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Chloride ingress into low carbon concrete in non-saturated condition: state of the art for on-site studies in the case of atmospheric tidal or splash area.

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Synopsis: The carbon footprint of cement production has led to increased interest in developing concrete with lower carbon emissions by incorporating supplementary cementitious materials (SCMs). However, the understanding of how chloride ingress behaves over the long term and under real-site conditions when SCMs are used remains incomplete. Many studies have been conducted in laboratory settings to explore the effects of SCMs, but their application in actual construction sites has been more recent. As a result, there is limited long-term data on the performance of these cementitious additions in real-world environments. Furthermore, to the best of our knowledge, there is no comprehensive database that catalogues the chloride profiles of concrete compositions that incorporate SCMs.

Assessing maritime durability requires a comprehensive understanding of the evolution of the chloride diffusion coefficient and concrete aging. It is essential to thoroughly investigate these factors, as they play a critical role in durability and provide input data for numerical models. This paper aims to study the effect of fly ash and silica fume on chloride propagation in concrete, addressing challenges in predicting chloride profiles and assessing durability by analyzing chloride profiles. A database containing over 210 chloride profiles of Ordinary portland cement, fly ash and silica fume concretes has been compiled. It includes 68 compositions from structures and samples exposed to real-life long exposures site conditions and 28 compositions of laboratory-fabricated samples exposed on-site.

The profiles were digitized and redrawn for analysis to comprehend the influence of SCM type, percentage of substitution, exposure conditions, and time (ranging from 0 to 60 years) on chloride propagation and surface concentration. Through this analysis, we aim to determine the contribution of each parameter and identify those with the highest impact on durability. The addition of SCMs significantly reduces chloride propagation, resulting in denser and less permeable microstructures. The distinctive bell-shaped chloride profile, characterized by an initial increase and subsequent decrease in chloride concentration, is not exclusive to tidal exposure or ordinary portland cement concrete.

Key words: Chloride profiles, cement, durability, supplementary cementitious materials SCM.

Gayelle Fahed, PhD candidate at Nantes Université, France, associated with the Research Institute in Civil and Mechanical Engineering (GeM), actively contributes with the RILEM Technical Committee TC EBD 298. The focus of the doctoral research is on the durability of low-carbon concrete in marine environments, with a particular emphasis on studying how hydrates interact with pore solutions and the subsequent impact on transport properties as seawater permeates low-carbon cementitious materials. The research involves a combination of experimental and numerical modeling efforts, involving the characterization of various low-carbon mortar compositions in terms of their mechanical and durability properties, as well as the use of numerical models to simulate chloride diffusion. The goal of the methodology is to validate and enhance the reactive transport model based on experimental results, with an aim to apply these findings over longer periods than what is typically possible with standard experimental methods.

Stephanie Bonnet, Professor in the Department of Civil Engineering at Nantes Université, France, and affiliated with the Research Institute in Civil and Mechanical Engineering (GeM), actively contributes to the RILEM Technical Committee TC EBD 298. Her research focuses on the durability of concrete within marine environments, the coupled transfers within cementitious materials, and the assessment of structural integrity using both destructive and non-destructive evaluations. Additionally, her work encompasses the eco-design of structures in harsh environments, employing durability models and Life Cycle Assessment (LCA) to enhance sustainability.

Anthony Soive, Senior researcher at CEREMA in Aix en Provence, France, is actively involved with the RILEM Technical Committee TC EBD 298. His research is centered on developing numerical chemo-mechanical tools to analyze the durability and mechanical integrity of concrete and soil treated structures exposed to different aggressive environment (chloride, sulfates, CO₂), prioritizing adherence to environmental standards. Soive employs an interdisciplinary strategy, utilizing simulation techniques to address complex engineering challenges, thereby enhancing the sustainability and resilience of infrastructure against environmental and mechanical stresses. Additionally, his leadership extends to supervising doctoral theses, further contributing to the advancement of civil engineering and environmental preservation research.

Introduction:

Infrastructure exposed to marine environments faces harsh conditions that accelerate its deterioration, resulting in substantial repair and maintenance expenses. The primary cause of concrete degradation in such environments is the ingress of chloride ions, attributed to exposure to sea spray and seawater. This ingress poses a significant threat to the durability and structural integrity of the concrete.

One promising approach to mitigate this issue involves incorporating mineral admixtures, such as fly ash, or silica fume, referred to as supplementary cementitious materials (SCMs). SCMs are commonly used in concrete, either blended with cements or added separately to the concrete mixture proportions. These materials, derived from industrial waste or by-products without additional clinkering processes, not only reduce the carbon footprint of concrete but also enhance its resilience against external aggressors, including chloride ingress. However, uncertainties remain regarding the long-term durability of low-carbon concrete in maritime conditions. Research [1], [2], [3] underscores that many analyses are conducted in accelerated and controlled laboratory settings, yielding results that may not accurately reflect the true aggressiveness of marine environments. Moreover, service life models often produce unsatisfactory outcomes due to variations in the chloride ingress process under real conditions compared to accelerated laboratory conditions. This discrepancy underscores the need for a thorough investigation into the development of chloride profiles, their corresponding diffusion coefficients, and the aging of concrete. Understanding these factors is vital for assessing the long-term performance of concrete and for providing necessary data for numerical models in this field of research. While several review articles have discussed chloride profiles in concrete, [4] in a recent publication, examined the role of chloride profiles in determining the service life of reinforced concrete structures, extending the discussion to the influence of various factors like exposure conditions water to binder ration and supplementary cementitious materials (SCMs) on these profiles, highlighting the importance of detailed research to inform engineering and mechanistic models for concrete durability. [3] in their study, assessed the chloride penetration in various exposure zones of an offshore concrete platform over five years, revealing orientation-dependent degradation and the influence of microclimatic factors such as wind, temperature, relative humidity, wetting-drying cycles, and solar radiation on chloride profiles. The research concluded that chloride ingress is affected by environmental factors, with wind-exposed sidewalls showing greater values of chloride superficial concentrations. However, it also noted that current service life prediction models may not fully account for these variations, underscoring the need for more comprehensive standards in assessing the longevity of marine-

exposed structures. [5] analyzed chloride ingress in different concrete formulations after a two-year marine exposure, rating their chloride resistance. Blast furnace slag concrete showed superior performance, with fly ash and silica fume mixtures also demonstrating effectiveness, whereas ordinary portland cement was less resistant. Their research emphasizes careful consideration when using early-age chloride migration coefficients for service life predictions, particularly in concretes with blended binders, highlighting the critical need for long-term exposure data to enhance the accuracy and dependability of service life estimations for concrete infrastructures. [6] research underscores the importance of long-term data in understanding chloride ingress and corrosion in concrete exposed to marine environments for over 20 years. It highlights the variability of chloride ingress across different zones and the effectiveness of multi-pozzolanic additions in reducing chloride penetration. The study calls for further investigation into the prediction models for service life, emphasizing the need for reliable long-term exposure data to ensure accurate assessments. Based on extensive mining of data from the literature, [7] trained, and tested, machine learning models for accurately predicting surface chloride concentrations, emphasizing the value and necessity of incorporating real-world exposure data.

