

A modeling framework to anticipate, mitigate, and adapt to the impact of climate change on the durability of civil infrastructure

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A modeling framework to anticipate, mitigate, and adapt to the impact of climate change on the durability of civil infrastructure

Suntharalingam Sharmilan

Ph.D. Thesis Month of defence 2023

DTU Sustain Department of Environmental and Resource Engineering Technical University of Denmark

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Ph.D. Thesis, Month 2023

The synopsis part of this thesis is available as a pdf-file for download from the DTU research database ORBIT: http://www.orbit.dtu.dk.

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Preface

This thesis is submitted as a partial fulfilment of the requirements for the Danish Ph.D. degree at the Technical University of Denmark. The study has been undertaken at the Department of Environmental and Resource Engineering, Technical University of Denmark, under the supervision of Associate Professor Alexander Michel and co-supervised by Professor Henrik Stang.

This Ph.D. project aimed to develop a modeling framework that enables designers and decision-makers to provide scientific, relevant, and usable knowledge to guide decisions related to climate change impacts. The thesis consists of two parts. Part I introduces the background, motivation, aim, and scope of the study and summarizes major research findings. Part II is a collection of three papers that treat important topics related to the research.

The project was financially supported by the Independent Research Fund Denmark (8022-00374B) (Danmarks Frie Forskningsfond).

Preface to published version

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Finally, I would like to thank my family and friends close to me for their constant support and encouragement during the past years.

Abstract

For human settlements all over the world, concrete is commonly used as a construction material for civil infrastructure. The long service life, ranging from 30 to 100 years or even more, of concrete infrastructure necessitates considering future climatic conditions in design, maintenance, and replacement planning. For proactive adaptation and decision-making regarding the maintenance of the infrastructure that society and the economy depend on, it is essential to understand and analyse the impact of climate change on concrete infrastructure.

Over the last few decades, while many studies have focused on concrete infrastructure deterioration in the literature, limited research has been conducted on the impact of climate change on the deterioration of concrete structures. However, while these few studies present the first step to enable designers and decision-makers to anticipate the impacts of climate change on concrete infrastructure, the studies and frameworks are limited in their capability to mitigate and facilitate proactive adaption, such as optimized material design, increased robustness, and more adapted maintenance strategies, etc. This limitation arises from their reliance on simplified predictive models with empirical formulas, as well as assumptions about the processes involved in the analysis of the impact of climate change on concrete infrastructure, for example, mass transport mechanisms into concrete, mass flux through boundary surfaces, and the integration effect of climate change on concrete deterioration. Also, predictive competencies are inadequate due to insufficient critical physical couplings between mass transport, chemical equilibrium, and material properties. To progress beyond the state-of-the-art, science-based models for concrete deterioration must be developed considering fundamentals and integrated with climate projection models to analyze the impact of climate change on concrete deterioration. Therefore, this study aimed to establish a modeling framework that enables designers and decision-makers to provide scientific, relevant, and usable knowledge to guide decisions related to climate change impacts.

A conceptual framework for predicting, mitigating, and adapting to the impacts of climate change on the durability of concrete infrastructure was developed, thereby enabling the establishment of more robust design approaches as well as more resilient and adapted maintenance strategies for existing concrete infrastructures. Initially, a multi-species reactive transport model (RTM) was established, including mass transport coupled with chemical equilibrium, for predicting the deterioration

of cement-based material through pore solution and solid phase changes under different environmental conditions. The prediction of concrete deterioration under actual environmental conditions, where concrete infrastructure is located in the real field, is more complex and often hardly comparable to results observed in labscale experiments, which may be due to fluctuations of climate conditions with time and the complex effect of boundary conditions. Therefore, the developed modeling framework was calibrated and tested in two case studies: *i*) data from the Solsvik field station, Norway, including observations of submerged concrete deterioration for more than 16 years, and *ii*) data from the Danish Technological Institute field station data, Denmark, including observations of concrete carbonation under atmospheric conditions for nearly eight years.

To account for the impact of climate change on concrete deterioration, the approach was further integrated with the statistical results of state-of-the-art climate models. For this study, the multi-model ensembles of global circulation models (GCMs) projections under the very high GHG emissions scenario (RCP8.5), which is produced by the Coupled Model Intercomparison Project phase 5 (CMIP5) initiative, were used to investigate the impact of climate change on concrete structure deterioration in the period between 2020 and 2100. To avoid the biases and spatial resolution of these global projections that hinder their use in regional applications, the multi-model climate projections at high spatial resolution were downscaled to local scales using the Delta statistical downscaling method. The downscaled multimodel climate projections were statistically analysed to determine the uncertainty of climate projections, *i.e.*, atmospheric temperature, relative humidity, and temperature and salinity level of seawater. Using distribution parameters from the climate projection for the RCP8.5 scenario, random samples were generated using the Latin hypercube sampling (LHS) technique. Using an integrated modeling framework, Monte Carlo simulations were performed to account for uncertainty information in the climate projections involved, and subsequently, an analytical probabilistic design approach was developed to identify critical climate projection outputs driving concrete deterioration in future climate projections. Finally, the results from the probabilistic design approach were used to investigate and identify more robust design approaches and more resilient and adapted maintenance strategies for concrete infrastructure, anticipating, mitigating, and adapting to the impacts of climate change on material deterioration.

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1 Introduction

1.1 Background

Crucial sets of civil infrastructure form the foundation for a high standard of living and facilitate global growth and development [1]. Deterioration of civil infrastructure (bridges, tunnels, roads, and buildings), together with increasing loads (e.g., traffic volume and weight), presents significant challenges to society in most developed countries [2-5]. Research and experience over the past 20 years show that planning, material, and construction costs are often dwarfed by the costs associated with deterioration, i.e., costs of inspecting, repairing, and maintaining civil infrastructure over its useful life [4,6]. Deterioration is affected not just by construction methods, material composition, and structural geometry but also by environmental boundary conditions [7]. Moreover, climate change may profoundly alter these environmental boundary conditions, especially over a longer term, changing deterioration processes and consequently affecting the safety, serviceability, and durability of civil infrastructure. The evidence for the changing climate and its impacts is substantial [8]. Climate change is responsible for adverse effects on human health [9,10], changes in ecosystem function [11], increases in the ocean [12], and atmospheric temperatures [12], as well as more frequent and severe droughts or rainfall, fires, and storms. While scientific consensus on trends in global mean temperature is strong, the impact of climate change on the deterioration of civil infrastructure is unclear to date and may cause considerable environmental and economic threats to society. For example, corrosion of reinforcement is identified as the leading cause of degradation in reinforced concrete civil infrastructure [13], and it consumes more than three percent of the world's GDP [3]. Corrosion has enormous direct and indirect costs; thus, even a slight acceleration of the deteriorating processes due to climate change may result in considerably higher maintenance and repair expenses [7]. However, there are currently no proper tools available for policymakers, designers, or decision-makers to allow them to anticipate, mitigate, and adapt to the impacts of climate change on civil infrastructure.

1.2 Concrete for civil infrastructure

For a wide range of applications in urban areas, concrete is commonly used as a construction material for civil infrastructure. Currently, 4.4 billion tons of cement are produced globally each year, but the Chatham House analysis predicts that by 2050, over 5.5 billion tons will be produced as poorer nations quickly urbanize

[14]. For civil infrastructure, concrete material is also easily accessible locally, reasonably priced, and has a wide range of applications with excellent material properties compared to other construction materials such as wood, steel, etc. Moreover, concrete significantly outperforms other construction materials regarding environmental sustainability when considering a structure's performance over the service life. This is due to concrete's inherent qualities, such as strength, resistance to fire, thermal capacity, and durability [15]. In addition, concrete infrastructure, such as buildings, bridges, tunnels, roads, offshore structures, etc., must meet society's expectations for durability and safety. Concrete's major weakness is its poor tensile strength and lack of ductility. Therefore, steel reinforcement is used to provide concrete more strength where it is required. When concrete is subjected to tensile stress, as it is in beams and slabs, steel reinforcement is used to provide the tensile capacity. Additionally, it provides extra shear capacity over and above that of the concrete in beams, supplementing the compressive and flexural strength in columns and walls [16,17]. Fig 1.1 presents a few examples of the application of reinforced concrete (RC) in construction.



Fig 1.1. Different infrastructures with applications of reinforced concrete: (a) Sydney Opera House [18], (b) Precast Concrete School in Chicago [19], (c) Hoover Dam [20], and (d) Sheikh Zayed Bridge [21].

The concrete cover in reinforced concrete structures protects the embedded steel reinforcement from corrosion when exposed to harsh environmental conditions. In concrete, a high alkalinity pore solution with a pH value between 12.5 and 14 is formed when the solution in the pores and solid phases of the typical Portland cement reaches an equilibrium state [22]. The high pH value in the pore solution facilitates the formation of a passive layer, which acts as a barrier and minimises the corrosion of steel reinforcement embedded in concrete [23,24]. However, the pH value starts to drop due to ionic ingress into concrete from the service environment and the rapid dissolution of gaseous $CO_{2(g)}$ into the alkaline pore solution during carbonation [4]. As a result of the change in the pore solution's alkaline environment, the passive layer becomes unstable [5–7], which is one of the major issues with the long-term durability of concrete structures [8–10]. However, reinforcement corrosion can be prevented or minimized through the proper selection of concrete mix (with low water-to-cement ratios (w/c) or supplementary cementitious materials (SCMs)) and cover thickness for environmental service conditions and high-quality construction. By creating a dense pore structure in concrete and selecting adequate cover thickness, the ingress of environmental chemical components into concrete, such as dissolved and gaseous carbon dioxide, chloride and other ions, moisture, and oxygen, can be limited. Also, the ingress may take several decades to reach the reinforcement surface [25]. However, following a proper mix design for a given environment and maintaining high-quality work is sometimes difficult in construction projects. As a result, achieving a dense pore structure of concrete and maintaining a proper cover thickness is often compromised in infrastructure constructions.

Moreover, the formation of cracks due to autogenous shrinkage, thermal shrinkage, and service loading is frequently observed in reinforced concrete structures. Therefore, the ingress of harmful chemical components from the environment increases through the pores and the cracked surface, which may lead to expedited initiation of deterioration [26–28]. For example, accelerated ingress of harmful substances has been observed in cracked concrete structures, leading to the initiation of corrosion of embedded steel in concrete as the concentration of ions reaches a specific critical threshold value, causing the passive film to be destroyed [29– 31]. Damages brought on by corrosion of steel, such as concrete cracking, spalling, delamination, and cross-sectional reduction of the reinforcement, can decrease a structure's load-bearing capacity, reduce its aesthetic appeal, and, in the most severe circumstances, result in deadly structural repercussions like failure [5,32,33].

1.3 Climate change

The advancement of industry opened up many possibilities for the global development of human civilization. However, these changes did not come without environmental consequences. Moreover, there is considerable concern that anthropogenic factors such as economic and population growth, particularly those involving greenhouse gas (GHG) emissions, are responsible for climate change [34–37]. According to the latest Intergovernmental Panel on Climate Change (IPCC) report in 2014 [38], anthropogenic greenhouse gas emissions are at their highest levels ever. Comparing the reported value of the overall anthropogenic radiative forcing estimate in the 5th IPCC Assessment Report (AR5) for 2011 to the value in the 4th IPCC Assessment Report (AR4), the value increased by 43% [39]. This increase results from the majority of GHG concentrations continuing to rise combined with an improved estimate of the radiative forcing from aerosols. There is no doubt that the climate system is warming, and many of the changes that have occurred since the 1950s have never been observed before across decades to millennia. As a result of the warming effect of the climate system, rises in sea level as well as a drop in relative humidity levels are observed with atmospheric temperature rises. The 5th IPCC report also highlighted that the $CO_{2(g)}$ concentration showed an upward trend from 280 parts per million in 1750 to 380 parts per million in 2005 [40]. The worst case scenario (RCP 8.5) in the 5th IPCC report predicts that the average temperature will rise by around 4.3°C in 2100 and that the $CO_2(g)$ content in the atmosphere will likely reach 1000 ppm [39]. The climate system is significantly impacted by these changes, particularly the rise in temperature, carbon dioxide levels, and decreases in relative humidity. As a result, these changes may significantly affect the durability of concrete infrastructures. In this context, there is currently widespread concern about how climate change may affect the durability of concrete structures.

1.4 Concrete structures under climate change

Over a more extended period, climate change may alter the service environment of reinforced concrete structures, accelerating degradation processes, particularly causing corrosion damage to steel bars and resulting in corrosion-induced cracking and spalling [41,42]. Therefore, the impact of climate change on the deterioration of concrete structures is currently considered a crucial problem from the perspective of the service life of concrete structures.

Yoon et al. carried out early research to develop a modified mathematical equation to assess the $CO_{2(g)}$ diffusion coefficient in concrete, although the suggested model ignores the effect of temperature change on concrete carbonation. The predicted results illustrated that carbonation depths would rise as a result of an increase in $CO_{2(g)}$ concentrations brought on by a changing climate [43]. Stewart *et al.* have presented advanced probabilistic and reliability-based approaches to predict concrete deterioration brought on by the changing climate in Australia. These approaches take into account variations in the probability of reinforcement corrosion and corrosion-induced damage caused by increases in atmospheric $CO_{2(g)}$ concentration, as well as variations in temperature and relative humidity [24,44]. In their studies, Stewart et al. predicted that by 2100, the risk of corrosion caused by carbonation might increase by 400% in specific regions in Australia. In addition, a 15% increase in temperature during that same timeframe increases the likelihood of damage by chloride-induced corrosion [24]. However, the model used in these studies is an approximation, as it does not take into account the time-dependent influence of climatic variables like $CO_{2(g)}$ concentration, temperature, and relative humidity. A spatial and time-dependent probability assessment also indicates that by 2100, the carbonation-induced and chloride-induced damage risks might increase by 16% and 3%, respectively. This indicates that by 2100, up to one in six structures may sustain expensive extra corrosion damage [44]. Lizhengli Peng et al. investigate the impact of climate change in three typical Chinese cities using the proposed model by Stewart et al. [44]. According to the findings, the mean carbonation depths for RC structures in China might increase by up to 45% by 2100 due to climate change. Additionally, it was predicted that by 2100, climate change might increase carbonation-induced damage to RC structures in China's temperate or cold temperature regions by 7 to 20% [45]. In order to predict the probability of corrosion initiation, the average proportion of corrosion damage, the probability of flexural and shear failure of typical RC beams, and the probability of failure of a typical pre-stressed concrete bridge over the next 100 years, Jianxin Peng et al. [46] used probabilistic approaches to account for uncertainty in material qualities, degradation processes, ambient $CO_{2(g)}$ levels, and loads and dimensions. They found that the proportion of corrosion damage for RC and Prestressed Concrete (PSC) structures is up to 540% more under the worst-case CO_{2(g)} emission scenario than in the best-case mitigation scenario. In contrast, the probability of flexural and shear failure in the worst-case scenario is around 6% and 18% greater, respectively, than in the best mitigation scenario [46]. Talukdar *et al.* [47] established a comprehensive carbonation model as a function of time that considers the effects of variations in humidity, temperature, ambient CO_{2(g)} concentrations, and chemical reaction rates to determine the depth of carbonation in unloaded concrete specimens [47]. The influence of climatic variations on the progression of carbonation-induced corrosion in non-pozzolanic, unloaded concrete for two major Canadian cities, Toronto and Vancouver, was examined by Talukdar et al. using the proposed model. The impacts might increase carbonation depths by around 45% over 100 years, which is predicted to be highly significant. Since Vancouver has higher relative humidity than Toronto, deeper carbonation levels are predicted in Toronto. However, the degradation rates for in-service structures under stress are probably significantly faster [48]. Furthermore, Talukdar et al. have proposed a model that considers fracture development brought on by global temperature change when estimating the service life of concrete structural elements. Predicted results show that concrete structures built in the year 2000 will begin to deteriorate after 30 years of exposure to climate change, while structures developed in 2020–2030 may need to start designing for climate change-related deterioration. For the worst-case scenario, concrete structures built in 2030 in regions where carbonation-induced corrosion might be a problem for a dry exposure class (moderate humidity, higher temperatures), it is reasonable to expect that buildings will start to exhibit a 15-20-year reduction in their service lifespan as a result of climate change, with damage being noticeable 40-45 years after construction [49]. Guofang Chen et al. proposed a carbonation model considering $CO_{2(g)}$ concentrations, temperature, and RH to predict the carbonation depth of concrete structures in different Chinese cities [41]. In this study, Chinese cities such as Harbin, Qingdao, and Ningbo are selected to represent the regions of severe cold, cold coastal, and temperate coastal climates, respectively. Based on the prediction of climate change trends by the 5th assessment report of IPCC and the local climate records in different areas, the carbonation of concrete with time over the 21st century was projected for the selected cities. The study's main findings include that the carbonation rate of concrete buildings is accelerated by climate change. In all three cities investigated, the carbonation rate continued to increase under the worst-case scenario for emissions, but under the best-case scenario, it will peak in the middle of the century before starting to decline. By the end of the century, climate change may cause concrete structures in China's regions with extreme cold, cold coastal climates, and moderate coastal climates to sustain an additional 20-160 percent of carbonation-induced damage [41]. Jiang et al. [50] developed a straightforward carbonation model for fatigue-damaged concrete using Monte Carlo simulations. In order to account for the time-variant fatigue damage and exposure conditions, they proposed an incremental approach. The findings

showed that the connection between the square root of service time and the carbonation depth would vary as a result of significant climatic changes [50].

In order to determine the effect of climate on maintenance, repair, and construction in ten different countries, Schweikert *et al.* [51] used a stressor-response approach. The analyzed results show that the cost of the effects of climate change on the road infrastructure networks of developing countries will be higher relative to developed countries through 2100, but it will start to happen as early as the 2020s. Compared to the reactive no adapt scenario, proactive adaptation actions can dramatically lower impacts and costs for all countries studied. Moreover, developed countries must spend a lot of money to respond to or adapt to the effects of climate change. For the area of the central Gulf Coast of the United States between Galveston, Texas, and Mobile, Alabama, Savonis *et al.* [52] conducted a regional evaluation of climate change and its possible consequences on transportation networks. They concluded from their analysis that rising temperatures will probably result in higher operational, maintenance, and construction costs for transportation. Increased frequency of intense precipitation events could cause visibility and flooding issues, disrupting transportation networks.

Moreover, many of the current infrastructure's vulnerabilities to frequent or permanent flooding will increase as the sea level rises; 72% of ports, 9% of rail lines, and 27% of major highways are constructed on terrain that is 122 cm (4 feet) or lower in elevation. Storm damage and service disruption could both increase with storm intensity: The majority of the region's main highways (64 percent of Interstates; 57 percent of arterials), nearly half of its rail miles, 29 airports, and nearly all of its ports are located below 7 meters (23 feet) of elevation, making them vulnerable to flooding and potential damage from hurricane storm surge. Using an infrastructure model modified to take into account specific climate impacts at northern latitudes, such as near-surface permafrost thaw, A.M. Melvin et al. [53] quantified the economic impacts of climate change on Alaska public infrastructure under relatively high and low climate forcing scenarios [representative concentration pathway 8.5 (RCP8.5) and RCP4.5]. Additionally, they established first-order estimations of possibilities and losses related to coastal erosion and the extension of the coastal ice-free season for 12 municipalities. They also assessed how proactive adaptation affected economic implications on certain infrastructure types. According to estimates, the cost of infrastructure-related climate damage without adaptation measures is expected to total \$5.5 billion (2015 dollars, 3% discount) for RCP8.5 and \$4.2 billion for RCP4.5 from 2015 to 2099. This indicates that reducing greenhouse gas emissions could save \$1.3 billion in damages this century. Different areas of the state saw different distributions of damages, with the interior and southcentral Alaska expected to experience the greatest losses. The main cause of damage was road flooding brought on by more precipitation, followed by building damage brought on by the thawing of the permafrost near the surface, while pipelines, trains, and airports all suffered less damage. The overall predicted cumulative costs were decreased by proactive adaptation to \$2.9 billion for RCP8.5 and \$2.3 billion for RCP4.5. Across four research eras, modification resulted in annual savings of 80-100% for road floods. Costs for damages and adaptation were higher for RCP8.5 than RCP4.5 for almost all infrastructure types and evaluation times. Losses attributed to coastal erosion were also predicted to be higher for RCP8.5. The impact of climate change on the road networks in Malawi, Mozambique, and Zambia was investigated by P.S. Chinowsky et al. [54] using a stressor-response approach. According to this extensive analysis, it was predicted that the three southern African nations could be faced with a potential \$596 million bill based on median climate scenarios to maintain and repair roads as a result of damages directly related to temperature and precipitation changes from potential climate change through 2050. According to a research by the committee on climate change and the U.S. transportation research board [55], climate change will significantly impact transportation, altering how U.S. transportation experts plan, design, build, operate, and maintain infrastructure. Moreover, long-term system adaptation to climate change will be influenced by decisions made today, particularly those pertaining to the redesign and retrofitting of existing or the location and design of new transportation infrastructure.

1.5 Research significance

The long service life, ranging from 30 to 100 years or even more, of concrete infrastructure necessitates considering future climatic conditions in design, maintenance, and replacement planning. For proactive adaptation and decision-making regarding the maintenance of the infrastructure that society and the economy depend on, it is essential to understand and analyse the impact of climate change on concrete infrastructure. Over the last few decades, while many studies have focused on concrete infrastructure deterioration in the literature, limited research has been conducted on the impact of climate change on the deterioration of concrete structures (see section 1.4). While these studies present the first step to enable designers and decision-makers to anticipate the impacts of climate change on concrete infrastructure, the studies and frameworks [51–55] are inadequate in their capability to mitigate and facilitate proactive adaption, such as optimized material design, increased robustness, and more adapted maintenance strategies, *etc*. This limitation arises from their reliance on simplified predictive models with empirical formulas, as well as assumptions about the processes involved in the analysis of the impact of climate change on concrete infrastructure, for example, mass transport mechanisms into concrete, mass flux through boundary surfaces, and the integration effect of climate change on concrete deterioration. Also, predictive competencies are inadequate due to insufficient critical physical couplings between mass transport, chemical equilibrium, and material properties. To progress beyond the state-of-the-art, science-based models for concrete deterioration must be developed considering fundamentals and integrated with climate projection models to analyze the impact of climate change on concrete deterioration. Therefore, this study aimed to establish a modeling framework that enables designers and decision-makers to provide scientific, relevant, and usable knowledge to guide decisions related to climate change impacts.

1.6 Research hypotheses and objectives

The central hypothesis of this Ph.D. study is that a modeling framework assessing the impact of climate change on material deterioration enables more robust design approaches and more resilient and adapted maintenance strategies for civil infrastructure. While material deterioration models and climate projections have matured over the past decades, key elements are missing to support such an integrated modeling framework. In this context, the following four research objectives were addressed:

- I. Development of a multi-species reactive transport model (RTM) based on gas-ion-solid phase interaction, which can predict the deterioration of cement-based material under different environmental conditions.
- II. Demonstration of the applicability and reliability of the developed RTM under actual environmental conditions through case studies.
- III. Development of a probabilistic modeling framework that integrates climate projection outputs and material deterioration to facilitate decisions for proactive adaptation.
- IV. Identification of critical climate projection outputs driving future material deterioration of civil infrastructure.

Such an integrated modeling framework enables designers and decision-makers to develop design and maintenance strategies anticipating, mitigating, and adapting

to the impacts of climate change on civil infrastructure. The development of such a tool provides a means to address some of the most pressing challenges in Danish society and worldwide [38,56]. Although establishing a generally applicable modeling framework 'to strengthen the knowledge base for decisions on investments in climate adaptation' [56] is a formidable task, this study was limited to material deterioration processes in concrete infrastructure under the fully submerged seawater and atmospheric carbonation exposure condition, *i.e.*, reinforcement corrosion related to service environmental conditions such as atmospheric CO_{2(g)} gas concentration, temperature, relative humidity, temperature and salinity level of sea-water, and precipitation level. Nevertheless, the project serves as a proof of concept for the overarching idea and provides the foundation for generalizing the approach and expanding the modeling framework to cover civil infrastructure more comprehensively, including various other deterioration phenomena such as sulfate attack, alkali–silica reaction, and freeze–thaw cycles.

1.7 Research approach and methods

The fundamental concept of the proposed framework is presented in Fig 1.2, which illustrates models for evaluating the impact of climate change on concrete deterioration. Initially, a multi-species reactive transport model (RTM) was established, including mass transport coupled with chemical equilibrium, for predicting the deterioration of cement-based material through pore solution and solid phase changes under different environmental conditions. The prediction of concrete deterioration under actual environmental conditions, where concrete infrastructure is located in the real field, is more complex and often hardly comparable to results observed in lab-scale experiments, which may be due to fluctuations of climate conditions with time and the complex effect of boundary conditions. Therefore, the developed modeling framework was calibrated and tested in two case studies: *i*) data from the Solsvik field station, Norway, including observations of submerged concrete deterioration for more than 16 years, and *ii*) data from the Danish Technological Institute field station data, Denmark, including observations of concrete carbonation under atmospheric conditions for nearly eight years.

To account for the impact of climate change on concrete deterioration, the approach was further integrated with the statistical results of state-of-the-art climate models. For this study, the multi-model ensembles of global circulation models (GCMs) projections under the very high GHG emissions scenario (RCP8.5), which

is produced by the Coupled Model Intercomparison Project phase 5 (CMIP5) initiative, were used to investigate the impact of climate change on concrete deterioration in the period between 2020 and 2100. To avoid the biases and spatial resolution of these global projections that hinder their use in regional applications, the multi-model climate projections at high spatial resolution were downscaled to local scales using the Delta statistical downscaling method. The downscaled multimodel climate projections were statistically analysed to determine the uncertainty of climate projections, *i.e.*, atmospheric temperature, relative humidity, and temperature and salinity level of seawater. Using distribution parameters from the climate projection for the RCP8.5 scenario, random samples were generated using the Latin hypercube sampling (LHS) technique. Using an integrated modeling framework, Monte Carlo simulations were performed to account for uncertainty information in the climate projections involved, and subsequently, an analytical probabilistic designing approach was developed to identify essential climate projection outputs driving material deterioration in future climate projections. Finally, the results from the probabilistic designing approach were used to investigate and identify more robust design approaches and more resilient and adapted maintenance strategies for concrete infrastructure, anticipating, mitigating, and adapting to the impacts of climate change on material deterioration.



Fig 1.2. Proposed framework for studying the impact of climate change on concrete deterioration.

1.8 Limitations and assumptions

The following limitations and assumptions are made to limit the scope of the work.

Mass transport calculation

- As a result of the faster heat transport capacity of concrete compared to mass transport into concrete, such as ions, gases, and moisture, the heat transfer model is not included in the reactive transport model. Furthermore, temperature changes at the boundary condition are assumed to be uniform and instantaneous throughout the depth of the concrete.
- The reactive transport model accounts for simulations of concrete deterioration in uncracked conditions. Therefore, transport parameters such as moisture conductivity, gas diffusion, and ionic diffusion through the pores are computed based on an uncracked condition in the pore structure of concrete.
- Due to cement-based materials being exposed to the solution, it is assumed that the composition of the boundary solution is not affected by ions leaching from the exposed surfaces of cement-based materials.
- Due to the corrosion of steel reinforcement in concrete, dissolved corrosion products begin to be transported through the pores. However, in this study, the transport of corrosion products through the pore solution is not included in the reactive transport model. Furthermore, it is assumed that the transport of corrosion products does not affect other mass transport processes such as moisture, gases, and ions.

Chemical equilibrium calculation

- The kinetic behaviour of dissolution and precipitation of solid phases is not considered in chemical equilibrium computations to predict changes in the phase assemblage in cement-based material. Additionally, dissolution and precipitation reaction rates are assumed to be equal for all hydrated solid phases.
- The assumption is made that chemical equilibrium between the gaseous phase in pores, pore solution, and hydrated solid phases is achieved within the assigned time step calculation.

• The mass transport calculation does not consider phase assemblage and porosity changes. However, at the end of each time step of chemical equilibrium calculation, the porosity changes corresponding to phase assemblage changes are implicitly considered in the subsequent mass transport calculation.

Impact of climate change analyses

- To study the impact of climate change on cement-based material exposed to seawater, two environmental climate parameters, i.e., salinity and temperature of seawater, were selected for the Monte-Carlo simulation.
- To study the impact of climate change on the carbonation of cement-based material exposed to atmospheric conditions, three environmental climate parameters, i.e., CO_{2(g)} concentration, temperature, and relative humidity were chosen for the Monte-Carlo simulation.
- The uncertainty of other climate projections, such as wind speed, wind direction, and precipitation, are not included in the impact of climate change analyses.
- Based on the complex mechanism of boundary conditions, the impact of climate change on the deterioration of concrete under other environmental conditions, such as tidal and splash zone offshore concrete structures, was not included in the present study.

1.9 Outline of the thesis

The thesis consists of nine chapters, including three appended papers. These chapters address concrete deterioration modeling, the effects of climate change on concrete deterioration, critical climate projections for concrete deterioration, and adaptation to climate change. A list of the chapters comprising the core of this thesis and its publications is given below.

Chapter 1 describes the background of the project, the aim and objectives of the thesis, the hypotheses and challenges of the research, and the general methodology used throughout the investigation.

Chapter 2 introduces concrete deterioration mechanisms under various environmental conditions, including the processes of reinforcement corrosion, associated reaction equations, and the dissolution and precipitation of solid phases. Chapter 3 describes the development of an RTM, including mass transport coupled with chemical equilibrium under different environmental conditions, such as submerged conditions (Paper I), cyclic drying and wetting conditions (Paper II), and atmospheric conditions (Paper III) to predict the durability of cement-based materials.

Chapter 4 demonstrates the applicability of the developed RTM to predict concrete deterioration under actual environmental conditions, where concrete is exposed to natural field conditions, comparing predicted results with experimental data obtained from two field stations, *i.e.*, Solsvik field station in Norway and Rødbyhavn field station in Denmark.

Chapter 5 outlines past and recent drivers of climate change, observed changes in the climate system, and future climate changes for different scenarios.

Chapter 6 highlights the impact of future climate change on concrete deterioration under different environmental conditions and sensitivity indices analysis to determine the critical climate projection for concrete deterioration.

Chapter 7 presents the adaptation methods to climate change based on predicted results from Chapter 6 and outlines limitations in current specifications for designing concrete structures to withstand climate change in selected case study locations, including the Solsvek and DTI field stations.

Chapter 8 comprises a summary of the discussions presented in Chapter 2 to Chapter 8, discusses research areas within the scope of this investigation where further work is needed, and the conclusions of the present study.

2 Mechanisms of concrete deterioration

Chapter 2 presents the mechanisms of reinforced concrete deterioration, focusing on chloride- and carbonation-induced corrosion. This chapter provides details of the chemical reactions that occur during the deterioration of cement-based materials due to interactions with the service environment. It also explores how these reactions affect the phase assemblage through the dissolution and precipitation of hydrated solid phases, along with changes in pore solution composition. Additionally, it briefly covers half-cell formation for corrosion initiation on the reinforcement surface and reactions in the cathode and anode cells.

2.1 Concrete exposed to seawater

For civil infrastructure in marine environments such as buildings, bridges, offshore platforms, and harbours, reinforced concrete materials are widely recommended based on cost and the most accessible construction. However, the service life of reinforced concrete structures in marine environments is shortened due to the penetration of chemical substances from the environment into the concrete, which is increasingly decisive for structural design, particularly in marine environments [57-60]. In marine environments, chloride-induced reinforcement corrosion and erosion of surface material are identified as the leading deterioration mechanisms [58,61–63]. Chloride ions alone in the exposure solution are not a threat to concrete. It is important to note that chloride ions in seawater are accompanied by other ions, including sodium, potassium, magnesium, carbonate, and sulfate ions, which are potentially aggressive to the concrete itself. These ions can impact chloride ingress by influencing the chloride-binding capacity of the paste, affecting the porosity of the concrete cover, or contributing to the deterioration of the concrete cover. Chloride profiles provide information about the concrete's overall chloride content at various depths from the exposed surface. As a result of exposure to seawater, chloride ions from the seawater start to penetrate the concrete through the exposed surface. In exposed concrete, a part of the transported chloride is physically absorbed by the silanol sites of the C-S-H phase, while a part is chemically bound and forms reaction products such as Friedel's salts or Kuzel's salt. At the same time, the remaining chloride exists as free chloride in the pore solution [58,61,63–65]. Free chloride ions in pore solution only move through the pores. The capacity of concrete to bind chlorides might decrease the amount of chloride in the pore solution, slowing down chloride ingress.

In order to ensure an adequate service life, such concrete structures must be planned and constructed with sufficient concrete cover thickness to protect the reinforcement throughout the intended service life and/or use proper binder compositions with high chloride ingress resistance. Therefore, understanding the governing mechanisms behind the deterioration of concrete under seawater exposure in marine environments has received much attention over the last few decades, as it is crucial for maintaining the prolonged and sustainable serviceability of concrete structures along with climate change.

2.1.1 Phase assemblage due to seawater exposure

The deterioration mechanism in concrete exposed to seawater can be understood through changes in the phase assemblage. Fig 2.1 shows a schematic summary of the zonation in concrete near the surface caused by seawater exposure, together with the related elemental profiles and observations acquired with Scanning Electron Microscopy - Energy Dispersive Spectroscopy (SEM-EDS) and light microscopy. Close to the exposure surface, elemental zonation in concrete can be observed, which is caused by variations in ion mobility and the solubility of reaction products [61]. In all concrete exposed to seawater, the same type of zonation near the surface, which is related to seawater ingress, is identified [61]. Furthermore, near-surface zonation is distinguished into three zones: magnesium-rich, sulfurrich, and chlorine-rich, based on variations in the elemental profile. Although the zones generally follow one another, it is common to see a slight overlap between the sulfur-rich and chlorine-rich zones.



Fig 2.1. Schematic overview of the different zones and the corresponding observations using light microscopy and SEM–EDS, e.g., from [61]. C–S–H: calcium silicate hydrate, M–S–H: magnesium silicate hydrate, MH: magnesium hydrate, and CC: calcium carbonate.

The chlorine-rich zone occurs at the end of the sulfur-rich zone, whereas chloride enrichment near the exposed surface is not observed in Fig 2.1. In the chlorinerich zone, chlorides are bound in calcium chloroaluminate hydrates such as Friedel's salts (see Eq 2.1) or Kuzel's salt (see Eq 2.2) or in various solid solutions between sulfate or carbonate AFm and chloride AFm [66,67]. Moreover, they can be adsorbed onto the C–S–H [63,68]. As a result of the low chloride-binding capacity of M–S–H and the higher solubility of AFm due to the low pH, low chlorine content might be observed in the magnesium-rich zone. As a result of the higher interaction between sulfates and both AFm and C-S-H in the sulfur-rich zone, chloride binding in the paste decreases within this zone. [68]. The beginning of the chloride enrichment zone depends on the region of the sulfur-rich zone, and the highest level in the chloride profile is observed just after the sulfur-rich zone. After that, the chlorine concentration gradually decreases in deeper depth from the exposed surface (see Fig 2.1).

$$C_{3}A_{(s)} + Ca(OH)_{2}_{(s)} + 2Cl_{(aq)} + 10H_{2}O_{(l)}$$

$$\rightarrow C_{3}A \cdot 3CaCl_{2} \cdot 10H_{2}O_{(s)} \text{ (Friedel's salt)} \qquad \text{Eq 2.1}$$

$$+ 2(OH)^{-}_{(aq)}$$

$$C_{3}A_{(s)} + 0.5Ca(OH)_{2}_{(s)} + 0.5CaSO_{4}_{(s)} + 2Cl_{(aq)} + 10H_{2}O_{(l)}$$

$$\rightarrow C_{3}A \cdot (CaCl_{2})_{0.5} \cdot (CaSO_{4})_{0.5}$$

$$\cdot 10H_{2}O_{(s)} \text{ (Kuzel's salt)}$$

Eq 2.2

Due to the concrete exposed to seawater, sulfate attack might be possible in regions close to the exposed surface. The interaction between the transported sulfate ions from seawater and the dissolved calcium hydroxide in the pore solution leads to the formation of gypsum (see Eq 2.3), and subsequently, in the presence of aluminate, the produced gypsum transforms into the ettringite phase near the exposed surface (see Eq 2.4). Furthermore, due to the higher molar volume of Ettringite, its formation can increase the solid volume, potentially leading to expansion and cracking [69,70]. In addition, the presence of gypsum and the Ettringite phase limits chloride binding [67,68,71].

$$SO_{4}^{2-}(aq) + Ca(OH)_{2(s)} \rightarrow CaSO_{4(s)} + 2(OH)^{-}(aq)$$
 (gypsum) Eq 2.3

Due to the concentration gradient between the seawater and the pore solution, magnesium is transported into the concrete, forming brucite in regions with highly alkaline pore solutions (see Eq 2.5). The brucite layer on the surface of the concrete might function as an impermeable and potentially concrete-protecting layer. However, the brucite layer is not dense enough to protect the underlying concrete due to a shortage of calcium hydroxide, a high water-cement ratio, or potential damage from mechanical activity such as erosion or abrasion. This might lead to the formation of non-cementing magnesium silicate hydrate (see Eq 2.6) as a result of the magnesium in the seawater reacting with the C-S-H phase through ion exchange between the Mg²⁺ ion and the Ca²⁺ in the C-S-H [72–75]. Elemental maps demonstrate that the magnesium-enriched zone has experienced considerable decalcification of hydrated solid phases and ion leaching (see Fig 2.1). This shows that magnesium was incorporated after the decalcification of the C–S–H phase near the exposed surface.

$$Mg^{2+}_{(aq)} + Ca(OH)_{2(s)} \rightarrow Mg(OH)_{2(s)} + Ca^{2+}_{(aq)}$$
 (brucite) Eq 2.5

$$Mg^{2+}_{(aq)} + CSH_{(s)}(decalcified) Eq 2.6$$

$$\rightarrow MSH_{(s)} + Ca^{2+}_{(aq)} (magnesium silicate hydrate)$$

A thin, dense crust layer on the exposure surface was observed on several exposed concrete in marine environments. In the concrete structure, the carbonates involved in crust development might originate from the air as well as from seawater [61]. The transported carbonates from seawater react with the phases of concrete that contain calcium, forming calcium carbonate in addition to creating a crust on the exposed surface (see Eq 2.7). Between the Mg-rich and the S-rich zones, a particular calcite morphology known as popcorn carbonation is usually found (see Fig 2.1). The C-S-H gel 'splits' into relatively large popcorn-like calcite clusters during the popcorn carbonation, along with a decalcified interstitial silicate-rich gel phase that frequently contains traces of Na and K. The formation of calcium carbonate may have a sealing effect near the exposed surface, delaying corrosion initiation. Additionally, the carbonates in the hydrated paste decrease the concrete paste's ability to bind chlorides [67,71].

$$H_2CO_{3(aq)} + Ca(OH)_{2(s)} \rightarrow CaCO_{3(s)} + H_2O_{(l)} \text{ (carbonate)}$$
Eq 2.7

The presence of sulfur and carbonate in concrete can cause the C-S-H phase to transform into thaumasite (see Eq 2.8) at lower temperatures (below 15 $^{\circ}$ C) [76,77].

$$CaCO_{3(s)} + CaSO_{4(s)} + CSH_{(s)} + H_2O_{(l)}$$

$$\rightarrow CaCO_3 \cdot CaSO_4 \cdot CaSiO_3 \cdot 15H_2O_{(s)} \text{ (thaumasite)} \qquad \text{Eq 2.8}$$

Sodium content in exposed concrete shows a particular behaviour, with enrichment in sodium observed in several exposed concrete samples. As a result of the decalcification of the C-S-H paste, it is predicted that only alkali aluminum silicates such as natrolite (see Eq 2.9) or a zeolitic phase (see Eq 2.10 and Eq 2.11) will form near the exposed surface [65,78]. This would be consistent with the sodium enrichment resulting from seawater exposure. Apart from the effects of the ingress of seawater ions such as chloride, sodium, sulfate, carbonate, and magnesium ions, the leaching of ions through the exposed surface will also effectively disrupt the phase assemblage of concrete. The dissolution of Portlandite and decalcification of the C–S–H phase occur as a result of the leaching of calcium and hydroxyl ions through the exposed surface [58,61,75].

$$2\text{AlO}_{2}^{-} + 2\text{Na}^{+} + 3\text{SiO}_{2} + 2\text{H}_{2}\text{O} \rightarrow \text{Na}_{2}\text{Al}_{2}\text{Si}_{3}\text{O}_{10} \cdot$$
Eq 2.9
2H₂O_(s) (natrolite)

$$2\text{AlO}_{2}^{-} + 2\text{Na}^{+} + 4\text{SiO}_{2} + 8\text{H}_{2}\text{O} \qquad \text{Eq 2.11}$$

$$\rightarrow \text{Na}_{2}\text{Al}_{2}\text{Si}_{4}\text{O}_{12} \cdot 8\text{H}_{2}\text{O}_{(s)} \text{ (zeolite Y)}$$

Over the last few decades, changes in the phase assemblage have been investigated using thermodynamic modeling to further understand the performance of concrete under seawater exposure. Using thermodynamic modeling, the predicted result of the effect of seawater on the solid hydrates phase is shown in Fig 2.2. The phases on the right side show the paste composition in the unaffected portion of the mortar, while the left side presents predicted results of the impact of adding more seawater on the formed hydrates, representing the gradual changes that occur closer to the exposed surface. The predicted phase composition for the non-exposed core of the sample consists of C-S-H, portlandite, ettringite, monocarbonate, siliceous hydrogarnet, and calcium carbonate. Due to concrete exposure to seawater, Friedel's salt phase forms to replace existing monocarbonate in the phase assemblage. The portlandite phase completely decomposes with higher seawater levels, and at the same time, a continuous increase in the total phase volume is observed in the predicted result. This results from the precipitation of additional phases, including ettringite, calcite, and brucite, due to the presence of sulfate, carbonate, and magnesium in the seawater. Due to a higher level of seawater exposure, the primary components in the phase assemblage, such as C-S-H and ettringite, begin to decompose completely, reducing the total volume of phases. Meanwhile, the formation of more M-S-H, hydrotalcite, brucite, and calcite is predicted in the phase assemblage.



Fig 2.2. Predicted volume of the phases in mortar upon exposure to increasing amounts of seawater in $[cm^3/100 \text{ g cement}]$ [65].

2.1.2 Chloride-induced corrosion

The formation of a thin passive layer on the surface of the reinforcement in reinforced concrete, as a result of the high pH (>12) in the pore solution, protects the reinforcement from corrosion while oxygen and water are present [79-81]. During concrete exposure to seawater, chloride ions start to ingress through pores into the concrete, and once a critical amount of chloride content is reached, also referred to as the critical chloride threshold, the formed passive layer is destroyed, and reinforcement corrosion is initiated in the presence of moisture and oxygen [82,83]. Chloride ingress into concrete is typically assessed by examining chloride profiles and analysing the chloride concentration at a depth of the reinforcement. The carbonation of concrete may further accelerate the dissolution of the passive layer by lowering the pH of the concrete [84–87]. The critical chloride threshold depends on many factors, such as the mix proportion of concrete, the chemical composition of the binder, pore solution composition, temperature, and construction process quality [88–91]. Generally, the critical chloride threshold is determined experimentally to predict reinforcement corrosion initiation due to seawater exposure [92,93].

The appearance of the surface of reinforced concrete after corrosion products is shown in Fig 2.3a. An overview of the electrochemical and physical mechanisms that lead steel to corrode in concrete is shown in Fig 2.3b. On the surface of the

reinforcement, two electrochemical half-cell reactions occur, *i.e.*, the anodic (oxidation) and the cathodic (reduction) half-cell reaction. Electrons are liberated during the anodic half-cell reaction by an electrical potential difference between the anode and cathode sites and subsequently pass through the steel to the cathode. In the cathodic half-cell reaction, the transported electrons are consumed. Finally, the ionic exchange process through the pore solution is needed to complete the electrical circuit. The anodic half-cell reaction, which may be stated as follows, is typically thought to represent the mechanism for the oxidation of iron.

$$Fe \rightarrow Fe^{+2} - 2e^{-}$$

$$Fe^{+2} + 2(OH)^{-} \rightarrow Fe(OH)_{2}$$

$$Eq 2.12$$

$$4Fe(OH)_{2} + 2H_{2}O + O_{2} \rightarrow 4Fe(OH)_{3}$$

At the cathode, the reduction of oxygen is commonly assumed, which can be given as follows:

$$0.50_2 + H_20 + 2e^- \rightarrow 2(0H)^-$$
 Eq 2.13

Due to the presence of chloride, chloride-induced corrosion at the steel surface involves the following reaction:

$$Fe^{+2} + 2Cl^- \rightarrow FeCl_2$$

 $FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$
Eq 2.14



Fig 2.3. Chloride-induced corrosion in concrete structures: (a) corrosion of steel reinforcement [82], and (b) overview of electrochemical and physical processes describing steel corrosion in concrete [94].

2.2 Concrete carbonation

Due to concrete exposure to atmospheric conditions, $CO_{2(g)}$ starts to transport into the concrete through the pore void by a partial pressure gradient of $CO_{2(g)}$ as well as total pressure differences, and simultaneously transported $CO_{2(g)}$ gas dissolves into the pore solution. The process of dissolved carbonates reacting with the hydrated solid phase is known as the carbonation of concrete. The carbonation of concrete depends on several factors such as porosity, saturation level, the diffusion coefficient of $CO_{2(g)}$, temperature, the chemical composition of pore water, and the dissolution rate of hydrated phases [95–98]. Once $CO_{2(g)}$ enters cement-based materials at pH > 10, gaseous $CO_{2(g)}$ starts to dissolve into the pore solution, after which it transforms into bicarbonate (HCO₃⁻) and carbonate ions (CO_{3}^{2-}) [99,100].

$$\text{CO}_2 + (\text{OH})^- \rightarrow \text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}^+$$
 Eq 2.15

At a lower pH value (pH < 8), $CO_{2(g)}$ gas dissolves and produces carbonic acid H_2CO_3 directly, which can subsequently dissociate into HCO_3^- and CO_3^{2-} ions at higher pH. [101].

$$CO_2 + H_2O \rightarrow H_2CO_3$$
 Eq 2.16

Since $CO_{2(g)}$ dissolves into the pore solution at pH 8–10, both mechanisms are possible [102,103]. Carbonation in concrete material is identified as a reactive transport process that depends on the internal conditions of the concrete (*e.g.*, pH, temperature, and super-saturation) [101], as well as the presence of contaminants

(a)

or additives [104–106]. The diffusion of gaseous $CO_{2(g)}$ is reduced by the saturation level of water in pores. At the same time, the potential of carbon dioxide for dissolution and reaction with ionic species in the pore solution is also subject to water availability in the pores [103]. Furthermore, during the carbonation process in concrete, the pH value starts to drop with the rapid dissolution of gaseous $CO_{2(g)}$ into the alkaline pore solution [102]. As a result of the change in the alkaline environment in the pore solution, the passive layer becomes unstable [80,102,107], which is one of the major issues with the long-term durability of concrete structures [108–110].

2.2.1 Phase assemblage due to carbonation

To understand the pH variations in pore solution and the order of destabilization of the various solid phases, several studies can employ thermodynamic modeling of cement-based material carbonation. The thermodynamic modeling results are shown in Fig 2.4 and illustrate the phase assembly of white Portland cement as a function of the quantity of $CO_{2(g)}$ that has interacted with the cement paste, as well as the accompanying drop in pH and the Ca/Si ratio of the calcium silicate hydrate (C-S-H). In both Fig 2.4(a) and (b), the unaffected portion of cement paste by carbonation is shown on the right-hand side, moving to the left as more $CO_{2(g)}$ reacts with the hydrated solid phase. The following steps can explain the carbonation of concrete: Initially, the monosulfate and hemicarbonate phases that may be present will destabilize to monocarbonate, causing minor changes in the solid volume [111,112]. The first major hydrated product in the cement-based material to decompose into calcium carbonate during carbonation is identified as portlandite, which results in a minor volume increase since calcite has a larger molar volume than portlandite, whereas the pH value is stable at approximately 12.5 [113,114]. Once all the portlandite is consumed by carbonation, the C-S-H phase begins to decalcify down to a Ca/Si ratio of 1.3. At the same time, the pH slightly decreases throughout this procedure. This decalcification process is not accompanied by any significant volume changes [111,115,116]. The monocarbonate phase in cementbased material decomposed into stratlingite, which consumes the silicon and aluminium released from C-S-H. The same Ca/Si ratio is maintained by continued consumption of C-S-H. Furthermore, the solid volume also changes as a result of this interaction. Monocarbonate has a larger molar volume than stratlingite; however, this is balanced by the production of calcium carbonate and consumption of C-S-H. Following the consumption of monocarbonate, the C-S-H continues to decalcify and decompose until its Ca/Si and pH reach 0.75 and 11, respectively. As

a result of the decalcification of C-S-H, the largest pH drop occurs in the pore solution. At a pH of about 10, ettringite decomposes after all the stratlingite is consumed. The formation of zeolites and gypsum bound the released aluminium and sulphur, respectively. At the same time, the pH value in the pore solution is decreased to 10 while the C-S-H decalcifies to a Ca/Si ratio of around 0.67. Further carbonation results in the decomposition of C-S-H into calcite and hydrated amorphous silica, and the pH decreases rapidly from 10 to 8.5. In the end, hydratelicite decomposes at a pH value of about 8.5.



Fig 2.4. Results of thermodynamic modeling: (a) the phase assemblage during carbonation of a white PC w/b = 0.5 and degree of hydration 90%, and (b) changes of pH and Ca/Si of the C–S– H during carbonation [117].

As a result of carbonation, the solid phases undergo variations that also affect the pore structure and the chemical composition of the pore solution. Thermodynamically predicted changes in the pore solution composition upon carbonation of CEM I_{0.55} mortar exposed to 1% $CO_{2(g)}$ and 60% RH is presented in Fig 2.5. Since more alkali ions (Na⁺ and K⁺) are sorbent by the decalcified C-S-H phase than the non-decalcified C-S-H phase, the concentration of alkali metal ions in the pore solution decreases during the carbonation process [78]. Due to carbonation, the sulphate concentration in the pore solution increases as a result of the decomposition of the Ettringite phase [102]. Due to carbonation, along with chloride ingress into concentration in the pore solution increases due to the decomposition of Friedel's salt and the C-S-H phase [118–120]. However, no chloride concentration increases are
found in the model prediction result (see Fig 2.5). This might be explained by thermodynamics, not including the release of physically absorbed chloride by C-S-H and monocarbonate phases on the pore surface.



Fig 2.5. Modelled changes in the pore solution composition (mmol/l) upon carbonation of CEM $I_{0.55}$ mortar under the 1% $CO_{2(g)}$ and 60% RH exposure condition [102].

2.2.2 Carbonation-induced corrosion

In concrete structures located in urban areas, one of the primary causes of reinforced concrete deterioration is carbonation-induced corrosion. In reinforced concrete, the carbonation process significantly reduces the pH value and changes the composition of the pore solution. Consequently, when the molar ratio between certain ionic components goes above or below the threshold values, the passive film formed on the reinforcement surface will be destroyed [121–123]. As the volume of precipitated corrosion products is larger than the initially consumed steel, the concrete around the reinforcement starts to crack and potentially delaminate. As cracks become more severe, spalling occurs, the concrete cover is pushed off, and the rebar becomes completely exposed, further accelerating the corrosion process, see Fig 2.6a.



Fig 2.6. Carbonation-induced corrosion in concrete structures: (a) corrosion and spalling of a concrete cover section by corrosion products [124], and (b) overview of carbonation caused by the penetration of $CO_{2(g)}$ and water [94].

Due to the carbonation of cement-based material, the pore solution composition in concrete plays an essential role in corrosion initiation and propagation. Complex interactions exist between the ions in the pore solution of carbonated concrete and steel reinforcement. Higher concentrations of chlorides and sulphates can accelerate the corrosion rate of carbon steel compared to hydroxyl concentrations and lower carbonate concentrations compared to bicarbonate concentrations in the pore solution. During the carbonation of concrete, the threshold value for corrosion initiation is defined by different molar ratios [102]. For CEM I_{0.55}, Fig 2.5 shows the predicted changes in $[Cl^-]/[(OH)^-]$, $[SO_4^{2--}]/[(OH)^-]$, and $[CO_3^{2--}]/[HCO_3^-]$ molar ratios, as well as the concentration of carbon (C) in the pore solution upon carbonation with and without zeolite formation. Zeolite formation is included in the model results as dashed lines, solid lines in the model where zeolite formation is suppressed, and dotted lines in the literature-based corrosion thresholds $[Cl^{-}]/[(OH)^{-}] > 0.6 [125], [SO_{4}^{2-}]/[(OH)^{-}] > 1.5 [126], and [CO_{3}^{2-}]/[HCO_{3}^{-}]$ >0.1 [127]. In the pore solution of non-carbonated mortar, the molar ratios of $[Cl^{-}]/[OH^{-}]$ and $[SO_{4}^{2-}]/[OH^{-}]$ are below the corrosion threshold levels. However, the pore solution mainly contains carbonates, leading to an exceptionally high $[CO_3^{2-}]/[HCO^{3-}]$ ratio. During the carbonation of mortar, the thermodynamically predicted results indicate that the molar ratios of [Cl⁻]/[OH⁻] and [SO₄²⁻]/[OH⁻] start to increase above the threshold values of 0.6 and 1.5, respectively, while $[CO_3^{2-}]/[HCO^{3-}]$ decreases below the threshold value of 0.1. Consequently, these changes are anticipated to accelerate the corrosion of reinforcement. In addition, the region where the molar ratio changes upon carbonation of mortar is consistent with the carbonation depth, and the pH value drops. During the carbonation of cement-based material, similar anodic and cathodic half-cell reactions are observed as mentioned in Eq 2.9 and Eq 2.10, respectively.



