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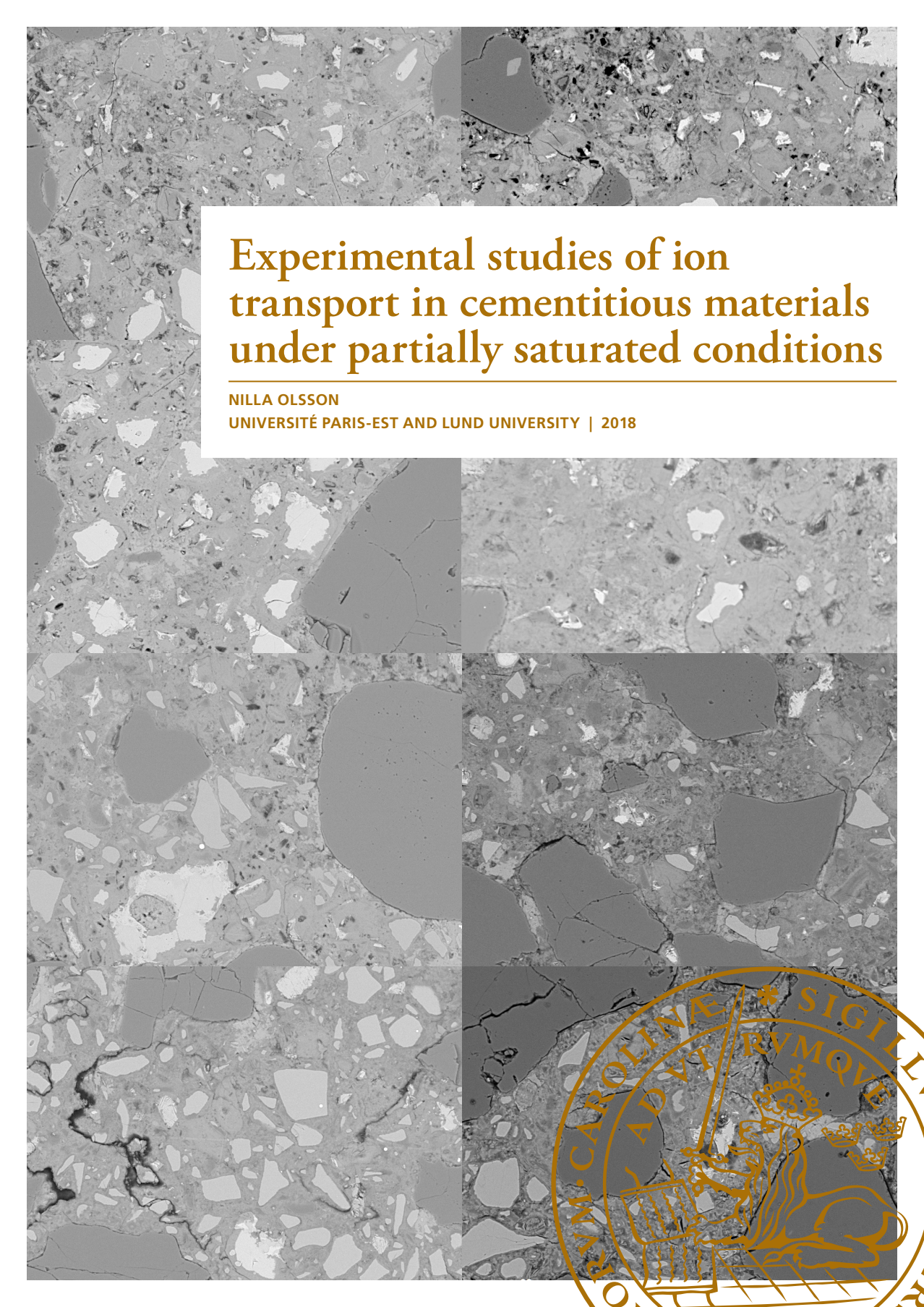
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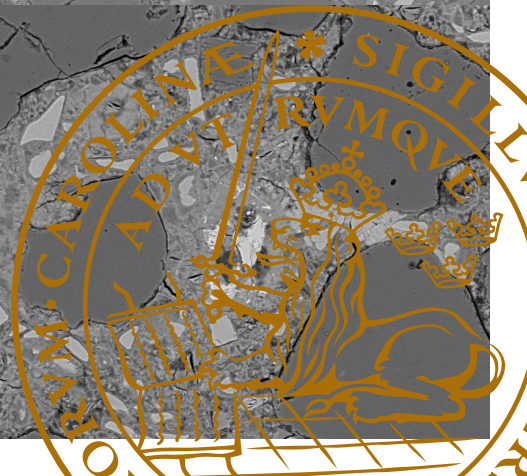
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Experimental studies of ion transport in cementitious materials under partially saturated conditions

NILLA OLSSON

UNIVERSITÉ PARIS-EST AND LUND UNIVERSITY | 2018





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Experimental studies of ion transport in cementitious materials under partially saturated conditions

Nilla OLSSON



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Experimental studies of ion transport in cementitious materials under partially saturated conditions

Nilla OLSSON



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Lund University, Faculty of Engineering
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*To Jens, Love, and Elise,
for your daily challenges,
thorough support, and endless love.*

Preface

The work behind this dissertation has been possible owing to collaborations, inspiring discussions, and genuine support from many people, and I would like to express my sincere gratitude to each one of them.

The research leading to this dissertation has been carried out at Division of Building Materials at Lund University, and at Materials Department FM²D Laboratory at Université Paris-Est. The work has received funding from Nanocem, SBUF, and NCC AB, which are greatly acknowledged. I would like to thank my supervisors, Lars-Olof Nilsson and Véronique Baroghel-Bouny, and my co-supervisor, Magnus Åhs, for their kind guidance, shared expertise, and loyal support.

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Finally, I would not have managed to finalize this work without the genuine support from my beloved friends. Thank you for listening to my frustrations and for your full support and love. I would also like to thank my parents and brother for their love and belief in me. Most of all, thank you Jens, Love, and Elise for your love, patience, and your everyday reminder of what is really important to me.

Lund, April 2018
Nilla Olsson

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Abstract

Cement production is responsible for a significant portion of manmade CO₂ emissions. This motivates the development of cementitious binders with a lower carbon footprint. Considering the emissions in a longer perspective, the durability of concrete structures is absolutely essential. Most degradation of concrete structures is closely related to both moisture transport and ion transport. Many studies have investigated these areas under saturated conditions. Owing to varying exposure conditions and self-desiccation, most concrete structures undergo large variations in moisture state during their service life. The coupling between ionic transport and moisture transport in cementitious materials under partially saturated conditions is still poorly understood. This project aimed to contribute to the knowledge in this area.

Service life models can be used to predict the performance of the material over time, but fundamental understanding of the underlying physical and chemical relations is critical for the development of accurate models. In this project, these physical relations of unsaturated ion transport were studied experimentally. The moisture dependency of ionic diffusion and ionic convection was investigated in two studies. The experimental investigations were performed on mortars with two water to binder ratios (0.38 and 0.53) and with four binders (OPC, 95% OPC + 5% silica fume, 60% OPC + 40% GGBFS, and 30% OPC + 70% GGBFS).

In the diffusion study, resistivity measurements and the Nernst-Einstein equation were used to evaluate the moisture dependency of the chloride diffusion coefficient, i.e., $D_{Cl}(RH)$ and $D_{Cl}(S)$. Desorption isotherms were determined using a gravimetric box method, and the conductivity of pore solutions was evaluated in two different ways. First, a simplified method was used. The limitation of this method is that it can only assess the pore solution composition for the OPC mortars. Second, a thermodynamic modeling tool, GEMS, was used to assess the pore solution composition and the chloride diffusion coefficient for all mortars. It was found that $D_{Cl}(S)$ is independent of w/b, but the relation differs between binders, and for the individual binders, there seems to be a relation between $D_{Cl}(RH)$ and the desorption isotherm.

Convective ion transport is more complicated to study because it is difficult to decouple ionic transport from moisture transport. For cementitious materials, it is difficult, or maybe impossible, to design an experimental setup where the ionic species are affected by convective transport only. Cementitious materials are by definition reacting with water, and therefore, there will be interactions between the solid phases and the pore solution, especially under non-saturated conditions.

Wick action experiments in combination with measurements of material properties were chosen for the investigation of convective ion transport. Chloride profiles and moisture profiles were evaluated with microXRF and ^1H NMR relaxometry, respectively. The measured profiles were discussed in relation to the moisture dependent material properties, such as chloride diffusion coefficients, moisture diffusion coefficients, chloride binding capacities, and desorption isotherms. It was concluded that there is a large variation in moisture dependency of the moisture diffusion coefficient, and that the variation cannot be related to the desorption isotherms. It was also shown that the composition of the binder is the key factor affecting the chloride penetration depth. The measured material properties are important parameters for prediction of chloride ingress and all are strongly affected by the binder composition.

Keywords: Cement, Mortar, Concrete, Ion transport, Moisture transport, Water vapor sorption, Supplementary cementitious materials, Silica fume, Ground granulated blast furnace slag.

Sammanfattning

Cementproduktion står idag för en ansevärd andel av världens koldioxidutsläpp, vilket driver utvecklingen av bindemedel med lägre koldioxidutsläpp. För utsläppen i ett längre perspektiv är dock de nya bindemedlens beständighet absolut avgörande. De flesta nedbrytningsmekanismer är direkt relaterade till både fukt- och jontransport. Dessa processer har undersökts i många studier, men huvudsakligen under fuktmättade förhållanden. På grund av varierande exponeringsförhållande och självuttorkning varierar dock fuktförhållandena i en betongkonstruktion mycket under dess livslängd och det saknas kunskap om relationen mellan jontransport och fukttransport under omättade förhållanden. Målet med detta projekt var att bidra med ny kunskap inom detta område.

Livslängdsmodeller kan användas för att prognostisera vad som händer i material över tid, men för att modellerna ska kunna ge tillförlitliga prognoser krävs grundläggande förståelse för de underliggande fysikaliska och kemiska relationerna i materialet. I detta projekt undersöktes dessa fysikaliska relationer experimentellt. Projektet är uppdelat i två studier där fuktberoendet hos jondiffusion respektive jonkonvektion undersöktes. Experimenten gjordes med bruk med två vattenbindemedelstal (0.38 och 0.53) och med fyra bindemedel (OPC, 95% OPC + 5% kiselstoff, 60% OPC + 40% GGBFS, och 30% OPC + 70% GGBFS).

I diffusionsstudien användes resistivitetmätningar och Nernst-Einsteins ekvation för att utvärdera fuktberoendet hos kloriddiffusionskoefficienten, d.v.s. $D_{Cl}(RH)$ och $D_{Cl}(S)$. Desorptionsisotermer mättes med en gravimetrisk boxmetod och konduktiviteten hos porlösningen bestämdes med två olika metoder. Först användes en förenklad metod för bestämning av porlösningens sammansättning. Begränsningen med denna metod är att den bara möjliggör bestämning av porlösningens sammansättning för bruk med OPC som bindemedel. Därför användes sedan även ett termodynamiskt modelleringsprogram, GEMS, för att bestämma porlösningens sammansättning och kloriddiffusionskoefficienten för alla bruk. Resultaten visade att $D_{Cl}(S)$ är oberoende av vattenbindemedelstalt, men att detta beroende varierar mellan de studerade bindemedlen. Resultaten visade även att det verkar finnas en relation mellan $D_{Cl}(RH)$ och desorptionsisotermer för de olika bindemedlen.

Konvektiv jontransport är mer komplicerat att studera eftersom det är svårt att särskilja jontransport och fukttransport. För cementbaserade material är det svårt, och kanske omöjligt, att designa ett experiment där jontransporten endast påverkas av den konvektiva fukttransporten. Cementbaserade material är per definition material som reagerar med vatten. Därför kommer det alltid att ske ett utbyte mellan porlösning och de fasta faserna, speciellt under icke mättade förhållanden.