To address the significant gap in structured databases for chloride profiles in concrete with SCMs, this project is designed to provide a comprehensive resource to support future research. It aims to refine our comprehension of chloride profiles in concrete with SCM by analyzing chloride ion profiles and concentrations in concrete samples from coastal settings, including those made from ordinary Portland cement and those enhanced with silica fume and fly ash. The project also involves determining the diffusion coefficients of chloride ions across various concrete mixes, thereby contributing to a better understanding of concrete's response to chloride exposure. The effort aligns with the broader objective of enhancing the predictability and reliability of service life models for marine-exposed concrete structures, underscoring the importance of long-term exposure data.

Structures exposure conditions and chloride penetration

Marine environments encompass three distinct exposure zones, each presenting unique challenges to concrete structures as shown by Fig. 1. The atmospheric zone is continually exposed to sea spray and high humidity levels, while the tidal zone experiences the cyclical submergence and desiccation caused by the ebb and flow of tides. In contrast, the submerged zone remains in constant and direct contact with seawater. The infiltration of chloride ions into concrete within these environments can lead to two distinct manifestations: they may exist as free chloride ions within the interstitial solution, or they can become fixed chloride ions, either through chemical bound within chloride-containing AFm's such as Friedel's or Kuzel's salt or physical interactions to compounds like calcium silicate hydrate (C-S-H) with the cementitious matrix.

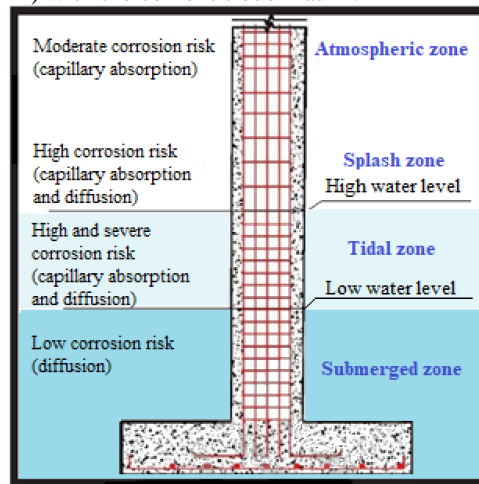


Fig. 1: Diagram of the different exposure areas and classes.

The ingress of chloride ions into concrete is therefore defined by a complex interaction between physical and chemical processes and involves multiple mechanisms including diffusion, adsorption, permeation and surface deposit of airborne salts, but it has been widely accepted that diffusion is the primary mechanism [1].

Chloride transport, driven by gradients in chloride concentration in the concrete is modelled as a one-dimensional diffusion process. Thus, the diffusion theory based on one-dimensional Fick's second law can be used to predict chloride transport in saturated condition with only diffusion phenomena, as is shown in Eq 1:

$$\frac{\partial C}{\partial t} = D_c \frac{\partial^2 C}{\partial x^2} \quad 1$$

For design and reevaluation purposes, engineers and researchers commonly employ the error function solution of Fick's second law of diffusion, as referenced in [8], [9], [10] and presented in Eq 2 and illustrated in Fig. 2 as a

prevalent method for predicting chloride ingress. This method involves the estimation of both the surface content, C_s , and the diffusion coefficient, D_c , by fitting experimental chloride profiles obtained starting from the C_{peak} , where C_{peak} is the maximum chloride concentration obtained for the profile. It's essential to acknowledge that this approach relies on assumptions of concrete homogeneity and does not take into consideration the convection effect. These assumptions, however, are subject to scrutiny, not only due to initial material variations but also because of the multitude of reactions occurring over time on the concrete surface exposed to seawater. Various strategies have been proposed to address this challenge. The international federation of concrete fib [8] introduces the concept of a transfer function Δx , which should be incorporated when calculating the ingress depth for splash and tidal exposures to account for rapid chloride ingress (via convection) to a specific depth. However, it's important to note that this adjustment does not apply to submerged exposure scenarios.

$$C(x, t) = C_0 + (C_{s,\Delta x} - C_i) \operatorname{erfc} \left(\frac{x - \Delta x}{\sqrt{4 * t * D_{app}(t)}} \right) \quad 2$$

where C_0 [weight-%/binder] is the initial chloride content in the concrete, $C_{s,\Delta x}$ [weight-%/binder] is the chloride content at the convection depth Δx [mm], D_{app} [m²/s] is the apparent diffusion coefficient

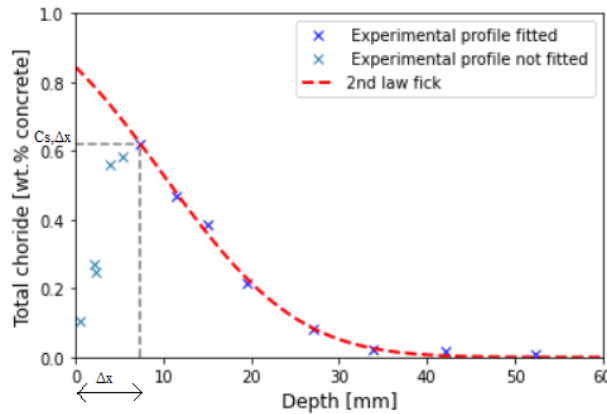


Fig. 2: Schematization of the chloride fitting curve of a chloride profile and the depth from which the process is considered diffusive.

Database about data on site

Chloride profile analysis is crucial in predicting the structural service life and planning inspection, maintenance, and repair schedule [11], [12]. To enable a comprehensive examination of chloride profiles, as well as variations in chloride surface concentrations over time and the associated phenomena, we established a database comprising 330 chloride profiles. This database combines data from both in-situ and laboratory conditions of marine exposure, covering a wide variety of concrete compositions and exposure durations of up to 60 years. The concretes included in the database originate from various parts of the world and feature a range of water-to-binder ratios from 0.23 to 0.84. Additionally, the concrete mixtures proportions incorporate different SCM's, including slag, silica fume, fly ash, and metakaolin, and are subjected to various exposure conditions such as tidal, atmospheric, and submerged environments. The database includes 75 concrete configurations from real-site exposure tests, comprising 68 samples collected during structural inspections and 28 laboratory-manufactured specimens exposed at real sites, as well as an additional 27 concrete configurations subjected to laboratory conditions for up to 20 years. These chloride profiles were sourced from diverse geographical locations, such as France, Portugal, Norway, Sweden, Scotland, Brazil, the Netherlands, Denmark, the Persian Gulf region, and Thailand.