Fig 2.7. Modelled changes in the $[Cl^-]/[(OH)^-]$, $[SO_4^{2--}]/[(OH)^-]$, and $[CO_3^{2--}]/[HCO_3^-]$ molar ratios and the carbon (C) concentration in the pore solution upon carbonation of CEM I_{0.55} mortar under 1% CO_{2(g)} and 60% RH [102].

3 Development of a multi-species reactive transport model

Chapter 3 introduces the theoretical background of transport models and the development of a multi-species reactive transport model for cement-based material, along with a definition of the relevant boundary conditions for different environmental conditions. Furthermore, the chapter presents a detailed description of a proposed reactive transport model, including mass transport coupled with chemical equilibrium to predict the deterioration of cement-based materials through pore solution and phase assemblage changes.

3.1 Overview of numerical models for predicting deterioration of concrete

Over the last few decades, there has been an increasing interest in models for evaluating and predicting the long-term durability of reinforced concrete structures exposed to severe environmental conditions. Such models have primarily been based on numerical transport models capable of predicting changes in concrete materials over the service life and may help select the cement composition and mix design and develop optimal maintenance and replacement strategies.

3.1.1 Modeling chloride penetration in concrete

Chloride ions in the pore solution are mainly transported into the concrete through pore spaces in the hydrated cement paste as well as through cracks. The transport of chloride ions into the concrete can be limited by considering different physical and chemical approaches. Chloride ingress in concrete depends on the concentration gradient and advection of moisture transport inside concrete material, service environmental conditions such as temperature and relative humidity, pore distribution, formed crack width, saturation degree, etc. The transportation of chloride ions into concrete is typically not the result of a single process because of the wide range of pore sizes and the fluctuating moisture content in the concrete as a result of the exposure conditions. Chloride can be transported into concrete using a combination of diffusion, permeation, and capillary sorption to move through pores caused by pressure gradients, chloride ion concentration gradients, and capillary sorption. Generally, empirical models for chloride penetration are underpinned by diffusion theories or Fick's law and connected with wide-ranging mathematical functions from laboratory works or field studies of existing reinforced concrete structures.

3.1.1.1 Chloride transport in concrete based on Fick's second law

Chloride ion transport into concrete is a non-steady state process that changes with time and space. Using Fick's second law, the non-steady-state diffusion processes of chloride ions are given in Eq 3.3.

$$\frac{\partial (C_{cl(x,t)})}{\partial t} = D_{cl(x,t)} \frac{\partial^2 (C_{cl(x,t)})}{\partial x^2}$$
Eq 3.1

Where, $C_{cl(x,t)}$ is the chloride concentration at depth (x) and time t, $D_{cl(x,t)}$ is the diffusion coefficient for the x-direction with the time, t. It is widely known that the chloride transport process into concrete is significantly influenced by binding capacity, chloride diffusivity, pore structure, and water content. Under typical circumstances, chloride transport in cementitious materials is an advection-diffusive phenomenon. Maekawa *et al.* [128] proposed a chloride transport model considering advection transport due to bulk movement as well as ionic diffusion due to concentration gradients. In this model, the chloride-binding model describes the equilibrium between chloride ions and bound chlorides, which is modelled as a non-linear function based on Langmuir's equation and calibrated with experimental results.

$$\frac{\partial(\phi SC_{cl})}{\partial t} + divJ_{Cl} - Q_{Cl} = 0$$
Where: Eq 3.2
$$J_{Cl} = -\left(-\frac{\phi S}{\Omega}\delta D_{Cl}\nabla C_{Cl} + \phi Su\nabla C_{Cl}\right)$$

Where
$$C_{cl}$$
 is the concentration of chloride ions in the pore solution, and J_{cl} is the total flux of chloride ions, and Q_{cl} is a sink term. The proposed method is restricted to chemical equilibrium and transport only connected to chloride. However, the movement and leaching of other cementitious ions can speed up concrete deterioration and disrupt its pore solution and phase assemblage. Furthermore, Lang-

muir's chloride binding equation varies with the binder composition type and exposure time. Therefore, it is hard to define the binding of chloride with Langmuir's equation.

3.1.1.2 Reactive transport model for chloride transport

Over the last decades, several numerical models have been developed to predict deterioration of cement-based material. Initially, such models were developed only considering multi-ionic transport [129–132]. Later, multi-ionic transport models were coupled with chemical equilibrium [133–136]. Currently, RTMs have been developed, including a multi-ionic mass transport model coupled with a chemical equilibrium, including surface complexation [137,138]. Here, the interactions between the pore solution and solid phases and the interactions between the C-S-H phase and the surrounding ions of the pore solution were included. In current RTMs, the Poisson-Nernst-Planck (PNP) equation derived using the hybrid mixture theory [139,140] is commonly used for the multi-ionic transport model in porous media. Among others, PHREEQC [141–143] is often adopted to perform chemical equilibrium between pore solution and solid phases, including surface complexation. In the current modeling approach, the governing equation for the multi-ionic transport through the pore solution is described by an extended version of the PNP equation as follows [133–135].

$$\begin{split} \epsilon^{l} \frac{\partial \left(c_{j}^{l}\right)}{\partial t} + c_{j}^{l} \frac{\partial \epsilon^{l}}{\partial t} \\ &= \nabla \cdot \left(D_{j}^{l} \epsilon^{l} \nabla c_{j}^{l} + D_{j}^{l} c_{j}^{l} \nabla \epsilon^{l} - A_{j}^{l} z_{j} \epsilon^{l} c_{j}^{l} \nabla \Phi\right) + V^{l,s} \epsilon^{l} \nabla c_{j}^{l} \quad \text{Eq 3.3} \\ &+ V^{l,s} c_{j}^{l} \nabla \epsilon^{l} + q_{j}^{g}; \end{split}$$

where c_j^l is the concentration of j^{th} species in the liquid phase, D_j^l is the effective diffusion coefficient of species j in the liquid phase, A_j^l is the ionic mobility of species j in the liquid phase, z_j is the valance of j^{th} species; Φ is the electrical potential, $V^{l,s}$ is the liquid velocity relative to the solid, q_j^g is the mass exchange term for chemical interactions between the species, and N is the total number of constituents in the liquid phase. In a cement-based material, an electrical double layer (EDL) will form on the pore surface due to interactions between the surface site of the C-S-H phase and the surrounding ions of the pore solution. As a result of the EDL formation, the diffusion of anions and cations will take a different pathway in the pore solution. Most of the anions diffuse through free water space, while the diffusion of cations occurs through the EDL [138,144,145]. In the current RTMs [133–135], the ion mass transport is performed only through free water space, whereas the ions in the EDL are considered stagnated ions, which means that part of the cations is neglected in the ion mass transport calculation. In addition, the ion mass transport in porous materials strongly depends on temperature [146], composition and ionic strength of pore solution [147,148], and pore structure [149,150]. Pore solution composition, phase assemblage, and pore structure will continuously vary in a cement-based material due to exposure to long-term environmental actions. The traditional PNP equation does not consider the effect of these changes. Moreover, most approaches accounting for surface complexation assume a fixed specific surface area of the C-S-H phase in cement-based materials over time [149]. Due to the reaction between pore solution and solid hydrated phases, the formation of new phases, as well as the precipitation and dissolution of solid hydrated phases, occur on the pore surface. As a result, the specific surface area of the C-S-H phase on the pore surface continuously changes in cementitious materials. Therefore, the ion absorption capacity of the pore surface by the silanol sites (\equiv SiOH) varies over time. Without considering these interactions, the predictive capabilities of such modeling approaches will always be limited.

In order to accurately predict the durability of cement-based materials exposed to various environmental conditions, RTMs should be developed with the following considerations: i) the flux of ions in both free water and the EDL must be considered for the actual multi-ionic transport calculation through a charged surface, ii) the effect of temperature, pore solution property, and pore structure changes must be accounted for in ion transport through a porous medium, iii) the exchange reaction between an ion in the pore solution and silanol sites (\equiv SiOH) needs to be included in the ion absorption on the pore surface in the surface complexation model, and v) for computation of the variation of the specific surface area of the C-S-H phase and the effect of pore structure changes on ion mass transport, a proper micro-pore structure model must be adapted as part of RTMs. Based on these perspectives, the development of a multi-species reactive transport model based on ion-solid phase interaction for saturated cement-based materials is presented in **Paper I**.

Over the last few decades, many studies have focused on developing RTMs for predicting concrete deterioration through changes in the composition of pore solution and phase assemblage due to the ingress of ions into concrete under submerged conditions [133,138,151,152]. However, only a few numerical modeling studies

based on the concept of multi-species and moisture transport coupled with chemical equilibrium were conducted for concrete in unsaturated conditions [135,153– 155]. Moreover, current modeling approaches are limited by considering simplified assumptions about the processes involved in the deterioration of cement-based materials under cyclic wetting and drying conditions, for example, the relationships between mass transport and moisture saturation in pores, chloride binding isotherm mechanisms due to the interaction between pore solution and solid phase, mass flux through boundary surfaces, and the integration effect of boundary condition. Also, the predictive capabilities of these modeling approaches are often limited due to the lack of fundamental relationships between phase assemblage changes, pore structure changes, and mass transport through pores. Using the current RTM [152], the leaching or ingress behaviour of ions in concrete exposed to saturated conditions can be adequately explained based on the ionic concentration gradient in the pore solution. However, predicting the leaching or ingress behaviour of ions in concrete exposed to cyclic wetting and drying conditions becomes challenging due to the complex interaction between ionic diffusion and moisture transport. Hence, current models are often inadequate for accurately predicting the changes in the composition of pore solutions and phase assemblage of cementbased materials under cyclic wetting and drying conditions. Due to the lack of a comprehensive conceptual explanation for the coupling of multi-ionic transport and moisture transport, the combined effect of moisture transport and electrochemical potential force on multi-ionic transport under unsaturated conditions is still unclear.

To achieve this objective, the reactive transport framework presented in **Paper I** should be extended to account for the deterioration of cement-based material, including moisture transport, and the effect of moisture fluctuation inside pores on multi-ionic transport. Moreover, chemical equilibrium calculations must include the equilibrium between the aqueous species in the pore solution, hydrated solid phases, and ionic absorption on the pore surface. A surface complexation model should be employed in the RTM framework to accurately replicate the chloride isotherm behavior, which includes forming an electrical double layer and exchanging interactions among the ionic solution in pores and the C–S–H surface site (\equiv SiOH). For interconnecting phase assemblage, pore structure, and mass transport, models for moisture conductivity and ionic diffusivity based on the pore structure and moisture distribution in pores must be adapted in the RTM framework. Based on these perspectives, the enhancement of a multi-species reactive transport model for cement-based materials under cyclic wetting and drying conditions is presented in **Paper II**.

3.1.2 Modeling carbonation of concrete

Due to the combination of gas and liquid transport into cement-based material under atmospheric conditions, modeling the carbonation process in cement-based material is generally quite complicated. The parameters influencing concrete carbonation can be divided into internal and external factors. The temperature, relative humidity, and $CO_{2(g)}$ concentration in the atmosphere are some examples of external factors, whereas internal factors are connected to concrete properties [156,157]. According to experiments using accelerated carbonation, a rise in $CO_{2(g)}$ concentration causes a greater depth of carbonation in concrete [128,158]. The highest rate of carbonation depth in mortar specimens is found for humidity between 40 and 60%, while a limited carbonation rate occurs for high or low relative humidity. Considerable reductions in carbonation depth are observed at relative humidity above 70%. It is confirmed that increased moisture storage inside the pore limits $CO_{2(g)}$ transport through accessible pore void spaces. Furthermore, specimens with different water-cement ratios exhibit a steady increase in the carbonation depth with temperature increases for 50% relative humidity [159]. Due to increases in both molecular activity and a faster rate of reactivity between the carbonate ions CO_3^{2-} and Ca^{2+} in the pore solution of concrete, as well as the diffusion of gaseous $CO_{2(g)}$ The carbonation rate steadily increases with temperature in exposed concrete through pore voids and carbonate ions through pore solution [47]. The mechanism of carbonation that will occur in the hydrated cement phase depends on the diffusion of $CO_{2(g)}$ gas and its dissolution process within the pore solution. The diffusion of carbon dioxide is mainly controlled by the concentration gradient, total pressure differences, pore structure of concrete, and saturation level of pore water in pores [128,157,160]. In order to predict the depth of carbonation in concrete, several models based on both concrete properties and exposure conditions have been proposed over the last few decades. The models for predicting the carbonation depth that are primarily based on Fick's laws are known as CO_{2(g)} diffusivity-based models. The following subsections provide a brief overview of such models based on Fick's laws.

3.1.2.1 Carbonation in concrete based on Fick's first law

In the early stages of modeling carbonation depth, the diffusion of $CO_{2(g)}$ gas through pores into concrete is considered based on Fick's first Law. Furthermore, in the condition where the steady state of diffusion of $CO_{2(g)}$ mass transport is driven by a concentration gradient [113,161]; the carbonation depth (C_{depth}) can be given by Eq 3.4.

$$C_{depth} = K\sqrt{t}$$
 Eq 3.4

Where K is the carbonation rate, and t is the exposure time. In this simplified model, the external and internal parameters, such as exposure conditions ($CO_{2(g)}$ concentration, temperature, and relative humidity at the boundary surface), pore structure, the reaction rate of $CO_{2(g)}$ with hydrated cement product, the saturation level of pore solution, and the effect on the carbonation depth of concrete are all embedded in one single constant, K, which limits the applicability of the model in a wider range. In concrete structures exposed to actual environmental conditions, the diffusion of $CO_{2(g)}$ through the unit area of concrete is not uniform and varies with the concrete material properties and environmental boundary conditions [113,159,162,163].

3.1.2.2 Carbonation in concrete based on Fick's second law

The carbonation of concrete can be affected by the concentration of atmospheric carbon dioxide in two different ways. Firstly, diffusion is the primary mechanism responsible for the transport of carbon dioxide into concrete, and the rate of diffusion will increase with the $CO_{2(g)}$ concentration gradient between the atmosphere and pores inside the concrete. Secondly, a higher $CO_{2(g)}$ concentration level at the boundary surface will result in a faster rate of carbonation [47,157]. Due to fluctuations in the atmospheric $CO_{2(g)}$ concentration and the reaction rate of $CO_{2(g)}$ with hydrated cement phases, the diffusion as well as the concentration of $CO_{2(g)}$ inside a pore will change with depth from the exposure surface and time [164,165]. Therefore, literature has focused on the non-steady-state of diffusion utilizing Fick's second Law, where the concentration of $CO_{2(g)}$ changes with time and space, t and x, respectively, as shown in Eq 3.5.

$$\frac{\partial (C_{CO_2})}{\partial t} = D_{CO_2} \frac{\partial^2 (C_{CO_2})}{\partial x^2}$$
 Eq 3.5

Where D_{CO_2} is the diffusion coefficient of $CO_{2(g)}$, and C_{CO_2} is the atmospheric concentration of $CO_{2(g)}$. The diffusion coefficient, D_{CO_2} depends on micropore structure, moisture content, temperature, and reaction rate of $CO_{2(g)}$ with hydrated phases as well as cracks in concrete. Eq 3.5 shows that the $CO_{2(g)}$ diffusion coefficient is a key factor in encouraging the development of models for determining the concentration of $CO_{2(g)}$ in order to predict carbonation depth. In these methods,

the effective diffusion coefficient of $CO_{2(g)}$ is empirically determined as a function of the water-to-cement ratio, carbon dioxide concentration at the boundary, temperature, relative humidity, water content, hydrated cement product, and potential use of supplementary cementitious materials (SCM). Using the solutions for Eq 3.5, along with considering internal and external factors for carbonation, several models have been proposed to compute carbonation depth in cement-based material. Considering a wide range of influence parameters on carbonation, the carbonation depth equation (Eq 3.8), which takes into account the diffusion coefficient, atmospheric $CO_{2(g)}$ concentration, and the amount of $CO_{2(g)}$ consumed by CaO was introduced by Yoon *et al.* [166].

$$C_{depth}(t) = \sqrt{\frac{2D_{CO_2}(t)}{a}}C_{CO_2}(t) t \left(\frac{t_0}{t}\right)^{n_m}$$

where

$$a = 0.75 C_{cem} C_{CaO} \alpha_{H} \frac{M_{CO2}}{M_{CaO}}$$

 $D_{aa}(t) = D_{aa}^{0} t^{-n_d}$

Where t_0 is the reference period (e.g., one year), t is time in years, $D_{CO_2}(t)$ and $C_{CO_2}(t)$ is the diffusion coefficient and atmospheric mass concentration of $C_{CO_2}(10^{-3}\text{kg/m}^3)$ at time t, respectively, n_d is the age factor for the diffusion coefficient of $CO_{2(g)}$, C_{cem} is cement content (kg/m³), C_{CaO} is the CaO content in cement, α_H is a degree of hydration, and M_{CaO} is the molar mass of CaO, and M_{CO2} is the molar mass of $CO_{2(g)}$. The age factor for microclimatic conditions (n_m) associated with the frequency of wetting and drying cycles is $n_m = 0$ for a sheltered outdoor environment and $n_m = 0.12$ for an unsheltered outdoor environment.

While using the proposed Eq 3.8 by Yoon *et al.* [166], it should be noted that the carbonation depth is computed considering the constant concentration of $CO_{2(g)}$ for all times up to time t. This shows the overestimation in carbonation depth calculation due to gradual increases in the concentration of $CO_{2(g)}$ with time up to the

peak value. Furthermore, the diffusion of $CO_{2(g)}$ increases with temperature. However, the effect of temperature on the diffusion of $CO_{2(g)}$ is not considered in the proposed carbonation model by Yoon *et al.* Considering the effects of changes in $CO_{2(g)}$ concentration and temperature, Stewart *et al.* [24] enhanced the carbonation depth model proposed by Yoon *et al.* [166] for assessing the impact of climate change in urban centres. This model includes the average $CO_{2(g)}$ concentration over a specific period, a factor to account for temperature's influence on the diffusion coefficient of $CO_{2(g)}$ ($f_T(t)$), and a factor to consider the increased $CO_{2(g)}$ levels in urban environments (k_{urban}). Thus, Eq 3.8 is rewritten for years starting from 2000 as:

$$X_{c}(t) = \sqrt{\frac{2 f_{T}(t) D_{CO_{2}}(t)}{a}} k_{urban} \int_{2020}^{t} C_{CO_{2}}(t) dt \left(\frac{t_{0}}{t - 1999}\right)^{n_{m}} t \ge 2000$$

Eq 3.7

where

$$f_{T}(t) = e^{\frac{E}{R} \left(\frac{1}{293} - \frac{1}{273 + T_{av}(t)}\right)}$$
$$T_{av}(t) = \frac{\sum_{i=2000}^{t} T(t)}{t - 1999}$$

Where T(t) is the temperature (°C) at time t, E is the activation energy of the diffusion process (40 kJ/mol), and R is the gas constant (8.314 x 10^{-3} kJ/mol K). However, this modeling approach cannot be applied or extended to predict carbonation in cement-based materials as a general practice due to the challenges of accommodating all internal and external factors and their interactions within such simplified empirical equations. On the other hand, this modeling approach is useful for developing the governing equations based on microscopic mechanisms for the carbonation phenomenon in cement-based materials under various environmental conditions. Based on this perspective, numerical methods were introduced to develop a carbonation depth model that can provide solutions in arbitrary space and time [167–169]. Studies describe the mass transport such as moisture and gaseous CO_{2(g)} and carbonation process in concrete to determine the carbonation depth by quantifying the remaining amount of calcium content phases and/or the formation of calcium carbonate in the concrete. Furthermore, some researchers have attempted to calculate the pH value of the pore solution by solving the ionic equilibrium between the pore solution and the hydrated solid cement phase [170–172].

Maekawa *et al.* [173,174] proposed a generalized computational method that can deal with pH fluctuations of pore water and deterioration of the concrete due to carbonation for arbitrary environmental conditions. To simulate carbonation phenomena in concrete, the equilibrium between gaseous and dissolved carbon dioxide, their transports, ionic equilibriums, and the carbonation reaction process are formulated based on thermodynamics and chemical equilibrium theory. The mass balance equation for a porous medium is expressed as

$$\frac{\partial \left[\varphi(1-S) \cdot \rho_{g} + S \cdot \rho_{d} \right]}{\partial t} + \nabla \cdot J_{CO_{2}} - Q_{CO_{2}} = 0$$
 Eq 3.8

Where:

$$J_{co2} = -(D_{dCO_2}\nabla\rho_d + D_{gCO_2}\nabla\rho_g)$$
$$Q_{CO2} = \frac{\partial(C_{CaCO_3})}{\partial t} = k[Ca^{2+}][CO_3^{2-}]$$

Where, φ is the porosity, S is the saturation of porosity, ρ_g is the density of gaseous carbon dioxide[kg/m³], ρ_d is the density of dissolved carbon dioxide in pore water [kg/m³], and J_{co2} is the total flux of dissolved and gaseous carbon dioxide [kg/m² s], D_{gCO2} is the diffusion coefficient of gaseous CO_{2(g)} in a porous medium [m²/s], and D_{dCO2} is the diffusion coefficient of dissolved CO_{2(g)} in a porous medium [m²/s], C_{CaCO3} is the concentration of calcium carbonate [mol/l], and k is the reaction rate coefficient [l/mol.s]. The proposed approach is limited to transport and chemical equilibrium related to carbon dioxide only. However, migration and leaching of other cementitious ions may accelerate the carbonation of concrete and disturb pore solution and phase assemblage of concrete. Furthermore, the carbonation of cement-based material is identified as a reactive transport process [103].

3.1.2.3 Reactive transport model for carbonation

Over the last few decades, several reactive transport models (RTMs) have been established to predict concrete carbonation [108,153,154,175]. For gaseous and

ion mass transport in porous media, the Poisson-Nernst-Planck (PNP) equation is typically used, which is derived from a hybrid mixture theory [176,177], whereas chemical equilibrium calculations are performed through specialized tools such as PHREEQC [141,143,178] or GEMS [179–181]. Among others, RTMs have been established that combine gaseous, multi-ionic, and moisture transport models with a chemical equilibrium [154].

Where, ϵ_p is the volume fraction of the liquid phase, ϵ^l is the volume fraction of the gas phase, C_j^g is the concentration of gas species j in the phase, D_j^g is the effective diffusion coefficient for gas j, q_j^g is the rate of mass exchange term for chemical interactions of the gaseous species, and M is the number of gas species building up the gas phase. However, current modeling approaches are limited by considering simplified assumptions about the processes involved in the carbonation of cement-based materials, for example, mass exchange mechanisms between gas phases and pore solution during the transport calculation, diffusion of gases associated with their dissolution process with pore solution, mass flux through boundary surfaces, and the integration effect of boundary condition. Also, predictive competencies are inadequate due to the lack of fundamental relationships between phase assemblage changes, pore structure changes, and mass transport through pores. Therefore, a practical interpretation of the relations between phase assemblage, pore structure, and mass transport is also needed to consider the impact of pore structure change on mass transport due to carbonation. In addition, current RTM models without considering ion absorption on the pore surface are insufficient to predict the actual changes in the phase assemblage and composition of pore solutions due to the carbonation process and the effects of carbonation on ionic transport. The dissolution of the C-S-H phase upon carbonation leads to the release or absorption of ions and alters the charge on the pore surface and the pore solution composition. As a result, ionic transport through the pore solution, as well as the rate of steel corrosion, will be affected by the pore solution composition. The lack of consideration of the interaction between the pore solution and the surface sites of the C-S-H phase on the pore surface in current models does not represent actual changes in pore solution composition upon carbonation, especially regarding free chloride concentration.

To progress beyond the state-of-the-art, the reactive transport modeling framework described in Paper I should be extended to account for the carbonation of cementbased materials, including multi-component gas and ionic transport coupled with moisture transport. To accurately replicate the variations in pore solution composition and the subsequent impact of these changes on steel corrosion, a surface complexation model should be employed, which includes the formation of an electrical double layer and exchange interactions among the ionic solution in pores and the C-S-H surface site (=SiOH). Therefore, chemical equilibrium calculations must include the equilibrium between the gas phases, aqueous species in the pore solution, hydrated solid phases, and ionic absorption on the pore surface. For interconnecting phase assemblage changes and mass transport, models for moisture conductivity, gas, and ionic diffusivity should be based on the properties of pore structure and storage of liquid water in pores, taking into account the impact of the pore structure and moisture content changes on mass transport. Based on these perspectives, the development of a multi-species reactive transport model based on gas-ion-solid phase interaction for the carbonation of cement-based materials is presented in Paper III.

3.2 Boundary conditions of concrete structures

Based on the location of concrete structures, service environments can be divided into different groups, such as marine, urban environments, and others. During the service life, the concrete structures in each location may be subjected to different deterioration scenarios, such as chloride-induced corrosion, carbonation-induced corrosion, sulfate attack, freeze-thaw cycle, *etc.*, which could affect the structural reliability and service life of the concrete structure. Reinforced concrete structures in the marine environment are mainly deteriorated by chloride-induced corrosion. However, reinforced concrete structures in urban areas exposed to the atmosphere also suffer from deterioration caused by carbonation-induced corrosion.

3.2.1 Marine environment

Exposure conditions to which concrete structures are subjected in the marine environment play a crucial role in the deterioration of concrete structures, giving rise to, *e.g.*, chloride penetration and the corrosion process of reinforcement. However, defining boundary conditions for numerical models in the marine area is challenging without understanding the inherent complexities. In an initial attempt, the boundary conditions may be simplified by considering the location of structural elements related to the seawater level. Exposure zones in the marine environment and relative corrosion rates depending on the exposure zone are shown in Fig 3.1. Within such an approach, five types of exposure zones can be introduced, *i.e.*, atmospheric, splash, tidal, submerged, and subsoil zones, including a seabed section based on seawater level for the concrete section. Moreover, different mechanisms of ionic and moisture penetration into concrete can be identified in each zone, which is mainly influenced by existing environmental conditions near the surface of the concrete.

The uppermost zone considered in the marine environment is the atmospheric zone, which is extended from the splash and tidal zone upwards. In this zone, atmospheric air mixes with moisture and salt, also known as airborne chlorides. The intensity of winds is different and more potent compared with on land. The concentration of airborne chloride depends on the intensity and pattern of waves and wind. Boundary conditions for numerical models are complex, and chloride ingress varies with airborne properties, relative humidity, precipitation, and temperature. The region between the highest and lowest levels of seawater is defined as the tidal zone, and the range typically varies with seasonal periods. The concrete surface in the tidal zone experiences cyclic wetting by seawater and drying in an

air atmosphere. The cyclic boundary condition is the most vulnerable exposure condition compared with fully submerged and atmospheric zones for reinforced concrete due to the accelerated ingress of various species and a high risk for chloride-induced corrosion. Hence, numerical modeling approaches should define the different boundary conditions for the wetting and drying periods. During the wetting period, the concrete is exposed to submerged conditions, whereas the boundary condition used in the atmosphere zone can be applied for the drying period. The splash zone is defined as the upper part of the tidal zone and extends from some distance below the mean low water level (MLWL) to about 1.5 to 2 times the distance above the MLWL. This zone may experience the splash from waves during high tide but is never fully submerged during high tide. The splash zone range depends on the local tide condition and wave height. The splash zone is the most critical zone for offshore structures due to the continuous contact with highly aerated seawater, the erosive effect of seawater spray, temperature fluctuation, and wave action. In this zone, salt ions accumulate, and structures experience the full effect of sea salt ions found in seawater. These actions become predominant in the presence of atmospheric oxygen and carbon dioxide, making both concrete and the embedded reinforcement vulnerable to damage and corrosion. A significant portion of an offshore structure is located in the submerged zone, below the low water level and above the sea bed. Here, the oxygen availability is low (about 3ppm), but the hydrostatic pressure increasing with depth can cause rapid penetration of harmful salt ions into the concrete. This is regarded as the least corrosive zone due to the lack of oxygen and carbon dioxide that accelerate rebar corrosion.



Fig 3.1. Exposure zones in marine environments and relative corrosion rate, depending on the exposure zone [182].

3.2.2 Urban environment

Carbonation is a common issue that inevitably affects reinforced concrete structures in urban areas. Mechanisms of carbonation of concrete in an urban area are mainly governed by the ingress of the gaseous phase of $CO_{2(g)}$ through pore voids and dissolved $CO_{2(g)}$ gas through pore solution into the concrete. The migration of gases and dissolved $CO_{2(g)}$ in concrete is driven by partial pressure and concentration gradients, respectively. Therefore, the deterioration of concrete depends on atmospheric parameters such as $CO_{2(g)}$ partial pressure, total atmosphere pressure, relative humidity, precipitation, wind speed, wind direction, and temperature when concrete structures are directly exposed to the atmosphere in an urban area. When there is no rain condition, the ions, gas, and moisture transport occurs through pores in concrete. During rainy conditions, the gas flux through the boundary surface is restricted due to increased saturation levels within the pore voids, and ions in the pore solution start to leach out from the concrete when exposed to runoff water on the concrete surface. Therefore, the boundary conditions for exposed concrete in urban areas should be defined separately for rainy and dry seasons, and distinctions should be made between indoor and outdoor to simulate the carbonation of exposed concrete.

3.2.3 Summary of boundary condition for numerical models

To accurately predict the deterioration of cement-based materials exposed to various environmental conditions, it is necessary to assign different boundary conditions to the developed RTM framework, such as concrete in fully saturated conditions leading to multi-ionic transports, *i.e.*, submerged zone in a marine environment, concrete in unsaturated condition leading to multi-ionic transport coupled with moisture transport, *i.e.*, tidal or splash zone in a marine environment, and concrete in typical indoor and outdoor atmospheric conditions leading to multiionic, moisture, and multi-component gas transport, *i.e.*, concrete structure in urban environmental condition. A summary of applied boundary conditions for numerical modeling and exemplary type of exposure conditions concerning the location to enable the prediction of deterioration are given in Table 3.1.

Environmen- tal condition	Marine environment				Urban environ- ment
Location	Atmospheric zone	Tidal zone or Splash zone		Submerged zone	In and outdoor atmospheric zone
Deterioration by	Airborne chlo- ride ingress and carbona- tion	Chlorde ingress and carbon- ation		Cloride in- gress	Carbonation
Boundary condition	-Airborne Cl concentration	Due to wet period	Due to dry pe- riod	-Seawater composition	$-CO_{2(g)}$ concentration
	-CO _{2(g)} con- centration -Temperature -Relative hu- midity -Precipitation -Wind speed and direction	-Seawater composition -Seawater Tempera- ture	-CO _{2(g)} con- centration eawater e e -Atmospheric Temperature e -Relative hu- midity -Precipitation -Wind speed and direction	- I emperature -Relative hu- midity -Precipitation -Wind speed and direction	

Table 3.1. Type of adequate boundary condition for RTM framework to predict the deterioration of reinforced concrete structures.

4 Durability of concrete under actual environmental conditions

The development of a reactive transport model under different boundary conditions was described in Chapter 4. Moreover, numerical predictions were compared to experimental data based on laboratory experiments to demonstrate the applicability of the RTM (see Papers I to III). However, in lab-scale experiments, the boundary conditions of exposed specimens often remain constant over the experimental period. Predicting concrete deterioration under natural environmental conditions is more complex and often not accurately represented by results observed in laboratory-scale experiments. The boundary conditions in actual environmental conditions, such as temperature, relative humidity, the partial and total pressure of gases, wind speed, and wind direction, vary with time. The combined, complex effect of varying boundary conditions on concrete deterioration can be favourable or unfavourable, and will vary from case to case. For example, even if the concrete is exposed to higher temperatures and $CO_{2(g)}$ concentration, increases in relative humidity might, in fact, decrease the carbonation of concrete. The ability of the developed RTM model to deal with varying boundary conditions is presented in Chapter 4 through the comparison of simulated results with experimentally measured data of concrete exposed to real climatic conditions.

4.1 General outline

In this study, the developed RTM modeling framework was calibrated and tested in two case studies: (i) to investigate concrete deterioration under submerged seawater exposure for more than 16 years using data from the Solsvik field station in Norway and (ii) to investigate concrete deterioration under urban environmental condition for nearly eight years using data from the Danish Technological Institute field station in Denmark.

4.2 Concrete deterioration under seawater exposure

4.2.1 Numerical example

To validate the developed RTM framework for concrete exposed to seawater at the Solsvik field station, a numerical study was conducted using the experimental conditions and results from [62,183] for comparison with the model simulation. The

Norwegian Public Roads Administration (NPRA) established the Solsvik field station along the Norwegian coast during the 1990s to study the deterioration of concrete induced by chloride ingress. Fourteen types of concrete beams with comparable water-to-binder ratios but prepared using different Portland cement blends and SCMs such as silica fume, fly ash, or slag were exposed at the site. For this numerical study, one specific concrete type (PC-SF) was selected with a lower content of SCMs in production. The experimental study includes among others, measurements of the Cl profile and total elemental contents, including calcium (Ca), sodium (Na), aluminum (Al), iron (Fe), magnesium (Mg), sulfur (S), and potassium (K), as well as solid phases (Portlandite and carbonate phase) for samples exposed to seawater. A brief overview of the exposure conditions, investigated materials, and field measurements are provided in the following, while more detailed information on sample preparation, exposure, and measurement campaign can be found in [62].

4.2.2 Materials

In October 1997, a 3 m \times 0.15 m \times 0.30 m concrete beam was prepared using 92% Portland cement (PC) type CEM I 42.5 N according to EN197-1 with 8 % silica fume (SF). The PC-SF concrete was proportioned with a water-to-binder mass ratio of 0.44. The mix design details of the concrete are given in Table 4.1, while the chemical composition of the PC and SF is given in Table 4.2.

Details of mix design	PC-SF
CEM I 42.5	378
Silica fume	34.0
Free water	181.0
Absorbed water	15.0
Fine aggregates 0-8mm	872.0
Coarse aggregates 0-8mm	898.0
SP 1	1.4
SP 2	1.1
Air entrainer	0.1
Fresh density	2382.0
Paste volume excl. air [Vol%]	33.0
Air content fresh mix [Vol%]	3.0
w/b = free water/(PC+S+FA+SF)	0.4

Table 4.1. Mix design of PC-SF concrete after [62].

Details of properties of PC	CEM I 42.5	SF
Chemical composition analysis [wt%]		
SiO ₂	21.3	95.1
Al_2O_3	4.1	1.0
Fe_2O_3	3.2	0.1
CaO	64.3	0.1
MgO	1.7	0.4
K ₂ 0	0.4	1.0
Na ₂ O	0.2	0.1
SO ₃	2.9	0.0

Table 4.2. Chemical composition [wt%] of the Portland cement (PC), silica fume (SF), after [62].

4.2.3 Curing condition

The PC-SF concrete beam was cast in October 1997 at a ready-mix concrete plant near the Solsvik field station. After casting, the concrete beam was kept outdoors at a temperature of -2 to 10 °C for 24 hours. After demolding, the concrete beam was cured under a plastic cover for six months outdoors.

4.2.4 Exposure condition

After curing, the PC-SF concrete beam was suspended at Solsvik bay on Sotra Island, near Bergen, Norway. The lower part of the beams was permanently submerged, the middle part was subjected to tidal fluctuations, and the top part was exposed to atmospheric and splash conditions. The details of lifting a beam at the Solsvik field station for testing and position for drilling cores in the concrete beam are presented in Fig 4.1. In August 2013, after nearly 16 years of exposure, the beam was lifted, and a core in the permanently submerged part of the beam, approximately 0.5 m from the lower edge of the beam, was cored for chemical analysis and moisture measurement.



Fig 4.1. The details of lifting a beam at Solsvik field station for testing (right) and position for drilling cores in the concrete beam, dimensions shown in [mm] (left) [183].

Seawater composition and temperature over the exposure period were needed for realistic numerical predictions of material deterioration. Therefore, Estimating the Circulation and Climate of the Ocean (ECCO Version 4 Release 3 or V4R3 for short) data [184], which includes satellite and in situ ocean observations, was used to retrieve exposure conditions, i.e., sea water temperature and salinity at Solsvik field station between 1997–2013. To assess the applicability of the interpolation method to ECCO data, ECCO data was interpolated to weather stations of the Norwegian Meteorological Institute (NMI) [185], located near the Solsvek field station, including Slåtterøy Fyr (SN48330), Ytterøyane Fyr (SN57770), and Troll A (SN76931). The weather station location and seawater temperature using interpolated ECCO data and NMI observed weather station data from 1997 to 2013 are shown in Fig 4.2a and b for comparison. The data in Fig 4.2 shows that the seawater temperature was not continuously registered for selected weather stations over the entire exposure period. However, interpolated ECCO data for each location agree well with observation data at the weather station (see Fig 4.2b). Therefore, in this numerical study, the interpolation method for ECCO data can be used to determine the exposure conditions for concrete exposed at Solsvik field station.



Fig 4.2. Location of weather observation station near the Solsvek field station and a comparison between ECCO Ocean Temperature and Salinity grid data (ECCO) and Norwegian Meteorological Institute (NMI) observation data for different weather stations.

The interpolated seawater temperature and salinity using ECCO data at Solsvek field station between 1998 and 2014 are shown in Fig 4.3a and b, respectively. In the present study, it is assumed that the seawater composition near the Trondheim fjord, Norway, is similar to that at the Solsvek field station. The composition of the seawater determined by inductive coupled plasma mass spectrometry (ICP-MS) [65] is given in Table 4.3. Further, the chloride content in seawater is adjusted with salinity changes over the exposure period. In the present study, the chloride content in seawater is related to the salinity of seawater as follows [186,187].

$$Cl_{m} = 0.5535 \cdot S_{sw}$$
 Eq 4.1

Where Cl_m is the mass content of chloride (g) and S_{sw} the salinity of seawater (g_salt/kg).



Fig 4.3. Temperature and salinity (ECCO data) for the Solsvek field station [184].

Element	Seawater [mmol/l]
Ca	8.76
CI	548
К	8.9
Mg	46.7
Na	411
S	26.9

Table 4.3. Elemental composition of exposure solution, after [65].

4.2.5 Input parameters and databases for numerical studies

In the numerical studies, the exposed specimen was assumed to be in a fully saturated condition, and the boundary conditions in the exposed specimen, such as seawater temperature and salinity levels, were assumed to be consistent with the interpolated values from ECCO data at the Solsvik field station. Input for the hydration model was determined based on the hydration of each clinker phase composition in the binder materials. The content of the main clinkers phases, alite, belite, aluminates, and ferrites, was determined by the Bogue equation. The soluble alkali sulfates (K_2SO_4 and Na_2SO_4) were determined using total alkali oxide and sulfate content in PC cement (see Table 4.2) and the proposed method by Taylor for sulfate distribution [188]. It is assumed that the remaining sulfates (SO_3), other than alkali-sulfates, basanite, and gypsum phases, accumulate as solid solutions in the major clinkers, especially alite and belite in PC. The remaining non-dissolved alkali oxide (K_2O and Na_2O) and magnesium oxide (MgO) are stored as minor content in the major clinkers. The resulting clinker composition of the PC cement is shown in Table 4.4.

Phase composition [wt%]		Present as a solid solution in the clinker phases [wt%]		
Alite ^a (C ₃ S)	53.14	CaO ^e	0.00	
Belite ^a (C_2S)	20.97	MgO ^c	1.70	
Aluminate ^a (C_3A)	5.45	K_2O^d	0.04	
Ferrite ^a (C ₄ AF)	9.74	Na ₂ 0 ^d	0.11	
Calcite ^b	4.32	SO ₃ ^f	0.80	
Gypsum ^c	3.62			
$K_2 SO_4^{d}$	0.67			
$Na_2SO_4^{d}$	0.21			
a - Determined by Bogue equation.		d - Calculated from total (Table 4.2) and soluble alkali con- tent [189].		
b - Calculated from the CO_2 content Table 4.2.		e - Calculated from the Free CaO content Table 4.2		
c - Calculated from the chemical analysis.		f - Calculated from the distribution of sulfate [188].		

Table 4.4. Clinker composition of the Portland cement (PC) [wt%].

In total, 74 ions were included in the multi-ionic mass transport model, whereas moisture transport was not considered under the assumption of full saturation. The phases, thermodynamic data, reaction equations, and thermodynamic data for ion adsorption on the C-S-H surface presented in [188,190] were used for the numerical investigation of PC-SF concrete under fully submerged conditions. In addition, the dissolution of $CO_{2(g)}$ in the exposure solution was allowed under atmospheric conditions.

Details of spatial discretization and time step used in the numerical study, together with assumed threshold pore radius, initial tortuosity, shape factor, and other constant values, are shown in Table 4.5. In general, using a relatively high number of elements to discretize the domain in numerical studies will increase the accuracy; however, computational costs will increase. Therefore, to balance accuracy and computational cost in the present investigations, the 20 cm 1D domain was discretized using 100 elements with a growth factor to create a finer mesh near the surface of the exposed boundary. The time step was decided through sensitivity indices studies for ion mass transport based on comparing total exposure time, computational costs, developed charged imbalance in the pore solution, and the truncated error in the boundary node. Chemical equilibrium was performed in every time step.

Model parameters	Value
No of spatial elements	100
Growth factor of spatial elements	2
Total spatial distance, (m)	0.2
Total exposure time, (years)	16
Time step, Δt (hr)	12
Threshold pore radius, r_{th} (nm)	2
Initial tortuosity factor, $f_{\tau,0}$	0.04
Shape parameter, c	1
Relative dielectricity, ζ_r	78.54
Dielectricity in a vacuum, ζ_0	8.85E-12
Faraday's constant, (C/mol)	96490
Gas constant, (J/(mol · K))	8.314

Table 4.5. Model parameters for numerical investigations.

4.2.6 Results and discussion

4.2.6.1 Phase assemblage of PC-SF concrete

The numerical results for PC-SF concrete after two months of outdoor curing at the Solsvek field station are shown in Fig 4.4. Results of the hydration model indicate that more than 92 % of alite and aluminate clinker are hydrated after two months of curing, whereas a slower reaction rate of belite was observed in PC-SF concrete specimens (see Fig 4.4a). The simulated phase assemblage contains C-S-H, Portlandite, Ettringite, monocarbonate, hydrogarnet, hydrotalcite, calcium carbonate, and unhydrated cement. Nearly 22% of the total PC-SF concrete volume consists of both hydrated and unhydrated cement, whereas the numerical results indicate that approximately 12% of the total volume is pore space after two months of curing (see Fig 4.4b). Dissolved ions will be present in the pore solution due to equilibrium reactions between the pore solution and hydrated phases. The numerically simulated composition of the pore solution of PC-SF concrete after two months of curing is given in Fig 4.4c. Alkali ions, such as Na⁺ and K⁺, dominate the composition of the pore solution in PC-SF concrete due to the higher dissolution rate of the alkali sulphates compared to the dissolution of the major clinkers. The Ca concentration is moderately higher due to the dissolution of Portlandite and C-S-H, whereas the presence of hydrogarnet and hydrotalcite phases limit the concentrations of Fe and Mg, respectively. The simulated results show that the pH value of the pore solution of the PC-SF concrete is approximately 13.08. Fig 4.4d

shows the simulated cumulative pore volume and pore size distribution of gel, capillary, and total pores of PC-SF concrete specimens after two months of outdoor curing. Numerical results indicate that nearly 1/3 and 2/3 of total pore volumes consist of gel and capillary pore, respectively, whereas two threshold pore radii were observed for the pore distribution. The pore size distribution shows that the peak lies between 0.1 to 1 μ m for non-exposed PC-SF concrete specimens. The threshold and peak pore radius considerably affect the ionic, gas, and moisture transport in the RTM model.



Fig 4.4. Numerical results for PC-SF concrete specimens after two months of outdoor curing under a plastic cover. (a) hydration of major clinkers phases and average degree of hydration, (b) phase assemblage, (c) composition of the pore solution, and (d) pore distribution.

4.2.6.2 Phase assemblage of exposed PC-SF concrete

The developed RTM was used to simulate the effect of seawater on the solid phases of exposed PC-SF concrete at the Solsvek field station. Results of the numerical simulations, i.e., phase assemblage for PC-SF concrete immersed in seawater solution for 1, 8, and 16 years, are shown in Fig 4.5. The right-hand side of the figures

displays the paste composition in the unaffected core, while the left-hand side illustrates the effect of exposure on the PC-SF concrete samples. For the non-exposed core, the simulated phase composition includes CSH, Portlandite, Ettringite, monocarbonate, hydrogarnet, hydrotalcite, calcium carbonate, and unhydrated silica fume and cement.

Upon exposure of the PC-SF concrete to seawater, Portlandite and monocarbonate decompose with a continuous increase in calcite content (see Fig 4.5). The observed changes in the phase assemblage result from the presence of Cl⁻ ions from the boundary solution, which start to substitute carbonate ions $(CO_3)^{2-}$ in the monocarbonate to form Friedel's salt. On the other hand, the formation of additional phases such as ferrihydrite-mc, brucite, magnesium silicate hydrate (MSHss), natrolite, and gypsum is observed near the surface of the exposed PC-SF concrete specimen due to the presence of sodium, sulfate, and magnesium in the seawater. In addition to the decomposition of monocarbonate and Portlandite, the decalcification of C-S-H and the dissolution of hydrogarnet and ettringite are observed near the exposed surface. The porosity near the exposed surface decreases mainly with calcite and MSHss formation because the molar volume of MSHss is comparably higher. Except for the region near the exposed surface (0-5mm section), a gradual decrease in pH value was observed with the leaching of some ions and decomposition of phases such as monocarbonate and Portlandite. In contrast, the decalcification of the C-S-H phase due to seawater exposure causes a sudden drop in pH value at the vicinity of the exposure surface (approximately 8.2 at the exposed surface for 16 years of exposure).



Fig 4.5. Numerically simulated phase assemblage for PC-SF concrete specimens using ECCO data for 1, 8, and 16 years of exposure at the Solsvek field station.

4.2.6.3 Elemental profiles of exposed PC-SF concrete

Fig 4.6a and b illustrate a comparison between simulated and experimentally determined (through TGA) Portlandite and the release of $CO_{2(g)}$ profiles for specimens exposed to seawater after 16 years of exposure, as well as simulated profiles for 1 and 8 years of exposure. The Portlandite and $CO_{2(g)}$ contents are presented in total phase content as the mass percentage of the dried PC-SF concrete at 105 °C. Results illustrate an increase in the release of $CO_2(g)$ in the outermost section (0– 3mm) due to seawater exposure over time (see Fig 4.6b). The formation of carbonate phases may result from either carbonation during sample preparation or the transport of $CO_{2(g)}$ dissolved in the boundary solution inside the PC-SF concrete sample during exposure. In the present study, the dissolution of $CO_{2(g)}$ in the exposure solution was considered under atmospheric conditions for which a good agreement between experimental and numerically simulated results is observed. Moreover, a decrease in Portlandite content near the exposed surface is observed over time. As previously discussed, the dissolution of Portlandite is increased by calcite formation. A gradual decrease in Portlandite is also found in the deeper, uncarbonated sections, i.e., both experimentally and numerically (see Fig 4.6).

Fig 4.7a and b show the simulated cumulative pore volume and pore size distribution of capillary, gel, and total pores of PC-SF concrete at a depth of 0.5mm from the exposed surface before and after exposure to seawater solution for 16 years. Numerical results for the cumulative pore volume indicate that seawater exposure appears to fill pores with newly formed phases such as calcite, ferrihydrite-mc, brucite, MSHss, and natrolite (see Fig 4.5). A slight decrease in the total pore volume of gel pores is found because decomposition of the C-S-H phase occurs due to carbonation and ingress of ions (see Fig 4.5). The effect is more pronounced for capillary porosity, for which nearly half of the capillary pore space is filled by newly formed phases. The peak radius considerably affects the ionic transport in the RTM model, influencing ion flux through a change in threshold porosity. The pore size distribution shows that the peak lies between 0.1 µm to 1 µm for all nonexposed and exposed PC-SF concrete. A more significant reduction in peak radius is observed for seawater exposure. For seawater exposure, the formation of additional phases affects the total porosity distribution and reduces the peak radius ten times smaller than non-exposed PC-SF concrete.

Numerically simulated the tortuosity factor for the PC-SF concrete after exposure to seawater solution for 16 years are given in Fig 4.8. Results of the numerical simulations illustrate changes in the tortuosity factor near the exposed surface for seawater exposure. The tortuosity factor is significantly reduced, indicating an increase in the length of the ion pathway. Consequently, the ion flux through the pore space near the PC-SF concrete's surface is reduced, forming new solid phases, although the boundary solution provides sufficient ion supply.



Fig 4.6. Comparison of experimentally determined and numerically simulated Portlandite and carbon content in PC-SF concrete specimens after 16 years of exposure to seawater at the Solsvek field station.



Fig 4.7. Cumulative pore volume and pore size distribution for PC-SF concrete specimens at a depth of 0.5mm from the exposed surface after 16 years at the Solsvek field station.



Fig 4.8. Tortuosity factor of PC-SF concrete specimens exposed to seawater for various exposure times at the Solsvek field station.

The simulated distribution of chlorides in PC-SF concrete exposed to seawater solution after 1, 8, and 16 years are shown in Fig 4.9, together with the experimentally measured after 16 years of exposure. The chloride profiles are thereby presented as total chloride contents per mass percentage of the dried PC-SF concrete (at 105 °C). Within the presented modeling framework, chlorides may be stored in free water and the EDL of the pore solution, physically bound on the pore surface, and chemically bound in, e.g., Kuzel's salt and Friedel's salt. The sum of all chlorides, i.e., free, physically, and chemically bound, is then provided as the total chlorides in the simulated result. Generally, the presented results indicate an excellent agreement between simulation and the experimental results for 16 years of PC-SF concrete exposure. The results show the peak behaviour in the chloride profile near the exposed surface (0-5mm section) of the PC-SF concrete due to the seawater exposure, as Cl from the boundary solution was immediately stored as Friedel's salt near the exposed surface (see Fig 4.5). Simultaneously, the peak region continuously moves deeper for all profiles with increasing exposure time. In addition, over time, the simulated and measured chloride profiles show a reduction in the chloride content at the surface (0-3mm section). The decrease in chloride content near the exposed surface is caused by the release of initially physically absorbed Cl⁻ ions from the surface sites of C-S-H due to the decalcification of the C-S-H phase, whereas the mass of dried PC-SF concrete at 105 °C increased in the surface region. Therefore, the normalized total chloride contents with the mass of the dried PC-SF concrete at 105 °C reduced after some exposure period.



Fig 4.9. Comparison between simulated and measured total chloride profiles of PC-SF concrete samples exposed to seawater after 16 years at the Solsvek field station. The notation M and E in the legend represent the model and experimental results, respectively.

A comparison between numerical and experimental results for calcium (Ca), aluminium (Al), iron (Fe), magnesium (Mg), sulfur (S), sodium (Na), and potassium (K) after 16 years of exposure to seawater is given in Fig 4.10 along with numerical results for 1 and 8 years. Total elemental distributions are presented as the mass percentage of the dried PC-SF concrete (at 105 °C). Generally, a good agreement between numerically simulated and experimentally determined elemental distribution is found for most parts of the spatial domain. As the exposure solution contains slightly less Ca than the pore solution of the PC-SF concrete (see Table 4.3 and Fig 4.4c), leaching of Ca is expected from the concrete due to electrochemical and potential gradients. However, in the outermost section (0-3mm) of the concrete region, the experimentally measured calcium profiles indicate enrichment in calcium. The simulated calcium profile can be explained through numerical simulation. The decalcification of the C-S-H phase occurs due to carbonation increasing the Ca concentration in the pore solution. As a result, numerical simulations predict the leaching of calcium through the exposed surface. Finally, the leached calcium reacts with dissolved carbon dioxide in the seawater, and a calcite crust is deposited on the exposed surface of the concrete, which is confirmed in the microscopic study presented in [61,65].

