

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Interaction of water with supplementary cementitious materials

Hydration mechanism, microstructure and moisture transport

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Division of Building Technology

Department of Architecture and Civil Engineering

CHALMERS UNIVERSITY OF TECHNOLOGY

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Abstract

Supplementary cementitious materials (SCMs) offer a sustainable solution to reduce carbon emissions from the production of cement and concrete. This dissertation explores the impact of SCMs and the related additives on the hydration process of cementitious materials, which affects their microstructure and transport properties. Water is involved in the whole life of the cementitious materials thereby determining the hydration, microstructure, and durability. Advanced techniques were employed in this study to investigate the impact of additives on the hydration of C_3S , alterations in water dynamics and microstructure induced by SCMs, and their correlation to transport properties. A device was designed to continuously monitor the effect of SCMs on early hydration, and it was subsequently updated to monitor the hardening process of concrete containing SCMs.

Results show that the dissolution theory fails to explain anomalous hydration of tricalcium silicate at high water to solid ratio. A new hypothesis in this study proposes that calcium silicate hydrate (C-S-H) primarily nucleates within the near-surface region, and this hypothesis bridges the gap between dissolution and protective layer theories. The precipitation involves primary particle nucleation and growth by particle attachment. Acceleration in C-S-H growth, instead of etch pit dissolution, may explain the rapid increase in reaction rate after the induction period. The hypothesis provides a thorough explanation for the impact of potassium salts and pH on the dissolution of C_3S and the precipitation of C-S-H. The newly designed device exhibits excellent performance in monitoring the interaction of water with cement and SCMs. The evolution of electrical conductivity in hydrating pastes closely relates to chemical reaction process. SCMs reduce the initial conductivity of pastes mainly by decreasing alkali concentration. The growth rate of the formation factor replicates the reactivity of different binders. Blending SCMs refines the pore structure, decreases pore connectivity and results in a higher formation factor. A percolation model can be used to demonstrate the relationship between volume of evaporable water and formation factor.

SCMs affect not only the pore structure of hardened cement-based paste (hcp), but also the phase assemblage and water dynamics. The effect of SCMs on mesoscale pore structure can be

well indicated by water vapour desorption isotherms, but effects of ion on water vapour equilibrium pressure must be considered when calculating the pore size distribution. A novel approach works well in evaluating the hydration degree of SCMs by use of water vapour sorption and thermodynamic modelling. Thermoporometry and broadband dielectric spectroscopy effectively characterise moisture distribution and water dynamics in hcp, respectively. SCMs have limited effects on the dynamics of structural water, primarily influencing water dynamics in small gel pores and interfacial polarization. The first drying process decreases the volume of unfrozen water ($< \sim 2.4$ nm) under any level of relative humidity. Gel pores coarsen significantly during the drying between 75 % and 50 %.

Change of microstructure alters the transport of moisture and chloride in hcp. The decrease in both moisture transport coefficient and chloride migration coefficient induced by SCMs is notably more significant at a higher water-to-binder ratio upon extended curing period. The modified moisture transport in blended systems is mainly due to pore structure refinement, specifically the reduction in pore connectivity. Both the formation factor and porosity of small pores determine the moisture transport in hcp, with the formation factor being more significant at high RH and the porosity of small pores being more significant at low RH. The effect of SCMs on chloride diffusion is mainly attributed to their influence on pore connectivity. A simplified model based on the formation factor can be used to estimate the chloride migration coefficient for the blended pastes and mortars.

The upgraded device provides a reliable non-destructive monitoring of concrete performance by measuring electrical conductivity and internal temperature accurately. Formation factor, maturity and ultrasonic pulse velocity are reliable indices for concrete strength; however, formation factor exhibits the optimal performance. This study provides insights into the mechanism of water interacting with cementitious materials and a new non-destructive method to promote the high-quality use of SCMs in sustainable concretes.

Keywords:

Supplementary cementitious materials; hydration; durability; electrical conductivity; formation factor; microstructure; moisture transport

Växelverkan mellan vatten och supplementary cementitious materials

Hydratiseringsmekanism, mikrostruktur och fuktransport

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Sammanfattning

Alternativa bindemedel (supplementary cementitious materials, SCMs) erbjuder en hållbar lösning för att minska koldioxidutsläppen från produktionen av cement och betong, som är en stor bidragande faktor till globala växthusgasutsläpp. Denna avhandling utforskar effekten av SCMs och relaterade tillsatser på hydratiseringsprocessen av cementbaserade material, vilka kan påverka dess mikrostruktur och transportegenskaper. Vatten är involverat i hela livet av cementbaserade material och avgör därmed hydratiseringen, mikrostrukturen och beständigheten. Avancerade tekniker användes i denna studie för att undersöka effekten av tillsatser på hydratiseringen av C_3S , mikrostrukturell förfining genom SCMs och dess relation till transportprocesser, samt bedöma förändringar i vattendynamiken. En enhet designades för att övervaka effekten av SCMs på tidig hydratisering och den uppdaterades senare för att övervaka härdningsprocessen av betong som innehåller SCMs.

Resultaten visar att upplösningsteorin misslyckas med att förklara anomal hydratisering vid höga vatten pulvertal. En ny hypotes i denna studie föreslår att C-S-H främst nukleeras inom när-ytan regionen, denna hypotes bygger en bro mellan upplösnings- och skyddandelagerteorier. När utfällning sker, uppstår en primärpartikel nukleering och tillväxt genom partikel sammanfogning. Accelerationen i C-S-H-tillväxt, istället för gropetsningsupplösning, kan förklara den snabba reaktionshastighetsökningen efter induktionsperioden. Hypotesen förklarar väl upplösning av C_3S och C-S-H-utfällning påverkad av kaliumsalter och pH-nivåer. Den utvecklade enheten fungerar bra vid övervakning av vatteninteraktioner med SCM. Utvecklingen av elektrisk ledningsförmåga i hydratiserande pasta relaterar nära till kemiska reaktionsprocesser och kan klassificeras i fyra faser. SCM minskar den initiala ledningsförmågan för pasta främst genom att minska alkalikoncentrationen. Tillväxthastigheten för formationsfaktorn indikerar reaktiviteten hos olika bindemedel. Inblandning av SCM förfinar porstrukturen genom att minska anslutningen mellan porer och resulterar i en högre formationsfaktor. Övervakning av ledningsförmåga demonstrerar visar på relationen mellan förångbar vattenvolym och formationsfaktorn, vilket underlättar in-situ övervakning av fuktinnehåll.

SCM påverkar inte bara porstrukturen i hårdade cementbaserade pastor (hcp), utan också dess fassammansättning och vattendynamik. Den mesoskala porstrukturen i pastor med SCM kan indikeras väl av vattenångadsorptionisotermer, men jonernas effekter på vattenångjämvikts tryck måste beaktas vid beräkning av porstorleksfördelning. En ny metod fungerar bra för att utvärdera SCMs hydratiseringsgrad genom användning av vattenångsorption och termodynamisk modellering. SCMs ökar både små och stora gel porvolym, mest märkbart vid ett vatten till bindemedel-förhållande på 0,35. Termoporometri och bredbandig dielektrisk spektroskopi karaktäriserar effektivt fuktfördelning och dynamik i hcps, respektive. SCM har begränsad effekt på dynamiken i strukturellt vatten, som främst påverkar vattendynamiken i små gel porer och interfacial polarisation. Den första torkningsprocessen minskar volymen av ofruset vatten ($< 2,4$ nm) under olika nivåer av relativa fuktigheter. Gel porer förstoras avsevärt under torkningen mellan 75 % och 50 %.

Porstrukturen hos hpc påverkas kraftigt av SCMs, vilket kan förändra transportegenskaperna för fukt och klorider. Minskningen av både fuktransportkoefficient och kloridmigrationskoefficient som orsakas av SCM är märkbart mer signifikant i hcp med högre vatten/ bindemedelstal efter en längre härdningsperiod. Förbättrad motståndskraft mot fukt i blandade system beror främst på en förfining av porstrukturen, särskilt minskningen av poranslutning. Både formationsfaktorn och porositeten hos små porer bestämmer fuktransportegenskaperna hos hcp, med formationsfaktorn som är viktigast vid hög relativa fuktigheter och porositeten hos små porer som är viktigast vid låg relativ luftfuktighet. Effekten av SCMs på kloridmotståndet beror på vatten/bindemedelsförhållandet, och en av de främsta orsakerna till minskningen av kloridinträngning är också minskningen av poranslutning som orsakas av SCM. En förenklad modell baserad på formationsfaktorn för hcp kan användas för att uppskatta kloridmigrationskoefficienten.

Den uppdaterade enheten ger tillförlitlig icke-destruktiv övervakning av betonghärdning genom att mäta elektrisk ledningsförmåga och intern temperatur noggrant. Formationsfaktorn och ultraljudspulshastigheten är tillförlitliga indikatorer för betongstyrka. Korrelationer mellan tryckhållfasthet och dessa index har etablerats, med bildningsfaktorn som uppvisar mycket högre noggrannhet. Denna studie ger insikter i mekanismen för vatteninteraktion med cementbaserade material och en ny icke-destruktiv metod för att främja tillämpningen av SCMs i hållbara betongar.

Nyckelord:

Alternativa bindemedel; hållbarhet; hydratisering; beständighet; elektrisk ledningsförmåga; formationsfaktor; mikrostruktur; fuktransport

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List of Publications

This dissertation is mainly based on the work presented in the following publications:

- I. L. Huang, L. Tang, H. Gu, Z. Li, Z. Yang, New insights into the reaction of tricalcium silicate (C_3S) with solutions to the end of the induction period, *Cem. Concr. Res.* 152 (2022) 106688. <https://doi.org/10.1016/j.cemconres.2021.106688>.
- II. L. Huang, L. Tang, I. Löfgren, N. Olsson, Z. Yang, Real-time monitoring the electrical properties of pastes to map the hydration induced microstructure change in cement-based materials, *Cem. Concr. Compos.* 132 (2022) 104639. <https://doi.org/10.1016/j.cemconcomp.2022.104639>
- III. L. Huang, L. Tang, L. Wadsö, I. Löfgren, N. Olsson, Z. Yang, Using water vapour and N_2 isotherms to unveil effects of SCMs on nanopores and evaluate hydration degree, *Cem. Concr. Res.* 164 (2023) 107042. <https://doi.org/10.1016/j.cemconres.2022.107042>.
- IV. L. Huang, H. Jansson, J. Swenson, L. Tang, Z. Yang, Distribution and dynamics of water in the blended pastes unraveled by thermoporometry and dielectric properties, (2023). Submitted manuscript.
- V. L. Huang, L. Tang, I. Löfgren, N. Olsson, Z. Yang, Y. Li, Moisture and ion transport properties in blended pastes and their relation to the refined pore structure, *Cem. Concr. Res.* 161 (2022) 106949. <https://doi.org/10.1016/j.cemconres.2022.106949>.
- VI. L. Tang, D. Boubitsas, L. Huang, Long-term performance of reinforced concrete under a de-icing road environment, *Cem. Concr. Res.* 164 (2023) 107039. <https://doi.org/10.1016/j.cemconres.2022.107039>.
- VII. L. Huang, L. Tang, I. Löfgren, N. Olsson, A. Ahmadi, O. Esping, Y. Li, Z. Yang, Non-destructive test system to monitor hydration and strength development of low CO_2 concrete, (2023). Submitted manuscript.

Additional Publications

Other publications that are related to the content of the thesis are listed below.

- VIII. L. Huang, Z. Yang, Early hydration of tricalcium silicate with potassium hydroxide and sulfate from pore solution and solid view, *Constr. Build. Mater.* 230 (2020) 116988. <https://doi.org/10.1016/j.conbuildmat.2019.116988>.
- IX. L. Huang, L. Tang, I. Löfgren, N. Olsson. Water distribution in green cementitious materials under different relative humidity, *proceedings of ERICA-CASH II Final Conference*, January, 25–27, 2021, Heidelberg, Germany.
- X. L. Huang, Water and alkali salts in the hydrating and hardened green cement-based materials: Hydration process, moisture content and transport, Licentiate thesis, Chalmers Tekniska Högskola (Sweden), 2022.
- XI. L. Huang, L. Tang, Z. Yang, The hydration and drying of concrete monitored by the array sensors, *proceedings of 24th NCR symposium*, August 17–19, 2022, Stockholm, Sweden.

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Abbreviations

w/b	Water to binder ratio
C_3A	Tricalcium aluminate
C_3S	Tricalcium silicate, alite
C-S-H	Calcium silicate hydrate
GEMS	Thermodynamic modelling software GEM-Selektor v3.7
hcp	Hardened cement-based paste
LT-DSC	Low temperature differential scanning calorimetry
PSD	Pore size distribution
RCM	Rapid chloride migration method
RH	Relative humidity
SCMs	Supplementary cementitious materials
SEM	Scanning electron microscopy
UPV	Ultrasonic pulse velocity
VFT	Vogel-Fulcher-Tammann equation
BET	Brunauer-Emmett-Teller

Major notations

σ_{ps}	Electrical conductivity of pore solution
σ_p	Electrical conductivity of paste
σ_c	Electrical conductivity of concrete
F	Formation factor
β	Pore connectivity index
D_v	Vapour diffusion coefficient at steady state
D_w	Total moisture transport coefficient
$D_{v,s}$	Vapour diffusion coefficient by semi-infinite drying
D_{RCM}	Chloride migration coefficient by RCM test
RH_s	Equilibrium relative humidity at the solution surface
RH_o	Observed relative humidity in cylinder pores
$a-F$	Average growth rate of formation factor
$a-UPV$	Average growth rate of ultrasonic pulse velocity
f_c	Compressive strength
ϕ	Water porosity
ϕ_c	Critical volume for percolation of water in hcp
Φ_0	Porosity at which the strength vanishes
E_a	Activation energy

1 Introduction

In this chapter, a concise background of the research area will be presented in section 1.1. The aim of this dissertation will be outlined in section 1.2. The following section, 1.3, will introduce the framework of this dissertation that internally links the different research topics. Finally, the limitations of experimental investigation and framework will be discussed in section 1.4.

1.1 Background

Risks of climate change have emerged gradually and some of them make direct influence on our daily life, such as causing the rise of the sea level and the increase in frequency of severe weather. Some others effects do not directly impact our current life but they are vital for future of homo sapiens [1]. To ensure a habitable climate for present and future generations, it is imperative to achieve the goal of net-zero by significantly reducing greenhouse gas emissions. Concrete is the most widely-used construction materials in the world due to its critical role in housing, transport infrastructure, hydroelectric dams and wind farms. Although the embodied CO₂ emission and energy for the production of one kilo of concrete is lower than most other construction materials, emission from cement clinker production becomes a challenging problem due to the massive demand of concrete [2]. The global production of cement in 2021 is around 4.3 Gt, among which China is accounting for about 55 %, followed by India (8 %), the European Union (4 %) and the United States (2 %) [3]. The total production is expected to grow up to 4.68 Gt in 2050 [4]. Traditional production process of ordinary Portland cement consumes fuel (e.g. coal) in the energy supply and releases massive CO₂ from the decomposition of calcium carbonate (accounting for approximately 60 % of the emissions). It is the third largest energy-consuming industry, which accounts for 6–7 % of anthropogenic CO₂ emissions and 4–5 % of greenhouse gases [5,6].

The effective solutions for reducing emission in the cement industry mainly include using green energy source, carbon capture and storage technologies, and reducing the Portland clinker

content in the cement. On the way to net-zero at 2050, it requires to make cement with clinker portion lower than 0.69 at 2025, and that lower than 0.56 also with 95 % of CO₂ from cement production stored [7]. Substituting clinker with supplementary cementitious materials (SCMs) is the most efficiency way to lower the clinker content in cement [8]. Furthermore, a prolonging of the service life by improving the durability of constructions is a good way to reduce emissions. In the net-zero emission scenario, the longer building lifetimes will result in a 13 % reduction in cement demand by 2050, compared to a baseline scenario with limited material efficiency [3].

SCMs significantly influence the hydration of ordinary Portland cement and the microstructure of hardened cement-based paste (hcp), which consequently affect the properties of fresh mix (setting time and rheology), the hardened properties, and thus the durability of concrete. Hydration of cement blended with SCMs is an interaction between water and these binders. This process involves the dissolution of minerals and the followed precipitation of hydration products from pore solution [9,10]. Water plays a crucial role in the reaction of cementitious materials. It acts as a “carrier” to dissolve ions from mineral surfaces and as “component” to form the chemical structure of hydration products.

Reaction of minerals in clinker with water would be altered by the SCMs. Escalante-García and Sharp [11] found that the hydrations of tricalcium silicate (C₃S), tricalcium aluminate (C₃A), and ferrite phase were accelerated by the replacement of SCMs, while pulverized fly ash did not accelerate C₃S hydration as much as other alternative materials. Hydration of dicalcium silicate (C₂S) was retarded by fly ash at higher temperatures, but it was accelerated by slag or volcanic ash. Many previous publications proposed that the driving force of early hydration is the undersaturation with respect to the dissolution of alite/tricalcium silicate (C₃S) [12–16]. The presence of limestone can accelerate this process by causing a higher undersaturation degree. Conversely, high concentrations of aluminum, which are dependent on the type and chemical composition of SCMs, have a retarding effect on the reaction. Interestingly, high calcium concentrations do not have any adverse effect on hydration kinetics [17,18].

The typical SCMs, such as slag and fly ash, generally have slower reaction rates than the main clinker phase, so it leads to a lower early strength as the SCMs replacement level is increased. Nevertheless, alkali metal sulfates can significantly enhance strength development at both early and later ages while improving workability [19]. After a sufficient curing time, it may induce a refinement in the pore structure, increase in bound water content and cumulative heat release, reduction in portlandite and calcium aluminate monosulfate (AFm) contents, and increase in ettringite content. The dosage of alkali metal sulfates can be adjusted to improve both early and long-term strength of the activated slags based binders [20].

Addition of alkali metal sulfates also impacts the hydration of C_3S [21,22], resulting in changes to the setting and rheology of fresh pastes, as well as the microstructure of both plain and blended concrete [23,24]. During the hydration process without introducing extra alkali salts, the calcium silicate hydrate (C-S-H) phase grows with a morphology of long needle-like structure which eventually link together. In contrast, the presence of alkali metal sulfates or calcium sulfates results in C-S-H growing in a dispersed and needle-like morphology. Furthermore, the sole addition of alkali metal ions causes the formation of a short tree-shaped C-S-H adhering to the surface of the unhydrated particles [22,25]. These different build-up patterns result in a significant difference in the pore structure, ultimately affecting the strength, shrinkage, and durability of the hardened cement-based materials.

The durability of concrete is characterized by its capacity to withstand adverse environmental factors, such as chemical exposure, weathering, and abrasion, while maintaining its initial shape, quality, and intended function [26]. The initial signs of durability issues manifest as material deterioration, which may not pose an immediate safety concern. However, they can gradually lead to structural damage, potentially endangering the integrity of the structures. The presence of water significantly influences the deterioration process of cement-based materials due to its control over transport properties [27,28] and corrosion reactions [29]. Moreover, water confined in hcp plays a critical role in the freezing-thawing damage [30,31] and alkali-silica reaction [32], as these processes are highly sensitive to the amount of water present. Therefore, understanding the effect of SCMs on interaction of water with hcp is crucial for the development of durable concrete structures.

Effects of SCMs on the chloride transport properties have been investigated through experimental and modeling approaches [33–36]. However, only a limited number of publications shed light on the moisture transport properties of hcp containing SCMs. Baroghel-Bouny [37] reported that the addition of 8 %–10 % silica fume in concrete reduced the apparent moisture diffusion coefficient of hcp at a saturation degree higher than 50 %. Saeidpour and Wadsö [38] conducted an investigation on the vapor diffusion coefficient of blended mortar during adsorption and desorption processes using a cup method. They observed that silica fume and slag could reduce vapor transport coefficient reduced by one order of magnitude, which was ascribed to the higher amount of gel pores and lower volume of capillary pores in the blended system. Olsson et al. [39] reported similar effects of silica fume and slag on vapor diffusion coefficient, and it was more pronounced at higher relative humidity levels. Linderöth [40] found that fly ash did not reduce the pore volume but still refined the pore structure. This caused a decrease in moisture diffusion coefficients by a factor of 2 to 5 after one-year curing. The addition of aggregates had very limited effect on the measured pore structure and sorption isotherms of mortar.

The moisture content is a significant factor that affects the chloride ingress in hcp. Chloride migration coefficient becomes higher at a higher moisture level [41]. This is crucial for the understanding and modelling of concrete structures exposed to different environments such as de-icing salt road and marine environments [42]. Leaching, as a kind of interaction with water, leads to change of the microstructure and a peak phenomenon in chloride profile of the exposed concrete. In addition, the splashing zone experiences high frequencies of wet-dry cycles, causing the anomalous chloride profiles in the near surface zone. These factors highlight the importance of considering the effect of moisture content on chloride ingress in hcp containing SCMs.

The deterioration processes are intrinsically determined by the interaction of water and ions in the microstructure of hcp [43,44]. Influence of SCMs on the microstructure and chemical structure of main hydration products, calcium-silicate-hydrate (C-S-H), has been a subject of significant research interest. Berodier and Scrivener [45] found that incorporating SCMs resulted in a lower volume of hydration products than in pastes made with ordinary Portland cement, which in turn increased the total porosity hcp. However, the pore structure was refined due to the filling effect of later age hydration products from SCMs. Several studies have reported that the addition of slag can reduce total porosity at an early stage and refine the pore structure [46]. In previous investigations, it was found that blending of silica fume, fly ash, slag, and metakaolin altered the elastic modulus of hydration products. The specific trend of change is closely related to the water to binder ratio (w/b) and the amount of SCMs [47,48]. It was also shown that the incorporation of SCMs has no effect on the performance of two different types of C-S-H, but it increases the percentage of high density C-S-H in hydration products [49]. A clear understanding of these changes in microstructure and properties is important for assessing the performance of concrete containing SCMs.

Water confined in the microstructure of hcp exhibits distinct structural and dynamical properties from bulk water [50–52]. Behavior of water in hcp at low temperature is a crucial factor in determining the frost damage of cement-based materials. The phase transition of freezable water to ice creates hydraulic pressure by expelling the unfrozen water, and it causes the cryo-suction process that forces the liquid to move towards the frozen sites [53]. These water migration processes are closely related to the distribution of freezable and unfrozen water in the porous matrix, as well as the dynamics of water confined in the nanosized pores. However, there is a lack of a comprehensive and general understanding of the confined water dynamics in hcp. Thus far, no investigation has been undertaken to explore the influence of SCMs on the water dynamics in hcp.

Use of SCMs for production of low CO₂ concrete affects the reaction kinetics, meaning deviation in early hardening properties such as setting time and the strength development. The

transition of a fluid to a hardened state during the hydration process governs the construction progress, the quality, and cost of the concrete structures. The hardening process determines the appropriate time for demoulding and further procedures. Furthermore, the evolution of the specific yield stress, as pointed out by Reiter et al. [54], is of great significance for digital fabrication (3D printing) due to the loading of concrete during fabrication. Traditional off-site quality control methods are time-consuming and require manual operation, making them inadequate for the quality control of fast or automated construction [55]. Additionally, hardening is known to be sensitive to temperature changes, so traditional methods must control the temperature and humidity of the environment, which can differ from the actual field site, particularly during the construction of large concrete structures [56]. Therefore, an efficient and high-quality non-destructive testing method would be very helpful in mitigating these problems in the use of SCMs in construction and digital fabrication.

1.2 Objectives

Replacement of cement clinker with SCMs is effective to reduce emissions in construction sectors. Slag and fly ash, sometimes with limestone, are the most widely and well-used alternative binders for making sustainable concretes. This thesis aims to investigate the interaction of water with the cement-based materials blended with large amount of these SCMs. The interaction at initial stage is called hydration in terminology of cement research. Reaction in this period will determine the workability of cement-based materials, which will also furtherly influence the performance of the materials at hardened state. Hydration of binders consumes the water and produces new phases to induce the transition of a flowable fresh state to a rigid hardened state thereby building links between particles. Space between the particles will be filled gradually as the hydration continues to reach a certain degree. Microstructure has been formed during the hydration and hardening process. It determines the deterioration process of the cement-based materials caused by the interaction with water and ions from the environment in service. To understand the effects of SCMs and their related ions on the above-mentioned properties, the subsequent problems have been tackled in the current work:

- How does water interact with the main mineral C_3S with the presence of C_3A , K_2SO_4 and KOH at the early stage thereby focusing on the nucleation of hydration products?
- How does the SCMs influence microstructure of pastes during the hydration up to the main peak, as determined by a novel in-situ monitoring method?
- What is the underlying mechanism between the interaction of water with the porous structure of the hardened pastes with SCMs and its reflection of the microstructure?

- How do SCMs modify the moisture and ion transport in hcp, and which parameter is the key determinant of the moisture and chloride transport properties?
- How does the upgraded non-destructive method work for onsite monitoring of hydration and strength development.

1.3 Thesis framework

This dissertation is dedicated to investigating the interaction of water with cementitious materials containing large volume of SCMs, spanning from the early stages to the long-term service. It mainly includes the content of 7 related papers as shown in Figure 1.1. Chapter 1 is about the background, objectives, framework, and limitations of this dissertation. Chapter 2 describes the information of materials, experimental procedures and test methods applied during the study. Chapter 3 to 6 demonstrates the main experimental results and discussions.

Chapter 3 starts with questioning the correlation between the dissolution rate and hydration rate of main minerals in the bulk pore solution. A novel hypothesis is proposed to understand the hydration mechanism with respect to the precipitation of C-S-H through a non-classical nucleation process. The research subject has expanded from pure minerals to SCMs substituting Portland cements. Effect of SCMs and w/b on the hydration induced microstructure change has been investigated in detail. This chapter comprises the content of paper I and II.

Chapter 4 consists of content from papers III and IV. Paper III presents a comparative study of pore structure in hcps with SCMs by water desorption isotherm. Dynamic water vapor desorption data were used to calculate the pore size distribution based on the principles of interaction between water and porous structure of hcp. Paper IV explores the correlation between water behavior and microstructure of hcp by thermoporometry method. The dynamics of water confined in nanopores were also characterized by broadband dielectric spectroscopy. The interaction of water with hcp was studied under various low temperatures conditions.

Chapter 5 comprises content of paper V and VI to discuss the effect of SCMs on the moisture and chloride transport in hcps. The moisture transport and chloride migration in the blended materials were correlated to the pore structure. Refinement effect of SCMs on the microstructure will be clearly indicated by a comprehensive analysis of various parameters indexing the pore structure.

Chapter 6 presents the main results of paper VII, in which an upgraded design of device was used to monitor the hydration and hardening of concrete containing SCMs. The monitored properties will be correlated with traditional indices measured by standard methods. The

function of upgraded device will be evaluated by comparison with the widely used method, ultrasonic pulse velocity test.

Chapter 7 concludes the major findings in this study and proposes prospects for future research to address the unresolved problems.

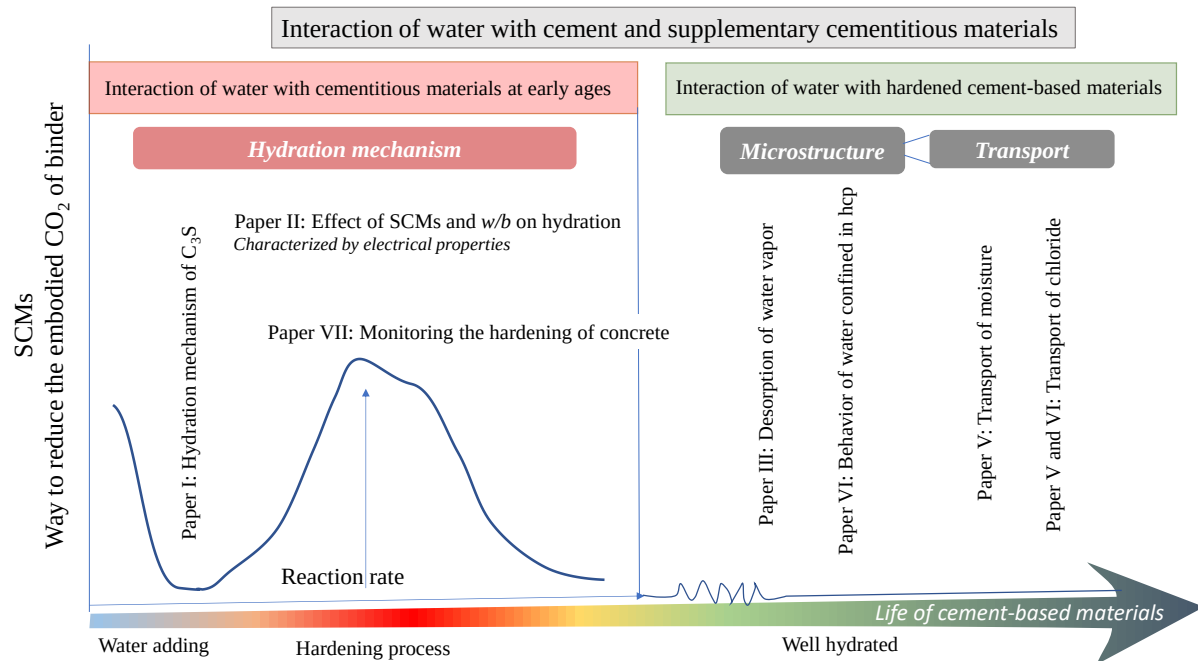


Figure 1.1. The research framework of this dissertation.

1.4 Limitations

The oxide compositions of binders were determined using X-ray fluorescence, and therefore they do not represent the actual concentration of dissolvable alkalis in materials. Because the conductivity of the pore solution is influenced by the types and concentrations of ions in pore solutions, solubility of the chemical composition is important for accurately predicting the electrical conductivity of the pore solution. To address this problem, a modification of the equation for calculating alkali concentration was introduced, but some discrepancies still exist between the calculated and actual concentrations due to the inaccurate evaluation of calcium and sulfate ions in the pore solution. Furthermore, this study was only focused on three kinds of SCMs, but there are many newly emerging alternative materials, such as calcined clay. Validation of the method with other SCMs is needed for promoting its application.

The method for determining water content in hcp neglects the effect of carbonation, which may overestimate the evaporable water content, although the effect is very minor in the early stages of hydration. Because the moisture transport coefficient was measured with small samples, the size effect needs to be considered if the model is to be applied for predicting moisture transport

in practical concrete structure.