For analysis purposes, all profile data were digitized using the "Engauge Digitize" image processing software [13]. Subsequently, we calculated the apparent chloride diffusion coefficient and surface concentration, excluding data points near the surface where a reduction in chloride content was observed, in accordance with the recommendations of fib 2006 [8]. For this article we will focus on various real-site exposures durations and conditions for the ordinary portland cement and the fly ash binder under saturated conditions. In all subsequent graphs, the legend's first part indicates the concrete composition: C for ordinary portland cement concrete, SF for silica fume, and FA for fly ash, followed by the exposure condition, the water-to-binder ratio, and the exposure period (see Fig. 3).

The document initially explores the database, delving into the various exposure zones, the use of Supplementary Cementitious Materials (SCMs), and the levels and distribution patterns of chloride concentration, particularly the bell-shaped profile, affect concrete. It specifically addresses selected references and the depicted curve references are detailed in Appendix 1.

Regarding the bell-shaped chloride profile observed in Figure 4(b), shows an increase in chloride concentration at shallower depths with a subsequent decrease at greater depths. While this profile is commonly associated with convection processes predominant in tidal exposure zones, its occurrence in all exposure zones suggests a more complex chloride ingress behavior. The presence of this pattern across different zones indicates the difficulty in distinguishing the zones based on chloride ingress characteristics alone. This observation necessitates a careful consideration of various environmental factors that influence chloride movement. The emergence of the bell-shaped profile under various conditions calls for a detailed approach in modeling chloride penetration, aiding in the accurate assessment of the durability of concrete structures in chloride environments.

Fig. 5 displays normal portland cement chloride profiles for short and long-time exposure (a) in Scotland and (b) in France. Both profiles demonstrate similar chloride distribution across different exposure conditions, with the highest concentrations found in tidal zones and very low concentrations throughout the penetration depth in atmospheric conditions. The profiles exhibit a higher chloride concentration near the surface in tidal zones that diminishes with depth, a trend that remains consistent irrespective of the exposure duration. This similarity could be due to several factors, such as the possibility that the initial rapid diffusion of chlorides could shift to a slower phase, suggesting that an equilibrium state in chloride penetration could be established relatively early in the concrete's lifespan. The data indicate that the rate of chloride entry can reach an equilibrium, leading to stable concentration gradients over time, which is an important consideration in predicting the service life of concrete structures in marine environments. The assumption that chloride concentration profiles reach an equilibrium or saturation state in concrete exposed to marine environments is supported by the results of various studies [7], [17]. However, the environmental dynamics of tidal zones could also play a role in the formation of these observed profiles, which is more or less the case with these profiles. As for the bridge exposed in France, it is located in a maritime environment but not in direct contact with the ocean, mostly in the estuary zone, so its tidal exposure condition is not true tidal compared to another structure in direct marine contact, which may explain the very low concentration at 60 years and the almost null concentration in atmospheric zone, given that the structure is located 10 km away from the seashore limit and in direct contact with the Jaudy coastal river which flows into the English Channel.

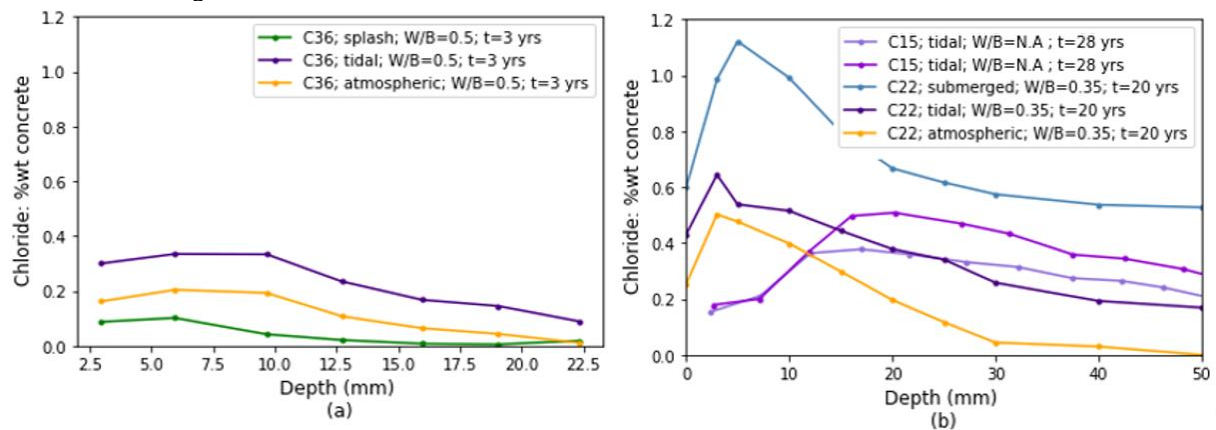


Figure 4: Chloride profiles for **ordinary portland cement** (a) 3 years of exposure of the naval complex of Stenave in Portugal (b) C22; 20 years of exposure of Träslövsläge field site in Sweden and 28 years for C15 in Saint Nazaire, France

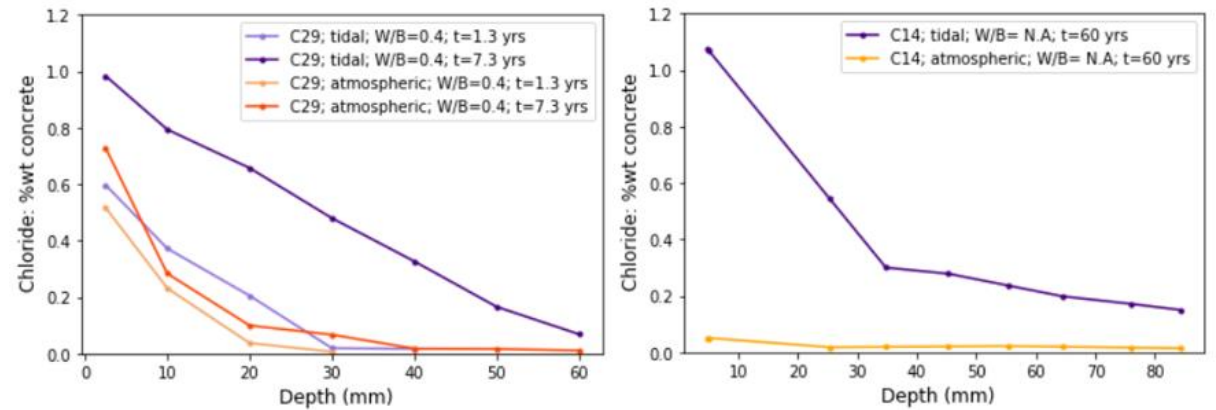


Fig. 5: Chloride profiles for **ordinary portland cement** exposed for (a) 1.3 and 7.3 years in Dornoch firth marine site in Scotland, (b) 60 years in a maritime bridge in France. The incorporation of silica fume tends to