For concrete exposed to seawater, leaching of Al and Fe is expected due to the lack of Al and Fe in the exposure solution. However, the leaching is restricted due to a slight concentration gradient between the boundary and pore solution (see Table 4.3 and Fig 4.4c), resulting in a slight decrease of Al and Fe profiles, as indicated by experimental results and numerical predictions. The presence of magnesium in the seawater solution leads to the ingress of magnesium in the PC-SF concrete samples. The magnesium content increased only in the outer sections (0-2mm) of samples exposed to seawater. Numerical results predict the formation of hydrotalcite, brucite, and M-S-Hss in the outer sections of the exposed samples (see Fig 4.5) as the transported magnesium ions react with other ions in the pore solution and precipitate as solid phases. Due to the presence of sulfur in the seawater solution, experimental and numerical results show increased sulfur content in the outer section (0-4mm) of the exposed sample. As a result, additional ettringite is formed after 1 and 8 years of exposure, as indicated in Fig 4.5. However, for the more prolonged exposure, the formed ettringite close to the exposure surface starts to decompose due to carbonation. Therefore, a reduction in sulfur profile was observed after 16 years of exposure (see Fig 4.10e).

Seawater solution contains more than three times the Na concentration of the pore solution of the PC-SF concrete (see Table 4.3 and Fig 4.4c); therefore, Na is expected to ingress into the samples due to electrochemical and potential gradients.

However, the measured and simulated sodium profiles indicate enrichment in sodium close to the exposed surface (0-1mm) for 1, 8, and 16 years of exposure. At the same time, the results illustrate a reduction in sodium content in the section located 1-3mm from the exposed surface. The numerical simulation shows that the transported Na replaces Ca in the C-S-H phase for more prolonged exposure, and a natrolite phase is formed close to the exposure surface. As a result, a rapid increase in the Na profile was observed in the vicinity of the exposure surface. The seawater solution contains only limited potassium concentrations compared to the pore solution (see Table 4.3 and Fig 4.4c), leading to continuous leaching of potassium ions from the exposed surface. In addition, initially physically absorbed potassium ions from the pore surface are released into the pore solution due to the decalcification of the C-S-H phase (see Fig 4.5).



Fig 4.10. Comparison of experimentally measured and numerically simulated total calcium(Ca), aluminium (Al), iron (Fe), magnesium (Mg), sulfur (S), sodium (Na), and potassium (K) content from profile ground PC-SF concrete samples after 16 years of exposure to seawater at the Solsvek field station.
4.3 Concrete deterioration under urban environment

4.3.1 Numerical example

To validate the developed RTM framework for concrete exposed to urban environments at a test site near the Danish Technological Institute (DTI), a numerical study was conducted using the experimental conditions and results from [191,192]. The test site near DTI for studying the carbonation of different types of concrete was established by Femern A/S in April 2010. Fifteen types of concrete with different blends of cement and SCMs were selected for testing by Femern A/S. To test the developed RTM, the reference concrete panels prepared with 100% Portland cement were investigated to study concrete carbonation. The experimental study measured the carbonation depth of exposed concrete using thymolphthalein in May 2018. A brief overview of the exposure conditions, investigated materials, and field measurements is provided in the following, while more detailed information on sample preparation, exposure, and measurement campaign can be found in [191,192].

4.3.2 Materials

The concrete panel with the dimensions 1.0 m x 1.0 m x 0.2 m was prepared using Portland cement (PC) type CEM I 42.5 N according to EN197-1. The PC concrete was proportioned with a water-to-binder mass ratio of 0.4 and a target air content of 4.5%. The mix design details of the concrete are given in Table 4.6, and Table 4.7 provides information on the chemical composition of the binder as measured by X-ray fluorescence according to EN 196-2 [191,192].

Details of mix design	PC
OPC cement (CEM I 42.5)	365
Water content	146.0
Aggregate 0/2	695.0
Aggregate 4/8	377.0
Aggregate 8/16	266.0
Aggregate 16/22	529.0
Amex SB 22 (AEA)	1.7
Glenium SKY 532SU (SP)	2.8
Air content fresh mix [Vol%]	4.5
w/b = free water/(PC+S+FA+SF)	0.4

Table 4.6. Mix design of PC concrete after [191].

Details of properties of PC	CEM I 42.5 ¹
Chemical composition analysis	[wt%]
SiO ₂	24.8
Al_2O_3	2.91
Fe_2O_3	2.34
CaO	65.6
MgO	0.75
K ₂ 0	-
Na ₂ O	0.40
SO ₃	2.24
CO ₂	0.15
Loss on ignition	0.65
Blaine surface [m ² /kg]	366
Density [kg/m ³]	3190

Table 4.7. Chemical composition [wt%] of the Portland cement (PC), after [191].

4.3.3 Curing condition

The casted concrete panel was kept indoors at room temperature (approximately 20 °C) for 24 hrs. After 24 hrs of maturity age, the casted concrete panel was demolded, and immediately after, the panel was tightly wrapped in plastic and stored indoors until the block had reached a minimum of 14 maturity days.

4.3.4 Exposure condition

After reaching 28 days of curing for maturity, the concrete panel was placed outdoors on the premises of the DTI and exposed to atmospheric conditions in April 2010. The placement of the concrete panel at the DTI and the positions for drilling cores for carbonation testing are shown in Fig 4.11.



Fig 4.11. The placement of the concrete panel at the DTI and the positions for drilling cores for carbonation testing.

Due to concrete being exposed to atmospheric conditions, the carbonation of concrete depends on various atmospheric parameters, e.g., CO_{2(g)} concentration, total atmospheric pressure, temperature, relative humidity, wind speed, wind direction, and precipitation. Modeling the effect of both wind and precipitation on the carbonation of concrete in an outdoor environment, along with other atmospheric parameters, is more challenging and requires further investigation. Therefore, atmospheric parameters, such as wind speed, wind direction, and precipitation, are not included in this study. Due to precipitation, ion leaching on the exposed surface of concrete can be observed, and the effect of this ion leaching on concrete deterioration in an urban environment over longer exposure periods cannot be neglected. However, this study accounts for ion leaching through the exposed surface when the atmospheric relative humidity reaches 100%, similar to the effect of precipitation. For the numerical simulation, the Roskilde Lufthavn weather station (SI-06170) belonging to the Danish Meteorological Institute (DMI) was selected to obtain observation data, such as temperature and relative humidity [193]. The observation data for the exposure period from 2010 to 2018 are shown in Fig 4.12. In this study, the average concentration of $CO_{2(g)}$ in the atmosphere is taken as 420 ppm from 2010 to 2018.



Fig 4.12. The observation data of Roskilde Lufthavn weather station (SI-06170) for the exposure period from 2010 to 2018 [193].

4.3.5 Input parameters and databases for numerical studies

The numerical simulations accounted for concrete properties and boundary conditions (atmospheric conditions) occurring in the field test. One side of the concrete specimen (1.0 x 1.0 m) was exposed to atmospheric conditions in the exposure field while simultaneously subjected to a wetting (at RH 100%) and drying process. Therefore, ionic flux through the exposed surface of the material is omitted in the ion mass transport calculation during drying conditions (due to lack of continuity of pore water with exposure), whereas moisture flux (in the form of vapour phase) through the exposed surface is accounted for in the moisture transport calculations. In addition, ion ingress and leaching are accounted for through the exposed surface in the mass transport calculations during wetting periods. Finally, gaseous ingress through the pore void is accounted for by assigning a flux through the exposed boundary surface in the mass transport calculations for gas. For the hydration model, the content of main clinkers phases alite, belite, aluminates, and ferrites was determined by the Bogue equation. The soluble alkali sulfates (K_2SO_4 and Na_2SO_4) were determined using total alkali oxide and sulfate content in PC cement (see Table 4.7) and the proposed method by Taylor for sulfate distribution [188]. It is assumed that the remaining sulfates (SO_3), other than alkali-sulfates, basanite, and gypsum phases, accumulate as solid solutions in the major clinkers, especially alite and belite in OPC. The remaining non-dissolved alkali oxide (K_2O and Na_2O) and magnesium oxide (MgO) are stored as minor content in the major clinkers. The resulting clinker composition of the PC cement is shown in Table 4.8.

Phase composition [wt%]		Present as a solid solution in the clinker phases [wt%]	
Alite ^a (C ₃ S)	53.49	CaO ^e	0.00
Belite ^a (C_2S)	30.67	MgO ^c	0.76
Aluminate ^a (C ₃ A)	3.78	K_2O^d	0.02
Ferrite ^a (C ₄ AF)	7.18	Na ₂ 0 ^d	0.22
Calcite ^b	0.34	SO ₃ ^f	0.57
Gypsum ^c	2.79		
$K_2 SO_4^{d}$	0.34		
Na ₂ SO ₄ ^d	0.42		
a - Determined by MAS NMR Spectroscopy [191]. d - Calculated from total (Table 4.7) and s tent [189].		(Table 4.7) and soluble alkali con-	
b - Calculated from the CO_2 content Table 4.7.		e - Calculated from the Free CaO content Table 4.7.	
c - Calculated from the chemical analysis.		f - Calculated from the distribution of sulfate [189].	

Table 4.8. Clinker composition of the white Portland cement (PC) [wt%].

In the present study, the $CO_{2(g)}$ gas constituent was only included in the multispecies gas transport, whereas two-phase moisture, i.e., liquid and vapour, was adapted in moisture transport. In total, 74 ions were included in the multi-ionic mass transport model during the numerical investigations. The phases, thermodynamic data, reaction equations, and thermodynamic data for ion adsorption on the C-S-H surface presented in [188,190] were used for the numerical investigation of carbonation of PC concrete exposed to atmospheric conditions. Details of spatial discretization and time step used in the numerical study, together with assumed threshold pore radius, initial tortuosity of ion and gas, shape factor, and other constant values, are shown in Table 4.9. In general, using a relatively high number of elements to discretize the domain in numerical studies will increase the accuracy; however, computational costs will increase. Therefore, to balance accuracy and computational cost in the present investigations, the 50mm 1D domain is discretized using a total of 50 elements with a growth factor to create a finer mesh near the surface of the exposed boundary. The time step was decided through sensitivity indices studies for ion mass transport based on comparing total exposure time, computational costs, developed charged imbalance in the pore solution, and the truncated error in the boundary node. Chemical equilibrium was performed in every time step.

Model parameters	Value
No of spatial elements	50
Growth factor of spatial elements	2
Total spatial distance, (mm)	15
Total exposure time, (days)	360
Time step, Δt (hr)	6
Threshold pore radius, r_{th} (nm)	2
Initial tortuosity factor, $f_{\tau,0}$	0.05
Initial gas tortuosity factor, $f^g_{ au,0}$	0.20E-5
Shape parameter, c	1
interfacial gas transfer coefficient	2.00 E-4
Relative dielectricity, ζ_r	78.54
Dielectricity in a vacuum, ζ_0	8.85E-12
Faraday's constant, (C/mol)	96490
Gas constant, (J/(mol · K))	8.314

Table 4.9. Model parameters for the numerical investigations.

4.3.6 Results and discussion

4.3.6.1 Phase assemblage of PC concrete panel

The numerical results for the PC concrete panel after reaching 28 days of maturity age at DTI are shown in Fig 4.13. Results of the hydration model indicate that more than 80% of alite and aluminate clinker are hydrated after 28 days of outdoor curing, whereas a slower reaction rate of belite was observed in the PC concrete panel (see Fig 4.13a). The simulated phase assemblage contains C-S-H, Portlandite, Ettringite, monocarbonate, hydrogarnet, hydrotalcite, calcium carbonate, and unhydrated cement. Nearly 19% of the PC concrete volume consists of both hydrated and unhydrated cement, whereas the numerical results indicate that approximately 11% of the total volume is pore space after 28 days of outdoor curing (see Fig 4.13b). Dissolved ions will be present in the pore solution due to equilibrium reactions between the pore solution and hydrated phases. The numerically simulated composition of the pore solution of PC concrete after 28 days of outdoor curing is given in Fig 4.13c. The composition of the pore solution in PC concrete is dominated by alkali ions, such as Na⁺ and K⁺, due to the higher dissolution rate of the alkali sulphates compared to the dissolution of the major clinkers. The Ca concentration is moderately higher due to the dissolution of Portlandite and C-S-H, whereas the presence of hydrogarnet and hydrotalcite phases limit the concentrations of Fe and Mg, respectively. The simulated results predict the pH value of the pore solution of the PC concrete to be 13.46. Fig 4.13d shows the simulated cumulative pore volume and pore size distribution of gel, capillary, and total pores of PC concrete after 28 days. Numerical results indicate that nearly 1/4 and 3/4 of total pore volumes consist of gel and capillary pore, respectively, whereas two threshold pore radii were observed in pore distribution. The pore size distribution shows that the peak lies between 0.1 to 1 μ m for non-exposed PC concrete.



Fig 4.13. Numerical results for PC concrete specimens after 28 days of sealed curing at 20 °C. (a) hydration of major clinker phases and average degree of hydration over 28 days of the curing period, (b) phase assemblage, (c) composition of the pore solution, and (d) pore distribution.

4.3.6.2 Moisture isotherm and transport parameters

Fig 4.14a compares the computed pore distribution of PC concrete at a depth of 1 mm from the exposed surface before and after exposure to atmospheric conditions at DTI for nearly eight years. The micro-pore structure directly affects the mass transport parameters, which mainly influence the carbonation of cement-based materials. During the carbonation of PC concrete, the numerical simulation predicts an increase in porosity at the exposed surfaces, followed by a slight decrease and constant porosity in the non-carbonated section of the sample. Numerical results illustrating the cumulative pore volume further indicate that the effect is more pronounced in fully carbonated PC concrete, for which the carbonation of hydrated phases nearly doubles the capillary pore space. Due to the transformation of the C-S-H phase into silica gel by the carbonation process, a gradual decrease in the interlayer and gel pores is observed.

Moreover, a shift in the pore size distribution towards larger pore diameters is also simulated. As a result, the peak radius in the pore distribution increases five times compared to non-exposed PC concrete. The computed moisture isotherms based on the pore structure development of PC concrete before and after $CO_{2(g)}$ gas exposure are shown in Fig 4.14b. As illustrated, the computed moisture isotherms indicate significant differences for PC concrete before and after carbonation. Moreover, it is shown that the water saturation level for carbonated PC concrete is lower than for non-carbonated PC concrete at particular relative humidities. Results of the simulation highlighting the impact of $CO_{2(g)}$ gas exposure, i.e., changes in the moisture conductivity and gas diffusivity as well as ionic diffusion, are presented in Fig 4.14c and d, respectively. The results indicate the increase in both transport parameters over the complete moisture range due to the carbonation of PC concrete. The most significant impact on $CO_{2(g)}$ gas diffusivity and moisture conductivity are found for lower and higher saturation, respectively. The larger pore structure and threshold pore radius of carbonated PC concrete considerably increase the ionic, gas, and moisture mass transport through the pore network.



Fig 4.14. Numerical results illustrating the effect of exposure on moisture isotherm and transport parameters at a depth of 1 mm from the exposed surface after 28 days of outdoor curing and exposure to atmospheric conditions for eight years. (a) pore distribution, (b) moisture isotherms, (c) $CO_2(g)$ gas diffusion, and (d) moisture conductivity. (a: absorption, d: desorption)

4.3.6.3 Solid phase composition of carbonated PC concrete

The presented modeling framework was used to determine phase changes of PC concrete caused by carbonation. Results of the numerical simulations, i.e., phase assemblage, pH value, and total porosity for PC concrete exposed to atmospheric conditions for eight years of exposure, are shown in Fig 4.15a. The right-hand side of the figures displays the paste composition in the unaffected core, while the left-hand side illustrates the effect of carbonation on the PC concrete sample. In Fig 4.15, the dotted lines represent the carbonation depth determined by the pore solution's simulated pH value of 9.7. In the carbonated zone, calcite, silica-gel, gyp-sum, gibbsite, ferrihydrite-mc, natrolite, and magnesium silicate hydrate mainly precipitate, while the decomposition of hydrated phases such as Portlandite, Ettringite, monocarbonate, CSHss, hydrogarnet, and hydrotalcite is observed.

Moreover, the increase of Mg²⁺ ions in the pore solution due to the dissolution of hydrotalcite form an MSHss phase as a more stable phase during carbonation. The carbonation process induces a decrease of Ca/Si, which increases the alkali uptake [78,102], which agrees with the numerical predictions. In the phase assemblage, the formation of a natrolite phase demonstrates the binding of alkali with C-S-H during the decalcification of the C-S-H phase. The carbonation front is identified as a thin layer ahead of the carbonation zone. After all accessible Portlandite is consumed in this zone, progressive decalcification of C-S-H, Ettringite, and monocarbonate phases was observed. As a result, the pH of the pore solution drops from nearly 13.46 to 7.58. In addition, the porosity in the carbonation front (region next to the carbonated zone) decreases mainly due to the formation of Ettringite, which has a comparably higher molar volume. The dissolution front contrasts with the carbonation front, in which the decalcification of Portlandite and calcite precipitation are observed without significant changes in porosity. Carbonation does not affect the phase assemblage and porosity in the non-carbonated zone.

Fig 4.15b illustrates simulated Portlandite and carbonate profiles for PC concrete after eight years of carbonation, along with the pH profile and carbonation depth. The Portlandite and carbonate contents are presented in total phase content as moles per 100g PC concrete. The simulated results show the progressive increase in carbonation depth through the dissolution of Portlandite and calcite precipitation. Additionally, the pH decrease coincides with the zone where the Portlandite content decreases and calcite content increases. Numerical results indicate a lack of Portlandite phase in the carbonated zone due to complete decomposition by carbonation. However, gradual changes in calcite content were observed in the simulated results, indicating carbonation continues through the reaction of transported $CO_{2(g)}$ with other phases, such as C-S-H, AFtss, or CO₂-AFm phases, after the complete decomposition of the Portlandite phase.



Fig 4.15. Numerical results for PC concrete exposed to atmospheric conditions for eight years. (a) phase assemblage, carbonation depth (C_{dep}) and pH value, (b) total Portlandite (CH) and carbonate (CC) content.

4.3.6.4 Carbonation depth profiles

Using a phenolphthalein pH indicator, the measured carbonation depth at ten different positions on the exposed PC concrete panel after eight years of exposure to atmospheric conditions at DTI and the box plot for the measured values are shown in Fig 4.16. In this study, the average carbonation depth in the exposed PC concrete panel, calculated from measurements at ten different positions, is 0.233 mm.



Fig 4.16. The carbonation depth in ten different positions in the exposed concrete panel after eight years of exposure

The simulated partial pressure of $CO_{2(g)}$ gas inside the pores after 3, 6, and 9 years of carbonation is shown in Fig 4.17a. During carbonation, the partial pressure of $CO_{2(g)}$ increases with its dissolution and finally reaches a stable value close to the partial pressure of $CO_{2(g)}$ gas applied at the boundary. The region where a stable

partial pressure value is nearly equal to the value at the boundary is consistent with the carbonation depth, which indicates a fully carbonated zone in a cement-based material. This study used experimentally measured carbonation depth in the exposed PC concrete panel, using phenolphthalein pH indicator as presented in Fig 4.17a, to adjust the initial tortuosity factor. Fig 4.17b compares simulated and experimentally measured carbonation depth in the exposed PC concrete. The presented results indicate excellent agreement between simulation and experimental results, with numerically simulated results well within the error margin of the phenolphthalein measurement.

Furthermore, numerically predicted results show that carbonation depth gradually increases in concrete nearly six years after exposure (Step-by-step increases in the simulated results show the simulated carbonation depth based on the refinement of finite element meshes). Due to concrete carbonation, initially, the surface of the concrete starts to carbonate, and the partial pressure of $CO_{2(g)}$ inside the pore at the surface gradually increases with the dissolution of $CO_{2(g)}$, which limits the transport of $CO_{2(g)}$ to further depth. Once the surface region of concrete reaches a state of complete carbonation, the carbonation depth gradually develops with the $CO_{2(g)}$ partial pressure in the pores.



Fig 4.17. Numerical results for PC concrete samples during carbonation (a) partial pressure of $CO_{2(g)}$ in pores, (b) comparison between predicted and measured carbonation depth.

5 Climate change and projections

Chapter 5 outlines the past and recent drivers of climate change, observed changes in the climate system, and future climate changes in different scenarios based on data presented in the fifth assessment report of the Intergovernmental Panel on Climate Change (IPCC, 2014). Climate change can be defined as a change in the state of the climate that persists for an extended period, typically decades or centuries. There is widespread concern that climate change is taking place today as a result of anthropogenic effects, especially related to greenhouse gas emissions.

5.1 Past and recent drivers of climate change

Recent anthropogenic emissions of greenhouse gases reached the highest level compared with recorded history, and recent climate changes impact more than before human and natural systems. The fifth assessment report of the Intergovernmental Panel on Climate Change (IPCC, 2014) indicated that atmospheric concentration levels of GHG have risen over the last 800,000 years [194]. Fig 5.1 shows the observed changes in atmospheric greenhouse gas concentrations such as carbon dioxide, methane, and nitrous oxide. Especially the concentrations of carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) in the atmosphere are reported to have significantly increased, 40%, 150%, and 20%, respectively, after 1750. The decadal rate change of CO₂(g) concentrations increased by approximately 2.0 \pm 0.1 ppm/yr between 2002 and 2011. The concentration of CH₄ was reported as a stable level for one decade since the late 1990s. However, recent measurements since 2007 show an increase in the concentration level of CH₄. The concentration of N₂O over the last three decades has steadily increased at a rate of 0.73 \pm 0.03 ppb/yr.

The radiative forcing of climate change during the industrial era (1750–2011) is given in Fig 5.2. Based on reported greenhouse gas emissions, the calculated total anthropogenic radiative forcing over 1750–2011 shows a warming effect of 2.3 [1.1 to 3.3] W/m2, for which a rapid increase was observed after 1970. Carbon dioxide, among other greenhouse gases, is reported as the single most prominent contributor to anthropogenic radiative forcing between 1750–2011. The reported value of the total anthropogenic radiative forcing estimate for 2011 increased by 43 percent compared with the value in the IPCC Fourth Assessment Report (AR4). A combination of continued growth in most GHG concentrations and an improved estimate of radiative forcing from aerosols causes this increase.



Fig 5.1. Observed changes in atmospheric greenhouse gas concentrations such as carbon dioxide (CO_2, green) , methane (CH_4, orange) , and nitrous oxide (N_2O, red) [194].



Fig 5.2. Radiative forcing of climate change during the industrial era (1750-2011) [194].

5.2 Observed changes in the climate system

5.2.1.1 Atmosphere

Globally averaged combined land and ocean surface temperature anomalies relative to the average from 1986 to 2005 are given in Fig 5.3. The results indicate that Earth's surface has been getting warmer continually in the last three decades compared to any preceding decade since 1850. The IPPC 2014 reported that the period from 1983 to 2012 was likely the warmest 30-year period of the last 800 years in the Northern Hemisphere. In addition, the globally averaged surface temperature, including land and ocean, between 1880 to 2012 increased by 0.85 °C [0.65 to 1.06]. Based on the most extended dataset available, the total increase between the average of the 1850-1900 period and the 2003-2012 period is 0.78 [0.72 to 0.85] °C. Changes in average precipitation over global land between 1901 and 1951 were reported as low. However, after 1951, it rose to a medium value.



Fig 5.3. Globally averaged combined land and ocean surface temperature anomalies relative to the average between 1986 and 2005 (Colors indicate different data sets) [194].

5.2.1.2 Ocean

Fig 5.4 shows the energy accumulation within the Earth's climate system, arctic (July to September average) and Antarctic (February) sea ice extent, and Global mean sea level relative to the mean between 1986–2005 for the longest-running data set. In the climate system, oceans are the primary source of energy storage, contributing to the earth getting warmer. It can be noticed that 90% of the total energy was accumulated in the ocean body between 1971 and 2010, whereas only 1% was stored in the atmosphere. The surface of the ocean body, i.e., the upper 75 m layer, shows an increase of 0.11 [0.09 to 0.13] °C per decade between 1971 to 2010.

In addition, salinity changes are observed on the surface of seawater. On the one hand, seawater becomes more saline due to the evaporation process, while on the other hand, with precipitation, seawater becomes fresher, and the salinity of seawater starts to reduce. These regional trends in ocean salinity provide indirect evidence for changes in evaporation and precipitation over the oceans and, thus, for changes in the global water cycle. Moreover, the global mean sea level rose by 0.19 [0.17 to 0.21] m between 1901-2010. The glacier mass loss and thermal expansion of the ocean body have been identified to contribute to about 75% of the observed global mean sea level rise after the 1970s. Between 1993 and 2010, the global mean sea level rise was, with high confidence, consistent with the sum of observed contributions from ocean thermal expansion due to warming, from changes in glaciers, the Greenland ice sheet, the Antarctic ice sheet, and land water storage. Seawater level changes mainly dominate seawater's salinity and pH value.



Fig 5.4. Observed data: (a) Energy accumulation within the Earth's climate system, which is given relative to 1971 and from 1971 to 2010, (b) sea ice extent in the Arctic and Antarctic region, and (c) global mean sea level relative to 1986–2005 mean for the longest running data set, and with all data sets aligned to have the same value in 1993, the first year of satellite altimetry data [194].

5.3 Future climate changes

5.3.1 The representative concentration pathways

The continuous emission of GHG will be the leading cause of future warming and long-lasting climate changes, increasing the likelihood of severe, irreversible impacts on people and ecosystems. An effort to limit greenhouse gas emissions is required worldwide to mitigate climate change and reduce infrastructure risks. The predicted greenhouse gas emissions for the future vary over a wide range, depending not only on socio-economic development such as population growth, lifestyle and behavioural changes, associated changes in energy and land usage, and technology but also on climate policies. Scenarios for climate projection are defined by a range of approaches and idealised experiments with Integrated Assessment Models (IAMs). Fig 5.5 shows that emissions of carbon dioxide ($CO_2(g)$) in the Representative Concentration Pathways (RCPs) and the associated scenario categories used in working group III (WGIII). Based on GHG emissions and atmos-

pheric concentrations, air pollutant emissions, and land use, four different pathways were defined as Representative Concentration Pathways (RCPs) for climate change projection. A wide range was covered by RCPs, such as a stringent mitigation scenario (RCP2.6), two intermediate scenarios (RCP4.5 and RCP6.0), and one scenario with very high GHG emissions (RCP8.5). These scenarios are used to assess the costs associated with emission reductions consistent with particular concentration pathways. For each defined scenario, climate change projection is obtained using climate models such as GCMs and Earth System Models (ESMs), which are used to simulate the carbon cycle. The GCMs simulate many climate aspects, including the temperature of the atmosphere and the oceans, precipitation, winds, clouds, ocean currents, and sea-ice extent. These climate projections, in turn, are used for impact and adaptation assessment.



Fig 5.5. Emissions of carbon dioxide (CO_2) in the Representative Concentration Pathways (RCPs) (lines) and the associated scenario categories used in WGIII (coloured areas show a 5 to 95% confidence interval) [194].

5.3.2 Projected changes in the climate system

5.3.2.1 Atmosphere

The global average surface temperature change is shown in Fig 5.6. In all defined emission scenarios, increases in surface temperature were observed over the 21st century. In the predicted climate projection for the early 21st century, a similar trend was identified between 2016–2035 and 1986–2005 and will likely be in the range of 0.3°C to 0.7°C. Climate change after this period (2016–2035) depends on committed warming caused by past anthropogenic emissions, as well as future anthropogenic emissions and natural climate variability. By the mid and end of the

21st century, significant changes in the projected climate change were identified between emissions scenarios. Relative to 1850–1900, global surface temperature changes will exceed 1.5°C at the end of the 21st century (2081–2100) for RCP4.5, RCP6.0, and RCP8.5. The increase of global mean surface temperature by the end of the 21st century (2081–2100) relative to 1986–2005 is likely to be 0.3°C to 1.7°C under RCP2.6, 1.1°C to 2.6°C under RCP4.5, 1.4°C to 3.1°C under RCP6.0 and 2.6°C to 4.8°C under RCP8.5. For the 21st century, GCM model predictions show that more intense and frequent extreme precipitation events will occur in many regions and that the changes in precipitation will not be uniform. An increase in annual mean precipitation under the RCP8.5 scenario was identified for high latitudes and the equatorial Pacific region, while mean precipitation will decrease in many mid-latitude and dry subtropical regions. At the same time, more intense and frequent extreme precipitation for most of the mid-latitude land masses.



Fig 5.6. The global average surface temperature change from 2006 to 2100 determined by multimodel simulations [194].



Fig 5.7. Change in average surface temperature based on multi-model mean projections for 2081–2100 relative to 1986–2005 under the RCP2.6 (left) and RCP8.5 (right) scenarios.

Change in average precipitation (1986-2005 to 2081-2100)



Fig 5.8. Change in average precipitation based on multi-model mean projections for 2081–2100 relative to 1986–2005 under the RCP2.6 (left) and RCP8.5 (right) scenarios [194].

5.3.2.2 Ocean, cryosphere, and sea level

For the 21st century, continuous warming will occur globally in the ocean body, and in comparison, the most substantial warming is predicted for the surface of the ocean body in the tropical and Northern Hemisphere subtropical regions. In the Southern Ocean region, the warming will be most pronounced in the deeper depths of the ocean. The acidification of the ocean body is observed globally for all RCP scenarios by the end of the 21st century, whereas recovery of acidification is predicted after the mid-century under RCP2.6. The decrease in surface ocean pH is in the range of 0.06 to 0.07 (15 to 17% increase in acidity) for RCP2.6, 0.14 to 0.15 (38 to 41%) for RCP4.5, 0.20 to 0.21 (58 to 62%) for RCP6.0 and 0.30 to 0.32 (100 to 109%) for RCP8.5. Year-round reductions in Arctic sea ice are observed in all RCP scenarios, and a nearly ice-free Arctic Ocean will be minimum in September before mid-century for RCP8.5. The reduction of near-surface permafrost extent (in the upper 3.5 m) at high northern latitudes is caused by global mean surface temperature increases. The permafrost area near the surface will be reduced by 37% (RCP2.6) to 81% (RCP8.5). At the same time, the global glacier volume, excluding glaciers on the periphery of Antarctica, will decrease by 15 to 55% for RCP2.6 and 35 to 85% for RCP8.5.

Due to changes in the global ocean temperature, glaciers, the Greenland ice sheet, the Antarctic ice sheet, and land water storage, the global mean sea level will rise faster than observed from 1971 to 2010 during the 21^{st} century. For the period between 2081–2100, relative to 1986–2005, the rise will likely be in the range of 0.26 to 0.55 m for RCP2.6 and 0.45 to 0.82 m for RCP8.5. By the end of the 21^{st} century, the sea level will likely rise in more than 95% of the ocean area. About 70% of the coastlines worldwide are projected to experience a sea level change within ±20% of the global mean.



Fig 5.9. Projections and a measure of uncertainty (shading) are shown for scenarios RCP2.6 (blue) and RCP8.5 (red): (a) Change in global mean sea level, (b) Change in ocean surface pH value [194].



Fig 5.10. Change in average sea level based on multi-model mean projections for 2081–2100 relative to the 1986–2005 period under the RCP2.6 (left) and RCP8.5 (right) scenarios [194].

6 Impact of climate change on the deterioration of concrete structures

Chapter 6 presents an estimation of the impact of climate change on the deterioration of concrete structures related to reinforcement corrosion. Concrete specimens and the location of exposure stations introduced in Chapter 6 were used for the analysis. The numerical simulations presented in Chapter 6 are based on material properties, thermodynamic databases, model discretization, etc., previously described and applied in Chapter 4.

6.1 General outline

The study investigated the impact of climate change on the deterioration of concrete structures, focusing on determining the critical climate projections that have the most influence on chloride ingress and carbonation of concrete. However, it should be noted that this approach for studying the impact of climate on the deterioration of concrete excluded material property variations such as cement, content of SCM, water-to-binder ratio, etc. The impact of climate change on the deterioration of concrete structures due to seawater exposure and atmospheric exposure conditions was investigated through chloride profiles and carbonation depths, respectively.

To account for the impact of climate change on concrete deterioration, the approach was further integrated with the statistical results of state-of-the-art climate models. Climate models are established based on physical principles, and each model has strengths and weaknesses in the applied physical approach and spatial grid scales. Therefore, differences between climate projections obtained from various models can be observed. For this study, the multi-model ensembles of global circulation models (GCMs) projections under the high GHG emissions scenario (RCP8.5), which is produced by the Coupled Model Intercomparison Project phase 5 (CMIP5) initiative, were used to investigate the impact of climate change on concrete structure deterioration in the period between 2020 and 2100. The selected General Circulation Models (GCMs) from the CMIP5 dataset for climate projection are summarized in .

Table 6.1. To avoid the biases and spatial resolution of these global projections that hinder their use in regional applications, using the observation data at the service location of the concrete structure and historical data of the multi-model, climate projections at high spatial resolution were downscaled to local scales using the Delta statistical downscaling method [195]. The downscaled multi-model climate projections were statistically analysed to determine the distribution parameters of climate projections. Using distribution parameters from the climate projection for the RCP8.5 scenario, random samples were generated using the Latin hypercube sampling (LHS) technique [196]. Using the developed integrated modeling framework, Monte Carlo simulations were performed to account for uncertainty information in the climate projections involved, and subsequently, an analytical probabilistic design approach was developed to identify critical climate projections.

GCM	Research centre
BCC-CSMI-1	Beijing Climate Centre, China Meteorological Administration, China
BCC-CSM1-1-M	Beijing Climate Centre, China Meteorological Administration, China
BNU-ESM	College of Global Change and Earth System Science, Beijing Normal University, China
CanESM2	Canadian Centre for Climate Modeling and Analysis, Canada
CCSM4	National Centre of Atmospheric Research, USA
CESM1-BGC	Community Earth System Model Contributors, USA
CESMI-CAMS	Community Earth System Model Contributors, USA
CESMI- FASTCHEM	Community Earth System Model Contributors, USA
CESM1-WACCM	Community Earth System Model Contributors, USA
CMCC-CESM	Centro Euro-Mediterranco per I Cambiamenti Climatici, Italy
CMCC-CM	Centro Euro-Mediterraneo per I Cambiamenti Climatici, Italy
CMCC-CMS	Centro Euro-Mediterranco per I Cambiamenti Climatici, Italy
CNRM-CM5	National Centre of Meteorological Research, France
CNRM-CM5-2	National Centre of Meteorological Research, France
CSIRO-Mk3-6-0	Commonwealth Scientific and Industrial Research Organization/Queens- land Climate Change Centre of Excellence, Australia
EC-EARTH	EC-EARTH consortium, The Netherlands/Ireland
FGOALS-g2	LASG, Institute of Atmospheric Physics, Chinese Academy of Sciences, China
FIO-ESM	The First Institute of Oceanography, SOA. China
GFDL-CM3	NOAA Geophysical Fluid Dynamics Laboratory, USA
GFDL-ESM2G	NOAA Geophysical Fluid Dynamics Laboratory, USA

Table 6.1. The details of employed GCM models from CMIP5 in this study.

GFDL-ESM2M	NOAA Geophysical Fluid Dynamics Laboratory, USA
GISS-E2-H	NASA Goddard Institute for Space Studies, USA
GISS-E2-H-CC	NASA Goddard Institute for Space Studies, USA
GISS-E2-R	NASA Goddard Institute for Space Studies, USA
GISS-E2-R-CC	NASA Goddard Institute for Space Studies, USA
HadCM3	Met Office Hadley Centre, UK
HadGEM2-AO	Met Office Hadley Centre, UK
HadGEM2-CC	Met Office Hadley Centre, UK
HadGEM2-ES	Met Office Hadley Centre, UK
INMCM4	Institute for Numerical Mathematics, Russia
IPSL-CM5A-LR	Institute Pierre Simon Laplace, France
IPSL-CM5A-MR	Institute Pierre Simon Laplace, France
IPSL-CM5B-LR	Institute Pierre Simon Laplace, France
MIROCS	Atmosphere and Ocean Research Institute (The University of Tokyo), Na- tional Institute for Environmental Studies, and Japan Agency for Marine- Earth Science and Technology, Japan.
MIROC-ESM	Japan Agency for Marine-Earth Science and Technology. Atmosphere and Ocean Research Institute (The University of Tokyo), and National Institute for Environmental Studies, Japan
MIROC-ESM- CHEM	Japan Agency for Marine-Earth Science and Technology, Atmosphere and Ocean Research Institute (The University of Tokyo), and National Institute for Environmental Studies, Japan
MPI-ESM-LR	Max Planck Institute for Meteorology. Germany
MPI-ESM-MR	Max Planck Institute for Meteorology, Germany
MRI-CGCM3	Meteorological Research Institute, Japan

6.2 Impact of climate change on concrete structure deterioration due to seawater exposure

In this study, the PC-SF concrete beam, which was exposed at the Solsvek field station to investigate concrete deterioration under actual seawater exposure conditions (see section 4.2), was selected to assess the impact of climate change on concrete deterioration due to chloride ingress. The material properties, input parameters, thermodynamic database, and spatial and temporal discretization details presented in Section 4.2 were adapted for this numerical simulation. Furthermore, utilizing both observational data from the Solsvek field station and historical data from a multi-model dataset, the multi-model projections of seawater temperature

and salinity at high spatial resolution for the period from 2020 to 2100 under the RCP8.5 scenario were downscaled to the Solsvek field station using the Delta statistical downscaling method. In the simulation, downscaled climate projections of seawater temperature and salinity were used to assign boundary conditions for the simulation. In this process, the uncertainty of downscaled projections of seawater temperature and salinity among the ensembles of the multi-model was assumed to be normally distributed, and distribution parameters of seawater temperature and salinity were determined from 2020 to 2100. Using the obtained distribution parameters, 500 random samples for seawater temperature and salinity projections were generated using the Latin hypercube sampling (LHS) technique from 2020 to 2100.

6.2.1 Impact of climate change based on the mean value of climate projection

6.2.1.1 Input data for mean value analysis

The estimation of the impact of climate change on the deterioration of concrete structures exposed to seawater is established through analysis based on the projected mean from generated random variables and reference values of temperature and salinity of seawater from 2020 to 2100. The reference data assumed constant climate projections between 2020-2100, i.e., keeping observed data from 2020 constant over the period. The projected mean and the reference value of temperature and salinity of seawater at the Solsvek field station are shown in Fig 6.1a and b, respectively. The increase in mean value changes of sea temperature for RCP8.5 was observed as nearly 4 °C in the year 2100, whereas salinity decreases continuously due to water rise caused by changes in the global ocean temperature, glaciers, the Greenland ice sheet, the Antarctic ice sheet, and land water storage.

6.2.1.2 Results and discussion for mean value analysis

The comparison of predicted phase assemblage in the exposed PC-SF concrete in the year 2100 applying the reference and mean values of seawater temperature and salinity projections are shown in Fig 6.2. In both exposure conditions, C-S-H, hydrogarnet, Portlandite, and monocarbonate decompose with a continuous increase in calcite content. In addition, the formation of additional phases such as ferrihydrite-mc, brucite, MSHss, Ettringite, and natrolite is predicted near the surface of the exposed concrete due to the presence of sodium, sulfate, and magnesium in the seawater. However, significant differences in phase assemblage in the region near the exposed surface (0-0.5 cm section) were predicted in the simulation. For the mean climate projection, the predicted phase assemblage indicates higher C-S-H dissolution and pH drop in the region close to the exposed surface. At the same time, decreases in porosity near the exposed surface were observed, which can be explained through the additional formation of Ettringite and MSHss (which have a comparably higher molar volume due to the temperature rise), whereas the formation of gypsum was also predicted in the simulation. The reduction of porosity limits the ingress of ions into the concrete, while the dissolution of the C-S-H phase will increase chloride transport into deeper depths.

The comparison of chloride ingress in the year 2100 applying the reference and mean values of water temperature and salinity projections is shown in Fig 6.3. The results indicate an increase in chloride ingress into concrete due to changes in temperature and salinity of seawater. The results further illustrate the peak behaviour in the chloride profile near the exposed surface (0-1 cm section) of the concrete due to both climate projections. The application of mean climate projections leads to a lower chloride content in the closer region of the exposure surface (0-6 cm) compared to the reference climate projection. At the same time, an increase in chloride content was observed in more profound depths. The developed multi-species reactive transport model can explain the observed variations in the predicted chloride profiles. Temperature increases lead to higher C-S-H dissolution, which results in a release of physically absorbed Cl⁻ ions from the surface sites of C-S-H. Subsequently, the released chloride is transported into the concrete due to increasing electrochemical and potential gradients. Furthermore, a decrease in seawater salinity limits the ingress of ions into concrete.



Fig 6.1. Comparison between the mean and the reference value of projections of (a) seawater temperature and (b) seawater salinity at the location of Solsvek field station based on the RCP8.5 scenario.



Fig 6.2. Comparison of solid phase composition of exposed concrete applying mean and reference value of climate projection.



Fig 6.3. Comparison of chloride profiles for concrete exposed to mean and the reference value of seawater temperature and seawater salinity at the location of Solsvek field station based on the RCP8.5 scenario.

6.2.2 Impact of climate change analyses based on the uncertainty of climate projection

6.2.2.1 Input data for uncertainty analyses

The uncertainty of chloride profile and critical climate projections for concrete deterioration under seawater exposure is studied using the Monte-Carlo simulation approach with generated random variables from an ensemble of multi-model climate projections between 2020 and 2100. The generated 500 independent samples of seawater temperature and salinity from an ensemble of multi-model climate projections at the Solsvek field station between 2020-2100, under the RCP8.5 scenario, are shown in Fig 6.4a and b, respectively. An increase in all generated temperature samples for RCP8.5 was observed between 2020 and 2100, whereas seawater salinity continuously decreased. Nearly 8 °C differences at the end of the year 2100 are observed between the upper and lower values of generated temperature samples, while the salinity level of samples spread over the range from 27 to 37 g-salt/kg.



Fig 6.4. Five hundred independent samples were generated from an ensemble of multi-model climate projections at the Solsvek field station between 2020-2100: (a) seawater temperature and (b) salinity of seawater.

The sensitivity indices analysis was conducted to identify critical climate projections for concrete deterioration under seawater exposure. Two different sensitivity indices analysis methods are employed: independent input and correlated input, depending on the correlation between the input data sets [197–199]. Therefore, initially, the generated data were analyzed to determine the correlation between projections of seawater temperature and salinity. A matrix plot for generated climate projection samples at the end of 2100 for RCP8.5 is shown in Fig 6.5, where the subplots in the diagonal show the histogram of the sample values while the subplots in the non-diagonal show the sample values of the two pairs of samples. The determined correlation coefficients among samples are shown in Table 6.2, indicating no significant correlation between climate projections for both temperature and salinity of seawater. Therefore, the non-correlation method is employed to determine the sensitivity indices of climate projection in this study.



Fig 6.5. Correlation between temperature and salinity of seawater in 2100 for RCP8.5 emission scenario.

Table 6.2. Determined correlation coefficients (CC) between temperature and salinity of seawater in the year 2100 for the RCP8.5 emission scenario.

CC	Temperature	Salinity
Temperature	1.0000	-0.0098
Salinity	-0.0098	1.0000

6.2.2.2 Results and discussion for uncertainty analysis

Using a Monte Carlo simulation approach, chloride profiles were simulated using the developed RTM framework for saturated conditions, applying randomly generated temperature and salinity projections under the RCP8.5 scenario. The predicted uncertainty chloride profiles at the end of the year 2100 are shown in Fig 6.6. In addition, the mean, 5, and 95% confidence intervals of chloride profiles are also indicated in Fig 6.6. In the exposed concrete, the ingress of Cl is observed up to a depth of approximately 20cm, whereas the peak behaviour for chloride profiles is predicted at a certain depth from the exposure surface (at nearly 1cm depth). The peak value of chloride profiles varies in the range of 0.47-0.62 % of dry mass of concrete. A decrease in the width of confidence intervals for the chloride profiles is observed at a depth of approximately 6 cm, which can be explained through the drop in peak chloride content due to temperature increases and decreases in the salinity of seawater (see also Section 6.2.1).



Fig 6.6. Predicted uncertainty of chloride profiles at the end of the year 2100.

In this study, predicted chloride profiles at a 95% confidence level are used to investigate the impact of climate on concrete deterioration under seawater exposure. The spatial and temporal variation of predicted chloride profiles at a 95% confidence level are shown in Fig 6.7. Increases in chloride profile at deeper depths are identified with exposure time, while a reduction in peak chloride concentration is observed at the same time. This behaviour is caused by the dissolution of the C-S-H phase near the exposure surface. In addition, the peak chloride concentration moves deeper into the concrete with exposure time, whereas a continuous decrease in chloride concentration in the vicinity of the exposure surface is predicted.



Fig 6.7. The spatial and temporal variation of predicted chloride profile at a 95% confidence level.

A sensitivity analysis between chloride content and climate projections was conducted to identify critical climate projections for concrete deterioration due to seawater exposure. In this study, variance-based sensitivity analysis was conducted using the binning method. For the sensitivity analysis, the predicted chloride contents (Y) at a particular depth from the exposure surface were sorted according to each climate projections variable (X_i), such as temperature and salinity of seawater. Then, the sorted chloride content was subdivided into 25 subsets to determine the sensitivity indices. The average value of each subset was computed as equivalent to E_{Xi} (Y|X_i), whereas the variance was estimated by V_{Xi} (E_{Xi} (Y|X_i)). Finally, a first-order sensitivity indices, $S_i = V_{Xi}$ (E_{Xi} (Y|X_i)) / V_Y , was calculated by dividing the variance of subset averages by the variance of chloride content.

Scatter plots of sorted chloride content at 3 and 8 cm depth from the exposure surface against values of each climate projection and calculated average chloride content for each subset are shown in Fig 6.8a and b, respectively. At both 3 and 8 cm depths, clear trends between chloride content and climate projections are observed. The analysis of the sensitivity indices of climate projections in 3 and 8 cm depth indicates that both increases in the seawater temperature and decreases in seawater salinity will be favourable to limiting total chloride content in shorter depths (0–6 cm). However, temperature increases will be identified as favourable, while the decreases in salinity will be unfavourable for increasing total chloride content in deeper depth (above 6cm depth). The calculated sensitivity indices of climate projections for chloride content at 3 and 8cm depth of exposure are given in Table 6.3. From the sensitivity indices values in Table 6.3 and subset averaging value trends in Fig 6.8, the impact of climate change on concrete deterioration under seawater exposure can be predicted and used to identify more robust design approaches and more resilient and adapted maintenance strategies for concrete infrastructure in a marine environment. This study shows that the temperature changes will mainly affect concrete deterioration in more shallow and profound depths. In both shallow and deeper depths from the exposed surface, the increase in seawater temperature is identified as the critical climate parameter for accelerating concrete deterioration. On the other hand, a decrease in seawater salinity limits concrete deterioration caused by seawater exposure at the Solsvek field station from 2020 to 2100.



Fig 6.8. Scatter plots of sorted chloride content against values for each climate projection and calculated average chloride content for each subset, (a) at 3 and (b) at 8 cm depth from the exposure surface.

Table 6.3. Sensitivity indices of climate projections.

Depth [cm]	Temperature	Salinity
3	0.729	0.327
8	0.564	0.491

6.3 Impact of climate change on concrete carbonation due to atmospheric exposure

In this study, the PC concrete panel, which was exposed at the DTI to investigate concrete deterioration under atmospheric environmental conditions (see section 4.3), was selected to assess the impact of climate change on concrete deterioration due to carbonation. The material properties, input parameters, thermodynamic database, and spatial and temporal discretization details presented in Section 4.3 were adapted for this numerical simulation. Furthermore, utilizing both observational data from the Roskilde Lufthavn weather station (SI-06170) belonging to the Danish Meteorological Institute (DMI) and historical data from a multi-model dataset, the multi-model projections of atmospheric temperature and relative humidity at high spatial resolution for the period from 2020 to 2100 under the RCP8.5 scenario were downscaled to the location of the DTI applying the Delta statistical downscaling method. In the simulation, downscaled climate projections of atmospheric temperature and relative humidity were used to assign boundary conditions for the simulation. In this process, the uncertainty of downscaled projections of atmospheric temperature and relative humidity among the ensembles of the multi-model was assumed to be normally distributed, and distribution parameters of atmospheric temperature and relative humidity were determined from 2020 to 2100. Five hundred random samples for atmospheric temperature and relative humidity projections were generated using the Latin hypercube sampling (LHS) technique from 2020 to 2100 using the obtained distribution parameters.

6.3.1 Impact of climate change based on the mean value of climate projection

6.3.1.1 Input data for mean value analysis

The impact of climate change on the carbonation of concrete exposed to an urban atmosphere was studied considering the projected mean from generated random variable and the reference values of atmospheric $CO_{2(g)}$ concentration, temperature, and relative humidity. The reference data assumed constant climate projections between 2020-2100, i.e., keeping the observed data from 2020 constant over the period. The projected mean and the reference value of atmospheric $CO_{2(g)}$ concentration, temperature, and relative humidity at the DTI are shown in Fig 6.9a, b, and c, respectively. Increases in mean temperature for RCP8.5 were observed at nearly 4°C in the year 2100, whereas a slight decrease in atmospheric relative humidity was found. However, the concentration of $CO_{2(g)}$ in the atmosphere for the

RCP8.5 scenario indicates a dramatic increase up to approximately 920 ppm at the end of year 2100.



Fig 6.9. Comparison between the mean and reference projection for the DTI field station in the period 2020-2100 based on the RCP8.5 scenario: (a) temperature, (b) relative humidity, and (c) $CO_{2(g)}$ concentration.

6.3.1.2 Results of mean value analysis and discussion

A comparison of the predicted phase assemblage in the reference concrete at the DTI field station in the year 2100 exposed to the mean and reference climate projections is shown in Fig 6.10. Under both exposure conditions, calcite, silica-gel, gibbsite, and natrolite mainly precipitate in the carbonated zone, while the decomposition of hydrated phases such as Portlandite, Ettringite, monocarbonate, CSHss, hydrogarnet, and hydrotalcite is observed. In addition, ferrihydrite-mc, MSHss, and brucite formed as minor content. Increases in porosity were predicted in the carbonated zone as a result of the dissolution and precipitation of phases by carbonation reactions. At the same time, a decrease in porosity is predicted in the carbonation front caused by the formation of ettringite, which has a comparably higher molar volume. For concrete, under the scenario of mean climate projections, deeper carbonation depths were predicted compared with the reference climate projection. For the mean climate projection, the effect of an increase in both $CO_{2(g)}$ concentration and temperature, as well as a slight decrease in relative humidity, lead to an increase in carbonation depth.

A comparison of predicted carbonation depth in concrete under mean and reference scenarios of climate projection between 2020-2100 is shown in Fig 6.11. Generally, a higher carbonation depth for the mean scenario is predicted compared to the reference scenario. The results further show that the carbonation depth in the mean climate projection starts to deviate around 2050, which is mainly caused by a rapid increase of $CO_{2(g)}$ concentration in the atmosphere. For the year 2100, nearly a 6mm difference in carbonation depth is predicted for the mean and reference scenario, which corresponds to an approximately 20% increase due to climate change.



Fig 6.10. Comparison of the predicted phase assemblage in concrete at 2100 exposed to the mean and reference climate projections.



Fig 6.11. Comparison of carbonation depth between 2020-2100 under mean and reference climate projection.

6.3.2 Impact of climate change based on the uncertainty of climate projection

6.3.2.1 Input data for uncertainty analyses

The uncertainty of carbonation depth profiles and critical climate projections for concrete deterioration under atmospheric conditions are studied using the Monte-Carlo simulation approach with generated random variables from an ensemble of multi-model climate projections between 2020 and 2100. The generated five hundred independent samples of temperature, relative humidity, and $CO_{2(g)}$ concentration from an ensemble of multi-model climate projections at the DTI between
2020-2100, under the RCP8.5 scenario, are shown in Fig 6.12a, b, and c, respectively. Based on reported greenhouse gas emissions, anthropogenic radiative forcing is calculated, and subsequently, climate change is predicted based on the calculated radiative forcing. Furthermore, the reported increase in atmospheric $CO_{2(g)}$ concentration for the RCP8.5 scenario is shown in Fig 6.9c. To cover a range of nearly ± 100 ppm around the reported atmospheric $CO_{2(g)}$ concentration, the coefficient of variation (COV) for $CO_2(g)$ concentration was assumed to follow a linear function, increasing from 0 in 2020 to a maximum value of 0.03 in 2100 for uncertainty analyses. In addition, the uncertainty of $CO_{2(g)}$ concentration was assumed to be normally distributed. An increase in all generated atmospheric temperatures and $CO_{2(g)}$ concentration samples for RCP8.5 was observed between 2020-2100, whereas a slight decrease in relative humidity was found for the same period. Nearly 10 °C temperature difference between the upper and lower values of generated temperature samples at the end of 2100 was observed, while the $CO_{2(g)}$ concentration for all samples spread over the range approximately from 800 to 1000 ppm.