Some assumptions in this dissertation may need further verification. It was assumed that the solvent exchange treatment by isopropanol had similar effects on morphology of hydration products for all samples, and the freeze-dry had the negligible effects on the sizes and number of etch pit on particles surface. This makes impact on the discussion based on the size of nucleated particles. The freezing and thawing experience will alter the microstructure and the moisture distribution in hcp. Although the experimental results showed that the fast low-temperature DSC test had minor nonreversible effects, the reversible effect needs to be assessed for a good understanding of real moisture state in hcp. For the estimation of hydration degree with desorption data, it was assumed that the water amount in the interlayer of C-S-H is similar in SCMs blended hcp. The presence of slag and fly ash reduces the Ca/Si ratio in C-S-H, and in turn it lowers the water content in the interlayers. Neglecting this change leads to an underestimation of the hydration degree due to the lower calculated C-S-H content based on water vapor sorption.

The primary focus of investigation was on the moisture transport properties of paste. However, the presence of aggregates in concrete results in different moisture transport behavior as compared to hcp. Hence, it is necessary to conduct further research to extend the applicability of the theory from hcp to concrete by considering the interfacial transition zone and volume of aggregates. Monitoring of concrete was conducted on a lab scale without considering the presence of reinforcement in practical. The steel bar is high conductive component and may alter the calibration factors, possibly limiting the use of parameters in this study to a real construction.

2 Materials and methods

This chapter presents an overview of the raw materials, the procedures employed for mixing and casting, and the measurement settings of various machines. Furthermore, an upgrade of test system for monitoring conductivity will be elaborated. In addition, methods are introduced to determine the moisture content in hcp.

2.1 Raw materials

2.1.1 Minerals and salts

Pure minerals, including triclinic tricalcium silicate (C_3S) and cubic tricalcium aluminate (C_3A), were procured from DMT Materials Technology Co., Ltd. The specific surface area of C_3A powder was measured to be $1.26 \text{ m}^2/\text{g}$ by BET method with N_2 sorption. C_3S powder has a purity of 98.57 % (Rietveld refinement results from [57]), with a specific surface area of $1.92 \text{ m}^2/\text{g}$. The information of particle size distribution of C_3S powder is available in [58]. Analytical reagents like sulfuric acid, $LiCl$, $NaCl$, KCl , KOH , K_2SO_4 and $Mg(NO_3)_2$ were employed for the experimental investigation as additives or relative humidity (RH) controller. Superplasticizer (PCE) used in the concrete samples was Master Glenium 5118 (with 17.5 % dry substance) purchased from Master Builder Solutions.

2.1.2 Cement and supplementary cementitious materials

The cement in all experiments is the Portland cement (CEM I 52.5 R) from CEMENTA with a Blaine surface of $525 \text{ m}^2/\text{kg}$. To substitute the Portland cement, three types of SCMs were used: ground granulated blast-furnace slag with a Blaine surface of $420 \text{ m}^2/\text{kg}$ from Thomas Cement, fly ash from CEMENTA, and limestone powder from Nordkalk. The type of limestone is Limus 15 with a D_{50} of $18 \text{ }\mu\text{m}$. Table 2.1 shows the chemical composition of each binder referred to [59]. The limestone consists of approximately 89 % calcite and 9 % SiO_2 . The detailed information about particle size distribution of the binders is presented in [58].

Table 2.1. Chemical composition of different binders (*LOI*: loss of ignition; δ_i : mole of chemical composition per gram binder).

Chemical Composition	CEM I 52.5 R		Slag		Fly ash		Limestone
	wt %	δ_i (mol/g)	wt %	δ_i (mol/g)	wt %	δ_i (mol/g)	wt %
CaO	62.2	1.11×10^{-02}	39.11	6.98×10^{-03}	5.1	9.11×10^{-04}	49.5
SiO ₂	19.6	3.06×10^{-03}	36.63	5.72×10^{-03}	54.6	8.53×10^{-03}	9.0
Al ₂ O ₃	4.5	4.41×10^{-04}	13.56	1.33×10^{-03}	22.4	2.20×10^{-03}	0.6
Fe ₂ O ₃	3	1.88×10^{-04}	0.49	3.06×10^{-05}	8.7	5.44×10^{-04}	0.3
SO ₃	3.5	4.38×10^{-04}	0.27	3.38×10^{-05}	0.8	1.00×10^{-04}	0.03
MgO	3.5	8.75×10^{-04}	8.52	2.13×10^{-03}	1.8	4.50×10^{-04}	-
K ₂ O	1.01	1.07×10^{-04}	0.57	6.06×10^{-05}	2.1	2.23×10^{-04}	0.3
Na ₂ O	0.27	4.35×10^{-05}	0.42	6.77×10^{-05}	1	1.61×10^{-04}	0.1
Cl	0.07	1.97×10^{-05}	0.009	2.54×10^{-06}	-	-	-
Sulfide	-	-	0.73*	-	-	-	-
<i>LOI</i>	2.5		-1.07		3.5		40.1

*Note: The sulfide in slag will be oxidized during the LOI test, so this induces an increase of weight. Although the hydration also makes oxidization of sulfide [60], we assume that its oxidization is rare due to the low hydration degree at the early age.

2.1.3 Aggregates

Aggregates used in the casting of fly ash blended concrete (C145) and slag blended concrete with *w/b* of 0.55 (C255) were siliceous type, and they were obtained from the building materials market in Gothenburg. The loose bulk density of the aggregates, which consists of sand and stones with a size distribution ratio of 85.2 %:14.8 % (1–4 mm: 4–10 mm), is $1.74 \times 10^3 \text{ kg/m}^3$, while the close packing density is $1.96 \times 10^3 \text{ kg/m}^3$. Different aggregates were used for casting the slag blended concrete with *w/b* of 0.45 (C245) and ternary concrete (C338). Sand with a density of $2.66 \times 10^3 \text{ kg/m}^3$ was sourced from Eurosand, and stones with a density of $2.85 \times 10^3 \text{ kg/m}^3$ were obtained from Skanska.

2.2 Preparation of samples

2.2.1 Hydration of minerals

The hydration of C₃S and C₃S:C₃A (wt, 90 %:10 %) mixture system was investigated using different solutions including deionized water, KOH solution, and K₂SO₄ solution. The solid to solution ratio was 0.5, and the samples were stirred for 1 min in a glovebox filled with N₂ gas and then cured under such an environment to avoid carbonation before hydration stopping. The hydration was stopped by two different methods, solvent exchange with isopropanol and freeze drying by immersing the samples into liquid nitrogen. The detailed description of sample treatment procedure can be found in paper I and VIII.

To investigate the hydration of C₃S under high solution to solid ratio conditions, 0.1 g of C₃S was mixed with 10 g (ratio of 100:1) and 20 g (ratio of 200:1) solutions in an ampere bottle. The mixture was then quickly placed into the channels of a calorimeter. To collect sufficient

solid residue for other tests, parallel experiments were conducted using materials five times the amount used in the calorimetry test. Solid residues were obtained by suction filtration, and they washed three times with an adequate volume of isopropanol to stop hydration. The washed residues were then vacuum dried at 40 °C for 48 h and sealed in a tube for analysis.

2.2.2 Preparation of cement-based materials

The mixture proportion of 11 paste samples is presented in Table 2.2. To create binary systems, Portland cement was substituted with 35 % fly ash or slag by weight. In the ternary system, Portland cement was replaced with 35 % slag and 16 % limestone. The pastes were mixed with three different *w/b* of 0.35, 0.45, and 0.55, except for the fly ash pastes with two *w/b* (0.35 and 0.45), as the future availability of fly ash is limited.

Table 2.2. The mixture proportion of pastes.

Samples	Binders				<i>w/b</i>
	Cement	Fly ash	Slag	Limestone	
P035	100 %	-	-	-	0.35
P045					0.45
P055					0.55
P135	65 %	35 %	-	-	0.35
P145					0.45
P235	65 %	-	35 %	-	0.35
P245					0.45
P255					0.55
P335	49 %	-	35 %	16 %	0.35
P345					0.45
P355					0.55

Pastes were mixed by a planetary mixer with 100 stainless steel balls (16 mm in diameter) in the bowl to ensure homogeneity. The mixer's agitator speed was set at 75 revolutions per minute with 7 rotations per revolution to prevent ball bouncing. Detailed description of mixing procedures was illustrated in the licentiate thesis [58]. After well-mixed, pastes were casted in different containers for further experiments.

Some specimens were cast in zip bags with dimensions of 150 mm × 200 mm. To facilitate the subsequent crushing, the freshly mixed pastes were rolled to a uniform thickness of approximately 1 mm prior to bag sealing. After a week of sealed curing, all samples were removed from the bags and crushed to particles with sizes around 1 mm. These particles were then cured in water within a sealed container of 1 L volume, with a control of the water mass (about 15 % of the particle mass) to ensure sufficient moisture but minimize leaching.

After being water-cured for two months, a portion of the particles was transferred to conditioning boxes maintained at four different levels of relative humidity (97.6 %, 75.5 %, 54.4 %, and 33 %), which were controlled by saturated salt solutions at 20 °C. Measurements

were conducted on samples that had been conditioned for 1.5 years. The total amount of evaporable water content in these samples was determined by subjecting the particles to vacuum drying at 25 °C for a week. Additionally, after 6-month curing a subset of each sample was conditioned at 11 % relative humidity, controlled by a saturated LiCl solution, for one year. The curing temperatures were held constant at 20 ± 1 °C throughout the experiment.

Some fresh paste was cast in polypropylene tubes and sealed with lips. To prevent inconsistencies caused by bleeding, the tubes were placed on a rotator at a speed of 12 rpm for 24 h. The samples were then stored in a curing room with a constant temperature of 20 °C for a period of 390 days (d). Afterwards, the tubes were wet cut properly from the top with a constant water flow using an electric diamond saw. Details about the cutting protocol are described in [28] for the measurement of moisture transport properties.

Table 2.3 shows the mixture proportion of concretes containing SCMs. Concretes were mixed using a self-falling mixer with a capacity of 50 liters. The water and binder were initially mixed for 2 min, and then the aggregates were gradually added to the mixer and mixed for an additional 5 min. The fresh concretes were cast into a container as depicted in Figure 1 (left side), and a board with an array of sensors was fixed in the container before casting. Once the container was filled to a specified height (10 mm above the first row of sensors), it was carefully vibrated if needed, and then sealed at the top to ensure minimal moisture loss. The samples were then placed in the laboratory room at either Chalmers (22 ± 1 °C) or Thomas concrete lab (19 ± 1 °C), and data collection from conductivity test began approximately 10–20 min after mixing with water.

Table 2.3. The mixture proportion of concretes (kg/m³).

Mix ID	Cement	Slag	Fly ash	Limestone	Water	PCE	Sand (<4 mm)	Coarse aggregate (4–10 mm)
C145	286		154		201	3.2	1411	246
C245	280	151			194	3.0	954	795
C255	247	133			209	2.7	1449	256
C338	242	173		79	187	4.0	953	780

2.3 Measurement procedures

2.3.1 Monitoring of electrical conductivity

Electrical conductivity of paste was tested by four electrodes positioned in the Wenner configuration [61]. The old setup of the device and measuring procedure have been illustrated in detail in paper II and licentiate thesis [58,59].

The monitoring system was upgraded in paper VII to measure the hydration of concrete at

various depths by accounting for temperature and dimension effect. Figure 2.1 presents the updated version based on the previous system, which includes an additional sensor to measure the temperature at each row. These sensors were calibrated to provide an accuracy of ± 0.2 °C. The measurement of each depth was performed sequentially, from the top to the bottom of the sample, and each instant measurement took approximately 0.1 seconds. Data were recorded every 5 min during the first 24 h and then every 10 min from 1 day to 7 d. Subsequent data was collected at selected ages, such as 14 and 28 d, to capture the later stages of hydration.

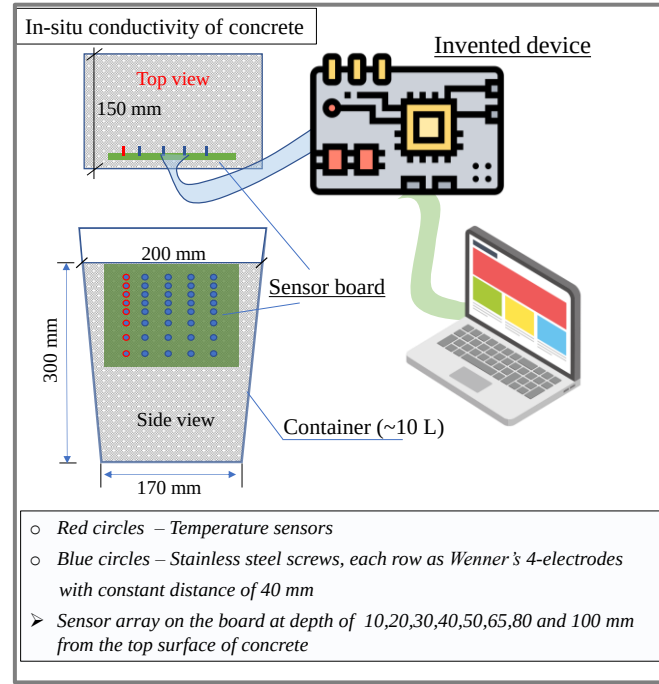


Figure 2.1. The setup for conductivity monitoring of concrete samples.

The impact of temperature on the electrical conductivity of concrete has been taken into consideration. The activation energy ($E_a = 13.375$ kJ/mol) was determined using the Arrhenius equation, Eq. (2.1), based on the measured conductivity in mimic pore solutions conditioned between 3 and 70 °C. In the equation, “ A ” represents the pre-exponential constant, “ R ” is the gas constant (8.314 J/K mol), and “ T ” represents the absolute temperature of the specimen.

$$\sigma = A \cdot e^{\frac{E_a}{RT}} \quad (2.1)$$

Wenner's method is used to calculate the electrical conductivity of concrete with assumption of a semi-infinite boundary, which is not always met in practical applications, particularly for the upper rows of sensors. The dimension factors at different depths have been modelled with COMSOL Multiphysics software. To account for the effects of temperature and dimension on electrical conductivity, Eq. (2.2) was used to calculate the conductivity of hydrating concrete at various depths. The average conductivity for each sample was calculated with data from the

second to the eighth row.

$$\sigma_c = \frac{I}{2\pi\Delta Vd} \gamma e^{\frac{Ea}{R}(\frac{1}{273.15+T} - \frac{1}{298.15})} \quad (2.2)$$

where σ_c is electrical conductivity of concretes normalized to 25 °C, I is the applied constant current between the outer two electrodes, ΔV is potential difference between the two middle electrodes, d is the distance between inner two electrodes and γ is the dimension factor at different depths.

2.3.2 Moisture transport

Moisture transport properties in the hcp were measured by the invented tube method, which enables to test both vapor diffusion under steady-state conditions (constant flux through the samples) and total moisture transport under non-steady-state conditions by a semi-infinite drying. The detailed information of tube method is presented in paper V [28] with the equations to calculate the moisture transport parameters.

Measurements of vapor diffusion in pastes were carried out across four different RH intervals, namely RH97–75 (97.6–75.5 % RH), RH85–75 (85.1–75.5 % RH), RH97–50 (97.6–50 % RH), and RH75–50 (75.5–50 % RH). In addition, semi-infinite drying tests were performed in two distinct RH conditions, namely 75.5 % RH within a box and 50 % RH within a climate room. To prevent any potential leakage from the tube edges, a thin circle of moisture-tight glue (LOCTITE® 60 Seconds Universal glue) was applied around the edge. Each sample was weighed at various conditioning times, and 3 parallel measurements were done for each.

2.3.3 Ultrasonic pulse velocity

Figure 2.2 illustrates the setup for monitoring of ultrasonic pulse velocity (UPV), using the IP-8 Ultrasonic Measuring System from Ultratest GmbH. The system comprises two channels equipped with an acoustic emission system, a controller, and a computer. A transmitter and a receiver are placed within the silicon mould facing each other and inserted into the inner empty cylinder. The protrusion of approximately 3 mm inside the cylinder ensures a dense connection to the fresh concrete at a measurement distance of 50 mm. The ultrasonic pulse was set at a frequency of 25 kHz, and the velocity in the hydrating concrete normally ranges from 100 m/s to 5000 m/s at about 20 °C. To compact the concrete samples, a mild vibration was applied immediately after casting, and the mould was then connected to the controller for automatic control by the computer. Ultrasonic waves were recorded at a constant interval of either 2 or 5 min. Each sample underwent three parallel measurements, and the average value was taken as the result.

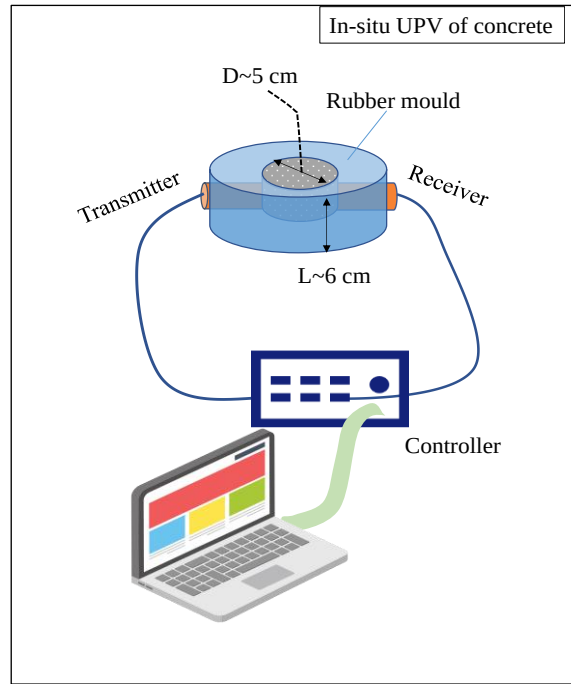


Figure 2.2. The setup for monitoring UPV in concrete samples.

2.3.4 Setting time

To measure the setting time of concrete, the penetration resistance test was carried out on the mortar part of the concrete mixture, in accordance with the traditional standard (ASTM C 403/C 403M – 05).

2.3.5 Compressive strength

Compressive strength measurements of the concrete samples were conducted in accordance with the EN 12390-3:2019 standard at several time points: 12 h, 24 h, 3 d, 7 d, 14 d, and 28 d. Notably, the dimensions of the C145 and C255 samples were $100 \times 100 \times 100 \text{ mm}^3$, while the C338 and C245 were cast as cubes of $150 \times 150 \times 150 \text{ mm}^3$. To ensure that a fair comparison could be made, the strength values of C145 and C255 were normalized using a dimension factor of 0.93 [62].

2.4 Methods

The licentiate thesis [58] has extensively covered several methods including X-ray diffraction, scanning electron microscopy (SEM), rapid chloride migration (RCM), and mercury intrusion porosimetry. Therefore, this dissertation will not describe the information of these techniques to avoid duplication.

2.4.1 Nitrogen sorption

A BET instrument (TriStar3000, Micromeritics) was used to measure the nitrogen sorption isotherm of samples. Before the sorption measurement, samples had been outgassed for 4 h with a continuous N₂ gas flow at 60 °C for a fast water removal. Adsorption isotherms were measured over the pressure range of 0.01–0.982 P/P_0 with an equilibrium interval of 10 s for each step at 77 K. Each sample has been repeated at least once, and the final value is an average of parallel tests.

2.4.2 Thermogravimetric analysis

The weight loss due to the decomposition of portlandite was measured by a thermogravimetric and differential thermal analysis instrument (SDT Q600, TA Instruments) with a Stanton Redcroft STA 780 simultaneous thermal analyser. Powder samples (dried at 11 % RH for 1 year) were heated at a rate of 10 °C/min under a continuous nitrogen flow (100 cm³/min) from 20 °C to 1000 °C.

2.4.3 Isothermal calorimeter

Hydration heat release of samples was measured using an isothermal calorimeter called I-Cal 2000 HPC, manufactured by Calmetrix. The instrument is specifically designed for measuring the isothermal heat flow of cement-based materials, which has two configurations with two or eight sample cells. These cells are well-insulated from each other by a wide air gap, ensuring a high level of precision and stability by eliminating any cross-influence. The temperature was maintained at a stable 20 °C with an accuracy of ± 0.001 °C. Two parallel measurements were conducted simultaneously to obtain an average value.

2.4.4 Moisture content

Moisture content in the hcp at early ages (10 h to 12 d) was determined with an easily implementing procedure described in [59] based on the solvent exchange by isopropanol and vacuum drying at 60 °C.

Moisture content in pastes after curing for 390 d was measured to calculate the moisture transport coefficient. Pastes were additionally crushed into particles with a size less than 2 mm and conditioned under various RH levels (97.6 %, 75.5 %, and 50 %) in a box where calcium hydroxide was placed to absorb CO₂. After one year, the particles were weighed and subjected to a vacuum drying process at 60 °C for 3 d to determine the evaporable water content.

2.4.5 Low temperature differential scanning calorimetry

The Q2000 TA equipment was used to conduct the test of heat flow in powder samples. Samples, weighing approximately 20 mg, were placed in hermetically sealed pans with lips. Samples were firstly cooled from 20 °C to -60 °C with a rate of 2 °C/min, and then equilibrated for 5 min before reheated to 20 °C with the same rate. Samples conditioned at 97 % RH were measured with a second cycle using the same protocol. To better compare the signals of the different binder systems, a normalization was done to obtain a similar starting point of all curves for better comparison. A mimic pore solution was made by adding 150 mmol/L KCl and 50 mmol/L NaCl into the extracted pore solution of CEM I paste with a *w/b* of 1, and it was then measured with the same temperature procedure for evaluating the heat of fusion of the pore water in hcp.

2.4.6 Broadband dielectric spectroscopy

The powder samples, obtained from well-conditioned particles, were subjected to dielectric permittivity testing. The broadband dielectric spectrometer (Novocontrol Alpha-N) was used to measure the complex dielectric permittivity in the frequency range of 10^{-2} – 10^6 Hz. Tests were performed isothermally in the temperature range of 130–300 K with a temperature increment of 5 K, and with temperature deviation controlled to be lower than ± 0.1 K. The powder samples (about 0.5 g) were tightly held with a thickness of 0.2 mm in between parallel gold-plated electrodes, with a diameter of 10 mm (see Figure 2.3).

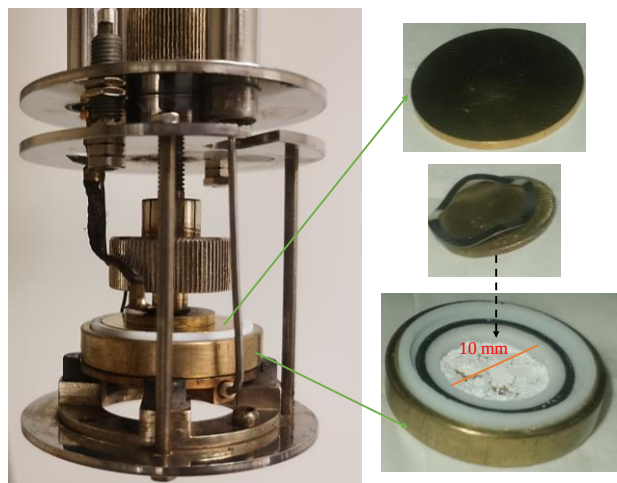


Figure 2.3. Holder for the broadband dielectric spectroscopy test of powder samples.

2.4.7 Dynamic water vapour isotherm

Water vapour desorption isotherms were measured on 6-month water cured samples. The measurement was carried out using a gravimetric water vapour sorption instrument, DVS (Advantage, Surface Measurements Systems, UK). The instrument continuously recorded the

mass of small samples during exposure to varying RH conditions. Samples weighing 40–60 mg were subjected to an RH sequence (95 %-90 %-80 %-70 %-50 %-40 %-35 %-30 %-20 %-10 %-0 %) at a constant temperature of 20 °C. To attain the criterion of mass loss rate lower than 0.0001 %/min, each RH step required a duration of 30–60 h. At least two samples were measured for each mix, and the final values are the average of parallel measurements.

2.4.8 Thermodynamic simulation

Thermodynamic modelling was carried out using GEM-Selektor v3.7, a freely available software for Gibbs energy minimization. The simulation was based on the cement database Cemdata18 [63] and the PSI-GEMS thermodynamic database [64]. It was applied to simulate the aqueous and gaseous species present in the pore solution of C_3S over a range of pH values.

The influence of SCMs on the phase assemblage was simulated by assuming that the clinker had a hydration degree of 92.2 % after being cured in water for 6 months at 20 °C (based on the portlandite content determined by Thermogravimetric analysis). This value closely aligns with that reported in [65], which used a similar clinker composition and curing conditions.

3 Interaction of water with cementitious materials at early age

This chapter will focus on the interaction of water with cementitious materials right after water addition to the main peak in hydration heat release. Theories for the early hydration of main minerals in cement are yet to have a good explanation for the result found in the experiments. Therefore, this chapter tries to propose a reasonable hypothesis for C_3S hydration using experimental results and thermodynamic simulation. In practical application, SCMs substituting partial cement is the most common scenario. The interaction of water with the blended binders will be demonstrated by an in-situ test method to monitor the electrical properties of hydrating paste. Electrical conductivity of pore solution will be calculated based on the concentration of alkali metal, hydroxide, sulfate, and calcium ions. The content of this chapter is sourced from paper I, paper II, and graphs in papers VIII and X.

3.1 Hydration of C_3S with solutions

This section explores the hydration of C_3S in various solutions. The preliminary result suggests that the dissolution theory regarding the thermodynamic property of the bulk pore solution is difficult to explain the hydration of C_3S with a high w/b . Therefore, the attention will be paid to the interfacial nucleation of C-S-H during hydration with normal w/b . A novel hypothesis has been proposed to provide a comprehensive understanding of the hydration process from the initial water contact to the end of induction period. The hydration evolution was monitored using an isothermal calorimetry test, while the composition and morphology of hydration products were determined by X-ray diffraction and SEM, respectively. GEMS simulation results provide significant information on the distribution of ion species in the pore solution.

3.1.1 Induction period

A significant number of prior investigations have categorized the hydration of C_3S into five distinct stages, as documented in [66]. Scrivener et al. [10] have simplified the classification

into three periods: I - up to the end of the induction period; II - the main hydration peak; and III - after the main peak. The debate continues as to whether the reaction during period I is controlled by the formation of a protective surface layer [67] or solely by the rate of dissolution [12]. The two prevailing theories that attempt to explain the sudden decline in heat release during the induction period are the protective membrane and the dissolution controlled by undersaturation of pore solution. These theories are comprehensively delineated and differentiated in [10]. Nonetheless, the protective membrane hypothesis has faced criticism mainly due to the lack of evidence through microscopic observations.

Figure 3.1 demonstrates that a high water to solid ratio merely results in an increased hydration rate at the main peak, without a significant impact on the duration of the induction period. However, more interesting results are observed in the cumulative heat release. It is observed that the cumulative heat release at the main peak is comparable among samples with a solution to C_3S ratio of 100, 200, and 200 (pH=4), which is approximately half of the heat release at 24 h. This observation indicates that the dissolution degree of the solid is similar at the end of the induction period, even with a very high water to solid ratio. As a result, the calcium concentration in the bulk pore solution is far from saturation with respect to the dissolution of C_3S . This conclusion is based on the theoretical calcium concentration from a complete dissolution of C_3S .

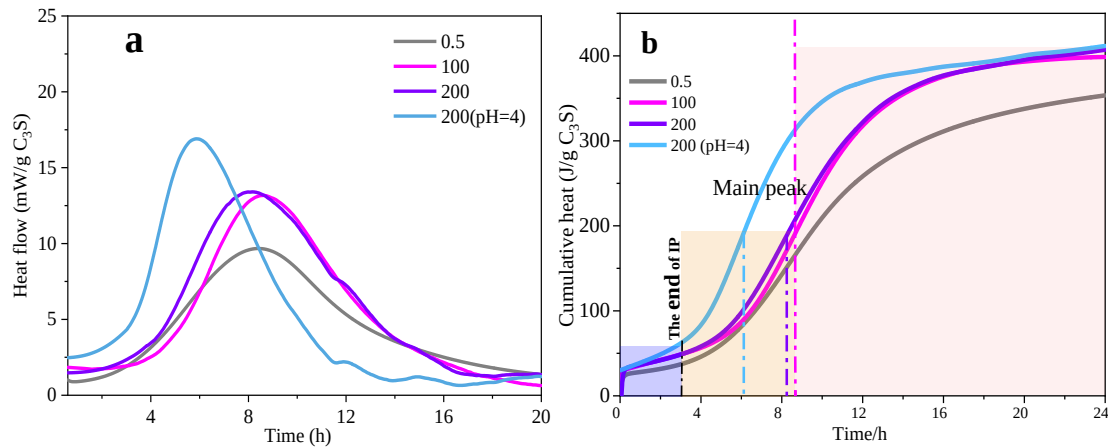


Figure 3.1. Graph “a” presents the hydration heat flow of C_3S with different deionized water to solid ratio (0.5, 100, 200) and sulfuric acid solution (pH=4) to solid ratio of 200. Graph “b” are the cumulative heat these samples, corresponding to Figure 2 in paper I [68].

C_3S with an empirical formula of Ca_3SiO_5 has a molar mass of 228.3 g/mol. To achieve a saturated state (>22.5 mmol/L [69,70]) with respect to portlandite at 25 °C, a water to solid ratio of 100 requires the consumption of more than 1/6 of C_3S ($22.5/131.4$ from Table 3.1). When the water to solid ratio is increased to 200, more than 1/3 of solid C_3S must be consumed to attain the saturated condition. A complete dissolution of C_3S with a water to solid of 600 only results in calcium concentration of 21.9 mmol/L in pore solution, which is slightly lower than

the saturated concentration of portlandite. Despite this, the precipitation of portlandite is still detected in the product at 4 h [68], which challenges the theory that the dissolution rate is controlled solely by the thermodynamic state of the bulk pore solution, as discussed in [16].

Table 3.1. The theoretical Ca^{2+} concentration from a complete dissolution of C_3S with a high water to solid ratio.

Water to solid ratio (by weight)	Volume of solvent (ml)	Mole of Ca in solid (mmol)	Complete dissolving Ca concentration (mmol/L)
100	100	13.14	131.4
200	200		95.7
600	600		21.9

Hydration heat flow of C_3S with and without C_3A is shown in Figure 3.2. The presence of C_3A evidently prolongs the starting point of the induction period. The majority of previous studies have proposed that the effect of aluminate on the hydration during the induction period is caused by inhibiting the dissolution of C_3S [71,72]. However, it should be noted that the “induction period” in these studies refers to the time from water addition to the end of the low-rate period. In contrast, this study tries to distinguish the inhibiting effect of aluminates on dissolution and nucleation processes. By replacing the concept of thermodynamic state between the solid and bulk pore solution with the state within the interfacial regions near the surface, we propose that the sharp decrease in heat release is a result of the increase in saturation degree within the near surface with respect to C_3S dissolution.

