechanical properties slightly reduced after the 2-month aging scheme under combined physical and chemical attacks. The developed composite kept the diffusivity of sulfate and chloride ions at low rate, and eventually prevented the chemical reaction between those ions with the matrix. In contrast, the plain material was spoiled after 90 freeze-thaw cycles in SL due to the volume expansion from water uptake and secondary ettringite.

This study contributes to the literature some understanding of the durability of ettringite-based binder and its fiber reinforced composite under the combined load from multiple chemicals and environmental factors. In addition, the destructive mechanisms in different environments and the role of fibrous reinforcement was distinguished. However, some further investigations are suggested for better understanding for this ettringite-based matrix and composite. First, the role of chloride ion and its activities in the destruction of LSG under freeze-thaw cycling needs clarifying. In addition, the interaction between SO$_4^{2-}$ and Cl$^-$, combined with the accelerated aging process from freeze-thaw cycles, is suggested. Second, the long-term mechanical performance and the prediction of service life of the developed composite is of interest since there was no data in the literature reported on fiber reinforced by-product-based ettringite composites.

![Images showing initial and final states of LSG and PP-LSG after different aging conditions](image-url)

**Fig. 8.** SEM images of plain (left) and reinforced LSG (right) after (a) 0 cycle, (b) 180 cycles in W, and (c) 180 cycles in SL; images taken at the fracture surface of samples after bending tests, except for LSG in (b) and (c) where the samples had destructed after aging.
Declarations of interest

None.

Acknowledgement

This work was done under MINSI-project (project number: A70189) funded by ERDF and FLOW-project (project number: 8904/31/2017) funded by Business Finland in the ERA-MIN 2 Research and Innovation programme (H2020 grant agreement No. 730238). The authors appreciate support from SSAB Europe Oy (Finland), Brasilit Saint-Gobain (Brazil), BASF (Germany), and Vanderbilt (USA) for providing the ladle slag, PP fiber, superplasticizer, and dispersing agent, respectively. Hoang Nguyen gratefully acknowledges the financial support from Tauno Tönning Foundation. The authors appreciate Alexandra Kaas for the help during data collection.

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