Fig 6.12. Generated 500 independent samples from an ensemble of multi-model climate projections for the DTI field station between 2020-2100 (a) temperature, (b) relative humidity, and (c) $CO_2(g)$ concentration.

A sensitivity analysis was conducted to identify critical climate projections for concrete deterioration under atmospheric conditions. The generated data samples were analysed to determine the correlation between projections of temperature, relative humidity, and $CO_{2(g)}$ concentration. A matrix plot for generated climate projection samples at the end of 2100 for RCP8.5 is shown in Fig 6.13, where the subplots in the diagonal show the histogram of the sample values while the subplots in the non-diagonal show the sample values of the two pairs of samples. The determined correlation coefficients among samples are shown in Table 6.4, indicating no significant correlation between the input data was identified (temperature, relative humidity, and $CO_{2(g)}$ concentration). Therefore, the non-correlation method is employed to determine the sensitivity indices of climate projections in this study.



Fig 6.13. Correlation between $CO_{2(g)}$ concentrations, temperature, and relative humidity in 2100 for the RCP8.5 emission scenario.

CC	Temperature	RH	Con_CO ₂ (g)
Temperature	1.000	0.032	0.023
RH	0.032	1.000	0.001
Con_CO ₂ (g)	0.023	0.001	1.000
Con_CO ₂ (g)	0.023	0.001	1.000

Table 6.4. Determined correlation coefficients (CC) between temperature, relative humidity and $CO_{2(g)}$ concentrations in 2100 for the RCP8.5 emission scenario.

6.3.2.2 Results of uncertainty analysis and discussion

Using a Monte Carlo simulation approach, carbonation depth profiles were simulated using the developed RTM framework for saturated conditions, applying randomly generated temperature, relative humidity, and $CO_{2(g)}$ concentration under the RCP8.5 scenario. The predicted uncertainty of the carbonation depth profiles is shown in Fig 6.14. In addition, the mean, 5, and 95% confidence level of carbonation depth profiles are also presented in Fig 6.14. In all simulations, a carbonation depth of less than 25mm was observed. Generally, the rate of carbonation decreases due to a gradual drop in the partial pressure of $CO_{2(g)}$ in the pore void with depth from the exposure surface. However, in all simulations, a decrease in the carbonation rate is not identified nearly after 2050. At the same time, the uncertainty of prediction of the carbonation depth continuously increases with exposure time, which is mainly caused by a rapid increase in atmospheric $CO_{2(g)}$ concentration.



Fig 6.14. Predicted uncertainty of carbonation depth profile.

A sensitivity analysis between carbonation depth and climate projections was conducted to identify critical climate projections for concrete deterioration under atmospheric climate conditions. The method presented in section 6.2.2.2 to determine the sensitivity indices was adapted here. Scatter plots illustrate the sorted carbonation depth against each climate projection at the end of the year 2100, and subsequently, the average for each subset was calculated, as shown in Fig 6.15. The results indicate linear trends between carbonation depth and climate projections. An increase in atmospheric temperature and $CO_{2(g)}$ concentration leads to an increase in the carbonation depth, while increases in relative humidity limit concrete carbonation. From the presented results, it can be concluded that atmospheric changes in temperature and $CO_{2(g)}$ concentration will be unfavourable, while changes in relative humidity will decrease carbonation depth in concrete. The calculated sensitivity indices of atmospheric climate projections for concrete carbonation are provided in Table 6.5. From the sensitivity indices values in Table 6.5 and subset averaging value trends in Fig 6.15, the impact of climate change on concrete deterioration under atmospheric exposure can be predicted and used to identify more robust design approaches and more resilient and adapted maintenance strategies for concrete infrastructure in urban environments. Changes in $CO_{2(g)}$ concentration will play a significant role in the carbonation of concrete compared to other climate parameters, whereas temperature was identified as the second most important parameter. Finally, it should be noted that the results of the present uncertainty analysis indicate that changes in relative humidity do not show a significant influence on carbonation depth.



Fig 6.15. Scatter plots of sorted carbonation depth against selected climate projection parameters and the average value of carbonation depth for each subset.

Table 6.5.	Sensitivity	indices	of climate	projections
	<i>.</i>			1 5

Location	CO ₂ (g)	Temp	RH	
At DTI	0.432	0.307	0.261	

7 Adaptations to climate change

In this chapter, adaptations to climate change based on predicted results from Chapter 6 and current durability design specifications are discussed for concrete structures under seawater and atmospheric exposure conditions. Furthermore, Chapter 7 outlines limitations in current specifications for designing concrete structures to withstand climate change in selected locations, including the Solsvek and DTI field stations.

7.1 General outline

Scenarios of adaptations to climate change are described based on simulations for concrete structure deterioration due to the climate projections for higher emission scenarios (RCP8.5) presented in IPCC 2014. Adaptation methods to counteract the impact of climate change on deterioration may include changes in material and geometrical properties of elements of the concrete structures, as well as the application of cathodic protection to prevent reinforcement corrosion. To protect concrete structures from deterioration due to the impact of climate change, an increase in cover thickness and concrete grade, choice of proper water-to-binder ratio, and binder composition are preferred options in the designing process without compromising reliability and serviceability.

The time to reach a threshold value of chloride at the surface of reinforcement and carbonation depth to reach reinforcement can be increased by adjusting the cover thickness of the concrete element. When increasing the cover depth, the time to corrosion initiation will be delayed. Adjusting cover thickness in the concrete infrastructure design under changing climate is the most apparent adaptation, as it is an easy and effective method for delaying corrosion initiation. High-grade, dense concrete reduces chloride transport and carbonation through pores, eventually delaying corrosion initiation. Furthermore, different binder compositions, including SCM materials such as fly ash, blast furnace cement, silica fume, and others, can reduce the transport of ions and gaseous species, which may result in increased durability of concrete structure. Surface and cathodic protection limit the ingress of harmful substances through exposed concrete surfaces. However, the direct and subsequent maintenance costs of these approaches may be too high compared with other adaptation methods.

7.2 Current specifications for the durability design of concrete structures

Current specifications for the durability design of concrete structures based on environmental classification, which can be used for the durability design of concrete structures, are briefly introduced. Current standards define a prescriptive system for specifying and ensuring the durability of (new) concrete structures. Within these prescriptive specifications, the durability of concrete structures is assumed to be guaranteed through the selection of concrete mix designs and construction methods, including parameters such as minimum cover thickness, water-to-cement ratio, minimum cement content, and minimum strength class of concrete to protect concrete structures from the different actions of the service environment.

7.2.1 Environmental conditions

For the durability design of (reinforced) concrete structures, environmental loading is typically characterized by exposure classes in current standards. For example, in EN206-1, the environmental loadings related to carbonation-induced and chloride-induced corrosion are described by exposure classes XC and XS, respectively. Here, class XC for carbonation-induced corrosion is further subdivided into four classes depending on the prevailing moisture condition, while XS is divided into three classes based on the location of a structure in seawater. Exposure classes related to environmental conditions in accordance with EN 206-1 are shown in Table 7.1.

Clas s	Description of the environment	An informative example where exposure classes may occur				
Corrosion induced by carbonation						
XC1	Dry or permanently wet	Concrete inside buildings with very low air humid- ity, Concrete permanently submerged in water				
XC2	Wet, rarely dry	Concrete surfaces are subject to long-term water contact; Many foundations				
XC3	Moderate humidity	Concrete inside buildings with moderate or high air humidity; External concrete sheltered from rain				
XC4	Cyclic wet and dry	Concrete surfaces subject to water contact, not within exposure class XC2				
Corros	sion induced by chlorides from seawate	ſ				
XS1	Exposed to airborne salt but not in direct contact with seawater	Structures near or on the coast				
XS2	Permanently submerged	Parts of marine structures				
XS3	Tidal, splash, and spray zones	Parts of marine structures				

Table 7.1. Exposure classes related to environmental conditions in accordance with EN 206-1.

7.2.2 Requirements for durability

According to EN 206-1, the concrete cover is defined by the distance between the surface of the reinforcement closest to the nearest concrete surface (including links and stirrups and surface reinforcement where relevant). In the design approach, the nominal cover value, which includes the minimum cover and its deviation, is used for the execution and specifications.

$$C_{nom} = C_{min} + \Delta C_{div}$$
 Eq 7.1

Where C_{nom} is the nominal cover, C_{min} is the minimum cover, and C_{div} (mm) is the expected deviation, which depends on quality control, and where ΔC_{div} is equal to 1.645s; here, s is the standard deviation of a concrete cover following a normal distribution. For typical quality control, the standard deviation is taken as 6mm. Therefore, the allowance for deviation is considered as $\Delta C_{div} = 10.0$ mm for nominal cover calculation.

Concerning the durability of concrete, the minimum cover values for reinforcement in normal-weight concrete, taking into account exposure classes and structural classes, are given by $C_{min,dur}$. For a design life of 50 years, structural class 4 (S4) is considered for all exposure classes. For different conditions such as working life, concrete strength, and element type, the recommended modifications to the structural class are given in Table 7.2. Based on each exposure classification and under the condition that a moderate level of maintenance is provided in EN 1992, the specifications for minimum concrete cover, $C_{min,dur}$ are given in Table 7.3. Each provided minimum concrete cover depends on the structural class (S1 to S6) and design service life (50 and 100 years).

Criterion	Exposure Class					
	X0	XC1	XC2/XC3	XC4	XSI	XS2/XS3
Design life of 100 years	increase class by 2					
Strength class	≥ C30/37 reduce class by 1	≥ C30/37 reduce class by 1	≥ C35/45 reduce class by 1	≥ C40/50 reduce class by 1	≥ C40/50 reduce class by 1	≥ C45/55 reduce class by 1
Member with slab ge- ometry (position of re- inforcement not af- fected by construction process)	reduce class by 1					
Special quality control of the concrete pro- duction ensured	reduce class by 1					

Table 7.2. Recommended structural classification.

Table 7.3. Values of minimum cover, $C_{min,dur}$, requirements with regard to durability for reinforcement steel following EN 10080.

Structural class	Exposure Class						
	X0	XC1	XC2/XC3	XC4	XS1	XS2	XS3
S1	10	10	10	15	20	25	30
S2	10	10	15	20	25	30	35
S3	10	10	20	25	30	35	40
S4	10	15	25	30	35	40	45
S5	15	20	30	35	40	45	50
S6	20	25	35	40	45	50	55

7.3 Chloride-induced deterioration

Reinforced concrete structures under the RCP8.5 scenario could be more vulnerable to the impact of climate change compared with other emission scenarios (RCP2.6, RCP 4.5, and RCP 6.5). Therefore, the adaption of methods to meet the challenges of, e.g., reinforcement corrosion under the RCP8.5 scenario, may be adequate to protect reinforced concrete under other climate change in other RCP scenarios. For different chloride threshold values, the vulnerability region for reinforcement corrosion initiation is predicted using a 95% confidence level plot (see Fig 6.7) for climate change in the RCP8.5 scenario, see Fig 7.1. The presented results allow choosing the nominal cover requirement based on the service life design (50 or 100 years) based on the minimum chloride threshold value. According to the current specifications in EN206-1, the nominal cover requirement for 50 and 100 years of service life of concrete structures under the XS2 exposure class is 40 and 50mm based on strength classes S4 and S6, respectively (see Table 7.3. Considering 50 years of service life, the predicted results under the RCP8.5 emission scenario show that 58, 50, 44, and 40mm covers are required for 0.2, 0.24, 0.28, and 0.32 chloride thresholds, respectively. Results of the numerical simulations indicate that concrete structures with a chloride threshold higher than 0.32 will be unaffected by the impact of climate change. However, the defined minimum cover thickness should be increased by 18, 10, and 4mm for 0.2, 0.24, and 0.28 chloride threshold values, respectively, to withstand the impact of climate change.



Fig 7.1. Predicted vulnerability region to chloride-induced reinforcement corrosion using a 95% confidence interval for different chloride threshold values.

For studying the impact of climate change on the service life of concrete exposed to seawater, the chloride content in different depths under reference and RCP8.5 climate change scenario is compared; see Fig 7.2. The numerical studies indicate that the time to corrosion initiation will be reduced in materials with lower chloride threshold values compared to the reference climate scenario. However, for materials with a higher chloride threshold value, the impact of climate change will be favourable, leading to a delay in corrosion initiation time. The increase in time to corrosion initiation is caused by the release of chloride due to the decomposition of the C-S-H phase in the vicinity of the exposure surface. The reduction in time to corrosion initiation increases with cover thickness for particular chloride threshold values, which means that the impact of climate change on deterioration is mainly observed for concrete with larger cover thicknesses.

By means of example, the reduction in time (in years and percentage) to initiation of reinforcement corrosion for different cover thicknesses and 0.2 and 0.24 threshold chloride values is given in Table 7.4 and Table 7.5, respectively. The presented results indicate that the reduction in time to corrosion initiation increases with cover thickness for both. Predicted changes are thereby in the range of 11.7-16.5% and 9.0-10.9% for materials with 0.20 and 0.24 chloride threshold values, respectively, implying that the impact of climate change on corrosion initiation decreases with the chloride threshold value.

The adaption of cover thickness appears to be the most accessible and straightforward design approach to reduce the impact of climate change on concrete deterioration. However, an increase in cover thickness is neither cost-effective nor sustainable due to increased material and resource consumption, which will also affect structural and architectural design. Therefore, other approaches for adaption, mainly connected to material selection, are required to reduce and counteract the impact of climate change. The ionic transport of aggressive species can be controlled by adjusting inherent material properties, such as the transport properties of substances. If the mix design of the material is conducted based on the concept of lowering the pore void without compromising strength and other material properties, the ingress of ions and gases can be reduced. As a result, the time for corrosion initiation will be delayed. In practice, selecting a higher strength grade of concrete is one approach to reduce the pore void and thus ingress, in addition to enhancing its mechanical properties. Yet, such an approach is again accompanied by an increase in material and resource consumption due to the higher cement content in the mix design.

On the other hand, rather than simply adjusting the concrete mix design and cover thickness, limiting the ionic and gas transport into deeper sections of concrete by increasing the chemical and physical binding of chloride ions with hydrated phases will be a more viable and cost-effective method to counteract climate change. For example, the presented RTM framework indicates that chlorides are chemically (e.g., Friedel's salt) and physically bound by the hydrated phase in the vicinity of the exposure surface, limiting the transport of chloride into more profound depths. However, the increase in chloride content in deeper depth is observed due to the decomposition of Friedel's salt and the C-S-H phase. Therefore, increasing the bound behaviour of chloride with hydrated phases using SCMs and other binder materials will be an advanced and cost-effective method to counteract climate change.



Fig 7.2. Predicted chloride content at different depths for reference and climate change scenario (RCP8.5).

Table 7.4.	Reduction in	service life	based on c	chloride t	threshold	(0.20%).
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Cover depth [cm]	Unchanged condition [year]	Climate change condition [year]	Reduction in cor- rosion initiation [year]	Reduction in corro- sion initiation [%]
2	2026.0	2025.3	0.7	11.7
3	2033.5	2031.7	1.8	13.3
4	2046.8	2042.9	3.9	14.5
5	2061.7	2054.8	6.9	16.5

Table 7.5. Reduction in service life based on chloride threshold (0.24%).

Cover depth [cm]	Unchanged condition [year]	Climate change condition [year]	Reduction in corro- sion initiation [year]	Reduction in corro- sion initiation [%]
2	2027.5	2026.8	0.7	9.0
3	2036.5	2034.9	1.6	9.8
4	2054.6	2050.6	4.0	11.7
5	2071.3	2065.7	5.6	10.9

7.4 Carbonation-induced deterioration

For studying the impact of climate change on the service life of concrete due to carbonation, predicted carbonation depths under reference and RCP8.5 climate change scenarios (95% confidence interval) were compared; see Fig 7.3. Results of the numerical studies indicate an increase in the difference in carbonation depth with exposure time. Generally, the carbonation rate reduces with time due to a drop in partial pressure in the pore void. However, this reduction in the carbonation rate is not observed under exposure to climate change scenarios in contrast to the reference scenario. The observed behaviour for the carbonation rate under climate change scenarios can be explained by the rapid increase of $CO_2(g)$ concentration at the boundary surface of the concrete.

Similar to the approach presented for chloride-induced deterioration, the minimum cover requirement can be based on the service life design (e.g., 50 or 100 years) and the results of the numerical simulations for the carbonation depth under climate change scenarios. According to current specifications in EN206-1 for carbonation-induced corrosion, the nominal cover requirement for 50 and 100 years of service life of concrete structures under the XC4 exposure class is 30 and 40mm based on strength class S4 and S6, respectively (see Table 7.3). Considering 50 years of service life, the predicted results for the RCP8.5 emission scenario show that the 20mm minimum cover thickness is sufficient to protect concrete exposed at the DTI field station from carbonation-induced corrosion. In general, the numerical simulations indicate that current guidelines for durability in terms of defined cover thickness are sufficient to withstand the impact of climate change. The primary reason for this observation is related to the annual relative humidity, which is above 75% compared to other regions in northern Europe. As a result, moisture occupies most of the pore space, which limits the $CO_{2(g)}$ transport through pores. This behaviour can be identified clearly in the sensitivity indices study for the relative humidity, as illustrated in Fig 6.15. Therefore, the relative humidity in the DTI field station protects the concrete from carbonation-induced corrosion due to climate change. However, the impact of climate change on concrete deterioration is mainly in concrete exposed to atmospheric conditions with low relative humidity.

The increase in carbonation depth (in percentage) due to climate change at the end of 2100 based on the reference scenario is provided in Table 7.6. The presented results indicate a continuous increase in carbonation depth with exposure time.

After 20 years of exposure, a 12.6% increase in carbonation depth is observed, which increases to 36.5% at the end of 2100. Even for concrete exposed to higher relative humidity, an increase of approximately 1/3 in carbonation depth is predicted. Therefore, the impact of climate change on carbonation-induced concrete deterioration in regions where a lower relative humidity is dominant will be considerably higher compared to regions with higher annual relative humidity, such as e.g. northern Europe.

To protect concrete exposed in regions with lower relative humidity, other methods than adjusting cover thickness (as described in section 7.3) can also effectively counteract concrete carbonation due to climate change. The design of concrete materials with lower porosity will increase the saturation level and reduce the moisture loss through the concrete surface. As a result, even if the concrete is exposed to lower relative humidity, the diffusion of $CO_2(g)$ through the pore void will reduce. Therefore, the reduction of porosity method mitigates the impact of climate change on concrete deterioration. In the context of chemical binder compositions, the design of materials with higher content of hydrated phases and lower reaction rates with carbonates such as C-S-H, AFm, and AFt will also be an effective method to delay carbonation and reduce the rate of carbonation.



Fig 7.3. Predicted carbonation depth for reference scenario and RCP8.5 emission scenario (95% confidence interval).

		-		
Age [years]	Reference scenario [mm]	Climate change scenario [mm]	Increase in car- bonation depth [mm]	Increase in car- bonation depth [%]
20	6.05	6.81	0.8	12.6
40	9.29	11.47	2.2	23.4
60	12.11	15.67	3.6	29.3
80	14.22	19.41	5.2	36.5

Table 7.6. Increase in carbonation depth due to climate change.

8 Conclusions and suggestions for further work

The overall objective of this thesis was to establish a modeling framework to predict, mitigate, and adapt to the impact of climate change on the material deterioration of civil infrastructure. The research findings are presented in Chapters 2 to 7. This chapter provides a summary and conclusions of the research findings of this study and how they relate to the overall objectives of the thesis. The chapter also discusses the current stage of the model framework for analysing the impact of climate change on concrete deterioration and the challenges and limitations that need to be addressed in future studies.

8.1 Summary

A conceptual framework for predicting, mitigating, and adapting to the impacts of climate change on the durability of concrete infrastructure was developed, thereby enabling the establishment of more robust design approaches as well as more resilient and adapted maintenance strategies for existing concrete infrastructures. Initially, a multi-species reactive transport model (RTM) was established, including mass transport coupled with chemical equilibrium, for predicting the deterioration of cement-based material through pore solution and solid phase changes under different environmental conditions. The prediction of concrete deterioration under actual environmental conditions, where concrete infrastructure is located in the real field, is more complex and often hardly comparable to results observed in labscale experiments, which may be due to fluctuations of climate conditions with time and the complex effect of boundary conditions. Therefore, the developed modeling framework was calibrated and tested in two case studies: i) data from the Solsvik field station, Norway, including observations of submerged concrete deterioration for more than 16 years, and ii) data from the Danish Technological Institute field station data, Denmark, including observations of concrete carbonation under atmospheric conditions for nearly eight years.

To account for the impact of climate change on concrete deterioration, the approach was further integrated with the statistical results of state-of-the-art climate models. For this study, the multi-model ensembles of global circulation models (GCMs) projections under the very high GHG emissions scenario (RCP8.5), which

is produced by the Coupled Model Intercomparison Project phase 5 (CMIP5) initiative, were used to investigate the impact of climate change on concrete structure deterioration in the period between 2020 and 2100. To avoid the biases and spatial resolution of these global projections that hinder their use in regional applications, the multi-model climate projections at high spatial resolution were downscaled to local scales using the Delta statistical downscaling method. The downscaled multimodel climate projections were statistically analysed to determine the uncertainty of climate projections, i.e., atmospheric temperature, relative humidity, and temperature and salinity level of seawater. Using distribution parameters from the climate projection for the RCP8.5 scenario, random samples were generated using the Latin hypercube sampling (LHS) technique. Using an integrated modeling framework, Monte Carlo simulations were performed to account for uncertainty information in the climate projections involved, and subsequently, an analytical probabilistic design approach was developed to identify essential climate projection outputs driving concrete deterioration in future climate projections. Finally, the results from the probabilistic design approach were used to investigate and identify more robust design approaches and more resilient and adapted maintenance strategies for concrete infrastructure, anticipating, mitigating, and adapting to the impacts of climate change on material deterioration.

8.2 Conclusions

The main conclusions of this Ph.D. thesis are presented in the following. Conclusions are drawn regarding the development of the RTM framework and its application to assess the impacts of climate change on concrete deterioration.

Development of a multi-species reactive transport model

Chapter 3 dealt with developing a multi-species reactive transport model for cement-based material and defining the relevant boundary conditions for different environmental conditions. Furthermore, Chapter 4 demonstrates the applicability of the developed RTM to predict concrete deterioration under actual environmental conditions, where concrete is exposed to natural field conditions, comparing predicted results with experimental data obtained from two field stations, i.e., Solsvik field station in Norway and Rødbyhavn field station in Denmark. From the work presented in Chapters 3 and 4, the following conclusion can be drawn:

- For understanding the deterioration of concrete through the pore solution composition and phase assemblage changes in cement-based materials, a reactive transport modeling framework is developed, including multi-component gas, multi-ionic, and moisture transport coupled with a chemical equilibrium computation.
- A set of modified Poisson Nernst-Planck equations for multi-ionic transport through an uncharged, 'free water' and charged, 'the electrical double layer,' including the effect of temperature, pore solution property, and pore structure changes, have been introduced for multi-ionic transport.
- A comprehensive method has been illustrated for determining the diffusion coefficient at infinite dilution of the aqueous species present in the pore solution in a cementitious material.
- The two-phase moisture transport model, which considers pore structure changes, is introduced with capillary pressure as the primary variable parameter.
- The consideration of boundary conditions and moisture flux through the exposed surface is demonstrated separately for wetting and drying conditions.
- Using Henry's law, the multi-component gas transport model was developed, including gas dissolution into the pore solution.
- A modeling approach for moisture conductivity and gas and ionic diffusivity based on the pore structure and moisture storage was presented to account for pore structure changes in mass transport.
- The significance of employing a surface complexation model is emphasized to predict the actual changes in the composition of the pore solution and evaluate the implications of these changes on steel corrosion.
- Numerical simulations were compared to experimental data to demonstrate the applicability of the RTM under saturated, drying-wetting, and atmospheric exposure conditions.

Impact of climate change on concrete deterioration

Chapter 6 highlights the impact of future climate change on concrete deterioration under different environmental conditions and sensitivity indices analysis to determine critical climate projections for concrete deterioration. Furthermore, Chapter 7 presents the adaptation methods to climate change based on predicted results from Chapter 6 and outlines limitations in current specifications for designing concrete structures to withstand climate change in selected case study locations, including the Solsvek and DTI field stations. From the work presented in Chapters 6 and 7, the following conclusion can be drawn:

- Total chloride concentration decreased due to climate change in the region closer to the exposed surface (0-6cm), whereas an increase in chloride content was observed in more profound depths (above 6cm depth). Therefore, the effect of climate change on chloride ingress can be observed at deeper depths in concrete exposed to seawater.
- The sensitivity indices analysis of climate change on concrete deterioration indicated that both temperature increases and decreases in the salinity of seawater are favourable to limiting corrosion initiation in depths between 0-6cm. However, temperature increases were identified as favourable, while the decreases in salinity were unfavourable for corrosion initiation in deeper depths (above 6cm depth). Furthermore, temperature changes are identified as a critical climate parameter to increase concrete deterioration in more profound depths.
- An increase in carbonation depth in concrete due to the projected atmospheric climate change. However, the predicted carbonation depth is less than 20mm. The rate of carbonation typically decreases over time. However, under the exposure of climate projection scenarios, such a decrease in the carbonation rate was not identified, which was mainly associated with a rapid increase in atmospheric CO_{2(g)} concentration.
- A linear trend between carbonation depth and atmospheric climate projection is observed. Further, the increase in atmospheric temperature and CO_{2(g)} concentration increases the carbonation depth, while a decrease in relative humidity limits concrete carbonation. Atmospheric temperature and CO_{2(g)} concentration changes will be unfavourable for concrete deterioration, while changes in relative humidity will be beneficial for concrete carbonation. Further, the determined sensitivity indices showed that changes in CO_{2(g)} concentration will play a significant role compared with other climate parameters for concrete carbonation, whereas temperature is the second most important parameter.
- According to a comparison of numerical predictions and values provided in the current EN206-1 specifications, model predictions indicated that reinforced concrete structures exposed to seawater at the Solsvik field station, Norway, could be vulnerable to the impact of climate change. Concrete materials with a chloride threshold larger than 0.32 are less impacted by climate change. For

concrete materials with a chloride threshold value lower than 0.32, the defined minimum cover thickness in the specification should be increased to withstand the impact of climate change. Further, the reduction in time to corrosion initiation based on the reference climate scenario varies approximately in the range of 11.7-16.5% and 9.0-10.9% for materials with 0.20 and 0.24 threshold chloride values, respectively. The difference in predicted time to corrosion initiation illustrated that the impact of climate change on corrosion initiation decreases with the chloride threshold value.

 According to the current EN206-1 specifications, numerical simulations for concrete exposed to the atmosphere at the DTI field station show that a 20mm minimum cover thickness is sufficient to protect concrete from carbonation-induced corrosion. Futhermore, the carbonation depth continuously increases with exposure time. Comparing the reference and RCP8.5 climate scenario, a 12.6% increase in carbonation depth was observed after 20 years of exposure, while an increase to 36.5% was found at the end of 2100.

8.3 Future studies

The developed multi-species RTM based on gas-ion-solid phase interaction was used to predict the deterioration of cement-based material under different environmental conditions. Further, the impact of climate change on concrete deterioration and critical climate projection outputs driving the material deterioration of civil infrastructure in the future were investigated. Based on the findings and conclusions of this study, the following recommendations for future work are listed:

- A calcite layer forms on the exposed concrete surface for long-term concrete exposure to seawater due to the direct reaction between leached ions and the hydrated cement phase. As a result, significant changes in phase assemblage and pore structure can be observed in the exposed concrete surface. In chemical equilibrium calculation, the reaction between the leaching of ions and the hydrated cement phase at the exposed surface should be considered to improve prediction results.
- The assumption is made that chemical equilibrium between the gaseous phase in pores, pore solution, and hydrated solid phases is achieved within the assigned time step calculation. Further, dissolution and precipitation reaction rates are assumed to be equal for all concrete phases. However, the reaction rate of each phase in concrete is different, and phases with a higher dissolution rate

disappear immediately. Therefore, the kinetic behaviour of phases should be considered in chemical equilibrium calculation to predict changes in phase assemblage.

- Cracks may form in concrete when exposed to severe environmental conditions. The mass transport of ions, moisture, and gases is significantly affected in cracked concrete compared with uncracked concrete. The current reactive transport model is designed to simulate concrete deterioration under uncracked conditions. In future studies, the diffusion parameters for ions and gases, as well as the conductivity terms for moisture in the mass transport equation, should be updated to account for cracked concrete.
- Boundary conditions in the tidal and splash zones are complex due to changes in seawater levels and wave propagation. Consequently, the mechanism of ion ingress through the concrete's boundary surface is not fully understood. Therefore, it is essential to thoroughly investigate the capability of the developed RTM approach to simulate the deterioration of cement-based materials under these complex environmental conditions by comparing numerical and experimental results.
- Considering the computational time, three environmental climate parameters, $CO_{2(g)}$ concentration, temperature, and relative humidity were chosen for the Monte-Carlo simulation to analyse the impact of climate change on the carbonation of concrete. However, uncertainties related to other parameters, such as wind speed, wind direction, and precipitation, were not included in the simulation. Therefore, future studies should investigate the combined effects of all climate parameters.
- The present study did not include the impact of climate change on concrete deterioration under various environmental conditions, such as atmospheric conditions and the tidal and splash zones of offshore concrete structures. Therefore, future studies should investigate the effects of climate change on concrete deterioration under these complex environmental conditions.

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10 Appended Papers

Paper I

"A multi-species reactive transport model based on ion-solid phase interaction for saturated cement-based materials"

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A multi-species reactive transport model based on ion-solid phase interaction for saturated cement-based materials



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ARTICLE INFO	ABSTRACT
Keywords: Reactive transport model Multi-ionic transport Chemical equilibrium Free water EDL PHREEQC_RM	This study established a reactive transport model (RTM) for saturated cement-based materials based on multi- ionic transport through an uncharged, 'free water' and charged, 'the electrical double layer' coupled with a chemical equilibrium model for interaction between pore solution and solid phase. A set of modified Poisson- Nernst-Planck equations, including the effect of temperature, pore solution property, and pore structure changes, have been introduced for multi-ionic transport. A comprehensive method has been illustrated for determining the diffusion coefficient at infinite dilution of the aqueous species present in the pore solution in a cementitious material. Numerical predictions were compared to experimental data to demonstrate the applica- bility of the RTM. For mortar specimens exposed to NaCl solution and seawater, numerical predictions agree well with experimentally determined Portlandite and carbonate in the phase assemblage, elemental distribution such

as chloride, sodium, potassium, magnesium, and sulfur adjusting the initial tortuosity factor.

1. Introduction

Reinforced concrete materials are widely used for civil infrastructure such as buildings, bridges, tunnels, roads, offshore structures, etc. However, in their service life, reinforced concrete structures located in a harsh environment are severely attacked by the ingress of substances from the service environment [1–4]. Furthermore, research and experience over the past 20 years show that planning, material, and construction costs are often dwarfed by the costs associated with material deterioration, i.e., costs of inspecting, repairing, and maintaining civil infrastructure over its useful life [5]. Therefore, numerical methods capable of predicting the changes in concrete materials over the service life help select the cement composition and mix design, optimize the cost for infrastructure, and predict the structure's lifetime.

Several numerical models were developed to predict deterioration, especially for cement-based materials, based on this perspective over the last two decades. Initially, deterioration models were developed only considering multi-ionic transport models [6–9]. Later, multi-ionic transport models were coupled with chemical equilibrium [10–13]. Currently, RTMs have been developed, including a multi-ionic mass transport model coupled with a chemical equilibrium including surface complexation [14,15]. Here, the interactions between pore solution and solid phases and the interactions between the C-S-H phase and the

surrounding ions of the pore solution were included. In the current RTM, the Poisson-Nernst-Planck (PNP) equation derived using the hybrid mixture theory [16,17] is commonly used for the multi-ionic transport model in porous media. PHREEQC [18–20] is adopted to perform chemical equilibrium between pore solution and solid phases, including surface complexation. However, the modelling approaches are restricted by simplifying assumptions and a large number of input parameters concerning the processes associated with the deterioration of cement-based materials. Predictive capabilities are also lacking due to the absence of essential relations between chemical reactions, pore structure changes, and ion mass transport. Without considering these interactions, the predictive capabilities of such modelling approaches will always be limited.

The electrical double layer (EDL) will form on the pore surface of cementitious materials due to interactions between the surface site of the C-S-H phase and the surrounding ions of the pore solution. As a result of the EDL formation, the diffusion of anions and cations will take a different pathway in the pore solution. Most of the anions diffuse through free water space, while the diffusion of cations occurs through the EDL [15,21,22]. In the current RTMs [10,12–14], the ion mass transport is performed only through free water space, whereas the ions in the EDL are considered stagnated ions, which means that part of cations is neglected in the ion mass transport calculation. In addition,

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the ion mass transport in porous materials strongly depends on temperature [23], composition and ionic strength of pore solution [24,25], and pore structure [26,27]. Pore solution composition, phase assemblage, and pore structure will continuously vary in a cement-based material due to exposure to long-term environmental actions. The effect of these changes is not taken into account by the traditional PNP equation. Moreover, most approaches accounting for surface complexation assume a fixed specific surface area of the C-S-H phase in the cementitious materials over time [13,14]. Due to the reaction between pore solution and solid phases, the formation of new phases, as well as the precipitation and dissolution of solid phases, occur on the pore surface. As a result, the specific surface area of the C-S-H phase on the pore surface continuously changes in cementitious materials. Therefore, the ion absorption capacity of the pore surface by the silanol sites (\equiv SiOH) varies over time.

In order to accurately predict the durability of cement-based materials exposed to various environmental conditions, RTMs should be developed with the following considerations: i) the flux of ions in both free water and the EDL must be considered for the actual multi-ionic transport calculation through a charged surface, ii) the effect of temperature, pore solution property, and pore structure changes must be accounted for in ion transport through a porous medium, iii) experimental results strongly indicate that C-S-H absorbs part of the ionic species in pore solution on the pore surface [28–36]. Thus, the exchange reaction between an ion in the pore solution and silanol sites (\equiv SiOH) needs to be included in the ion absorption on the pore surface in the surface complexation model, and v) for computation of the variation of the specific surface area of the C-S-H phase and the effect of pore structure changes on ion mass transport, a proper micro-pore structure model must be adapted as part of RTMs.

2. Modelling approach

2.1. Outline of reactive transport model (RTM)

The present study outlines the framework for a RTM, which can predict the spatial and temporal variation of pore solution composition and solid phases for various cement compositions and different exposure conditions. A schematic description of the phenomena and processes included in the RTM is shown in Fig. 1. The available space in pore distribution for ion mass transport and the schematic illustration of ion mass transport due to interaction between the ions and solid phase is described in Fig. 1a and Fig. 1b, respectively. The underlying framework of the RTM is thereby dealt with within two different time domains, i.e., the early-stage development of cementitious materials during the curing period and the deterioration processes of cementitious materials due to exposure to long-term environmental actions. The modelling part of early-stage material development and material deterioration is illustrated through regions A and B, respectively, in Fig. 1c. The RTM is established for saturated conditions within the present study, including multiple constitutive models, i.e., cement hydration, micropore structure, multi-component ionic transport models through free water and the EDL, and chemical equilibrium models.

During early-stage material formation, the incorporated hydration model determines the degree of cement hydration from input data of the mix design, composition of cement, and curing conditions. Subsequently, results from the hydration model are used to calculate the amount of pure phases (EQ) and solid solution phases (SS), the composition of pore solution, amount of absorbed ions on pore surface, and water content. During the deterioration process, the hydration model determines the degree of hydration for the remaining unhydrated cement with the exposure condition for each time step and the new



Fig. 1. Schematic diagram of the proposed multi-species reactive transport model.

equilibrium state of solid phases, the concentration of ions in free water and the EDL, amount of absorbed ions on the pore surface, and water content is computed applying the equilibrium phase theory. The geochemical model PhreeqcRM determines the chemical equilibrium, accounting for pore solution, pure and solid solution phases, and surface complexation in this study. For the computation of the material's microstructure, the total porosity of interlayer, gel, and capillary pores and the distribution of gel and capillary pores are determined from the phase assemblage provided by the geochemical computation. The effective diffusion coefficient of ions is subsequently calculated based on computed pore structure and pore solution property, whereas threshold porosity is also determined with updated pore structure. Finally, multicomponent ion transport through free water and the EDL is established with updated boundary conditions.

In the present study, the model proposed by Parrot and Killoh [37], a set of equations to describe the hydration rate of individual major clinker at each time step, is used for the hydration model. The reliability of the Parrot and Killoh approach for different types of water-cement ratio, blended cement, relative humidity, and temperature is described in [38–41]. The pore structure model proposed by Maekawa et al. [42] is adapted to compute the microstructure in this study. The adaption provides a more reliable modification, adapted to various cement and water-cement ratios considering the dissolution and precipitation of solid phases through chemical equilibrium calculations [42]. The details of the ion mass transport model, chemical equilibrium model, and numerical studies of the developed RTM for saturated cement-based material are illustrated in the following sections.

2.2. A multi-component ion transport model

2.2.1. General outline

Under the assumption of saturated conditions, all pores of cementitious materials are assumed to be filled with the pore solution during transport calculation. Thus, in the present study, a moisture transport model is not adapted, and the effect of moisture transport on the flux of ions is not included in the ion mass transport model. An electrical double layer (EDL) will form in cementitious materials due to the interaction between ions in the pore solution and silanol sites (≡SiOH) of the C-S-H phase in the pore surface. The water in the EDL (charged water) and water in the middle of the pore (uncharged water) are defined as EDL water and free water, respectively (see Fig. 1b). The ion diffusion and pathway of ions along an EDL water space are different from free water space. Therefore, the multi-ionic transport model will be developed using a one-dimensional FEM method in free water and the EDL separately. In addition, the effect of temperature, pore solution properties, and pore structure changes are implemented in the multi-ionic transport model. Moreover, it is considered that pores below a certain threshold radius are not accessible for multi-ionic transport (even if the pores are saturated) due to the formation of an EDL and high electrical potentials (see Fig. 1a). In the present study, the proposed model based on threshold radius (r_{th}) by Yuya Takahashi et al. [43] is used to calculate threshold porosity (φ_{th}).

2.2.2. Balance equations

This section will discuss the balance equations for the ion constituents in free water and the EDL separately. The mass balance equation for the j^{th} ion constituents in the free water of pore solution is,

$$\frac{\partial \left(\varphi_{gc} \varepsilon_{f}^{l_{j}} \rho_{f}^{l_{j}}\right)}{\partial t} + \nabla \left\{ \left(\varphi_{gc} - \varphi_{lh}\right) \varepsilon_{f}^{l} \rho_{f}^{l_{j}} v_{f}^{l_{j}} \right\} - q_{f}^{l_{j}} = 0$$
(1)

where φ_{gc} is the sum of gel and capillary porosity, φ_{th} is the threshold porosity, e_f^i is the saturation level of free water in the pore volume, $\rho_f^{i_i}$ is the mass density of the j^{th} ion constituent in the free water, which is related to the mass and volume as $\rho_f^{i_f} = M_f^{i_f}/V_f$, where $M_f^{i_f}$ and V_f are the mass of j^{th} ion constituent in the free water and volume of free water, respectively, and v_{j}^{l} is the absolute velocity of the j^{th} ion constituent in the free water. The property q_{j}^{l} denotes the mass gain of the j^{th} constituents in free water from all other constituents present in the phase due to chemical reactions. The mass balance equation for the j^{th} ion constituent in the EDL of the pore solution can be written as,

$$\frac{\partial \left(A_s t_d \rho_d^{l_j}\right)}{\partial t} + \nabla \left\{ (A_s - A_{th}) t_d \rho_d^{l_j} \nu_d^{l_j} \right\} - q_d^{l_j} = 0$$
⁽²⁾

where A_s is the surface area of the pore occupied by the pore solution, t_d is the thickness of the EDL, A_{th} is the surface area of the threshold porosity, ρ_d^l is the mass density of the j^{th} ion constituent in the free water, which is related to the mass and volume as $\rho_d^l = M_d^l/V_d$, where M_d^l and V_d are the mass of j^{th} ion constituent in the EDL and volume of the EDL, respectively, and v_d^l is the absolute velocity of the j^{th} ion constituent in the EDL. The property q_d^l denotes the mass gain of the j^{th} ion constituent in the EDL from all other constituents present due to chemical reactions.

2.2.3. Constitutive equations

This section discusses the constitutive equations leading to the governing equations for ion mass transport in free water and the EDL based on the approach presented in [15,16]. The cement-based material is considered as a non-deformable rigid porous material with constant porosity within the transport calculations. Moreover, for fully saturated conditions, all pores in the material are considered filled with liquid water. Thus, the following relations are valid in this case: $V_s + V_p = 1$, V_s $= V_{uc} + V_{ph} + V_{ag}$ and $V_p = \varphi_{lr} + \varphi_{gc} \bullet (\varepsilon_f^l + \varepsilon_d^l)$ where V_s and V_p is the volume fraction of solids and total porosity in the material, respectively, φ_{lr} is interlayer porosity, and ε_d^l is the saturation level of water in the EDL. The following constitutive equation for the diffusion flows $v^{l_r, l}$ as derived in Bennethum and Cusham [17], is subsequently adapted for multi-ionic transport.

$$r^{l_j} \rho^{l_j} v^{l_j,l} = -\rho^{l_j} \nabla \mu^{l_j} + \rho^{l_j} g^{l_j} - \rho^{l_j} z^j E_T$$
(3)

where r^{l_j} is the resistivity tensor for the j^{th} ion constituents, g^{l_j} is the gravity for the j^{th} ion constituents, μ^{l_j} is the chemical potentials for the j^{th} ion constituents, and E_T is the total electrical field. In the constitutive equation for the diffusion flow of ions, the charge character of all ionic constituents of the solution is allowed to affect the diffusion of the considered j^{th} ion constituent, which is included in the last term on the right-hand side. Moreover, the ionic diffusion flow depends on the constitution of the chemical potentials of the diffusing species in the solution. In the present approach, the chemical potential, which was introduced without the electrical field term in Bennethum and Cusham [17], is used, and the activity coefficient is adapted for the influence of the composition of the pore solution as follows:

$$\mu^{l_j} = \mu_0^{l_j} + R_m^{l_j} T \ln(\rho^{l_j} \gamma^{l_j}) \tag{4}$$

where $\mu_0^{l_i}$ is the reference chemical potential for the j^{th} ion constituent in the liquid phase, γ^{l_i} is the activity coefficient for the j^{th} ion constituent in the liquid phase, and $R_m^{l_i}$ is the gas constant for the j^{th} ion constituent in the liquid phase. The constitutive equation for the diffusive flow, i.e., Eq. (3), is subsequently modified with the introduced chemical potential in Eq. (4),

$$\rho^{l_j} v^{l_j,l} = r^{l_j-1} R_m^{l_j} T \left(-\nabla \rho^{l_j} - \frac{\rho^{l_j}}{\gamma'} \nabla \gamma^l - \frac{\rho^{l_j} z^j}{R_m^{l_j} T} \nabla \Phi_T \right)$$
(5)

where the total electric field intensity is described as the gradient of the total electric intensity potential Φ_T as $E_T = \nabla \Phi_T$. Since the effect of gravity, g^{l_j} on the diffusive flow of ions is negligible, the term is omitted in Eq. (5).

2.2.4. Governing equations

The governing equations for the multi-ionic transport in free water

and the EDL are derived using the introduced balance equation and appropriate constitutive equations. In fully saturated conditions, it is assumed that the moisture in the porous media is in a static condition, and thus, the velocity of the liquid phase can be neglected. Hence, the diffusion velocity of the j^{th} ionic species $v^{l_j, l}$ is considered equal to the absolute velocity of the j^{th} ionic species v^{l_j} in the porous material. Moreover, it is assumed that the following relations are valid for ion flow in free water and the EDL, respectively; $v_f^{l_i} = v_f^{l_i, l}$ and $v_d^{l_i} = v_d^{l_i, l}$, where $v_f^{l_i, l}$ is the diffusion velocity of the *j*th ionic species in free water and $v_d^{l_i l}$ is the diffusion velocity of the j^{th} ionic species in the EDL. To transform the mass flow equation into moles, the mole mass term, M^{l_j} of the ionic species is introduced. The mass concentration ρ^{l_j} and the mole concentrations C^{l_j} are related through $\rho^{l_j} = M^{l_j} C^{l_j}$ and the gas constant, R, which is related to $R_m^{l_j}$ through $R = M^{l_j} R_m^{l_j}$. Here, v^j is the valence of the j^{th} ionic species and the charge z^{j} is related to the valance by the Faraday constant F_C and the mole mass through $v^j F_C = z^j M^{l_j}$. For multi-ionic transport in free water, Eqs. (1) and (5) are combined via a velocity condition and represented in mole quantities, assuming no chemical reactions during ionic transport occur, i.e., $q_f^{l_i} = 0$,

$$\varphi_{gc} \varepsilon_{f}^{l} \frac{\partial C_{f}^{l_{j}}}{\partial t} = \nabla \left\{ D^{l_{j}} \left(1 + \frac{\partial ln\gamma_{j}}{\partial lnC_{j}^{l_{j}}} \right) \left(\varphi_{gc} - \varphi_{th} \right) \varepsilon_{f}^{l} \nabla C_{f}^{l_{j}} + A^{l_{j}} \nu^{j} \left(\varphi_{gc} - \varphi_{th} \right) \varepsilon_{f}^{l} C_{f}^{l_{j}} \nabla \Phi_{f}^{T} \right\}; j = 1, 2, 3..., N$$

$$(6)$$

where C_{f}^{l} is the mole concentrations of ions in free water. Similarly, Eqs. (2) and (5) are combined based on the velocity condition and formulated in mole quantities for multi-ionic transport in the EDL, assuming no chemical reactions during ionic transport, i.e., $q_{d}^{l} = 0$,

$$A_{s}t_{d}\frac{\partial C_{d}^{l_{j}}}{\partial t} = \nabla \left\{ D^{l_{j}} \left(1 + \frac{\partial ln\gamma_{j}}{\partial lnC_{d}^{l_{j}}} \right) (A_{s} - A_{th})t_{d}\nabla C_{d}^{l_{j}} + A^{l_{j}}\nu^{j}(A_{s} - A_{th})t_{d}C_{d}^{l_{j}}\nabla \Phi_{d}^{T} \right\}; j = 1, 2, 3..., N$$

$$(7)$$

where $C_d^{l_i}$ is the mole concentrations of ions in the EDL. D^{l_i} and A^{l_i} are the diffusion constant and ionic mobility, respectively, and are identified in the multi-ionic transport equation for free water and EDL as

$$D^{l_j} I = r^{l_j - 1} \frac{RT}{M^{l_j}}; A^{l_j} I = r^{l_j - 1} \frac{F_C}{M^{l_j}}$$
(8)

The first term on the right-hand side of Eqs. (6) and (7) describes the self-diffusion of ions. Here, the term $\partial \ln \gamma_j / \partial \ln C^l$ represents the effect of the mixture composition of all ions on the diffusion of individual ions. The second term accounts for the effect of the electrical potential on the ion diffusion in the mixture. The electric intensity potential in free water (Φ_f^T) and the EDL (Φ_d^T) are determined using Gauss's law separately. The obtained electric potential equation for free water is,

$$\nabla \left\{ \left(\varphi_{gc} - \varphi_{th} \right) \varepsilon_f^l \zeta_0 \zeta_r \nabla \Phi_f^T \right\} = \left(\varphi_{gc} - \varphi_{th} \right) \varepsilon_f^l F_C \sum_{j=1}^N v^j C_f^{l_j} \tag{9}$$

While the electric potential equation for the EDL can be written as follows,

$$\nabla\left\{(A_s - A_{th})t_d\zeta_0\zeta_r\nabla \boldsymbol{\varPhi}_d^T\right\} = (A_s - A_{th})t_dF_C \sum_{j=1}^N \nu^j C_d^{j_j}$$
(10)

where ζ_0 and ζ_r are the relative dielectricity coefficient and the dielectricity coefficient of vacuum, respectively. The finite element formation for the set of governing equations of the multi-ionic transport is described in Appendix A.

2.2.5. Diffusion coefficient of ions

The diffusion coefficient of ions in a porous material depends on pore structure [26,27] and pore solution properties such as the composition of the solution, ionic strength [24,25], and temperature [23]. In the

present approach, the effective diffusion coefficient is used after applying several corrections to the diffusion coefficient of an ion at infinite dilution. The diffusion coefficient at infinite dilution of individual ions at a reference temperature ($T_0 = 298.15$ K) is adjusted by the temperature, composition, and ionic strength of the solution and tortuosity factor to determine the effective diffusion coefficient. The tortuosity factor depends on the pore structure of the material. The effective diffusivity $D_{l,T}^{eff}$ of the i^{th} ion for the multi-component ion transport model is given as

$$D_{i,T}^{eff} = f_{\tau} \cdot f_{Tem} \cdot f_{I_i} \cdot D_{i,T_0}^{\infty} \cdot \left(1 + \frac{\partial ln\gamma_i}{\partial lnC^{l_i}}\right)$$
(11)

where D_{i, T_0}^{∞} is the diffusion coefficient at infinite dilution of the i^{th} ion at a reference temperature $(T_0), f_{\tau}$ is the tortuosity factor, and f_{Tem} and f_{I_s} are correction factors for temperature and ionic strength, respectively. The effect of the solution composition $(1 + \partial \ln \gamma_i / \partial \ln C^l)$ on the diffusion coefficient of ions is implicitly accounted for in the ion mass transport equation. The diffusion coefficient at infinite dilution is obtained from the limiting conductivities of ions $(\lambda_{i,T}^{\infty})$ by the following Eq. [44],

$$D_{i,T}^{\infty} = \frac{RT\lambda_{i,T}^{\infty}}{z_i^2 F^2}$$
(12)

Due to the presence of a charge-coupling mechanism between the ions, the diffusion coefficient at infinite dilution of many of the aqueous species present in the pore solution of cementitious materials is not determined experimentally. Various models for determining the diffusion coefficient at infinite dilution have been proposed over the past several decades. However, none of the models has led to a comprehensive set of equations suitable for estimating diffusion coefficient at infinite dilution for cementitious ion species [45–47]. Therefore, in this study, the values of unknown $D_{i, T0}^{\circ}$ of ions are estimated empirically as a function of both the size and charge property of the ion. According to Nernst, Stokes, and Einstein [44,46], the ionic stokes radius can be expressed in terms of the limiting conductivities

$$\mathbf{r}_{st}^{i} = \left(\frac{F^{2}}{6\pi N_{A}}\right) |z_{i}| / \eta_{w} \lambda_{i,T}^{\infty}$$
(13)

where N_A is the Avogadro's number and η_w the viscosity of water. From Eqs. (12) and (13), the ionic diffusion coefficient can be derived as inversely proportional to the formal charge and stokes radius of ions,

$$D_{i,T}^{\infty} = k \cdot \left(\frac{1}{|z_i| \ r_{st}^i}\right); \tag{14}$$

where:

$$k = \left(rac{RT}{6\pi N_A \ \eta_w}
ight)$$

To determine an empirical function for the diffusion coefficient at infinite dilution of ions present in cement-based materials, experimentally reported diffusion coefficient at infinite dilution at a reference temperature of 298.15 K, $D_{i,T=298}^{\infty}$, and the van der Waals radius of ions (calculated using the Calculator Plugins module of the chemical structure visualization tool MarvinSketch, Version 21.10, ChemAxon (htt ps://chemaxon.com/), is used. It was found that the experimentally measured value of $D_{i,T=298}^{\infty}$ is strongly correlated to the approximate van der Waals radius and charge of the ion, as shown in Fig. 2.