För att studera konvektiv jontransport gjordes wick action experiment. Efter wick action exponering mättes kloridprofiler och fuktprofiler med mikroXRF respektive ^1H NMR relaxometri. De uppmätta profilerna diskuterades i relation till fuktberoende materialegenskaper, såsom kloriddiffusionskoefficienter, fuktdiffusionskoefficienter, kloridbindningskapacitet och desorptionsisoterm. Fuktdiffusionskoefficienter mättes parallellt i denna studie. Dessa resultat visade att det finns stora variationer i fuktberoendet mellan de olika bindemedlen och att dessa variationer inte kan kopplas till desorptionsisotermerna. I studien visades även att bindemedlet sammansättning är den egenskap som tydligast påverkar inträngningsdjupet av klorid. De uppmätta materialegenskaperna är dock alla viktiga parametrar för prognostisering av kloridinträngning och alla dessa materialegenskaper påverkas av bindemedelssammansättningen.

Nyckelord: Cement, Bruk, Betong, Jontransport, Fukttransport, Sorptionsisoterm, Tillsatsmaterial, Kiselstoft, Masugnslag.

Résumé

La production de ciment est responsable d'une part importante des émissions de CO₂ générées par les activités humaines, ce qui pousse au développement de liants cimentaires ayant une empreinte carbone plus faible. Pour les émissions dans une perspective plus longue, la durabilité des structures en béton est absolument essentielle. La plupart des dégradations des structures en béton sont étroitement liées au transport d'humidité et au transport d'ions. De nombreuses recherches ont été faites dans ce domaine dans des conditions saturées. En raison des conditions d'exposition variables et de l'auto-dessiccation, la plupart des structures en béton subissent d'importantes variations de degré de saturation pendant leur vie. Le couplage entre le transport ionique et le transport d'humidité dans des matériaux cimentaires dans des conditions partiellement saturées est encore mal compris. Ce projet visait à mieux comprendre les phénomènes dans ce domaine.

Les modèles de durée de vie peuvent être utilisés pour prédire les performances du matériau au cours du temps, mais la compréhension des relations physiques et chimiques impliquées est essentielle pour le développement de modèles précis. Dans ce projet, les relations physiques de transport d'ions en conditions insaturées ont été étudiées expérimentalement. La dépendance de la diffusion ionique et de la convection ionique avec l'humidité a été étudiée dans deux cas. Les études expérimentales ont été réalisées sur des mortiers avec deux rapports eau / liant (0,38 et 0,53) et avec quatre liants (OPC, 95% OPC + 5% de fumée de silice, 60% OPC + 40% de laitier et 30% OPC + 70% de laitier).

Dans l'étude de la diffusion, des mesures de résistivité et l'équation de Nernst-Einstein ont été utilisées pour évaluer la dépendance à l'humidité du coefficient de diffusion des chlorures, c'est-à-dire $D_{Cl}(HR)$ et $D_{Cl}(S)$. Les isothermes de désorption ont été déterminées par une méthode gravimétrique, et la conductivité des solutions interstitielles a été évaluée de deux manières différentes. Tout d'abord une méthode simplifiée a été utilisée. La limitation avec cette méthode est qu'elle permet seulement de déterminer la composition de la solution interstitielle pour les mortiers de CEM I. Ensuite, un outil de modélisation thermodynamique, GEMS, a été utilisé pour déterminer la composition de la solution interstitielle et le coefficient

de diffusion des chlorures de tous les mortiers. Il a été observé que $D_{Cl}(S)$ était indépendant de w/b, mais que la relation obtenue différait selon les liants. De plus, pour chaque liant, il semble y avoir une relation entre $D_{Cl}(HR)$ et l'isotherme de désorption.

Le transport ionique par convection est plus compliqué à étudier étant donné qu'il est difficile de découpler le transport ionique du transport d'humidité. Pour les matériaux cimentaires, il est difficile, voire impossible, de concevoir un montage expérimental où les espèces ioniques sont uniquement affectées par le transport par convection. Les matériaux cimentaires réagissent par définition avec l'eau et il y aura par conséquent interaction entre les phases solides et la solution interstitielle, en particulier dans des conditions non saturées.

Des essais en "wick action", combinés avec la mesure des propriétés du matériau, ont été choisis pour l'étude du transport ionique convectif. Les profils de concentration en chlorures et les profils de teneur en eau ont été déterminés par microfluorescence X et relaxométrie RMN 1H , respectivement. Les profils mesurés ont été discutés en relation avec les propriétés du matériau dépendant de l'humidité, tels que le coefficient de diffusion des chlorures, le coefficient de diffusion hydrique, la capacité de fixation des chlorures et l'isotherme de désorption. Il a été conclu que le coefficient de diffusion hydrique variait largement avec l'humidité, et que cette large variation ne pouvait pas être attribuée aux isothermes de désorption. Il a également été montré que la composition du liant était le facteur clé affectant la profondeur de pénétration des chlorures. Les propriétés des matériaux mesurées sont des paramètres importants pour la prédiction de la pénétration des chlorures et sont toutes fortement influencées par la composition du liant.

Mots-clés: Ciment, Mortier, Béton, Transport ionique, Transport d'humidité, Sorption de vapeur d'eau, Additions minérales, Fumée de silice, Laitier de haut fourneau granulé moulu.

List of appended publications

This thesis is based on the following publications, which are appended at the end of the thesis.

- Paper I Olsson, N., Baroghel-Bouny, V., Nilsson, L.-O., Thiery, M., *Non-saturated ion diffusion in concrete – New laboratory measurements*. Proceedings of the 1st International Congress on Durability of Concrete, 18–21 June 2012, Trondheim, Norway.
- Paper II Olsson, N., Baroghel-Bouny, V., Nilsson, L.-O., Thiery, M., *Non-saturated ion diffusion in concrete – A new approach to evaluate conductivity measurements*. Cement and Concrete Composites 40 (2013) 40–47.
- Paper III Olsson, N., Lothenbach, B., Baroghel-Bouny, V., Nilsson, L.-O., *Unsaturated ion diffusion in cementitious materials – The effect of slag and silica fume*. Cement and Concrete Research, 108 (2018) 31–37.
- Paper IV Olsson, N., Nilsson, L.-O., Åhs, M., Baroghel-Bouny, V., *Moisture transport and sorption in cement based materials containing slag or silica fume*. Cement and Concrete Research, 106 (2018) 23–32.
- Paper V Olsson, N., Abdul Wahid, F., Nilsson, L.-O., Wong, H.S., Baroghel-Bouny, V., *Wick action in mature mortars with binary cements containing slag or silica fume – The relation between chloride and moisture transport properties under non-saturated conditions* (submitted to Cement and Concrete Research, February 2018).

The contributions of the authors to the papers appended to this thesis are as follows:

- Paper I NO planned and carried out the experiments, analyzed the data, and wrote the manuscript. VBB, LON, and MT contributed in planning the experiments and commented on the manuscript.
- Paper II This is a revised version of Paper I. The conference paper (Paper I) was selected to be presented in the plenum and to be published in a special issue of Cement and Concrete Composites.
- Paper III NO planned the study, analyzed the data, and wrote the manuscript. NO and BL performed the GEMS calculations together. BL, VBB, and LON commented on the manuscript.
- Paper IV NO planned and carried out the experiments, analyzed the data, and wrote the manuscript. LON and MÅ contributed to the analysis and commented on the manuscript. VBB commented on the manuscript.
- Paper V NO planned and prepared the specimens, analyzed the data, and wrote the manuscript. FAW performed the microXRF analysis. CT performed the NMR measurements and wrote the method section for NMR analysis. LON contributed in planning the experiments and commented on the manuscript. HSW wrote the method section for microXRF analysis and commented on the manuscript, and VBB commented on the manuscript.

Nomenclature

Symbols

$D_{Cl}(RH)$	Chloride diffusion coefficient in bulk material as a function of relative humidity	(m ² /s)
$D_{Cl}(S)$	Chloride diffusion coefficient in bulk material as a function of degree of saturation	(m ² /s)
D_i	Diffusion coefficient of ion i in bulk material	(m ² /s)
D_{0i}	Diffusion coefficient of ion i in pore solution	(m ² /s)
D_{tot}	Total moisture transport coefficient, with vapor content as driving potential	(m ² /s)
D_v	Moisture diffusion coefficient, with vapor content as driving potential	(m ² /s)
w	Moisture content by volume	(kg/m ³)
S	Degree of saturation	(-)
σ	Conductivity of bulk material	(S/m)
σ_0	Conductivity of pore solution	(S/m)

Abbreviations

C-S-H	Calcium silicate hydrate
C ₃ S	Tricalcium silicate (alite)
C ₂ S	Dicalcium silicate (belite)
C ₃ A	Tricalcium aluminate (aluminate)
C ₄ AF	Calcium ferro aluminate (ferrite)
CH	Calcium hydroxide (portlandite)
C/S	Calcium to silica ratio
¹ H NMR	¹ H neutron magnetic resonance
IGP	Intraglobular pore
K ₂ O	Potassium oxide
LGP	Large gel pores
microXRF	Micro X-ray fluorescence
Na ₂ O	Sodium oxide
OPC	Ordinary Portland cement
RH	Relative humidity
SCMs	Supplementary cementitious materials

SEM-EDS	Scanning electron microscope with energy-dispersive X-ray spectroscopy
SF	Silica fume
SGP	Small gel pores
slag	Ground granulated blast furnace slag (GGBFS)
w/b	Water to binder ratio

1 Introduction

In this chapter, a general background and motivation for this research project is provided. The investigated research questions and how they are addressed in the appended publications are outlined. The most important limitations are also stated.

1.1 Background

Durability of concrete structures is of major importance to society, and most degradation of concrete structures is closely related to the transport of moisture and ions, inside or outside of the material. Chloride ingress, sulfate attack, alkali silica reactions, carbonation, and leaching are all related to ion transport. Ion transport is strongly dependent on the moisture content of the material, and all concrete structures undergo a variation in moisture distribution over time owing to self-desiccation from hydration and the surrounding climatic conditions. These variations cause ion and moisture movements within the material and in many cases, degradation of the material [1]. Service life models are often used to predict the performance of the material over time, and important input data to these models are the ion and moisture transport properties of the material [2].

The transport properties are related to the microstructure of the material, which is formed during the hydration of cementitious binders. The composition of the binder strongly affects the resulting hydration products and their structure [3, 4]. The production of ordinary Portland cement (OPC) is responsible for a considerable portion of manmade CO₂ emissions. This motivates the development of new binders with lower environmental impact. One way of reducing the environmental impact is through partial substitution of OPC with supplementary cementitious materials (SCMs) [5-7].

There is a lack of knowledge on transport properties in blended systems, and the need for more experimental data on the effect of SCMs and water to binder ratio (w/b) on unsaturated transport was recently pointed out in a review [8]. To enable the use of service life models for prediction of durability of concrete structures with

new cementitious binders, there is a need for better understanding of the coupling between microstructural properties and durability [6]. An increased understanding of the moisture dependency of ion transport is a key factor.

1.2 Aim and research questions

The aim of the present research project is to experimentally investigate ion transport in cementitious materials in unsaturated conditions. The investigation is focused on the effect of w/b ratio and the addition of SCMs. The SCMs investigated in this project are ground granulated blast furnace slag (slag) and silica fume (SF). The investigation is summarized by the following research questions:

1. Can resistivity measurements be used for the assessment of the moisture dependency of ionic diffusion coefficients?

Papers I, II, and III

2. How is ionic diffusion related to the moisture content of the materials?

Papers I, II, and III

3. Can moisture transport be related to any other microstructural property of the material?

Paper IV

4. How is moisture sorption changed with age?

Paper IV

5. What are the key factors affecting the simultaneous moisture and ion transport during wick action experiments?

Paper V

6. What relations can be established between the material properties and measured ion and moisture profiles during wick action exposure?