The occurrence of a delayed starting point, as shown in Figure 3.2b, can be attributed to the inhibiting effect on dissolution by Al species absorbed on the surface of C_3S . During this period, the pH value of the pore solution is typically below 12.6. As hydration progresses, the pH increases and the effect of Al on dissolution is eliminated [73,74]. It means that the Al in solution has little influence on the dissolution of C_3S during induction period. This finding is consistent with the result that the lowest point of heat release rate in C_3S with C_3A is even higher than that of pure C_3S during induction period (Figure 3.2a). The ending time of low-rate period is delayed by the presence of aluminate due to the inhibition of both dissolution and precipitation, which is similar to the effect found in [75].

The addition of KOH and K_2SO_4 has been found to mitigate the effect of C_3A on the induction period and even shorten its duration. In particular, the heat flow of samples in KOH solution is much higher than the others in this period, indicating a higher dissolution rate of C_3S in KOH solution than in other solutions when the nucleation of the hydration products takes over the hydration process. The presence of K^+ ions and high pH in the solution accelerates nucleation, resulting in a reduction in the duration of induction period. K_2SO_4 eliminates the effect of Al by reducing the concentration of Al through ettringite precipitation. Although C_3A has little effect on the starting point induction period in K_2SO_4 solution, it does reduce its duration, and

as such, further attention should be paid to the nucleation and growth of the hydration products.

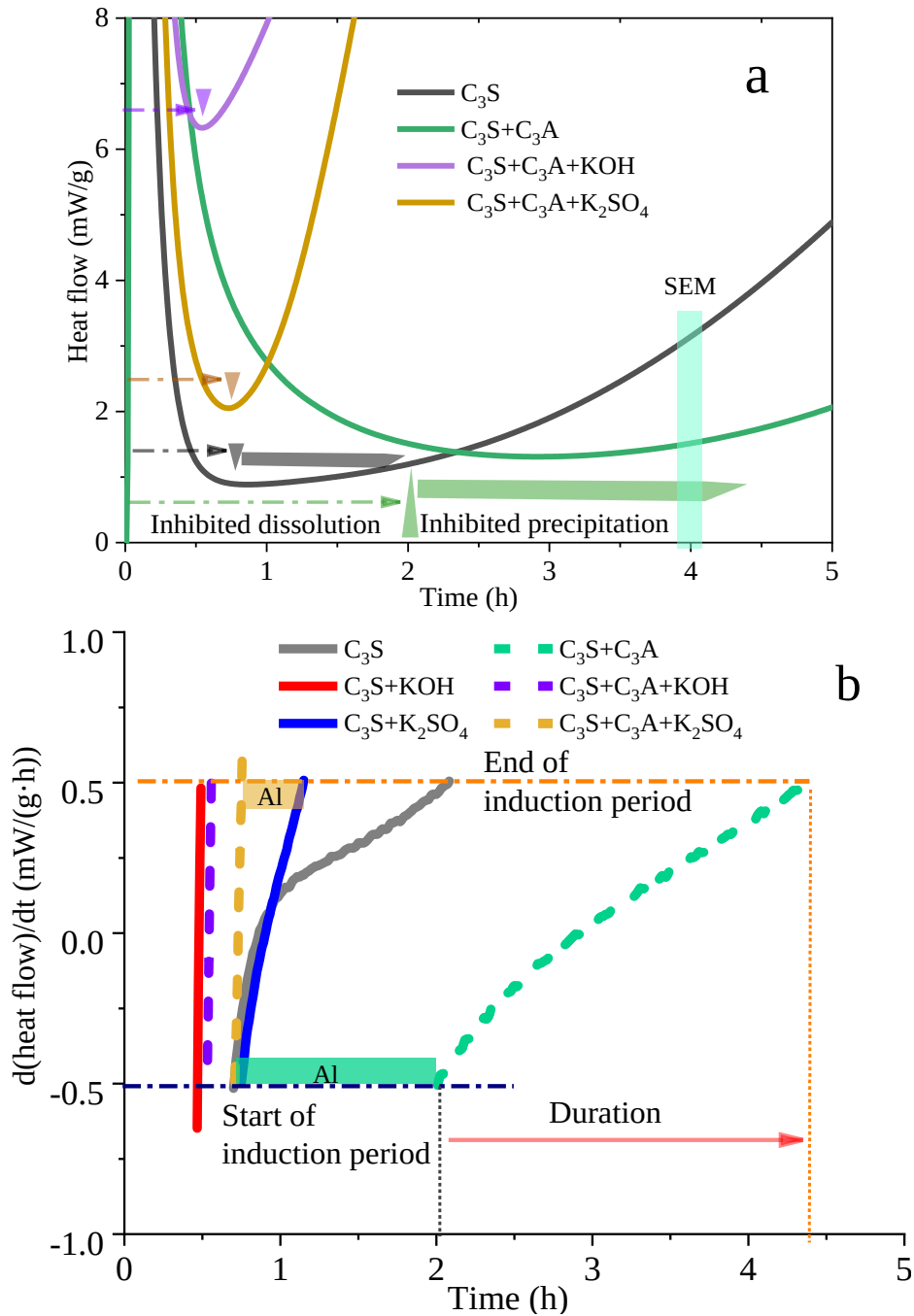


Figure 3.2. Hydration heat flow of C_3S with the presence of C_3A and additives in the first 5 h (a). Induction period of C_3S hydrating in solutions with and without C_3A (b). Samples were mixed with a water to solid ratio of 0.5 and cured at 25 °C, corresponding to Figure 7 in paper I.

3.1.2 Main peak

Figure 3.3 presents heat release at the main peak from hydration of C_3S in different solutions. After the low-rate period the interaction between water and C_3S will proceed to an acceleration period during which time the growth of hydration products occurs, the heat release of C_3S hydrating in K_2SO_4 solution at 20 °C overtakes the other two mixes and maintains the

maximum until deceleration period at about 10 h. KOH induces the time of main peak appears much earlier than the others at 25 °C, but the maximum hydration rate is still observed in K₂SO₄ solution. This indicates that K₂SO₄ has the most enhancement of the growth of hydration products at acceleration period.

In previous studies, two hypotheses, namely the diffusion layer hypothesis and the impingement hypothesis, have been proposed to explain the heat evolution at the main peak. However, these hypotheses were unable to provide a satisfactory explanation for some experimental evidence [10]. In recent years, another two hypotheses, namely the confined growth and dissolution limitation hypotheses, have been introduced and critically evaluated. Moreover, the hypothesis about the C-S-H growth seems to be quantitatively supported through a needle model [76]. However, the underlying mechanism behind the formation of C-S-H needles is still lacking a fundamental explanation.

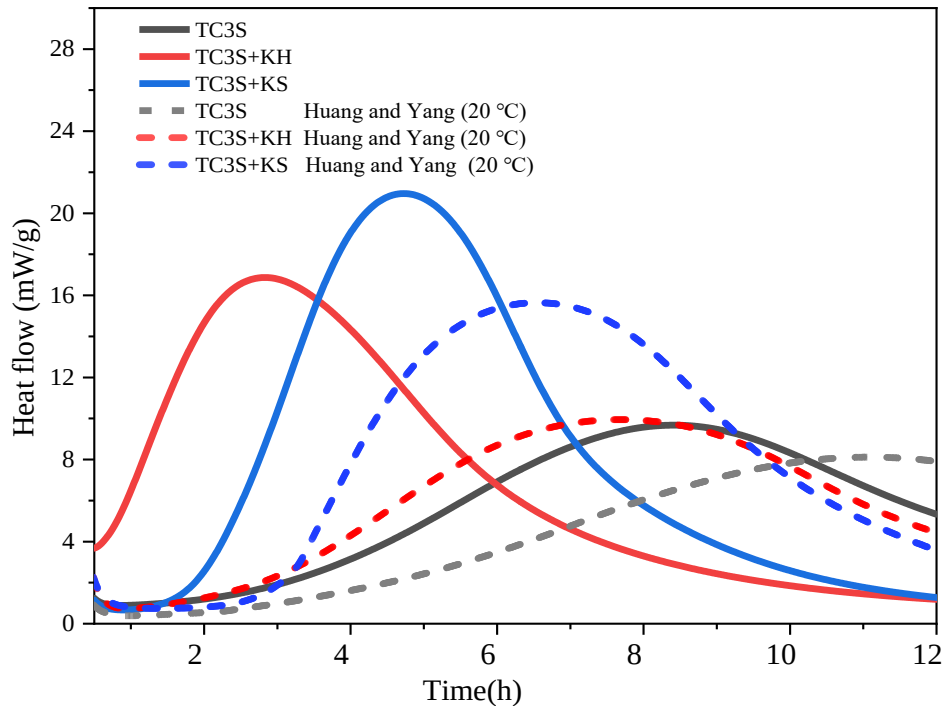


Figure 3.3. Hydration heat flow of C₃S with deionized water, KOH and K₂SO₄ from 0.5 to 12 h. The solid line is hydration data with a water to solid ratio of 0.5 at 25 °C from [68], and the dash line is hydration data with a water to solid ratio of 2 at 20 °C.

Results in this study (see Figure 3.4) provide the evidence for the nucleation of a primary mono floc (0), formation of a dimer floc (1), a single strip from the nearly oriented attachment (2) and the clusters from a strip attachment (3) or primary particles attaching to strips. This implies that the precipitation of C-S-H is very similar to the crystallization process of some other polymers or minerals [77,78], which starts from the nucleation of primary mono flocs that are poorly crystalline nanoparticles or colloidal. The mono floc may correspond to the intermediate C-S-H phase during the precipitation process as highlighted in the previous investigations

[79,80]. As it is thermodynamically metastable, it tends to aggregate into strips through oriented attachment within a local region. As the precipitation of mono floc and strips increases, the mono floc will attach to the strip and strips will agglomerate to form more stable clusters or blocks. The primary mono floc seems to be a globular grain with size smaller than ~60 nm. The presence of C_3A , KOH and K_2SO_4 will alter the size of mono floc as well as the orientation of particle attachment, resulting in a variation in length of strips (needles) and morphology of products.

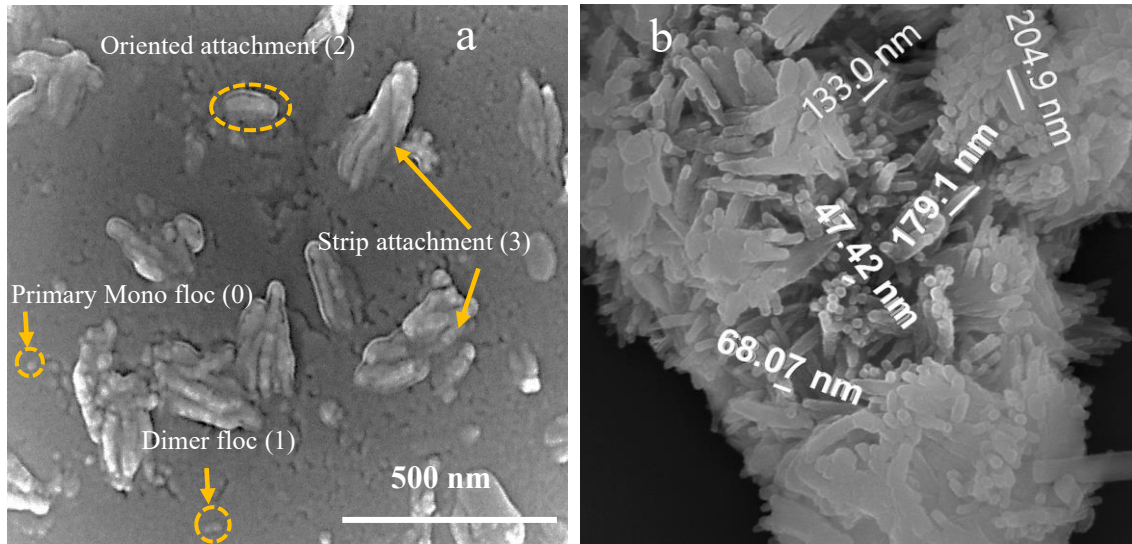


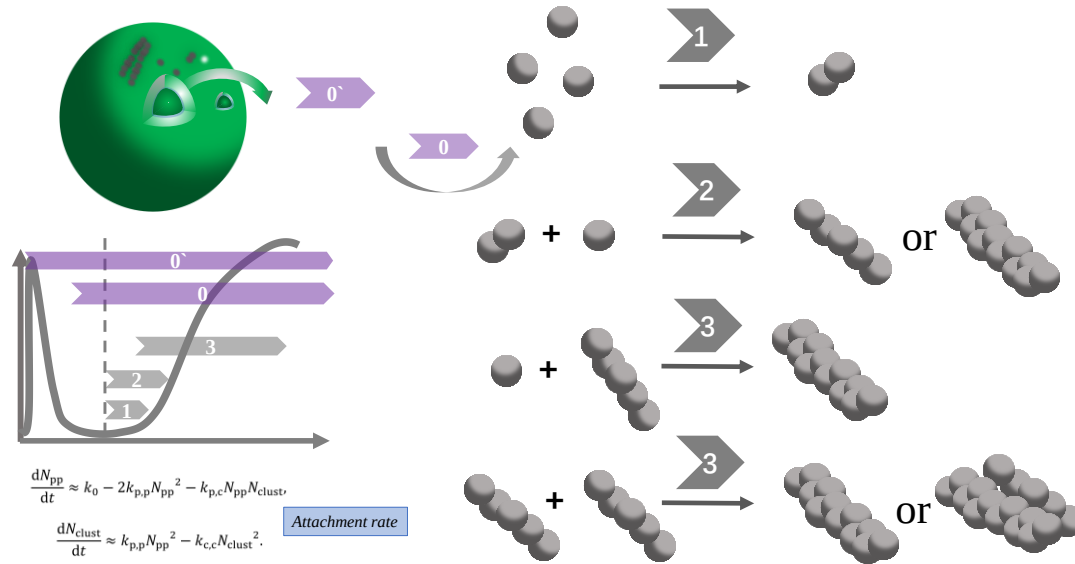
Figure 3.4. SEM images of C_3S hydrated in deionized water at 25 °C. The hydration was stopped at 4 h after water addition by freeze-drying. An image with higher magnification was provided to give a clear picture of the particles on the surface (a) [68]. Nucleation of primary mono-flocs and dimer flocs was detected above or near the etch pit. C-S-H grows by nearly oriented attachment and block attachment. Hydration products of C_3S with K_2SO_4 solution at 20 °C stopped at 4.5 h by solvent exchange (b) [22].

3.1.3 Hydration mechanism up to the main peak

The reaction of C_3S in water can mainly be classified into five stages. Stage I is a fast dissolution in the first few minutes right after contacting with water. Stage II is the state for approaching dissolution equilibrium with respect to C_3S within the local zone near the surface. In stage III a new surface equilibrium with respect to nucleation of hydration products would be established. Afterwards it goes into stage IV with the surface nucleation, and Stage V will follow when the precipitation of hydration products takes over by attachment to growth.

Stage I and II corresponds to the first dissolution peak in the hydration heat flow, which is controlled by the dissolution rate of minerals (0th process illustrated in Figure 3.5). After these two stages, the rate of reaction is limited by the nucleation and growth rate of the main products C-S-H. Nucleation of C-S-H is a colloidal assembly process similarly found in the crystallization of many other minerals [77,78]. The kinetics of this process is a key to understand the hydration mechanism in the main peak of hydration. The pH value is a critical

parameter to control the nucleation (0 process) and dimer assembly (1 process), since it determines the calcium and silicate ion species in pore solution (see the results from GEMS modellings in [68]). Al ions have an inhibiting effect on the dissolution to affect the process 0' and change the kinetic of nucleation of C-S-H. Presence of other inorganic ions such as K^+ , SO_4^{2-} will alter the attaching process (2 to 3) as well.



The packing of globular particles produce more sites for nucleation and attachment

Figure 3.5. Illustration of hydration process up to the main peak time from the nucleation perspective.

The presence of some organic substances has been observed to increase the solubility of C-S-H [81], as indicated by an increase in calcium concentration. This effect brings the solubility of C-S-H closer to, and sometimes even higher than, the equilibrium line of C_3S hydration. The interaction between organic admixtures and Si ions results in the release of more ions into the bulk solution from the near surface region, leading to a higher silicate ion concentration in the solution than in the pure system. This modification of the double layer reduces the concentration of Si and Ca in the near surface region, which in turn requires a higher supersaturation state for the precipitation of primary C-S-H on the surface with these admixtures. Furthermore, some organics such as PCE can stabilize the primary floc [82], hindering the attachment between primary particles.

3.2 Hydration of cement blended with SCMs

A device for instantaneous monitoring of electrical conductivity was designed, with a focus on understanding the relationship between the conduction and structure of paste. This section presents the correlation between the electrical properties, hydration process and structure evolution in the hydrating Portland cement and the blended pastes. The evaporable water content in paste was measured by a newly designed procedure, so that it enables the calculation

of the electrical conductivity of the pore solution based on the chemical composition of the binders and the volume of evaporable water. The formation factor was calculated to distinguish the effect of pore solution and structure on conduction. The change of liquid connection has been evaluated during the hydration. The average growth rate of the formation factor is defined to indicate the setting and hydration reactivity of cementitious materials.

3.2.1 Hydration induced conduction change

The process of cement hydration can be divided into two simplified stages: the dissolution of solid minerals in water, which increases the ion concentration in the liquid pore solution; the precipitation of hydration products to create solid network. Figure 3.6 depicts change of conduction in paste during the hydration, which is mainly caused by the changes in volume of solid particles and liquid pore solution. The electrical conductivity of solid particles is approximately 1×10^{-8} mS/cm. This value is much lower than the typical ionic conductivity of pore solution, $\sigma_s = 10\text{--}200$ mS/cm [83]. Thus, the dry solid component can be considered as an insulative element ($\sigma_s \rightarrow 0$).

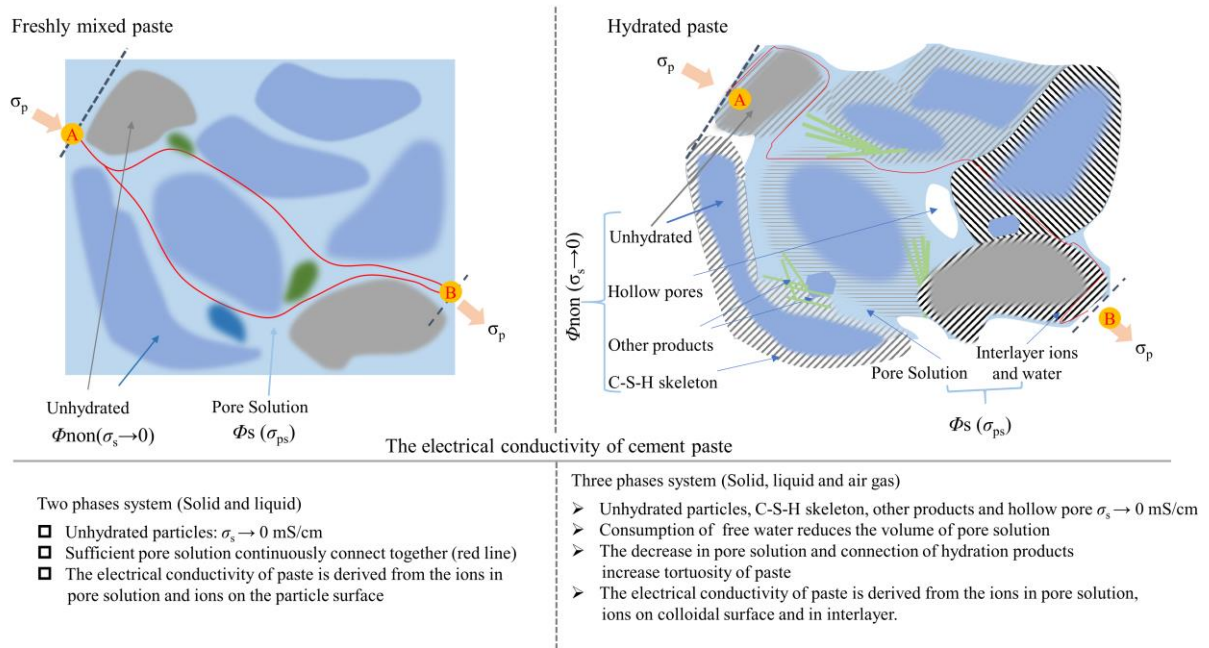


Figure 3.6. A graphical representation of the temporal evolution of electrical conductivity during the hydration process.

3.2.2 Conductivity of pore solution over time

The pore solution is the primary conductive component in the paste, and the ionic conductivity of the solution depends on the type and concentration of ions. The concentration of highly soluble alkalis can be determined by using the evaporable water content and chemical composition of binders (see Table 2.1). The electrolyte conductivity of the pore solution can be represented as the sum of the molar conductivity of each ion species [84]. The detailed

procedure and equations for calculation of ionic conductivity of pore solution have been elaborated in paper II [59], assuming that alkali metal oxide has a fast dissolution to a certain percentage in the first few minutes.

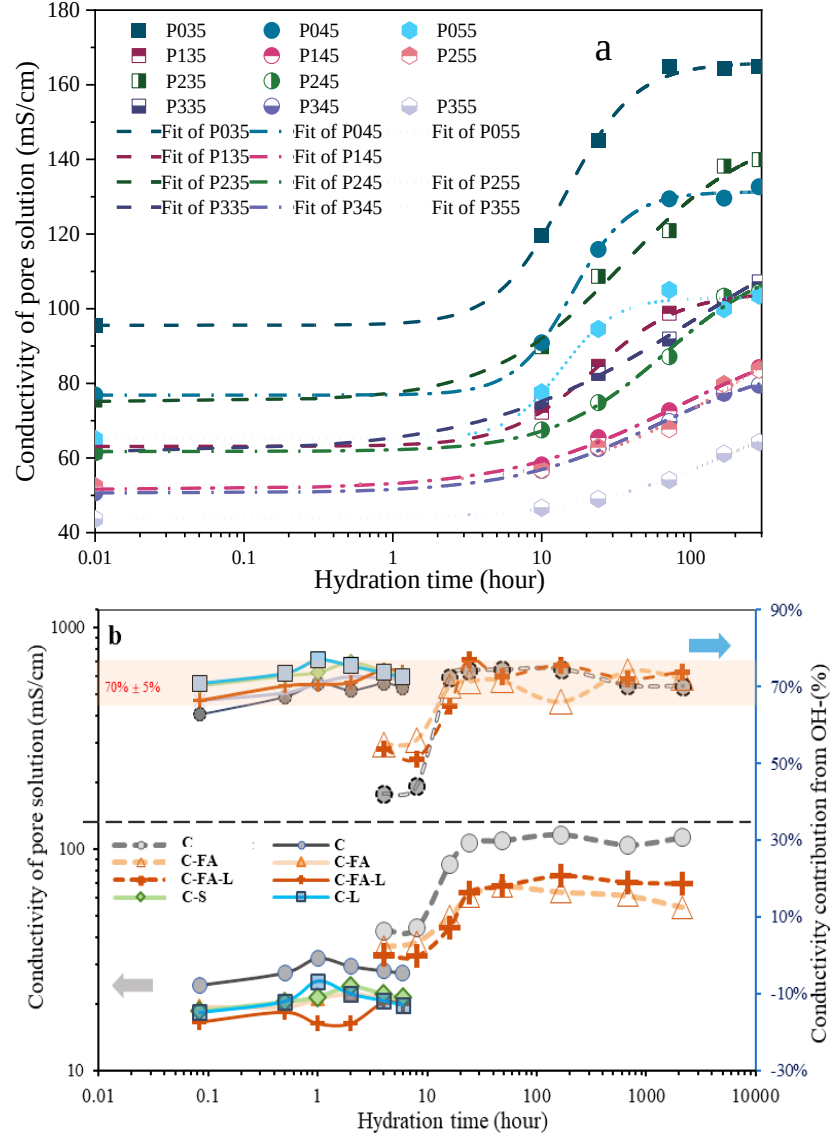


Figure 3.7. Calculated conductivity of pore solution. (a)- the values in this study. (b)- the conductivity value calculated based on the concentration of squeezed pore solution from literatures: solid line from [17] with $w/b=0.75$, and dash line from [85] with $w/b=0.5$. Notes, C: Portland cement; FA: fly ash; S: slag; L: limestone, corresponding to Figure 7 in paper II.

Figure 3.7a illustrates the calculated conductivity of pore solution in paste samples along with the regression lines. It shows that an increase in w/b results in a decrease in electrical conductivity of the pore solution as a higher w/b lowers the concentration of alkali ions by introducing more evaporable water into the paste. Blending SCMs reduces the electrical conductivity of pore solution, which is consistent with data from published papers based on the squeezed pore solution data (see Figure 3.7b). It was also discovered in the previous investigation [68] that blending SCMs reduces the electrical conductivity of pore solution.

Even though the fly ash used in [67] has high alkali content (3.9 % K₂O and 0.9 % Na₂O), the concentrations of K⁺, Na⁺, and hydroxide in the fly ash blended pastes are similar with those in pastes with identical quartz replacement, supporting the assumption that alkalis in fly ash have a very low solubility.

The measured conductivity of paste is lower than the calculated conductivity of pore solution because the presence of cement particles breaks the connection between pore solution. The chemical composition of Portland cement used in this study is highly similar to that of cement used in [85], so the calculated conductivity of P055 (light blue hexagon in Figure 3.7a) based on chemical composition is close to that of ordinary Portland cement with w/b of 0.5 based on the data of squeezed pore solution (dashed line sphere in Figure 3.7b). Hydroxide ion is the major conductive ions in the pore solution of cement-based materials which accounts for around 70 % of the electrical conductivity (see Figure 3.7b). The electrical conductivity of pore solution remains almost constant until it has a sharp increase after about 6 h. The evolution of conductivity of pore solution is well regressed by the Hill function [59]. The fitted lines exhibit the same trend as the evolution of the value calculated from the squeezed pore solution. This verifies that method in this study can effectively quantify the specific conductivity of pore solution without the need to extract the solution from the paste or use any expensive equipment, as summarised in [86], to measure the ion concentration of squeezed pore solution.

3.2.3 Evolution of microstructure

To differentiate the impact of pore solution and microstructure, the formation factor (F) was introduced. It was originally proposed by Archie [87] to describe the relationship between the electrical conductivity of sandstone and its permeability or porosity. F is now commonly used in cement-based materials to indicate the diffusivity of ions in hcp, which shares a porous nature with sandstone, according to the definitions in [88,89].

$$F = \sigma_{ps}(t)/\sigma_p(t) \quad (3.1)$$

where $\sigma_p(t)$ represents the conductivity of the bulk paste, while $\sigma_{ps}(t)$ indicates the conductivity of pore solution at a given hydration time, t . In this study, $\sigma_p(t)$ is equivalent to the conductivity of naturally saturated hcp. $\sigma_p(t)$ was measured by the designed device, and data of $\sigma_{ps}(t)$ was generated from the regression line in Figure 3.7.

F of the porous matrix is determined by porosity and pore connectivity, which can be described by the equation [88,90]:

$$F = \frac{1}{\phi\beta} \quad (3.2)$$

where ϕ is the porosity of paste and β is the pore connectivity index. In this study, the water

accessible porosity was used to calculate the pore connectivity index.

Figure 3.8 shows the evolution of formation factor in pastes with various binders up to 180 d. Initially, F remains constant for a period of 2 to 9 h, which varies depending on the w/b and types of SCMs. The initial F is higher than 1, and it decreases with increasing w/b . It is followed by a sharp increase after the constant period, whose phenomenon is similar to the percolation of solid at the setting time found in ultrasound tests [91]. The effect of w/b on F is magnified during the fast growth period. The ratio of F in hcp, with a w/b ratio of 0.35, to that in hcp with a w/b ratio of 0.45 was found to be 1.90, 2.57, 3.90, and 2.05 for CEM I, fly ash, slag, and ternary systems, respectively. The differences in F of binary and ternary slag pastes become negligible after 28 d. The fly ash blended pastes exhibit the highest increase in F up to 180 d. Figure 3.8 b shows that as the hydration process continues, the β value decreases significantly from the point of water addition until 24 h. Despite the slag blended systems having a higher volume of evaporable water than CEM I pastes with identical w/b , the β value of slag blended pastes is lower than CEM I, as demonstrated by the data for P235 and P335 in Figure 5 of paper II [59]. This difference results in a higher F value for the slag blended paste. Therefore, the dissimilarities in F values among various binder systems primarily stem from variations in β .

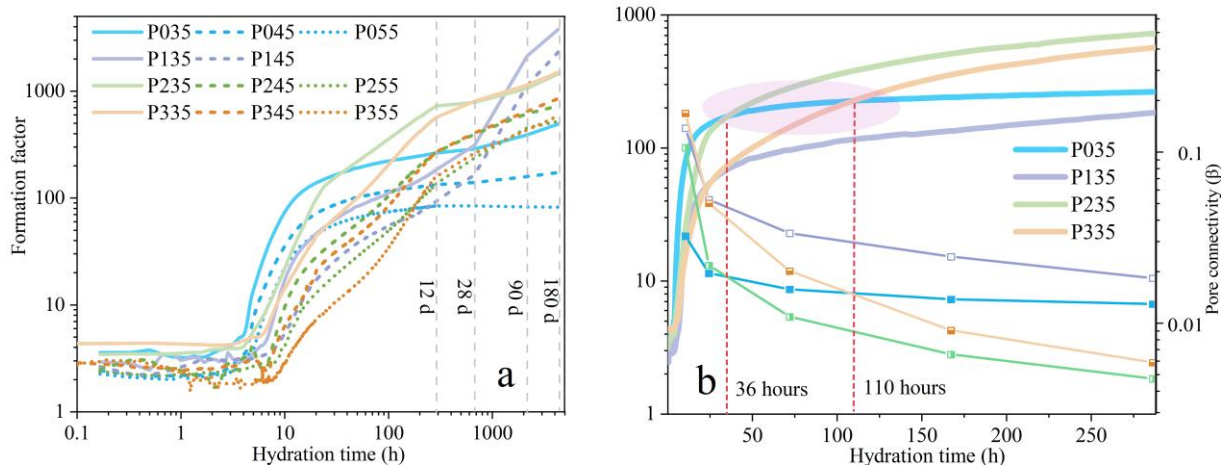


Figure 3.8. Evolution of formation factor for all pastes (a) and pore solution connectivity of binders with w/b of 0.35 over time, adopting from Figure 8 in paper II.