From Fig. 2, the diffusion coefficient at infinite dilution, $D_{i,T=298}^{\infty}$ can be expressed as a function of $1/(|z_i| r_{st}^i)$ for neutral, cations, and anions as

$$D_{i,T=298}^{\infty} = 3.752 \times 10^{-9} \left(\frac{1}{|z_i| r_{st}^i} \right) - 7.64 \times 10^{-11}$$
(15)

The estimated diffusion coefficient of typical ions in the pore solution



Fig. 2. Fitted linear regressions of $D_{i, T=298}^{\infty}$ values as a function of $1/(|z_i| r_{si}^i)$.

of a cementitious material at infinite dilution and for a temperature of 298.15 K is presented in Table B.1. The molar conductivities of ions change with the ionic strength of the pore solution at a constant temperature. To account for the influence of the ionic strength of solution on the diffusion coefficient at infinite dilution, the model proposed by Appelo [48] is used

$$f_{I_s} = exp\left(\frac{-a_{1i}A |z_i| \sqrt{I_s}}{1 + \kappa a}\right)$$
(16)

where:

$$\kappa a = \kappa \sqrt{I_s} \ \frac{a_{2i}}{1 + I_s^{0.75}}$$

where a_{1i} and a_{2i} are coefficients, *A* the Debye-Hückel parameter (0.51 (mol/dm³)^{-0.5} at 25 °C), κ the Debye length, and I_s the ionic strength. The limiting ionic conductivities and, equivalently, the diffusion coefficient at infinite dilution are dependent on temperature. For a wide range of temperatures, the temperature dependence of limiting ionic conductivities is reported by Smolyakov's equation [23]

$$f_{Tem} = \left(\frac{\eta_{298}^0}{\eta_T^0}\right) \left(\frac{T}{298.15}\right) exp\left(\frac{d_i}{T} - \frac{d_i}{298.15}\right)$$
(17)

where η_T^0 is the viscosity of pure water (Pa·s) at *T* in Kelvin and d_i a coefficient. The tortuosity is calculated based on changes of the pore structure due to dissolution and/or precipitation of solid phases determined by chemical equilibrium as follows [13],

$$f_{\tau} = f_{\tau,0} \left[exp\left(log\left(\frac{1}{f_{\tau,0}}\right) \left(1 - \left(\frac{1}{P_t}\right)^c \right) \right) \right]$$
(18)

where f_{τ} is the tortuosity factor at time step t, $f_{\tau,0}$ the initial tortuosity factor, c a shape factor, and P_t a penalty factor, which is described as the ratio of the total porosity at time step t, φ_t , and initial porosity, φ_0 .

2.3. Chemical equilibrium

In the chemical modelling, the mass exchange terms q_{\perp}^{l} and q_{d}^{l} from the governing Eqs. (1) and (2) for chemical interactions between ions and solid phases are solved by the external geochemical PHREEQC code [18,19]. The PHREEQC module is commonly used as a general-purpose geochemical reaction model to simulate interactions between water, minerals, gases, ion exchangers, surface complexation, and solid solutions [10,12,14,15]. However, in reactive transport modelling, transferring cell solution data between multi-ionic transport calculations and chemical equilibrium calculations is tedious and inefficient for running millions of calculations. Therefore, for the compatibility between the transport module and the chemical module with sufficient fast parallel processing in all time steps, the PHREEQC_RM module with an operatorsplitting approach for the reactive transport model is used [49]. In both modules (i.e., PHREEQC and PHREEQC_RM) the mass action law is applied for aqueous species, pure phase, and solid solution reaction to obtain chemical equilibrium between aqueous species and solid phases. The stoichiometric coefficient and equilibrium constant for the reaction of aqueous species, phases, and solid solution phases are defined through a thermodynamic database.

2.3.1. Surface complexation model

It is widely accepted that the pore surface in a cement-based material binds a part of ions present in the pore solution physically see, e.g., [28-36]. The physical binding of ions affects the pH value of the pore solution by absorbing alkali ions (Na⁺ and K⁺) as well as the mass transportation of Cl⁻ and various other ions. Surface complexation allows for accounting for two mechanisms to describe the physical binding of ions. Absorption of ions to a pore surface by an exchange reaction between ionic species in pore solution and the silanol sites (=SiOH) of the C-S-H, and non-adsorbed ions captured in the EDL present at the solid-solution interface. In the present modelling approach, the total moles of the surface site are calculated by assigning a value to the surface site density, the specific surface area, and the C-S-H product in the phase assemblage. In the pore surface, a charge imbalance will be developed due to the reaction of ion species in the pore solution and the silanol sites (=SiOH) of the C-S-H, which results in the formation of two distinct layers in the pore solution, i.e., free water and the EDL (see Fig. 1b). In the present study, the charge density on the surface and surface potential are related using the Dzombak and Morel approach [50]. The Donnan approach is used to determine the diffuse-layer composition by balancing the surface charge accumulation and computed by the Boltzmann equation.

3. Numerical examples

The numerical study compares experimental conditions and results from [51] to model predictions to test and validate the developed reactive transport model. The experimental study compares, among others, Cl profile, total elemental contents, i.e., sodium (Na), potassium (K), magnesium (Mg), and sulfur (S), as well as solid phases (Portlandite and carbonate phase) over time for samples exposed to various solutions. A brief overview of the investigated materials and measurements is provided in the following, while more detailed information on sample preparation, exposure, and measurement campaign can be found in [51].

3.1. Materials

Mortars samples were prepared in 125 ml cylindrical sealed HDPE bottles using ordinary Portland cement (OPC) type CEM I 42.5 R according to EN197-1 with 6 % silica fume (SF). The PC mortar was proportioned with a water-to-binder mass ratio of 0.40 and a sand-to-binder mass ratio of 2.5:1. The mix design details of the mortar are given in Table 1, while the chemical composition of the OPC, SF, and sand is given in Table 2.

3.2. Exposure conditions

Two different exposure solutions were used in the experimental study [51], i.e., NaCl solution and seawater. The seawater sample was collected from the Trondheim fjord, Norway, whereas the NaCl solution was prepared to have the same chloride concentration as the seawater. The measured element composition of the exposure solution is given in Table 3. After 21, 90, and 180 days of exposure, samples were investigated to determine the elemental mass content of chloride (Cl), potassium (K), sodium (Na), magnesium (Mg), and sulfur (S) relative to the

Table 1Mix design of mortars, after [51].

Mix composition	Mass [g]
PC	1522.8
SF	97.2
Water	638.6
Sand	4050.0
Superplasticizer	4.9
Air entraining admixtures	6.1

Table 2

Chemical composition [wt%] and physical characteristics of the ordinary Portland cement (OPC), silica fume (SF), and sand, after [51].

	OPC	SF	Sand					
Chemical composition analysis [wt%]								
SiO_2	19.6	95.1	95.8					
Al_2O_3	4.5	1.0	1.6					
TiO ₂	0.3	0.0	0.1					
MnO	0.1	0.0	0.0					
Fe ₂ O ₃	3.5	0.1	0.7					
CaO	61.6	0.1	0.1					
MgO	2.4	0.4	0.1					
K ₂ O	1.0	1.0	0.7					
Na ₂ O	0.5	0.1	0.0					
SO3	3.4	0.0	0.0					
P_2O_5	0.2	0.1	0.0					
CO_2	2.4							
Free CaO	2.5							
K ₂ O water-soluble	0.9							
Na ₂ O water-soluble	0.3							
LOI 950C	2.4	2.0	0.3					
Blaine [cm²/g]	3900.0							
Density [g/cm ³]	3.12	2.3	2.66					
BET [m ² /g]		19.19						

mass of dried mortar at 105 $^{\circ}$ C and phase mass content of Portlandite and carbonate relative to the mass of dried mortar at 900 $^{\circ}$ C. In addition, to identify concentration gradients between the exposure solutions and the pore solution of the mortars, the authors studied the pore solution composition of non-exposed reference samples after three years of sealed curing at 20 $^{\circ}$ C.

3.3. Input parameters and databases for numerical studies

Experimental samples were assumed to be fully saturated during the numerical studies, and the temperature was kept constant throughout the exposure period. Input for the hydration model was determined based on the hydration of each clinker phase composition in the binder materials. The content of main clinkers phases alite, belite, aluminates, and ferrites was determined by XRD-Rietveld [51]. The distribution of alkalis content between sulfates and oxides in OPC was calculated based on the measured data of total and soluble alkalis presented in Table 2. The content of calcite is calculated by CO_2 content in OPC. The sulfate content as a substituent in the major phases, especially alite and belite in OPC, is determined using the proposed method of Taylor [52]. It is assumed that the remaining sulfates other than alkali-sulfates and sulfates in the major clinkers are accumulated as gypsum phases. The

Table 3

Elemental composition of the exposure solutions, after [51].

Element	Seawater [mmol/l]	NaCl solution [mmol/l]
Ca	8.8	
Cl	548.0	545.0
К	8.9	
Mg	46.7	
Na	411.0	545.0
S	26.9	

resulting clinker composition of the OPC cement is shown in Table 4.

The ionic composition of the boundary solution (i.e., either NaCl or seawater) was determined using PHREEQC based on the measured elemental composition presented in Table 3, which is presented in Table B.1. In total, 74 ions were included in the multi-ionic mass transport model during the numerical investigations. The CEMDATA18 database [53] (http://www.empa.ch/cemdata) is used to describe reactions and thermodynamic properties for various substances and phases found in cementitious systems. In a CaO $- Al_2O_3 - SiO_2 - CaSO_4 - CaCO_3 - H_2O_3$ systems, C-S-H gel is formed as the major hydrate described by the solid solution CSHQss model proposed by Kulik [54] in the present study, whereas two end members for KSiOH and NaSiOH are provisionally added to improve predictions of pH and composition of the OPC pore water [53]. Moreover, Portlandite (CH), Ettringite (AFtss), monocarbonate (CO3-afm), hydrogarnet (HGss), hydrotalcite (Ht), and calcite (CC) are included in the thermodynamic database for numerical investigations. In addition, Kuzel's salt and Friedel's salt phases, primarily for chemical binding of Cl⁻, magnesium silicate hydrate (MSHss), ferrihydrite-mc (FeOOH), brucite, gibbsite (Gb), gypsum (Gp), straetlingite, and natrolite phases are added in the database to simulate exposure to NaCl and seawater solution. An overview of the dissolution reactions and corresponding equilibrium constants used in the numerical study are shown in Table C.1.

The selected ideal solid solution, CSHQss, contains a mix of CSHQ-TobH, CSHQ-TobD, CSHQ-JenH, CSHQ-JenD, NaSiOH, and KSiOH as endmembers, which have been found as stable phases and in good agreement with measured and calculated alkali concentrations in chemical equilibrium calculations for OPC cement [53]. The surface site of the crystal structure of the C-S-H phase has not been entirely determined. Various models can be found in the literature, including Viallis-Terrisse et al.'s model [31], considering one kind of surface site called silanol (=SiOH). Pointeau et al. [29] mentioned that C-S-H consists of two different sites, i.e., silanol (\equiv SiOH) and silandiol (=Si(OH)₂) sites, while Heath et al. [55] considered that silicon (=SiOH) and calcium (-CaOH) sites dominate the surface of C-S-H. Based on the availability of surface site data, in the present study, the proposed surface site model by Viallis-Terrisse et al. [31] is used in the surface complexation model. The density of silanol sites of the C-S-H phase is assumed to be equal for all CSHQss endmembers, with a value of 4.878 sites/nm^2 .

For absorption reactions between ions in the pore solution and surface sites, Ca^{2+} , $(SO_4)^{2-}$, $(OH)^-$, Cl^- , and alkali ions Na^+ and K^+ are included in the surface complexation model. Reaction equations and thermodynamic parameters, log(K), for ion adsorption on the C-S-H surface are shown in Table C.2 [21]. The equilibrium constants for ion reactions onto silanol sites of CSHQss endmembers are assumed to be equal. In addition, the specific surface area per mole of C-S-H, A_{ss}, and the thickness of the EDL, t_d , are required for the surface complexation model. The specific surface area, A_{ss} , is calculated by the following

Fable 4		
Clinker composition	of the ordinary Portland	cement (OPC) [wt%].

Phase composition	[wt%]	Present a	as a solid solution in the clinker phases [wt%]
Alite ^a (C ₃ S)	55.7	CaO ^e	2.5
Belite ^a (C ₂ S)	15.4	MgO ^c	2.4
Aluminate ^a (C ₃ A)	5.7	K2O ^d	0.1
Ferrite ^a (C ₄ AF)	10.9	Na_2O^d	0.2
Calcite ^b	5.5	SO ₃ ^f	1.2
Gypsum ^c	2.3		
$ m K_2SO_4^d m K_2SO_4^d$	1.7		
$Na_2SO_4^d$	0.7		

^a Determined by XRD-Rietveld [51].

^b Calculated from the CO₂ content Table 2.

² Calculated from the chemical analysis.

^d Calculated from the total and soluble alkali content Table 2.

^e Calculated from the Free CaO content Table 2

^f Calculated from the distribution of sulfate [52].

equation,

$$A_{ss} = \frac{f_{CSH}^{A_{int}} A_{int} + f_{CSH}^{A_{gl}} \circ \left(\int_{0}^{\infty} dA_{gl}^{r} + \int_{0}^{\infty} dA_{cp}^{r}\right)}{n_{CSH}}$$
(19)

where A_{int} is the total surface area of the interlayer, dA_{gl}^{r} the surface area of a gel pore for a pore radius, dA_{cp}^{r} the surface area of a capillary pore for a pore radius r, $f_{CSH}^{A_m}$ and $f_{CSH}^{A_{gl},p}$ the fraction of the C-S-H surface in the interlayer, gel, and capillary pore surface, respectively, and n_{CSH} the total moles of the C-S-H product. The pore structure model determines the surface area of the interlayer, gel, and capillary porosity. It is thereby assumed that the C-S-H phase occupies 65 % of the gel and capillary pore surface, and C-S-H forms the interlayer. Therefore, the values for $f_{CSH}^{A_m}$ and $f_{CSH}^{A_{gLP}}$ are set to 1.0 and 0.65, respectively. The thickness of the EDL, t_s , depends on the ionic strength of the pore solution and is set to be proportional to the Debye length, κ , ($t_d = \chi \kappa$, where χ is the proportionality coefficient) in the present study. The Debye length (for electrolyte solution) is determined as follows

$$\kappa = \sqrt{\frac{\zeta_0 \, \zeta_r k_B T}{2N_A e^2 I_s}} \tag{20}$$

where, k_B is the Boltzmann constant and e the elementary charge. In this study, the proportionality coefficient, χ , is set to 1.55 after [14]. Details of spatial discretization and time step used in the numerical study, together with assumed threshold pore radius, initial tortuosity, shape factor, and other constant values, are shown in Table 5. In general, using a relatively high number of elements to discretize the domain in numerical studies will increase the accuracy; However, computational costs will increase. Therefore, to balance accuracy and computational cost in the present investigations, the 30 mm 1D domain is discretized using a total 50 of elements with a growth factor to create a finer mesh near the surface of the exposed boundary. The time step is decided through sensitivity studies for ion mass transport based on comparing total exposure time, computational costs, developed charged imbalance in the pore solution, and the truncated error in the boundary node [56]. Chemical equilibrium is determined every second time step, which is sufficient to reach a minimum level of accumulated ion concentration in the pore solution.

4. Results and discussion

4.1. Phase assemblage of reference mortar samples

The numerical results for the hydration of major clinker phases, the average level of hydration of cement, and the phase assemblage for the reference mortar sample after three years of sealed curing at 20 $^{\circ}$ C are shown in Fig. 3. Results of the hydration model indicate that >90 % of alite and aluminate clinker are hydrated after three years of sealed curing and that the dissolution rates for belite and ferrite are significantly slower in the reference mortar specimen. The predicted phase

Table 5

Model pa	arameters	for t	he	numeric	al in	nvesti	igati	ons
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Model parameters	Value
No of spatial elements	50
Growth factor of spatial elements	2
Total spatial distance, (m)	0.030
Total time, (days)	180
Time step, Δt (h)	6
Threshold pore radius, r _{th} (nm)	5
Initial tortuosity factor, $f_{\tau, 0}$	0.075
Shape parameter, c	1
Relative dielectricity, ζ_r	78.54
Dielectricity in a vacuum, ζ_0	8.85E-12
Faraday's constant, (C/mol)	96,490
Gas constant, (J/(mol • K))	8.314

assemblage contains C-S-H, Portlandite, Ettringite, monocarbonate, hydrogarnet, hydrotalcite, calcium carbonate, and unhydrated cement. The simulated phase assemblage for OPC cement is thereby in good agreement with reported results in, e.g. [53,57]. Nearly 31 % of the total mortar volume consists thereby of both hydrated and unhydrated cement, whereas the numerical results indicate that approximately 12 % of the total volume is pore space after three years of sealed curing. Due to the equilibrium between pore solution and hydrated phase of a standard Portland cement, pore solution is formed with high alkalinity, which maintains the pH value of the pore solution generally between 12.5 and 14 [58]. The simulated results show that the pH value of the pore solution of the reference mortar is approximately 13.22.

Dissolved ions in the pore solution will be transported among others by electrochemical potential forces, and these transported ions will subsequently affect the dissolution and precipitation of phases. Thus, validating the pore solution composition against experiment data is crucial for RMT modelling. More than 70 ions are considered in the present study, for which experimental determination is cumbersome. Hence, the elemental concentration of selected ions in the pore solution is compared with the available experimental results for the reference mortar sample in Fig. 4. Presented results indicate that numerical results are in good agreement with experimental results obtained through ICP-MS [51], apart from Fe and Mg, for which the model predicts lower concentrations in the pore solution. The discrepancy may be due to the influence of other factors such as the concentration of other elements, ionic strength, etc., on the dissolution rate of Fe and Mg containing solid phases, i.e., hydrogarnet and hydrotalcite. Therefore, the choice of phases and the dissolution rate of phases within the thermodynamic modelling framework strongly affect and control the composition and concentration of the pore solution. In the present study, incorporating a hydration model and the selected phase assemblage (see Fig. 3) allows capturing the trend for most of the elements in the pore solution.

4.2. Mortar samples exposed to NaCl and seawater solution

4.2.1. Solid phase composition

The presented modelling framework was used to determine the effect of NaCl and seawater on the solid phases of exposed mortar samples. Results of the numerical simulations, i.e., phase assemblage for OPC mortar specimens immersed in NaCl and seawater solution for 180 days, are shown in Fig. 5. The right-hand side of the figures displays the paste composition in the unaffected core, while the left-hand side illustrates the effect of exposure on the mortar samples. For the non-exposed core, the predicted phase composition includes CSH, Portlandite, Ettringite, monocarbonate, hydrogarnet, hydrotalcite, calcium carbonate, and unhydrated cement.

Upon exposure of the mortar sample to NaCl solution, Friedel's salt and ettringite (Aftss) are formed in the vicinity of the exposed surface, whereas Portlandite and monocarbonate decompose with a continuous increase in calcite content (see Fig. 5a). The observed changes in the phase assemblage result from the presence of Cl- ions from the boundary solution, which start to substitute carbonate ions $(CO_3)^{2-}$ in the monocarbonate to form Friedel's salt, see, e.g., Balonis et al. [59]. The released carbonate ions subsequently react with Ca²⁺ ion in the pore solution to form calcite. The Ca^{2+} deficit in the pore solution causes an increase in the dissolution rate of Portlandite and monocarbonate until both phases are decomposed near the exposed surface. Moreover, leaching of selected ions is observed from the exposed mortar specimen as the concentration of most ions (considered in the RTM model) is close to zero in the boundary solution. In addition, a minute decrease in the volume of solid phases is observed near the exposed surface due to the leaching of ions.

In the case of seawater exposure, the formation of Friedel's salt as observed for exposure to NaCl was not predicted (see Fig. 5b). On the other hand, the formation of additional phases such as ettringite, ferrihydrite-mc, brucite, and gypsum is predicted near the surface of the



Fig. 3. Numerical results for reference OPC mortar sample. (a) Hydration of major clinkers phases and average degree of hydration over three years, (b) phase assemblage for mortar specimens after three years of sealed curing at 20 °C.



Fig. 4. Comparison between calculated and experimentally determined (by ICP-MS on expressed pore solution) [51] composition of the pore solution for reference OPC mortars after three years of sealed curing.

exposed mortar specimen due to the presence of sulfate, carbonate, and magnesium in the exposure solution. A similar trend was noticed for the mortar specimen exposed to NaCl solution in connection to monocarbonate and Portlandite. Both phases continuously decompose with exposure time until fully dissolved near the exposed surface. The decomposition of monocarbonate and Portlandite is thereby accompanied by an increase in calcite content as observed for the mortar specimen exposed to NaCl solution. In addition to the decomposition of monocarbonate and Portlandite, the decalcification of C-S-H and the dissolution hydrogarnet are observed near the exposed surface. The porosity near the exposed surface decreases mainly with the ettringite formation because the molar volume of ettringite is comparably higher. For both exposure condition and except the region near the exposed surface (0-2 mm section), the gradual decreases in pH value was observed together with the leaching of some of ions and decomposition of phases such as monocarbonate and Portlandite, whereas the decalcification of higher Ca/Si ratio C-S-H phase (CSHQ-JenD) due to seawater exposure causes a sudden drop in pH value at the vicinity of the exposure surface (approximately 11.83 at the exposed surface).

Fig. 6 illustrates a comparison between predicted and experimentally determined (through TGA) Portlandite and carbonate profiles for specimens exposed to NaCl and seawater, respectively, after various times of exposure. The Portlandite and carbonate contents are presented in total phase content as the mass percentage of the dried mortar at 900°C. Results illustrate an increase in the carbonate content in the outermost section (0–5 mm) for both exposure solutions over time (see Fig. 6b). The formation of carbonate phases may result from either carbonation



Fig. 5. Numerical predictions of phase assemblage for OPC mortar specimens exposed to NaCl (left) and seawater solution (right) for 180 days.



Fig. 6. Comparison of experimentally determined [51] and numerical predictions of Portlandite and carbonate content after 21, 90, and 180 days of exposure to NaCl and seawater solution, Phase contents were measured through TGA on profile ground OPC mortar and expressed as wt% of mortar dried at 900 °C (left: NaCl, right: seawater).

during sample preparation or transport of CO_2 dissolved in the boundary solution inside the mortar sample during exposure. In the present study, the dissolution of CO_2 in the exposure solution was considered under atmospheric conditions for which a good agreement between experimental results and numerical predictions is observed. Moreover, a reduction in Portlandite content near the exposed surface is observed for both exposure conditions over time. As previously discussed, the dissolution of Portlandite is increased by calcite formation. A gradual decrease in Portlandite is also found in the deeper, uncarbonated sections, i.e., both experimentally and numerically (see Fig. 6a). The dissolution of Portlandite in the uncarbonated area results thereby from the leaching of $(OH)^-$ ions, which is accompanied by the transport of Ca^{2+} ions inside the mortar.

4.2.2. Pore structure

Fig. 7a and Fig. 7b show the simulated cumulative pore volume and pore size distribution of capillary, gel, and total pores of OPC mortar at a depth of 0.1 mm from the exposed surface before and after exposure to NaCl and seawater solution for 180 days. Numerical results for the cumulative pore volume indicate seawater exposure appear to fill pores with newly formed phases, whereas NaCl exposure shows leaching behaviour. For both exposures scenarios, a slight decrease in the total pore volume of gel pores is found because decomposition of the C-S-H phase occurs due to exposure (see Fig. 5). The effect is more pronounced for seawater exposure, for which nearly half of the capillary pore space is filled by newly formed phases, while an increase in total porosity of capillary pores is observed due to NaCl exposure. The peak radius has a considerable effect on the ionic transport in the RTM model, influencing ion flux through a change in threshold porosity. The pore size distribution shows that the peak lies between 10 nm and 1 μm for all non-exposed and exposed mortar specimens. A more significant reduction in peak radius is observed for seawater exposure than NaCl exposure. For seawater exposure, the formation of additional phases affects the total porosity distribution and reduces the peak radius ten times smaller than non-exposed OPC mortar, whereas a considerable change is not found for NaCl exposure.

Numerical predictions of the tortuosity factor for the OPC mortar specimens after exposure to NaCl and seawater solution for 180 days are given in Fig. 8. Results of the numerical simulations illustrate changes in the tortuosity factor near the exposed surface for both NaCl and seawater exposure. For seawater exposure, the tortuosity factor is significantly more reduced than NaCl exposure, indicating an increase in the length of the ion pathway. Consequently, the ion flux through the pore space near the mortar's surface is reduced, forming new solid phases, although the boundary solution provides sufficient ion supply. A peak reduction in the tortuosity factor was observed at a certain depth from the exposed surface, marking the transition between decrease and increase in the total volume of solid phases.

4.2.3. Chloride profiles

The predicted and experimentally measured distribution of chlorides in mortar exposed to NaCl and seawater solution after 21, 90, and 180 days are shown in Fig. 9. The chloride profiles are thereby presented as total chloride contents per mass percentage of the dried mortar (at 105 °C). Within the presented modelling framework, chlorides may be stored in free water and the EDL of the pore solution, physically bound on the pore surface, and chemically bound in, e.g., Kuzel's salt and Friedel's salt. The sum of all chlorides, i.e., free and physically and chemically

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Fig. 7. Cumulative pore volume and pore size distribution for OPC mortar specimens at a depth of 0.1 mm from the exposed surface after 180 days (left: NaCl, right: seawater).



Fig. 8. Tortuosity factor of OPC mortar specimens exposed to NaCl and seawater solution for various exposure times (left: NaCl, right: seawater).

bound, is then provided as the total chlorides in the predicted result. Generally, the presented results indicate an excellent agreement between simulation and the experimental results for most parts of the spatial and time domains for all exposed mortar specimens. Deviations between experimental and numerical results are observed for the surface region (0–2 mm section). These deviations may be caused by troublesome sample preparation from the mortar surface for chloride content measurements as well as the casting of mortar, including variations in the mix proportion at the mortar surface due to preparation and bleeding. For all exposure times, the predicted and measured total Cl results indicate that seawater exposure seems to lead to a higher chloride content than exposure to NaCl solution at the same depth from the exposed surface (see Fig. 9b).

On the other hand, the results show the peak behaviour in chloride profile near the exposed surface (0–3 mm section) of the mortar due to the NaCl exposure because the Cl from NaCl boundary solution was immediately stored as Friedel's salt near the exposed surface (see Fig. 9a). In addition, over time, the predicted and measured chloride



Fig. 9. Comparison between predicted and measured [51] total chloride profiles of OPC mortar samples exposed to NaCl and seawater solution after 21, 90, and 180 days, expressed at wt% of mortar dried at 105 °C (left: NaCl, right: seawater).

profiles for both exposure conditions show a reduction in the chloride content at the surface (0–1 mm section). The decrease in chloride content near the exposed surface is caused by the release of initially physically absorbed Cl⁻ ions from the surface site of C-S-H due to the decalcification of higher Ca/Si ratio C-S-H phase (CSHQ-JenD), whereas the mass of dried mortar at 105°C increased in the surface section. Therefore, the normalized total chloride contents with the mass of the dried mortar at 105°C reduced after some exposure period.

4.2.4. Elemental profiles

Results of the numerical simulations comprising profiles of total elements, the composition of free water, composition of the EDL, absorbed element on the surface sites, and composition of surface sites for the mortar specimens exposed to NaCl and seawater solution for 180 days are given in Fig. 10. The quantity for all compositions is expressed as moles of an element per m³ volume of mortar. As illustrated in Fig. 10a, changes in the elemental composition are observed mainly near the exposed surface, while the ingress of Cl and leaching of K are observed up to a depth of approximately 15 mm. The ingress of Mg and S is identified only for seawater exposure as the exposure solution contains certain amounts of Mg and S, whereas a unique shape in Ca and Na profiles were found from the simulation results.

The free water and EDL compositions are expressed as the content of an element instead of the ionic concentration in Fig. 10b and Fig. 10c, respectively. For example, Ca concentration in solution indicates the sum of the concentration of Ca^{2+} in different species such as Ca^{2+} , Ca $(OH)^+$, etc. For NaCl exposure, the ingress of Na and Cl ions through free water is observed; simultaneously, Na ions in the EDL are moving outwards. Moreover, leaching is observed for K and S, while the concentration of Ca and Mg increases near the exposed surface, despite a lack of supply from the exposure solution. Upon mortar sample exposure to seawater solution, Na and Cl profile tendency is the same as for NaCl exposure. The leaching of K is lower compared to samples exposed to NaCl due to the presence of K in the seawater solution. S, Ca, and Mg profiles indicate ingress inside the mortar due to higher concentrations in the exposure solution than the pore solution.

Fig. 10d and Fig. 10e show the amount of absorbed elements onto surface sites and the composition of surface sites in the C-S-H phase after 180 days of exposure to NaCl and seawater solution. The right-hand side of the figures displays unaffected surface sites, while the left-hand side of the figures shows the effect of transported ions on the silanol sites. Initially absorbed alkali ions, i.e., for both NaCl and seawater exposure, Na and K, onto the surface sites are released to the pore solution due to leaching of ions and decalcification of C-S-H phase near exposure surface (see Fig. 5). On the other hand, the absorption reaction of Ca and Cl

increased on the surface sites compared to the initial stage of absorption. A peak in the absorbed element profile of Ca and Cl is observed at a certain depth, caused by a release of absorbed Ca and Cl due to the decalcification of the C-S-H phase near the exposure surface. In the case of NaCl exposure, some of the absorbed S is released and leached through the exposure surface. In contrast, a certain amount of transported S from the boundary solution is absorbed onto the surface sites for seawater exposure.

A comparison between numerical and experimental results for sodium (Na), potassium (K), magnesium (Mg), and sulfur (S) after 21, 90, and 180 days of exposure to NaCl and seawater is given in Fig. 11. Total elemental distributions are presented as mass percentage of the dried mortar (at 105 °*C*). In general, a good agreement between numerically predicted and experimentally determined elemental distribution is found for most parts of the spatial as well as time domain for all exposed mortar specimens.

Both exposure solutions, i.e., seawater and NaCl solution, contain >3-times the Na concentration than the pore solution of the mortars (see Table 3 and Fig. 4); therefore, Na is expected to ingress into the samples due to electrochemical and potential gradients. However, except for the outermost section (0-1 mm) of the mortar specimen exposed to NaCl, the measured and predicted sodium profiles indicate enrichment in sodium only in deeper sections from the exposed surface (3-15 mm). At the same time, the results illustrate a reduction in sodium content in the section located 1-3 mm from the exposed surface. The presented modelling framework provides an explanation for the observed (experimentally and numerically) sodium distribution. Initially, transported sodium ions are absorbed on the pore surface through the reaction between ions and surface sites of the C-S-H. Later, the absorbed sodium ions are released from the pore surface due to the lowering pH value, and the released sodium ions are subsequently transported inside the mortar due to the concentration gradient between the boundary and pore solution. Thus, sodium enrichment is observed in the deeper section.

The exposure solutions contain only limited potassium concentrations (in the case of seawater and none for NaCl) compared to the pore solution (see Table 3 and Fig. 4), leading to continuous leaching of potassium ions from the exposed surface. In addition, initially physically absorbed potassium ions from the pore surface are released to the pore solution (see Fig. 10a). The modelling framework captures the effect of leaching very well on the profile of potassium over time for both exposures.

The presence of magnesium in the seawater solution leads to the ingress of magnesium in the mortar samples. However, the magnesium content increased only in the outer sections (0-2 mm) of samples



Fig. 10. Profiles for OPC mortar specimens exposed to NaCl and seawater solution for 180 days (left: NaCl, right: seawater): a) total elemental concentration, which is the summation of the element included in the free pore solution, the EDL, hydrates, and surface sites, b) free water composition, c) EDL composition, d) surface absorption, and e) surface sites on the C-S-H phase.



Fig. 11. Comparison of experimentally measured (by ICP-MS) [51] and numerical predictions for total sodium (Na), potassium (K), magnesium (Mg), and sulfur (S) content from profile ground OPC mortar samples after 21, 90, and 180 days of exposure to NaCl and seawater solution, expressed as wt% of mortar dried at 105 °C (left: NaCl, right: seawater).

exposed to seawater. Numerical results predict the formation of hydrotalcite and brucite in the outer sections of the exposed samples (see Fig. 5) as the transported magnesium ions react with other ions in the pore solution and precipitate as solid phases. For samples exposed to NaCl solution, leaching of magnesium is expected due to the lack of Mg in the exposure solution. However, the leaching is restricted due to a slight concentration gradient between boundary and pore solution as well as the dissolution of the initially formed hydrotalcite (see Fig. 5 and Fig. 10a), resulting in a temporal increase of magnesium in the pore solution. Thus, the magnesium concentration in samples exposed to NaCl remains unchanged, as indicated by experimental results and numerical predictions.

Sulfur is not present in the NaCl solution, whereas the seawater solution contains slightly more sulfur (see Table 3 and Fig. 4) than the pore solution of the unexposed mortar. Due to the presence of sulfur in the seawater solution, experimental and numerical results show an increased sulfur content in the outer section (0–4 mm) of the exposed sample. As a result, additional ettringite (solid solution) is formed, as indicated in Fig. 5. For samples exposed to NaCl, sulfur leaching occurred due to concentration gradients in the pore solution. However, only a minor reduction in the sulfur content is observed in the outer section (0–4 mm) of the exposed mortar.

5. Conclusions

A reactive transport model (RTM) was developed for saturated cement-based materials based on multi-ionic transport through an uncharged, 'free water' and charged, 'EDL' coupled with a chemical equilibrium model for interaction between the pore solution and solid phase. A set of modified Poisson-Nernst-Planck (PNP) equations, including the effect of temperature, pore solution property, and pore structure changes, were introduced for multi-ionic transport through free water and the EDL. The diffusion coefficient at infinite dilution of many of the aqueous species present in the pore solution in cementitious material was expressed as a function of van der Waals radius and charge of the ion.

Numerical predictions were compared to experimental data to demonstrate the potential of the RTM. Comparisons include the variation of total element content, solid-phase composition, free water and EDL composition, absorbed elements onto surface sites, and composition of surface sites of C-S-H phase for mortar specimens exposed to NaCl solution and seawater from Trondheim fjord in Norway. Excellent agreements (in both spatial and time domains) between experimentally determined and numerical predictions were found comparing Portlandite and carbonate in the phase assemblage, total chloride (Cl), elemental distribution of sodium (Na), potassium (K), magnesium (Mg),

Appendix A. Finite element formulation

and sulfur (S) for all exposed specimens adjusting only the initial tortuosity factor. Furthermore, the developed RTM provides an explanation for the observed elemental distribution, phase assemblage, and pore structure in all exposed mortar specimens. The results indicate the importance of considering multi-ionic transport through free water and the EDL for cement-based material due to exposure to the environment. Moreover, considering the effect of temperature, pore solution properties, and pore structure changes on multi-ionic transport in porous media significantly improve model prediction.

CRediT authorship contribution statement

All persons who meet authorship criteria are listed as authors, and all authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in the concept, design, analysis, writing, or revision of the manuscript. Furthermore, each author certifies that this manuscript or similar content in manuscript has not been and will not be submitted to or published in any other publication before its appearance in the *Cement and Concrete Research*.

The specific contributions made by each author are listed below.

Author's name	Roles of author
Suntharalingam Sharmilan	Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization
Henrik Stang	Validation, Resources, Supervision, Project administration, Funding acquisition
Alexander Michel	Validation, Resources, Writing - Review & Editing, Visualization, Supervision, Project administration, Funding acquisition

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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The present approach solves the governing equations through the finite element method (FEM) for the multi-ionic transport. For the finite element formulation, the governing Eqs. (6), (7), (9), and (10) are transformed into weak forms dividing the system of equations in a spatial domain and a time domain using a weight function *w* for the spatial domain and a weight function *W* for the time domain. Galerkin's approximation is used for the discretization of the one-dimensional spatial scheme using linear spatial elements [60,61]. The Green-Gauss theorem is used in the ion mass transport terms to separate the boundary flow conditions. An implicit single-step approach is used to solve the problem in the time domain. The complete coupled set of equations is solved simultaneously to avoid staggering schemes between separate solutions of state variables. A modified Newton-Raphson iteration scheme is used to improve the FEM solution of the non-linear governing equations for the employed single time-stepping scheme. The modified iteration scheme reduces computational time compared to the complete scheme while minimizing the residual of the problem [9,62]. The weak forms of the local differential equations, i.e., Eq. (6), for the concentration of the ionic species in the free water solution of the porous material, are

$$\int_{t_1}^{t_2} W \int_V w \varphi_{gc} e_f^j \frac{\partial C_f^{l_j}}{\partial t} dV dt = -\int_{t_1}^{t_2} W \int_V (\nabla w)^T D^{l_j} \left(1 + \frac{\partial ln \gamma_j}{\partial ln C_f^{l_j}} \right) \left(\varphi_{gc} - \varphi_{ih} \right) e_f^l \nabla C_f^{l_j} dV dt - \int_{t_1}^{t_2} W \int_V (\nabla w)^T A^{l_j} v^j \left(\varphi_{gc} - \varphi_{ih} \right) e_f^l C_f^{l_j} \nabla \Phi_f^T dV dt + \int_{t_1}^{t_2} W \oint_S J_f^{l_j} n dS dt; j$$

$$= I, 2, 3 \dots, N$$
(A.1)

,

where a time increment is used in the integration, starting with t1 and ending with t2, J_{i}^{i} the mass density flow of ions at the boundary surface dS of free water, and n the outward drawn normal to this surface. The weak forms of the local differential equations, i.e., Eq. (7) for the concentration of the ionic species in the EDL of the porous material, are

$$\int_{t_1}^{t_2} W \int_V W A_s t_d \frac{\partial C_d^{i_j}}{\partial t} dV dt = -\int_{t_1}^{t_2} W \int_V (\nabla w)^T D^{l_j} \left(1 + \frac{\partial ln\gamma_j}{\partial lnC_d^{l_j}} \right) (A_s - A_{th}) t_d \nabla C_d^{l_j} dV dt - \int_{t_1}^{t_2} W \int_V (\nabla w)^T A^{l_j} v^j (A_s - A_{th}) t_d C_d^{l_j} \nabla \Phi_d^T dV dt + \int_{t_1}^{t_2} W \int_S J_d^{l_j} n dS dt; j = 1, 2, 3 \dots, N$$
(A.2)

where J_d^l is the mass density flow of ions at the boundary surface dS of the EDL. The weak form of the Poisson type of Eq. (9) determining the electrical potential in the free water is given by

$$\int_{t_1}^{t_2} W \int_{V} (\nabla w)^T (\varphi_{gc} - \varphi_{th}) \varepsilon_f^t \zeta_0 \zeta_r \nabla \Phi_f^T dV \, dt = -\int_{t_1}^{t_2} W \int_{V} w (\varphi_{gc} - \varphi_{th}) \varepsilon_f^t F_C \sum_{j=1}^N v^j C_f^{j} dV \, dt + \int_{t_1}^{t_2} W \oint_{S} J_f^{\Phi} n dS \, dt \tag{A.3}$$

where J_f^{ϕ} is the electrical displacement at the boundary surface of the free water space. The weak form of the Poisson type of Eq. (10) determining the electrical potential in the EDL is given by

$$\int_{t_1}^{t_2} W \int_V (\nabla w)^T (A_s - A_{th}) t_d \zeta_0 \zeta_r \nabla \Phi_d^T dV \, dt = -\int_{t_1}^{t_2} W \int_V w (A_s - A_{th}) t_d F_C \sum_{j=1}^N v^j C_d^j dV \, dt + \int_{t_1}^{t_2} W \oint_S J_d^{\Phi} n dS \, dt \tag{A.4}$$

where J_d^{ϕ} is the electrical displacement at the boundary surface of the EDL. The state variables in the weak formulations are approximated by the general expansion $N \bullet a$, where N is the global shape function, and a contains the nodal state variables. In the one dimensional case, the local linear shape function is given as $[1 - x/l_e, x/l_e]$, where l_e is the element length. The arbitrary spatial weight function w is approximated with the same general expansion following Galerkin's method. The state variables are approximated by the shape functions N, i.e.

$$w = c^{I}N^{I}; C_{f}^{I} = Na_{f}^{\phi}; \Phi_{f}^{I} = Na_{f}^{\phi};$$

$$C_{d}^{I} = Na_{d}^{J}; \Phi_{d}^{T} = Na_{d}^{\phi}$$
(A.5)

where c^T is an arbitrary matrix of the spatial weight function, and yields $c^T = c$. The weak formulations are formed using the gradient of the shape functions *N*, the approximate gradient of the state variables is denoted by *B*. The gradient of the weight function and the state variables may be written as follows:

$$\nabla w = c^T B^T; \nabla C_f^{l_j} = B a_f^j; \nabla \Phi_f^T = B a_f^{\phi};$$

$$\nabla C_d^{l_j} = B a_d^j; \nabla \Phi_d^T = B a_d^{\phi}$$
(A.6)

Applying assumptions (A.5) and (A.6), the weak formulations (see Eqs. (A.1)–(A.4)) can be brought to the form

$$\frac{C(a_{n+1}-a_n)}{\Delta t} + K(a_n + \Theta(a_{n+1}-a_n)) - (f_n + \Theta(f_{n+1}-f_n)) = 0$$
(A.7)

where *C* represents the total damping of the complete coupled set of equations and *K* and *f*, are the total stiffness of the problem and the load vector, respectively. Δt is time increment, and Θ is the time integration parameter. The time integration parameter Θ is restricted to $0 \le \Theta \le 1$, in which $\Theta = 0$ represents a truly explicit scheme, and $\Theta = 1$ is a truly implicit scheme. The total damping matrix of the total coupled problem (A.7) can be written as

	Г							٦	
	C_f^1	0	0	0	0	0	0	0	\dot{a}_{f}^{1}
	Ő	•.	0	0	0	0	0	0	:
	0	0	C_f^N	0	0	0	0	0	\dot{a}_{f}^{N}
C à	0	0	0	0	0	0	0	0	\dot{a}^{\varPhi}_{f}
$C \cdot a =$	0	0	0	0	C_d^1	0	0	0	\dot{a}_d^1
	0	0	0	0	0	۰.	0	0	:
	0	0	0	0	0	0	C_d^N	0	\dot{a}_d^N
	0	0	0	0	0	0	0	0	\dot{a}_d^{Φ}
	L								

According to the weak form Eqs. (A.1)–(A.4), sub-matrices of C in Eq. (A.8) are identified, as

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$$C_f^i = \int_V N^T \varphi_{gc} \varepsilon_f^i N dV; C_d^i = \int_V N^T A_s t_d N \, dV \tag{A.9}$$

In order to shorten the notation, the abbreviation $\hat{a} = a_n + \Theta(a_{n+1} - a_n)$ is introduced. The stiff-ness part of the total coupled problem described in Eq. (A.7) can be formed as

(A.8)

 $K \cdot \hat{a} =$

 $K_{\ell}^{1} = 0 = 0$

 $0 \quad 0 \quad 0 \quad 0 \quad E_{d}^{j}$

 V_f^1

0 0 0 0

(A.10)

The submatrices of K in Eq. (A.10) are identified as (using the weak Eqs. (A.1)–(A.4))

 $E_d^N = K_d^{\Phi}$

 \widehat{a}_{f}^{1}

 $\vdots \\ \widehat{a}_{f}^{N} \\ \widehat{a}_{f}^{\Phi}$

 \widehat{a}_d^1 \vdots \widehat{a}_d^N

 \widehat{a}_d^{Φ}

$$\begin{aligned} K_{f}^{j} &= \int_{V} B^{T} D^{j} \left(I + \frac{\partial ln \gamma_{j}}{\partial ln C_{f}^{j}} \right) \left(\varphi_{gc} - \varphi_{ih} \right) \varepsilon_{f}^{j} B dV; \end{aligned} \tag{A.11} \\ & V_{f}^{j} &= \int_{V} B^{T} A^{j} v^{j} \left(\varphi_{gc} - \varphi_{ih} \right) \varepsilon_{f}^{j} F_{c} v^{j} N dV; \end{aligned} \\ & E_{f}^{j} &= \int_{V} N^{T} \left(\varphi_{gc} - \varphi_{ih} \right) \varepsilon_{f}^{j} F_{c} v^{j} N dV; \end{aligned} \\ & K_{f}^{\Phi} &= \int_{V} B^{T} \left(\varphi_{gc} - \varphi_{ih} \right) \varepsilon_{f}^{j} \zeta_{0} \zeta_{r} B dV; \end{aligned} \\ & K_{d}^{d} &= \int_{V} B^{T} D^{j} \left(I + \frac{\partial ln \gamma_{j}}{\partial ln C_{d}^{j}} \right) (A_{s} - A_{ih}) t_{d} B dV; \end{aligned} \\ & V_{d}^{j} &= \int_{V} N^{T} (A_{s} - A_{ih}) t_{d} C_{c}^{j} B dV; \end{aligned}$$

The coupled problem, as described in Eq. (A.7), is arranged as explained in Eqs. (A.8) and (A.10) is solved for a_{n+1} in each considered time step. Eq. (A.7) yields for determining a_{n+1}

$$a_{n+1} = \left(\frac{C}{\Delta t} + \Theta K\right)^{-1} \left[\left(\frac{C}{\Delta t} - (1 - \Theta) K\right) a_n + f_n + \Theta(f_{n+1} - f_n) \right]$$
(A.12)

For ion mass transport, a truly explicit time-stepping scheme ($\Theta = 0$) is used as a convenient method for solving the system of governing equations. In addition, for improving the solution of the non-linear governing equation, a modified version of the Newton-Raphson algorithm is used based on consideration of computational time to complete the scheme for minimizing the residual of the problem. The residual vector ψ is calculated using a truly implicit scheme ($\Theta = 1$) in Eq. (A.7) as follows:

$$\psi^{i-1} = \frac{C_{n+1}^{i-1}}{\Delta t} \left(a_{n+1}^{i-1} - a_n \right) + K_{n+1}^{i-1} \cdot a_{n+1}^{i-1} - f_{n+1}$$
(A.13)

where *i* is the iteration number and n + 1 indicates that the mass and stiffness matrices are updated with the solution in each iteration. In a modified Newton-Raphson method, the iteration scheme is established between Eq. (A.13) and a modified Taylor expansion without considering the higher-order terms for minimizing the residual of the problem [9,60,62]. The improved result a_{n+1}^i is determined in each iteration as,

$$a_{n+1}^{i} = \left(\frac{C_{n+1}^{i-1}}{\Delta t} + K_{n+1}^{i-1}\right)^{-1} \left[\left(\frac{C_{n+1}^{i-1}}{\Delta t} + K_{n+1}^{i-1}\right) \cdot a_{n+1}^{i-1} - \delta \cdot \psi^{i-1} \right]$$
(A.14)

where δ is a constant acceleration factor, which is used for reducing computational time, Eqs. (A.13) and (A.14) are solved sequentially until a sufficient convergence criterion is reached.

Appendix B. Diffusion properties and boundary values

The properties for ionic constituents together with the ionic composition of boundary conditions are given in Table B.1.

Table B.1

Properties for ionic components and boundary conditions for numerical example (see Section 3)

Id	$D^{\infty}_{l,\ T=298} * 10^{-8}$	$A_{i, T=298} * 10^{-7}$	ν_i	BC_NaCl	BC_seawater
Al(OH) ²⁺	0.0829	0.3227	2	-	-
$Al(SO_4)^+$	0.1365	0.5313	1	-	_
$Al(SO_4)_2^-$	0.1125	0.4380	$^{-1}$	-	_
					(continued on next page)

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Table B.1 (continued)

Id	$D_{i,\ T=298}^{\infty} * 10^{-8}$	$A_{i, T=298} * 10^{-7}$	v_i	BC_NaCl	BC_seawater
Al ³⁺	0.0603	0.2348	3	_	_
AlHSiO ²⁺	0.0630	0.2452	2	_	_
AlO ⁺	0.1787	0.6953	1	_	-
AlO ₂	0.1659	0.6459	-1	_	-
AlO ₂ H	0.1626	_	_	-	_
AlSiO ₅ ⁻³	0.0371	0.1445	-3	_	-
CH₄	0.1909	_	_	_	-
CO ₂	0.1805	_	_	_	_
$CO_3^{\tilde{2}-}$	0.0788	0.3066	-2	-	-
$Ca(HCO_3)^+$	0.1258	0.4897	1	_	-
$Ca(HSiO_3)^+$	0.1201	0.4675	1	_	-
Ca(OH) ⁺	0.1428	0.5560	1	_	2.61E-09
Ca ²⁺	0.0736	0.2863	2	_	7.79E-03
CaCO ₃	0.1289	_	_	_	-
CaSiO ₃	0.1227	-	-	-	-
CaSO ₄	0.1212	_	-	-	9.69E-04
Cl^{-}	0.2067	0.8046	-1	5.45E-01	5.48E-01
ClO_4^-	0.1494	0.5816	$^{-1}$	-	-
Fe(OH) ²⁺	0.0774	0.3013	2	-	-
Fe(SO ₄)	0.1317	_	-	-	-
$Fe(SO_4)^+$	0.1317	0.5125	1	-	-
$Fe(SO_4)_2^-$	0.1084	0.4221	1	-	-
Fe ²⁺	0.0862	0.3353	2	-	-
Fe ³⁺	0.0549	0.2136	3	-	-
$Fe_2(OH)_2^{4+}$	0.0261	0.1016	4	-	-
$Fe_3(OH)_4^{5+}$	0.0157	0.0610	5	-	-
FeCO ₃	0.1427	_	-	-	-
FeCl ⁺	0.1561	0.6074	1	-	-
FeCl ²⁺	0.0742	0.2888	2	-	-
FeCl_2^+	0.1410	0.5486	1	-	-
FeCl ₃	0.1303	-	-	-	-
FeHCO ₃ ⁺	0.1370	0.5332	1	-	-
FeHSO ⁺	0.1274	0.4959	1	-	-
FeHSO ₄ ⁺	0.0599	0.2331	2	-	-
FeHSiO ₃ ⁺	0.0608	0.2368	2	-	-
FeO ⁺	0.1665	0.6480	1	-	-
FeO ₂	0.1554	0.6050	-1	-	-
FeO ₂ H	0.1530	-	-	-	-
FeOH ⁺	0.1624	0.6323	1	-	-
H'	0.3050	1.1871	1	1.21E-07	1.20E-07
H ₂	0.2720	-	-	8.07E-26	8.0/E-26
H_2S	0.1885	-	-	-	-
HCO_3	0.1621	0.6309	-1	-	-
H5	0.1538	0.7545	-1	-	-
п50 ₃ исо-	0.1350	0.5954	-1	-	2.03E-20
HSO4	0.1432	0.5051	-1	-	3.19E-08
H3IO3 V ⁺	0.1288	0.5775	-1	-	- 9.7EE 02
KOH	0.1253	0.3012	1	-	1.22E 10
KON	0.1233	- 0.4273	- 1	-	1.22E-10 1.46E 04
$M_{\sigma}(CO_{\pi})$	0.1058	0.4275	-1	-	1.405-04
$M_{g}(HCO_{a})^{+}$	0.1434	0 5580	- 1		
$Mg(HSiO_2)^+$	0.1344	0.5330	1		
$M_{\sigma}(OH)^+$	0.1754	0.6826	1		3 95E-07
Mg(SO ₄)	0.1353	-	-		6.95E 07
$M\sigma^{2+}$	0.1008	0 3923	2	_	3.95E-02
MgSiOa	0.1377	-	-	_	-
$Na(SO_4)^-$	0.1208	0.4700	_1	_	5 30E-03
Na ⁺	0.1576	0.6135	1	5 45E-01	4.06E-01
NaCO ⁻	0.1284	0.4999	-1	-	-
NaHCO ₃	0.1272	_	-	_	-
NaOH	0.1451	_	_	1.70E-08	1.26E - 08
02	0.2069	-	_	-	-
OH-	0.2271	0.8837	-1	7.81E-08	7.78E-08
s ²⁻	0.0966	0.3759	-2	-	-
$S_2O_3^{2-}$	0.0658	0.2560	-2	_	_
SO ²	0.0739	0.2875	-2	_	6.34E-28
SO ²⁻	0.0698	0.2716	$^{-2}$	_	1.35E-02
$Si_4O_{10}^{4-}$	0.0188	0.0732	-4	_	
SiO ₂	0.1576	_	_	_	-
SiO2	0.0715	0.2782	2		-

Appendix C. Thermodynamic database

The dissolution reaction of phases and corresponding thermodynamical data based on the CEMDATA18 database [53] are shown in Table C.1.

Table C.1

Thermodynamic properties of the phases at 25 °C in the chemical equilibrium model.