diminish the level of chloride transport but does not affect the classification of concrete according to the exposure conditions. Fig. 6 (a) presents the chloride profiles of silica fume-enriched concrete, revealing the highest chloride concentrations in tidal exposures, succeeded by splash and atmospheric exposures. When comparing all the exposure conditions the chloride content does not depend only on the conditions. In some cases, no variation between the different exposure conditions is detected [18]. Comparing the results of Fig. 6 (b), which illustrates chloride concentrations in submerged versus tidal exposures over a decade, shows only marginal disparities. The tidal exposure exhibited slightly higher peaks and marginally deeper chloride penetration. One explanation for the similar observations could be that the actual exposure conditions were to a large extent similar. The cores for chloride analysis from the tidal zone were submerged approximately half of the time, with assumed frequent wetting from waves. Moreover, in the case of heavy organic growth with barnacles and mussels on the structure not only on the submerged part of the structure, but also in the tidal zone, it can play a role in preventing the drying and accumulation of chloride at the evaporation front. Consequently, this could explain why the maximum chloride content is only slightly elevated in the tidal exposure profiles compared to the submerged exposure profiles. Such nuances underscore the importance of detailed, localized studies for a comprehensive understanding of chloride ingress mechanisms. The absence of a bell-shaped profile could be attributed to less precision in the measurement of the chloride profile, potentially obscuring any minor peaks that might suggest a bell shape. This highlights the importance of accuracy in data collection to capture all relevant phenomena

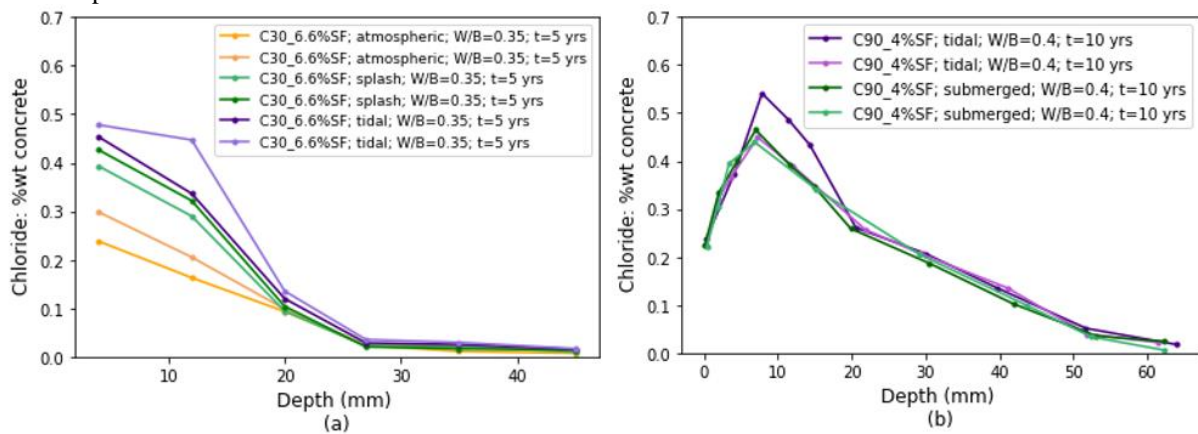


Fig. 6 : Chloride profiles for concrete *with silica fume* for (a) 5 years in the Bandar Imam Khomeini in the Persian Gulf, (b) 10 years in at the Fehmarn Belt Exposure Site, Rødbyhavn, Denmark.

Incorporating fly ash at a 25% replacement level in concrete does not result in the expected variations in chloride profiles across different exposure conditions, as evidenced by Fig. 7, which depicts concrete exposed at the Rødbyhavn maritime site in Denmark. In tidal conditions, chloride profiles show slightly higher concentrations at the surface compared to submerged conditions, with greater penetration depth. However, the difference in maximum chloride concentration remains minimal, both at 2 and 10 years.

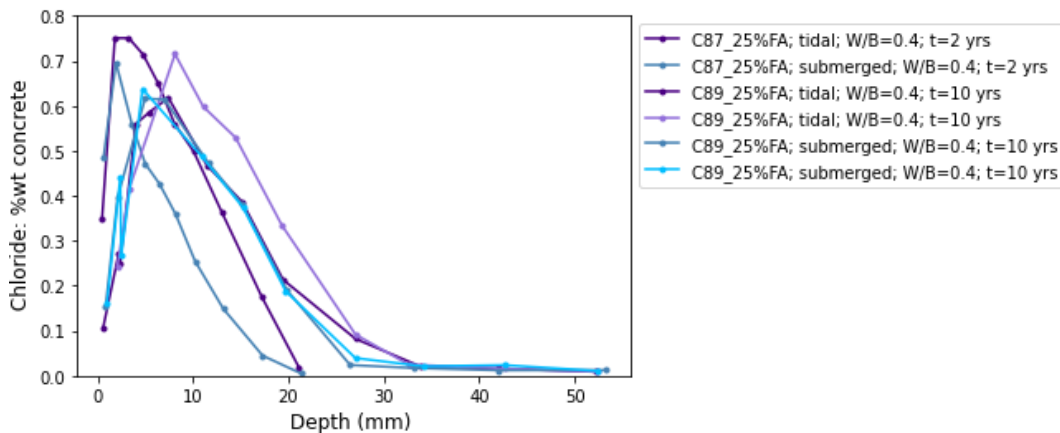


Fig. 7: Chloride profiles for concrete *with 25% Fly ash* exposed in the Fehmarn Belt Exposure Site, Rødbyhavn, Denmark for 2 and 10 years

The notion that chloride ingress in concrete strictly adheres to a gradient from tidal to splash to submerged zones does not hold universally. Investigations reveal that the interaction of various factors, such as sample placement, biological growth on surfaces, and temperature fluctuations, can disrupt this expected pattern. Particularly in tidal zones, the variance in wetting and drying cycles, influenced by aspects like sample depth and proximity to tidal ranges, might cause conditions that resemble splash zones. Additionally, the exposure condition and water-to-binder ratio are predominant factors influencing surface chloride concentration, with tidal zones generally showing higher concentrations. The complexities observed necessitate precise, site-specific studies to accurately assess the impact of environmental conditions on chloride penetration in maritime concrete structures.