For analyzing the change rate of microstructure, the average growth rate of F ($a-F$) is defined as Eq. (3.3): where $F(t)$ is the F of paste at hydration time t .

$$a-F = \frac{F(t)}{t} \quad (3.3)$$

As shown in Figure 3.9, the progression of $a-F$ for CEM I paste can also be classified into three phases. The $a-F$ in Period I has a sharp decrease followed by a constant period. It involves mineral dissolution, ettringite precipitation, and C-S-H nucleation. The $a-F$ in Period II exhibits a sharp increase because a rapid growth of ettringite, C-S-H, and portlandite joints particles to block the connectivity of pore solution. In Period III $a-F$ displays a decreasing trend due to the

slowing down of hydration and water consumption. For blended paste, period IV corresponds to a new peak during deceleration, indicating a refining of the pore size due to the later age hydration of SCMs. These periods correlate to the changes of connectivity and size of pores in the pastes during hydration.

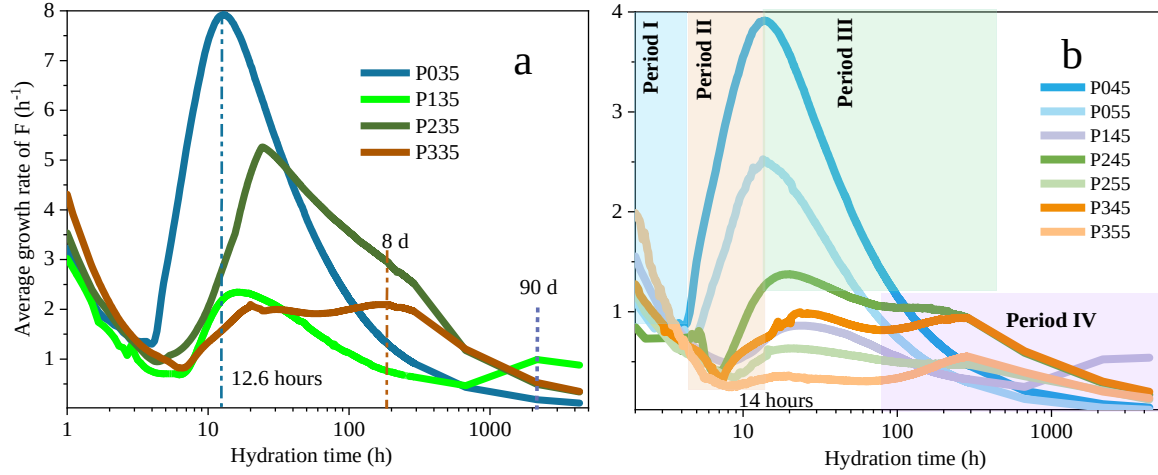


Figure 3.9. Evolution of a - F over hydration time, adopting from Figure 9 in paper II.

3.2.4 Moisture content and formation factor

The electrical conductivity of cement-based materials depends on the composition of the paste, which consists of insulative dry solid and conductive liquid solutions (Figure 3.6). After an extension of the percolation theory to the continuum cases [92,93], a general formula similar to Archie's law describes the conductivity of cement-based materials.

$$\sigma_p = a * \sigma_{ps} * (\phi - \phi_c)^m \quad (3.4)$$

After the substitution of conductivity with F , we get:

$$F = 1/a * (\phi - \phi_c)^{-m} \quad (3.5)$$

In this study, the conductive component is assumed to comprise ions in pore water and layer water, with ϕ representing the volume of evaporable water. ϕ_c is the critical volume required for percolation of the conductive component, while m and a represent the shape factor and the constant, respectively. Figure 3.10 and R^2 in Table 6 of paper II [59] indicate that the regression curve matches the experimental data well.

The shape factor and percolation threshold are affected by the type of binders. Systems with complex shapes, such as sand and chalk, have a higher shape factor (1.6) compared to single-shaped particle systems. Calcium montmorillonite has the highest shape factor of 3.28 [94]. The difference in the threshold for percolation may improve the understanding and modelling

of mass transport in concrete containing SCMs by some lattice models.

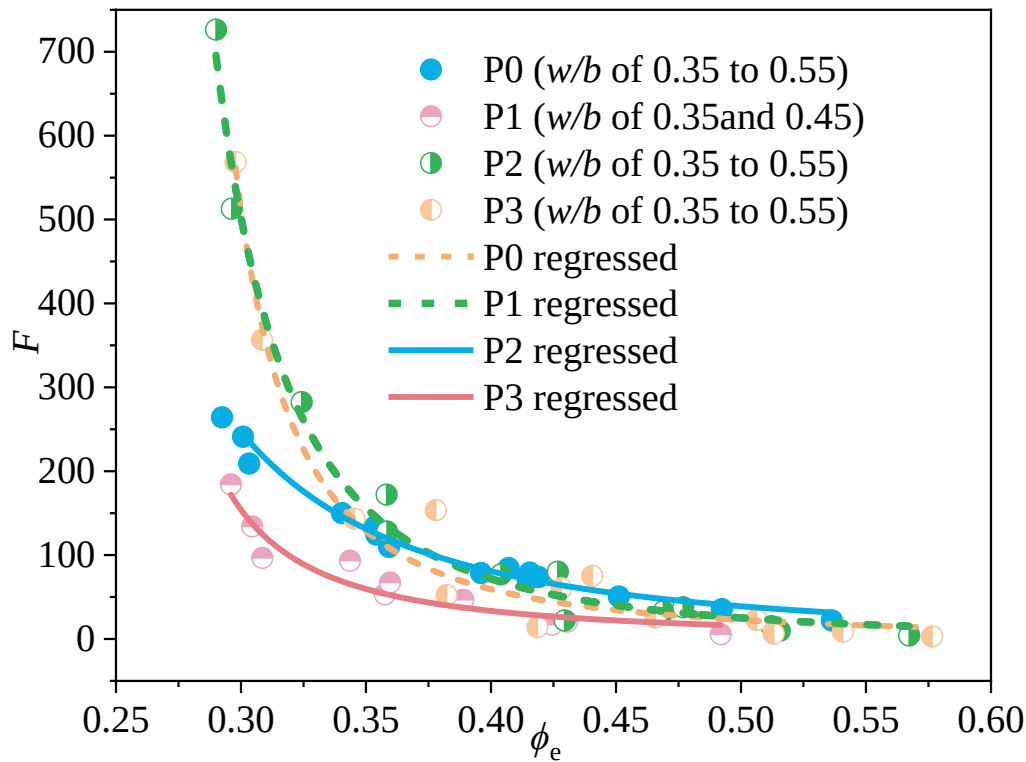


Figure 3.10. Relationships between the volume of evaporable water (ϕ_e) and formation factor (F). P0, P1, P2 and P3 correspond to CEM I, the fly ash, slag, and ternary blended pastes, respectively: adopting from Figure 13 in paper II.

3.3 Chapter summary

The mechanism of cementitious materials reacting with water at the early age is a complicated scientific problem. Reaction of the main mineral, C_3S , has not been thoroughly understood to date. Experimental studies have shown that the dissolution theory can hardly explain the anomalous interaction at high water to solid ratio. Therefore, a theory based on the crystallization and precipitation process of the main hydration products has been proposed. The hypothesis suggests that C-S-H primarily nucleates within the near-surface region, bridging the gap between dissolution and protective layer theories. The precipitation of C-S-H is a nonclassical nucleation process involving primary particle nucleation and growth by particle attachment. The acceleration of C-S-H growth rather than etch pit dissolution may explain the rapid reaction rate increase after the induction period. The dissolution of C_3S and precipitation of C-S-H are affected by potassium salts and pH levels.

The interaction of water with supplementary cementitious materials is a more complex process than that with C_3S . Therefore, a more comprehensive detection method based on conductivity was used to monitor the interaction process at early age. Electrical conductivity evolution in

hydrating pastes relates closely to chemical reaction processes and can be classified into four stages during early hydration. Differences in the connectivity of pore solution primarily account for the variations in the F of pastes with different binders. The w/b ratio impacts the electrical conductivity and F of pastes by altering the alkali concentration in pore solution and increasing pore connectivity. The growth rate of the formation factor can indicate the reactivity of different binders. Blending SCMs refines the pore structure, decreasing pore connectivity. Monitoring conductivity can demonstrate the relation between evaporable water volume and formation factor, facilitating in-situ monitoring of moisture, alkali ion concentration, and pore connectivity.

4 Interaction of water with hardened cement-based materials

The hardened cement-based paste is a complex porous matrix with a wide range of pore sizes from 0.5 nm to tens of micrometers. Due to the hydrophilic nature of cementitious materials, the surface of the pore wall interacts strongly with water. Understanding the interaction between the pore structure and water is essential to develop effective strategies for improving the durability of cement-based materials. The effect of SCMs on water-related relaxation processes in hcp with different RH levels has been quantitatively illustrated for the first time in cement-based materials research. This chapter comprises the content of paper III and IV.

4.1 Desorption isotherms

Water vapour isotherm is very useful for understanding the moisture-related behavior of cement-based materials and its relationship with pore structure. It has been utilized for modelling moisture transport, understanding drying shrinkage mechanisms [95,96], and exploring microstructural changes during the drying process [97]. This section presents the effect of SCMs on nanopores in hardened pastes, which was investigated by dynamic water vapour desorption. C-S-H content was determined from sorption data, and portlandite content was determined by thermogravimetric analysis. The hydration degree of SCMs was evaluated by the means of GEMS simulation.

4.1.1 Effect of SCMs and w/b on isotherms

Figure 4.1 shows that the type of SCMs and w/b make impact on the desorption isotherms. While paste mixing with w/b of 0.35, the replacement with SCMs increases the moisture content (W_e) in the hcp under the whole range RH intervals from 11 % to ~95 %. Moreover, the effect of SCMs on desorption isotherms is dependent on the w/b of the pastes. An increase in w/b causes an increase in moisture content of CEM I pastes at all RH conditions. However, the increase in moisture content of the blended pastes mainly occurs at RH above 40 % as the w/b increases to be larger than 0.45 [44]. A similar phenomenon has been reported by Olsson

et al. [39] in desorption data of the well hydrated (water curing for 4 years) pastes blended with slag. Effects of SCMs introduce additional complexities to the prediction of moisture state and transport in concretes containing SCMs.

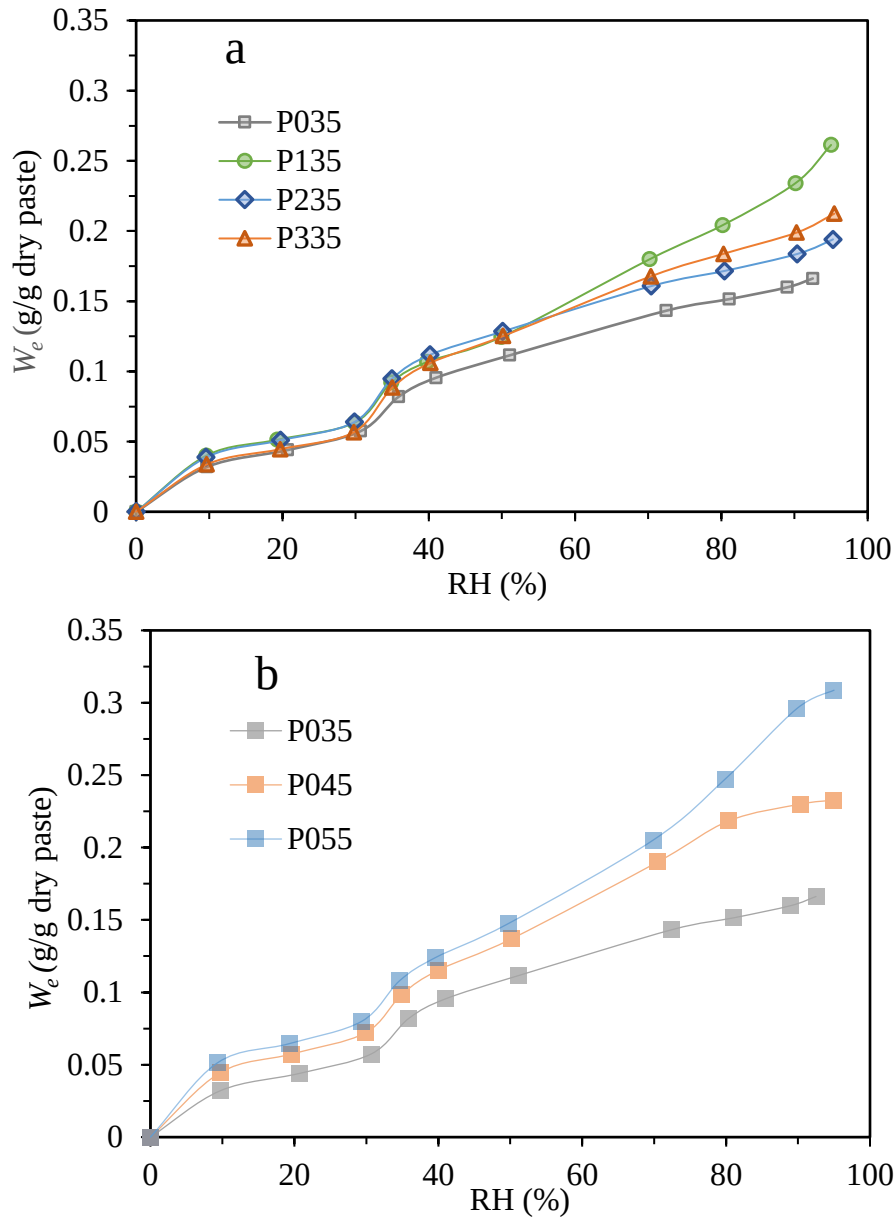


Figure 4.1. Water vapour desorption isotherms of pastes measured at 20 °C. Plots in a are comparisons between different binder systems with the same w/b, exemplifying with w/b of 0.35. Plots in b are comparison between different w/b for CEM I paste, refer to [44] for more detailed data.

4.1.2 Calculating the pore size distribution

The BJH method has been widely used to estimate the pore size distribution (PSD) in cementitious materials using data from water vapour desorption [96,98,99], which was initially proposed by Barrett, Joyner, and Halenda [100] for determining the pore size distribution in porous materials based on N₂ sorption isotherm. Although the pore geometry in hcp is more intricate than the assumed cylindrical shape in this approach, and cavitation occurs during the

desorption process [101,102], the computed results can provide valuable insights for comparative analysis, such as the present study. To calculate the pore size distribution, a physically adsorbed layer of molecules on pore surfaces needs to be considered. The radius of an open cylinder pore (r_p) is determined by adding the thickness t_h to Kelvin diameter r_k ($r_p = r_k + t_h$). The correlation between the statistical thickness of the water film and RH in hcp was initially discovered by Hagymassy et al. [103]. Badmann [104] developed this to describe the correlation using two parameters, K_1 and K_2 . Parameters for pastes in this study were determined by a trial-error method to adjust the constants for different binder systems to ensure a good match between the measured and calculated total pore volume.

This method uses the Kelvin equation to establish a relationship between the radius of the condensed liquid in cylindrical pores and the relative humidity (represented by RH_k). However, ions in a solution can affect the equilibrium vapour pressure on the plane surface (p_s), which is different from the pressure on the pure water surface (p_0). Raoult's law [105,106] provides an empirical expression of the correlation between the ion concentration and the RH on the plane surface (RH_s), as shown in Eq. (4.1). The total moles of ions in the solution are represented by " n_i ", and " n_w " refers to the moles of water in the solution. Consequently, the observed relative humidity value (RH_o) is a result of both curvature and ion effects, which can be described by Eq. (4.2).

$$RH_s = \frac{p_s}{p_0} = \frac{n_w}{n_w + n_i} \quad (4.1)$$

$$RH_o = RH_k RH_s \quad (4.2)$$

The influence of ions on the RH_s of the pore solution has not been considered in previous studies [96,98,99], where the observed RH_o was used as RH_k . Figure 4.2 presents a comparison of the calculated PSD with the RH_s of the pore solution and pure water. Although the ions in the pore solution have a minor influence on the calculated width and volume of pores with a diameter less than 10 nm, neglecting the ion effects results in a significant underestimation of the size and volume of capillary pores (width greater than 12 nm). Therefore, it is crucial to include the influence of ions on the surface pressure of the pore solution when determining the PSD using the BJH method on water vapour desorption isotherm.

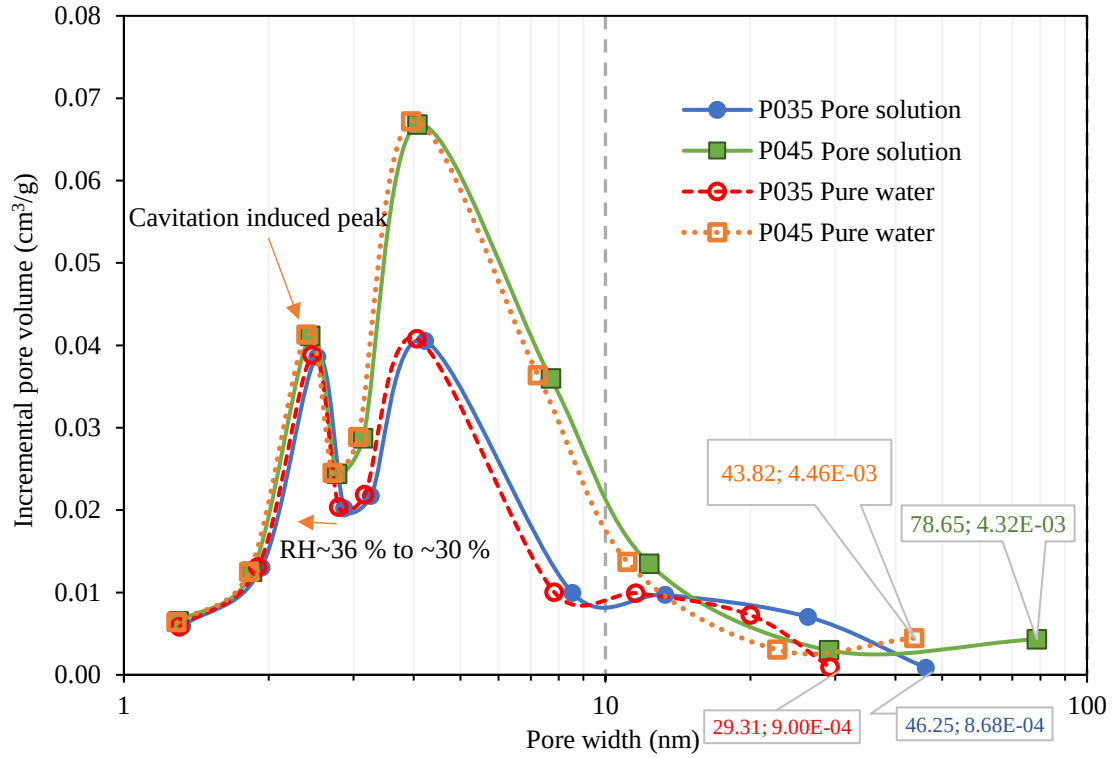


Figure 4.2. The effect of ions in pore solution on the calculated PSD of hcps, exemplifying with CEM I pastes, corresponding to Figure 4 in paper III.

Figure 4.3 illustrates the pore size distribution obtained using the BJH method to analyze the water vapour isotherm data. The pore widths, calculated as the diameter of open cylinder pores, are between 1–90 nm. It means that water vapour desorption analysis can provide effective indication of mesoscale pore structure in hcp. It should be noted that a sudden decrease in the moisture content drying from 36 % to 30 % RH can be attributed to cavitation occurring in larger pores [101,102]. It is not useful to designate the calculated volume at this interval to pores of a specific size. However, it is noteworthy for comparative purposes in evaluating the volume of ink-bottle gel pores in various binder systems. Incorporation of SCMs leads to a minor reduction in the volume of interlayer space in hcp. The use of both slag and fly ash results in an increase in the value of cavitation-induced peaks, indicating a refinement of the large gel pores and the reduced pore connectivity. At higher w/b , the refinement effect of slag and fly ash is more pronounced, leading to a larger difference between binary and CEM I hcp. The blending of slag and fly ash significantly increases the volume of open large gel pores (3.3–12.3 nm), with the most significant effect observed for hcp with a w/b of 0.35.

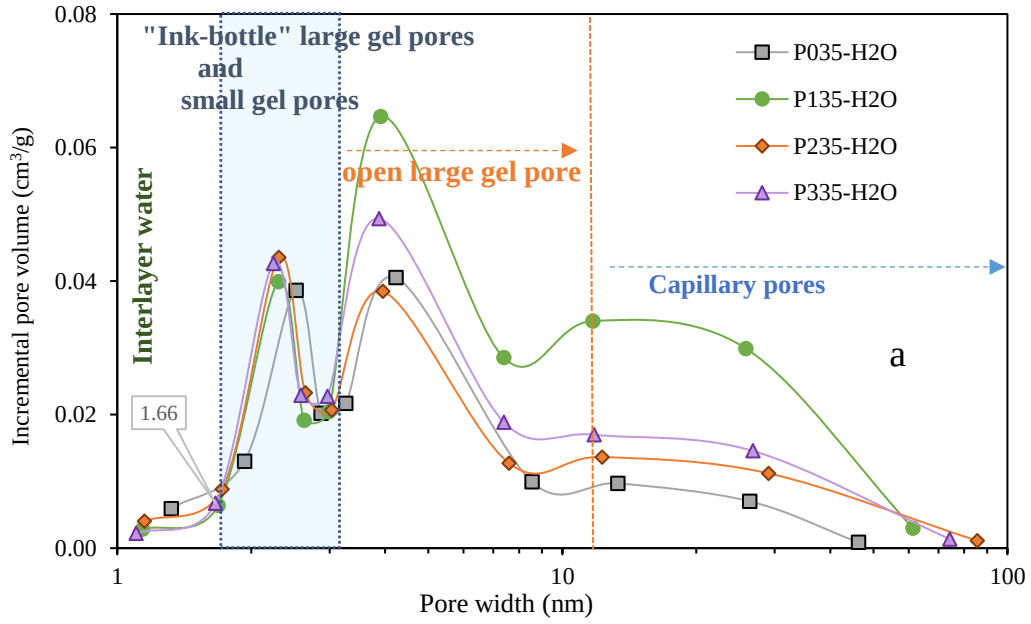


Figure 4.3. The PSD in hcp calculated by BJH method from water vapour desorption, exemplifying with pastes with w/b of 0.35, refer to [44] (paper III) for the detailed information of all pastes.

4.1.3 Evaluation of hydration degree

Moisture content at 20–25 % RH is associated with water in the interlayer space of C-S-H. Bonnaud et al. [107] conducted molecular dynamic simulations and discovered that interlayer water began to dry at approximately 20 % RH. The mesoporous structure of C-S-H gives it a specific surface area at least one order of magnitude greater than other hydration products. When the RH falls below the condensation point in the gel pores, most of the moisture in hcp is adsorbed in the interlayer space of C-S-H. Using the common atomic structure of $1.65\text{CaO} \cdot \text{SiO}_2 \cdot 1.75\text{H}_2\text{O}$ from [108] or $1.69\text{CaO} \cdot \text{SiO}_2 \cdot 1.80\text{H}_2\text{O}$ from [109], the evaporable water (dried at ~ 0 % RH) in the C-S-H structure is roughly 7.3×10^{-3} mol/g (or 0.131 g/g) dried C-S-H, with approximately 0.55 mole of chemically bound water attached to Ca or Si atoms [110]. This value is close to the experimental result (0.1 g/g) in [111] and very similar to the value used in [96,99] for calculating the C-S-H content. Assuming SCMs have few effects on the evaporable water in the interlayer of C-S-H, Eq. (4.3) can be used to estimate the C-S-H content in all hcps in this study.

$$W_{CSH} = \frac{n_{e,20}}{\bar{n}_{w,CSH}} \quad (4.3)$$

where $n_{e,20}$ (mol/g) is the amount of water adsorbed in hcp at 20 % RH (partially shown in Figure. 4.1), $\bar{n}_{w,CSH}$ is the amount of evaporable water in C-S-H with respect to the weight dried at ~ 0 % RH (7.3×10^{-3} mol/g), and W_{CSH} is the weight of C-S-H in the dried hcp. The

amount of C-S-H in pastes have been calculated and presented in paper III [44].

Thermodynamic modelling has been popularly employed to investigate the influence of SCMs on the hydration process and phase assemblage in cementitious materials. It was also used in this section to evaluate the effect of SCMs hydration degree on the phase assemblage in hcp. Figure 4.4 shows the hydration phases in the hcp with different hydration degree of fly ash. The hydration degree of CEM I is set to 92.2 %, which is calculated by dividing the measured content of portlandite in P055 (22.0 % by thermogravimetric analysis) with the portlandite content in the fully hydrated paste (23.87 % by GEMS). The focus centers on the quantities of the two main hydration products, namely C-S-H and portlandite. In the case of the fly ash binary hcp, portlandite will decrease due to consumption by the pozzolanic reaction of fly ash. Moreover, the amount of C-S-H will increase with the hydration degree, during the process before a complete consumption of fly ash. Theoretically, a hydration degree of 38 % will consume all portlandite in P145. Beyond this hydration degree, the content of C-S-H will decrease due to the formation of strätlingite.

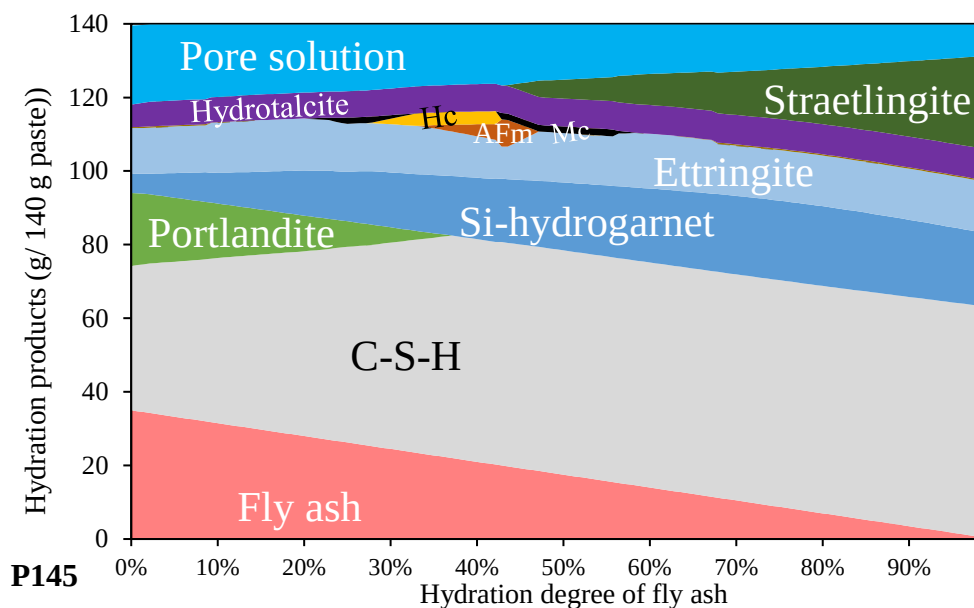


Figure 4.4. Phase assemblage of hydration products with the increase in hydration degree of fly ash, refer to paper III [44] for data of other binder systems.

To validate the method using water vapour sorption data to calculate the hydration degree of SCMs, the amount of portlandite was measured through thermogravimetric analysis. The hydration degree of SCMs is evaluated by its linear correlation to the amount of C-S-H and portlandite [44]. Figure 4.5 illustrates the hydration degree of fly ash and slag based on the measured portlandite content and the calculated C-S-H content. The good agreement between

the hydration degree estimated by these two methods confirms the reliability of water vapor desorption for assessing the C-S-H content and hydration degree. An increase in w/b will enhance the hydration of fly ash and slag. The calculated hydration degree of fly ash falls within the range of 20 %–30 %, which is consistent with previously reported data for hcps blended with 35 % fly ash under similar curing conditions [112,113]. The calculated hydration degree of slag in binary and ternary hcps ranges from 40 % to 52 % and 43 % to 59 %, respectively. These values are similar with the measured degree of hydration for slag blended hcps with a w/b of 0.42, as reported in previous studies [114].

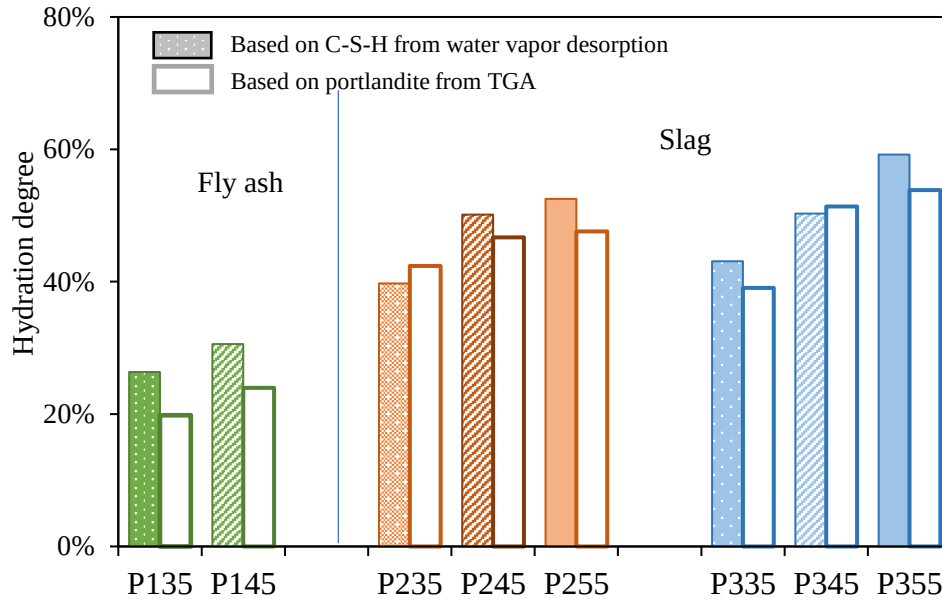


Figure 4.5. Hydration degree of fly ash and slag in the blended hcp after a 6-month water curing calculated by use of GEMS and water vapor isotherm data, corresponding to *Figure 10* in paper III.

4.2 Water behavior in hcp at low temperature

The nanosized confinement of water in hcp will change the thermodynamics of liquid-phase transformations during the freezing and melting experience. This kind of confinement will also change the dielectric response and dynamics of water. In this section low-temperature differential scanning calorimetry (LT-DSC) was employed to quantify the distribution of water confined in different pores during drying under various RH levels. It sheds light on the water distribution in gel and capillary pores with respect to freezable and unfrozen (supercooled) water. Broadband dielectric spectroscopy was used to investigate the dynamics of water confined in the hcp. Various relaxation processes were observed, corresponding to the local chemical environment of C-S-H microstructure, which contributes to a comprehensive understanding of the C-S-H structure.