Paper V

1.3 Limitations

Unsaturated ion transport in cementitious materials is a broad research topic, and several major aspects were not included in this project as follows:

- Modeling: This is an experimental project and modeling or development of models is not included.
- At unsaturated conditions, the chemical composition of the pore solution will change and the water activity in the pore system will decrease. The possible effects of this decrease in water activity on the stability of hydrates are not discussed.
- Binding of ions to the charged pore walls and in solid phases is another factor affecting ion transport. The effect of the unsaturated pore system on the binding properties is not investigated.
- Ion transport is by definition the transport of charged species. The system tries to maintain electroneutrality, and therefore, there will be electrochemical aspects that affect the ion transport. The fact that the pore system has charged pore walls will also affect transport, possibly to a larger extent, at low relative humidity (RH). These aspects are not investigated.
- The effect of an unsaturated pore system on gas transport.

2 The porous nature of cementitious materials

In this chapter, the hydration of the most common cementitious materials, OPC with SCMs, is briefly described. The description focuses on the aspects of hydration that are most relevant for this project. These are further discussed in the appended publications. The formation of the pore structure is generally described in Section 2.2, and the motivation for the materials used in this project is given in Section 2.3.

2.1 Hydration of OPC and SCM reactions

Concrete is the most widely used construction material in the world. It contains aggregates, water, a cementitious binder, and admixtures. Historically and currently, OPC is the major constituent in cementitious binders [5]. The main minerals in OPC clinker are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and calcium ferro aluminate (C_4AF). However, there are several other minor elements incorporated in clinker minerals, which affect the structure causing deviation from that of the pure mineral. To highlight the differences compared to pure minerals, clinker minerals are often referred to as alite (C_3S), belite (C_2S), aluminate (C_3A), and ferrite (C_4AF). The proportions between the major elements in OPC can be observed in the ternary diagram of $CaO-SiO_2-Al_2O_3$ in Figure 2.1 A).

Currently, a portion of OPC is often substituted by other materials, commonly referred to as SCMs. SCMs are added to the binder for various reasons, and one of the major reasons at present is their lower emission of carbon dioxide (CO_2). They also affect the workability and durability, and often lower the cost for the producer. SCMs that are commonly used in cementitious materials are industrial byproducts, such as slag, fly ash (FA), and SF. Natural materials such as metakaolin and natural pozzolans can also be used. The important properties of SCMs are that they are reactive and a significant portion of the material is calcium, silicon, or aluminum oxides. These elements are favorable owing to their high mobility on solution and

the fact that they are available in large amounts in the earth's crust. The most common compositions of the main SCMs are shown in Figure 2.1 A). As can be observed, SCMs generally contain less calcium and more silicon and/or aluminum than OPC.

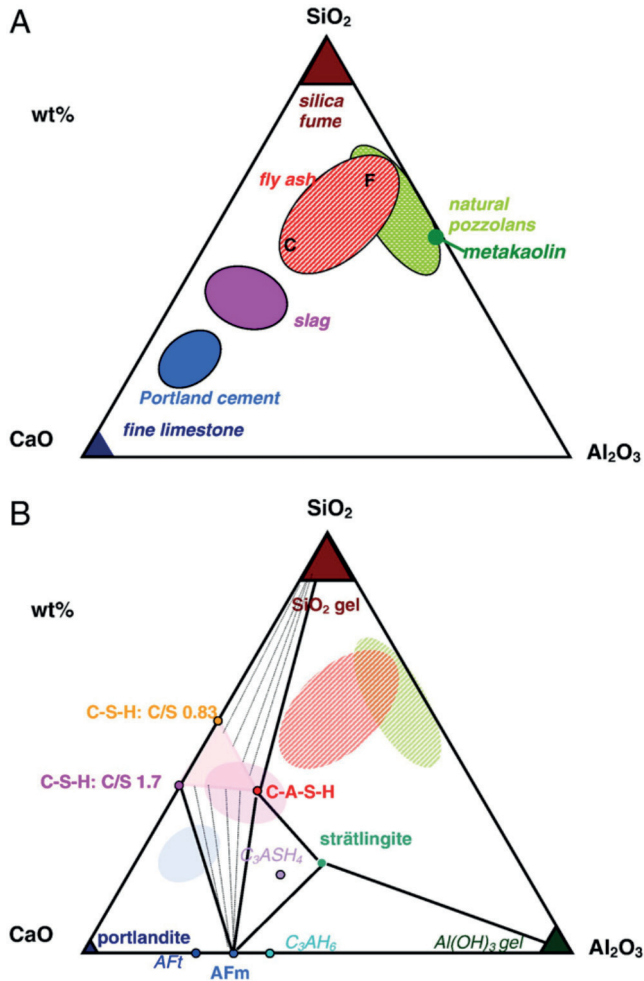


Figure 2.1 Ternary diagram of CaO-SiO₂-Al₂O₃ for cementitious materials.

A) Composition of anhydrous OPC and the most common SCMs.

B) Composition of the most common hydrates in cementitious materials with the composition of the original anhydrous materials in A) shaded underneath.

The figure is adopted from [4].

The chemical and mineralogical compositions of the raw materials used in this project are provided in Papers I–V.

The solid structure in cementitious materials is formed from reactions between the cementitious binder and water, i.e., hydration of the minerals in the binder. During this process, water is consumed, hydrates are precipitated, and the porous structure of the material is formed. The hydration of OPC has been widely investigated; however, it is a series of complex reactions, which is still not fully understood [3, 9, 10]. For the investigations in this project, the dissolution of alkalis is important as alkalis are the main cations in pore solution at later ages. Alkalis, mainly sodium and potassium, are present in OPC as minor elements incorporated in the clinker minerals and as highly soluble sulfate salts. The sulfate salts are dissolved rapidly during contact with water. The sodium oxide (Na_2O) and potassium oxide (K_2O) in the clinker minerals are dissolved at a slower rate during the dissolution of the clinker minerals.

Several hydrates are formed during the hydration of OPC. The main hydration phase is calcium silicate hydrate (C-S-H). The porous structure in cementitious materials is closely related to the structure of C-S-H and its space-filling properties. A key factor affecting the space-filling properties of the hydrates is the mobility of the ions in solution. Calcium and silicon have high mobility and therefore better ability to form hydrates and fill spaces in between the original grains. By contrast, iron and magnesium have lower mobility, and therefore, their hydrates tend to precipitate close to or within the original grain. The most common hydrates in cementitious binders and their chemical composition are shown in Figure 2.1 B).

For the investigations in this project, the formation of calcium hydroxide (CH), often referred to by its mineral name, portlandite, is important as well. The reactivity of the SCMs is strongly related to the pH, and a high pH of the pore solution is required for the reactions to start. The high pH of the pore solution is maintained by the portlandite buffering the pore solution with hydroxide ions (OH^-). The dissolved calcium ions (Ca^{2+}) are also consumed when more C-S-H is formed during the hydration of SCMs. When a large portion of the OPC is substituted by SCMs, all portlandite is consumed and the pH of the pore solution is decreased. The possible degree of substitution varies between different SCMs owing to their different chemical and mineralogical compositions.

In OPC systems, the clinker minerals have different reactivities and are dissolved during different phases of the hydration process. Because the SCM reactions are dependent on the hydration products from the OPC, i.e., the portlandite, the SCM reactions are initiated later than the clinker reactions. Several researchers have

investigated these reactions. It is a complicated series of reactions that are sensitive to several factors such as temperature, pH, water activity, presence of minor elements, and available space, and the kinetics of the reactions are still not fully understood. Currently, the SCM reactions are generally believed to start after approximately the first day or so. Moreover, before this, the SCMs affect the clinker reactions owing to their filler effect, i.e., providing more sites for nucleation of C-S-H [11, 12].

The C-S-H formed from OPC and SCMs has different properties. The chemical composition of C-S-H can differ on both the amount of incorporated water and the calcium to silica ratio (C/S). Alumina can also substitute for silica in C-S-H. Many SCMs have a higher alumina content than OPC, which yields higher incorporation of Al in the C-S-H. The structure of the C-S-H formed is related to the C/S. Generally, C-S-H has a nanocrystalline structure in the short range, but is amorphous at larger scales. C-S-H formed from OPC has a C/S close to two and a fibrillar structure of C-S-H forms. When SCMs are added to the system, the C/S decreases and the structure of C-S-H becomes more foil-like [13].

The relation between the microstructural properties such as C/S, morphology, and amount of C-S-H to moisture and ion transport properties are discussed in Paper III and Paper IV. The composition of pore solutions is used for the analysis in Paper I, Paper II, and Paper III. In Paper I and Paper II, an analytical method was used to assess the composition of the pore solution, and in Paper III, the composition of the pore solution is determined through thermodynamic modeling.

2.2 Pore structure and moisture sorption

The pore structure of cementitious materials is of major importance for durability, as this is the structure where the transport of moisture and ions occurs. Initially, the pore structure consists of the volume filled with the mixing water and the air voids formed during mixing and compaction. The air voids are in the size range of centimeters to millimeters and, generally, these remain filled with air during the hydration process. When hydration starts, the minerals in the binders are dissolved in the mixing water, and the solid phases, i.e., the hydrates, precipitate. During this process, pores of different sizes are formed within the C-S-H gel and in between the hydrates. The pore structure is increasingly refined, and the capillary pores decrease in volume and size. The total volume of the hydration products is smaller than the volume of the mixing water and the binder; this reduction is commonly referred to

as chemical shrinkage. Owing to this difference in volume, parts of the pore system are emptied.

Theoretically, the evolution of the pore structure continues until the system reaches its chemical equilibrium. However, the precipitated hydrates are sensitive to the composition of the surrounding pore solution and most concrete structures undergo a variation in moisture and ion distribution over time. Therefore, in reality, the pore structure of the material changes with time. This topic is further discussed in Paper IV.

As stated above, the main space-filling hydration product is C-S-H. Therefore, the structure of C-S-H is important for the overall pore structure of the material. The C-S-H in cementitious materials does not have a fixed mineral structure. The C/S and the amount of incorporated water vary depending on the composition of the pore solution. The C-S-H has a layered structure and is often compared to an imperfect version of the natural minerals tobermorite and jennite, or their combination.

The pore structure of C-S-H has been discussed by several authors and different models have been suggested [14-20]. The latest research suggests a colloidal model as illustrated in Figure 2.2 A). It is based on units of layers of C-S-H that are structured together in globules. The moisture in between the layers of C-S-H is referred to as interlayer water, and the pores in the globules are referred to as intraglobular pores (IGP). These pores are smaller than 1 nm in pore radius. The globules are packed together in globule flocs. Pores are formed in between the globules in the globule floc. These pores are called gel pores and are divided into two groups based on their size. Small gel pores (SGP) are pores smaller than 3 nm in pore radius, and large gel pores (LGP) have a radius in the range of 3–12 nm. It was recently suggested by Muller *et al.* [19] that LGP are not the characteristic of the C-S-H structure because their volumes decrease with the growth of C-S-H, as illustrated in Figure 2.2 B). They suggest that these pores are formed between the hydrates, i.e., interhydrate pores.