Effect of SCM

Research findings indicate that the resistance to chloride penetration in various examined concrete types is significantly influenced by the composition of the binder used in the concrete mixture proportions.

Fig. 8 displays the chloride profiles measured after a 5-year exposure in the submerged area of Rødbyhavn field in the Netherlands, featuring a set of five concrete types: C82, which is regular Portland cement concrete; C83, containing 15% of the binder mass as fly ash; C84, with 4% of the binder mass as silica fume; and C85, which includes 4% of the binder mass as silica fume and 12% as fly ash. For instance, as shown in Fig. 8, chloride penetration is notably lower and shallower in Concrete C85_12%FA_4%SF when both supplementary cementitious materials (SCMs) are combined.

Fig. 9 shows chloride levels in (a) submerged and (b) tidal exposures over a ten-year period for C88: normal Portland cement concrete, C89_25%FA with 25% of the binder mass as fly ash, and C90_4%SF with 4% of the binder mass as silica fume, including two samples of each composition. Concrete with silica fume exhibits the lowest surface concentration and penetration depth, whereas compositions with fly ash have nearly the same surface concentration as normal portland cement but with a shallower penetration depth.

Based on the data presented, it can generally be inferred that the effectiveness of binder types in providing high resistance to chloride ingress can be ranked as follows: (1) combinations of portland Cement, Fly Ash, and Silica Fume, (2) blends of portland cement and fly ash, (3) blends of portland Cement and Silica Fume, and (4) pure portland cement. The enhanced resistance to chloride ingress from the inclusion of mineral additives like fly ash or silica fume is well-supported by numerous studies. [19], [20], [21], [22], [23], [24]. This hierarchy underscores the significant influence of supplementary cementitious materials on the microstructure.

[20] concluded that using FA as an addition to a concrete mixture proportions, exhibit significantly lower total chloride content for all depths from the surface, apart from a thin layer near the external surface. [25] concluded that the resistance to chloride penetration of concrete is significantly increased with the incorporation of fly ash and the increase is enhanced with an increase in fly ash fineness.

Incorporating silica fume (SF) into the mix proportions of concrete leads to significant changes in microstructure, enhancing strength and reducing permeability, thereby lowering chloride transport. This process involves SF reacting with calcium hydroxide, resulting in the formation of C-S-H gel, which aids in the hardening of concrete [26]. The reduction in the chloride binding capacity is reported by many researchers [24] and associated to the fact that silica fume reduces the amount of aluminates phases in concrete that are able to chemically bind chlorides and produces C-S-H that seem to have lower chloride sorption than C-S-H generated from cement hydration [27], [28], [29]. [30] concluded that the use of silica fume markedly enhanced the resistance of concrete mixtures against chloride diffusion as shown by Fig. 8. The normal portland cement mixture had the highest chloride penetration depth when compared to compositions with various replacement level of FA or SF. And more replacement level of SF resulted in more reduction of apparent chloride diffusion coefficient of concrete with an optimum percentage of 12% of SF.

In summary, the incorporation of slag, fly ash or silica fume into concrete mixtures serves as an effective strategy to reduce the concentration of chlorides capable of penetrating the concrete. Each SCM brings its unique properties to the mixture, leading to denser and less permeable microstructures that enhance the chloride resistance of maritime structures.

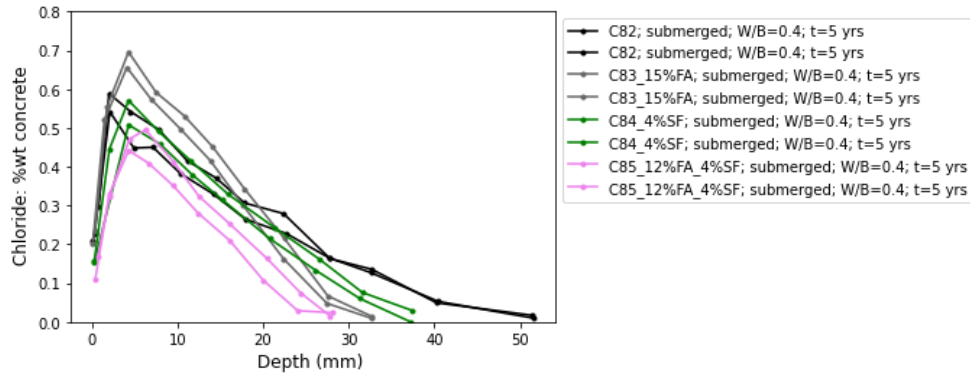


Fig. 8: Chloride profiles for ordinary portland cement concrete (black), 15% of mass binder as FA (grey), and 4% of mass binder as SF (green) and 12% of mass binder as FA combined with 4% of mass binder as SF (magenta) in submerged exposure of 5 years in Rødbyhavn for field in Netherlands

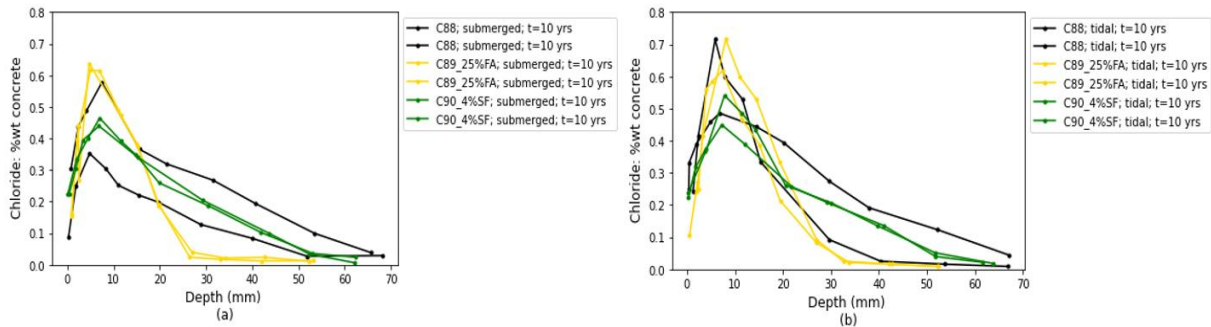


Fig. 9: Chloride Ingress Profiles in the Fehmarn Belt Exposure Site, Rødbyhavn, Denmark for ordinary portland cement concrete (black), 25% of mass binder as FA (yellow) and 4% of mass binder as SF (green), ($W/B=0.4$).