Details of phase		Reaction equation	log K
Pure phases	Notation		
Calcite	Calcite	$CaCO_3 = CO_3^{2-} + Ca^{+2}$	-8.480
Hydrotalcite	Ht	$Mg_4Al_2O_7(H_2O)10 + 6H^+ = 4Mg^{2+} + 2AlO_2^- + 13H_2O$	27.981
Monocarbonate	CO3-AFm	$Ca_{4}Al_{2}CO_{9}(H_{2}O)11 + 4H^{+} \rightleftharpoons CO_{3}^{2-} + 4Ca^{2+} + 2AlO_{2}^{-} + 13H_{2}O$	24.530
Portlandite	CH	$Ca(OH)_2 + 2H^+ \rightleftharpoons Ca^{2+} + 2H_2O$	22.800
Brucite	Brucite	$Mg(OH)_2 + 2H^+ \Rightarrow Mg^{2+} + 2H_2O$	16.840
Friedel salt	Friedel salt	$Ca_{4}Al_{2}Cl_{2}(OH)12(H_{2}O)4 + 4H^{+} = 2Cl^{-} + 4Ca^{2+} + 2AlO_{2}^{-} + 12H_{2}O$	28.730
Kuzel salt	Kuzel salt	$\text{Ca}_4\text{Al}_2\text{Cl}(\text{SO}_4)0.5(\text{OH})12(\text{H}_2\text{O})6 + 4\text{H}^+ \leftrightarrows \text{Cl}^- + 4\text{Ca}^{2+} + 0.5\text{SO}_4^{2+} + 2\text{AlO}_2^- + 14\text{H}_2\text{O}$	27.470
Ferrihydrite-mc	FeOOH	$FeOOH = FeO_2^- + H^+$	-19.600
Gibbsite	Gibbsite	$Al(OH)_3 \Rightarrow AlO_2^- + H^+ + H_2O$	-14.670
Gypsum	Gypsum	$CaSO_4(H_2O)2 \Rightarrow Ca^{2+} + SO_4^{2+} + 2H_2O$	-4.581
Straetlingite	SiO2-Afm	$\operatorname{Ca_2Al_2SiO_7(H_2O)8} + 2\mathrm{H^+} \rightleftharpoons 2\mathrm{Ca^{2+}} + 2\mathrm{AlO_2^-} + 9\mathrm{H_2O} + \mathrm{SiO_2}$	4.108
Natrolite	Natrolite	$Na_2(Al_2Si_3)O10(H_2O)2 = 2AlO_2^- + 2Na^+ + 3SiO_2 + 2H_2O$	-30.200
Solid solutions	End member		
AFtss	SO4-AFt	$(({\rm H_2O})2){\rm Ca_6Al_2(SO_4)3(OH)12({\rm H_2O})24} + 4{\rm H^+} \leftrightarrows 6{\rm Ca^{2+}} + 3{\rm SO_4^{2-}} + 2{\rm AlO_2^{-}} + 34{\rm H_2O}$	11.100
	SO4-AFt{30}	$Ca_{6}Al_{2}(SO_{4})3(OH)12(H_{2}O)24 + 4H^{+} = 6Ca^{2+} + 3SO_{4}^{2-} + 2AlO_{2}^{-} + 32H_{2}O$	11.702
HGss	Si0.84-HG	$AlCa_{3}AlO_{6}(SiO_{2})0.84(H_{2}O)4.32 + 4H^{+} \rightleftharpoons 3Ca^{2+} + 2AlO^{2-} + 6.32H_{2}O + 0.84SiO_{2}$	25.781
	Si0.84-(fe)HG	$(FeFeO_3)(Ca_3O_3(SiO_2)0.84(H_2O)4.32) + 4H^+ \rightleftharpoons 2FeO_2^- + 3Ca^{2+} + 6.32H_2O + 0.84SiO_2$	19.981
CSHQss	CSHQ-TobH	$(CaO)0.6667(SiO_2)1(H_2O)1.5 + 1.3334H^+ \rightleftharpoons 0.6667Ca^{2+} + 2.1667H_2O + SiO_2$	8.287
	CSHQ-TobD	$(({\rm CaO})1.25({\rm SiO}_2)1({\rm H}_2{\rm O})2.75)0.6667 + 1.66675{\rm H}^+ \leftrightarrows 0.833375{\rm Ca}^{2+} + 2.6668{\rm H}_2{\rm O} + 0.6667{\rm SiO}_2$	13.655
	CSHQ-JenH	$(CaO)1.3333(SiO_2)1(H_2O)2.1667 + 2.6666H^+ = 1.3333Ca^{2+} + 3.5H_2O + SiO_2$	22.179
	CSHQ-JenD	$(CaO)1.5(SiO_2)0.6667(H_2O)2.5 + 3H^+ = 1.5Ca^{2+} + 4H_2O + 0.6667SiO_2$	28.730
	NaSiOH	$((NaOH)2.5SiO_2H_2O)0.2 + 0.5H^+ \leftrightarrows 0.5Na^+ + 0.7H_2O + 0.2SiO_2$	5.649
	KSiOH	$((\text{KOH})2.5\text{SiO}_2\text{H}_2\text{O})0.2 + 0.5\text{H}^+ \rightleftharpoons 0.5\text{K}^+ + 0.7\text{H}_2\text{O} + 0.2\text{SiO}_2$	5.764
MSHss	M075SH	$Mg1.5Si_{2}O5.5(H_{2}O)2.5 \rightleftharpoons 1.5Mg^{2+} + 2SiO_{2} + 3OH^{-} + H_{2}O$	-28.800
	M15SH	$Mg1.5SiO3.5(H_2O)2.5 = 1.5Mg^{2+} + 1SiO_2 + 3OH^- + H_2O$	-23.570

The surface reactions considered in the numerical simulation and corresponding equilibrium constants, logK are given in Table C.2.

Table C.2

Equilibrium constants, log(K), for considered surface reactions [21].

Reaction equation	log (K)
$ \begin{split} & \equiv SiOH + OH^- \rightleftharpoons \equiv SiO^- + H_2O \\ & \equiv SiOH + Ca^{2+} \rightleftharpoons \equiv SiOCa^- + H^+ \\ & \equiv SiOH + Ca^{2+} + SO_4^- \rightleftharpoons \equiv SiOCaSO_4^- + H^+ \\ & \equiv SiOH + Ca^{2+} + CI^- \rightleftharpoons \equiv SiOCaCI + H^+ \\ & \equiv SiOH + Na^+ \rightleftharpoons \equiv SiONa + H^+ \\ & \equiv SiOH + K^+ \rightleftharpoons \equiv SiOK + H^+ \end{split} $	-12.700 -9.400 -6.000 -8.900 -13.640 -13.640
$\equiv \text{SiOH} + \text{Cl}^- \rightleftharpoons \equiv \text{SiOHCl}$	-0.350

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Paper II

"Enhancement of a multi-species reactive transport model for cement-based materials under cyclic wetting and drying conditions"

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Enhancement of a multi-species reactive transport model for cement-based materials under cyclic wetting and drying conditions



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ABSTRACT

To understand the underlying phenomena that drive concrete deterioration under cyclic environmental conditions in the marine environment, a reactive transport model (RTM) for unsaturated cement-based materials has been established in this study, including multi-ionic and moisture transport coupled with a chemical equilibrium computation. The two-phase moisture transport model, which considers pore structure changes, is introduced with capillary pressure as the primary variable parameter. The modified Poisson-Nernst-Planck (PNP) equations were illustrated for multi-ionic transport through pore solution under unsaturated conditions. A modelling approach for moisture conductivity based on the pore structure and moisture storage was presented to account for pore structure changes on the mass transports. The consideration of boundary conditions and moisture flux through the exposed surface is demonstrated for wetting and drying conditions, separately. Numerical results for mortar samples subjected to NaCl solutions under various cyclic wetting and drying conditions were in good agreement with experimentally measured moisture gain and total chloride content. Under more prolonged wetting conditions, the deeper influence depth and a wider range of moisture fluctuation lead to an increase in concrete deterioration. For all cyclic wetting conditions, the precipitation of Friedel's salt is predicted, which subsequently limits the transport of chloride ions to deeper depths from the exposed surface. A peak in the chloride profile is observed near the exposed surface. Meanwhile, the peak region continuously expands and moves deeper into the specimens with increasing wetting time duration and exposure times, consistent with Friedel's salt precipitation. In contrast, the chloride content near the exposure surface shows a significant decrease due to the decomposition of the C-S-H phase caused by ion leaching and carbonation of the exposed surface.

1. Introduction

For civil infrastructure in marine environments such as buildings, bridges, offshore platforms, and harbours, reinforced concrete materials are widely recommended based on cost and the most accessible construction. However, the service life of reinforced-concrete buildings is shortened due to contaminants from the service environment infiltrating concrete, which is increasingly decisive for the structural design, particularly in marine environments [1–7]. In marine environments, chloride-induced reinforcement corrosion and

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erosion of surface material are identified as the leading deterioration mechanisms [6,8–10]. Moreover, the effect of seawater on the hydrated solid phases of cement-based materials becomes more intricate due to the presence of various aggressive ions, such as sodium, potassium, magnesium, carbonate, sulfate, and chloride ions [6,10]. The degradation of concrete structures imposes a substantial burden on preventive measures, necessitating not only proactive routine maintenance but also expenses for strategic planning, inspection, and testing. Additionally, indirect costs such as traffic delays and productivity losses further contribute to the overall financial impact [11–13].

In marine environments, the exposure of concrete structures can be categorized into various zones, such as submerged, splash, tidal, and atmospheric zones, based on the location of structural elements in relation to the seawater level. In each zone, various ionic and moisture penetration mechanisms can be identified, primarily influenced by the respective environmental condition. Compared to other exposure conditions in different zones, the deterioration of reinforced concrete structures located under low tide or permanently immersed conditions is limited. This limitation results from the inadequate transport of ions and oxygen without any contribution from advection caused by moisture transport. However, the concrete sections in the tidal and splash zone are severely attacked by the ingress of ions together with aggressive moisture fluctuation due to cyclic wetting and drying conditions [4,14–18]. Thus, mass transport and moisture fluctuation are closely associated with the performance and durability of concrete structures. Meanwhile, the mechanism of ionic ingress or leaching coupled with moisture transport through pores in unsaturated conditions is generally quite complicated [19-21]. Understanding the governing mechanisms behind the deterioration of concrete under cyclic wetting and drying environmental conditions in marine environments has received much attention over the last few decades, as it is crucial for maintaining the prolonged and sustainable serviceability of concrete structures. Numerical simulations can be an effective method for predicting the deterioration of concrete structures and providing valuable insights into the underlying phenomena that drive concrete deterioration under cyclic environmental conditions. In addition, numerical tools that can predict changes in concrete structures that are located in marine environments can be used to select environmentally suitable binder and mix designs, reduce infrastructure costs, make cost-effective decisions regarding the timing for repair and replacement of structural elements during the service period, and estimate the lifespan of concrete structures.

Over the last few decades, many studies have focused on developing RTMs for predicting concrete deterioration through changes in the composition of pore solution and phase assemblage due to the ingress of ions into concrete under submerged conditions [22-25]. However, only a few numerical modelling studies based on the concept of multi-species and moisture transport coupled with chemical equilibrium were conducted for concrete in unsaturated conditions [26-29]. Moreover, current modelling approaches are limited by considering simplified assumptions about the processes involved in the deterioration of cement-based materials under cyclic wetting and drying conditions, for example, the relationships between mass transport and moisture saturation in pores, chloride binding isotherm mechanisms due to the interaction between pore solution and solid phase, mass flux through boundary surfaces, and the integration effect of boundary condition. And also, predictive competencies are inadequate due to the lack of fundamental relationships between phase assemblage changes, pore structure changes, and mass transport through pores. Using the current RTM [22], the leaching or ingress behaviour of ions in concrete exposed to saturated conditions can be adequately explained based on the ionic concentration gradient in the pore solution. However, predicting the leaching or ingress behaviour of ions in concrete exposed to cyclic wetting and drying conditions becomes challenging due to the complex interaction between ionic diffusion and moisture transport. Hence, current models are often inadequate for accurately predicting the changes in the composition of pore solutions and phase assemblage of cement-based materials under cyclic wetting and drying conditions. Due to the lack of a comprehensive conceptual explanation for the coupling of multi-ionic transport and moisture transport, the combined effect of moisture transport and electrochemical potential force on multi-ionic transport under unsaturated conditions is still unclear.

This study aimed to develop a comprehensive multi-species reactive transport model coupled with moisture transport to understand the underlying phenomena that drive concrete deterioration under cyclic environmental conditions in a marine environment. To achieve this objective, the reactive transport framework presented in Ref. [22] is extended to account for the deterioration of cement-based material, including moisture transport, and the effect of moisture fluctuation inside pores on multi-ionic transport. Moreover, chemical equilibrium calculations include the equilibrium between the aqueous species in the pore solution, hydrated solid phases, and ionic absorption on the pore surface. To accurately replicate the chloride isotherm behaviour, a surface complexation model is employed in this study, which includes forming an electrical double layer and exchanging interactions among the ionic solution in pores and the C–S–H surface site (\equiv SiOH). For interconnecting phase assemblage, pore structure, and mass transport, models for moisture conductivity and ionic diffusivity based on the pore structure and moisture distribution in pores are adapted in the RTM framework. Finally, numerical studies were conducted, and numerically predicted results were compared to experimentally measured values reported in Ref. [30] for understanding the underlying phenomena that drive concrete deterioration under cyclic environmental conditions in the marine environment, specifically regarding changes in pore solution composition and phase assemblage.

2. Modelling approach

2.1. Outline of modelling approach

The framework presented in Ref. [22] for an RTM which is established for saturated conditions, is extended for analysing the deterioration of cement-based materials under cyclic wetting and drying conditions by adapting additional sub-models, multi-ionic transport coupled with moisture transport, a hysteresis model for determining the moisture storage in pores, and a conductivity model for moisture transport. The framework for the proposed RTM in unsaturated cement-based material is presented in Fig. 1. The RTM framework is addressed in two distinct time domains: the initial stage involving the development of cement-based materials during the

curing period and the subsequent deterioration processes resulting from exposure to environmental conditions. In Fig. 1, regions A and B represent the modelling of early-stage material development and material deterioration, respectively. Using the proposed RTM for unsaturated conditions, the following parameters can be predicted: the spatial and temporal changes in pore structure, moisture content, moisture distribution in the pore, vapour pressure, capillary pressure, internal relative humidity, ionic composition in free water and the electrical double layer (EDL), absorbed ions on pore surface, and phase assemblage such as pure phases (EQ) and solid solution phases (SS) for cement-based material. The following sections provide explanations of the moisture and multi-ionic transports, considerations of chemical equilibrium, and simulation studies conducted using the proposed RTM approach for analysing the deterioration of mortar specimens under various cyclic wetting and drying conditions.

2.2. Governing system of equations for mass transport

2.2.1. General outline

A one-dimensional finite element method (FEM) approach is employed to establish the transport of multiple ionic species through free water, the electrical double layer (EDL), and the two-phase moisture transport in unsaturated cement-based materials. For any arbitrary time and spatial discretization, the ionic concentration in the pore solution, vapour pressure, capillary pressure, relative humidity in the pore void, and moisture distribution in the pore structure are mathematically simulated according to ionic and moisture transport models and applied boundary conditions. In calculating mass transport through pores, cement-based materials are assumed to be rigidly porous and non-deformable and have a consistent porosity. In addition, it is assumed that under unsaturated conditions, all the pores of the material are occupied with condensed water and vapour phases. Consequently, the following relationships can be applicable under unsaturated conditions: $V_s + V_p = 1$ and $V_p = \varphi$ ($\varepsilon_l + \varepsilon_v$) where φ is the total porosity, V_s and V_p are the volume fractions of the solid and void space in the cement-based material, respectively, and ε_l and ε_v are the saturation of water and void in the pores, respectively.

2.2.2. Moisture transport model

A moisture transport model for unsaturated cement-based material is established considering two-phase moisture flow, i.e., vapour and liquid water transport through porous media. The moisture transport in porous media is driven by vapour pressure, capillary pressure, and temperature gradients. In unsaturated porous media, liquid water moves due to gradients in capillary pressure, while water vapour transports through the void space in pores driven by the vapour pressure gradient [31–38]. The level of contribution of thermal diffusion to the overall moisture flow is a subject of ongoing debate in the scientific community. Moreover, compared to capillary pressure and vapour pressure gradient, thermal diffusion mechanisms have a relatively minor impact on moisture transport [39,40]. Therefore, in this study, the effects of temperature changes on moisture transport are neglected during moisture transport calculation. Nevertheless, transport parameters, i.e., liquid water conductivity, ionic diffusion coefficients, and vapour conductivity, are updated to account for the impact of temperature before each time step of transport calculation.

In cement-based material, it is assumed that the moisture and ion mass transport only occurs through the gel and capillary pores, whereas the physically bound water in the interlayer pores is considered immobile. In the current modelling strategy, the governing equation for moisture transport is derived based on the total moisture mass balance of vapour and condensed water in gel and capillary pores. The mass conservation equation is formulated for a representative volume (REV), considering the moisture capacity, moisture flux, and sink term. Using the Kelvin equation, the capillary pressure of condensed water is set as the primary variable to perform



Fig. 1. The framework of the proposed multi-species reactive transport model for cement-based materials under unsaturated conditions.

moisture transport in porous materials. The presented framework accounts for variations in transport parameters, i.e., vapour and liquid water conductivity, due to changes in both pore structure and moisture distribution. In a general form, the mass balance equation for moisture transport may be expressed as

$$\rho_l \varphi \left(\frac{\partial \varepsilon_l}{\partial P_c}\right) \frac{\partial P_c}{\partial t} = -\nabla \left\{ \left(K_{vap}(\theta_l) + K_l(\theta_l) \right) \nabla P_c \right\} + q_l \tag{1}$$

Where φ is the total porosity, e_l the saturation of condensed water, ρ_l the density of pore water $[\text{kg}/\text{m}^3]$, $K_{vap}(\theta_l)$ and $K_l(\theta_l)$ represent the conductivity of vapour and liquid water $[\text{kg}/\text{Pa} \cdot \text{m} \cdot \text{s}]$, respectively, P_c the capillary pressure, and q_l the sink term. The moisture capacity, which is associated with capillary pressure, is represented by the first term on the left-hand side of Eq. (1). The value of $\partial e^l / \partial P_c$ in the moisture capacity term depends on the moisture isotherms of the porous material. The first term on the right-hand side of Eq. (1) represents the total moisture flux within the REV. The second term (q_l) accounts for variations in the total porosity of the cement-based material, as well as other effects, such as moisture changes in pores caused by unreacted cement hydration and/or interaction between pore solution and solid phases. In this study, it is assumed that there are no hydration, chemical reactions, and pore structure changes during the moisture transport calculation, i.e., $q_l = 0$.

In cement-based material, vapour transport will occur through the non-water-filled pore space, and Knudsen diffusion is used to determine vapour diffusion through various pore radii. The vapour conductivity due to the capillary pressure gradient, $K_{vap}(\theta_l)$ for arbitrary temperature, T, is formulated based on the integral in the following formula, accounting for the influence of vapour diffusivity on the pore structure and moisture storage [41].

$$K_{vap}(\theta_l) = \left(\frac{p_{v,sat}}{\rho_l(R_v T)^2}\right) \frac{D_v(T)}{\Omega} \int_{r_c}^{\infty} \frac{1}{1+N_k} dV_v N_k = \frac{l_m}{2r}$$
(2)

Where $p_{v,sat}$ is the saturated vapour pressure [Pa], *h* the relative humidity, R_v the gas constant of vapour [J/kg · K], $D_v(T)$ the vapour diffusivity in free space at temperature T [m²/s], Ω a parameter representing the three-dimensional tortuosity of the pore structure $(\Omega = (\pi/2)^2)$, N_k the Knudsen number, l_m the mean free path of gas molecules [m], r_c the pore radius [m] corresponding to the point at which an interface between liquid water and vapour phase is formed, and V_v the volume of void pore space for vapour transport [m³]. The conductivity of liquid water through the pores depends on the pore structure and moisture content. The following model, based on the distribution of pores and occupied liquid pore water content, is adapted to determine the conductivity of liquid water, $K_l(\theta_l)$ Due to a capillary pressure gradient [41]:

$$K_{l}(\theta_{l}) = \frac{\rho_{l} \varphi_{gc}^{2}}{50\eta_{l}} \left(\int_{0}^{r_{c}} r \, dV_{l} \right)^{2}$$
(3)

Where *r* is the pore radius [m], φ_{gc} the sum of gel and capillary porosity ($\varphi_{gc} = \varphi_{gl} + \varphi_{cp}$), V_l the volume of condensed water [m³], and η_l the viscosity of pore water. Due to interactions between the pore water and hydrated phases in cement-based material, dissolved ions are present in the pore water. The presence of ions, the impact of the water molecule's polarity, the long-range pressures acting on the pore water by the adjacent porous structure, or a combination of any of these influences may cause the pore solution to behave in a non-ideal manner [41]. In the liquid water conductivity model, the effect of temperature changes and the non-ideal behaviour of pore solution on liquid water transport is considered through the viscosity parameter. The actual viscosity of the pore solution under non-ideal conditions at temperature T can be expressed as follows using thermodynamic considerations [41]:

$$\eta_i = \eta_i^i \exp\left(\frac{G_e}{RT}\right) \tag{4}$$

Where η_l^i is the viscosity of pore solution under ideal conditions $[kg/m \cdot s]$, G_e the excess of the free energy required for ideal flow conditions that activate flow [J], and *R* the gas constant [J/mol · K]. The Gibbs free energy, G_e , resulting from the interaction of the pore solution and pore structure, may be described in terms of the characteristics of the pore structure and changes in the relative humidity inside pores [see section 4.2]. The relationship between the pore pressure (P_l) and the relative humidity inside the pores (h) can be defined using Kelvin's thermal equilibrium state between vapour and condensed water as,

$$P_l = \frac{\rho_l RT}{M_w} ln(h)$$
(5)

Where P_l is the pore water pressure [Pa] and M_w the molecular mass of the liquid water [g/mol]. In cement-based materials, it is typically observed that the absorption and desorption curves of typical moisture isotherms exhibit different paths. Additionally, it is apparent that the desorption curves consistently appear above the adsorption curves, and the presence of hysteresis loops can also be identified [34,42,43]. The hysteresis phenomenon in a moisture isotherm model can be addressed by considering the influence of trapped liquid water within the pore structure during drying. In this modeling framework, the model proposed by Maekawa et al. [41] to describe the hysteresis behavior of pore structure in cement-based materials, based on the concept of entrapped liquid water within

the pore structure, is utilized for computing the moisture content and its distribution in the pores.

2.2.3. Multi-ionic transport coupled with moisture transport

The multi-ionic transport strongly depends on the advection of pore water under unsaturated conditions [44–46]. For ion transport through pore solution in unsaturated conditions, the previously presented modified Poisson-Nernst-Planck (PNP) equation in Ref. [22] has been further enhanced to incorporate the influence of bulk moisture flow on ionic transport. It is assumed that the free water (uncharged water) is located in the middle of the pore, and the EDL (charged water) forms on the pore surface. Thus, the velocity of liquid water close to the pore surface can be neglected due to the no-slip condition between the pore solution and pore surface, and the thickness of the EDL is small compared to the pore diameter. Hence, the water in the EDL is considered non-moveable water in the current approach. Therefore, the effect of liquid water flow through pores on ionic mass transport is applied only to ions in free water. The governing equation for ion transport, including advection terms in free water according to the velocity condition, is given by,

$$\varphi \varepsilon_{f}^{l} \frac{\partial C_{f}^{l_{j}}}{\partial t} + \varphi C_{f}^{l_{j}} \frac{\partial \varepsilon_{l}}{\partial t} = \nabla \left\{ D^{l_{j}} \left(1 + \frac{\partial \ln \gamma_{j}}{\partial \ln C_{j}^{l_{j}}} \right) (\varphi - \varphi_{th}) \varepsilon_{f}^{l_{j}} \nabla C_{f}^{l_{j}} + D^{l_{j}} (\varphi - \varphi_{th}) C_{f}^{l_{j}} \nabla \varepsilon_{l} + A^{l_{j}} v^{j} (\varphi - \varphi_{th}) \varepsilon_{f}^{l_{j}} \nabla \Phi_{f}^{T} \right\} - \overline{V}^{l,s} (\varphi - \varphi_{th}) \varepsilon_{f}^{l_{j}} \nabla C_{f}^{l_{j}}$$

$$- \overline{V}^{l,s} (\varphi - \varphi_{th}) C_{f}^{l_{j}} \nabla \varepsilon_{l} + q_{f}^{l_{j}}; j = 1, 2, 3 \dots, N$$

$$(6)$$

Where $C_f^{l_j}$ and γ_j are the mole concentrations and activity coefficient of the j^{th} ion species in free water, φ_{th} the threshold porosity, ε_f^l the saturation of free water, $\overline{V}^{l,s}$ the velocity of water with regard to the rigid porous material, v^j the valence of the j^{th} ion species, D^{l_j} and A^{l_j} are the diffusion coefficient and mobility of the j^{th} ion species, respectively, and q_j^l the mass exchange term in free water due to chemical interactions between ions and the solid phases. Similarly, the governing equation for ion transport in the EDL according to the velocity condition is given by,

$$A_{s}t_{d}\frac{\partial C_{d}^{l_{j}}}{\partial t} = \nabla \left\{ D^{l_{j}} \left(1 + \frac{\partial \ln \gamma_{j}}{\partial \ln C_{d}^{l_{j}}} \right) (A_{s} - A_{th}) t_{d} \nabla C_{d}^{l_{j}} + A^{l_{j}} v^{i} (A_{s} - A_{th}) t_{d} C_{d}^{l_{j}} \nabla \Phi_{d}^{T} \right\} + q_{d}^{l_{j}}; j = 1, 2, 3..., N$$

$$\tag{7}$$

Where $C_d^{l_j}$ is the concentration of the *j*th ion species in the EDL, A_s and A_{th} the portion of a pore's surface that is covered by the pore solution and the threshold porosity, respectively, t_d the thickness of the EDL, and $q_d^{l_j}$ the mass exchange term in the EDL due to chemical interactions between ions and solid phases. Gauss's law is used to calculate the intensity of electrical potential in free water and the EDL (Φ_t^T and Φ_d^T), respectively) individually. The equation for free water's acquired electric potential is,

$$\nabla \left\{ \left(\varphi - \varphi_{th} \right) \varepsilon_f^l \zeta_0 \zeta_r \nabla \Phi_f^r \right\} = \left(\varphi - \varphi_{th} \right) \varepsilon_f^l F_C \sum_{j=1}^N \nu^j C_f^{lj} \tag{8}$$

The following equation can be used to represent the electrical potential for the EDL.

$$\nabla \left\{ \left(A_s - A_{th} \right) t_d \zeta_0 \zeta_r \nabla \Phi_d^T \right\} = \left(A_s - A_{th} \right) t_d F_C \sum_{j=1}^N \nu^j C_d^{l_j} \tag{9}$$

Where ζ_0 and ζ_r are the relative and vacuum dielectricity coefficient, respectively, and F_C the Faraday constant. In this study, the effective diffusion coefficient, $D_{i,T}^{eff}$ and effective ionic mobility, $A_{i,T}^{eff}$, introduced in Ref. [22] are used, accounting for pore structure, pore solution properties, and temperature changes. The liquid water flow governs the advection force on ions during transport through the porous material. Liquid water flow will only occur through a fully saturated pore due to the capillary pressure gradient in an unsaturated porous material. Thus, the advection velocity of ions, $\overline{V}^{l,s}$, is formulated using the liquid water conductivity term and Darcy law as,

$$\overline{V}^{l,s} = \frac{\Omega K_l(\theta_l)}{\rho_l \varphi \varepsilon_l} \nabla P_c \tag{10}$$

2.2.4. Boundary conditions of ionic and moisture transport model

The boundary condition for moisture and ionic transport should be adequately defined in the RTM to predict ionic transport coupled with moisture transport realistically due to cyclic wetting and drying conditions. During drying conditions (directly exposed to the atmospheric condition), moisture transport occurs in the form of vapour and liquid water within the pores of the material. At the same time, moisture loss occurs due to vapour flux from the concrete's surface to the surroundings, mainly driven by the vapour pressure gradient between the surface of the material and the atmosphere. This process of moisture loss is defined as the evaporation of moisture from the surface of porous material. The moisture evaporation from wet pore surfaces depends on water saturation level, pore structure, moisture conductivity, and formed boundary air layer adjacent to the material's surface [29,47–50]. The isothermal evaporation from wet porous surfaces is driven by advection and/or vapour diffusion. In the case of a dense pore surface (with pore sizes < 1000 µm) subjected to natural airflow conditions (airflow velocity < 4 m/s), the primary factor influencing moisture loss is the dispersion of vapour, while the impact of advection on moisture loss can be neglected [47]. The airflow direction near the evaporating surface is assumed to be parallel to a flat surface and considered a laminar flow. The parallel air velocity starts from U = 0 at z = 0 (due to the no-slip condition at the surface) and gradually asymptotically increases to $U = U_{\infty}$ (free-stream air velocity, m/s) at a

considerable distance away from the surface [51]. Moreover, the boundary layer thickness is defined as the region thickness where the airflow velocity $U < 0.99U_{\infty}$. The boundary layer thickness depends on surface roughness, free air velocity, temperature, etc. Additionally, the boundary layer thickness is inversely associated with the free-stream velocity, as demonstrated by numerous experimental studies [48,51,52]. The model proposed by Shahraeeni et al. is utilized in this study to compute the boundary layer thickness, δ_m [48].

$$\delta_m = 2.26 * 10^{-3} U_{\infty}^{-1/2} \tag{11}$$

The proposed model for the evaporation flux through boundary surface, \dot{e} , (kg/m²s) based on a 2-D plan by Haghighi et al. [47], may be defined as

$$J_e^s = k_e D_a^v \left(\rho_s^v - \rho_e^v \right) \tag{12}$$

Where k_e is the relative evaporation rate, D_a^v the diffusivity of vapour in air (m^2/s) , ρ_s^v the density of vapour at the surface (kg/m^3) , and ρ_a^v the density of vapour in the air (kg/m^3) . Considering vapour diffusion through pore surface over a boundary layer, an analytical expression for the evaporation rate is proposed by Schlünder et al. [50], as

$$k_e = \frac{1}{1 + \frac{2}{\pi} \frac{P}{\delta_m} \sqrt{\frac{1}{4\theta_{surf}}} \left[\sqrt{\frac{\pi}{4\theta_{surf}}} - 1 \right]}$$
(13)

Where θ_{surf} is the relative wetted surface area, the valid range of θ_{surf} is $\leq \pi/4$, *P* represents available pore space of wet patches, $P = \sqrt{\pi r_c^2}$, and r_c the radius of cylindrical pores. The evaporation of moisture depends on the internal moisture transport to the surface and, subsequently, the evaporation of moisture from the surface to the atmosphere. For low saturation conditions in cement-based material, the moisture flux through a pore at the surface (J_{yl}^s) is low compared to the evaporation flux through the boundary surface (J_{el}^s) . Thus, the moisture loss occurs through the boundary surface at the rate of moisture flux through a pore at the surface. Therefore, moisture flux through the boundary surface is calculated based on the conductivity term at the surface. On the other hand, for a high saturation level, sufficient moisture content is present at the surface of the porous material to allow moisture loss through the boundary surface at the evaporation rate. Therefore, in the current study, the moisture flux from the surface to the atmosphere is defined by two conditions and determined as follows.

$$f_l^s = K_{vl}(\theta_l)_s \frac{(P_c^s - P_c^e)}{\delta_m} \quad \text{if } J_e^s \ge J_{vl}^s$$

$$f_l^s = k_e \left(\frac{p_{v,sut} h^e}{\rho_l(R_v T)^2}\right) D_a^v \left(P_c^s - P_c^e\right) \quad \text{if } J_e^s < J_{vl}^s$$

$$(14)$$

Where $K_{vl}(\theta_l)_s$ is the moisture conductivity at the surface of a material $(K_{vl}(\theta_l)_s = K_{vap}(\theta_l)_s + K_l(\theta_l)_s)$, P_s^s the capillary pressure at the surface, P_e^e and h^e the capillary pressure and relative humidity in the environment, respectively. In addition, when considering ion mass transport, ionic flux through the surface of the material is not allowed under dry boundary conditions $(f_l^s = 0)$ due to a lack of continuity of liquid water with atmospheric boundary conditions. This is accomplished by setting the ionic flow term at the boundary node to zero during the solution of the ionic transport equations. Thus, moisture loss occurs in the vapour phase under dry boundary conditions based on moisture mass flux through the boundary surface, and ion ingress or leaching is omitted through the boundary surface. Moreover, the pore water pressure and relative humidity at the boundary are determined by the transport equations for moisture and the moisture flux through the boundary surface, resulting in values that differ from environmental conditions such as relative humidity and vapour pressure at the surface of the concrete. Due to direct contact with a boundary solution (submerged condition), the developed hydraulic pressure on the concrete surface is assigned as a boundary condition to solve the moisture transport equations. Direct contact of the boundary solution with the exposed concrete surface results in the application of the concretrations of ions present in the boundary solution as boundary conditions for solving the ion mass transport equations, whereas ion ingress or leaching continues through the boundary solution as boundary conditions for solving the ion mass transport equations, whereas ion ingress or leaching continues through the boundary solution as boundary conditions for solving the ion mass transport equations, whereas ion ingress or leaching continues through the boundary solution as boundary conditions for solving the chemical equilibrium calculation, the compos

2.2.5. Finite element formulation

1-

The finite element method (FEM) is used to solve the governing equations for the ions and moisture transport under wet and dry conditions. Using a weight function w for the spatial domain and a weight function W for the time domain, the governing equations Eqs. (1) and (6)-(9) are separated into a spatial domain and a time domain for the finite element formulation. Utilizing Galerkin's approximation, the one-dimensional spatial scheme with linear spatial components is discretized [53,54]. The Green-Gauss theorem is applied to separate the boundary flow conditions in the mass transport. Every step implicitly solves the problem in the time domain.

The entire connected set of equations is solved at once to prevent the staggered schemes between individual solutions of state variables. A modified Newton-Raphson iteration strategy is adapted to enhance the FEM solution of the system equations while also speeding up computation [55,56].

2.3. Chemical equilibrium model

The external geochemical PhreeqcRM algorithm, which allows for adequate fast parallel processing while maintaining compatibility between the transport module and the chemical module, is used in the chemical equilibrium computation to solve the mass exchange terms q_l , $q_f^{l_j}$, and $q_d^{l_j}$ from the governing Eqs. (1), (6) and (7) for chemical interactions between ions and hydrated phases [57–59]. To achieve chemical equilibrium among aqueous solution and solid phases, the geochemical program employs the mass actions law for aqueous species, pure phase, and solid solution reaction [60–62]. A thermodynamic database determines the stoichiometric coefficients and equilibrium constants for the reaction of aqueous species, pure phases.

3. Numerical examples

The proposed reactive transport model for unsaturated conditions is investigated by comparing model predictions with the experimental data presented in Ref. [30]. The experimental study compares moisture changes of different mortars subjected to various boundary conditions, including wetting and drying, moisture gain due to cyclic wetting and drying conditions, and Cl profiles over time. Comprehensive details on specimen preparation, exposure condition, measurement procedure, and results can be obtained in Ref. [30], whereas a brief description of the material and measured results is given in the following.

3.1. Materials

Two sets of mortar samples (OPC35 and OPC50) were prepared using ordinary Portland cement (OPC) in cylindrical moulds with a diameter of 50 mm and a height of 100 mm. The binder-to-sand ratio was kept constant at 1:2.25, while the water-to-binder ratios for the OPC35 and OPC50 specimens were adjusted to 0.35 and 0.50, respectively. Table 1 provides information about the mortar mix design. The chemical composition of cement (OPC), classified in the JIS R 5210, is obtained from Ref. [63] and given in Table 2.

3.2. Exposure conditions

To study the moisture conductivity of OPC mortar specimens after sealed curing for 28 days at 20 °C, all mortar samples (OPC35 and OPC50) were kept in a dry environment (60% RH and 20 °C) using a control chamber for 30 days. After drying, one set of mortar specimens was exposed to 99.5% RH for an additional 30 days, while another set was kept in water-submerged conditions for that period. During the exposure period, the mass gain or loss of each specimen was measured while it was being dried at 60% relative humidity, wet at 99.5% relative humidity, and immersed in water. Furthermore, after being sealed-cured for 28 days at 20 °C, another set of OPC50 mortar specimens was subjected to three different types of wetting and drying cycles to examine moisture migration and the ingress of ions from the boundary solution. In this exposure condition, the alternating cycles comprised wetting due to water submerging and drying due to storage in 60% RH over three days, in which the three-day cycles are split into periods of 1% wetting – 99% drying, 10% wetting – 90% drying, and 40% wetting – 60% drying, respectively. In addition, different types of solutions were used for the wetting process of specimens. One set of samples was wetted with a 3% NaCl solution and another with a 6% NaCl solution. In total, six experiments were conducted, comprising two types of boundary solutions and three types of wetting and drying cycles. For each specimen, the mass gain or loss was measured during the initial cycles of wet and dry conditions. Also, the chloride profiles of each specimen were measured using the potentiometer titration technique after exposure periods of 1, 7, and 12 months. For more comprehensive information regarding the experimental setup and the measured results, reference is made to Ref. [30]. Table 3 provides the elemental composition of the two different types of exposure solutions.

3.3. Input parameters for numerical studies

The specimen size and boundary conditions for the numerical studies are simulated as described in the experiment. In the experiment, the top surface of the mortar specimens was allowed for wetting and drying, while the remaining surfaces were coated with epoxy to protect from moisture gain or loss. The hydration of the binder is computed from the degree of hydration of each clinker in cement. The main and some minor clinkers phases, such as alite, belite, aluminate, ferrite, calcite, bassanite, and gypsum, were determined by XRD-Rietveld [63]. The soluble alkali sulfates (K_2SO_4 and Na_2SO_4) were determined using total alkali oxide and sulfate content in OPC cement (see Table 2) and the proposed method by Taylor for sulfate distribution [64]. The sulfates (SO_3) that are neither alkali-sulfates, basanite, or gypsum phases are thought to concentrate as solid solutions in the major clinkers, particularly alite and belite in OPC. The remaining non-dissolved alkali oxide (K_2O and Na_2O) and magnesium oxide (MgO) are stored as minor content in the major clinkers. Table 4 displays the calculated clinker composition of the OPC cement.

The ion transport model comprised a total of 74 ions, whereas moisture transport included two phases of moisture, i.e., vapour and

Table 1			
Mix design	of mortars	after	[30]

Type of mortar	Cement [kg/m ³]	Sand [kg/m ³]	Water [kg/m ³]
OPC35	635	1429	222
OPC50	580	1305	290

Table 2

Chemical composition [wt%] and physical properties of the OPC, after [63].

	OPC
Chemical composition analysis [wt%]	
SiO ₂	20.23
Al_2O_3	5.39
Fe ₂ O ₃	3.04
CaO	64.64
MgO	0.92
K ₂ O	0.31
Na ₂ O	0.30
SO ₃	1.91
Cl	0.03
LOI 950C	2.40
Blaine [cm ² /g]	3300
Density [g/cm ³]	3.16

Table 3

Elemental composition of exposure solutions, after [30].

Element	3% NaCl solution [mmol/l]	6% NaCl solution [mmol/l]
Na	513.3	1026.6
Cl	513.3	1026.6

liquid water. The thermodynamic data of phase reaction and ionic adsorption on the pore surface described in Ref. [1] were used for the numerical analysis of OPC mortars under dry and wet conditions. Additionally, under ambient circumstances, CO_2 gas dissolution into the exposure solution was permitted. Table 5 shows the estimated threshold value of porosity, initial tortuosity, and other variables along with details of the spatial and temporal discretization employed in the numerical simulation. The 100 mm 1D domain of the mortar specimen is discretized using 50 elements with a growth method considering accuracy and computational cost. According to the duration of exposure, computational time, accumulation of charge imbalance of ions in the pore water, and the truncation error at the node of the exposed surface [65], sensitivity analyses for ionic transport under unsaturated conditions were used to define the

Table 4

Clinker composition of the ordinary Portland cement (OPC) [wt%].

Phase composition [wt%]		Present as a solid solution in the clinker phases [wt%]		
Alite ^a (C ₃ S)	58.60	CaO ^c	0.00	
Belite ^a (C ₂ S)	17.20	MgO ^a	0.77	
Aluminate ^a (C ₃ A)	6.97	$K2O^{d}$	0.10	
Ferrite ^a (C ₄ AF)	9.90	Na_2O^d	0.20	
Calcite ^a	3.75	SO ₃	1.19	
Bassanite ^a (CaSO4 ·0.5H2O)	2.01	-		
Gypsum ^a (CaSO4 ·2H2O)	0.43			
$K_2SO_4^b$	1.66			
Na ₂ SO ₄ ^b	0.69			
a - Determined by XRD-Rietveld [63].		d - Calculated from the total in Table 2 and soluble alkali content.		
b - Calculated from the distribution of sulfate [64]. c - Calculated from the chemical analysis.		e – Calculated from the total in Table 2, basanite, gypsum, and soluble alkali content.		

Table 5

Model parameters for numerical investigations.

Model parameters	Value
No of spatial elements	50
Growth factor of spatial elements	2
Total spatial distance, (m)	0.1
Total exposure time, (days)	360
Time step, Δt (hr)	1
Threshold pore radius, r _{th} (nm)	2
Initial tortuosity factor, $f_{r,0}$	0.09
Shape parameter, <i>c</i>	1
Relative dielectricity, ζ_r	78.54
Dielectricity in a vacuum, ζ_0	8.85E-12
Faraday's constant, (C/mol)	96490
Gas constant, $(J/(mol \bullet K))$	8.314

time step.

4. Results and discussion

4.1. Phase assemblage of OPC35 and OPC50 mortar specimens

For OPC35 and OPC50 mortar samples, the predicted results of individual and total hydration of clinkers over a 28-day curing period and the phase assemblage after 28 days of curing at 20 °C temperature are presented in Fig. 2. According to the hydration model prediction, at the end of the curing period, the alite and aluminate clinker in the OPC35 and OPC50 samples are approximately 80% hydrated, while belite and ferrite dissolve at significantly slower rates. However, higher dissolution of belite and ferrite is observed in the OPC50 sample compared with OPC35 because the higher water content in pores increases the interaction between unreacted clinker particles and water. As shown in Fig. 2b, the predicted phase assemblage in both OPC35 and OPC50 samples consists of calcium silicate hydrate (CSHss), Portlandite (CH), Ettringite (AFtss), monocarbonate (CO3-AFm), hydrogarnet (HGss), hydrotalcite (Ht), calcium carbonate (calcite), and unreacted cement content (UnhyCemt). After 28 days of sealed curing, the OPC35 and OPC50 samples contain 13.5% and 20% of the total volume as pore spaces, respectively. Meanwhile, the combined volume of the hydrated solid phases and the remaining unreacted cement in the mortar specimens occupy approximately 32% and 30% of the space, respectively. As a result of the denser pore structure in OPC35 samples compared to OPC50 samples, there is a reduction in the contact between pore water and unreacted cement particles. This leads to a higher content of unreacted cement in OPC35, even after pore water is still available in pores. The simulated results indicate that the pH of the mortar pore solutions for OPC35 and OPC50 is approximately 13.14 and 13.09, respectively, which are consistent with the experimentally measured values for typical Portland cement [66].

At the end of the 28-day curing period, Fig. 3 illustrates the numerically predicted pore solution composition in OPC35 and OPC50 mortar samples. The mole fraction among the hydrated phases varies with the water-to-cement ratios, leading to slight variations between the predicted composition of the pore solution in OPC35 and OPC50 mortars. In both mortar samples, the pore solution composition is primarily dominated by alkali ions such as Na^+ and K^+ due to the higher dissolution rate of alkali sulphates compared to the dissolution of the major clinkers. The decalcification of the Portlandite and C–S–H phases results in a slightly higher calcium concentration, while the precipitation of the hydrotalcite and hydrogarnet phases limits the concentrations of Fe and Mg in the pore solution under ambient conditions in the simulation, a certain amount of carbon (C) concentration in the pore solution is observed in the simulated results.

The pore structure of mortar significantly influences the flux of ions and moisture across the exposed surface, as well as the internal mass transport through the pore space. The presented modelling approach considers moisture conductivity and ionic diffusivity, which are based on the pore structure and moisture storage, to address the impact of pore structure change on mass transport. After 28 days of



Fig. 2. Numerical results for OPC35 and OPC50 mortar samples. (a) individual and total hydration of clinker over 28 days of the curing period, (b) phase assemblage for mortar specimens at the end of the 28-day curing period at 20 °C temperature. (left: OPC35, right: OPC50).



Fig. 3. The numerically predicted composition of the pore solution of OPC35 and OPC50 mortar specimens after 28 days of curing at 20 °C temperature.



Fig. 4. Pore size distribution and cumulative pore volume of OPC35 and OPC50 mortar specimens after 28 days of sealed curing at 20 °C. (left: OPC35, right: OPC50).

curing at 20 °C temperature, the multi-level of pore distribution and cumulative porosity of the OPC35 and OPC50 mortar specimens, such as gel (blue), capillary (green), and total pores, which represent the sum of gel and capillary pores (red) are shown in Fig. 4a and b, respectively. Solid lines represent the modelled results of pore distribution, while dashed lines illustrate the cumulative porosity. As per the numerical prediction, OPC50 mortar exhibits a more significant formation of capillary pores than OPC35 mortar. However, no significant differences are observed in gel pore formation between OPC35 and OPC50 mortars, as both mortars exhibit nearly the same moles of C–S–H gel formation (see Fig. 2). Due to the formation of gel and capillary pores during the sealed curing period, the OPC50 mortar shows a higher overall total pore volume (the combined sum of gel and capillary pores). Moreover, the simulated pore distribution reveals that the peak radius of the pore structure in OPC50 mortar is five times greater compared to OPC35 mortar. As a result, the ionic and moisture transport through pore space is expected to be higher in OPC50 mortar.

Fig. 5a compares the predicted absorption and desorption curves (moisture isotherms) for OPC35 and OPC50 mortars. In the simulated results, a difference between the absorption and desorption curves for OPC35 and OPC50 mortars is observed, which may be attributed to the presence of trapped water in the pore structure caused by the inkbottle effect. Moreover, the computed moisture isotherms indicate significant differences for OPC mortars with different water-to-cement ratios. And also, the absorption and desorption curves of OPC35 mortar lie above the curves for OPC50. It is shown that the water saturation level for OPC35 is higher than OPC50 at specific relative humidity. The computed vapour and liquid water conductivity for OPC35 and OPC50 mortar specimens are presented in Fig. 5b and c, respectively. The numerical simulation demonstrates a significant difference in vapour and liquid water conductivity throughout the entire moisture range for the two different water-to-cement ratios. For a high water saturation (above 0.4), moisture transport through the pores of mortar is mainly driven by liquid water, whereas the contribution of vapour transport is negligible, as most pores are occupied with condensed liquid water, and limited space is available for vapour transport. Vapour transport governs moisture transport for saturation levels below 0.4 because the fully saturated water flow channels significantly decrease under low pore saturation. It should be noted that vapour transport is also decreased at very low water saturation (see Fig. 5b) because higher energy is needed to evaporate water stored in very narrow pores. Fig. 5d shows the overall moisture conductivity for OPC50 mortar than



Fig. 5. Numerical results for OPC35 and OPC50 mortar samples in absorption and desorption condition after 28 days of sealed curing at 20 °C. (a) moisture isotherms, (b) vapour conductivity, (c) liquid conductivity, and (d) moisture conductivity. (a: absorption, d: desorption).

OPC35 due to the available space for transport. Hence, based on the computed moisture conductivity, OPC50 is expected to experience faster moisture ingress than OPC35.

4.2. Moisture transport due to wetting and drying

In the cement-based materials, the non-ideal behaviour was identified in the transport of liquid water through pores [41,67,68]. To account for water behaviour transitioning from an ideal to a non-ideal state due to an interaction between pore water and pore structure, Maekawa et al. [41] introduced the liquid water conductivity model, including a time-lag phenomenon. In this study, the proposed model by Maekawa et al. [41] for considering the time-lag phenomena in cement-based material is modified to accommodate RTM in unsaturated conditions. The additional energy for the activation of flow, G_e , in Eq (4) is computed with a delayed pore humidity parameter, H_d , and pore structure characteristics. Using the Kelvin chain model, the delayed pore humidity, H_d , is modelled as a



Fig. 6. Comparison of numerical and experimental results for OPC35 and OPC50 mortar samples [30]. (a) moisture gain of OPC35 and OPC50 mortar after drying at 60% RH for 30 days and wetting at 99.5% RH for 30 days, (b) moisture gain of OPC35 and OPC50 mortar after drying at 60% RH for 30 days and submerged wetting for 30 days. (left: 99.5% RH, right: submerged).

function of the actual pore humidity, H, and time history of pore humidity. By comparing predicted and measured moisture gain of the two different mortars (OPC35 and OPC50) under various dry and wet conditions. The extra activation energy, G_e , at any point and time is proposed as,

$$G_{e} = G_{max}H_{d} \tag{15}$$

Where

 $G_{max} = 4100$ for dry boundary conditions

 $G_{max} = 14946 * \varphi_{gc} + 2532.4$ for wet boundary conditions

$$\frac{dH_d}{dt} = \frac{H - EH_d}{\eta_d}; \quad \eta_d = 12(1 + 30H_d^2); \quad E = 0.9;$$

Where η_d and *E* are dashpot viscosity and spring stiffness of the Kelvin chain model, respectively. The compared results between the predicted and measured moisture gain in two different mortars (OPC35 and OPC50) under various dry and wet conditions, which were used to model the extra activation energy, are shown in Fig. 6. The model of activation energy due to dry boundary conditions (see Eq. (15)) reveals that the non-linear behaviour of pore water viscosity does not depend on pore structure. This is because moisture gain or loss takes place through the boundary in the form of vapour due to the vapour pressure gradient. On the other hand, pore structure plays a significant role in the viscosity changes of pore solution under wet boundary conditions, specifically in submerged conditions. This is because the hydraulic pressure, acting on the boundary surface, compresses the pore solution within the rigid pore structure, leading to changes in the viscosity of the pore solution.

Under cyclic wetting and drying conditions, the drying front (DF) and wetting front (WF) of concrete are essential parameters in concrete durability design. They provide specific details about the region where the ingress of ions can rapidly deteriorate the concrete [69,70]. The moisture profile of OPC35 and OPC50 after 30 days of drying at 60% RH and 30 days of wetting under two different conditions, i.e., 99.5% RH and submerged, are illustrated in Fig. 7a and b, respectively. Based on the simulated results, there are significant differences observed between OPC35 and OPC50 concerning the drying front in 60% RH (DF60), wetting front in 99.5% RH (WF995), and wetting front in submerged conditions (WFsub). The depth of the drying front at 60% RH (DF60) is found to be greater in OPC50 compared to OPC35. Additionally, the OPC50 mortar specimen, upon dry condition, exhibits a higher level of moisture loss, which can be attributed to its coarser pore structure, as shown in Fig. 4. This coarser pore structure leads to enhanced moisture conductivity towards the boundary surface and increases the evaporation rate of moisture at the exposed surface. Apart from the wetting front of OPC35 under submerged conditions (WFsub in OPC35), the wetting fronts of OPC35 and OPC50 in all exposure conditions do not extend beyond the drying front. Therefore, the predicted results indicate that ionic and moisture transport does not significantly affect the region beyond the drying front. However, it is essential to acknowledge that cement-based material exposed to a single exposure cycle may provide limited information for making decisions on material deterioration. Therefore, it is necessary to conduct analyses of cement-based materials under cyclic wetting and drying conditions to determine the influential depth of moisture transport for the durability design of concrete (see section 4.3.2).

4.3. Mortar samples exposed to NaCl solution under cyclic wetting and drying conditions

4.3.1. Phase assemblage of exposed mortar specimens

The proposed modelling approach was employed to evaluate the changes in the phase assemblage of mortar specimens under exposure to NaCl solutions at various concentrations and cyclic drying and wetting conditions. Fig. 8 illustrates the predicted phase composition for OPC mortar samples exposed to wet and dry cycles in 3% and 6% NaCl solutions with 1-h, 9-h, and 33-h cyclic wetting



Fig. 7. Numerical results for OPC35 and OPC50 mortar samples. (a) moisture profile of OPC35 mortar at 99.5% RH and submerged conditions for 30 days, (b) moisture profile of OPC50 mortar at 99.5% RH and submerged conditions for 30 days. (left: 99.5% RH, right: submerged).



Fig. 8. The predicted phase assemblage for OPC50 mortars exposed to 3% and 6% NaCl with 1hr, 9hr, and 33 h wetting cycles for 12 months (left: 3% NaCl, right: 6% NaCl).

for 12 months. In Fig. 8, the right-hand side shows the section of the unaffected core, while the left-hand side displays the region of specimens exposed to NaCl solution. The simulation result shows that the phase assemblage of the unaffected portion of mortar specimens includes calcium silicate hydrate, Portlandite, Ettringite, hydrogarnet, hydrotalcite, monocarbonate, calcite, and unreacted cement content. Due to the mortar specimen being exposed to 3% and 6% NaCl solutions during all cyclic wetting conditions, the calcite phase starts to precipitate close to the exposed surface due to the reaction between transposed $(CO_3)^{2-}$ ions and released Ca^{2+} ions from the dissolution of Portlandite, Ettringite, monocarbonate, and C–S–H. Furthermore, it is observed that the moles of Portlandite, Ettringite, monocarbonate decomposition, and calcite precipitation vary with cyclic wetting periods.