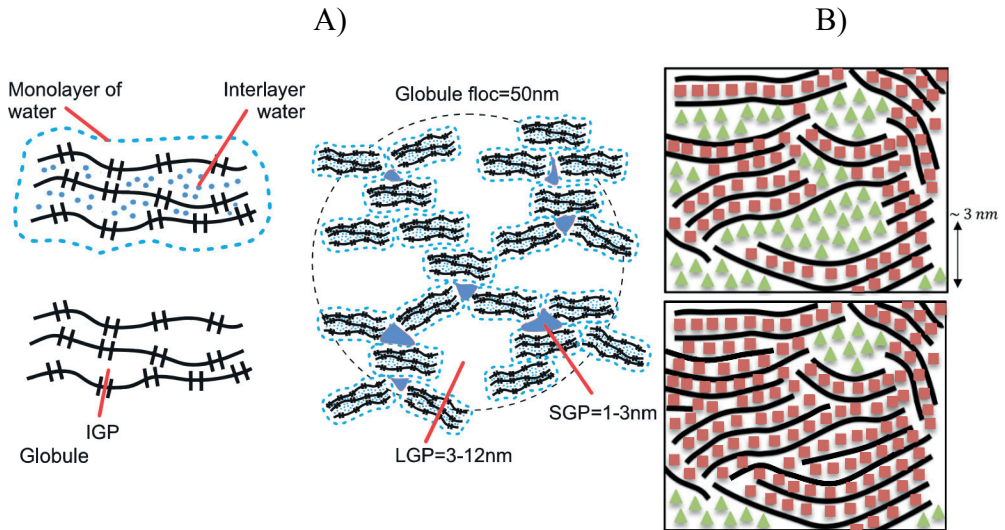


Figure 2.2 A) Illustration of the structure of C-S-H based on Jennings model CM-II. The figure is adopted from [21] based on [18].
B) Suggestion of a refinement of the CM-II model by Muller [22] and Muller *et al.* [19]. Solid lines represent the layers of C-S-H, red squares are interlayer water, and green triangles are gel water. The upper part of the figure shows an early pore structure, and the bottom part shows the same structure at late age when more layers of C-S-H are formed in the large gel pores.

Parts of the originally water filled volume are not filled with hydration products. The pores in between the hydrates that are larger in size than the interhydrate pores are called capillary pores [19, 20]. It should be noted that the definition of gel pores and capillary pores currently deviates from the early definition by Powers and Brownyard [14]. In their work, the gel water was defined as the water in the system that is affected by the absorbing forces on the pore walls, and capillary water is considered as “free water,” i.e., not structured or constrained by the charged pore walls [23].

The volume of capillary pores in a cementitious system is related to the w/b and the ability of the binder to fill the initial water volume with hydration products. This ability, often referred to as space-filling ability, varies between binders [12]. The observed differences between binders are not fully understood; however, they are clearly related to both the volume of the precipitated hydrates and the mobility of ions in the system. Currently, there is also reasonable agreement that a lack of space

is an important factor affecting the growing hydrates, and this is the main factor that limits the growth of C-S-H at later ages [10].

The amount of moisture in a material at a specified RH is shown by the sorption isotherm of the material. When a cementitious material is in equilibrium at 100% RH, the air voids formed during mixing and compaction are still filled with air. It should be noted, however, that when the material is in equilibrium at 100% RH, the RH within the material is lower than 100% RH owing to the high ionic strength in the pore solution. The air voids can be water filled through vacuum saturation, or if that material is submerged in water for a long time, i.e., when there is enough time for the air in the pores to be transported by the water-filled pore system through diffusion. The other parts of the pore system are water filled when the material is in equilibrium at 100% RH. When the RH is decreased, the pore system is gradually emptied. The large capillary pores are emptied first, followed by the interhydrate pores, gel pores, and IGP. However, the emptied pores will also contain some moisture as capillary condensate and adsorbate on the pore wall. In this way, the pore structure remains interconnected, even though the volume that is no longer water filled will change the transport through the pore structure. Several material properties can be derived from the sorption isotherm, e.g., pore size distribution and inner surface.

It can be noted that the use of the term “capillary” is somewhat confusing. On one hand, the term is used to describe the largest pores in the pore system, i.e., “capillary pores” that are larger in size than LGP with a size of up to approximately 12 nm. On the other hand, the term “capillary condensate” is used to describe the nature of the moisture fixation in the pore structure. Moisture fixation in cementitious materials results from two processes: adsorption and capillary condensation. Up to an RH of approximately 45%, moisture fixation occurs through adsorption. Above this RH, the moisture fixation is a combination of adsorption and capillary condensation. The limit of approximately 45% RH refers to the Kelvin equation and the smallest pore radius where the water molecules are believed to be able to form a meniscus in the pore system, i.e., form a “capillary condensate.” The capillary condensation according to the Kelvin equation occurs in the range of approximately 45% to 100% RH, and the material contains capillary condensate in this range [14]. However, the definition of “capillary pores” as larger than approximately 12 nm is not related to the pore radius given by the Kelvin equation. These pores are gradually emptied from 100% to approximately 90% RH. At lower RH values, these pores only contain moisture as adsorbate on the pore surfaces, but there is still capillary condensate in the smaller pores, i.e., the LGP or interhydrate pores. Because of the different definitions, it can be more confusing when terms such “capillary moisture” or “capillary water” are used.

Depending on the geometry of the pore structure in a material, the sorption isotherm will differ between absorption and desorption. The phenomenon is referred to as hysteresis and is important for the understanding of RH and moisture content in cementitious materials [21]. This topic is not investigated in detail in this project. Here, all investigations are performed on water-cured samples and the material is regarded to be on the first desorption isotherm. Owing to the self-desiccation of cementitious materials, this is not perfectly true, especially for materials with low w/b.

In Paper IV, desorption isotherms at two ages, namely 8 months and 4 years, are presented. The evolution of the pore structure between these ages is discussed. The desorption isotherms are also discussed in relation to moisture transport properties and other microstructural properties as mentioned in Section 2.1.

2.3 Choice of materials for this project

The experiments in this project were performed on mortars. Siliceous sand materials according to EN 196-1 with sizes of 0–2 mm were used as aggregates. Four binders, which were mixed to two w/b, were used. The binders used were OPC, and three binary binders with SF (5% by mass) or slag (40% and 70% by mass). These were mixed to 0.38 and 0.53 w/b. Further details are given in Papers I–V.

As stated above, transport in concrete occurs in the pore structure of the paste, but the aggregates still affect transport. This effect has been investigated by several researchers and it has potentially several origins, e.g., the effect of the interface between the aggregates and the paste (interfacial transition zone), the filler effect of the inert particles on hydration, and the fact that the solid grains act as obstacles to transport. However, the size of aggregates also affects the feasibility of using experimental techniques, e.g., the size of the largest aggregates determines what sample size is suitable in cup tests. These are the reasons that mortars were used, i.e., to include the effects of aggregates and at the same time avoiding the largest fraction of aggregates and smaller samples and shorter exposure times in some of the experiments.

The binders were chosen based on those commonly used in civil engineering structures, except for the blend with 70% slag, which is more of an extreme than common choice. Slag was favored compared to FA owing to its better homogeneity over time in chemical and mineralogical composition. Differences in chemical and

mineralogical composition affect hydration and the development of the pore structure, and therefore, complicate comparisons between different studies.

The 0.38 and 0.53 w/b were chosen as one low and commonly used w/b, where the reactions are limited, yielding a low degree of hydration. The higher w/b was chosen to be slightly above what is commonly used in civil engineering structures. The aim was to investigate materials with more initial pore volume, and systems where a significantly higher degree of hydration is expected. It should be noted that the w/b was calculated on equivalent volume ratio, i.e., the volume of binder in relation to the volume of water is equal for all binders. Owing to the differences in density of the raw materials, the w/b differs slightly between binders. The aim of this concept is to enable comparison of the binders' ability to fill the initial capillary pore volume, i.e., the volume of the mixing water.

3 Transport in cementitious materials

In this chapter, transport in cementitious materials is discussed. The discussions and the whole project focus on transport when the pore system is unsaturated, i.e., partially filled with water.

As stated earlier, moisture is closely related to the degradation of concrete structures, because the water in pore systems is the solvent for the ionic species. Generally, ion transport in cementitious materials is described by two major transport mechanisms: diffusive ion transport and convective ion transport. Diffusive ion transport is the transport of ions due to differences in ionic concentration. In a case with pure diffusive ion transport, the material has no moisture gradient and no moisture transport occurs. In this case, there are differences in ionic concentration within the moisture phase, which cause the diffusive ion transport. Convective ion transport is the transport of ions with moisture transport. In a case with pure convective ion transport, the material has no differences in ionic concentration within the moisture phase, and ions are only transported due to a moisture gradient causing moisture transport.

However, in cementitious materials, diffusive ion transport and convective ion transport can rarely or never be separated in an unsaturated pore system in reality. When the ionic concentrations change due to diffusion, the water activity changes, which induces moisture transport. Convective ion transport causes concentration gradients, which induce ionic diffusion. To complicate things further, the interaction between the solid phases and the pore solution has a major impact on transport and needs to be considered in cementitious materials.

These phenomena have been investigated in this project. In Paper I, Paper II, and Paper III, diffusive ion transport and its moisture dependency is discussed, and in Paper IV, the moisture dependency of pure moisture transport is discussed. In these papers, the measured transport properties are discussed in relation to microstructural properties, as outlined in Chapter 2. In Paper V, chloride and moisture profiles after wick action exposure are presented. These profiles are discussed in relation to the transport properties and sorption isotherms presented in Paper III and Paper IV.

3.1 Moisture transport

Moisture transport in cementitious materials occurs in the pore structure formed during the hydration of the cementitious binder. Microcracks and cracks due to loads or restraints also affect transport [24]. These effects are considered to have minor influence on the experimental setups used in this project and are therefore not further investigated or discussed.

Moisture transport in cementitious materials is generally described by two major physical transport mechanisms: water vapor diffusion and liquid water flow. Diffusion is transport due to variations in concentration between different parts of the material, or between the material and the surrounding atmosphere. Diffusion can be described with water vapor content as the transport potential (see Eq. 1).

$$q_v = -D_v \cdot \frac{dv}{dx}, \quad (1)$$

where q_v ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) is the moisture flux in vapor phase, D_v ($\text{m}^2\cdot\text{s}^{-1}$) is the moisture diffusion coefficient, v ($\text{kg}\cdot\text{m}^{-3}$) is the vapor content, and x (m) is the distance. The liquid water flow through materials is due to differences in pore water pressure and is described by Darcy's law as given in Eq. 2 [25].

$$q_l = -\frac{k_p}{\mu} \cdot \frac{dP_w}{dx}, \quad (2)$$

where q_l ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) is the liquid moisture flux, k_p ($\text{kg}\cdot\text{m}^{-1}$) is the permeability, μ ($\text{Pa}\cdot\text{s}$) is the dynamic viscosity, P_w (Pa) is the pore water pressure, and x (m) is the distance.

The total moisture transport, q_{tot} , is the combination of diffusive and liquid moisture transport as given in Eq. 3.

$$q_{tot} = -D_{tot} \cdot \frac{dv}{dx} \quad (3)$$

Here, q_{tot} ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) is the total moisture flux, D_{tot} ($\text{m}^2\cdot\text{s}^{-1}$) is the total moisture transport coefficient, v ($\text{kg}\cdot\text{m}^{-3}$) is the vapor content, and x (m) is the distance.

In reality, however, it is not possible to separate water vapor diffusion and liquid moisture transport in cementitious materials. Owing to the complex pore structure with pores in a large range of sizes, transport will occur as a series of different transport mechanisms. To estimate the moisture dependency of moisture transport in cementitious materials, experimental methods are used. These methods are based on measurements of the total moisture transport and cannot distinguish between water vapor diffusion and liquid flow [26]. This disables the analysis of the contribution of each type of moisture transport on ionic transport.