To accurately evaluate the impact of increasing fly ash (FA) content, it's crucial to keep the water-to-binder ratio constant. Consequently, Fig. 10 showcases the effects of 5 years of tidal chloride ingress in Chonburi Province, Thailand, for W/B ratios of (a) 0.45, (b) 0.55, and (c) 0.65. Results indicate that both fly ash and W/B strongly affected chloride diffusion in concrete; higher fly ash replacement and lower W/B clearly produced better chloride resistance in concrete under a marine environment.

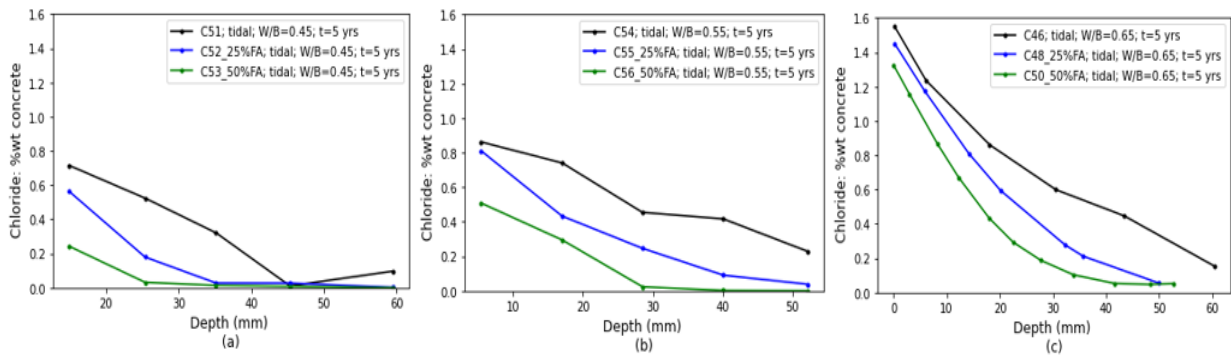


Fig. 10: Chloride Ingress profiles after 5 years of tidal exposure in Chonburi Province in Thailand for various water to binder for ordinary portland cement concrete (black), 25% of mass binder as FA (blue) and 50% of mass binder as SF (green), ($W/B=0.45$).

Chloride surface concentration and convection depth: Case of the bell shape

Chloride profiles in concrete typically decrease with depth, but unique bell-shaped profiles are sometimes observed, as seen in Figure 4(b), Fig. 6(b), Fig. 7, Fig. 8 and Fig. 9. These profiles show an increase in chloride concentration from the surface to a peak at a certain depth, followed by a decrease. This distinctive profile is attributed in the existing literature to convective phenomena induced when concrete is exposed to tidal influences. Over time, a subtle reduction in chloride content at the surface compared to deeper sections is attributed to pronounced leaching in the outermost zone of the samples [4], [31]. Notably, the bell-shaped profile is observed in both tidal and submerged conditions for concretes incorporating supplementary cementitious

materials (SCMs) and in atmospheric conditions for ordinary portland cement concrete. It is important to acknowledge that the bell-shaped profile may exist in actual structural elements. However, during chloride profile analysis, the presence of the bell shape may go unnoticed if the analysis is not finely resolved within the initial few millimeters, as this phenomenon occurs within the first 10mm.

In seawater, a diverse array of ions, including magnesium, sulfate, and carbonate ions, in addition to calcium, potassium, and hydroxyl ions leaching, exerts a substantial influence on the ingress of chloride ions. These processes alter the microstructural properties and binding capacity of the concrete paste, leading to changes in the porosity of the outer concrete surface and the potential for surface scaling [18]. When examining concrete exposed to marine environments, a common observation is the existence of elemental zonation. This typically manifests as a surface layer enriched with magnesium, followed by a sulfur-enriched zone, and ultimately a chloride-enriched zone. This phenomena clarifies why chloride concentrations are not highest at the concrete surface, a pattern observed in scenarios featuring convection zones and submerged exposures alike[32]. Fig. 11 presents the variation in chloride peak concentration as a function of exposure time in submerged conditions over a range of 2 to 5 years, alongside the variation in the peak positions. Chloride concentration tends to increase with exposure time for all the compositions presented. However, for the ternary mixture, the maximum surface concentration tends to be more limited, but the position of this highest concentration gradually shifts with prolonged exposure time.

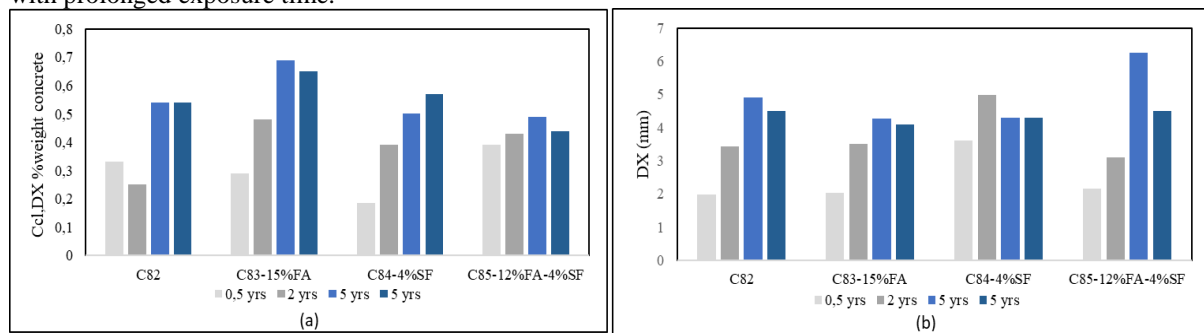


Fig. 11:(a) Maximum chloride peak concentration variation function on exposure time, (b) peak position function of time.