4.2.1 Freezing and melting

Figure 4.6a presents a typical freezing and melting curve of hcp equilibrium under 97 % RH with CEM I paste as an example. The freezing-melting curve exhibits a significant hysteresis, with the average melting temperature being higher than the average freezing temperature. It is a common phenomenon observed in many porous media [115]. This can partially be attributed to the geometrical hindrance effect caused by the pore shape. Furthermore, the attractive potential from the pore wall induces a compression effect, resulting in a non-monotonic correlation between the freezing temperature and pore diameter due to the competition between hindrance and compression [116]. In cases of extreme confinement, water molecules are inhibited from forming an ice structure to avoid crystallization [50].

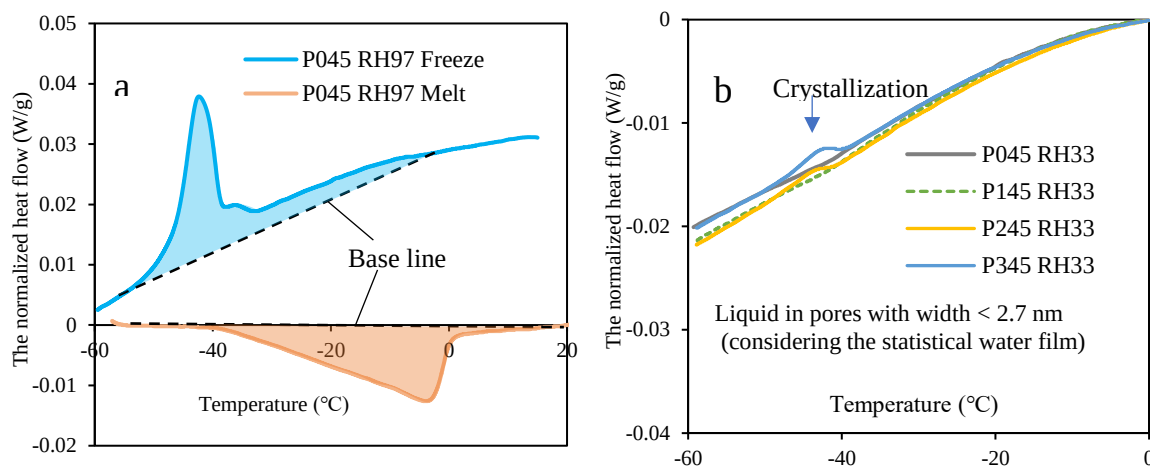


Figure 4.6. Example of low temperature DSC curve for hcp, with OPC paste conditioned under RH of 97 % (a) and pastes conditioned under RH of 33 % (b): corresponding to Figure 1 in paper IV.

Sun and Scherer [117] suggested that water in pores with a width smaller than 4.5 nm did not undergo ice formation during the cooling process. In addition, Bager and Sellevold [118] observed no ice formation in hardened cement paste with equilibrium at 33 % and 11 % RH. White cement paste at 33 % RH also did not exhibit any exothermic peak indicative of ice formation [119]. However, as shown in Figure 4.6b, crystallization of ice was detected in slag blended pastes (P245 and P345) at 33 % RH, while no ice was found in P045 and P145. This intriguing observation may be attributed to the refined small neck of ink-bottle pores. During the drying process, it may be difficult to dry the inner part of these pores. The expulsion of water from interlayer or small gel pores to larger pores during the cooling process, similar to the freezing process of montmorillonite [120], may also result in this phenomenon.

4.2.2 Thermoporometry to determine moisture distribution

Based on the thermodynamic characteristics of water-ice phase transition in porous matrix, the correlation between phase change temperature and pore size can be expressed by the Gibbs-

Thomson equation [117,121].

$$r_p = \frac{A}{\Delta T_s} + \delta \quad \dots\dots\dots (4.4)$$

In this equation, the radius of the cylinder pore is denoted as r_p (nm), and the undercooling is represented by ΔT_s (°C), which is positive when the temperature is below the melting point of the bulk ice crystal. The constant A is determined by the surface energy between water and the cement-based material, whilst the constant δ is related to the layer of unfrozen water and the shape of the pore. The shape of the pore is typically assumed to be cylindrical, and for the freezing process, the values of A and δ are taken as 64.67 nm and 0.57 nm, respectively. For the melting process, the values are 32.33 nm and 0.69 nm, respectively [117].

Taking into account the baseline for LT-DSC and the variation in heat capacity of the different phases (liquid, ice crystal, and porous body), the quantity of ice formed at temperature T can be computed using Equation (4.5) due to the narrow temperature intervals in the data collection [117].

$$m_c(T + n\Delta T) = m_c(T) + \sum_1^n \frac{\Delta T}{2} \left[\frac{Q(T+n\Delta T-\Delta T)-Q_0}{qh_f} + \frac{Q(T+n\Delta T)-Q_0}{qh_f} \right] \exp \left[\frac{\Delta T(C_{pC}-C_{pL})}{h_f} \right] \quad \dots\dots\dots (4.5)$$

where $m_c(T)$ represents the ice mass at temperature T , and ΔT denotes the temperature interval that was set to 0.02 °C in this study. h_f (J/g) denotes the heat of fusion for pore water, $Q(T)$ (W/g) represents the heat flow into the sample, Q_0 (W/g) is the baseline in heat flow, q (°C/s) is the heating rate, C_{pL} (J/g/°C) denotes the heat capacity of the pore liquid, and C_{pC} (J/g/) represents the heat capacity of the ice crystal. The baseline of LT-DSC is estimated by fitting a linear line from the onset of freezing to approximately -55 °C.

Figure 4.7 presents the distribution of ice volume in cement paste under various RH levels. The curves for hcp equilibrium with 33 % RH are not included due to limited crystallization. As expected, the ice volume in hcp decreases as the RH decreases. The hysteresis phenomenon during freezing and melting processes is observed under all RH levels. When the temperature is converted to pore width using Eq. (4.4), the hysteresis effect becomes more noticeable, particularly in terms of the minimum pore width required for ice crystal formation. The freezing curves suggest that the critical pore width for ice formation is around 4 nm, implying that no ice will form in pores smaller than this value. However, previous studies have detected crystallization peaks in silica nanopores with diameters as small as 3 nm [122], and molecular dynamic modeling has indicated a critical nucleation radii of 1 nm [123]. The critical pore size for melting curves is approximately 2.4 nm, suggesting that the melting curves are more suitable for evaluating moisture distribution in hcp.

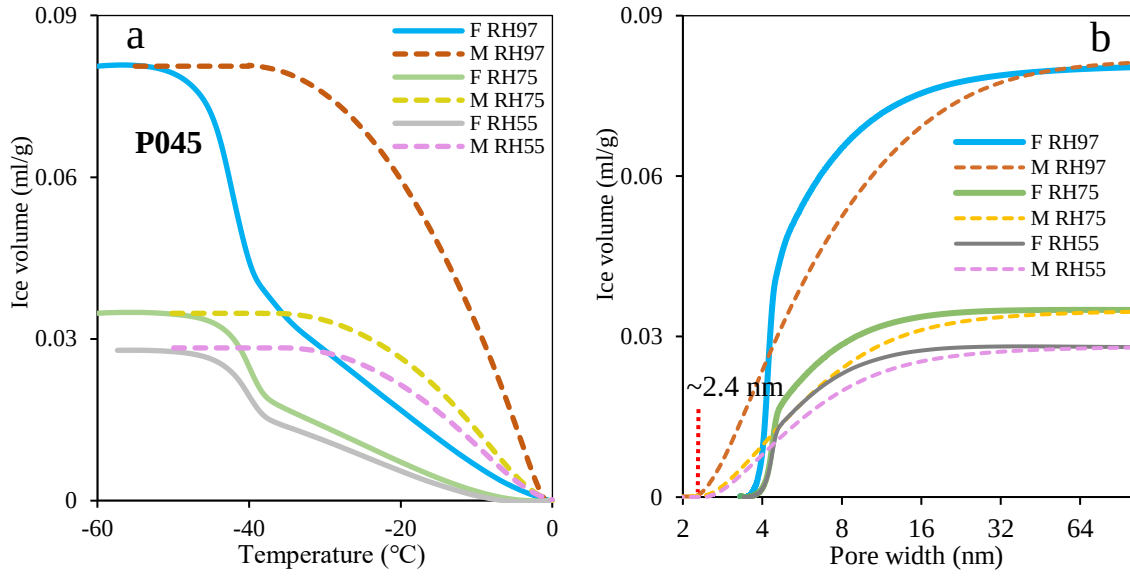


Figure 4.7. Ice volume distribution in P045 under different RH conditions. (a) Calculated ice volume under RH of 97 %, 75 %, and 55 % using Eq. (4.5), and (b) corresponding ice volume in nanopores based on Eq. (4.4) with respect to freezing (F) and melting (M) process: *Figure 2* in paper IV.

Figure 4.8 illustrates the detailed distribution of evaporable water in P045 and P145 during the drying process, categorized into four different intervals: < 2.7 nm, 2.7–10 nm, 10–20 nm, and > 20 nm. The change of water confined in the interlayer and gel pores is easily distinguishable from the data obtained from P045 and P145. The results indicate that water confined in the interlayer and small gel pores (< 2.7 nm) does not present any increase during the drying process. Under 75 % RH, water in capillary pores is almost fully evacuated, and there is a loss of more than half of the water in large gel pores [124] or interhydrate spaces (2.7–10 nm) [125,126]. The LT-DSC data reveals only a small loss of freezable water during a drying to 55 % RH compared to 75 % RH, and the major loss is detected in water confined in the interlayer and small gel pores. This can be ascribed to a coarsening of gel pores. A drying process at 33 % RH induces a minor increase in unfrozen water due to the movement of C-S-H sheets.

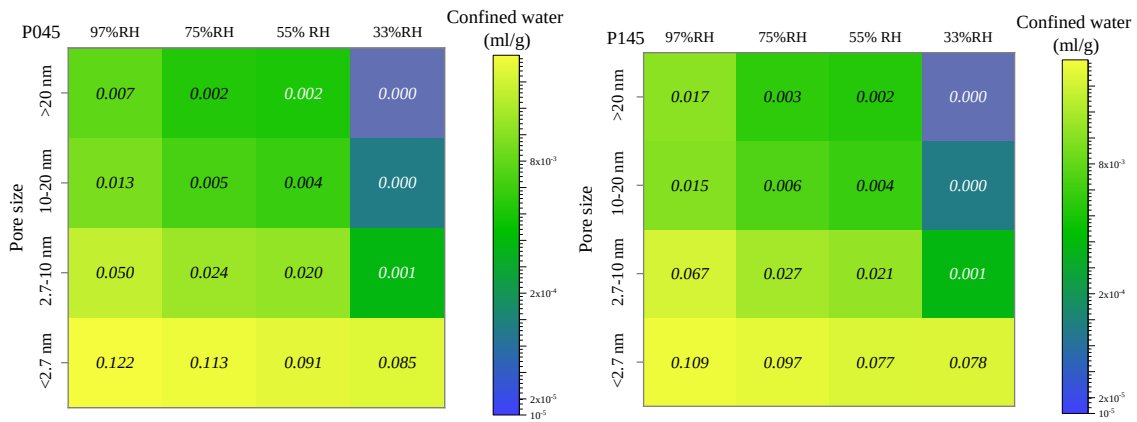


Figure 4.8. Moisture redistribution in P045 and P145 during the desorption equilibrium (*Figure 6* in paper IV).

4.2.3 Dynamics of water confined in hcp

Figure 4.9 shows that the comparison between the relaxation time of P145 with RH of 97 % and 33 %. Four relaxation processes were detected relating to the water behavior. The relaxation process 1 (R1) has the fastest relaxation dynamic and the lowest activation energy, which is attributed rotation/reorientation of hydroxyl in Si-OH environment [127]. Relaxation process 2 (R2) is the second fastest process, and it is more reasonable to be assigned as the dynamic of water molecular hydrating the silanol groups [128] or water confined in pores of smaller than 1 nm [129]. Relaxation process 3 (R3) is dynamics of the unfrozen water in pore with reduced hydrogen bonds and mixed with dynamics of hexagonal ice (ice I_h). Relaxation process 4 (R4) is a Maxwell–Wagner process, relating to interfacial polarization between liquid and solid face [130]. The saddle-like temperature dependence of relaxation time in between $1000/T$ of 3 and 4 is ascribed to the loss of evaporable water in matrix. This somehow can explain why R4 is missing in samples with RH of 33 %.

Relaxation of structural water (R1 and R2) is a β -process with Arrhenius dependence. The supercooled water in gel pores seems to have a Vogel–Fulcher–Tammann (VFT) dependence at high temperature range. This fragile-to-strong transition (from VFT to Arrhenius) occurs in supercooled water confined hydrophilic porous matrix [50,52]. However, the data in this study is insufficient for getting such a conclusion. R4 also has an Arrhenius dependence in temperatures below 250 K.

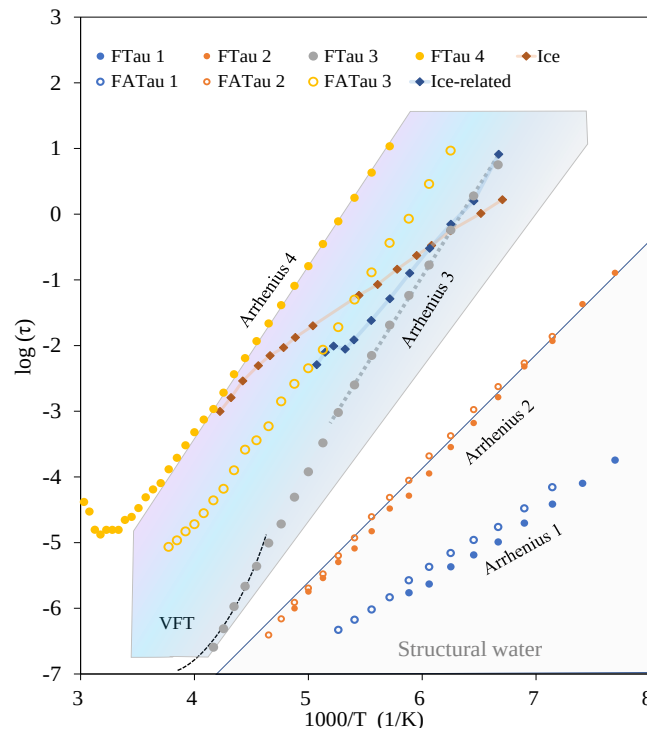


Figure 4.9. Comparison of relaxation times of P145 at RH of 97 % (FTau*) and 33 % (FATau*). Data of ice I_h relaxation from [131] and ice-related relaxation in frozen tri-propylene glycol solution [132] are shown for comparison: Figure 9 in paper IV.

The comparison of fitting results with Arrhenius equation is presented in Table 4.1. The activation energy required for R1 lies in the range of 19.65 to 24.85 kJ/mol. These values are higher than the activation energy of Si-OH relaxation in xonotlite (17.28 kJ/mol or 0.18 eV) [127], but they are lower than that of the similar relaxation in Co-montmorillonite [133]. Fly ash and a further replacement of limestone seem to reduce the activation energy and increase the $\log(\tau_0)$, but the effect is very limited. A drying of P145 at 33 % RH has almost no effects on both activation energy and the $\log(\tau_0)$ of structural water compared with a conditioning at 97 % RH. Activation energy of R2 in binder systems has a value between 34.79 and 37.42 kJ/mol. The behavior of R2 is similar with that of process 2 observed in synthetic C-S-H [134] and tobermorite [127]. The activation energy of R3 is similar to the activation energy of diffusion of glassy bulk water (45 kJ/mol [135]) and lower than the activation energy of ice I_h relaxation (~ 50 kJ/mol [131,136]). The addition of fly ash increases the activation energy of R3, which is likely due to the lower ion concentration in the pore solution. The effect of slag on this process is mainly observed in the non-Arrhenius temperature range; thus, P245 exhibits similar activation energy and $\log(\tau_0)$ as P045. When CEM I is partially replaced with limestone, the activation energy of R3 decreases. In comparison to CEMI paste, fly ash results in a lower activation energy of R4. Slag has little effect on the activation energy of R4, but it increases the value of $\log(\tau_0)$.

Table 4.1. Regression of the temperature dependence of water related relaxation processes in hcp with RH of 97 % and P145 with RH of 33 %.

Mix ID	Relaxation	Slope (k)	$\log(\tau_0)$	R^2	E_a (kJ/mol)
P045	R1	1.237	-13.25	0.998	23.67
	R2	1.946	-15.78	0.999	37.24
	R3	2.607	-17.02	0.996	49.90
	R4	2.896	-16.52	0.997	55.42
P145	R1	1.119	-12.39	0.998	21.41
	R2	1.818	-14.89	0.999	34.79
	R3	2.671	-16.97	0.998	51.11
	R4	2.500	-13.29	0.999	47.84
P245	R1	1.297	-13.63	0.997	24.82
	R2	1.836	-15.11	0.998	35.13
	R3	2.582	-16.91	0.996	49.41
	R4	2.870	-15.68	0.996	54.92
P345	R1	1.027	-11.85	0.998	19.65
	R2	1.944	-15.73	1	37.20
	R3	2.196	-14.50	0.994	42.02
	R4	2.831	-15.68	0.999	54.17
P145RH33	R1	1.146	-12.36	0.998	21.93
	R2	1.832	-14.85	0.999	35.06
	R3	2.484	-14.68	0.998	47.53

4.3 Chapter summary

Water vapour desorption isotherm provides effective information of the mesoscale pore structure in hcp. It is essential to consider the effect of ions on the equilibrium pressure of water vapour on a plane surface when calculating the pore size distribution using the BJH model. The novel approach based on water vapour sorption and thermodynamic modelling performs well in the evaluating the hydration degree of SCMs. It has been observed that the presence of SCMs markedly increases the moisture in hcp at RH above 50 %. This is attributed to their effect on increasing the volume of large gel pores and capillary pores. Cavitation occurs during the desorption of water vapour at RH between 36 % and 30 %, which can result in an overestimation of the volume of the small gel pores. Nonetheless, the increase in the cavitation-induced value reveals the refinement effect of SCMs. Furthermore, the dilution effect from SCMs provides essential extra water for achieving full hydration of the clinker.

During the drying process, moisture in hcp undergoes a redistribution due to the dynamic microstructural changes. Thermoporometry is an effective method for characterising the moisture distribution. The melting curve is preferable to the freezing curve for evaluating water confined in hcp, and it enables to perform measurement of the water confined in pores larger than ~2.4–2.7 nm. Regardless of the temperature to which the water is frozen, water in pores smaller than the critical value, including interlayer and partial gel pores, will not form a tetrahedral ice structure. The influence of SCMs on the distribution of moisture has been found to extend beyond the equilibrium state at 97 % RH to affect redistribution during the drying process down to 33 % RH. Although some discrepancies in the discussion of dynamic pore structure changes during the initial drying process have been observed between previous publications [137–139], this study affirms that, under equilibrium conditions, the drying process does not induce any increase in volume of pores smaller than 2.7 nm. A severe coarsening of small pores occurs during the drying process between RH values of 75 % and 55 %. SCMs have a limited effect on the dynamics of structural water, primarily influencing the dynamic of water in small gel pores and interfacial polarization.

5 Effect of SCMs on moisture and chloride transport

Moisture transport properties play crucial roles in determining the performance of cement-based materials during construction process and the long-term service. The humidity levels in the concrete substrate before applying any covering material are directly linked to the risk of cracking and mould growth. Moisture also influence the transport of CO₂, O₂, and chloride ions in concrete, which ultimately determine the deterioration process of reinforced concrete structures [37,140]. Effect of SCMs on both water transport and chloride migration in cement-based material will be investigated to provide better understanding for the design of more durable cement-based materials. The impact of SCMs on pore structure in pastes will be analyzed by interpreting various parameters. Finally, the moisture and chloride transport characteristics of pastes blended with different SCMs will be comprehensively compared to the pore structure parameters. This chapter summarises the content of paper V and VI.

5.1 Moisture transport

This section elaborates moisture transport properties of hcp measured by a novel method with the corresponding procedures, as described in [28,58]. This method enables the measurement of both water vapour diffusion coefficient (D_v) at steady state, total moisture transport coefficient (D_w) and water vapour diffusion coefficient by semi-infinite drying ($D_{v,s}$) for the same sample in a single procedure. The influence of w/b and SCMs on the moisture transport properties will be discussed in detail.

5.1.1 Water vapour diffusion at steady state

Figure 5.1 presents D_v of hcp measured by the tube method within four different RH intervals. It is important to note that all “ D_v ” values in the figures represent the average diffusion coefficient within a specific RH interval. It has been observed that a higher RH interval leads to a higher deviation within three parallel tests. However, it is worth mentioning that the tube

method shows a lower level of deviation compared to the cup method, as reported in [38]. Therefore, the tube method, as described in detail in paper V, is a reliable and valid alternative to traditional cup methods for measuring vapour diffusivity under steady-state conditions.

For pastes with w/b of 0.35, the fly ash binary paste has the lowest D_v within all RH intervals, with a value smaller than half of that in CEM I paste (P035). Effect of slag on the vapour diffusion at steady state depends on the RH intervals. It induces a reduction in coefficient measured in RH intervals above 75 % but enforces a minor increase in coefficient between RH of 75 and 50 %. The impact of SCMs on vapour diffusion reduction is more pronounced at the higher w/b and at RH intervals above 62.8 % (between 75.5 % and 50 %). For example, the D_v of slag blended paste is only 0.52, 0.29, and 0.14 of CEM I paste for w/b ratios of 0.35, 0.45, and 0.55, respectively. A higher w/b causes an increase in the vapour diffusion coefficient for all pastes. An increase of the w/b from 0.35 to 0.55 induces an elevation in the coefficient of slag blended and CEM I paste, with a factor of approximately 2.5 and 10, respectively. The further replacement of CEM I with limestone generally leads to an increase in the vapour diffusion. However, this effect is negligible at the higher RH intervals.

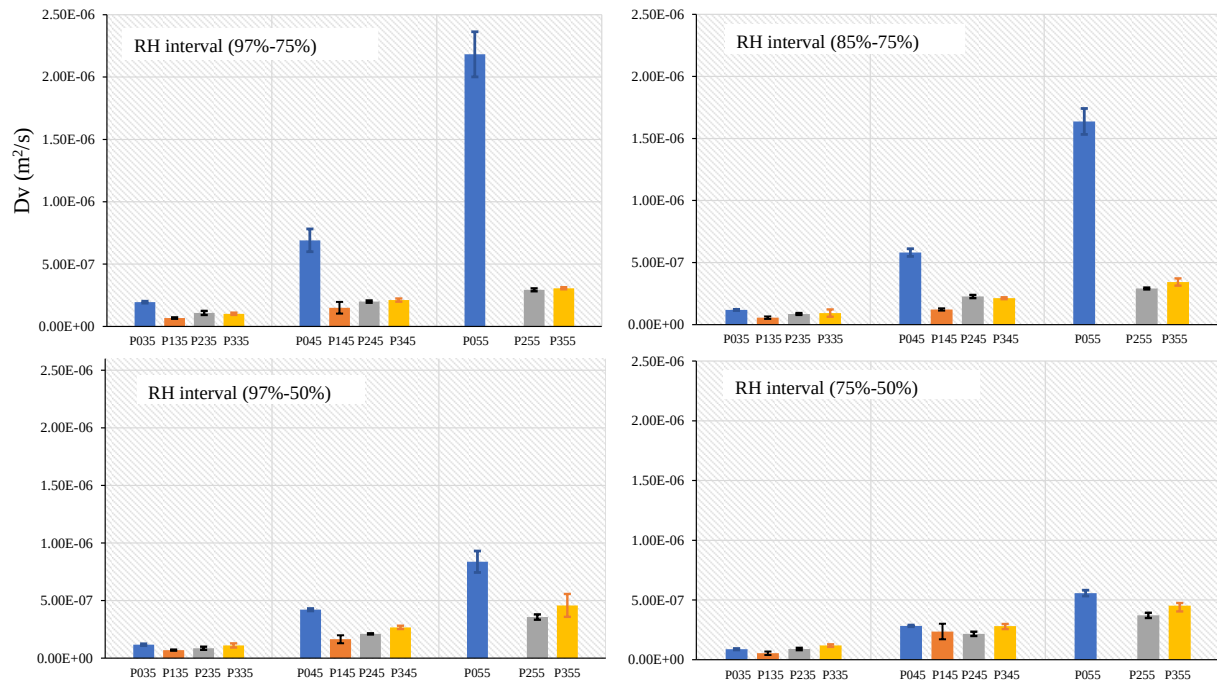


Figure 5.1. Water vapour diffusion coefficient of hcp measured by the tube method in four different RH intervals.

Apparently, the measured vapour diffusion coefficient depends on the RH intervals. There is a significant increase in the D_v of CEM I pastes as RH increases. D_v of pastes blended with SCMs seems to be independent on RHs. However, An increase in the D_v can be observed as the RH level reaches a higher range (94.6 % to 97.6 %) in both the adsorption and desorption processes, as depicted in [38]. As shown in Figure 5.2, moisture transport in cement-based materials involves the transportation of both gas (vapor) and liquid phases under non-saturated

conditions, where the pore volume is only partially filled with the liquid phase. The dominance of either process depends on saturation state. Before the liquid phase achieves contiguous connection (percolation) at the critical RH condition, the moisture transport process is dominated by vapor diffusion. In contrast, a Darcian transport of the liquid phase is prominent after percolation, resulting in particularly high transport coefficients. Therefore, at high RH intervals, the results from the cup method will overestimate vapor diffusion due to liquid flow mixing. Baroghel-Bouny [37] provided a detailed explanation of this phenomenon. The RH dependence of measured D_v is well described by equation (14) in paper V [28], and Figure 5.2 presents the representative results in the top left corner.

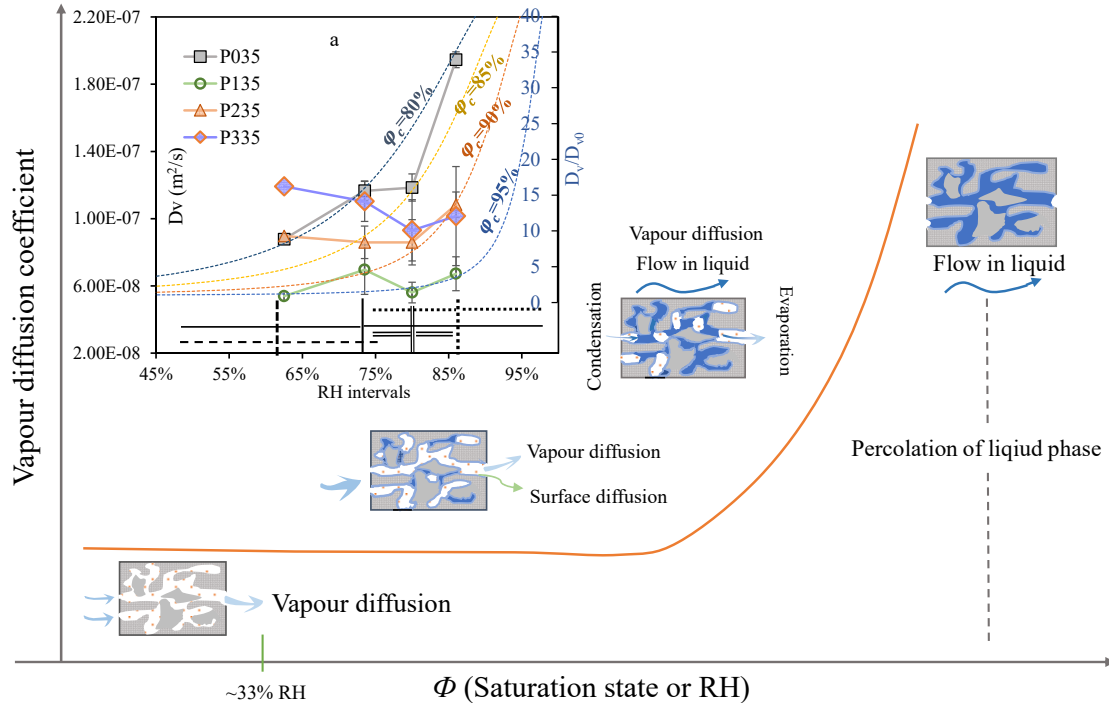


Figure 5.2. Illustration of dependence of water vapour diffusion coefficient, exemplifying with w/b of 0.35.

5.1.2 Moisture transport during the first drying

The total moisture transport coefficient (D_w) can be measured by the semi-infinite drying. Using D_w and the moisture content at the drying RH enables to calculate the water vapour diffusion coefficient under the drying process ($D_{v,s}$). This has been demonstrated in paper V in detail.

Figure 5.3 shows the moisture transport coefficient for hcps dried at RH of 75 % and 50 %. Pastes dried at 75 % RH exhibit lower D_w values compared to those dried at 50 % RH. D_w is dependent on the moisture content of cement-based materials. As the degree of saturation increased from zero, D_w decreased and reached its minimum value at a saturation degree of 0.5-0.8. Once the liquid percolation threshold was reached, D_w increased with the saturation

degree [37]. Blending SCMs leads to a significant decrease in D_w during drying at both 50 % and 75 % RH. While drying at RH of 50 %, the reduction in D_w caused by SCMs is most noticeable in the hcp with fly ash and a w/b of 0.45. With a further replacement of limestone, the effect of slag in D_w weakens, resulting in a D_w of ternary paste almost twice as that of the binary paste containing slag.

The effect of drying RH on $D_{v,s}$ is comparable to its effect on D_w . However, the variation in $D_{v,s}$ between different RH levels is less pronounced than that in D_w . This phenomenon is particularly noticeable in blended paste, which may be due to the greater moisture capacity of blended pastes compared to CEM I paste. Effect of SCMs on water vapor diffusion at drying will be amplified at a higher w/b , which is similar with the finding in water vapor diffusion at steady state.