The precipitation of Friedel's salt occurs when there is a sufficient ingress of CI^- ions to replace carbonate ions $(CO_3)^{2-}$ in monocarbonate [71]. The predicted results demonstrate the precipitation of Friedel's salt for all cyclic wetting conditions, which subsequently limits the transport of CI^- ions to deeper depths from the exposed surface. Meanwhile, the mole of Friedel's salt formation increases with wetting time due to extended interaction with the boundary solution. Due to the presence of Na⁺ ions in the exposure solution, the formation of alkali aluminium silicates is expected to occur in all exposure conditions. However, alkali aluminium silicates form as a natrolite phase close to the exposed surface under more prolonged cyclic wetting conditions such as the 9hr and 33hr cyclic wetting period. In the vicinity of the exposed specimens, it is also possible to observe the decomposition of C–S–H and hydrogarnet phases along with the precipitation of new phases, including ettringite and ferrihydrite-mc (FeOOH). Due to mortar exposure to a longer duration of wetting in both 3% and 6% NaCl solutions, the decomposition of C–S–H leads to the formation of silica gel and magnesium silicate hydrate (MSHss) at the surface. In addition, the leaching of ions, as well as the dissolution of phases such as C–S–H, Portlandite, Ettringite, monocarbonate, and hydrogarnet, leads to a reduction in the solid phase volume in the region close to the exposed surface of the mortar. The dissolution of the solid phase increases with wetting time duration as a result of higher leaching of ions due to the interaction of hydrated solid phases with the boundary solution. For both the 9-h and 33-h cyclic wetting conditions,
considerable drops in the pH value of the pore solution were observed, along with the leaching of specific ions and the dissolution of phases. Moreover, the decomposition of the C–S–H phase in mortar samples exposed to 3% and 6% NaCl solutions results in a decrease in pH value to approximately 6.35 and 6.38 near the exposed surface for samples exposed to 33-h cyclic wetting conditions.

4.3.2. Moisture migration due to cyclic wetting and drying conditions

The predicted moisture gain and loss in mortar exposed to 1hr, 9hr, and 33 h cyclic wetting for the first few cycles are shown in Fig. 9. The numerical predictions and the experimentally measured moisture variations in OPC50 mortar specimens exposed to various cyclic wetting conditions are in good agreement. The numerical simulation shows increased maximum moisture gain and loss with wetting duration. In all exposure conditions, the rate of moisture gain during the wetting period is higher compared to the rate of moisture loss during the drying period. In addition, the rate of moisture gain and loss during each wetting and drying cycle decreased over time. The increased moisture migration leads to a more intense advection flux of ions through the boundary surface. As a result, higher chloride penetration and potential deterioration of the mortar specimens are expected.

The changes in the moisture profile and moisture isotherms at a depth of 2.5 mm from the exposure surface of OPC50 mortar samples, exposed to 3% NaCl with 1 h cyclic wetting and 6% NaCl with 33 h cyclic wetting, are presented in Fig. 10a and b, respectively. In Fig. 10a, the changes in the moisture profile over time are visualized by variations in the line colour, ranging from light to dark. The drying and wetting actions in each cycle influence the moisture profiles. The final moisture profile under moisture equilibrium conditions, where moisture loss and gain are equal in each cycle, is represented by a dark line. The influence depth, i.e., areas in which the saturation changes actively under cyclic boundary conditions, is clearly identified in Fig. 10a. The predicted moisture profile shows a more significant moisture loss was observed in the 1 h cyclic wetting condition compared to the 33 h cyclic wetting conditions. However, the influence depth is higher in the 33 h cyclic wetting conditions than in the 1 h cyclic wetting conditions. The computed moisture isotherms at 2.5 mm depth from the exposed surface based on the pore structure development of OPC50 mortar and moisture isotherms indicate significant differences for OPC50 mortar under shorter and longer wetting conditions. It can be noticed that the moisture fluctuation inside pores is more pronounced for 33hr cyclic wetting conditions compared to 1 h cyclic conditions. As a result of a deeper influence depth and a more extensive range of moisture fluctuation, concrete deterioration increases with the wetting period.

4.3.3. Chloride profiles

In the exposed mortar specimens, the total chloride content may include free chlorides in the pore solution (Cl_f), chloride physically absorbed on the surface site of the C–S–H phase (Cl_p), and chemically bound chloride (Cl_c) in the form of salts, such as Kuzel's and Friedel's salt. In this numerical study, the total chloride (Cl_{Tot}) as a percentage of the mass of the binder (m_b) is determined as follows

$$Cl_{IoI} = \left(\frac{Cl_f + Cl_p + Cl_c}{m_b}\right) \times 100$$
(16)

Fig. 11 illustrates the numerically simulated and experimentally determined chloride content in mortar exposed to 3% and 6% NaCl with 1hr, 9hr, and 33hr of cyclic wetting for 1, 7, and 12 months. The chloride content in the figure is presented as a percentage of the mass of the binder. The results in Fig. 11 demonstrate good agreement between the numerically simulated and measured values for mortar samples under various cyclic conditions. From the numerical studies, the following sequence of chloride storage mechanisms



Fig. 9. Moisture gain and loss in OPC50 mortar specimens exposed to 1hr, 9hr, and 33 h cyclic wetting conditions.



Fig. 10. Numerical results for OPC50 mortar samples exposed to different boundary conditions (left: in 3% NaCl with 1 h cyclic wetting, right: in 6% NaCl with 33 h cyclic wetting). (a) changes in moisture profile under cyclic wetting and drying conditions, (b) moisture isotherms at 2.5 mm depth from the exposed surface. (a: absorption, d: desorption).

may be identified; initially, chloride ions start to penetrate mortar specimens due to cyclic wetting conditions. Subsequently, the transported chloride ions are absorbed by the surface sites of the C–S–H phase; after reaching a certain amount of free chlorides in the pore solution, which is adequate to replace carbonate ions $(CO_3)^{2-}$ in monocarbonate, chloride ions are chemically bound as Friedel's salt. Compared to mortar specimens exposed to 3% NaCl solution, samples exposed to 6% NaCl exhibit higher chloride contents for all cyclic wetting conditions. The numerical simulation provides an explanation for the higher chloride contents observed in the 6% NaCl exposure. It is indicated that the exposure of the mortar specimen to a 6% NaCl boundary solution results in higher electrochemical and potential differences between the boundary solution and pore water, leading to increased chloride ingress into the exposed mortar specimens.

A chloride profile peak is observed near the exposed surface in all exposed mortar specimens. This peak region continuously expands and moves deeper into the specimens with increasing wetting duration and exposure times. On the other hand, the chloride content near the exposure surface (0–3 mm section) significantly decreases under all exposure conditions. Various hypotheses have been proposed to explain the chlorine content peak and the chloride profile reduction near the exposed surface. The presence of sulfur in the exposure solution and its accompanying ingress has been attributed to reduced chloride binding [72,73]. On the other hand, specimens exposed to NaCl solutions without sulfur content also exhibit the peaking behaviour [74]. Additionally, the carbonation process in cement-based materials can lead to a decrease in chloride absorption [73]; However, the numerical prediction demonstrated that the peaking behaviour in the chloride profiles for exposure to 6% NaCl becomes more apparent with time compared to exposure to a solution of 3% NaCl, while the carbonation level remains nearly the same in both exposed specimens (see Fig. 8). As a result of ion leaching, the pH is decreased, and the C–S–H phase starts to decompose, which raises the calcium content in the pore water and increases chloride adsorption. Recent studies report that the presence of calcium content in cement is essential to increase the binding capacity of chloride [9,75].

The presented multi-species reactive transport model provides an explanation for the peak and reduction behaviour in Cl profiles. In the mortar specimens exposed to a 6% NaCl solution for 33 h cyclic wetting after 12 months of exposure, a relation between physically bound chlorides and Ca^{2+} concentration in free water (see Fig. 12b and d) is observed. The simulated results demonstrate that the release of absorbed Cl- ions from the pore surface due to the decomposition of the C–S–H phase upon carbonation, accompanied by a drop in the pH due to the leaching of ions, results in a decrease in the total chloride profile within the 1–3 mm region of the exposure surface (see Fig.s. 12b and 8). The peak in Cl content is formed by combining the absorbed chloride by the C–S–H phase and the chloride content in the precipitated phase, such as Friedel's salt, for all exposure conditions. The increase and movement of the peak region into the deeper region are thereby compatible with the precipitation of Friedel's salt (see Fig. 8). It should be further noted



Fig. 11. Comparison between predicted and measured total chloride profiles of OPC50 mortar samples exposed to 3% and 6% NaCl with 1hr, 9hr, and 33 h wetting for 1, 7, and 12 months, expressed at wt% by mass of binder (left: 3% NaCl, right: 6% NaCl).

that the peak behavior and gradual increase of the peak over time close to the exposed surface limit the penetration of Cl^- ions into deeper sections.

4.3.4. Elemental profiles in exposed mortar specimens

For the mortar samples exposure to 3% NaCl solution for 1hr and 6% NaCl solution for 33hr of cyclic wetting over the course of a year, the results of the numerical studies, which included total elemental content, the pore solution composition, absorbed elemental composition, and C–S–H surface sites, are presented in Fig. 12. The amount of content in Fig. 12 is presented in terms of moles per m³ volume of mortar. The most prominent variations can be observed in the chloride and potassium contents between the pore solution of the mortar and the NaCl exposure solution (see Fig. 3 and Table 3). The exposure solutions have about three orders of magnitude more chlorine than the pore solution, whereas the quantity of potassium is approximately two orders of magnitude lower. For mortars exposed to both 3% and 6% NaCl solutions, the elemental profile changes are mostly seen close to the exposure surface, whereas the penetration of Cl and K leaching can be predicted up to a depth of about 5 cm. However, Cl penetration and leaching of K varies with wetting conditions and time. Moreover, potassium leaching releases absorbed potassium from the pore surface, while the ingress of chloride increases chloride binding (see Fig. 12a).

Due to the absence of magnesium in the NaCl solution, it is expected that the leaching of magnesium will occur in samples exposed to a shorter wetting time (1hr). However, the leaching of magnesium is limited by lower concentration differences, as well as the presence of the hydrotalcite phase in a stable form (see Fig. 3), resulting in negligible magnesium leaching through the exposure surface. Thus, the magnesium content in the samples remains unchanged (see Fig. 12a), as indicated by numerical predictions.



Fig. 12. Profiles for OPC50 mortar specimens exposed to 6% NaCl and 1hr and 33hr cyclic wetting for 360 days (left: 3% NaCl for 1hr wet, right: 6% NaCl for 33hr wet): a) total elemental concentration, which is the summation of the element included in the free pore solution, the EDL, hydrates, and surface sites, b) free water composition, c) EDL composition, d) surface absorption, and e) surface sites on the C–S–H phase.

However, for longer wetting times (33hr), the pH value near the exposure surface starts to drop due to the leaching of ions, resulting in the complete dissolution of the hydrotalcite phase, which leads to a sudden increase in magnesium concentration in the pore solution with limited deeper leaching of magnesium (see Fig. 12b and c). Exposure to 6% NaCl solution for a shorter cyclic wetting (1hr) resulted in a slight apparent decrease in the sulfur content close to the exposure region due to the leaching of sulfur and the absence of sulfur in the NaCl solution. On the other hand, sulfur leaching increased for 33 h cyclic wetting due to the extended interaction between pore solution and exposure solutions, as well as the dissolution of the ettringite phase near the exposed surface. In addition, a sudden drop in bound sulfur content can be observed in the region close to the exposed surface due to the complete decomposition of the C–S–H phase (see Fig. 12e).

Sodium exhibits a particular behaviour; initially, for both shorter and longer cyclic wetting (1hr and 33hr), sodium ions start to

ingress into the mortar specimen due to differences in concentration, and subsequently, the transported sodium ions are absorbed by the surface site of C–S–H. During the C–S–H phase decomposition occurring close to the exposed surface with a longer exposure time, sodium ions release from the pore surface. Finally, a clear sodium enrichment is observed, forming a natrolite phase close to the exposed surface by the interaction of transported and released bound sodium and the decalcification of C–S–H. Furthermore, the decalcification of C–S–H phase causes more sodium to be bound in the substance because C–S–H with low Ca/Si can be able to absorb more alkali ions [76], which is clearly shown in predictions of the presented multi-species RTM (see Fig. 12). However, under more prolonged wetting conditions (33hr wetting), no physically bound sodium is observed near the exposed surface (within 0–0.5 mm depth) because the C–S–H phase is completely decomposed in that region (see Fig. 8). For both 1hr and 33hr cyclic wetting conditions, a reduction in total calcium is predicted near the exposure region, which is mainly associated with the leaching of Ca²⁺ ions. However, the binding of additional calcium by the C–S–H phase is observed over depth (see Fig. 12d) because the calcium released from the dissolution of monocarbonate and Portlandite is precipitated as the calcite phase and bound together with chloride ions in the C–S–H (\equiv SiOCaCl). For longer cyclic wetting conditions (33hr wetting), the dissolution of the C–S–H close to the exposed region increases while the pH value drops, resulting in a peak of calcium concentration in free water (see Fig. 8). In addition, a dramatic decrease in bound calcium near the exposed surface (0–0.5 mm) is predicted due to the complete decomposition of the C–S–H phase (see Fig. 12d).

5. Conclusions

To understand the underlying phenomena that drive concrete deterioration under cyclic environmental conditions in the marine environment, the reactive transport modelling framework presented in Ref. [22] was extended, including multi-ionic and moisture transport, coupled with a chemical equilibrium computation for determining a stable state among the pore solution and solid phase. To accurately replicate the chloride isotherm behaviour, a surface complexation model is employed in this study, which includes forming the electrical double layer and exchanging interactions among the ionic solution in pores and the C–S–H surface site (\equiv SiOH). A moisture transport model for porous media is introduced with capillary pressure as the primary parameter, considering two-phase moisture transport, i.e., vapour and liquid water. The conductivity terms for vapour and liquid water, based on the pore distribution and moisture storage in pores, are adapted throughout simulations to account for pore structure changes during dissolution and precipitation of solid phases upon exposure. For ion transport through pore solution in unsaturated conditions, a previously presented set of modified Poisson-Nernst-Planck (PNP) equations in Ref. [22] were extended, accounting for the effect of moisture fluctuation.

For analysing the deterioration of cement-based material under cyclic environmental conditions, the consideration of boundary conditions and moisture flux through the exposed surface is demonstrated for wetting and drying conditions, separately. Using the proposed RTM framework, numerical investigations were performed on mortar specimens subjected to different drying and wetting boundary conditions, and the predicted results were then compared to the experimentally measured values reported in Ref. [30]. By comparing predicted and measured moisture gain in two different types of porous materials under various drying and wetting conditions, a model was proposed to describe the activation energy (in the context of a time-lag model) that is crucial for understanding the liquid water flow through porous media under drying and wetting boundary conditions. For cyclic drying and wetting with different NaCl solutions, the presented model results included the changes in moisture storage, elemental composition, phase assemblage, pore water composition, absorbed ions on pore surface, and composition of C–S–H surface sites.

Numerical results for mortar samples exposed to 3% and 6% NaCl solutions under various cyclic wetting and drying conditions were in good agreement with experimentally measured moisture content changes and total chloride content. The numerical predictions indicate that moisture fluctuation inside pores and influence depth are more prominent during prolonged wetting conditions. As a consequence of the deeper influence depth and a more comprehensive range of moisture fluctuation, concrete deterioration increases with the duration of wetting. For all cyclic wetting conditions, the precipitation of Friedel's salt is observed, which subsequently limits the transport of chloride ions to deeper depths from the exposed surface. Meanwhile, the formation of Friedel's salt increases with wetting time duration due to prolonged interaction with the boundary solution. On the other hand, the dissolution of the solid phase close to the exposed surface increases with wetting time duration as a result of higher leaching of ions. Furthermore, considerable drops in the pore solution's pH value were observed for more prolonged wetting conditions. The ingress of chloride increases with the concentration of the exposure solution due to higher electrochemical and potential differences between the boundary solution and pore water. A peak in the chloride profile is observed near the exposed surface in all exposed mortar specimens. Meanwhile, the peak region continuously expands and moves deeper into the specimens with increasing wetting time duration and exposure times, consistent with Friedel's salt precipitation. On the other hand, the chloride content near the exposure surface shows a significant decrease due to the decomposition of the C–S–H phase by the leaching of ions and carbonation of the exposed surface.

CRediT authorship contribution statement

Suntharalingam Sharmilan: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Henrik Stang:** Validation, Resources, Supervision, Project administration, Funding acquisition. **Alexander Michel:** Validation, Resources, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Diffusion properties and boundary values

The characteristics of ions and ionic composition of boundary solutions are shown in Table B1.

 Table B.1

 Property of ions and ionic composition of boundary solutions for numerical example (see Section 3)

Id	$D^{\infty}_{i,T=298}*10^{-8}$	$A_{i,T=298} * 10^{-7}$	v_i	BC_3%NaCl	BC_6%NaCl
$Al(OH)^{2+}$	0.0829	0.3227	2	-	_
$Al(SO_4)^+$	0.1365	0.5313	1	_	_
$Al(SO_4)_2^-$	0.1125	0.4380	-1	_	_
Al ³⁺	0.0603	0.2348	3	_	_
AlHSiO ²⁺	0.0630	0.2452	2	_	_
AlO ⁺	0.1787	0.6953	1	_	_
AlO ₂	0.1659	0.6459	-1	_	_
AlO ₂ H	0.1626	_	_	_	_
AlSiO ₅ ⁻³	0.0371	0.1445	-3	_	-
CH4	0.1909	_	_	2.274E-02	2.274E-02
CO_2	0.1805	_	-	2.262E-02	2.261E-02
CO_{3}^{2-}	0.0788	0.3066	-2	9.541E-11	8.898E-11
$Ca(HCO_3)^+$	0.1258	0.4897	1	_	_
$Ca(HSiO_3)^+$	0.1201	0.4675	1	_	_
$Ca(OH)^+$	0.1428	0.5560	1	_	_
Ca ²⁺	0.0736	0.2863	2	_	_
CaCO ₂	0.1289	_	_	_	_
CaSiO ₃	0.1227	_	_	_	_
CaSO ₄	0.1212	_	_	_	_
Cl-	0.2067	0.8046	-1	5.137E-01	1.027E + 00
ClO_4^-	0.1494	0.5816	-1	_	-
Fc(OH) ²⁺	0.0774	0.3013	2	_	-
Fe(SO ₄)	0.1317	_	-	_	_
$Fe(SO_4)^+$	0.1317	0.5125	1	_	-
$Fe(SO_4)_2^-$	0.1084	0.4221	1	_	-
Fe ²⁺	0.0862	0.3353	2	_	-
Fe ³⁺	0.0549	0.2136	3	_	-
$Fe_2(OH)_2^{4+}$	0.0261	0.1016	4	_	-
$Fe_3(OH)_4^{5+}$	0.0157	0.0610	5	_	-
FeCO ₃	0.1427	_	_	_	_
FeCl ⁺	0.1561	0.6074	1	_	_
FeCl ²⁺	0.0742	0.2888	2	_	-
FeCl ⁺	0.1410	0.5486	1	_	_
FeCl ₃	0.1303	_	_	_	_
FeHCO ₃ ⁺	0.1370	0.5332	1	_	-
FeHSO₄	0.1274	0.4959	1	_	-
FeHSO ₄ ²⁺	0.0599	0.2331	2	_	_
FeHSiO ²⁺	0.0608	0.2368	2	_	_
FeO ⁺	0.1665	0.6480	1	_	_
FeO ₂	0.1554	0.6050	-1	_	_
FeO ₂ H	0.1530	-	_	_	_
FeOH ⁺	0.1624	0.6323	1	-	_
H^+	0.3050	1.1871	1	1.228E-04	1.288E-04
H_2	0.2720	-	-	9.816E-10	9.729E-10
H_2S	0.1885	-	-	-	-
HCO_3^-	0.1621	0.6309	-1	1.071E-04	1.009E-04
HS ⁻	0.1938	0.7545	-1	-	-
HSO_3^-	0.1530	0.5954	-1	-	-

(continued on next page)

Table B.1 (continued)

Id	$D^{\infty}_{i,T=298} * 10^{-8}$	$A_{i,T=298} * 10^{-7}$	vi	BC_3%NaCl	BC_6%NaCl
HSO ₄	0.1452	0.5651	-1	-	-
HSiO ₃	0.1484	0.5775	$^{-1}$	_	-
\mathbf{K}^+	0.1288	0.5012	1	_	-
КОН	0.1253	_	-	-	-
KSO ₄	0.1098	0.4273	-1	-	-
Mg(CO ₃)	0.1476	_	-	_	-
$Mg(HCO_3)^+$	0.1434	0.5580	1	-	-
$Mg(HSiO_3)^+$	0.1344	0.5231	1	_	-
$Mg(OH)^+$	0.1754	0.6826	1	-	-
Mg(SO ₄)	0.1353	_	-	_	-
Mg ²⁺	0.1008	0.3923	2	-	-
MgSiO ₃	0.1377	_	-	_	-
Na(SO ₄) ⁻	0.1208	0.4700	$^{-1}$	-	-
Na ⁺	0.1576	0.6135	1	5.137E-01	1.027E + 00
NaCO ₃	0.1284	0.4999	-1	3.932E-10	6.382E-10
NaHCO ₃	0.1272	_	-	1.559E-05	2.786E-05
NaOH	0.1451	_	-	6.916E-12	1.236E-11
O_2	0.2069	-	-	-	-
OH^-	0.2271	0.8837	-1	3.316E-11	2.803E-11
S ²⁻	0.0966	0.3759	$^{-2}$	-	-
$S_2O_3^{2-}$	0.0658	0.2560	-2	-	-
SO_{3}^{2-}	0.0739	0.2875	-2	-	-
SO_{4}^{2-}	0.0698	0.2716	-2	-	-
$Si_4O_{10}^{4-}$	0.0188	0.0732	-4	-	-
SiO ₂	0.1576	_	-	_	-
SiO ₃ ²⁻	0.0715	0.2782	-2	-	-

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Paper III

"A multi-species reactive transport model based on gas-ion-solid phase interaction for the carbonation of cement-based materials" Suntharalingam Sharmilan, Henrik Stang, and Alexander Michel

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A multi-species reactive transport model based on gas-ion-solid phase interaction for the carbonation of cement-based materials

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6

7 Abstract

8 This study presents a reactive transport modelling framework for understanding carbonation 9 processes through pore solution composition, phase assemblage changes in cement-based 10 materials, and pore solution composition changes on steel corrosion. The study emphasizes the 11 significance of considering pore structure changes on mass transport and utilizing a surface 12 complexation model for predicting changes in pore solution composition and comprehending its 13 influence on steel corrosion. A clear enrichment in sodium and potassium content in carbonated 14 regions is observed upon carbonation, which leads to a decrease in alkali concentration in the pore 15 solution, and alkali ions are transported toward the carbonated zone. Simultaneously, the opposite 16 behaviour is observed for both the sulphur and chloride content. The increase in the concentration 17 of sulphur and chloride in the pore solution was observed upon the decomposition of the solid 18 phase. Calcium ions are transported to the carbonated zone, further increasing calcite formation

19 near the exposed surface.

20 **Keywords** Multi-component gas transport, carbonation process, gas dissolution, reactive transport

21 model, chemical equilibrium.

22 **1. Introduction**

23 In many different civil engineering applications, reinforced concrete structures are widely used. A 24 high alkalinity pore solution with a pH value between 12.5 and 14 is formed when the solution in 25 the pores and solid phases of the typical Portland cement reach equilibrium [1]. The high pH value in the pore solution facilitates the formation of a passive layer, which acts as a barrier and 26 27 minimises the corrosion of steel reinforcement embedded in concrete [2,3]. The pH value starts to 28 drop with the rapid dissolution of gaseous CO₂ into the alkaline pore solution during carbonation 29 [4]. As a result of the change in the pore solution's alkaline environment, the passive layer becomes 30 unstable [5–7], which is one of the major issues with the long-term durability of concrete structures [8–10]. In marine environmental conditions, chloride ingress co-occurs with carbonation, and their 31 32 combined impact results in the severe corrosion of reinforced concrete structures [11–14]. Since 33 concrete carbonation is critical for ensuring a long and durable service life of concrete structures, 34 the study of the durability of concrete associated with carbonation has received much attention,

35 especially when concrete is made with low-clinker blends [1,4,15–17].

36 The carbonation of cement-based material is defined as a reactive transport process in which the 37 saturation level of pore solution in the pores reduces the diffusion of gaseous CO_2 through the non38 water-filled pore space. At the same time, the potential of carbon dioxide for dissolution and 39 reaction with ionic species in the pore solution is also subject to water availability in the pores 40 [16]. Once CO₂ enters cement-based materials at pH > 10, gaseous CO₂ starts to dissolve into the 41 pore solution, which after that transforms into the forms of bicarbonate (HCO3⁻) and carbonate ions (CO₃²⁻). At pH < 8, the CO₂ is directly hydrated as carbonic acid (H₂CO₃), which can then 42 43 further break into two components: HCO_3^{-1} and $CO_3^{2^{-1}}$. Since CO_2 dissolves into the pore solution 44 at pH 8–10, both mechanisms are possible [4,16]. In the pore solution, calcium ions that have been 45 re-solubilized from the solid products like Portlandite (Ca(OH)₂) react with carbonate ions to precipitate calcium carbonate [4,17–19]. Similarly, while the destabilisation of Ettringite occurs 46 47 due to carbonation, other substances like gypsum, calcite, and aluminium hydroxide start precipitating [4,16]. Moreover, carbonation leads to decalcifying calcium silicate hydrate (C-S-H) 48 49 [20]. The ability of the C-S-H phase to absorb alkali ions such as Na⁺ and K⁺ increases due to the 50 Ca/Si ratio decreasing during carbonation [4,21]. As a result of carbonation, the solid phases 51 undergo variations that also affect the pore structure and the chemical composition of the pore 52 solution. The amount of alkali ions in the pore solution decreases due to the sorption of alkali ions 53 by the decalcified C-S-H. Meanwhile, the free Cl content increases as a result of the decomposition 54 of the C-S-H phase, whereas the sulphate concentration increases upon the carbonation of 55 Ettringite [21].

56 As a result of the dissolution and/or precipitation of solid phases during carbonation, the porosity 57 and pore size distribution undergo significant changes, which has a considerable influence on mass transport [22–24]. Moreover, changes in the pore solution composition in cement-based materials 58 59 may be fundamental for understanding the carbonation process and the corrosion mechanism of embedded steel in concrete structures. Therefore, studying the pore solution composition changes 60 due to carbonation is particularly interesting for monitoring concrete structures. However, 61 relatively few studies and information are available on pore solution composition changes upon 62 63 carbonation [4,25]. Concrete is often carbonated in a dry environment, resulting in minimal free 64 water in pores and challenging pore solution extraction [4,25,26]. Furthermore, the deterioration 65 of concrete and understanding the governing mechanism for carbonation through accelerated experimental studies where samples are exposed to higher CO₂ concentrations may be vastly 66 different and thus difficult to interpret [27-30]. Therefore, numerical simulations can be a 67 compelling method to predict the deterioration of concrete structures and gain insight into the 68 69 underlying phenomena driving the carbonation processes through the pore solution composition and phase assemblage changes [8,16,31–34]. In addition, numerical tools that can predict changes 70 71 in cement-based materials throughout the service life can be used to select environmentally 72 suitable binder and mix designs, reduce infrastructure costs, and estimate the lifespan of buildings that are located in different environmental conditions, such as marine environments, urban 73 74 environments, etc.

- 75 Over the last few decades, several reactive transport models (RTMs) have been established to 76 predict concrete carbonation [8,31,32,35]. Among others, RTMs have been established that 77 combine gaseous, multi-ionic, and moisture transport models with a chemical equilibrium [31].
- 78 Simple diffusion or diffusion-advection equations are used for gaseous transport through the non-
- 79 water-filled pore space. For ion mass transport in porous media, the Poisson-Nernst-Planck (PNP)

80 equation is typically used, which is derived from a hybrid mixture theory [36,37], whereas 81 chemical equilibrium calculations are performed through specialized tools such as PHREEQC [38–40] or GEMS [41–43]. However, current modelling approaches are limited by considering 82 83 simplified assumptions about the processes involved in the carbonation of cement-based materials, for example, mass exchange mechanisms between gas phases and pore solution during the 84 transport calculation, diffusion of gases associated with their dissolution process with pore 85 solution, mass flux through boundary surfaces, and the integration effect of boundary condition. 86 Also, predictive competencies are inadequate due to the lack of fundamental relationships between 87 88 phase assemblage changes, pore structure changes, and mass transport through pores. Therefore, 89 a practical interpretation of the relations between phase assemblage, pore structure, and mass 90 transport is also needed to consider the impact of pore structure change on mass transport due to 91 carbonation. In addition, current RTM models without considering ion absorption on the pore 92 surface are insufficient to predict the actual changes in the phase assemblage and composition of 93 pore solutions due to the carbonation process and the effects of carbonation on ionic transport, for 94 example, to analyse chloride ingress together with carbonation in concrete exposed to marine 95 environmental conditions [44-46]. The dissolution of the C-S-H phase upon carbonation leads to 96 the release or absorption of ions and alters the charge on the pore surface and the pore solution 97 composition. As a result, ionic transport through the pore solution, as well as the rate of steel corrosion, will be affected by the pore solution composition. The lack of consideration of the 98 interaction between the pore solution and the surface sites of the C-S-H phase on the pore surface 99 100 in current models does not represent actual changes in pore solution composition upon 101 carbonation, especially regarding free chloride concentration.

102 This study aimed to develop a reactive transport modelling framework, including multi-component 103 gas, multi-ionic, moisture transport, and chemical equilibrium computation for understanding 104 carbonation processes through the pore solution composition and phase assemblage changes in 105 cement-based materials that are exposed to different boundary conditions and the effect of the 106 composition of pore solution change on steel corrosion. To achieve this goal, the reactive transport 107 modelling framework described in [47] is expanded to account for the carbonation of cementbased materials, including multi-component gas and ionic transport coupled with moisture 108 109 transport. To accurately replicate the variations in pore solution composition and the subsequent 110 impact of these changes on steel corrosion, a surface complexation model is employed in this study, which includes the formation of the electrical double layer and exchange interactions among 111 the ionic solution in pores and the C-S-H surface site (=SiOH). Therefore, chemical equilibrium 112 113 calculations include the equilibrium between the gas phases, aqueous species in the pore solution, 114 hydrated solid phases, and ionic absorption on the pore surface. For interconnecting phase assemblage changes and mass transport, models for moisture conductivity, gas, and ionic 115 116 diffusivity are based on the properties of pore structure and storage of liquid water in pores, taking into account the impact of the pore structure and moisture content changes on mass transport. 117 Finally, two numerical studies were conducted. In the first numerical study, numerically predicted 118 119 results were compared to experimentally measured values reported in [17] for understanding 120 carbonation processes through the pore solution composition and phase assemblage changes in 121 cement-based materials and the influence of pore solution composition changes on steel corrosion. 122 In order to demonstrate the applicability of the RTM to predict the carbonation of cement-based

- 123 materials prepared with a different water-to-cement ratio under various environmental conditions,
- the reported carbonation test results in [48] were compared to simulated results in a second numerical study.

126 **2. Modelling approach for carbonation of cement-based materials**

127 2.1 Outline of proposed RTM

128 The framework presented in [47] for an RTM in saturated cement-based material was extended to 129 allow for analyzing the carbonation of cement-based materials by adapting additional sub-models, 130 such as the multi-component gas and ionic transport models, which are fully coupled with moisture 131 transport, a model to include the gas phase in chemical equilibrium calculations, a hysteresis model 132 for determining the moisture storage in pores, a conductivity model for moisture, and a diffusivity 133 model for multi-component gas transport. The framework for an RTM for simulating the 134 carbonation of cement-based materials is outlined in Fig 1a. The RTM framework is addressed in 135 two distinct time domains: the initial stage involving cement-based materials during the curing 136 period and the subsequent deterioration processes upon carbonation. In Fig 1a, regions A and B 137 represent the modelling of early-stage material development and material deterioration, 138 respectively. Using the proposed RTM for simulating the carbonation of cement-based materials, 139 the following parameters can be predicted: the spatial and temporal changes in the concentration 140 and partial pressure of gaseous phase in pores, moles of dissolved gas, moisture content, vapour 141 and liquid pressure, internal relative humidity, ionic composition in free water and the electrical 142 double layer (EDL), and phase assemblage such as pure phases (EQ) and solid solution phases 143 (SS) for cement-based material under carbonation. The accessible pore space in pore structure for 144 ionic, moisture, and gaseous transport and a graphical description of mass transport due to 145 carbonation of cement-based material are demonstrated in Fig 1b and Fig 1c, respectively. The following sections provide explanations of the ion, moisture, and gas transport, considerations of 146 147 chemical equilibrium, and simulation studies conducted using the proposed RTM approach for 148 analyzing carbonation in mortar specimens.



149

Fig 1.a Framework of the proposed RTM for carbonation of cement-based materials. b. The accessible pore space in the pore structure for ionic, moisture, and gas transport. c. A graphical description of mass transport due to carbonation of cement-based material. CC: calcite, CH: Portlandite, AFt: Ettringite, AFm-CO3: monocarbonate, Gp: gypsum, CSH: calcium silicate hydrate, MSHss: magnesium silicate hydrate, and SI-gel: Silica-gel.

155 2.2 Governing system of equations for mass transport

156 2.2.1 General outline

157 Multi-ionic, moisture, and gas transport through a pore in unsaturated cement-based material are

158 constructed using a one-dimensional FEM technique. For any time and spatial discretization, the

ionic and gas concentration, vapour pressure, capillary pressure, relative humidity in the non-

160 water-filled pore space, and pore solution distribution in the pore structure are simulated according

- 161 to ionic, gas, and moisture transport models and applied boundary conditions. In this study, the
- 162 cement-based material is assumed to be a non-deformable and rigidly porous material with

163 constant porosity within the transport calculations. Therefore, the porosity changes are not 164 considered during the mass transport calculation. However, at the end of each time step of chemical 165 equilibrium calculation, the porosity changes corresponding to phase assemblage changes are

166 implicitly taken into account in the subsequent mass transport calculation. Furthermore, pore

- 167 solution and gaseous components such as vapour and $CO_2(g)$ are expected to occupy all pores in
- 168 the material under unsaturated conditions. As a result, the following relationships apply in this
- 169 situation: $V_s + V_p = 1$ and $V_p = \varphi(\varepsilon_l + \varepsilon_v)$ where V_s and V_p are the volume fractions of the solid
- and void parts in the material, respectively, φ is the total porosity, and ε_l and ε_v is the saturation
- 171 of the pore solution and void in the pore, respectively.

172 2.2.2 Moisture transport model

Modelling of moisture transport for an unsaturated cement-based material is developed considering two-phase moisture transport, i.e., pore water and vapour, through porous media. In the present modelling approach, the governing equation for moisture transport was derived according to the total moisture mass balance of vapour and pore water in gel and capillary pores [49]. The mass balance equation of moisture transport with capillary pressure as a primary variable is given as

$$\rho_l \varphi \left(\frac{\partial \varepsilon_l}{\partial P_c} \right) \frac{\partial P_c}{\partial t} = -\nabla \left\{ \left(K_{vap}(\theta_l) + K_l(\theta_l) \right) \nabla P_c \right\} + q_l$$
(1)

179 Where φ is the total porosity, ε_l the saturation of pore water, ρ_l the density of pore water [kg/m³], 180 $K_{vap}(\theta_l)$ and $K_l(\theta_l)$ represent the conductivity of vapour and pore water [kg/Pa·m·s], 181 respectively, P_c the capillary pressure, and q_l the term used to describe water loss by hydration and 182 differences in pore water distribution brought on by porosity changes. It is assumed that there are 183 no hydration and pore structure changes during the transport calculation, i.e., $q_l = 0$. The vapour 184 conductivity and liquid water conductivity proposed by Maekawa et al. [24] are adopted in the 185 present RTM.

186 2.2.3 A multi-species ionic transport model coupled with moisture fluctuations

187 Due to the formation of the EDL in cement-based material, the diffusion of ions will follow a 188 different path within the pore solution. Most anions and cations diffuse through free water space 189 and the EDL, respectively [47]. For ion transport through free water (uncharged water) and the 190 EDL (charged water) under unsaturated conditions, the previously presented set of modified 191 Poisson-Nernst-Planck (PNP) equations in [47] are further enhanced to account for the influence 192 of moisture fluctuation in the pores. Free water is typically present within the pore's middle region, 193 while the electric double layer (EDL) develops on the pore's surface. Due to the no-slip condition, 194 the velocity of liquid water near the pore surface can be neglected, and the thickness of the EDL 195 is small compared to the typical pore diameter (see Fig 1b). Hence, the water in the EDL is 196 considered non-moveable water in the present approach. Therefore, the effect of liquid water flow 197 through pores on ionic transport is considered only for ions in free water. Moreover, pores with a 198 diameter smaller than approximately 7 nm are completely covered by an EDL [50]. Due to the

199 formation of a fully covered EDL and the presence of high electrical potentials on the pore surface, 200 an assumption is made that pores with a radius below a certain threshold (r_{th}) are inaccessible for multi-ionic transport [51], even if the pores are saturated (see Fig 1b). In this study, the threshold 201 202 porosity (φ_{th}) and the surface area of pores below the threshold pore radius (A_{th}) are calculated based on the distribution of pores and an assumed threshold pore radius. Similarly, the portion of 203 204 a pore's surface (A_s) that is covered by the pore solution is computed based on the distribution of 205 pores and the pore radius (r_c) corresponding to the point at which an interface between the pore solution and vapour phase is formed (see Fig 1b). In free water, the governing equation for multi-206 207 ionic transport under the velocity condition is:

$$\varphi \varepsilon_{f}^{l} \frac{\partial C_{f}^{l_{j}}}{\partial t} + \varphi C_{f}^{l_{j}} \frac{\partial \varepsilon_{l}}{\partial t} = \nabla \left\{ D^{l_{j}} \left(1 + \frac{\partial \ln \gamma_{j}}{\partial \ln C_{j}^{l_{j}}} \right) (\varphi - \varphi_{th}) \varepsilon_{f}^{l} \nabla C_{f}^{l_{j}} + D^{l_{j}} (\varphi - \varphi_{th}) C_{f}^{l_{j}} \nabla \varepsilon_{l} + A^{l_{j}} \upsilon^{j} (\varphi - \varphi_{th}) \varepsilon_{f}^{l} C_{f}^{l_{j}} \nabla \Phi_{f}^{T} \right\} - \overline{\nu}^{l,s} (\varphi - \varphi_{th}) \varepsilon_{f}^{l} \nabla C_{f}^{l_{j}} - \overline{\nu}^{l,s} (\varphi - \varphi_{th}) C_{f}^{l_{j}} \nabla \varepsilon_{l}$$

$$(2)$$

; $j = 1, 2, 3 \dots, N$

208 Where $C_{f}^{l_{j}}$ and γ_{j} are the mole concentrations and activity coefficient of the j^{th} ion in free water, 209 ε_{f}^{l} the saturation of free water, $\overline{V}^{l,s}$ the velocity of water with regard to the rigid porous material, 210 v^{j} the valence of the j^{th} ion, and $D^{l_{j}}$ and $A^{l_{j}}$ are the diffusion coefficient and mobility of the j^{th} 211 ion, respectively. Similarly, the governing equation for ions transport in the EDL according to the 212 velocity condition is given by,

$$A_{s}t_{d}\frac{\partial C_{d}^{l_{j}}}{\partial t} = \nabla \left\{ D^{l_{j}} \left(1 + \frac{\partial \ln \gamma_{j}}{\partial \ln C_{d}^{l_{j}}} \right) (A_{s} - A_{th}) t_{d} \nabla C_{d}^{l_{j}} + A^{l_{j}} \nu^{j} (A_{s} - A_{th}) t_{d} C_{d}^{l_{j}} \nabla \Phi_{d}^{T} \right\}$$

$$(3)$$

; $j = 1, 2, 3 \dots, N$

Where $C_d^{l_j}$ is the concentration of the j^{th} ion in the EDL, A_s the portion of a pore's surface that is covered by the pore solution, and t_d the thickness of the EDL, which is computed based on the Debye length [47]. Gauss's law is used to calculate the intensity of electric potential in the EDL and free water (Φ_f^T and Φ_d^T) individually. The equation for free water's acquired electric potential is,

$$\nabla \left((\varphi - \varphi_{th}) \,\varepsilon_f^l \,\zeta_0 \,\zeta_r \nabla \Phi_f^T \right) = (\varphi - \varphi_{th}) \,\varepsilon_f^l F_C \sum_{j=1}^N v^j \,C_f^{lj} \tag{4}$$

218 The following equation can be used to represent the electric potential for the EDL.

$$\nabla \left((A_s - A_{th}) t_d \zeta_0 \zeta_r \nabla \Phi_d^T \right) = (A_s - A_{th}) t_d F_C \sum_{j=1}^N v^j C_d^{l_j}$$
(5)

219 Where ζ_0 and ζ_r are the relative and vacuum dielectricity coefficients, respectively, and F_c the 220 Faraday constant. In this study, the effective diffusion coefficient, $D_{i,T}^{eff}$ and effective ionic 221 mobility, $A_{i,T}^{eff}$, introduced in [47] are used, accounting for pore structure, pore solution properties, 222 and temperature changes.

$$D_{i,T}^{eff} = f_{\tau} \cdot f_{Tem} \cdot f_{I_s} \cdot D_{i,T_0}^{\infty} \cdot \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln C^{l_i}}\right)$$
(6)

$$A_{i,T}^{eff} = \frac{F_C}{RT} \cdot D_{i,T}^{eff}$$
(7)

223 Where D_{i,T_0}^{∞} is the diffusion coefficient at infinite dilution of the i^{th} ion at a reference temperature 224 $(T_0), f_{\tau}$ the tortuosity factor, and f_{Tem} and f_{I_s} correction factors for temperature and ionic strength, 225 respectively.

226 2.2.4 A multi-component gas transport model coupled with moisture transport

227 Due to concentration gradients as well as a total gas pressure gradient, gas components can be 228 transported through the non-water-filled pore space (see Fig 1b). Concentration gradients cause 229 molecular diffusion, Knudsen diffusion, and surface diffusion of gases, whereas the differences in 230 total pressure drive a bulk flow of the gaseous phase through unsaturated pores. In the present 231 study, surface diffusion (since its contribution to the overall transport is hard to assess precisely) 232 and total pressure gradient are neglected [52,53]. Moreover, due to the low density of the gaseous 233 phase and the stable atmospheric pressure at the boundary, the convection term is excluded from 234 the transport equation for the gas phase. This is because the relatively lower momentum of the gas phase is insufficient to generate sufficient force for driving convection flow through the non-water-235 filled pore space [31]. As a result, the mass balance equation for the components of the j^{th} gas in 236 237 the pore is given as follows:

$$\frac{\partial \left(\varphi \left(1-\varepsilon^{l}\right) \rho_{v}^{g_{j}}\right)}{\partial t} + \nabla \cdot \left\{ \nabla \left(D_{eff}^{g_{j}}(\theta_{l}) \varphi \left(1-\varepsilon^{l}\right) \rho_{v}^{g_{j}}\right) \right\} - q_{g-l}^{g_{j}} = 0$$
(8)

; $j = 1, 2, 3 \dots, M$

Where $\rho_v^{g_j}$ is the density of the j^{th} gas phase, which can be written as $\rho_v^{g_j} = M_v^{g_j}/V_v$, where $M_v^{g_j}$ 238 and V_v are the mass and volume of j^{th} gas phase in the non-water-filled pore space, respectively, 239 and $D_{eff}^{g_j}(\theta_l)$ the effective diffusion of the j^{th} gas constituent through the non-water-filled pore 240 space. The first term on the left-hand side of Eq. (8) defines the gas capacity in a representative 241 242 volume (REV), the gas content in the non-water-filled pore space. Gas flux by a diffusion process 243 is described by the first term in Eq. (8) on the right. The gas mass exchange between the gas and pore solution is indicated by the parameter $q_{a-l}^{g_j}$. It is assumed that no reaction takes place between 244 245 the dissolved gaseous phase and hydrated phases during mass transport calculations. However, gas 246 dissolution into the pore solution co-occurs with the gaseous transport through the non-water-filled 247 pore space. Therefore, the mass transfer term between the gas phase in the non-water-filled pore space and the dissolved gas phase in the pore solution, $q_{g-l}^{g_j}$ in gas transport Eq. (8) cannot be 248 neglected during transport calculation. In this study, the gas mass exchange term, $q_{g-l}^{g_j}$ is defined 249 250 as the dissolution mass of gases in the pore solution as,

$$q_{g-l}^{g_j} = \frac{\partial \left(k_t \, A_{g-l} \, \varphi \, \varepsilon^l \, \rho_{ag}^{g_j}\right)}{\partial t} \tag{9}$$

Where k_t and A_{g-l} are the interfacial gas transfer coefficient of the j^{th} gas constituent between 251 the gas phase and pore solution and the contact surface area between the gas phase and pore 252 solution, and $\rho_{ag}^{g_j}$ the density of the dissolved j^{th} gas phase in the pore solution. As the water 253 254 saturation in the pores increases, the diffusion of gaseous CO₂ through the non-water-filled pore space and the contact area available to dissolve gaseous CO₂ into the pore solution decreases. To 255 account for these mechanisms, the parameters such as $D_{eff}^{g_j}$ and A_{g-l} are adapted to limit the 256 257 diffusion and dissolution of gaseous CO₂, respectively, in this gas transport model. Henry's law [54], which describes the relation between gas solubility in the pore solution and partial pressure 258 259 of the gas phase, is used to illustrate the equilibrium between the gaseous and dissolved gas phases.

$$C_{ag}^{g_j} = \frac{K_H \,\varphi_g \, P_v^{g_j}}{\gamma_g} \tag{10}$$

260 Where $C_{ag}^{g_j}$ is the molality of the j^{th} gas constituent, K_H Henry's law constant, φ_g the fugacity 261 coefficient, γ_g the activity coefficient of the j^{th} gas phase in pore solution, and $P_v^{g_j}$ the partial 262 pressure of the j^{th} gas phase in the non-water-filled pore space. The ideal gas law of the j^{th} gas 263 phase in terms of the mass density of the j^{th} gas phase in the non-water-filled pore space is,

$$P_{v}^{g_{j}} = \frac{\rho_{v}^{g_{j}} R T}{M_{g_{j}}}$$

$$\tag{11}$$

264 Where M_{g_j} is the mole mass of the j^{th} gas phase and R the gas constant [J/mol·K]. By using 265 Henry's law Eq. (10) and the ideal gas law Eq. (11), the gas mass exchange term Eq. (9) can be 266 written in terms of the density of the j^{th} gas phase in the non-water-filled pore space as,

$$q_{g-l}^{g_j} = \frac{\partial \left(k_t \, A_{g-l} \, \varphi \, \varepsilon^l \, H_K \, \rho_v^{g_j}\right)}{\partial t} \tag{12}$$

Where

$$H_K = \left(\frac{K_H \ \varphi_g \ R \ T}{\gamma_g}\right)$$

267 The mass concentration $\rho_v^{g_j}$ and the mole concentrations $C_v^{g_j}$ are related through $\rho_v^{g_j} = M_{g_j} C_v^{g_j}$. 268 Combining Eqs. (8) and (12) yield the multi-gas transport in the non-water-filled pore space 269 represented in mole quantities as,

270

$$\varphi (1 - \varepsilon^{l}) \frac{\partial C_{v}^{g_{j}}}{\partial t} - \varphi C_{v}^{g_{j}} \frac{\partial \varepsilon^{l}}{\partial t}$$

$$= \nabla \left\{ D_{eff}^{g_{j}}(\theta_{l}) \varphi (1 - \varepsilon^{l}) \nabla C_{v}^{g_{j}} - D_{eff}^{g_{j}}(\theta_{l}) \varphi C_{v}^{g_{j}} \nabla \varepsilon^{l} \right\}$$

$$- k_{t} A_{g-l} \varphi \varepsilon^{l} H_{K} \frac{\partial C_{v}^{g_{j}}}{\partial t} - k_{t} A_{g-l} \varphi C_{v}^{g_{j}} H_{K} \frac{\partial \varepsilon^{l}}{\partial t}$$

$$; j = 1, 2, 3 ..., M$$
(13)

271 2.2.4.1 **Diffusion coefficient of gas**

In the case of gas transport through a narrow pore, gas molecules will frequently collide with the pore walls. Thus, Knudsen diffusion theory is applied to account for the colloidal effect of gas in the non-water-filled pore space. The effective diffusion of the j^{th} gas constituent through the nonwater-filled pore space, $D_{eff}^{g_j}(\theta_l)$ for an arbitrary temperature, *T*, is formulated as follows, accounting for the dependence of gas diffusivity on pore-structure saturation (see Fig 1a) [24,55].

$$D_{eff}^{g_j}(\theta_l) = \frac{f_\tau^g \cdot D_a^{g_j}(T, P_g)}{\Omega \varphi (1 - \varepsilon^l)} \int_{r_c}^{\infty} \frac{1}{1 + N_k} dV_v$$
(14)

Where

$$N_k = \frac{\lambda_{j,a}}{2r}$$

277 Where $D_a^{g_j}(T)$ is the gas diffusivity in free air space at temperature T [m²/s], f_{τ} the tortuosity 278 factor, Ω the three-dimensional tortuosity of a pore (= ($\pi/2$)²), N_k the Knudsen number, l_m the 279 mean free path of gas molecules [m], r_c the pore radius [m] at the liquid and vapour contact, and 280 V_v the volume of vacant micro-pore space for gas transport [m³]. For the binary mixture of the *j*th

gas constituent and air, the following formula is used to compute the mean free path of j^{th} gas constituent in the air $(\lambda_{i,a})$ at temperature T [56].

$$\lambda_{j,a} = \frac{k_B T}{\pi \left(\left(\sigma_j + \sigma_a \right) / 2 \right)^2 P_T} \frac{1}{\sqrt{1 + \left(M_j / M_a \right)}}$$
(15)

Where k_B is the Boltzmann constant, P_T the total pressure, σ_j and σ_a the collision diameters for the j^{th} gas constituent and air, respectively, and M_j and M_a the molecular weights of the j^{th} gas constituent and air, respectively. By considering phase assemblage changes, the chemical equilibrium calculation determines the variations in porosity, which are subsequently employed to compute the tortuosity [57].

$$f_{\tau}^{g} = f_{\tau,0}^{g} \left[exp\left(log\left(\frac{1}{f_{\tau,0}^{g}}\right) \left(1 - \left(\frac{1}{P_{t}}\right)^{c}\right) \right) \right]$$
(16)

288 Where f_{τ}^{g} represents the tortuosity factor at time step t, $f_{\tau,0}^{g}$ the initial tortuosity factor, c a shape

factor, and the ratio of the total porosity at time step t, φ_t , and the starting porosity, φ_0 is defined as the penalty factor, P_t . The diffusion coefficient of the j^{th} gas constituent, $D_a^{g_j}(T)$ is evaluated

through the kinetic gas theory applying the Wilke and Lee method [58],

$$D_a^{g_j}(T) = \frac{\left[3.03 - \left(0.98/M_{j,a}^{1/2}\right)\right] \cdot T^{3/2}}{P_T M_{j,a}^{1/2} \sigma_{j,a}^2 \Omega_D} \cdot 10^{-7}$$
(17)

Where

$$M_{j,a} = 2[(1/M_j) + (1/M_a)]^{-1}$$

Where
$$M_j$$
 and M_a are molecular weights of j^{th} gas constituent and air, respectively [g/mol], P_T

the pressure [bar], $\sigma_{j,a}$ the characteristic length of the intermolecular force law [A°], and Ω_D the diffusion collision integral.

295 2.2.5 Finite element formulation

296 The finite element method (FEM) was used to solve the governing equations for ion, gaseous, and 297 moisture transport under unsaturated environments. Using a weight function w for the spatial 298 domain and a weight function W for the time domain, the governing equations Eqs. (1)-(5), and 299 (13) are separated into a spatial domain and a time domain for the finite element formulation. 300 Utilizing Galerkin's approximation, the one-dimensional spatial scheme with linear spatial 301 components was discretized [59,60]. The Green-Gauss theorem was applied to separate the 302 boundary flow conditions in the mass transport. Every step implicitly solves the problem in the 303 time domain. To prevent the staggering schemes between individual solutions of state variables, 304 the entire connected set of equations was solved at once. A modified Newton-Raphson iteration 305 strategy was adapted to enhance the FEM solution of the system equations while also speeding up 306 computation [61,62].