Conclusion

In summary, despite the inherent uncertainties in the data presented, our analysis of the compiled information sheds light on the complex interplay between structural exposure conditions, chloride penetration, and various influencing factors. From this comprehensive examination, several key findings emerge:

- The influence of exposure conditions on chloride ingress in concrete is significant, with tidal and splash zones presenting considerable challenges. Notably, factors such as the presence of organic growth or the hydraulic profile can cause the tidal zone's response to mirror that of submerged conditions, indicating deviations from conventional expectations. This highlights the importance of detailed, location-specific investigations to enhance our understanding of the complex mechanisms of chloride penetration in concrete under various environmental conditions.
- Concrete incorporating Supplementary Cementitious Materials (SCMs) demonstrates a notable reduction in the chloride penetration. Based on the presented data, binder could be ranked in terms of their effectiveness in providing high resistance to chloride ingress as follows: (1) combinations of portland cement, fly ash, and Silica Fume, (2) blends of portland cement and fly ash, (3) blends of portland cement and silica fume, and (4) pure portland cement.
- The bell-shaped chloride profile, marked by an initial rise and subsequent fall in chloride levels, is not unique to tidal exposures but rather a result of physicochemical reactions near the concrete surface. In some instances, the peak of this profile might not be discernible due to a limited number of measurement points at the first few millimeters. The depth at which this peak occurs can vary and is an important aspect to consider when evaluating the ingress of chlorides into concrete structures.

Appendix 1

Table 3: Chloride profile references.

Number of the mixture presented in the graphs	Associated bibliographic reference
C36	[33]
C15	[34]
C22	[6]
C29	[35]
C14	[36]
C30_6.6%SF	[37]
C90_4%SF	[18]
C87_25%FA	[5]
C89_25%FA	[18]
C82	[38]
C83_15%FA	[38]
C84_4%SF	[38]
C85_12%FA_4%SF	[38]
C88	[18]
C51	[39]
C52_25%FA	[39]
C53_50%FA	[39]
C54	[39]
C55_25%FA	[39]
C56_50%FA	[39]
C46	[39]
C48_50%FA	[39]
C50_50%FA	[39]

References:

- [1] L. Pang and Q. Li, "Service life prediction of RC structures in marine environment using long term chloride ingress data: Comparison between exposure trials and real structure surveys," *Constr. Build. Mater.*, vol. 113, pp. 979–987, Jun. 2016, doi: 10.1016/j.conbuildmat.2016.03.156.
- [2] D. R. Vieira, A. L. R. Moreira, J. L. Calmon, and W. K. Dominicini, "Service life modeling of a bridge in a tropical marine environment for durable design," *Constr. Build. Mater.*, vol. 163, pp. 315–325, Feb. 2018, doi: 10.1016/j.conbuildmat.2017.12.080.
- [3] R. A. de Medeiros-Junior, M. G. de Lima, P. C. de Brito, and M. H. F. de Medeiros, "Chloride penetration into concrete in an offshore platform-analysis of exposure conditions," *Ocean Eng.*, vol. 103, pp. 78–87, Jul. 2015, doi: 10.1016/j.oceaneng.2015.04.079.
- [4] K. De Weerd, W. Wilson, A. Machner, and F. Georget, "Chloride profiles – What do they tell us and how should they be used?," *Cem. Concr. Res.*, vol. 173, p. 107287, Nov. 2023, doi: 10.1016/j.cemconres.2023.107287.
- [5] H. E. Sørensen, U. Jönsson, and C. Munch-Petersen, "Chloride penetration into concrete – Comparison of results from field exposure tests and laboratory tests," 2014, doi: 10.13140/RG.2.1.4088.2960.
- [6] D. Boubitsas, T. Luping, and P. Utgenannt, "Chloride Ingress in Concrete Exposed to Marine Environment -Field data up to 20 years' exposure," p. 145.
- [7] R. Cai *et al.*, "Prediction of surface chloride concentration of marine concrete using ensemble machine learning," *Cem. Concr. Res.*, vol. 136, p. 106164, Oct. 2020, doi: 10.1016/j.cemconres.2020.106164.
- [8] International Federation for Structural Concrete, Ed., *Model code for service life design fib34*. in Bulletin / International Federation for Structural Concrete Model code, no. 34. Lausanne: International Federation for Structural Concrete, 2006.
- [9] M. Collepardi, A. Marcialis, and R. Turriziani, "The kinetics of chloride ions penetration in concrete," vol. II *Cemento*, 67, 157-164, 1970.
- [10] L. Tang, L.-O. Nilsson, and P. A. M. Basheer, *Resistance of Concrete to Chloride Ingress*, 0 ed. CRC Press, 2011. doi: 10.1201/b12603.