The fine pore structure in cementitious materials yields a large specific surface area. Therefore, these materials may have a substantial volume of moisture in the adsorbate covering the surfaces of the pore structure. For other porous materials such as amorphous silica and porous glass, moisture transport as surface diffusion can occur in the adsorbed moisture on the pore walls [27, 28]. In a later study on cementitious materials [29], it is stated that surface diffusion is of minor importance. One argument for this statement is that the charged pore walls attract the water molecules, which limit their mobility and decrease transport. However, in materials such as dense cementitious materials with a fine pore structure, surface diffusion could be the main transport mechanism. A recent study by Jacobsen *et al.* [30] investigates the mobility of water in C-S-H. They concluded that the changed structure of C-S-H in systems with SCMs (sugar cane ash in this case), affects the mobility of water close to the surface. The results show that the interaction between water and pore wall is stronger in systems with SCMs, yielding a decreased transport.

The connection between pores of different sizes is of major importance to transport. This effect is often discussed in terms of connectivity between the pores, or tortuosity of the pore structure. The tortuosity of the pore structure can be described as a factor that relates the distance in macro scale to the real distance for a molecule to go through the pore structure. The relation between moisture transport and desorption isotherms, amount of C-S-H, C/S, and morphology of C-S-H is discussed in Paper IV. In this study, a climate box method and a dynamic sorption balance were used to assess desorption isotherms at 8 months and 4 years, respectively. Cup tests were used to assess $D_{tot}(RH)$. The results from the cup tests were evaluated as the fundamental potential, which was then used for the evaluation of $D_{tot}(RH)$. Some of the major results in Paper IV are shown in Figure 3.1. In this study, it is concluded that there is a significant difference in moisture dependency of D_{tot} , as observed in Figure 3.1 A).

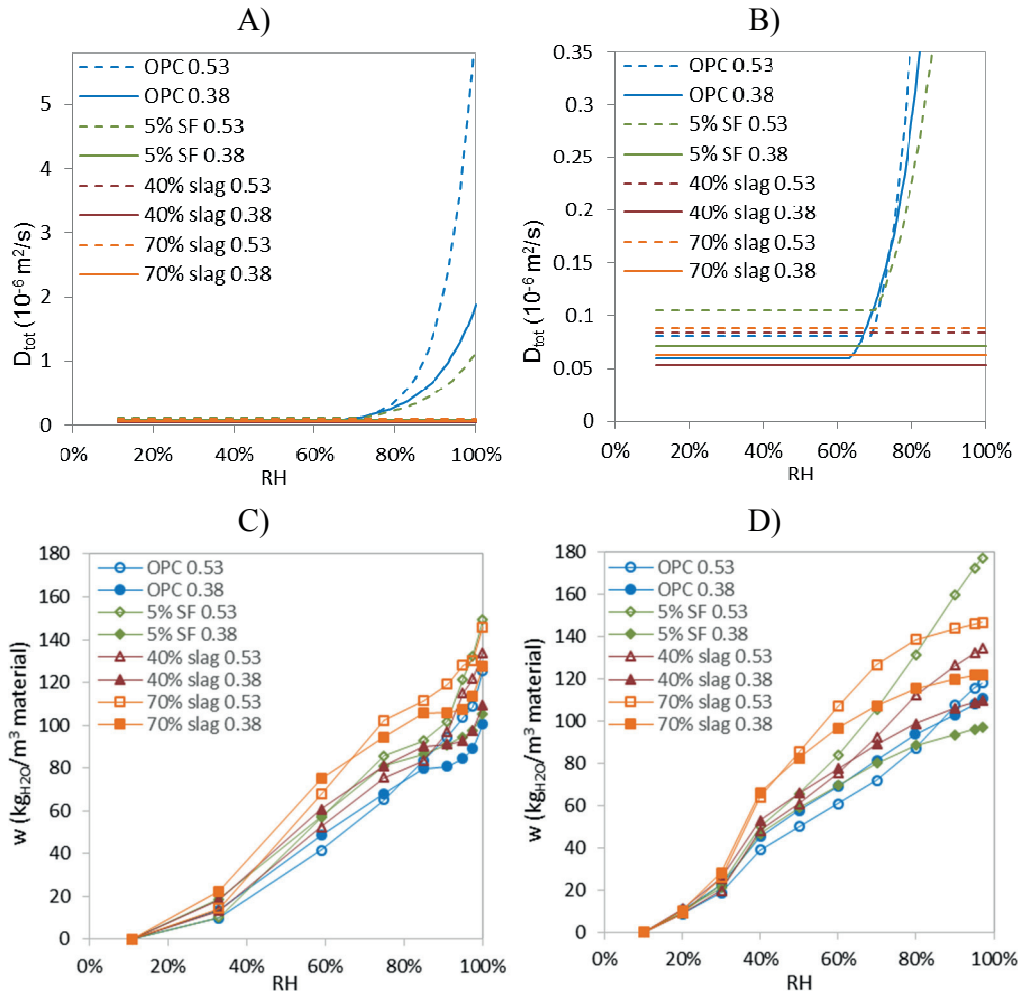


Figure 3.1 Results presented in Paper IV [31].

A) Moisture dependency of moisture diffusion coefficients, D_{tot} .

B) Moisture diffusion coefficients in A), but with a changed y-axis to show the moisture transport at low D_{tot} .

C) Desorption isotherms at 8 months.

D) Desorption isotherms at 4 years.

The results in Figure 3.1 A) and B) show that three mortars have a clear moisture dependency, whereas the others do not. The results in Figure 3.1 B) show that below 70% RH, the w/b is more dominant for moisture transport than the type of binder. By comparing the results in Figure 3.1 A) with C) and D), it can be observed that the moisture content is of the same order of magnitude for all mortars based on the large differences in D_{tot} . No relation between moisture content and moisture transport could be identified.

The results in Figure 3.1 C) and D) also show that the pore structure is refined from 8 months to 4 years for all mortars. The refinement is most pronounced for the mortars with slag. This conclusion is important because cementitious materials are commonly regarded as mature at the age of approximately 8 months. However, in the perspective of moisture sorption, the results in Figure 3.1 C) and D) show that a significant evolution of the pore structure occurs at a later age. The conclusions drawn from a specific experiment may therefore be completely different depending on the age of the material. Further details on the experimental setups and evaluation are given in the paper.

3.2 Ion transport

3.2.1 Ionic Diffusion

Diffusion is one of the physical transport mechanisms for ionic transport in cementitious materials. Diffusion is the transport of ions due to differences in ionic concentration between different positions in the material. The concentration gradient induces differences in chemical potential, and ions are transported from a higher to lower concentration. Similarly, as for moisture diffusion, ionic diffusion is conventionally described by Fick's first law as given in Eq. 4.

$$q_i = -D_i \cdot \frac{dC_i}{dx}, \quad (4)$$

where q_i ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) is the flux of ion i in the bulk material, D_i ($\text{m}^2\cdot\text{s}^{-1}$) is the ionic diffusion coefficient of ion i , C_i ($\text{kg}\cdot\text{m}^{-3}$) is the ionic concentration of ion i in the pore solution, and x (m) is the distance [32]. Ionic diffusion is by definition the transport of charged species and the electrochemical effects are not considered using Fick's law. However, for accurate prediction of ionic diffusion in multi-species

systems such as the pore solution in cementitious systems, the electrochemical effects need to be considered. For prediction of diffusive transport of several ions, the Nernst-Planck equation can be used [33].

For prediction of ionic diffusion, the diffusion coefficient of all ionic species in the solution needs to be assessed. Chloride is a hazardous agent for concrete structures because the chloride ions are well known to initiate reinforcement corrosion. Several standardized test methods are used to measure the chloride diffusion coefficient, D_{Cl} , for cementitious materials in saturated conditions. The evaluated diffusion coefficients are related to the test method and are not necessarily comparable [34].

There is no generally accepted method to measure the chloride diffusion coefficient in partially saturated conditions, and different approaches have been used to investigate this mechanism. This topic is further discussed in Paper I, Paper II, and Paper III. In these papers, resistivity measurements and the Nernst-Einstein equation are used to evaluate the moisture dependency of the chloride diffusion coefficient, $D_{Cl}(RH)$ or $D_{Cl}(S)$. The Nernst-Einstein equation relates the conductivity of bulk material to the ionic diffusion coefficient. The Nernst-Einstein equation is given in Eq. 5.

$$\sigma/\sigma_0 = D_i/D_{0i} \quad (5)$$

Here, σ (S/m) is the bulk material conductivity, σ_0 (S/m) is the pore solution conductivity, D_i (m^2/s) is the calculated diffusion coefficient for ion i in the bulk material, and D_{0i} (m^2/s) is the diffusion coefficient of ion i in pore solution.

To be able to use the Nernst-Einstein equation, the pore solution conductivity is required. The chemical composition of the pore solution can be used to calculate the conductivity of the pore solution. In Paper I and Paper II, a simplified method was used to calculate the pore solution composition for OPC mortars and the Nernst-Einstein equation was then used to calculate the moisture dependency of the chloride diffusion coefficients, $D_{Cl}(RH)$ and $D_{Cl}(S)$. In Paper III, a thermodynamic modeling program, GEMS, was used to enable the calculation of pore solution composition for all mortars. The calculated conductivity of pore solutions used in Paper III is shown in Figure 3.2. As can be expected, the conductivity increases with decreasing moisture content. However, owing to the interaction between the pore solution and solid phases, the increase in conductivity is not linearly proportional to the decrease in moisture content.

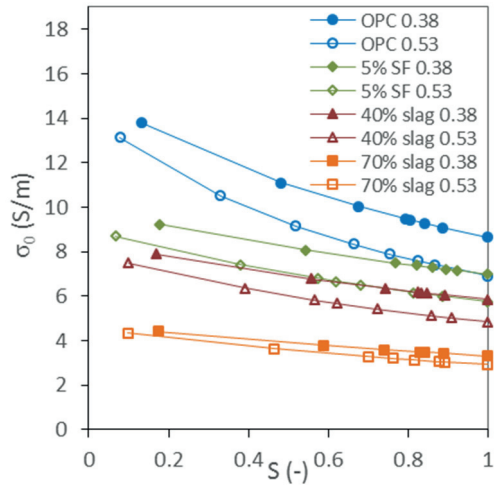


Figure 3.2 Calculated conductivity of pore solutions presented in Paper III [35].

The main results presented in Paper III are shown in Figure 3.3, Figure 3.4, and Figure 3.5. The differences between Figure 3.3 A) and B) highlight the need for considering the conductivity of the pore solution when resistivity measurements are used to assess the transport properties in cementitious materials.

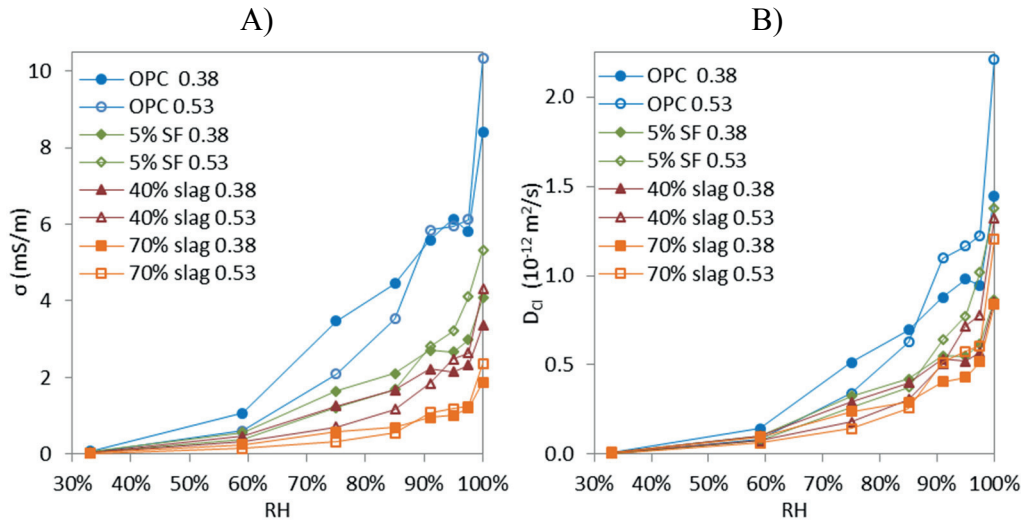


Figure 3.3 Results presented in Paper III [35].
A) Measured conductivity of the bulk material, $\sigma(RH)$.
B) Calculated chloride diffusion coefficient, $D_{Cl}(RH)$.