307 2.3 Chemical equilibrium model

308 The geochemical PhreeqcRM algorithm was employed in the chemical equilibrium computation, 309 enabling efficient parallel processing while ensuring compatibility between the transport and chemical modules. This algorithm was used to solve the mass exchange terms. q_l , $q_f^{l_j}$, $q_d^{l_j}$ and $q_{q-l}^{g_j}$ 310 from the governing equations (1)-(3) and (13), accounting for the chemical interactions between 311 312 gas, ions, and hydrated phases [38-40,63]. In the geochemical solver, the chemical equilibrium 313 calculation for interactions between gas phases, aqueous species in pore solution, and hydrated 314 solid phases, including surface absorption, is performed using the mass action laws derived from 315 thermodynamics [47]. Here, the heterogeneous mass-action equations in terms of partial pressure 316 and an equation for total pressure describe the equilibrium between the multi-component gas and aqueous phases [39]. Furthermore, all gas components in the gas phase are expected to be 317 318 substances of ideal gas behaviour. 319 3. Numerical examples

320 Two numerical studies were conducted. The first numerical study investigated carbonation 321 processes through the pore solution composition and phase assemblage changes in cement-based 322 materials using experimental results for white Portland cement (wPc) under specific environmental 323 conditions reported in [17] and the influence of the pore solution composition changes on steel 324 corrosion. Results of the experimental study comprise the content of Portlandite and carbonate 325 phases over time for specimens exposed to a controlled CO₂(g) environmental condition and the 326 carbonation depths as measured by phenolphthalein. In order to show the applicability of RTM to 327 predict the carbonation of cement-based materials prepared with a different water-to-cement ratio 328 under various environmental conditions, a second numerical study was conducted. The second 329 numerical simulation used the reported carbonation test results for mortar specimens under various 330 temperature and humidity conditions [47]. In the experimental studies [48], carbonation tests were 331 conducted using a constant temperature and relative humidity test tank with a carbon dioxide gas 332 concentration of 10% to determine the effect of relative humidity and temperature on the 333 carbonation of mortar specimens. Materials and measurements used in these two investigations are briefly summarized here, while [17] and [48] provide more details on preparing the mortar specimens, environmental conditions, and testing methods for numerical examples 1 and 2, respectively.

337 3.1 Materials

338 In the experimental study [17] used for the first numerical simulation, mortar samples were 339 prepared in 40×40×160 mm³ moulds using white Portland cement (wPc, CEMI 52.5N). A water-340 to-cement mass ratio of 0.50 and a binder-to-sand mass ratio of 1:3 were used to prepare the wPc 341 mortars. The mortar samples underwent a 24-hour curing process in a humid cabinet that was kept 342 at a humidity level of 90% and a temperature of 20±1 °C. The mortar specimens were demolded 343 and then cured in demineralized water for 91 days at 20 °C. Table 1 provides the mix design for 344 the wPC mortar. White Portland cement (wPc), categorized in CEMI 52.5N, with a chemical 345 composition determined in c, is shown in Table 2 for numerical example 1.

346 Furthermore, in the experimental study presented in [48] and adapted for the second numerical 347 simulation, experiments were conducted, selecting different temperature and humidity levels as 348 external environmental conditions and water-cement ratios as factors for internal material 349 conditions. The mortar specimens were prepared using Portland cement (PC) with various watercement ratios, namely w/c-55% (PC55), w/c-60% (PC60), w/c-65% (PC65), and w/c-70% (PC70), 350 351 in 40×40×160 mm³ moulds for carbonation tests. The mortar specimens were demolded after 24 352 hours of air curing. After demolding, standard curing was performed for 28 days at 20°C 353 temperature. Before exposure to carbonation, aerial curing was performed for about ten days in a 354 constant temperature and humidity room with a relative humidity of 50% until mass equilibrium 355 was nearly accomplished. Table 1 provides information about the PC mortar's mix design. For 356 numerical example 2, the chemical composition of Portland cement (PC) classified in CEMI 52.5N 357 was obtained from [64] and given in Table 2.

358 Table 1. Mix design of mortars, after [17] and [48].

Mix Composition	Example 1		Exar	nple 2	
Mass [kg/m ³]	wPc50	PC55	PC60	PC65	PC70
Cement	511.1	504.1	459.9	424.9	403.7
Water	255.5	277.3	275.9	276.2	282.6
Sand	1533.2	1441.8	1481.0	1508.6	1509.7

Table 2. Chemical composition [wt%] and physical characteristics of (white) Portland cement (wPc), after [17] and [64].

Details	Example 1	Example 2	
Details	wPc	PC	
Chemical composition analysis [wt%]			
SiO ₂	21.81	20.23	
Al ₂ O ₃	3.56	5.39	
Fe ₂ O ₃	0.24	3.04	
CaO	66.13	64.64	
MgO	1.10	0.92	
K ₂ O	0.43	0.31	
Na ₂ O	0.04	0.30	
SO ₃	3.37	1.91	
CO ₂ (g)	0.37	1.65	

CaCO ₃	3.10	3.75
Gypsum	4.10	2.44
Free lime	1.91	-
Cl	0.03	0.025
LOI 950C	2.40	2.40
Density [kg/m ³]	3080	3160
Blaine fineness [m ² /kg]	387	330

361 3.2 Exposure conditions

362 In the experimental study presented in [17], which is used as the basis for the first numerical 363 simulation, wPc mortar specimens were kept in a controlled environment with 1% CO₂(g) 364 concentration (v/v) for 280 days at $57 \pm 1\%$ relative humidity and 20 °C. After exposure to CO₂ 365 for 0, 7, 14, 21, 28, 56, 91, and 280 days, carbonation depths were measured using phenolphthalein. In addition, thermo-gravimetric analysis (TGA) was used to assess Portlandite and carbonate 366 367 content relative to 100g mass of ignited mortar samples at 800 °C in the carbonated and non-368 carbonated areas of exposed mortars after 28 and 91 days. In the experimental study conducted in [48] and used for the second numerical simulation, the carbonation test for mortar specimens was 369 370 carried out by using a constant temperature and humidity test tank with a carbon dioxide gas 371 concentration of 10% and promoting tests under four different temperatures, i.e., 15.0 °C, 22.5 °C, 372 30.0 °C, and 37.5 °C, and four different relative humidity, i.e., 35% RH, 50% RH, 65% RH, and 373 80% RH. After 1, 3, 7, 14, 28, 42, and 56 days of exposure, carbonation depths were measured by 374 spraying a 1% phenolphthalein solution on a split section of mortar specimens.

375 3.3 Input parameters and databases for numerical studies

376 In the two numerical studies, specimen size and boundary conditions are simulated according to 377 the experiments' descriptions. In both experiments, one side of the mortar specimens was exposed 378 to carbonation, and the other surfaces were sealed with epoxy resin. Upon carbonation, moisture 379 loss or gain in the mortar specimens occurs through the exposed surface. However, due to the lack 380 of pore solution continuity with the exposure environment, ionic ingress or leaching through the 381 exposed surface does not occur in the exposed mortar specimens. Therefore, the mass transport 382 calculations consider gaseous ingress and moisture flux (in the form of vapour phase) through the 383 exposed surface.

384 The hydration of the binder was computed from the degree of hydration of each clinker in the 385 cement. For numerical examples 1 and 2, the main clinker contents, such as alite, belite, aluminates, and ferrites, were measured using MAS NMR Spectroscopy [17] and XRD-Rietveld 386 387 [64], respectively. The proposed approach of Taylor [65] and chemical analyses are used to 388 determine minor contents, which include soluble alkali sulfates (K₂SO₄ and Na₂SO₄), non-389 dissolved alkali oxides (K₂O and Na₂O), magnesium oxide (MgO), and gypsum. The calculated 390 clinker content in wPC and PC cement, which are used in example 1 and example 2, respectively, 391 is shown in Table 3.

 ³⁹² Table 3. Clinker composition of the white Portland cement (wPc) and Portland cement (Pc) [wt%]

 Phase composition [wt%]
 Present as a solid solution in the clinker phases [wt%]

-			-	
	wPc (Example 1)	Pc (Example 2)	wPc (Example 1)	Pc (Example 2)

Alite ^a (C ₃ S)	65.6	58.60	CaO ^e	1.97	0.00
Belite ^a (C_2S)	14.9	17.20	MgO ^c	1.13	0.77
Aluminate ^a (C ₃ A)	9.30	6.97	K ₂ O ^d	0.04	0.10
Ferrite ^a (C ₄ AF)	0.75	9.90	Na ₂ O ^d	0.02	0.20
Calcite ^b	3.15	3.75	SO ₃ ^f	0.99	1.19
Bassanite ^a	0.00	2.01			
Gypsum ^c	4.54	0.43			
K ₂ SO ₄ ^d	0.74	1.66			
$Na_2SO_4^{d}$	0.04	0.69			

a - Determined by MAS NMR [17] and XRD [64].

b - Calculated from the CO₂ content Table 2.

c - Calculated from the chemical analysis.

d - Calculated from total (Table 2) and soluble alkali content [65].

e - Calculated from the Free CaO content Table 2 f - Calculated from the distribution of sulfate [65].

393 In the numerical studies, the multi-ionic transport contained 74 ions in total and the $CO_2(g)$ gas 394 phase in the gas transport, whereas two-phase moisture, i.e., liquid and vapour, were adapted in 395 moisture transport calculation. The reactions among gas, ions, and hydrated phases present in the 396 cement-based material and their thermodynamic properties were defined using the CEMDATA18 397 database [66] (http://www.empa.ch/cemdata) in the chemical equilibrium model. In addition, the 398 thermodynamic data for zeolite phases that contain K and Na such as phillipsite(K), 399 phillipsite(Na), clinoptilolite(K), clinoptilolite(Na), chabazite(K), chabazite(Na), mordenite(K), 400 mordenite(Na) and natrolite [67-69] were adapted for the database. The CSHQss model [70,71] 401 for the major hydrated component (C-S-H) in cement-based material was incorporated for the 402 numerical studies. At the same time, KSiOH and NaSiOH are also included as endmembers for 403 the C-S-H phase to enhance simulation results of the pore solution composition as well as pH value 404 [66]. The thermodynamic database also included calcite (CC), Ettringite (AFt_{ss}), monocarbonate (CO3-AFm), Portlandite (CH), hemicarbonate (HC), hydrotalcite (Ht), and hydrogarnet (HGss). 405 406 To model the carbonation of mortar specimens, other phases were included in the database, 407 including zeolite phases, gypsum (Gp), aluminium hydroxide (Al(OH)_{mic}), silica-gel (Silica_{am}), 408 brucite, Friedel salt, Kuzel salt, ferrihydrite-mc (FeOOH), magnesite (Mgs) and magnesium 409 silicate hydrate (MSH_{ss}). Table A. 1 summarises the reaction processes and their equilibrium constants employed in the numerical analysis. The introduced surface complexation model in [47], 410 411 including the absorption reaction of the surface site (=SiOH) of the C-S-H phase with ions in the 412 pore solution and their equilibrium constants, was adapted in the numerical simulations. Table 4 413 provides information on the spatial and temporal discretization and the tortuosity factor for ions and gas movement, gas transfer coefficient, and other parameters for the numerical simulations. 414 415 For considering accuracy and computational cost in numerical examples 1 and 2, the 15 mm and 30 mm 1D domains of mortar specimens are discretized using 50 and 60 elements with a growth 416 factor method to create a finer mesh near the surface of the exposed boundary, respectively. 417 418 Sensitivity analyses for the carbonation of mortar were used to define the time step accounting for 419 the duration of exposure, computational time, accumulation of charge imbalance of ions in the 420 pore solution, and the truncation error in the exposed surface node [72].

421	Table 4. Model	parameters for the	numerical
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Table 4. Model parameters for the numerical investigations.						
Model parameters	Example 1		Example 2			
Model parameters	wPc50	PC55	PC60	PC65	PC70	
No of spatial elements	50	60	60	60	60	
Growth factor of spatial elements	2	2	2	2	2	
Total spatial distance, (mm)	15	30	30	30	30	

Total exposure time, (days)	360	42	42	42	42
Time step, Δt (hr)	6	6	6	6	6
Threshold pore radius, r _{th} (nm)	2	2	2	2	2
Initial tortuosity factor, $f_{\tau,0}$	0.05	0.06	0.075	0.08	0.085
Initial gas tortuosity factor, $f_{\tau,0}^{g}$	0.05	0.06	0.075	0.08	0.085
Shape parameter, <i>c</i>	1	1	1	1	1
Interfacial gas transfer coefficient, $k_{(t=293.15)}$	100	300	300	300	300

422 4. Results and discussion

423 4.1 Numerical example 1

424 The simulation results for wPc mortar specimens after 91 days of sealed curing at 20°C are 425 presented in Fig 2. According to the model proposed by Parrot and Killo [73] for clinker hydration, 426 the results of the hydration model show that over 95% of the alite and aluminate clinker is hydrated, 427 while belite exhibits a slower reaction in wPc mortar specimens (see Fig 2a). As shown in Fig 2b, 428 the simulated phase assemblage consists of C-S-H, Portlandite, Ettringite, monocarbonate, 429 hemicarbonate, hydrogarnet, hydrotalcite, and unreacted cement. Moreover, the numerical 430 prediction indicates that around 12% of the volume of mortar specimens is pore space after 91 431 days of sealed curing, whereas nearly 31% of the whole mortar volume comprises both hydrated 432 and unreacted cement. Fig 2c highlights the numerically determined composition of the pore 433 solution of the wPc mortar specimen. Since the faster rate of alkali sulphate dissolution compared 434 to the dissolution of the main clinkers, the composition of the pore solution in wPc mortar is 435 dominated by alkali ions, such as Na⁺ and K⁺. Due to the solubility of major hydrated phases such as Portlandite and C-S-H, the concentration of calcium (Ca) in the pore solution is comparatively 436 437 higher than that of other elements. Meanwhile, the precipitation of hydrotalcite and hydrogarnet 438 phases decreases the concentrations of iron (Fe) and magnesium (Mg), respectively. According to 439 the simulated results, the pH of the pore solution in the wPc mortar is approximately 13.03, which 440 is in the reported range of pH values in [1]. Fig 2d illustrates the predicted cumulative pore volume 441 and pore size distribution of wPc cement mortars after 91 days of curing at 20 °C. Numerical 442 results indicate that nearly one-third (1/3) and two-thirds (2/3) of the total pore volumes, excluding 443 interlayer porosity, are occupied by gel and capillary pores, respectively, whereas two threshold 444 pore radii were observed in pore distribution. According to the distribution of the pores for non-445 exposed wPc mortar specimens, the peak appears to be in the range of 0.1 to 1 µm. The threshold 446 and peak pore radius considerably affect the ionic, gas, and moisture transport in the RTM model.

447



449

Fig 2. Numerical results for wPc mortar specimens after 91 days of sealed curing at 20 °C. (a)
hydration of clinkers and average hydration of cement over 91 days of the curing period, (b) phase
assemblage, (c) composition of the pore solution, and (d) pore size distribution.

452 assemblage, (c) composition of the pole solution, and (d) pole size

453 4.1.1 Moisture isotherm and transport parameters

454 The predicted pore distribution of wPc mortar at a depth of 0.1 mm from the exposed surface is 455 compared in Fig 3a before and after 360 days of exposure to 1% CO₂(g) at 20 °C and 57% RH. 456 The mass transport parameters, such as the moisture conductivity and the diffusion coefficient of 457 the gas phase, primarily governing the carbonation rate of cement-based materials are directly 458 impacted by the pore structure changes. The numerical simulation of carbonation in wPc mortar 459 shows an increase in porosity near the exposed surface (in the fully carbonated zone), followed by 460 a decrease within the continuous carbonation region (see Fig 5). The simulated porosity changes demonstrate a comparable trend to that observed in other published experimental findings, e.g., 461 462 [74-77]. Additionally, numerically predicted results showing the cumulative pore volume indicate that the effect is more pronounced in completely carbonated wPc mortar, where the carbonation 463 of hydrated phases increases the capillary pore space near the exposed surface. During the 464 465 carbonation process, a continuous decrease is observed in the interlayer and gel pores, which can be attributed to the decalcification of the C-S-H phase and its subsequent transformation into silica 466

467 gel. The distribution of pore sizes is also predicted to move towards larger pore diameters. As a 468 result, the peak radius in the pore distribution increases five times compared to non-exposed wPc 469 mortar. The computed moisture isotherms based on the pore structure development of wPc mortar 470 before and after CO₂(g) gas exposure are presented in Fig 3b. As illustrated, the computed moisture isotherms show significant differences for wPc mortar before and after carbonation. Moreover, it 471 472 is shown that the water saturation level for carbonated mortar is lower than for non-carbonated 473 mortar at particular relative humidities. The simulation results illustrate that $CO_2(g)$ exposure 474 significantly affects moisture conductivity and gas diffusivity parameters of wPc mortar, as shown 475 in Fig 3c and Fig 3d, respectively. The results indicate that the carbonation of wPc mortar close to 476 the exposed surface has increased mass transport parameters over the entire moisture range. 477 Moreover, the carbonation of wPc mortar shows considerable effects on CO₂(g) diffusivity at 478 lower saturation levels and significant increases in moisture conductivity at higher saturation 479 levels. A similar trend in the simulated transport parameters, including moisture conductivity and 480 gas diffusivity, was observed in the experimental findings as reported, e.g., in [78–80].



Fig 3. Numerical results for wPc mortar samples at a depth of 0.1 mm from the exposed surface in absorption and desorption after 91 days of sealed curing at 20 °C and exposed to 1% CO₂(g) at 20 °C and 57% RH for 360 days. (a) pore size distribution, (b) moisture isotherms, (c) CO₂(g) gas diffusion, and (d) moisture conductivity.

486 4.1.2 Carbonation depth profiles

487 This study used experimentally measured carbonation depths in exposed wPc mortar specimens 488 [17], using phenolphthalein pH-indicator as presented in Fig 4a, to adjust the initial tortuosity 489 factor. A more significant deviation between simulated and measured values is found after 91 days 490 of exposure. However, numerically simulated results are well within the error margin of the 491 phenolphthalein measurement. Furthermore, numerically simulated results indicate a continuous 492 reduction of carbonation rate over time, governed by the development of the $CO_2(g)$ partial 493 pressure in the pores with depth from the exposed surface. The simulated partial pressure of $CO_2(g)$ gas inside the pores after 28, 91, and 360 days of exposure is shown in Fig 4b. Upon carbonation 494 495 of the wPc mortar specimen, the partial pressure of $CO_2(g)$ in the pores gradually increases due to 496 its dissolution into the pore solution. Subsequently, the developed partial pressure in the pores 497 helps transport CO₂ gas to greater depths from the exposed surface. The region of developed partial 498 pressure in the pores is compatible with the carbonation depth and pH value drops, indicating a 499 fully carbonated zone in cement-based material.



500

Fig 4. Numerical results for wPc mortar samples during carbonation (a) simulated carbonation depth compared with measured carbonation depth [17], and (b) partial pressure of CO₂(g) in pores.

503 4.1.3 Solid phase composition of carbonated mortar

504 The phase changes in wPc mortar caused by carbonation were determined using the proposed 505 modelling approach. Fig 5 shows the results of the numerical studies, including phase assemblage, 506 pH value, and total porosity for wPc mortar specimens exposed to 1% CO₂(g) at 20 °C and 57% 507 RH for 28, 91, and 360 days. The phase assemblage in the non-carbonated portion is shown on the 508 right side of the figures, while the impact of carbonation on the exposed mortar specimen is 509 presented on the left. The carbonation depth in Fig 5 is represented by dotted lines, based on the 510 pH value dropping below 9.7 in the pore solution. The carbonation and dissolution fronts gradually 511 move with exposure time toward the inside of the material. In Fig 5, the numerically predicted results show the experimentally identified zones and their progressive behaviour [9]. In the 512 513 carbonated zone, calcite, silica-gel, gypsum, aluminium hydroxide, ferrihydrite-mc, magnesite, magnesium silicate hydrate, and zeolite phases such as clinoptilolite(K) and mordenite(Na) mainly 514

515 precipitate, while the decomposition of existing hydrated phases such as Portlandite, Ettringite, 516 monocarbonate, hemicarbonate, C-S-H_{ss}, hydrogarnet, and hydrotalcite is observed. The numerical 517 simulation shows that alkali binds with the decalcification of the C-S-H phase, leading to the 518 formation of zeolite phases such as clinoptilolite(K) and mordenite(Na) during the carbonation 519 process, which is consistent with the experimentally reported findings [4,81]. The thin layer in 520 front of the carbonated zone is known as the carbonation front. The pH value of the pore solution 521 subsequently decreases from approximately 13.03 to 7.83. Moreover, the simulated range of pH 522 value drop in the pore solution upon carbonation is consistent with reported results in [4,82]. In addition, the porosity in the carbonation front decreases mainly due to the formation of Ettringite, 523 524 which has a comparably higher molar volume. The dissolution front contrasts with the carbonation front, in which the decalcification of Portlandite and calcite precipitation is predicted, showing a 525 gradual decrease in porosity. 526



Fig 5. Numerical predictions of phase assemblage, carbonation depth, and pH value for wPc mortar
specimens during carbonation for 28, 91, and 360 days. CZ: carbonated zone, CF: carbonation
front, DF: dissolution front, and NC: non-carbonated zone.

531 Fig 6a and b compare the predicted and measured contents of Portlandite and carbonate for mortar 532 specimens after 28 and 91 days of carbonation, respectively. The total phase content of the Portlandite and carbonate is shown as moles per 100g of ignited mortars (800 °C). Most parts of 533 534 the spatial and temporal domains show high agreement between predicted and measured 535 Portlandite and calcite content. Moreover, the experimental results validate numerical predictions on the gradual increase in carbonation depth caused by the dissolution of Portlandite and calcite 536 precipitation. Additionally, a pH reduction occurs in the region where the amount of calcite 537 increases and the amount of Portlandite decreases, consistent with results described in [4,17,83]. 538 539 Upon carbonation, numerical results indicate a complete decomposition of the Portlandite phase 540 in the region of carbonation depth. However, increases in calcite content were observed even after pH values dropped below 9.7, which indicates carbonation continues due to the transported CO₂ 541 542 reacting with other phases, such as C-S-H, AFtss, and CO₂-AFm phases, after the complete 543 decomposition of the Portlandite phase.



544

Fig 6. Comparison of experimental measurements [17] and numerical predictions of total Portlandite (CH), carbonate (CC), and the fraction of carbonate (CCo) formed by carbonation of phases apart from Portlandite after 28 and 91 days of carbonation. The data are given in terms of molar contents per 100 g of ignited mortars (800 °C).

549 The underlying mechanisms of the carbonation process of various phases and the development of 550 pH are challenging to study through a single-phase assemblage presented in Fig 5. Therefore, the dissolution of phases and calcite precipitation, including the pH profile, at 1mm depth from the 551 exposure surface were studied, and predicted results are presented in Fig 7. According to the 552 553 anticipated results, Portlandite is the first major hydration product to decompose and transform 554 into calcite after around 20 days of exposure, while other hydrated phases are stable during 555 carbonation. The results further illustrate a stable pH of approximately 13.03 during the carbonation process, identified as the dissolution front (see Fig 7). Once all accessible Portlandite 556 557 has been decomposed, the higher Ca/Si (2.25) CSHQ-JenD phase begins to decalcify down to a 558 Ca/Si ratio of 1.33, 1.25, and 0.67, similar to the Ca/Si ratio of the CSHQ-JenH, CSHQ-TobD, and 559 CSHQ-TobH phase, respectively. As a result, the total C-S-H phase, except for CSHQ-JenD phase 560 content, increases due to the decalcification of the CSHQ-JenD phase up to nearly 27 days of 561 exposure. At the same time, the decomposition of monocarbonate and the formation of Ettringite 562 are also predicted. However, the decalcification process of CSHQ-JenD and other phase changes does not significantly alter the pH of the pore solution. After 27 days of exposure, CSHQ-JenH 563 564 and CSHQ-TobD start to decompose, whereas CSHQ-TobH and AFt phases continuously increase 565 up to 33 days of exposure. As numerical results indicate, the pH value in the pore solution starts to decrease gradually, which is shown as the first drop in Fig 7. The second drop in pH to 9.74 is 566 567 observed after nearly 33 days of exposure once almost all C-S-H except CSHQ-TobH and AFt_{ss} 568 are decomposed by carbonation. Afterwards, mainly decalcification of the CSHQ-TobH phase continues up to 38 days of exposure at a nearly stable pH of 9.74. Finally, a third drop in pH value 569 570 to 7.26 is predicted alongside the complete decomposition of the CSHQ-JenH, CSHQ-TobD, and 571 CSHQ-TobH phase.



572

573 Fig 7. Numerical results illustrating changes in the phase content and pH profile at 1mm depth of 574 exposed wPc mortar.

575 4.1.4 Elemental profiles

576 The modeling approach results, including changes in elemental composition, free water and EDL concentration, absorbed ions on the pore surface, and surface sites of the C-S-H phase for the 577 578 mortar specimen after 360 days of carbonation, are given in Fig 8. The elemental profile of the 579 unaffected core is shown on the right side of the figures, while the carbonation impact on the 580 mortar sample is presented on the left. As shown in Fig 8a, the decomposition of hydrated phases 581 and the precipitation of new solid phases lead to significant changes in the elemental composition 582 of the carbonated zone. The increase in C elemental profile is predicted up to a depth of 583 approximately 0.8cm due to CO₂(g) transport in the gaseous and dissolved state. Fig 8b illustrates 584 an increase in the moles of dissolved $CO_2(g)$ gas through the elemental content of C in both free 585 water and the EDL, which is consistent with the developed partial pressure of $CO_2(g)$ gas in the 586 pores (see Fig 8a).

587 Upon carbonation, a clear enrichment in both sodium and potassium content is observed as a result

588 of the formation of zeolite phases that contain Na (mordenite(Na)) and K (clinoptilolite(K)) in the

589 carbonated zone due to the interaction of the released absorbed sodium from the pore surface and

the decalcification of the C-S-H phase (see Fig 5 and Fig 8d). As a result, the concentration of both

- 591 sodium and potassium starts to decrease in the pore solution (see Fig 8b and c), and subsequently, 592 both Na and K in the pore solution of the non-carbonated zone are transported to the carbonated
- zone due to the concentration difference in the pore solution between the carbonated and non-
- 594 carbonated zones. Thus, an increase in sodium content in the carbonated zone is observed in Fig
- 595 8a. At the same time, the opposite behaviour is observed for both the sulphur and chloride content.
- 596 The concentration of sulphur and chloride in free water increases due to the decomposition of the
- 597 AFt_{ss} phase and C-S-H phase as well as the release of both absorbed sulphur and chloride from the
- 598 pore surface through the decomposition of the C-S-H phase (see Fig 6 and Fig 8d), which results 599 in a concentration gradient (of approximately more than two orders of magnitude) in the pore
- 600 solution between the carbonated and non-carbonated zone. As a result, sulphur and chloride
- 601 content decrease in the carbonated zone due to the transport toward the non-carbonated zone.
- 602 The direct comparison of the predicted free Na, K, S, and Cl content in the pore solution of wPc 603 mortar specimens (non-shaded bars) with the measured pore solution composition in the Pc 604 (CEM1) mortar specimens by cold water extraction (CWE) before and after carbonation [4] 605 (shaded bars) is shown in Fig 9. For both non-carbonated and carbonated mortar, the proposed 606 RTM framework underestimates the free Na, K, S, and Cl content compared to the measured amounts [4]. This can be attributed to a discrepancy in consideration of alkali ions as well as other 607 608 ions' absorption by the surface sites of the C-S-H phase in the surface complexation model used 609 and/or the release of some of the loosely absorbed ions from the pore surface during cold water 610 extraction. However, a similar trend between the predicted pore solution composition in wPc 611 mortar specimens and the measured amounts in Pc mortar specimens [4] can be observed. Upon 612 carbonation, the numerical simulation indicates a gradual decrease in the concentration of free 613 alkali, particularly sodium and potassium, along with an increase in sulfur and chlorine 614 concentration.
- 615 Due to the formation of the MSH_{ss} and magnesite phases due to the dissolution of hydrotalcite (Fig
- 616 5), the concentration of Mg in the pore solution increased, which indicates the instability in the
- 617 Mg elemental profile in the carbonated zone. In the carbonated zone, the precipitation of a calcite
- 618 phase during the carbonation slightly reduces the Ca^{2+} ion concentration in the pore solution. As
- 619 a result, Ca²⁺ ions in the non-carbonated zone are transported by a concentration gradient to the
- 620 carbonated zone, increasing further calcite formation.



622 Fig 8. Profiles for wPc mortar specimens during carbonation for 360 days. a) elemental composition, which is the summation of the element included in the free pore solution, the EDL, 623 624 hydrates, and surface sites, b) free water composition, c) EDL composition, d) surface absorption, 625 and e) surface sites on the C-S-H phase.





Fig 9. Comparison of the predicted free Na, K, S, and Cl content in the pore solution of wPc mortar (w/b-0.50) with the measured pore solution composition in the Pc mortar (w/b-0.55) [4] before 628 629 and after carbonation. (UC: non-carbonated, C: carbonated). The non-shaded and shaded bars

630 represent the predicted and measured results, respectively.

4.1.5 Free chloride concentration due to carbonation 631

632 Under marine environments, the carbonation of cement-based materials promotes chloride ingress, 633 subsequently increasing the risk of corrosion for embedded steel reinforcement. The capability of 634 the proposed RTM modelling framework, including the surface complexation model, was used to 635 investigate the interaction mechanism between free chloride concentration and carbonation. The predicted free chloride concentration in the wPc mortar specimen before and after carbonation 636 with (W_{EDL}) and without considering EDL formation (WO_{EDL}) is presented in Fig 10. When 637 considering the EDL formation, the predicted result shows an increase in free chloride 638 639 concentration upon carbonation, consistent with the measured chloride concentration in the 640 carbonated Pc mortar specimen [4] (see Fig 9). However, when the EDL formation is not 641 considered, no considerable changes in the free chloride concentration within the pore solution are 642 observed. By incorporating the surface complexation model, the proposed modeling framework 643 can explain the experimentally observed increase in chloride concentration. Initially, the pore 644 surface absorbs chloride ions through the interaction between ions and surface sites of the C-S-H. 645 Upon the carbonation, the pore surface releases the absorbed chloride ions as a consequence of the decomposition of the C-S-H phase. As a result, a free chloride concentration increase in the pore 646 solution is observed during carbonation. Hence, for a more accurate prediction of the changes in 647 648 free chloride concentration in the pore solution (and, ultimately, initiation of reinforcement 649 corrosion), incorporating the interaction between the pore solution and pore surface is crucial in 650 the RTM modelling framework.



652

Fig 10. Predicted chloride concentration in wPc mortar specimens before and after carbonation with (W_{EDL}) and without considering EDL formation (WO_{EDL}) . (UC: non-carbonated, C: carbonated).

656 4.1.6 Effect of composition of pore solution on corrosion due to carbonation

Upon carbonation of cement-based material, several factors can influence the corrosion of steel 657 658 reinforcement. Among these, the composition of the pore solution is of utmost importance for 659 understanding the corrosion process of embedded steel reinforcement in concrete. Upon carbonation of wPc mortar for 360 days of exposure, Fig 11 illustrates the simulated changes in 660 molar ratios of [Cl⁻]/[OH⁻], [SO₄²⁻]/[OH⁻], and [CO₃²⁻]/[HCO³⁻] with (W_{EDL}) and without 661 considering EDL formation (WO_{EDL}), as well as pH value and carbonation depth. Increases in the 662 corrosion rate of steel reinforcement [84] may be observed for concentrations of chlorides and 663 664 sulfates higher in relation to the hydroxyl concentration [85,86] and carbonate concentrations 665 lower than bicarbonate in the pore solution. In the pore solution of non-carbonated mortar, the molar ratios of $[Cl^-]/[OH^-]$ and $[SO_4^2-]/[OH^-]$ are below the corrosion threshold levels. However, 666 the pore solution mainly contains carbonates, leading to an exceptionally high $[CO_3^{2-}]/[HCO^{3-}]$ 667 ratio. When EDL formation is taken into consideration during the carbonation of mortar, the 668 simulation results indicate that the molar ratios of [Cl⁻]/[OH⁻] and [SO₄²⁻]/[OH⁻] start to increase 669 above the threshold values of 0.6 and 1.5, respectively, while $[CO_3^{2-}]/[HCO^{3-}]$ decreases below 670 the threshold value of 0.1. Consequently, these changes are anticipated to accelerate the corrosion 671 of reinforcement. In addition, the region where the molar ratio changes upon carbonation of mortar 672 673 are consistent with the carbonation depth, and the pH value drops. When the formation of the EDL 674 is not taken into account, the molar ratios of [Cl⁻]/[OH⁻] in both carbonated and non-carbonated regions are above the threshold value of 0.6. However, changes in the molar ratios of $[SO_4^{2-}]/[OH^-]$ 675 676 and $[CO_3^{2-}]/[HCO^{3-}]$ show a somewhat similar trend as observed in the predicted results when considering the EDL formation. The predicted variations in the pore solution highlight the 677 678 significance of incorporating surface complexation into the RTM modelling framework for 679 investigating the corrosion of steel reinforcement, particularly based on the molar ratios of 680 [Cl⁻]/[OH⁻].


682

Fig 11. Numerical predictions of molar ratios for $[Cl^-]/[OH^-]$, $[SO_4^{2-}]/[OH^-]$, and $[CO_3^{2-}]/[HCO^{3-}]$, pH value, and carbonation depth upon carbonation of wPc mortar for 360 days of exposure. The dotted lines show the threshold value of mortar ratios for corrosion ($[Cl^-]/[OH^-]$ >0.6, $[SO_4^{2-}]/[OH^-] > 1.5$, $[CO_3^{2-}]/[HCO^{3-}] > 0.1$) [4].

687 4.2 Numerical example 2

688 4.2.1 Applicability of RTM under various relative humidity conditions

689 In this study, the simulated carbonation depth using the proposed RTM framework, achieved by 690 adjusting the initial tortuosity factor (see Table 4) based on experimentally measured carbonation depth of PC mortar samples prepared with different water-to-cement ratios at 50.0% relative 691 humidity and 30°C temperature [48], while considering a functional description (With FD) of the 692 693 relationship between phase assemblage changes, pore structure changes, and mass transport 694 through pores, is presented in Fig 12a. To demonstrate the importance of the functional description 695 in the modelling framework, the simulated carbonation depth without considering it (Without FD) 696 for the adjusted initial tortuosity factor mentioned above is presented in Fig 12b. Without 697 considering a functional description, the simulated result indicates an underestimate of carbonation 698 in exposed Pc mortar specimens. Upon carbonation, the variation in pore distribution close to the 699 exposure surface, as well as increases in porosity due to phase assemblage changes, were observed 700 in simulated results. Therefore, gas mass transport through the non-water-filled pore space 701 increases upon carbonation, further accelerating the carbonation process in the Pc mortar 702 specimen. Therefore, when accounting for pore structure changes on mass transport through pores 703 using the proposed functional description, an increase in the carbonation rate for all specimens was 704 observed in Fig 12b. Furthermore, using an adjusted initial tortuosity factor for carbonation depth 705 in mortar samples at 50.0% relative humidity and 30°C temperature, the proposed functional 706 description for accounting for pore structure changes in mass transport through pores was 707 examined under various relative humidity conditions. Fig 13 compares simulated and measured 708 carbonation depth of PC mortar samples prepared with different water-to-cement ratios, 35.0%, 709 50.0%, 65.0%, and 80.0% relative humidity, respectively, and 30 °C temperature. A good 710 agreement between simulated and experimentally measured values is observed for the carbonation 711 depth of mortar specimens exposed to different relative humidity, which indicates that the

712 proposed model, including a functional description of the relation between phase assemblage 713 changes, pore structure changes, and mass transport through pores, can be utilized to predict the 714 carbonation process of cement-based material exposed to various ranges of relative humidity. As 715 illustrated in Fig 13, mortar specimens with a higher water-to-cement ratio show higher 716 carbonation for all relative humidity levels. Numerical results indicate that changes in relative 717 humidity around mortar specimens have a more significant effect on carbonation depth and further 718 suggest that very low as well as high relative humidity levels slow down the carbonation rate in 719 cement-based material. Moreover, mortar specimens exposed to 50% relative humidity show the 720 most considerable carbonation depth compared with other exposure conditions (see Fig 13e). The 721 carbonation depth of mortar specimens exposed to 80% relative humidity is significantly lower 722 than in exposure conditions with lower relative humidity. The simulation outcome demonstrates that when a mortar specimen is exposed to higher relative humidity, such as 80% or more, the 723 724 moisture storage inside the pores of the mortar increases significantly compared to exposure to 725 lower relative humidity (see Fig 3b). As a result of limited space for gas mass transport, 726 carbonation depth in mortar specimens exposed to 80% relative humidity considerably decreases at a higher saturation level of moisture. 727



728 729

Fig 12. Comparison between simulated and measured carbonation depth [48] of Pc mortar samples prepared with different water-to-cement ratios, 50.0% relative humidity, and 30 °C temperature 730 731 (a) with (With FD), and (b) without considering a functional description of the relation between 732 phase assemblage changes, pore structure changes, and mass transport through pores (Without 733 FD).





Fig 13. Comparison between simulated and measured carbonation depth [48] of Pc mortar samples prepared with different water-to-cement ratios, 35.0%, 50.0%, 65.0%, and 80.0% relative humidity, respectively, and 30 °C temperature (a) w/c-0.55, (b) w/c-0.60, (c) w/c-0.65, (d) w/c-

738 0.80, and (e) for 42 days of exposure.

739 4.2.2 Applicability of RTM under various temperature conditions

740 Using an adjusted initial tortuosity factor (see Section 4.2.1), simulated results without considering 741 the temperature effect on the interfacial gas transfer coefficient (Without TE), along with the 742 experimentally measured carbonation depth of PC mortar samples prepared with different water-743 to-cement ratios at 50.0% relative humidity and 15°C temperature [48], are presented in Fig 14a. 744 Simulated results, disregarding the temperature effect on the interfacial gas transfer coefficient, 745 indicate an overestimate of carbonation in exposed PC mortar specimens. The increase in 746 temperature accelerates both the dissolution of gas into a pore solution and the diffusion coefficient 747 of the gas phase. Nevertheless, based on the mass balance equation for gas transport, increased gas 748 dissolution into the pore solution reduces the quantity of gas phase transport through the non-749 water-filled pore space. By reducing the moles of gas transport through the air void space, a 750 decrease in the carbonation rate can be anticipated in cement-based materials. Therefore, it was 751 decided that the effect of temperature on the dissolution of the gas phase into the pore solution can be considered by adjusting the interfacial gas transfer coefficient. By comparing simulated and 752 753 measured carbonation depth under various temperatures, a relation for the interfacial gas transfer 754 coefficient accounting for temperature is proposed as

$$k_t = k_{(t=293.15)} \cdot \exp\left(\frac{E_0}{RT_0} - \frac{E_0}{RT}\right)$$
(18)

Where $k_{(t=293,15)}$ is the interfacial gas transfer coefficient of the j^{th} gas constituent between the 755 gas phase and pore solution at a reference temperature (t = 293.15 K), E_0 the reference activation 756 757 energy for gas dissolution ($E_0 = 25220 \text{ J/mol}$), R the universal gas constant, T_0 the reference 758 temperature ($T_0 = 293.15$ K), and T the absolute temperature (K). After incorporating the effect of 759 temperature on gas dissolution (With TE), an improvement in the predictability of the proposed 760 RTM was observed compared to the simulated results that did not account for the effect of 761 temperature on gas dissolution, as shown in Fig 14b. Furthermore, the proposed function for 762 accounting for the effect of temperature on gas dissolution was examined for various PC mortar 763 specimens prepared with different water-to-cement ratios under various temperature conditions. 764 Fig 15 shows a comparison between simulated and measured carbonation depths for PC mortar 765 samples prepared with different water-to-cement ratios exposed to 15.0 °C, 22.5 °C, 30.0 °C and 37.5 °C, and 50% of relative humidity. The simulated carbonation depth incorporating the 766 767 proposed temperature effect on gas dissolution agrees well with experimentally measured values 768 for mortar specimens exposed to various temperatures. The results show that the specimens for 769 each water-cement ratio exhibit a steady increase in the carbonation depth with temperature 770 increases.





Fig 14. Comparison between simulated and measured carbonation depth [48] of Pc mortar samples

prepared with different water-to-cement ratios, 50.0% relative humidity, and 15 °C temperature
(a) without (Without TE), and (b) with accounting temperature effect on the interfacial gas transfer

(a) without (Without TE), and (Icoefficient (With TE).





Fig 15. Comparison between simulated and measured carbonation depth [48] of Pc mortar samples

with different water-to-cement ratios exposed to $15.0 \circ C$, $22.5 \circ C$, $30.0 \circ C$, and $37.5 \circ C$, respectively, and 50% relative humidity. (a) w/c-0.55, (b) w/c-0.60, (c) w/c-0.65, (d) w/c-0.80, and

780 (e) for 42 days of exposure.

781 **5.** Conclusions

782 For understanding carbonation processes through the pore solution composition and phase 783 assemblage changes in cement-based materials and the influence of pore solution composition 784 changes on steel corrosion, the reactive transport modelling framework presented in [47] was 785 extended, including multi-component gas, multi-ionic, and moisture transport coupled with a 786 chemical equilibrium computation. Using Henry's law, the multi-component gas transport model 787 was developed, including gas dissolution into the pore solution. A modelling approach for moisture 788 conductivity and gas and ionic diffusivity based on the pore structure and moisture storage was 789 presented to account for pore structure changes on mass transport.

790 By adjusting the initial tortuosity factor based on carbonation depth, the results of the first 791 numerical study demonstrate good agreements in both spatial and temporal domains between the 792 measured and numerically predicted content of Portlandite and carbonate. The zones related to the 793 carbonation process, such as the carbonated zone, carbonation front, dissolution front, and non-794 carbonated zone, were clearly identified in the numerical simulation. Initially, the Portlandite 795 phase was decomposed upon carbonation, whereas other hydrated phases were stable. After the 796 complete decomposition of the Portlandite phase, the C-S-H phase with a higher Ca/Si ratio 797 (CSHQ-JenD) starts to decalcify, and subsequently, the lower Ca/Si C-S-H phases and AFt form. 798 Simultaneously, the decomposition of monocarbonate is also predicted. Finally, all C-S-H phases 799 and AFt were completely decomposed. During this carbonation process, three drops in the pH 800 value were observed.

801 The significance of employing a surface complexation model is emphasized in this study to predict 802 the actual changes in the composition of the pore solution and evaluate the implications of these 803 changes on steel corrosion. The simulation results show that changes in the phase assemblage 804 accompany changes in the composition of the pore solution. A fundamental understanding of the 805 carbonation process, particularly related pore solution changes, is indispensable to elucidating the 806 mechanisms of steel corrosion in reinforced concrete. A clear enrichment in sodium and potassium 807 content in carbonated regions is observed upon carbonation. As a result, the concentration of both 808 sodium and potassium starts to decrease in the pore solution, and alkali ions are transported toward 809 the carbonated zone. At the same time, the opposite behaviour is observed for both the sulphur and 810 chloride content. The increase in the concentration of sulphur and chloride in the pore water was 811 observed due to the dissolution of the solid phases. Calcium ions are transported to the carbonated 812 zone, further increasing calcite formation near the exposed surface. Upon carbonation of wPc 813 mortar, the molar ratios of [Cl⁻]/[OH⁻] and [SO₄²⁻]/[OH⁻] in the pore solution start to increase above the threshold values of 0.6 and 1.5, respectively, while $[CO_3^{2-}]/[HCO^{3-}]$ falls below the 814 815 threshold value of 0.1 as the bicarbonate concentration increases. It indicates that pore solution

816 composition changes upon carbonation promote reinforcement corrosion. In addition, the region

817 where the molar ratio changes upon carbonation of mortar is consistent with the carbonation depth,

818 and the pH value drops.

819 In the second numerical study, the applicability of the proposed RTM was examined across various 820 conditions of temperature and relative humidity. Within the framework of the RTM, the 821 importance of accounting for changes in pore structure on mass transport upon carbonation is 822 demonstrated by comparing the simulated carbonation depth with the measured value for mortar 823 specimens exposed to various relative humidity conditions. Numerical results indicate that mortar 824 specimens exposed to high or low relative humidity exhibit lower carbonation depths. On the other 825 hand, the highest carbonation rate occurs at a relative humidity range between 40% and 60%. 826 Furthermore, a relation for the interfacial gas transfer coefficient was proposed to account for the 827 impact of temperature on gas dissolution into pore solution. Numerical results highlighted that an 828 increase in temperature results in a steady increase in the carbonation depth of the mortar

specimens.

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835 Appendix A. Thermodynamic database

Table A. 1 presents the dissolution reaction of phases and associated thermodynamical information
based on the CEMDATA18 database [66].

Details of Phase		Reaction equation	log K
Pure phases	Notation		-
Calcite	Calcite	$CaCO_3 \rightleftharpoons CO_3^{2-} + Ca^{+2}$	-8.480
hemicarbonate	HC	$(CaO)3Al_2O_3(CaCO_3)0.5(CaO_2H_2)0.5(H_2O)11.5 + 5H^+ \Leftrightarrow 0.5CO_3^{-2} + 4Ca^{+2} + 2AlO_2^{-} + 14.5H_2O$	40.870
hydrotalcite	Ht	$Mg_4Al_2O_7(H_2O)10 + 6H^+ \Rightarrow 4Mg^{2+} + 2AlO_2^- + 13H_2O$	27.981
monocarbonate	CO ₂ -AFm	$Ca_4Al_2CO_9(H_2O)11 + 4H^+ \Leftrightarrow CO_3^{2-} + 4Ca^{2+} + 2AlO_2^{-} + 13H_2O$	24.530
Portlandite	СН	$Ca(OH)_2 + 2H^+ \rightleftharpoons Ca^{2+} + 2H_2O$	22.800
AlOHmic	Al(OH)mic	$Al(OH)_3 \rightleftharpoons AlO_2^- + H^+ + H_2O$	-14.670
silica gel	silica gel	$SiO_2(H_2O)2 \rightleftharpoons SiO_2 + 2H_2O$	-3.018
Ferrihydrite-mc	FeOOHmic	$FeOOH \Leftrightarrow FeO_2^- + H^+$	-19.600
Brucite	Brucite	$Mg(OH)_2 + 2H^+ \Leftrightarrow Mg^{2+} + 2H_2O$	16.840
Friedel salt	Friedel salt	$Ca_4Al_2Cl_2(OH)12(H_2O)4 + 4H^+$ $\Rightarrow 2Cl^- + 4Ca^{2+} + 2AlO_2^- + 12H_2O$	-2.714
Kuzel salt	Kuzel salt	$Ca_{4}Al_{2}Cl(SO_{4})0.5(OH)12(H_{2}O)6 + 4H^{+}$ $\Leftrightarrow Cl^{-} + 4Ca^{2+} + 0.5SO_{4}^{2+} + 2AlO_{2}^{-} + 14H_{2}O$	-19.600
Gypsum	Gypsum	$CaSO_4(H_2O)2 \rightleftharpoons Ca^{2+} + SO_4^{2+} + 2H_2O$	-4.581
Magnesite	Mgs	$MgCO_3 = CO_3^{-2} + Mg^{+2}$	-8.288
Natrolite	NAT	$Na_2(Al_2Si_3)O10(H_2O)2 \Rightarrow 2AlO_2^- + 2Na^+ + 3SiO_2 + 2H_2O$	-26.6

838 Table A. 1 Thermodynamic properties of the phases at 25°C in the chemical equilibrium model.

Phillipsite(K)	PHI(K)	$K_{2.5}(Al_{2.5}Si_{5.5}O_{16})(H_2O)5 \Rightarrow 2.5AlO_2^- + 2.5K^+ + 5.5SiO_2 + 5H_2O$	-42.60
Phillipsite(Na)	PHI(Na)	Na _{2.5} (Al _{2.5} Si _{5.5} O ₁₆)(H ₂ O)5	-39 375
		$\Rightarrow 2.5 \text{AlO}_2^- + 2.5 \text{Na}^+ + 5.5 \text{SiO}_2 + 5 \text{H}_2 \text{O}$	-57.575
Clinoptilolite(K)	CLI(K)	$K_{1.01}(Al_{1.01}Si_{4.99}O_{12})(H_2O)2.3$	-26.80
		$= 1.01 \text{AlO}_2 + 1.01 \text{K}^+ + 4.99 \text{SiO}_2 + 2.3 \text{H}_2\text{O}$	20100
Chabazite(K)	CHA(K)	$K_2(Al_2Si_4O_{12})(H_2O)4 \Leftrightarrow 2AlO_2^- + 2K^+ + 4SiO_2^- + 4H_2O_2^-$	-32.30
Chabazite(K)	CHA(Na)	$Na_2(Al_2Si_4O_{12})(H_2O)6 \Leftrightarrow 2AlO_2^- + 2Na^+ + 4SiO_2^- + 6H_2O$	-31.9
Mordenite(K)	MOR(K)	$K_{0.65}(Al_{0.65}Si_{5.35}O_{12})(H_2O)2.3$	-22.00
		$\Rightarrow 0.65 \text{AlO}_{2}^{-} + 0.65 \text{K}^{+} + 5.35 \text{SiO}_{2} + 2.3 \text{H}_{2} \text{O}$	
Mordenite(Na)	MOR(Na)	$Na_{0.72}(Al_{0.72}Si_{5.28})012(H_20)2.71$	-22.5
		$\Rightarrow 0.72 \text{AlO}_2^- + 0.72 \text{Na}^+ + 5.28 \text{SiO}_2^- + 2.71 \text{H}_2 \text{O}_2^-$	
Solid solutions	Fnd member		
Solid Solutions	End memoer	$((H_0)^2)_{C_2} = A_0 (S_0)^3 (OH)^{12} (H_0)^{24} + 4H^+$	
AFtss	SO4-AFt	$((11_20)_2)Ca_6Hi_2(30_4)_3(01)_12(11_20)_24 + 411$ $\leftarrow 6C_2^2 + 2SO_2^2 + 2A1O_2 + 2AHO_2$	11.100
		$\rightarrow 0Ca + 550_4 + 2A10_2 + 5411_20$	
	SO4-AFt{30}	$Ca_{6}Ai_{2}(30_{4})3(01)12(1i_{2}0)24 + 411$ $\leftarrow 6C_{2}^{2+} \pm 3SO^{2-} \pm 3AiO^{-} \pm 32HO$	11.702
		\rightarrow 0Ca + 550 ₄ + 2Al0 ₂ + 52l1 ₂ 0	
		$(A FeO_2)(Ca_2O_2(SiO_2)0.84(H_2O)4.32) + 4H^+$	
HGss	Si0.84-(Al)HG	$\leq \text{Fe}O_2^- + 3Ca^{+2} + AlO_2^- + 6.32H_2O_2^- + 0.84SiO_2^-$	22.280
		$(FeFeO_2)(Ca_2O_2(SiO_2)0.84(H_2O)4.32) + 4H^+$	
	Si0.84-(Fe)HG	$\Rightarrow 2FeO_2^- + 3Ca^{2+} + 6.32H_2O + 0.84SiO_2$	19.981
COLLO		$(CaO)0.6667(SiO_2)1(H_2O)1.5 + 1.3334H^+$	0.007
CSHQss	CSHQ-TobH	$\Rightarrow 0.6667 \text{Ca}^{2+} + 2.1667 \text{H}_2\text{O} + \text{SiO}_2$	8.287
		$((CaO)1.25(SiO_2)1(H_2O)2.75)0.6667 + 1.66675H^+$	12 (55
	CSHQ-TODD	$\Rightarrow 0.833375 Ca^{2+} + 2.6668 H_2 O + 0.6667 SiO_2$	13.655
	CSUO IsaU	$(CaO)1.3333(SiO_2)1(H_2O)2.1667 + 2.6666H^+$	22 170
	Сэпұ-зепп	$\Leftrightarrow 1.3333 \text{Ca}^{2+} + 3.5 \text{H}_2\text{O} + \text{SiO}_2$	22.179
	CSUO Imp	$(CaO)1.5(SiO_2)0.6667(H_2O)2.5 + 3H^+$	28 720
	CSHQ-JenD	$\Rightarrow 1.5 Ca^{2+} + 4H_2O + 0.6667 SiO_2$	28.750
	NaSiOH	$((NaOH)2.5SiO_2H_2O)0.2 + 0.5H^+ \Leftrightarrow 0.5Na^+ + 0.7H_2O + 0.2SiO_2$	5.649
	KSiOH	$((KOH)2.5SiO_2H_2O)0.2 + 0.5H^+ \Rightarrow 0.5K^+ + 0.7H_2O + 0.2SiO_2$	5.764
		·	
MSHss	M075SH	$Mg1.5Si_205.5(H_20)2.5 \Leftrightarrow 1.5Mg^{2+} + 2SiO_2 + 30H^- + H_2O$	-28.800
	M15SH	$Mg1.5SiO3.5(H_2O)2.5 \Leftrightarrow 1.5Mg^{2+} + 1SiO_2 + 3OH^- + H_2O$	-23.570

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