- [11] O. T. de Rincón *et al.*, “Chloride profiles in two marine structures—meaning and some predictions,” *Build. Environ.*, vol. 39, no. 9, pp. 1065–1070, Sep. 2004, doi: 10.1016/j.buildenv.2004.01.036.
- [12] E. Bastidas-Arteaga, A. Chateaneuf, M. Sánchez-Silva, Ph. Bressolette, and F. Schoefs, “A comprehensive probabilistic model of chloride ingress in unsaturated concrete,” *Eng. Struct.*, vol. 33, no. 3, pp. 720–730, Mar. 2011, doi: 10.1016/j.engstruct.2010.11.008.
- [13] “Engauge Digitizer,” SourceForge. Accessed: Feb. 14, 2024. [Online]. Available: <https://sourceforge.net/projects/digitizer/>
- [14] M. Valipour, F. Pargar, M. Shekarchi, S. Khani, and M. Moradian, “In situ study of chloride ingress in concretes containing natural zeolite, metakaolin and silica fume exposed to various exposure conditions in a harsh marine environment,” *Constr. Build. Mater.*, vol. 46, pp. 63–70, Sep. 2013, doi: 10.1016/j.conbuildmat.2013.03.026.
- [15] Q. Li, K. Li, X. Zhou, Q. Zhang, and Z. Fan, “Model-based durability design of concrete structures in Hong Kong–Zhuhai–Macau sea link project,” *Struct. Saf.*, vol. 53, pp. 1–12, Mar. 2015, doi: 10.1016/j.strusafe.2014.11.002.
- [16] International Conference on Durability of Building Materials and Components, *Durability of building materials and components 7: testing, design and standardisation : proceedings of the seventh International Conference on Durability of Building Materials and Components, 7DBMC : Stockholm, Sweden, 19-23 May, 1996*, First edition. in Testing, Design and Standardisation ; Volume Two. London ; Taylor & Francis, 1996. doi: 10.4324/9781315025018.
- [17] H.-W. Song, C.-H. Lee, and K. Y. Ann, “Factors influencing chloride transport in concrete structures exposed to marine environments,” *Cem. Concr. Compos.*, vol. 30, no. 2, pp. 113–121, Feb. 2008, doi: 10.1016/j.cemconcomp.2007.09.005.
- [18] S. Fjendbo, H. E. Sørensen, K. De Weerd, U. H. Jakobsen, and M. R. Geiker, “Correlating the development of chloride profiles and microstructural changes in marine concrete up to ten years,” *Cem. Concr. Compos.*, vol. 131, p. 104590, Aug. 2022, doi: 10.1016/j.cemconcomp.2022.104590.
- [19] M. C. G. Juenger and R. Siddique, “Recent advances in understanding the role of supplementary cementitious materials in concrete,” *Cem. Concr. Res.*, vol. 78, pp. 71–80, Dec. 2015, doi: 10.1016/j.cemconres.2015.03.018.
- [20] V. G. Papadakis, “Effect of supplementary cementing materials on concrete resistance against carbonation and chloride ingress,” *Cem. Concr. Res.*, vol. 30, no. 2, pp. 291–299, Feb. 2000, doi: 10.1016/S0008-8846(99)00249-5.
- [21] M. Raghav, T. Park, H.-M. Yang, S.-Y. Lee, S. Karthick, and H.-S. Lee, “Review of the Effects of Supplementary Cementitious Materials and Chemical Additives on the Physical, Mechanical and Durability Properties of Hydraulic Concrete,” *Materials*, vol. 14, no. 23, p. 7270, Nov. 2021, doi: 10.3390/ma14237270.
- [22] S. Samad and A. Shah, “Role of binary cement including Supplementary Cementitious Material (SCM), in production of environmentally sustainable concrete: A critical review,” *Int. J. Sustain. Built Environ.*, vol. 6, no. 2, pp. 663–674, Dec. 2017, doi: 10.1016/j.ijbsbe.2017.07.003.
- [23] M. Panjehpour, A. A. A. Ali, and R. Demirboga, “A Review for Characterization of Silica Fume and Its Effects on Concrete Properties,” *Int. J. Sustain. Constr. Eng. Technol.*, vol. 2, no. 2, Art. no. 2, 2011, Accessed: Nov. 05, 2022. [Online]. Available: <https://publisher.uthm.edu.my/ojs/index.php/IJSCET/article/view/343>
- [24] K. E. Hassan, J. G. Cabrera, and R. S. Maliehe, “The effect of mineral admixtures on the properties of high-performance concrete,” *Cem. Concr. Compos.*, vol. 22, no. 4, pp. 267–271, Jan. 2000, doi: 10.1016/S0958-9465(00)00031-7.
- [25] P. Chindapasirt, C. Chotithanorm, H. T. Cao, and V. Sirivivatnanon, “Influence of fly ash fineness on the chloride penetration of concrete,” *Constr. Build. Mater.*, vol. 21, no. 2, pp. 356–361, Feb. 2007, doi: 10.1016/j.conbuildmat.2005.08.010.
- [26] J. M. R. Dotto, A. G. de Abreu, D. C. C. Dal Molin, and I. L. Müller, “Influence of silica fume addition on concretes physical properties and on corrosion behaviour of reinforcement bars,” *Cem. Concr. Compos.*, vol. 26, no. 1, pp. 31–39, Jan. 2004, doi: 10.1016/S0958-9465(02)00120-8.
- [27] X. Shi, N. Xie, K. Fortune, and J. Gong, “Durability of steel reinforced concrete in chloride environments: An overview,” *Constr. Build. Mater.*, vol. 30, pp. 125–138, May 2012, doi: 10.1016/j.conbuildmat.2011.12.038.
- [28] C. Arya, N. R. Buenfeld, and J. B. Newman, “Factors influencing chloride-binding in concrete,” *Cem. Concr. Res.*, vol. 20, no. 2, pp. 291–300, Mar. 1990, doi: 10.1016/0008-8846(90)90083-A.
- [29] “(26) Pore solution composition and chloride binding capacity of silica-fume cement pastes | Hala Emad El-Dain Fouad - Academia.edu.” Accessed: Nov. 05, 2022. [Online]. Available: https://www.academia.edu/748985/Pore_solution_composition_and_chloride_binding_capacity_of_silica_fume_cement_pastes

- [30] A. Dousti, R. Rashednia, B. Ahmadi, and M. Shekarchi, "Influence of exposure temperature on chloride diffusion in concretes incorporating silica fume or natural zeolite," *Constr. Build. Mater.*, vol. 49, pp. 393–399, Dec. 2013, doi: 10.1016/j.conbuildmat.2013.08.086.
- [31] K. D. Weerdt, "Comparing chloride ingress from seawater and NaCl solution in Portland cement mortar," *Cem. Concr. Res.*, 2019.
- [32] Y. Yi, D. Zhu, S. Guo, Z. Zhang, and C. Shi, "A review on the deterioration and approaches to enhance the durability of concrete in the marine environment," *Cem. Concr. Compos.*, vol. 113, p. 103695, Oct. 2020, doi: 10.1016/j.cemconcomp.2020.103695.
- [33] A. Costa and J. Appleton, "Chloride penetration into concrete in marine environment—Part I: Main parameters affecting chloride penetration," *Mater. Struct.*, vol. 32, no. 4, pp. 252–259, May 1999, doi: 10.1007/BF02479594.
- [34] I. Othmen, S. Bonnet, and F. Schoefs, "Statistical investigation of different analysis methods for chloride profiles within a real structure in a marine environment," *Ocean Eng.*, vol. 157, pp. 96–107, Jun. 2018, doi: 10.1016/j.oceaneng.2018.03.040.
- [35] W. J. McCarter, G. Starrs, B. T. Linfoot, and T. Chrisp, "Performance of concrete in XS1, XS2 and XS3 environments," *Mag. Concr. Res. - MAG CONCR RES*, vol. 60, pp. 261–270, Jan. 2008, doi: 10.1680/mac.2008.60.4.261.
- [36] PERFDUB, "Pont X - Synthèse des données de durabilité." PERFDUB, Jan. 2020.
- [37] M. Safedian and A. A. Ramezani pour, "Assessment of service life models for determination of chloride penetration into silica fume concrete in the severe marine environmental condition," *Constr. Build. Mater.*, vol. 48, pp. 287–294, Nov. 2013, doi: 10.1016/j.conbuildmat.2013.07.006.
- [38] S. Poulsen, H. Sørensen, and U. Jönsson, "Chloride ingress in concrete blocks at the Rødbyhavn marine exposure site - Status after 5 years," Aug. 2018.
- [39] W. Chalee, C. Jaturapitakkul, and P. Chindaprasirt, "Predicting the chloride penetration of fly ash concrete in seawater," *Mar. Struct.*, vol. 22, no. 3, pp. 341–353, Jul. 2009, doi: 10.1016/j.marstruc.2008.12.001.