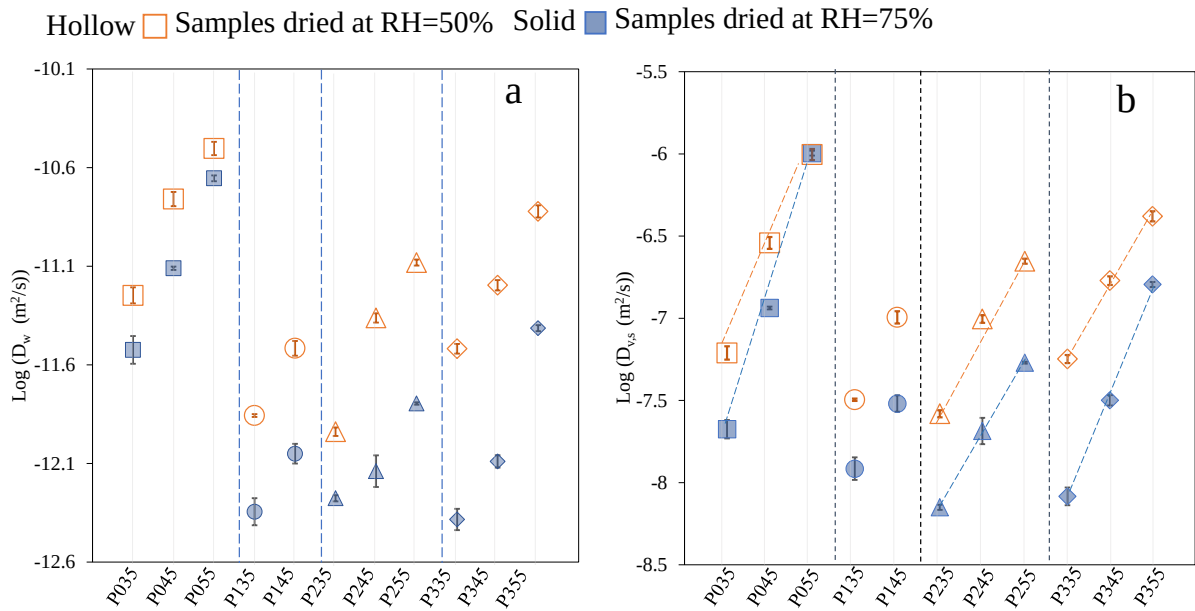


Figure 5.3. The total moisture transport coefficient D_w and water vapor diffusion coefficient during semi-infinite drying $D_{v,s}$ at RH=50 % and 75 % (20 °C), respectively: a- D_w of all pastes; b- $D_{v,s}$ of all pastes: adopting from Figure 2 in paper V.

5.2 Effect of SCMs on chloride migration

Chloride migration coefficient in cement-based material is crucial for predicting the service life of concrete structures exposed to marine and saline environment. This parameter is time-dependent and decreases over time due to the continuous hydration of binders, following an empirical power function [141,142]. Table 5.1 presents the chloride migration coefficient of various pastes at different curing times, tested by the rapid chloride migration (RCM) method. Generally, the chloride migration coefficient (D_{RCM}) decreases as curing time increases, except for P055, which shows an unexpected increase. Additionally, an increase in w/b causes an increase in D_{RCM} , although the influence of w/b on D_{RCM} of slag binary paste at 180 d is

relatively weak. Blending of SCMs in reduces the chloride migration coefficient, particularly in pastes with a longer hydration time and higher w/b ratios. Fly ash has the strongest effect on the reduction of DRCM after 180 d. Interestingly, D_{RCM} of P055 exhibits an increase with hydration time after 28 d, which has also been observed in some previous studies [141,142]. It was found that Portland cement-based concrete may have a higher chloride migration coefficient at a later age when the w/b ratio is relatively high (> 0.5).

Table 5.1. The D_{RCM} of pastes cured to 28, 90 and 180 d.

Time/days	Chloride migration coefficient ($\times 10^{-12} \text{ m}^2/\text{s}$)										
	P035	P045	P055	P135	P145	P235	P245	P255	P335	P345	P355
28	8.02	15.56	21.08	8.90	11.35	5.12	5.82	7.29	5.79	5.39	6.40
90	5.84	11.67	26.28	2.27	3.67	3.17	3.85	4.52	2.70	3.64	3.81
180	3.52	10.46	26.15	0.84	1.51	2.50	2.60	2.91	1.76	1.94	3.71

In the practical application scenario, the exposure environment is much severer than the lab room. Figure 5.4 presents a comparison of the chloride profile in concretes after a 20-year exposure under a de-icing salt road environment in Sweden. It shows that substituting Swedish structural cement with 5 % silica fume has little impact on chloride penetration. However, the benefits of reducing chloride content become more apparent when the replacement ratio increases to 10 % silica fume. For the concrete made with Finnish rapid Portland cement containing 10–15 % limestone filler, blending of ground granulated blast-furnace slag seems to have very limited effect on the penetration front of the chloride at w/b of 0.4. It even caused an increase in the chloride content at depth lower than 20 mm. However, its inhibiting on the chloride ingress is much evident in concrete with w/b of 0.5, especially in the depth larger than 20 mm. It implies that the effect of slag on the chloride migration in practical environment still depends on the binder types and w/b .

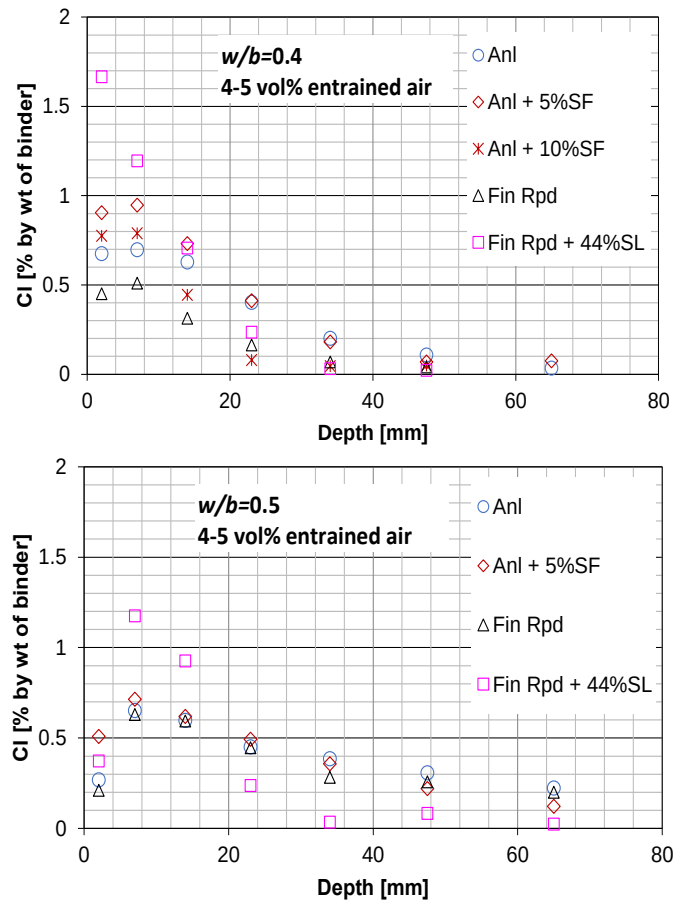


Figure 5.4. The chloride profile in concretes after an exposure of 20 years under a de-icing salt road environment adopted from Figure 4 in paper VI [42]. Notes: Anl- Swedish structural cement, SF- Silica fume, SL- Finnish ground granulated blast-furnace, Fin Rpd- Finnish rapid Portland cement blended with 10–15 % limestone filler.

5.3 Refinement of pore structure

Mercury intrusion porosimetry measurement is a useful method for obtaining comparative indices of pore structure in cement-based materials by testing the threshold diameters of intrudable pore space. The pore size corresponding to the peak in the $dV/d\log(D)$ curve is known as the critical entry pore size [143]. Figure 5.5 shows that under sealed curing conditions after 390 d, the incorporation of fly ash in pastes with w/b of 0.35 and 0.45 induces a decrease in the critical entry pore size. Conversely, the use of slag results in a minor increase in this critical size compared with CEM I paste. This means that in the change of critical entry pore size cannot explain the much lower moisture transport coefficients of the blended pastes (as shown in Figure 5.1 and 5.3), which was considered to be a significant factor controlling moisture transport in previous publications [39,144]. It has been observed that slag can reduce the critical entry pore size of pastes at a later age when cured in water [9]. This is because such a curing provides adequate amount of water in the large capillary pores, which enables the hydration products to precipitate and fill these pores during the later hydration of slag. However, the sealed curing may not induce this effect due to the limited availability of water.

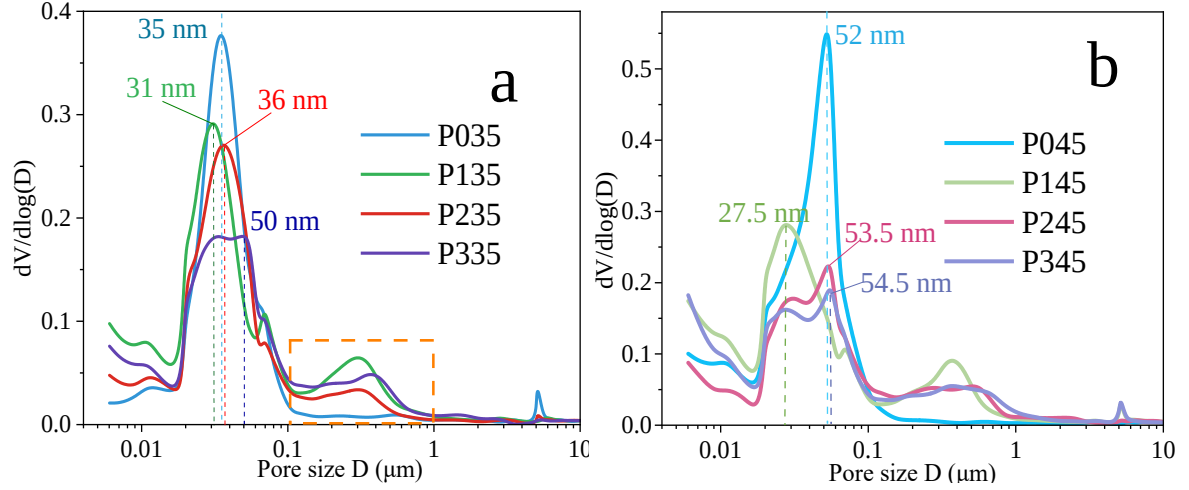


Figure 5.5. Pore size distribution of hcp after a sealed-curing for 390 d measured by mercury intrusion porosimeter, adopted from Figure 6 in paper V [28].

Formation factor and pore connectivity are related to the transport properties of cement-based materials as described by equation (1) in paper V. To find out the real refinement effect of SCMs, these two parameters have been calculated and presented in Table 5.2. Blending of SCMs decreases not only the conductivity of pore solution but also the pore connectivity and inverse of F . The tendency of pore connectivity (β) with respect to variations in w/b and binder types is similar to that of $1/F$. As the w/b increases, both $1/F$ and β present a significant increase. Fly ash causes a substantial reduction in $1/F$ compared with CEM I paste, with a reduction factor of approximately $1/8.5$ and $1/20$ in pastes with w/b of 0.35 and 0.45, respectively. The $1/F$ the slag blended pastes is also much lower than that of CEM I paste with the same w/b , 0.45, and 0.55, respectively. The ternary pastes exhibit a similar $1/F$ or β as the slag binary pastes. It is apparent that the real refinement effect of SCMs is to reduce the pore connectivity.

Table 5.2. Properties of pastes at approximately 1 year (390 d), including electrical conductivity, pore solution conductivity, inverse of F , porosity, and pore connectivity.

Sample	Electrical conductivity (mS/cm)		$1/F$	Φ	β
	Paste	Pore solution			
P035	0.251	165.9	1.52×10^{-03}	0.19	7.84×10^{-03}
P045	0.701	131.3	5.34×10^{-03}	0.26	2.07×10^{-02}
P055	1.249	102.9	1.21×10^{-02}	0.35	3.45×10^{-02}
P135	0.019	104.4	1.78×10^{-04}	0.24	7.48×10^{-04}
P145	0.026	96.0	2.71×10^{-04}	0.28	9.82×10^{-04}
P235	0.075	149.6	4.98×10^{-04}	0.19	2.60×10^{-03}
P245	0.128	114.5	1.12×10^{-03}	0.23	4.85×10^{-03}
P255	0.167	111.6	1.50×10^{-03}	0.27	5.46×10^{-03}
P335	0.070	133.3	5.26×10^{-04}	0.20	2.60×10^{-03}
P345	0.085	86.9	9.75×10^{-04}	0.24	4.01×10^{-03}
P355	0.111	78.0	1.42×10^{-03}	0.25	5.60×10^{-03}

5.4 Transport properties in relation to pore structure

5.4.1 Correlation between D_v , F and porosity

As D_v in hcp is moisture-dependent, Figures 5.6a–c show separate plots for correlations at different RH intervals. D_v at RH97–75 presents a linear relation to the $1/F$ of hcp. This indicates that the pore connectivity, rather than porosity, determines D_v at high RH intervals. The blended pastes exhibit much lower pore connectivity than CEM I pastes, which results in a much lower vapor diffusion coefficient at high RH intervals compared to CEM I pastes. As RH interval decreases to RH97–50, the connectivity of the pore solution declines significantly, causing a de-percolation of liquid phase. Therefore, the moisture transport process is primarily determined by porosity, as depicted in Figure 5.6d.

Even though both $1/F$ and β of the blended pastes are substantially lower than that of CEM I (Table 5.2), the D_v of blended pastes is similar to that of CEM I with the same w/b in RH75–50. Furthermore, the slope of the regression line in the blended hcp increases with the decrease of RH levels. It implies that the major determinant of D_v shifts from pore connectivity to porosity. It is noteworthy that the data of fly ash blended pastes with w/b of 0.45 deviate from the fitting line of the blended pastes, owing to their much lower pore connectivity compared to the slag blended hcp.

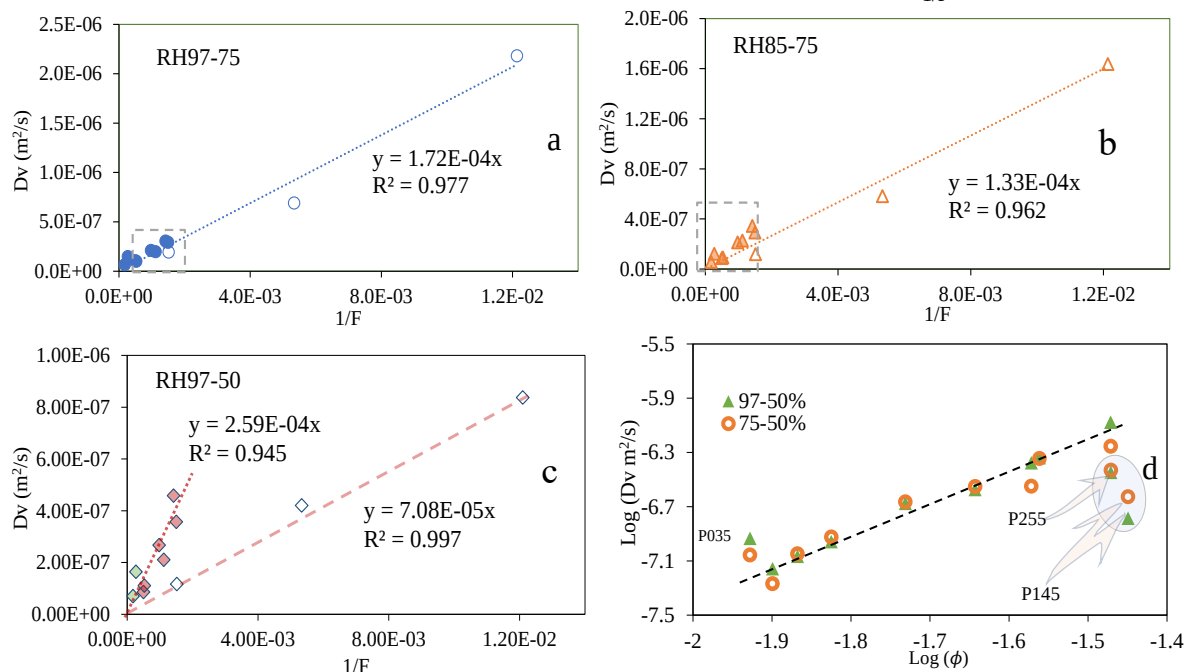


Figure 5.6. The water vapour diffusion coefficient in relation to $1/F$ and porosity. The hollow marks are the data of CEM I, the solid marks are the data of the blended pastes and the marks filled with green color are fly ash blended pastes.

5.4.2 Relationship between D_{RCM} and $1/F$

The ion transport coefficient in the paste linearly correlates to the pore structure parameter F and its transport coefficient in the pore solution [88,90]. If we assume that the binding capacity of the hydration products can be neglected, the non-steady-state migration of chloride under an applied electric field, D_{RCM} , can be estimated by the use of F . D_{ps} , the chloride migration coefficient in the bulk pore solution, is often assumed to be 2.03×10^{-9} (m²/s) [33], although The value could potentially be smaller as a result of interactions with other ions in pore solution.

$$D_{RCM} = \frac{D_{ps}}{F} \quad (5.1)$$

Figure 5.7 shows that in general the D_{RCM} of all the pastes is located close to the modelled line (dash line in Figure 5.7). However, the data of pastes with w/b of 0.35 deviate from the general curve. Because pastes with a sealed curing were used to measure the conductivity, the pastes with w/b of 0.35 are far from the saturation state under this curing condition. However, the D_{RCM} was tested under the nearly saturated condition which might result in a deeper chloride penetration depth thus a higher value of D_{RCM} . The data of Chidiac and Shafikhani [145] has been normalized to the volume of mortar to fit in the figure. It shows that D_{RCM} of all the mortar generally locates close to the modelled line as well. Therefore, it can be concluded that the pore connectivity or F of hcp should be a key controlling factor on the chloride migration in cement-based materials.

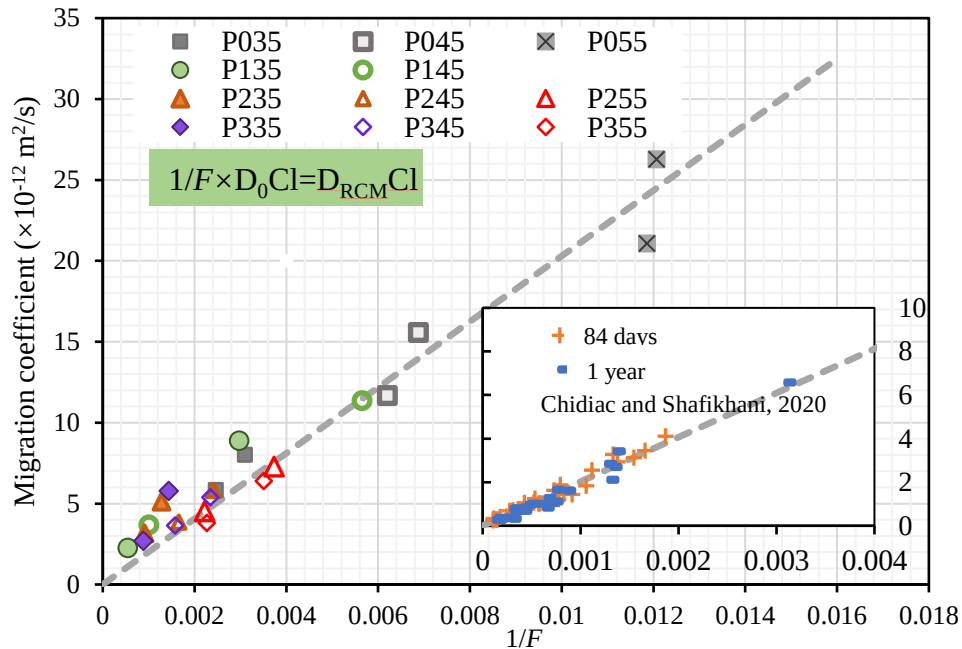


Figure 5.7. The correlation between chloride migration coefficient and $1/F$ with data in this study at curing time of 28 and 90 d and data adopted from [145].

5.5 Chapter summary

SCMs evidently reduce the moisture transport coefficient of hcp after curing for 390 d. Slag decreases the chloride transport rate in the hcp, and effect of fly ash on improvement of chloride resistance shows after 90 d curing. Both fly ash and slag have a great reducing effect on the pore connectivity in the pastes after a long-term curing. The ternary pastes with limestone have the similar F with the binary slag blended pastes after 1 year. A higher w/b provides more water for the later hydration of fly ash and slag, which increases their refining effect on the pore structure. Thus, increasing the w/b amplifies the impact of SCMs on moisture transport and chloride migration coefficient in hcp. Moisture content in hcp plays a crucial role in the moisture transport due to water condensation in its porous structure. Blended pastes exhibit a more complex pore structure, resulting in that vapour diffusion coefficient (D_v) of the blended pastes shows a very weak RH dependence at measured RH intervals.

There are many parameters describing pore structure of hcp, such as porosity, pore connectivity, pore size distribution, the critical entry pore size, and formation factor. Critical entry pore size is not the main controlling factor for moisture transport. The improved resistance to moisture in the blended system is primarily attributed to the pore structure refinement. The refinement effect mainly reflects on the reduction in pore connectivity. The moisture transport properties in the hcp are determined by both the formation factor and the porosity of small pores, specifically volume of the middle capillary and mesoscale pores. However, at high RH the formation factor is the primary factor affecting moisture transport, whilst at low RH, the porosity of small pores is the main factor. Effect of SCMs on the chloride resistance of concrete depends on the w/b , and the effect of slag is pronounced after 20-years of exposure under a road environment for mixture with w/b of 0.5. A highly simplified model was developed to estimate the chloride migration coefficient with only one measured parameter F of hcp. This model is valid to calculate the D_{RCM} of both plain and blended pastes as well as mortars.

6 Monitoring the hardening process of the blended concrete

Traditional methods for testing the hardening of concrete require the strict control of temperature and humidity, which is very different from the field conditions. The non-destructive test is useful for ensuring the application quality of SCMs in field construction. It is also essential for the digital fabrication. This chapter will present an upgraded system based on the previous version in paper II to replicate the setting and strength development of concrete containing SCMs. The content of this chapter is from paper VII.

6.1 Electrical conductivity

6.1.1 Calibrating the dimension effect

The calculation of electrical conductivity using Wenner's method assumes a semi-infinite boundary condition. However, in practical applications, the size of the concrete specimen does not satisfy this boundary, particularly for the upper rows of sensors. To investigate the impact of dimension on the calculation of electrical conductivity, a numerical simulation was performed using COMSOL Multiphysics with a geometry similar with that of the container (see Figure 6.1). In this simulation, the AC/DC mode was employed with the electric current conservation equation, and the boundary conditions were set such that all surfaces of the geometry were insulative. The matrix was set to a constant electrical conductivity of 0.1 mS/cm, and a constant input current of 0.1 mA was applied from point A to point B.

The simulated potential difference between V2 and V1 was used to calculate the electrical conductivity by Wenner's method. The dimension factor (γ) was evaluated by dividing the given conductivity with the calculated one. Figure 6.1 shows that γ is about 1.96 at the first row and decreases with depth. From these simulated results the relationship between γ and the depth of sensors (x) can be established. The simulated values have been validated with the standard

solutions (KCl), and it is confirmed to be very close to the experimental value (see table in Figure 6.1).

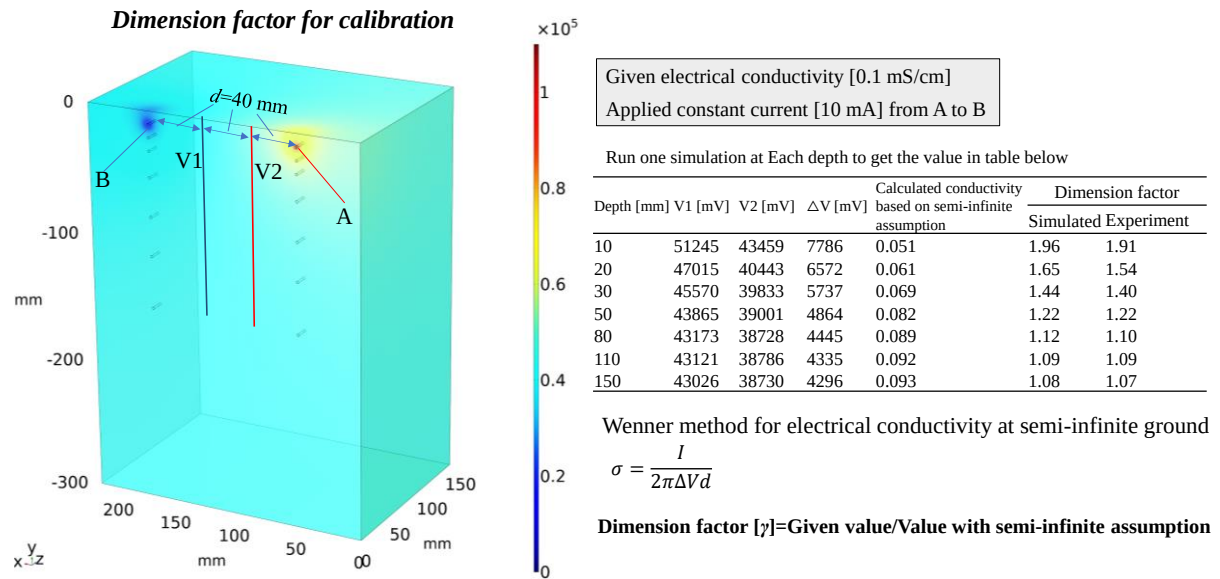


Figure 6.1. Evaluation of dimension factor by the numerical simulation and experiments, corresponding to Figure 2 in paper VII.

6.1.2 From paste to concrete

After including the temperature and dimension factor, the real-time electrical properties of hydrating concrete were calculated and shown in Figure 6.2. To calculate the formation factor (F) of concrete sample, the conductivity of pore solution is assumed to be the same as that in paste (as shown in Figure 3.7). This treatment is based on two assumptions: (1) the presence of aggregates has very limited influence on the hydration of binders; (2) the temperature change induced by the heat release shows minor effects on the ion concentration of pore solution. It should also be noted that the conductivity of pore solution in C338 is estimated by multiplying value of paste with w/b of 0.35 by a dilution factor of 1.09 ($= 0.38/0.35$).

$$F_c = \sigma_{ps}(t)/\sigma_c(t) \quad (6.1)$$

where $\sigma_c(t)$ is the monitored electrical conductivity of concretes.

The influence of aggregates on the electrical characteristics is assessed by comparing formation factor of concrete specimens (F_c) with that of pastes (F_p) with the same w/b ratio. This ratio is also equivalent to the ratio between conductivity of pastes and that of concrete.

Figure 6.2 presents the electrical conductivity, F of concrete and the ratio of F between concrete and paste. Compared to conductivity of pastes, a similar tendency of evolution was detected during the hydration of concrete. The upgraded system (in paper VII) is better than the old version (paper II) in monitoring electrical conductivity before final setting, since it can obtain more stable and smooth data due to a modification on eliminating polarization effects. During

the continuous decrease from 4 h to 20 h, a peak occurs in electrical conductivity of all samples. The time for this peak coincides with the second reaction period of aluminate with the presence of sulfates. The second aluminate peak causes a subsequent depletion of sulfate ions in the pore solution [146], so concentration of hydroxyl ions will increase in order to maintain electrical balance. As hydroxyl ions are more conductive than sulfate ions, the conductivity of the pore solution increases (see C255 in Figure 6.2a).

The initial formation factors are almost constant. The ternary concrete has the highest formation factor over hydration time up to 168 h. Although the formation factor of C255 is lower than C145 before 86 h due to a higher w/b , it grows higher than that of fly ash binary concrete afterwards. Figure 6.2c shows that aggregates will reduce the electrical conductivity of matrix by a factor of 2–7. Before setting, the factor is nearly equivalent to the ratio between the value of solid/water in concrete and that in pastes by volume. As the hardening process progresses from 6 h to 16 h, the factor increases to a peak and then decreases significantly to values similar with the ratio of volume fraction of mixing water in pastes and that in concretes.

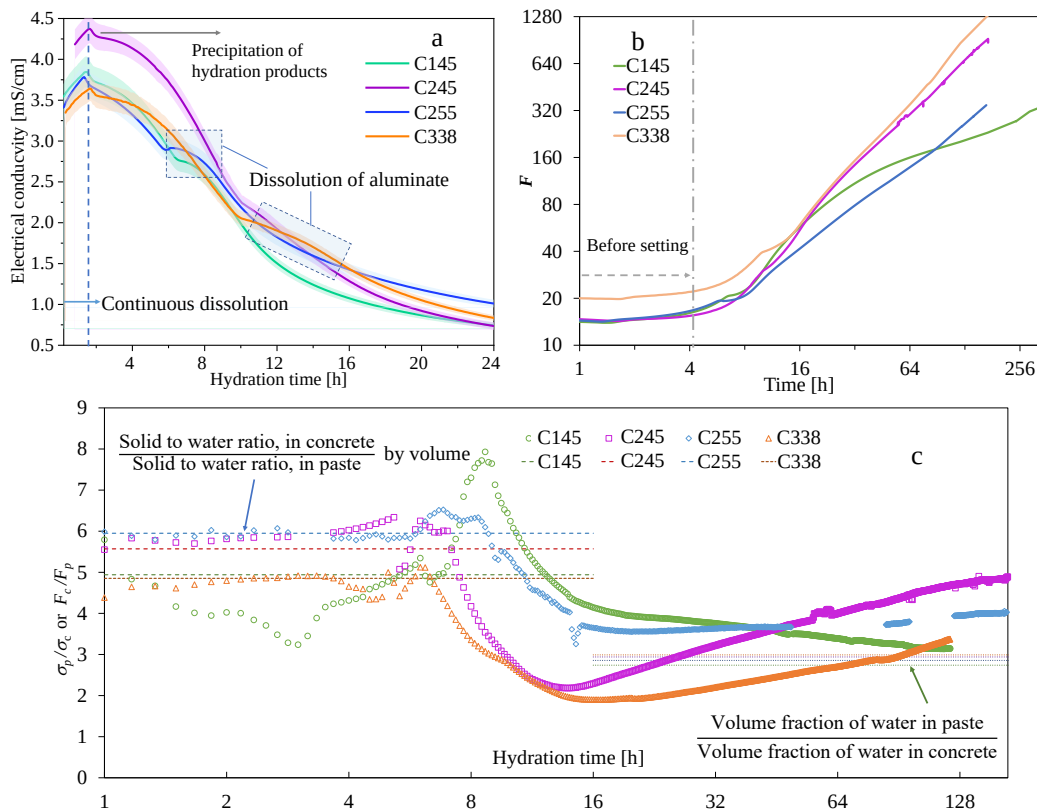


Figure 6.2. The monitored electrical properties of concretes: graph a – evolution of electrical conductivity; graph b – formation factor of concretes; graph c – the difference between electrical properties of paste and concrete, note that C338 was evaluated based on P335: corresponding to Figure 3 in paper VII.