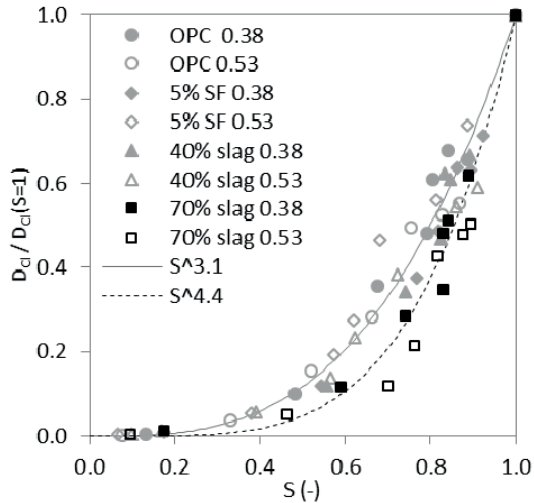


Figure 3.4 Results presented in Paper III [35]. Relative chloride diffusion coefficient related to the degree of saturation of material.

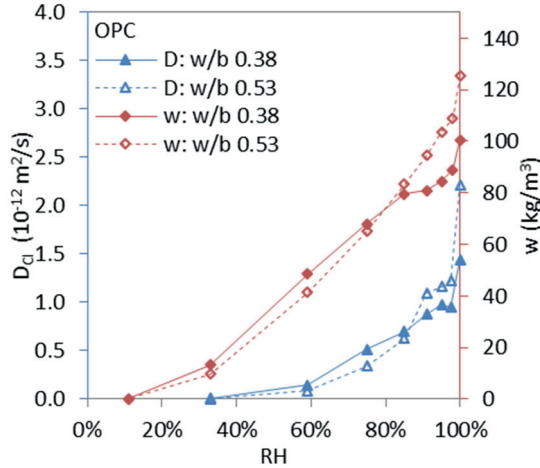


Figure 3.5 Results presented in Paper III [35]. Calculated chloride diffusion coefficients and desorption isotherms for OPC mortars.

Figure 3.4 shows the chloride diffusion coefficients normalized to their values at saturation, i.e., $D_{cl}/D_{cl}(S=1)$ related to the degree of saturation, S . From these results, it was concluded that this dependency does not seem to be significantly affected by w/b , but the composition of the binder affects the relation. In Paper III, it was also concluded that for the individual binders, there seems to be a relation between the moisture content and $D_{cl}(RH)$, which is exemplified by the results for OPC mortars in Figure 3.5. It is interesting to note that from these results, it seems that the diffusion of ions depends on the moisture content in the material, whereas the results in Figure 3.1 show that moisture transport is not related to the moisture content in the material. Further details on experimental setups and evaluation are given in the paper.

3.2.2 Interaction between pore solution and solid phases

As discussed in Section 2.2 above, the evolution of the material continues until the system is thermodynamically at equilibrium, but in reality, this point is never reached. During the service life of a concrete structure, there will be interactions between the material and the surrounding atmosphere, and the kinetics of some reactions is very slow, which also adds to changes of the material over time. Leaching, chloride ingress, and carbonation are examples of degradation processes where ionic species or substances are transported into or out of the material, which

changes the composition of the pore solution. The changed pore solution composition induces interactions between solid phases and the pore solution, e.g., dissolution of solids, ion exchange, and precipitation of new solid phases.

During chloride ingress, chloride is present in the material in several phases. Conventionally, the total chloride content is described with a chloride binding isotherm that shows the relation between “free chlorides,” i.e., chloride ions in the pore solution, and “bound chlorides,” i.e., chemically bound chloride in solid phases and physically bound chloride adsorbed on the pore walls. It should be mentioned that the chloride binding isotherms differ between binders and that the relation is not linear [34].

The chemically bound chloride is mainly present as chloroaluminate hydrates such as Friedel’s and Kunzel’s salts. The formation of these salts can be related to the aluminate content of the binder. The physically bound chloride is adsorbed on the surfaces of C-S-H [36] where OH⁻ is exchanged for Cl⁻ [37]. The amount of physically bound chloride is related to the amount of C-S-H.

Chloride binding and chloride binding isotherms are discussed in the literature, e.g., in [34, 36-42]. It is well recognized that several factors affect the chloride binding capacity of cementitious materials. The aluminate content and the amount of C-S-H are mentioned above, but the pH of the pore solution, temperature, C/S of C-S-H, carbonation, cation of the chloride salt, sulfate ions, addition of SCMs, and degree of reaction of SCMs are also important factors discussed in the literature. Some of these factors are related to each other but the exact relations are still not fully understood. It should also be mentioned that there is no consensus in the literature on the influence of these factors, in particular, when the effect of SCMs is discussed. Similarly, as for moisture transport, chloride binding isotherms are measured as a global relationship and it is not possible to investigate the effect of the individual parameters mentioned above, based on what is globally observed.

There is a lack of studies that investigate the effect of a partially saturated pore system on the interaction between the pore solution and solid phases. The effect of water activity on some cement hydrates has been investigated [43-45], but more knowledge on alkali adsorption and other hydrates is required. The surfaces of C-S-H are known to affect ionic transport in saturated conditions [37]. These surfaces are initially negatively charged, which creates an electrical double layer that increases the diffusion of anions and decreases diffusion of cations. This effect could potentially be increased in partially saturated condition when the large capillary pores are emptied and transport is limited to moisture in capillary

condensate and thin layers of adsorbed moisture on the pore walls. This lack of knowledge limits the possibilities of investigating and fully understanding non-saturated ion transport.

The results presented in Paper I, Paper II, Paper III, and Paper V are based on the assumption that a decreased water activity in the pore system has a minor influence on the interaction between the pore solution and the solid phases. In Paper I, Paper II, and Paper III, the distribution of alkalis between the pore solution and solids is assumed to be similar for all RH, and in Paper V, a similar assumption is made for chloride binding.

In Paper V, the total chloride content is measured in selected points for comparison with chloride profiles measured with microXRF and to obtain an estimation of the chloride binding capacity of the solid phases. In this study, it is concluded that the composition of the binder and its chloride binding capacity are important parameters for the prediction of chloride ingress. It is also concluded that for denser materials with limited moisture transport and no moisture dependency in D_{tot} , the chloride binding capacity seems to be increasingly important for the chloride penetration depth. These conclusions further intensify the need for more knowledge on the effect of a partially saturated pore system on the interaction between the pore solution and solid phases.

3.2.3 Convective ion transport

Liquid moisture transport in cementitious materials with a pore solution containing ionic species will be coupled with ion transport. The ionic species in the solution will be transported with the liquid flow of moisture. This mechanism is often referred to as convective ion transport. In a case with pure convective ion transport, ions are only transported owing to a moisture gradient causing moisture transport and no other mechanism influences transport. This, however, is never the case in cementitious materials.

In cementitious materials, the ionic species in the pore solution have different diffusion coefficients and their interactions with the solid phases vary. These differences induce electrical fields and differences in concentration, which affect the transport and cause ionic diffusion. Simultaneously, a changed ionic strength of the pore solution affects the water activity of the solution. Owing to the moisture dependency of moisture transport, a changed water activity will affect moisture transport in a non-saturated pore system. Consequently, ionic transport and moisture

transport in partially saturated cementitious materials are closely related and difficult to study separately.

In this project, two experimental studies were planned to investigate convective ion transport in partially saturated cementitious systems. The first study is on mortars exposed to wick action. This study is further discussed in Section 3.3, and the results are presented in Paper V. The second study on convective ion transport is a study that aimed at investigating convective ion transport at a well-defined moisture state in a two-step drying experiment similar to that in the study described in [46]. This study was not finalized owing to lack of time within the project. However, some interesting findings from the work are discussed in the following sections.

With the two-step drying method, it should be possible to quantify the total ionic transport in a material at the specified RH. In this method, the ionic species in the pore solution of the original material are used for the investigation, e.g., the alkalis sodium and potassium. The alkalis were chosen because a large portion of the total alkali content is present in the pore solution and because of their relatively high mobility in solution. However, despite these properties, the differences in alkali content within the material are small and difficult to measure. Åhs *et al.* [46] investigated OPC mortars and used SEM-EDS analysis to investigate the potassium profiles.

The aim of this project was to investigate a wider range of RH and binders, and therefore, SEM-EDS analyses were found to be extremely time consuming. Other methods such as LA-ICP-MS and microXRF were evaluated for the analysis, but unfortunately, these methods were not able to detect the differences in alkali distribution within the material, probably because of the extremely low signal to noise ratio. However, it was found that profile grinding in combination with XRF analysis can be a suitable method to measure the alkali profiles. One mortar specimen with 0.38 w/b and 70% slag binder was analyzed with this method. Profile grinding was performed at École polytechnique fédérale de Lausanne (EPFL), in cooperation with Prof. Karen Scrivener, and XRF analyses were performed at Heidelberg Cement Technology Center in cooperation with Dr. Jan Skocek. The composition of the mortar was similar to that in the other studies, but in this study, the specimens were sealed-cured. For the selected specimen, the RH after self-desiccation was 78%. After two years of sealed curing, one surface was exposed to 33% RH and the other surfaces were sealed. The results are shown in Figure 3.6.

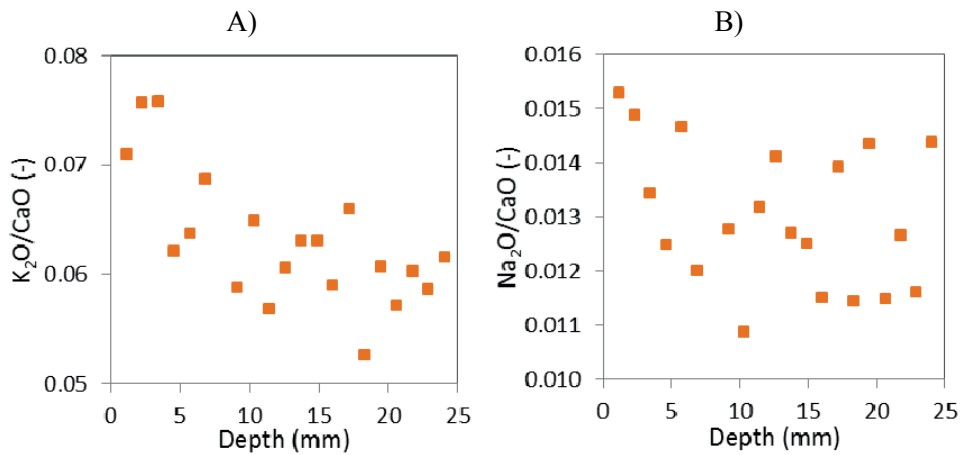


Figure 3.6 Alkali profiles from XRF analysis as **A)** potassium content and **B)** sodium content. The specimen was exposed to drying at 0 mm.

From the results in Figure 3.6, it appears that the method can detect a potassium distribution. The results for sodium are not as clear. It could be because the variation in sodium content in the sample is below the limit of detection for the technique, or that no accumulation of sodium has occurred close to the drying surface. Obviously, nothing can be concluded from a single measurement, but with this in mind, some observations can be made. The accumulation of potassium from 0 to approximately 5 mm in the sample in Figure 3.6 A) indicates that convective ion transport occurs in this mortar at 78% RH. It also shows that the convective transport due to the moisture gradient is larger than the ionic diffusion acting in the opposite direction.

It would be interesting to relate this ionic transport to measured transport properties, e.g., the transport properties presented in Paper III and Paper IV. These transport properties are, however, measured on wet-cured specimens and therefore, may not be fully accurate for the sealed-cured specimens in the two-step drying experiment. With this uncertainty in mind, it is interesting to note that the mortar in Figure 3.6, i.e., 70% slag and 0.38 w/b, has little moisture transport and no moisture dependency in moisture transport. Despite this, the results in Figure 3.6 suggest that convective ion transport occurs in this material, and that this transport mechanism is predominant. The moisture dependency of the alkali diffusion coefficients can be compared to the moisture dependency of chloride diffusion coefficient in Paper III. This is possible because the only factor that differs in the Nernst-Einstein equation is the self-diffusion coefficient of the ionic species in the solution, D_{oi} (m²/s), which is a constant. From Figure 3.3, it can be observed that at 75% RH, ionic diffusion is

limited and D_{Cl} is approximately 25% of its value at saturation. Figure 3.6 suggests that this diffusive transport is subordinate. However, further measurements would be required to conclude the relations between moisture transport, convective ion transport, and ionic diffusion from the two-step drying experiment.

3.3 Wick action experiments

Wick action experiments were chosen to investigate convective ion transport under partially saturated conditions. The basis for these wick action experiments is that the specimens are in contact with an ionic solution on one side, and the opposite sides of the specimens are exposed to air with a controlled RH. The moisture gradient induces moisture transport and convective ion transport through the specimens. The water will evaporate at the drying surface, but the ionic species will precipitate either at the drying surface or within the specimen. The experimental conditions are described in detail in Paper V.

This experimental setup was chosen based on a sensitivity analysis with models, from which it was concluded that the drying condition and the moisture transport properties of the material seemed to be crucial for the appearing ion distribution. This effect is partly because when modeling moisture transport, the moisture flux is separated into liquid water transport and water vapor transport. The liquid transport contributes to ion transport, whereas the gas phase does not. For trying to investigate these relations experimentally, specimens were exposed to wick action, and moisture transport and moisture sorption properties of the mortars were measured separately. The measured moisture transport and moisture sorption properties are reported in Paper IV.

In the experimental wick action study, the specimens exposed to wick action were in contact with a sodium chloride solution on the wet side, and either 33% or 75% RH on the dry side. The chloride and moisture distributions were measured as described in Paper V. However, as for the evaluation of the two-step drying experiment, it was important to find suitable methods for evaluation of the ion and moisture profiles. The commonly used method for evaluation of chloride profiles with grinding and titration was rejected owing to the large number of specimens to be evaluated, and the desire to obtain a relatively high resolution in the profile. Several other methods such as SEM-EDS, require dried and polished samples. This sample preparation is time consuming, but more importantly, both drying and polishing might interfere with the ion distribution and affect the measured profile. The chloride profiles were finally evaluated using MicroXRF because this technique

enables analysis of a freshly broken surface. The measurements were performed in cooperation with the Imperial College in London, UK.

3.3.1 Chloride profiles

The measured chloride profiles are shown in Figure 3.7. These results show that for OPC mortars, chlorides have penetrated the specimens, which is in contrast to the mortars with SCMs that showed significantly smaller penetration depths. In Paper V, it was concluded that for mortars exposed to wick action, the binder composition is a key parameter for prediction of chloride penetration depths, and that w/b and drying RH are of minor importance. In this paper, chloride penetration is also discussed in relation to the transport properties reported in Paper III and Paper IV and chloride binding properties. From these discussions, it is concluded that for mortars with a large moisture transport and moisture dependency in D_{tot} , convective ion transport is the predominant transport mechanism. However, for dense mortars with little moisture transport and no moisture dependency in moisture transport, chloride binding and ionic diffusion are of higher importance and need to be considered.

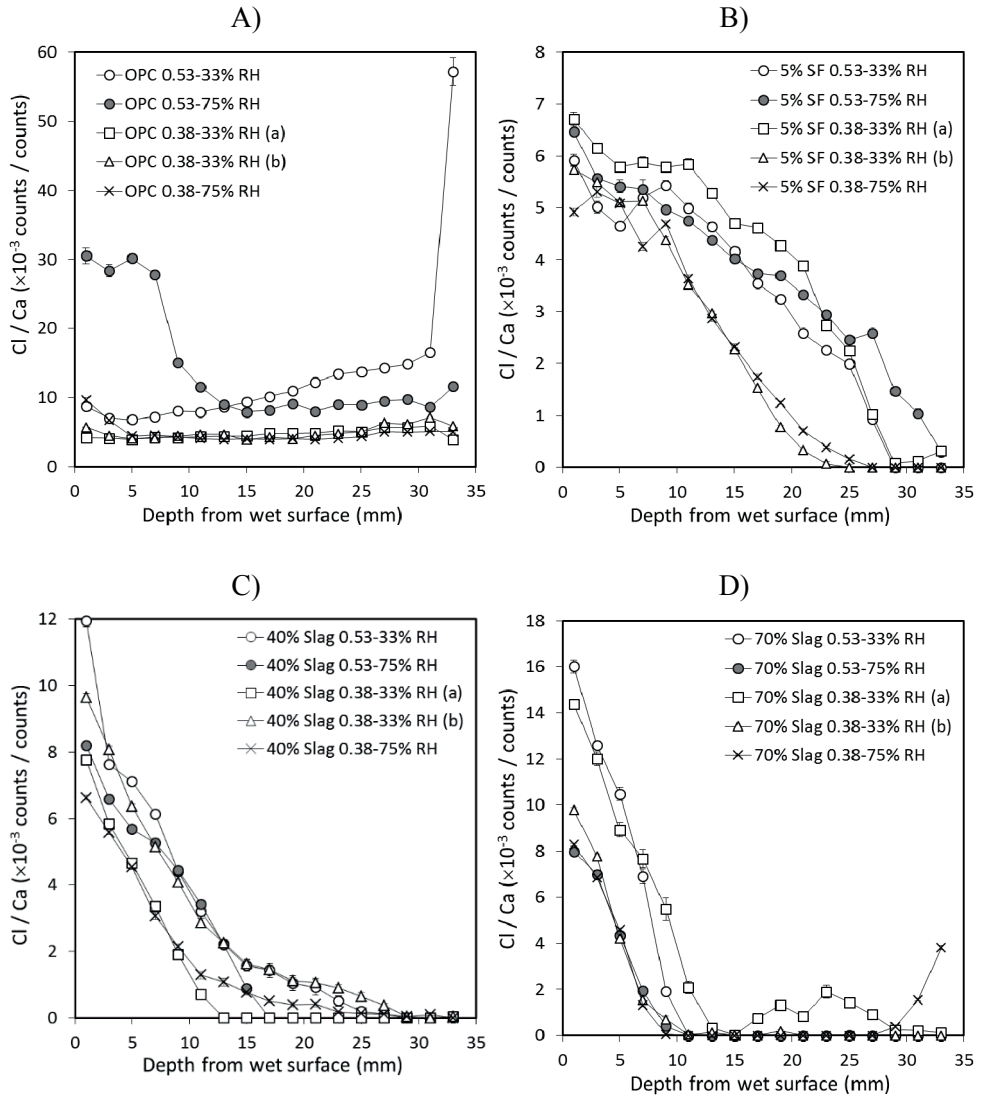


Figure 3.7 Chloride profiles after wick action exposure of mortars with A) OPC, B) 5% SF, C) 40% slag, and D) 70% slag. Results presented in Paper V [47].

3.3.2 Moisture profiles

The moisture profiles were finally evaluated with ^1H NMR relaxometry in cooperation with the Technical University of Munich, Germany (TUM). However, as reported in Paper V, some profiles could not be evaluated owing to lack of specimens. Originally, the evaluation of moisture profiles was planned to be performed using gamma-ray attenuation, but unfortunately, this technique was not available when the measurements were conducted. Other suitable methods were considered prior to choosing the ^1H NMR relaxometry at TUM. The same technique but with a different instrumentation at another laboratory was evaluated without success. X-ray absorption was evaluated and chosen for the evaluation, though with a little hesitation. During the test measurements, large differences in intensity were observed between subsequent images of the same area of the sample. In other studies performed at the same laboratory, e.g., in [48], this problem has been addressed through normalization of the intensity in overlapping regions between images. Based on this, it was decided to use this method for evaluation of all moisture profiles in the wick action study. However, despite thorough attempts to evaluate moisture profiles from these measurements, the results did not show sensible profiles.

The results from the NMR measurements at TUM are shown in Figure 3.8 and Figure 3.9 A). The results are presented and discussed in detail in Paper V. As expected, the results show that the specimens are capillary saturated in the parts adjacent to the exposure solution. In Figure 3.8, in cases A), B), and D), the samples are capillary saturated all the way through the sample, which is explained by the presence of NaCl in the system. The chloride profiles were measured after 30 months of wick action exposure, in contrast to the moisture profiles that were measured after 48 months of exposure. As discussed above, the reason for this delay was the difficulty in finding a suitable method for the determination of moisture profiles. The different exposure times complicate the analysis of the relation between chloride and moisture profiles.

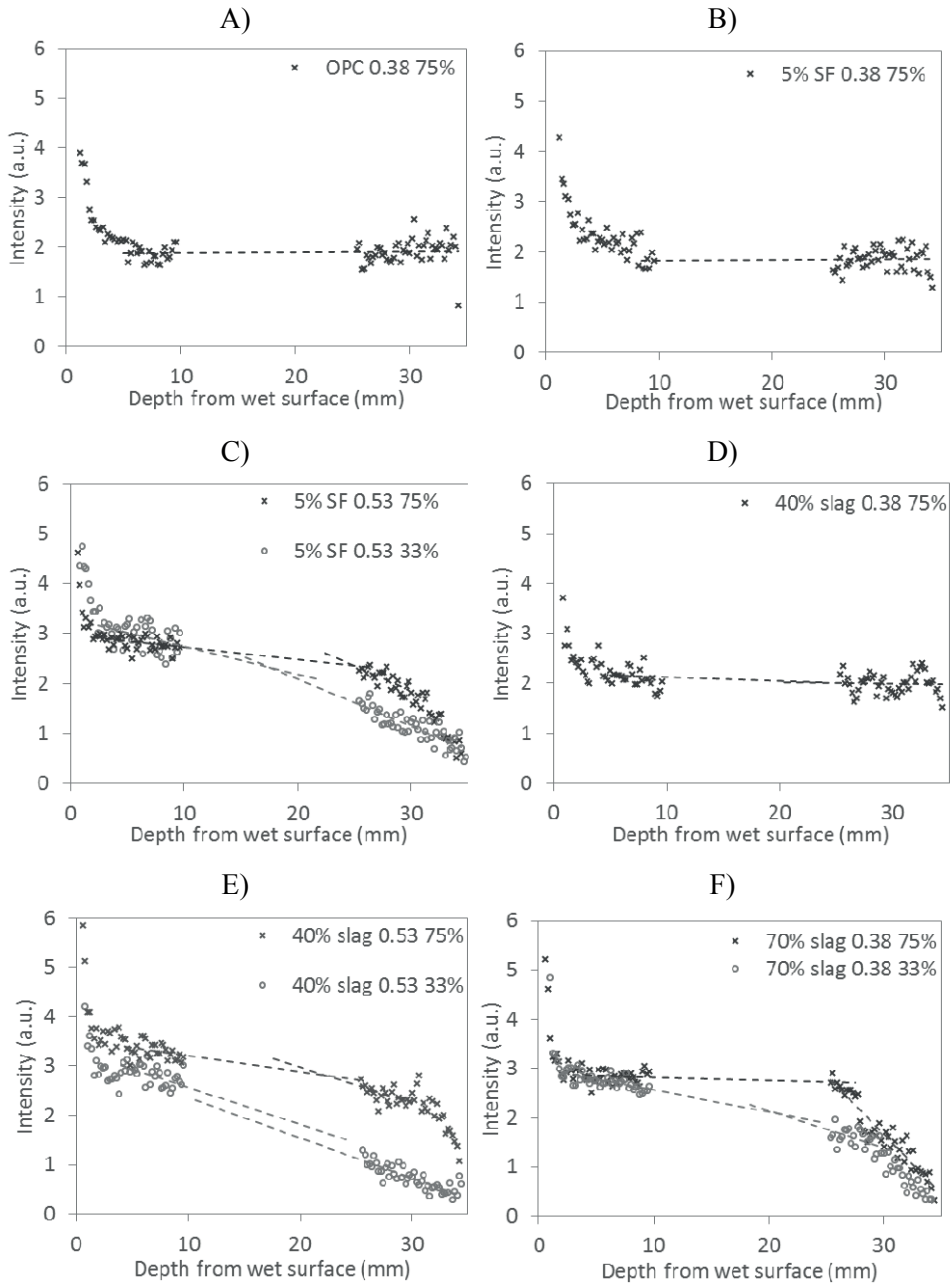


Figure 3.8 Moisture profiles after wick action exposure of mortars. Results presented in Paper V [47].