6.2 Ultrasonic pulse velocity

According to Figure 6.3, the ultrasonic pulse velocity (UPV) of concrete remains nearly constant before 2 h due to the limited consumption of free water. This period corresponds to the induction time of cement hydration, during which the UPV of the fresh concrete is primarily

governed by the volume fraction of solids. Some slight variations in the sequence may occur due to temperature effects. After the slow rate period, the precipitation of hydration products starts to build connections between particles, leading to an increase in UPV. The growth of particle connection is faster in C145 than in C255 owing to the lower w/b , which results in a higher UPV of C145 than that of C255 after 4 h.

The square of UPV (v^2) has a linear correlation with elasticity parameter of materials is, which can be described by the dynamic Young's modulus and dynamic Poisson's ratio [147]. Therefore, the change rate of elasticity can be inferred from the value of dv^2/dt , as shown in Figure 6.3b. C245 has the highest dv^2/dt in the first 4 h. The increase in dv^2/dt of C145 occurs later than C245, but the curve shape of these two concretes is similar. From 4 h to 8 h, C255 has the lowest dv^2/dt due to its high w/b . This could also result from the low growth rate of solid connection caused by the dispersive distribution of the precipitated hydration products on particle surfaces [68,148]. From 12 h to 18 h, there is an increase in the growth rate of elasticity in C245 and C338 due to the aluminate reaction. The higher peak indicates that the dynamic modulus of C338 grows faster than C245, likely due to the accelerating effect of fine limestone powder on hydration after 4 h.

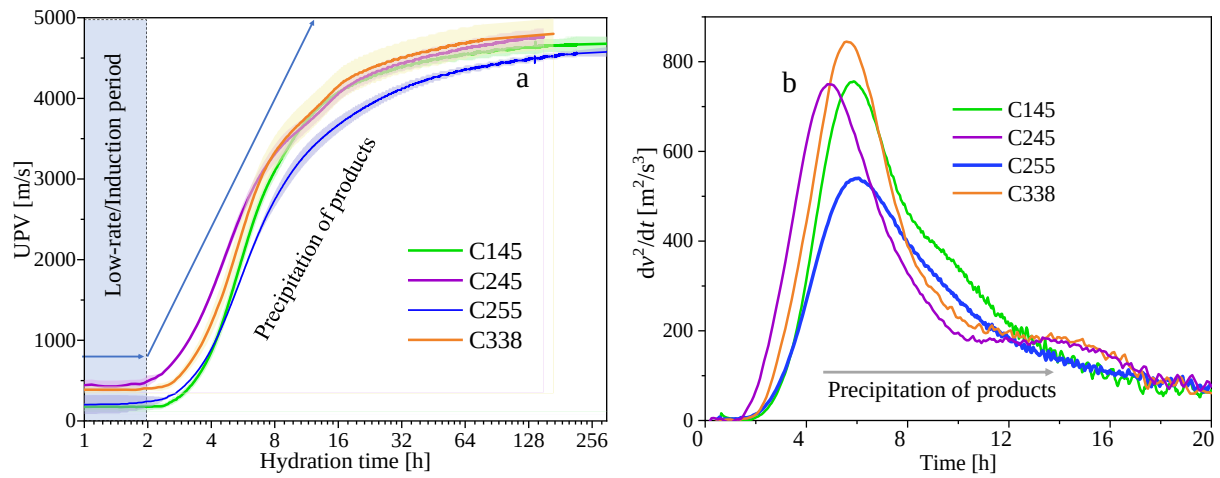


Figure 6.3. Monitored UPV in hydrating concrete (a) and dv^2/dt , corresponding to Figure 5 in paper VII.

6.3 Comparison with traditional methods

6.3.1 Penetration resistance

The percolation theory of consolidation has been extensively employed to comprehend the mechanics of soil during its drying process [149]. Although Pellenq and Damme [150] emphasized that the setting of cement-based materials differs from soil hardening by “wetting” rather than “drying”, the physics underlying concrete setting is similar to soil drying in that both processes involve the formation of solid networks to a percolation point for a transformation from a plastic to an elastic state. To establish a quantitative description of the

elastic modulus during hydration, percolation theory based on the hardcore/soft-shell model was employed [151]. The regression results by using the equations (6) and (7) in paper VII within a certain time interval indicate the initial setting of concrete. The transition from a semi-solid to a solid state can be indexed by the inflection point of the average growth rate of formation factor ($a-F$). The $a-F$ is calculated by dividing the formation factor by hydration time [59]. The inflection time of average growth rate of UPV ($a-UPV$) was determined using the same protocol.

Table 6.1 summarises the critical time and setting time of all the concrete samples, and Figure 6.4 shows the correlation between critical time and setting time. The critical time of $a-F$ is a good indicator of both the initial and final setting, with a strong linear correlation, regardless of the influence of temperature. The inflection time of UPV can also indicate the final setting time in a similar way but it has a weaker correlation to the initial setting time.

Table 6.1. Critical time of $a-F$ and $a-UPV$ in percolation (t_0), the inflection time and setting time.

Sample	Critical time [h]				Setting time [h]	
	t_0 of UPV	t_0 of F	Peak of $a-UPV$	Inflection time of $a-F$	Initial setting	Final setting
C145	2.80	2.68	7.00	8.48	3.81	6.82
C245	1.80	4.08	5.67	7.33	4.83	6.56
C255	2.40	2.41	7.25	8.58	3.73	6.97
C338	2.34	3.56	6.64	7.72	4.41	6.31

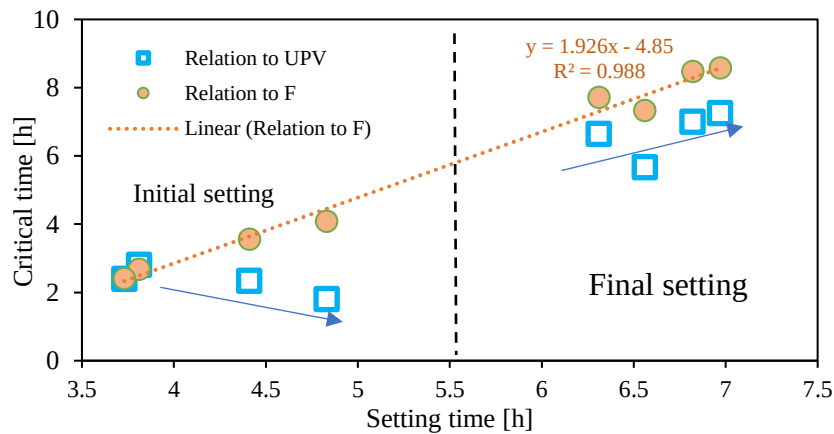


Figure 6.4. Correlation between critical time of monitored data and setting time of concrete: corresponding to Figure 10 in paper VII.

6.3.2 Compressive strength

The mechanical properties of porous materials depend on the pore structures of the matrix. Several empirical functions have been proposed to describe the relationship between porosity and compressive strength of concrete [152,153]. Schiller [154] reported a logarithmic function as a typical expression. Formation factor relates to water accessible porosity according to Archie's law [87]. By combining Archie's law and Schiller's empirically function, Eq. (6.2) is obtained to describe the correlation between compressive strength and formation factor.

$$f_c = K \left(\ln \Phi_0 - \frac{\ln a}{m} \right) + \frac{K}{m} \ln F \quad (6.2)$$

where f_c is the compressive strength, K is the constant parameter, and Φ_0 is porosity at which the strength practically vanishes. Parameters a and m share the same definition in Eq. (3.5). This equation describes the volume of pores filled with conductive liquid, so it may exclude the empty pores and air void in the non-saturated concrete matrix. However, the samples in this study cured under sealed condition so the matrix is a naturally saturated state with few empty air voids. In practical utilization, the saturation degree of the matrix should be taken into consideration.

Consequently, a logarithmic function was used as the base for regression between strength and F . Figure 6.5a depicts a linear relationship between the compressive strength of concretes containing SCMs and natural logarithm of the formation factor $\ln F$, with a coefficient of determination (R^2) of 0.99. This finding is a remarkable quantitative description that can be used for in-situ monitoring of strength development of the blended concretes. Moreover, it is independent of both curing ages and binder types. On the other hand, Figure 6.5b displays the correlation between compressive strength and electrical conductivity of concretes. Although the R^2 value is high at 0.96, Figure 6.5d illustrates that the deviation in value predicted by electrical conductivity is significantly higher than that by F . This is mainly because ion concentration of pore solution affects the electrical conductivity of concretes.

For a theoretical description using physical principles, Luping [155] introduced a model based on Griffith's theory, which includes the average pore radii to describe the relationship between compressive strength and pore structure. Kumar and Bhattacharjee [156] furtherly simplified the correlation. This study used the simplified function and the Archie's law to build a correlation between compressive strength and formation factor as Eq. (6.3). C_1 and C_2 are constant parameters. The detailed derivation of this equation has been elaborated in paper VII.

$$f_c = \frac{C_1 - C_2 F^{-\frac{1}{m}}}{\sqrt{F^{-\frac{1}{m}}}} \quad (6.3)$$

Figure 6.5c shows the correlation between $F^{-1/m}$ ($m = 2$) and compressive strength is quite good with a regression result of $R^2=0.99$. Hence, the compressive strength can be well indicated by the formation factor in both the empirical and theoretical description.

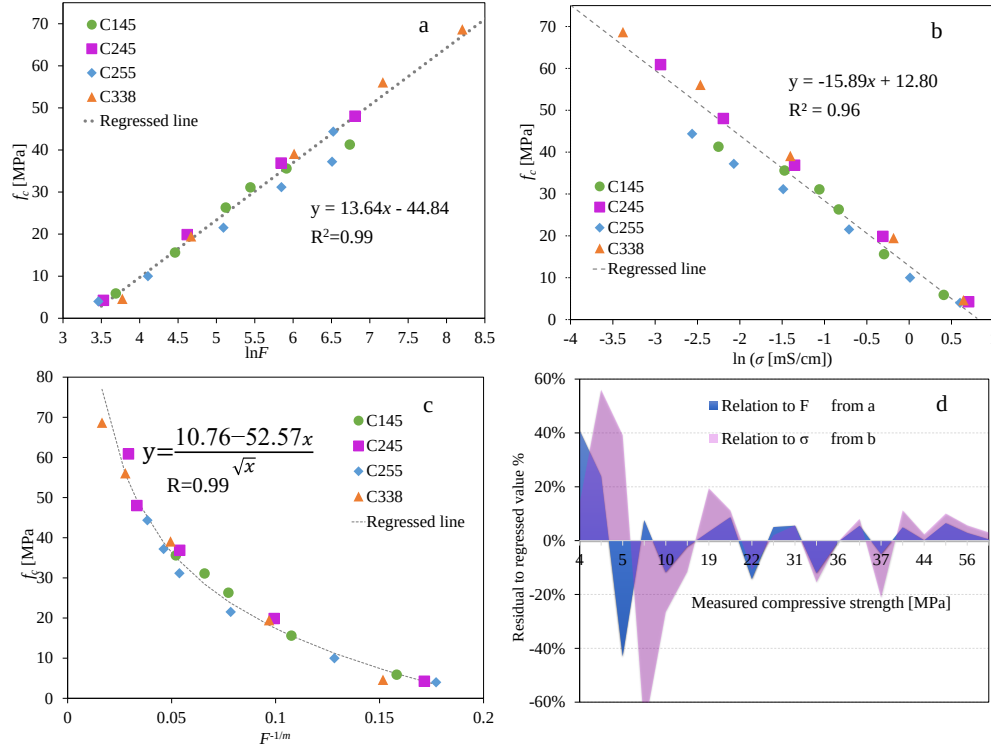


Figure 6.5. Quantitative correlations between compressive strength and electrical properties in different functions, corresponding to Figure 13 in paper VII.

To highlight advantage of using formation factor, Figure 6.6 displays the regressions between compressive strength and ultrasonic pulse velocity (UPV). Numerous empirical relationships for correlating value of UPV (v) and compressive strength have been documented in a review paper [157]. The results in this study can be regressed with an exponential expression as Eq. (6.4).

$$f_c = A \cdot e^{B \cdot v} \quad (6.4)$$

where A and B are constant parameters related to the concrete mix. Despite with R^2 of 0.96, there is a significant deviation of data points from the regression line in the case of C145 and C255.

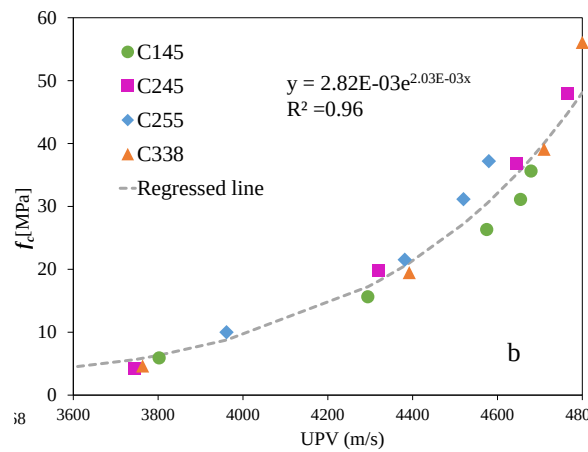


Figure 6.6. Quantitative correlations between compressive strength and UPV: Figure 13 in paper VII.

6.4 Chapter summary

The upgraded device can properly measure the electrical conductivity of hydrating concretes with SCMs at various depths, meanwhile accounting for the dimension factor. Moreover, the temperature sensors integrated within the device provide test of the internal temperature with adequate accuracy at different depths, which is also useful for normalizing the electrical conductivity to a reference temperature.

Both the formation factor and UPV serve as good indicators for the hardening process of concrete up to final setting. The development of UPV and formation factor undergoes a sudden change during the hardening process, which can be explained by the percolation theory. The inflection time of formation factor shows a linear correlation with the initial and final setting time of concrete. Although all indices (including electrical conductivity, formation factor and UPV) can indicate the development of compressive strength in concretes, the formation factor is the most reliable indicator as it appears to be independent of binder types, mixing proportions, and curing ages. Quantitative descriptions have been established for the compressive strength in relation to all the indices, among which two correlations between compressive strength and formation factor exhibit the highest accuracy.

7 Conclusions and future research work

7.1 Conclusions

Supplementary cementitious materials (SCMs) are one of the promising options to reduce the emissions from production of cement and concrete. Most of them have a lower reactivity than cement clinker, so activators are commonly added to mitigate this issue. Both the SCMs and activators alter the hydration of the blended binders, change the microstructure of hardened cementitious materials, and thus impact the transport process related to the durability. Water plays a crucial role in the hydration reaction, in the microstructure of hydration products and in the deterioration process of cement-based materials. This study has revealed the limitations of dissolution theory and based on this, proposed a new hypothesis to explain the mechanism in early hydration of C_3S . A novel non-destructive method was developed to detect the microstructure change during the setting and hardening process. A new approach for assessing the hydration degree of SCMs has been proposed by use of thermodynamic simulations and water vapour isotherm. The proposed moisture transport testing method enables an effective detection of steady-state and transient moisture transport coefficients. The key structural parameters for moisture and ion transport in cementitious materials have been identified, and a simplified model has been proposed for an accurate prediction of chloride migration coefficient in the blended cementitious systems.

Hydration of C_3S at early age is not solely controlled by the dissolution rate of minerals. The duration of the induction period is mainly determined by the nucleation rate of hydration products in localized areas on the surface. The new hypothesis proposed in this study is focused on the crystallization and precipitation process of the main hydration products, which provides a better explanation of early hydration mechanism. It suggests that C-S-H primarily nucleates within the near-surface region and its precipitation involves a nonclassical nucleation process. Additionally, the effect of potassium salts and pH levels on the dissolution of C_3S and

precipitation of C-S-H can be well explained by the proposed hypothesis.

The process of water interacting with cement and SCMs is more complex than it with C_3S , so a non-destructive method was proposed to monitor early-age interactions based on electrical conductivity test. The evolution of electrical conductivity in hydrating pastes closely relates to chemical reaction and can be classified into four stages. The formation factor, calculated by dividing the pore solution conductivity by the paste conductivity, accurately reflects the evolution of pore structure during the hydration process. The differences in formation factors observed among various cementitious systems primarily derive from disparities in the pore solution connectivity. Blending SCMs refines the pore structure, better indexed by the decreased pore connectivity, which results in a much higher formation factor of hcp. Conductivity monitoring demonstrates the relationship between evaporable water volume and formation factor, facilitating in-situ monitoring of moisture content in cement-based materials.

SCMs not only impact the pore structure but also change the phase assemblage and the water structure in the local environment of C-S-H. Water vapour desorption isotherm is an effective test for detecting the mesoscale pore structure in pastes with SCMs. When calculating pore size distribution using the BJH model, it is important to consider the effect of ions on water vapour equilibrium pressure on a plane surface. The proposed novel approach performs well to evaluate the hydration degree of SCMs based on water vapour sorption and thermodynamic modelling. Cavitation during desorption results in an overestimation of small gel pore volume, but it somehow implies the refinement effect of SCMs on pore structure. Replacing CEM I with slag and fly ash increases both small and large gel pore volumes.

Interaction of water with hcp under low temperature can be effectively unraveled by Thermoporometry for characterising moisture distribution and broadband dielectric spectroscopy for detecting water dynamics. The melting curve performs better than the freezing curve for testing water confined in pores larger than 2.4–2.7 nm. Water in smaller pores, including interlayer and a part of gel pores, cannot form a tetrahedral ice structure during the cooling process. SCMs affect not only moisture distribution equilibrium at 97 % RH but also influence moisture redistribution during a drying down to 33 % RH. Despite controversies in previous publications on pore structure changes during the first drying, this study confirms that the drying process does not induce any increase in volume of unfrozen water ($< \sim 2.4$ nm) under equilibrium conditions. Gel pores coarsen severely during the drying between 75 % and 55 % RH. SCMs have limited effects on the dynamics of structural water, and they primarily influence dynamics of water in small gel pores and the interfacial polarization.

SCMs have a significant impact on the pore structure, thus altering moisture and chloride transport in cement-based materials. The reduction in moisture transport coefficient and

chloride migration coefficient caused by SCMs is more pronounced at a higher w/b and after a longer curing. Pore structure refinement, specifically the reduction in pore connectivity, is the primary reason for the decrease in moisture transport coefficient of blended systems. The moisture transport properties in hcp are determined by both the formation factor and the porosity of small pores, with the formation factor being the primary factor at high RH and the porosity of small pores being the primary factor at low RH. The effect of SCMs on chloride resistance also mainly derives from the refinement of pore structure, which depends on the w/b and curing ages. A simplified model based on the formation factor can be used to estimate the chloride migration coefficient of hcp and mortars.

A reliable non-destructive monitoring method is useful for promoting the use of SCMs in concrete. The upgraded device properly measures the electrical conductivity and internal temperature of hydrating concretes with SCMs. Both formation factor and UPV are good indicators for the hardening process of concrete. The formation factor is the most reliable indicator for compressive strength development and is independent of SCMs types, mixing proportions, and curing ages. Quantitative descriptions have been established for the compressive strength in relation to the monitored indices, and Correlations between compressive strength and formation factor exhibit the best prediction

7.2 Future research work

Hydration during the main peak controls the setting and hardening of cement-based materials. This study paid more attention to early hydration up to the end of induction period, but a concept model has been proposed for understanding the hydration of C_3S after the induction period. It is of great interest to further develop an analytic model based on the conceptual model to provide a quantitative description for the precipitation of hydration products at the main peak.

The electrical conductivity test has been verified as a very effective method to monitor the moisture related interaction process in SCMs at relative early age. The main purpose of the project is to develop a method for assessing the moisture drying in the blended concrete. Therefore, a clear correlation between the moisture content and electrical conductivity in concrete is meaningful topic in further research. Chloride ingress, carbonation and the combined effects will also change both the moisture and ion concentration in concrete. Exploring the function of the device for monitoring these processes in low-carbon concretes is very interesting as well.

The refinement effect of SCMs on the pore structure and its impact on moisture and ion transport depend on the later age hydration. Thus, it is essential to conduct further research on the effect of curing conditions on the pore structure and spatial distribution of hydration products. This can be achieved by combining different advanced tests to reveal differences in phase assemblage and local pore distribution in hcp after different long-term curing regimes. Such studies not only enhance our understanding of the impact of SCMs on the durability of concrete but also contribute to a deeper comprehension of the mechanisms governing hydration at later stages.

Experimental results from this study provide abundant data for validation of models that predicts moisture transport based on pore size distribution or pore network in blended pastes. Another topic for future research is the development of a moisture transport and fixation model based on pore structure. Models that incorporate the effect of the interfacial transition zone are also necessary to predict moisture content and diffusion in concrete containing various kinds of SCMs.

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Paper I

New insights into the reaction of tricalcium silicate (C₃S) with solutions to the end of the induction period

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New insights into the reaction of tricalcium silicate (C_3S) with solutions to the end of the induction period

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ABSTRACT

Although dissolution theory is widely used, in certain circumstance, it seems to be unable to explain the hydration of C_3S . In this article, more attention is paid to the nucleation of hydration products. We find that the precipitation of C-S-H is a nonclassical nucleation process. It starts with nucleation of primary particles and then grows by particle attachment. A sharp increase in the reaction rate after induction period may come from the accelerating growth rate of C-S-H instead of dissolution of etch pits. The duration of induction period relates to the size of primary floc. Potassium salts influence the primary globule floc size and mitigate the effect from Al. The pH impacts ion species in solution to affect the dissolution and precipitation. A hypothesis regarding the dissolution of C_3S and nucleation of C-S-H within the near-surface region may narrow the gap between dissolution theory and protective layer theory.

1. Introduction

The hydration of cement is a sophisticated process, but the research of it is of great significance for both practical and scientific interest. During the past decades, there were several reviews on the investigation of the hydration mechanism. Even though it has been studied for so many years, some problems remain unsolved or under argument for the hydration of some pure minerals. The hydration of C_3S has attracted considerable attention because it is the main constituent of ordinary Portland cement. Having a better understanding of its hydration is a critical step to unveil the mechanism of the cement hydration. A majority of the previous studies classified C_3S hydration into 5 regions as in [1], and Scrivener et al. [2] simplified this into 3 periods: I- up to the end of the induction period (IP); II- the main hydration peak; III- hydration after the main peak. Whether the reaction in period I is controlled by the formation of a protective layer covering the surface [3] or only the dissolution rate [4] is still hotly debated. The duration of period I and the reaction rate at this period would be affected by many factors, including intrinsic properties (particle size, doping of impure elements and annealing treatment) and external factors (inorganic salts, organic chemicals and temperature). Herein we present a short review on some

interesting investigations about how these factors impact the hydration of C_3S or cement during the IP.

1.1. Particle size/specific surface area and annealing

The size of mineral particles has an impact on the reaction of C_3S during the IP. Costoya [5] performed a systematic work to assess the hydration of C_3S with different particle size distributions, ranging from 6 up to 240 μm . The lowest heat flow from the hydration of coarse particles is lower than that of the fine particles during IP, and the duration of the induction period (DIP) for the large particles is longer than the small ones. A higher specific surface area can shorten the DIP [6,7]. An annealing treatment of C_3S at 650 °C results in a longer IP without much influence on its particle size distribution. Some authors hold the opinion that the unannealed C_3S and the smaller particles had a higher dissolution rate during the IP due to a higher defects density on the surface [5,6,8]. However, the surface defects may have little effects on the dissolution rate of minerals such as calcite [9], silicates [10], and the annealed C_3S [11].

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1.2. Doping elements

The incorporation of trace elements and the annealing treatment of clinker induce polymorphs of C_3S [12,13]. C_3S in different crystal systems has a distinct hydration heat release rate to the end of the IP [14]. Triclinic crystal has the shortest IP while the monoclinic system has much longer IP. The doping of 2.5% Cr, Ni and Zn can stabilize the C_3S in T_2 , T_2 and M_2 crystals, respectively, and M_2 C_3S doped with Zn has the longest IP [15]. Although C_3S doped with Cr and Ni are in the same crystal system, the reactivity presents evident differences. Monoclinic C_3S doped with excessive Cu prolongs the IP up to 250 h [16]. These effects may also result from the trace elements dissolved into the pore solution. Gineys et al. [17] noticed that Cu, Zn and Pb in the solution increased the duration of IP of cement hydration. Dietmar Stephan [18,19] reported that the incorporation of Mg, Al and Fe below 1% changed the crystal structure of C_3S , but they had little influence on the DIP and the hydration rate during the IP. Bazzoni [20] also found that doping of Mg and Zn had an impact on the main peak but it induced very limited effect on the DIP. Most of the published papers unilaterally connect the effect from doping to its influence on the dissolution rate of C_3S [21–25]. Its effect on nucleation and growth of hydration products deserves attention as well.

1.3. Water/binder ratio, inorganic and organic admixtures

Water plays a key role in the hydration of C_3S . According to [22], the water to binder ratio (from 0.4 to 0.97) has little effect on the IP of triclinic C_3S (henceforth noted as TC_3S) and cement. Recently, Naber et al. [23] reported that the water to C_3S ratio (w/c) may have some effects on the reaction rate up to 5 h. However, in their study the saturated $Ca(OH)_2$ (CH) solution was used and the reaction rate was indicated by ex-situ X-ray diffraction (XRD) and thermogravimetric analysis (TGA) of samples dried at 60 °C. The results from Brown et al. [24] indicated that the w/c hardly affects the Ca^{2+} concentration in the IP, which means that the increase of w/c will augment the dissolving amount of the solid ingredient to gain a critical supersaturation condition in this period.

Inorganic chemicals in the solution make impact on the DIP as well. The saturated $CaSO_4$ solution prolonged the DIP but $CaCl_2$ solution narrowed this period [25]. Many other soluble chlorides ($MgCl_2$, $NiCl_2$ and YCl_3) presented a reducing effect on the DIP. An interesting small peak occurred in the long IP (about 15 h) when C_3S was hydrated in a $CuCl_2/CuSO_4$ solution [26]. $NaOH$ [27,28] and KOH [29] evidently shortened the DIP. A high alkalinity even induced the hydration process to get rid of the IP [30]. Some nanosized insoluble inorganics also presented a reduction in the DIP. It is recognized as a seeding effect not only on the hydration in IP but more evidently on the main hydration peak. C-S-H seeds (precipitated from aqueous solutions of sodium silicate and calcium nitrate) effectively shortened the IP of C_3S and cement hydration [31]. It is interesting that afwillite seed (prepared from C_3S hydration) evidently enhances the main peak but has little effect on the IP [32]. This implies that the effect from C-S-H seed on DIP can hardly be explained by providing nuclei to accelerate hydration. Nanosized $CaCO_3$ [33] and TiO_2 [34] shortened the IP and increased the lowest hydration rate from C_3S or cement in the IP.

Many organic admixtures that have strong complexation with Ca ions will prolong the IP, such as sucrose, tartaric acid and succinic acid [35]; lignosulfonates, glucose and sodium gluconate [36]; cellulose ethers [37]; D-glucitol, D-galactitol and D-mannitol [38]; and polycarboxylate polymers [39]. Some of these admixtures have weak influence on the dissolution kinetics of pure C_3S and even increase its dissolution rate, which can be deduced from the pore solution evolution in [38]. The popular explanation for the retarding effect from organic admixtures will be summarized in the next paragraph.

1.4. Limitation of current theories for the IP

The two most popular theories for explaining the rapid decrease in the heat release during early hydration are protective membrane and dissolution controlled by undersaturation. These theories are well summarized and distinguished in [2]. The dissolution theory may be better for explaining the emerge of the IP than the protective membrane, but it seems to be inapplicable for explaining the retarding effect of organic admixtures by only considering the relationship between dissolution rate and thermodynamic of bulk pore solution. This theory tries to explain the retarding effect by the reason that the ions or molecules adsorbed on the particle surface passivate the active sites and block the dissolution of defects, like dislocations outcropping on the surface, or point defects [4,40]. However, the dissolution rate is increased by some organic retarders as highlight in the above paragraph. Moreover, it is doubtful that the longer IP of the annealed C_3S can be explained by the dissolution theory, because the surface defects may have little effect on the dissolution rate of minerals. Therefore, it is more reasonable to ascribe the long DIP to the inhibition of the nucleation and growth of hydration products (Portlandite or C-S-H) induced by the admixtures [35,41–43]. This inhibiting effect will delay the starting time of the acceleration period to increase the IP.

This paper presented our study on the hydration of TC_3S with solutions, which started with deionized water and sulfuric acid. The preliminary results indicate that it is difficult to explain the hydration of C_3S with a high w/c by the dissolution theory. Therefore, we focused on a deep analysis on the interfacial nucleation of C-S-H and the dissolution etch pits on TC_3S surface with normal w/c. In the discussion section, we try to use a hypothesis to provide a holistic explanation for the hydration process from water contact to the end of the IP. The hydration evolution was monitored by an isothermal calorimetry test. The composition and morphology of hydration products were determined by XRD and scanning electron microscopy (SEM). GEMS simulation results supplied a significant information on the distribution of ion species in the pore solution.

2. Experiments and simulation

2.1. Materials and procedures

Triclinic C_3S is the same materials used in [29] with a purity of 98.57% and a specific surface area of 1.92 m^2/g . The particle size distribution is presented in Fig. 1. The majority of C_3S has a size smaller than 10 μm . The sulfuric acid solution (pH = 1 and 4) was diluted from the AR sulfuric acid (CAS:7664-93-9). All of the materials were preserved at 25 ± 1 °C before mixing. The hydration heat test of C_3S with very high solution/solid ratio was operated by mixing 0.1 g C_3S with 10 g (100/1) and 20 g (200/1) solutions in the ampere bottle, respectively, within 30 s before putting them into calorimeter channels. To get enough solid residue for the XRD test, the parallel experiments were

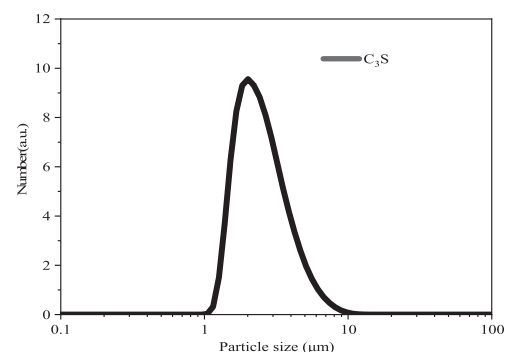


Fig. 1. Particle size distribution of C_3S powder.

carried out by using five times as much materials as in the calorimetry test. One more hydration experiment with a w/c of 600 was performed to check the dissolution of C_3S . All samples were only stirred at the initial mixing for about 1 min. After hydration for 4 h the solid residues were obtained by suction filtration and then cleaned with an adequate volume of isopropanol for three times to stop the hydration. The washed residues were vacuum dried at 40 °C for 48 h and then preserved in a sealed tube for XRD analysis.