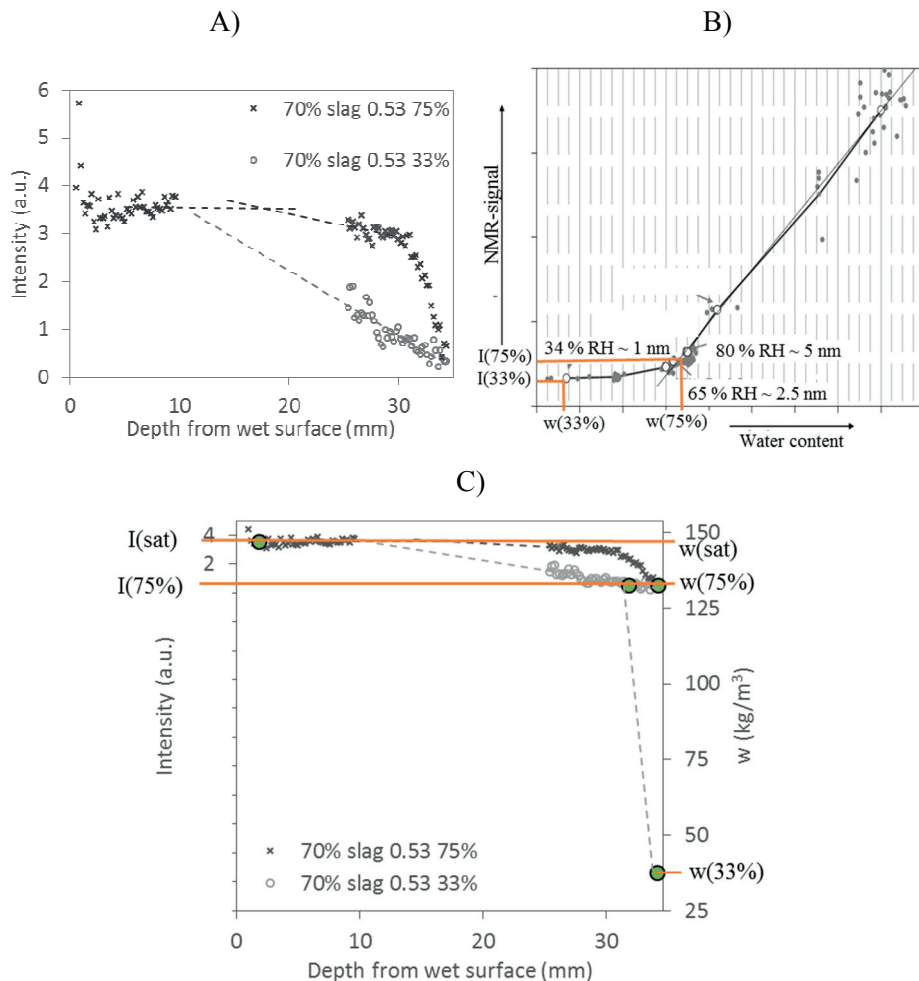


Figure 3.9 A) Moisture profiles after wick action exposure of mortar with 70% slag and 0.53 w/b as intensity measured by NMR.
 B) A general calibration curve illustrating the non-linear relation between measured NMR-signal intensity and water content based on data from [49].
 C) The same moisture profiles as in A), but here, the effect of the calibration curve in B) is demonstrated. The results are presented in Paper V [47].

Another complication for the interpretation of the moisture profiles from NMR measurements is the non-linear relation between the measured response from samples, i.e., measured intensity and moisture content [49, 50]. From the moisture profiles in Figure 3.8 and Figure 3.9 A), it appears that the moisture content close to the drying surface is nearly similar for the two exposure conditions, i.e., 75% and

33% RH, respectively. This could be reasonable for specimens with precipitation of NaCl on the surface. However, for most specimens, chloride has not penetrated them, and these specimens should have different moisture contents at 75% and 33% RH. The reason for this inaccurate appearance of moisture profiles is the differences in sensitivity of the NMR equipment to water in different pore sizes, which yield the non-linear relation between intensity and moisture content shown in Figure 3.9 B). Figure 3.9 A) shows the primary results for 70% slag and 0.53 w/b mortar and in B), a general calibration curve is shown. Figure 3.9 C) shows the same moisture profiles as in A), but here, an axis for moisture content in kg/m^3 is inserted, and the effect of the calibration curve in B) is demonstrated. To quantitatively evaluate moisture profiles from NMR measurements of moisture content, an accurate calibration curve is required.

3.3.3 Moisture profiles related to pore solution composition

The presence of ions in the pore solution complicates the relation between the measured moisture profiles and the measured material properties, i.e., $w(RH)$, $D_{tot}(RH)$, and $D_{Cl}(RH)$, which are measured with no additional ionic species in the system in this project. The sodium chloride from the exposure solution will increase the ionic strength of the pore solution and decrease its RH. This affects the desorption isotherm and the pore structure will be capillary saturated at humidity levels lower than 100% RH. A changed desorption isotherm changes the basis for moisture and ionic transport. For materials with a clear moisture dependency in transport, the ionic strength of the pore solution should hypothetically affect the transport properties, i.e., $D_{tot}(RH)$ and $D_{Cl}(RH)$, in this case.

In this project, the moisture diffusion coefficients and chloride diffusion coefficients are evaluated as a function of RH. As discussed in [51], different moisture potentials can be used to describe transport. The desorption isotherm can be used to recalculate $D_{tot}(RH)$ into $D_{tot}(w)$ or $D_{tot}(S)$, and similarly for $D_{Cl}(RH)$. The choice of potential is important. RH is closely related to the driving potential of the basic physics of moisture transport, i.e., the moisture content of gas phase and Kelvin radius. However, the moisture-filled pore volume, i.e., w or S , has a closer relation to the connectivity of the moisture phase. This property might be of higher importance for ionic transport because RH is largely affected by the ionic strength of the pore solution. This is a topic that requires further research.

The effect of these changed transport properties on the measured moisture profiles is discussed in Paper V. Based on the calibration curve in Figure 3.9 B), the

measured intensity profiles should be proportional to the moisture content profiles in the RH interval of 75–100%. However, the moisture profiles for specimens exposed to 75% RH in Figure 3.8 and Figure 3.9 A) do not agree with what can be expected from the measured moisture transport properties and desorption isotherms in Figure 3.1. One part of the explanation for this is probably the changed ionic strength of the pore solution as discussed above.

The results presented in Paper V contribute to new understanding of the key parameters influencing chloride penetration in cementitious materials with SCMs. These results constitute valuable data for the development of mass transport models for cementitious systems and for the development of new binders. However, it is also emphasized that there is a lack of knowledge on the interaction between ions in the pore solution and solid phases, especially for partially saturated conditions. Additionally, it is concluded that the relation between the ionic diffusion, pore solution ionic strength, RH, moisture content, and degree of saturation needs to be clarified to understand ion transport in cementitious materials under partially saturated conditions.

4 Concluding remarks

The conclusions from the investigations in this project, as outlined in Section 1.2 (Aim and research questions), are discussed and presented in the appended papers. The main conclusions are summarized in this section.

Main conclusions from Paper I, Paper II, and Paper III:

- Resistivity measurements and the Nernst-Einstein equation can be used to investigate the moisture dependency of ionic diffusion coefficients in cementitious materials. However, the variation in pore solution composition with moisture content in the material and binder composition needs to be considered.
- $D_{Cl}/D_{Cl}(S=1)$ is relatively independent on w/b for the individual binders (for the investigated range of w/b and binders), but the relation differs slightly between binders.
- There seems to be a clear relation between $D_{Cl}(RH)$ and the moisture content, w , for the individual binders, although the variation between binders is large.

Main conclusions from Paper IV:

- Between 70% and 100% RH, three mortars show a clear moisture dependency $D_{tot}(RH)$, whereas the other five mortars do not. Below 70% RH, there is no moisture dependency for any mortar and the w/b is more dominant for moisture transport than the type of binder.
- No clear relation could be identified between $D_{tot}(RH)$ and w , C/S or amount of C-S-H. However, it should be noted that the comparison is performed with properties measured at different ages.
- The pore structure is refined from 8 months to 4 years for all mortars and the refinement is most pronounced for mortars with slag.

Main conclusions from Paper V:

- The composition of the binder is the key factor affecting the chloride penetration depth in the wick action experiment. For the studied range of w/b and RH, w/b and moisture potential are of minor importance.
- For mortars with a moisture dependency in $D_{tot}(RH)$, this factor seems to have a large impact on the chloride penetration depth. However, for mortars with no moisture dependency in $D_{tot}(RH)$, chloride binding and possibly $D_{Cl}(RH)$ seem to be the governing parameters for chloride ingress.

5 Future research

Based on the outcome of the investigations in this project, I have the following proposals for future research:

- The use of resistivity measurements is an efficient method for prediction of ionic diffusion properties in cementitious systems. The composition of the pore solution is required to assess the ionic diffusion properties from these measurements. There is a lack of knowledge on alkali sorption in blended cementitious systems and at different RH values. This knowledge is required to improve thermodynamic modeling tools and to accurately predict pore solution composition in cementitious systems.
- There is a need for better understanding of how moisture and ionic transport properties are affected by aging and refinement of pore structure with time.
- As for the effect of SCMs on the moisture transport properties, it should be possible to find a relation between the expected volume of reaction products of SCMs and the available pore volume when the reaction of SCMs occurs. It should be investigated if it is possible to predict the moisture dependency of moisture transport from w/b, substitution level of SCM, and space-filling ability of SCMs.
- There is a need for improved methods on determination of moisture profiles in cementitious materials. In particular, there is a need for quantitative nondestructive methods with appropriate accuracy that can be used in every laboratory and that can be applied to cementitious materials with varying aggregate contents and binder compositions.
- The results from the wick action experiments can be used in a modeling study for developing more precise models and for enhanced understanding of the relation between ion profiles, moisture profiles, and material properties. There is a need for improved models that can predict this type of combined transport. This modeling study should be combined with a

sensitivity analysis on the effect of the different input data required for the model.

- Chloride binding is a key factor for prediction of chloride penetration depths in materials with low moisture transport. There is a need for understanding of how chloride binding is affected by a partially saturated pore system.

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