Further experiments were carried out with a solution to C_3S ratio of 0.5 at 25 °C. The solutions include deionized water (TC_3S), 0.06 g/mL KOH solution (KH) and 0.06 g/mL K_2SO_4 solution (KS). The samples were stirred for 1 min in a glovebox with N_2 gas and then cured in the box before they were taken out to stop hydration. The hydration was stopped at 0.5 h for SEM analysis. The procedure for stopping the hydration and drying is the same as the high w/c system.

The cubic tricalcium aluminate (C_3A) purchased from DMT Materials Technology Co., Ltd. was used to replace a part of the C_3S to make a C_3S : C_3A mixture system (90%:10% by weight). The specific surface area of C_3A powder is 1.26 m²/g. The hydration experiments of mixture system with deionized water, KH, and KS were performed with a solution to solid ratio of 0.5 at 25 °C in a glovebox. It was stopped at 4 h by immersing the samples into liquid nitrogen and then samples were quickly moved into a freeze-drying machine at -50 °C and 0.7 Pa for 3 days. The same procedure was used to stop the hydration of a reference sample (pure C_3S with deionized water).

2.2. Methods

The specific surface area of C_3A was measured by the same method applied to C_3S in [29]. The XRD of the hydration products was determined by a Rigaku International Corporation D/max 2550 VB3+/PC diffractometer (Cu K α radiation). The measurements were conducted in the range of 5–45° (2 θ) with a step of 0.05°, a counting time of 1 s/step, a tube voltage of 40 kV and a current of 100 mA.

The Au-plated hydration particles were detected by a Nova NanoSEM 450 scanning electron microscope. The accelerating voltage and beam current for the images were 10 kV and 0.5 nA, respectively.

The hydration heat release was tested by the TAM Air Isothermal Calorimeter from TA Instruments (TAM air C80, Thermometric, Sweden). The sample was only stirred within the initial 30 s and then measure in quiescence.

Thermodynamic modeling was carried out by using the Gibbs free energy minimization program GEM-Selektor v3.7. The cement database Cemdata'18 [44] and PSI-GEMS thermodynamic database [45] were used to simulate the general aqueous, and gaseous species in the pore solution of C_3S with a gradient of pH values.

3. Results

3.1. Hydration of TC_3S with high solution to solid ratios

TC_3S with an empirical formula of Ca_3SiO_5 ($Ca_2SiO_4 \cdot CaO$) has a molar mass of 228.3 g/mol. a w/c of 100 needs to consume more than 1/6 of Ca (22.5/131.4 from Table 1) in the solid to achieve a saturation state (>22.5 mmol/L [24,46]) with respect to portlandite at 25 °C. When the water/solid ratio is up to 200, it needs to consume more than 1/3 of

Table 1
The ideal Ca^{2+} concentration from a complete dissolving of C_3S in a high water/solid ratio.

w/c (by weight)	Volume of water (mL)	Mole of Ca in solid (mmol)	The ideal Ca concentration (mmol/L)
100	100	13.14	131.4
200	200		95.7
600	600		21.9

solid C_3S to get this saturated condition. However, the heat flow in Fig. 2a shows that a high w/c only induces a higher hydration rate at the main peak, but it has no evident influence on the duration of the IP. Furthermore, the accumulative heat release in Fig. 2b shows that the heat release from the start of the IP to the main peak is similar among samples with the solution to C_3S ratio of 100, 200, and 200 (pH = 4). This value is about half of the heat release at 24 h. It implies that the dissolution degree of the solid is similar at the end of IP even with a rather high w/c, so the Ca concentration in the bulk pore solution from the high w/c is far from equilibrium during IP. 0.05 mmol/L H_2SO_4 solution (pH = 4) makes the main peak occur earlier, increases the heat release rate before 6 h, but has few effects on the ending time of the IP. An increase in the H_2SO_4 concentration up to 0.05 mol/L (pH = 1) alters the reaction of C_3S into one heat release peak without the IP. The high H^+ concentration in solution will bring a neutralization effect which results in a high heat release at the first peak, because the ionic O in C_3S undergoes a fast electrophilic attack from H^+ [21]. This also results in a different precipitation process, which will be further indicated by XRD.

Hydration products at 4 h were detected and presented in Fig. 3. It shows that gypsum is the main product of C_3S reacting with a high concentration H_2SO_4 (pH = 1). Most of the C_3S has reacted with sulfuric acid before 4 h. The dissolution of C_3S in H_2SO_4 solution (pH = 1) and precipitation of gypsum is a consecutive process without the occurrence of an IP. The w/c has little influences on the precipitation of CH at 4 h, which time is near the end of the IP. We can observe that the majority of solid residue is C_3S in good crystalline state even for a w/c of 600. A complete dissolution of C_3S with a w/c of 600 can only get 21.9 mmol/L Ca^{2+} in pore solution (Table 1), which is slightly lower than the saturation concentration (22.5 mmol/L) of portlandite. Moreover, the high diffraction intensity of C_3S indicates that its dissolution rate in such a high w/c is rather lower than the expected value referring to the dissolution theory. Apparently, the low Ca concentration in the solution (less than 21.9 mmol/L) implied an undersaturated state in the IP but it still resulted in the precipitation of CH (as shown in Fig. 3). This phenomenon can hardly be explained by the theory that the hydration rate is mainly controlled by dissolution rate with respect to the thermodynamic state of the bulk pore solution, as discussed in [47].

3.2. Hydration of TC_3S with KOH and K_2SO_4 solution

Many investigations focused on the dissolution of tricalcium/dicalcium silicate during the early hydration age based on a highly diluted solution [47–50]. These results could be well illustrated by the dissolution theories from geochemistry for silicates or other minerals [9,10,51], which are not coupled with the precipitation of new phases during dissolution. However, as mentioned in the previous section, the dissolution theory regarding the thermodynamic properties of the bulk solution is not so effective for explaining the hydration with a high w/c. This section will focus on the coupled nucleation and growth of hydration products during the IP.

Fig. 4 presents the hydration heat flow of TC_3S with deionized water, KH and KS, respectively. We define the IP as a time interval between the first and second peaks, during which the first derivative of the heat flow is between -0.5 mW/(g·h) and 0.5 mW/(g·h). The light was shed on the period from the starting point to the end of the IP. Comparing with 20 °C, a temperature of 25 °C brings an earlier starting point for samples with deionized water or KS. The IP starts at about 0.75 h after water addition except for KH (at about 0.5) at 25 °C, but this time is about 1 h for all samples at 20 °C. The IP ends up earlier in the hydration of samples at a higher temperature. This effect is so evident for samples with KH and KS, decreasing from 1.75 to 0.50 h and 2.28 to 1.15 h, respectively. K_2SO_4 has a great increasing effect on the main peak that is even larger than KOH, but the DIP is still longer than the sample with KOH. This is similar to the influence from sodium salts [27]. It may be related to the growth of products, which requires a focus on the early precipitated phases.

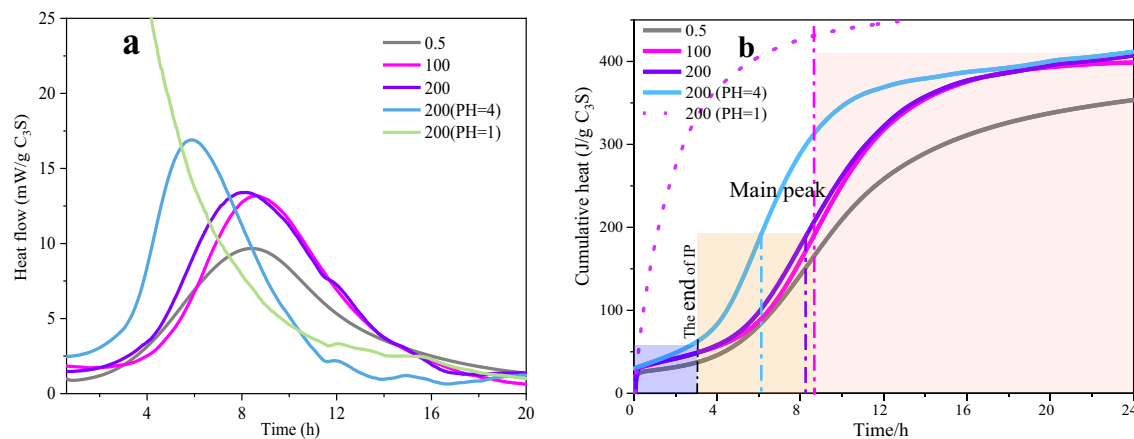


Fig. 2. Curves in “a” are the hydration heat flow of TC₃S with different w/c (0.5, 100, 200) and a sulfuric acid to C₃S ratio of 200 with two different pH values (pH = 4 and 1). Curves in “b” are the cumulative heat of samples with a w/c of 0.5, 100, 200 and a sulfuric acid to C₃S ratio of 200 (pH = 4 and 1).

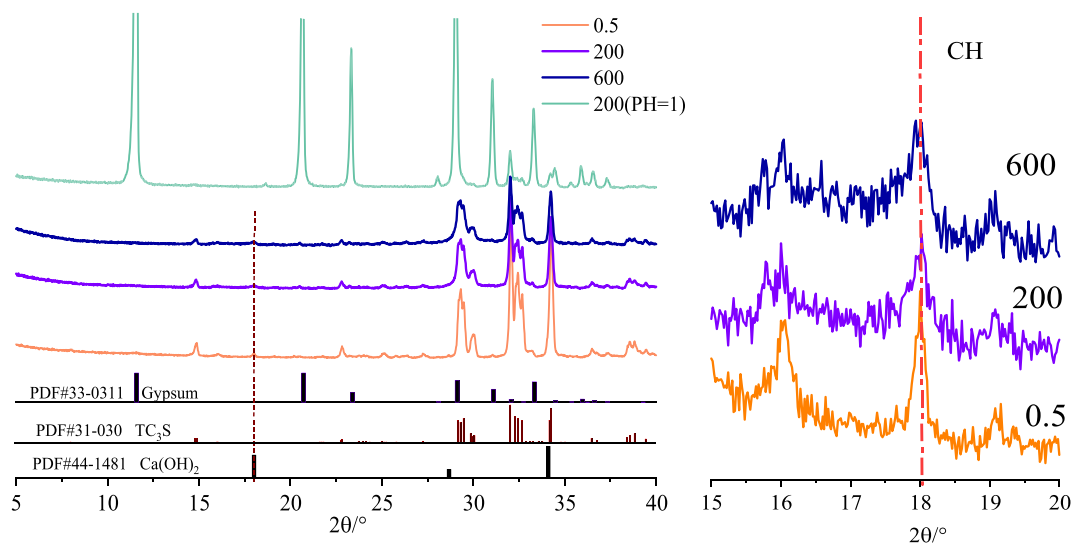


Fig. 3. XRD patterns of hydration products from samples with a w/c of 0.5, 200, and 600 and a sulfuric acid to TC₃S ratio of 200 (pH = 1). The hydration of sample was stopped at 4 h after water addition by isopropanol exchange.

Fig. 5 shows the surface of TC₃S hydrated in deionized water. It should be noted that the surface was treated with isopropanol, so it is different from the original hydrating surface. There is no distinguishable dissolution pit on the surface. However, we can observe many strips which were called needles in other published studies [27,52,53]. An enlarged image shows a clearer feature for the strips, and the strips consist of globule flocs. According to Jennings [54], these globule flocs with a size about 50 nm are from the packing of globules with a smaller size of 4–10 nm. From the Gaussian distribution of the measured values, it shows that the mean diameter of the globule flocs is about 63 nm.

The morphology of hydration products is more reasonable to be explained by a nonclassical nucleation theory. It is crystallization by particle attachment (CPA), which means a crystallization process by the addition of particles, ranging from multi-ion complexes to the fully formed nanocrystals [55]. In contrast, classical nucleation theory is crystallization through monomer by monomer addition [56]. As summarized in [55], particle attachment is influenced by the structure of the solvent and ions at solid-solution interfaces and in confined regions of the solution between solid surfaces. This nucleation process has been proven in the nucleation of many minerals, such as gypsum [57], iron oxyhydroxide nanoparticles [58], CaCO₃ [59], and silicates [60]. By applying this theory, we found that nucleation of C-S-H in the IP firstly

comes with a formation of primary globule flocs (Fig. 5), which may be formed from polymerization of mono silicic complexes into dimeric structures [61]. This happens within a confined region between the surface and solution, because this region has a higher concentration of ions or complexes compared to the bulk solutions. From this point of view, the hydration in a highly diluted system is possible to have a precipitation of CH. Moreover, the dissolution equilibrium during the IP may build up within the interfacial regions instead of between the solid and bulk pore solution. Some correlations may exist between the thermodynamics of the interfacial region and bulk solution, but it is ambiguous to connect the hydration kinetic in the IP directly with the ion concentration in the bulk pore solution when the correlation is not clearly revealed.

The SEM images of the early hydration products from TC₃S with KH and KS are shown in Fig. 6. The strips on the surface of the sample in the KH (Fig. 6a) is much thinner than those precipitated in the deionized water (Fig. 5), and many strips even pack together to form a dense cluster. This is similar to the morphology of C-S-H precipitated from the hydration in sodium alkali solution [27,62]. Previous research paid attention to the needle length without considering the thickness of the needles that represents the diameters of the primary globule size. The mean thickness of the strips in KH is about 18 nm. Whereas the strips in

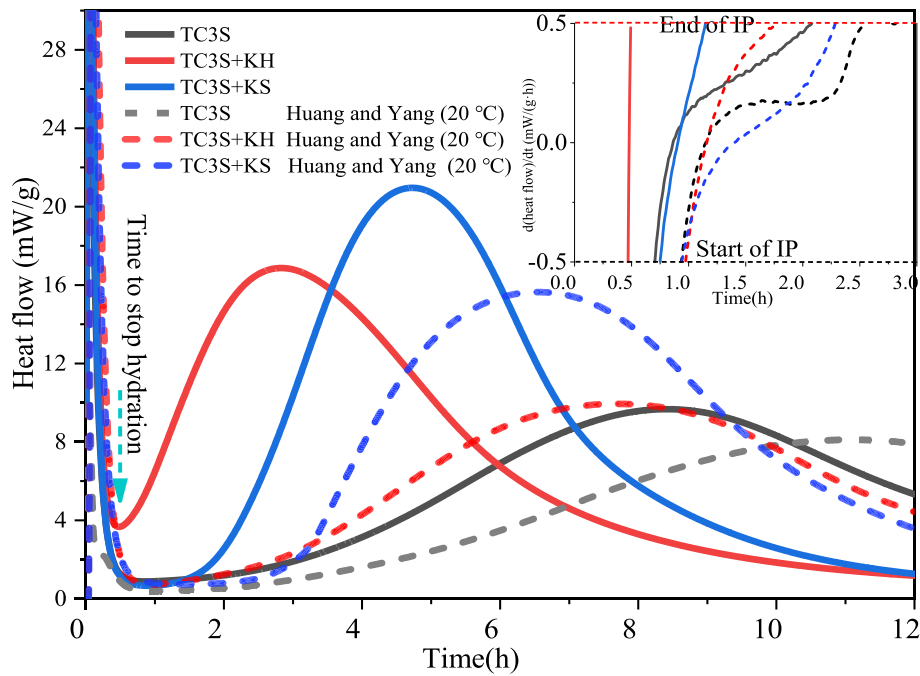


Fig. 4. Hydration heat flow of TC₃S with deionized water, KH and KS. The solid line is hydration data with a $w/c = 0.5$ at 25 °C, and the dash line is hydration data with a $w/c = 2$ at 20 °C, adopting from [29].

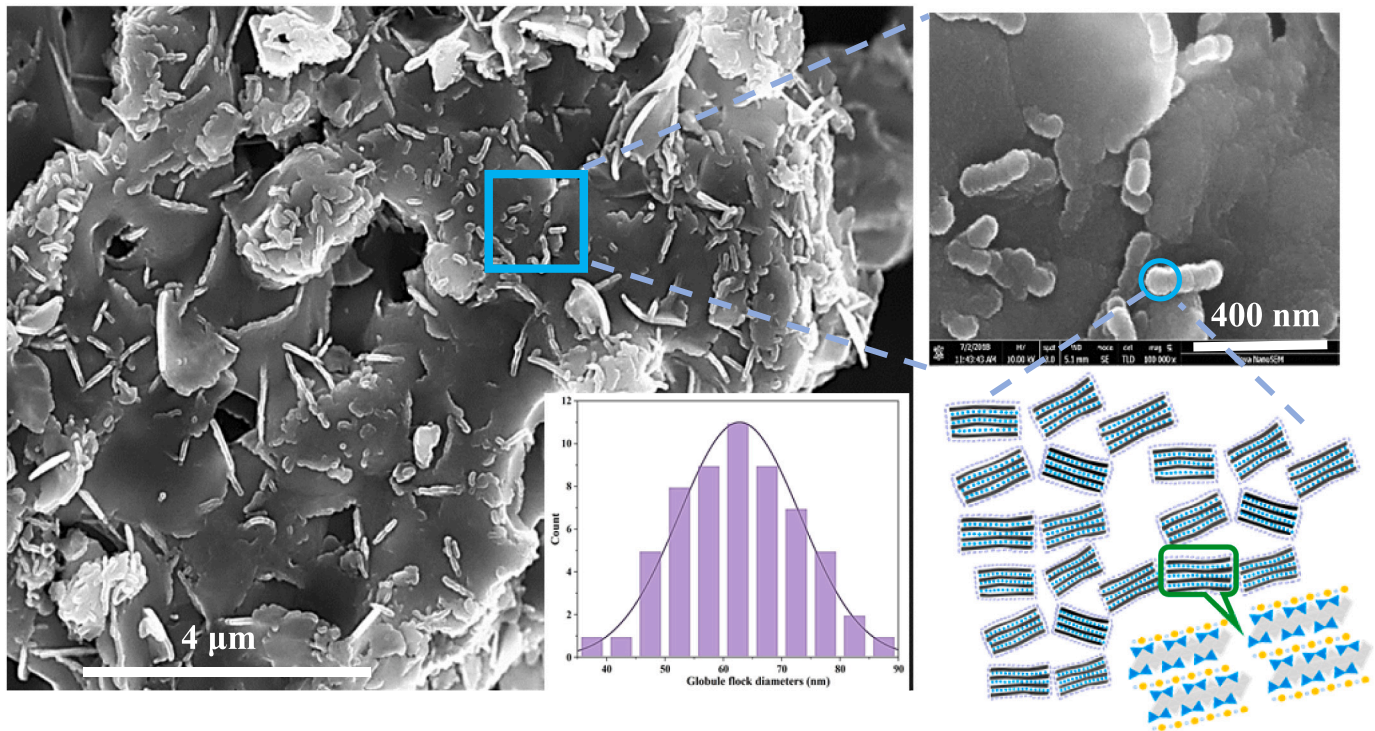


Fig. 5. SEM image of TC₃S hydrated with deionized water. The hydration was stopped at 0.5 h after water addition by isopropanol exchange. An enlarged image was provided to give a clearer picture of the particles on the surface. The diameter of the globule flocs was counted with the Nano measurer software. The structure of the globule flocs was illustrated based on Jennings model.

KS have a thickness about 49 nm, and this is much larger than the products precipitated in the KH. Furthermore, CH on the surface is well nucleated in large crystal, with some sizes larger than 500 nm. The correlations between the DIP (Fig. 4) and globule floc size will be further analyzed in the discussion section.

3.3. Hydration of TC₃S with C₃A

Fig. 7a shows the heat flow of TC₃S with C₃A, and Fig. 7b presents the comparison of the IP between hydration of TC₃S with and without C₃A. The presence of C₃A evidently prolongs the starting point of the IP. It increases this time to 2 h after water addition, which is much longer than

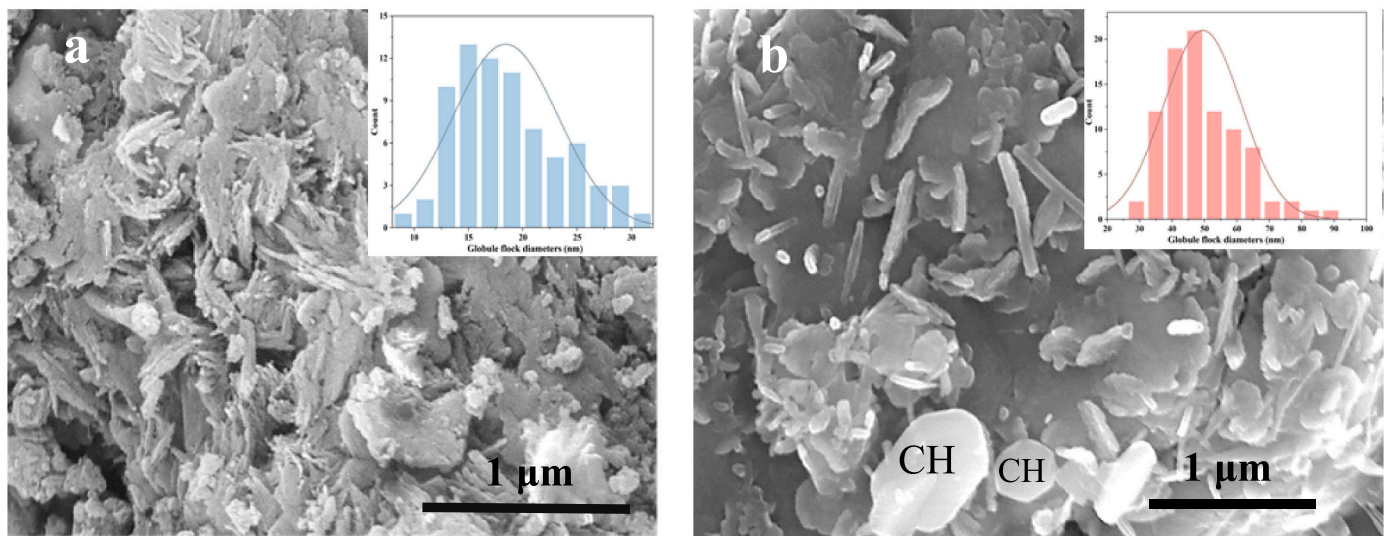


Fig. 6. SEM images of TC₃S hydrated in KOH (a) and K₂SO₄ (b) solutions, respectively. The hydration was stopped at 0.5 h after water addition by isopropanol exchange.

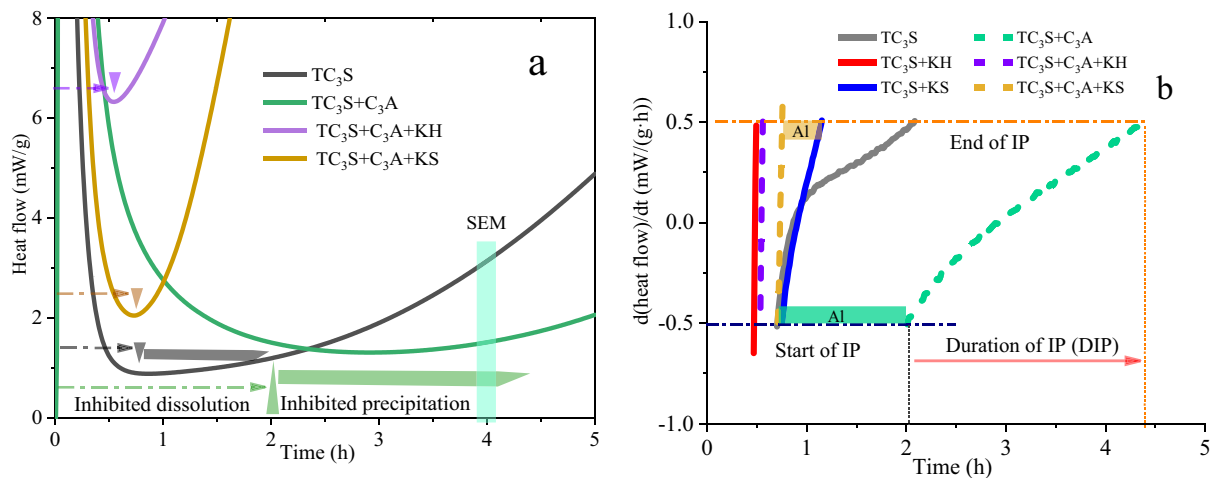


Fig. 7. Hydration heat flow of TC₃S with the presence of C₃A (a). The intervals of IP from TC₃S hydrating in solutions with and without C₃A (b). Samples were mixed with a w/c of 0.5 and cured at 25 °C.

the pure C₃S. A majority of the previous work hold the opinion that the prolonged IP came from inhibiting of C₃S dissolution [63,64], but the “Induction period” in their work was from water addition to the end of the low heat release rate period. Herein, we distinguish the inhibiting effect from aluminates on dissolution and nucleation. If we replace the concept of thermodynamic state between the solid and bulk solution with the state within the interfacial regions near the surface, according to [52], the sharp decrease in the heat release comes from an increase in saturation degree within the near surface with respect to C₃S dissolution. The delayed starting point of the IP (shown in Fig. 7b) is due to the inhibiting effect on dissolution by absorbing Al species on the surface of C₃S. In this period, the pH value is normally lower than 12.6. As hydration proceeds, the pH increases to a value larger than 13; this effect on dissolution will be eliminated [65,66]. As found in many published articles, the coverage effect of Al is negligible when pH is higher than 12.5 [67] and even at 10 for Ca_{0.87}Al_{1.29}SiO_{4.81} [68]. When it comes to the start of IP, the pH of the pore solution in C₃S with C₃A is up to 12.5–13 [63], so the Al in solution have little effect on the dissolution of C₃S during this period. This is consistent with the result that the lowest heat release rate of C₃S with C₃A in IP is even higher than that of pure C₃S in IP (Fig. 7a). The ending time of the IP is delayed partially due to

the inhibition of dissolution so the increment in DIP is shorter than the delayed starting time of the acceleration period, which is similar to the effect found in [69]. The increase in DIP by C₃A is much more effective in a previous article with a more reactive C₃A [63]. It comes from the inhibiting effect on both dissolution and nucleation.

KH and KS can eliminate the effect from C₃A on the IP and even shorten the DIP. The starting point of the IP from mixture system in KH is close to that of pure C₃S in KH because a high pH from KOH can avoid the suppression on the dissolution from Al ions. Moreover, the lowest heat release rate from the sample in KH is much higher than that of other samples (Figs. 4 and 7a). It implies that the dissolution rate of C₃S in KH is higher than that in other solutions when the nucleation of the hydration products takes over the hydration process. The K⁺ and high pH in solution accelerate the nucleation, resulting in a reduction of the DIP. KS also can eliminate the effect from Al due to the reduction of the Al concentration by the precipitation of ettringite. Although C₃A has little influence on the starting point of C₃S in KS, it reduces the DIP. To reveal this, more attention should be paid to the nucleation and growth of the hydration products.

Fig. 8 presents the SEM images of TC₃S hydrated with deionized water. The hydration was stopped at 4 h by freeze-drying, which is

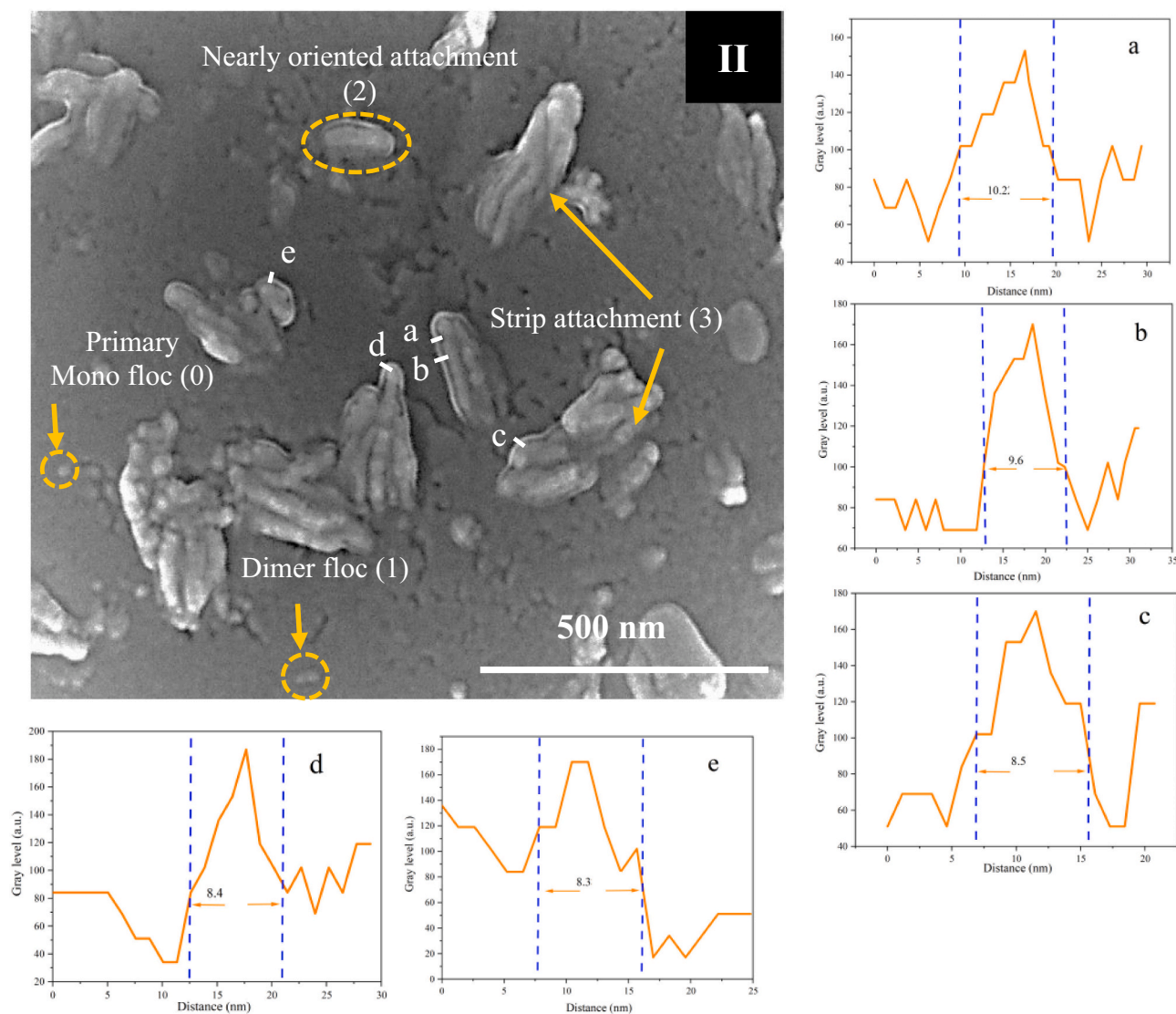
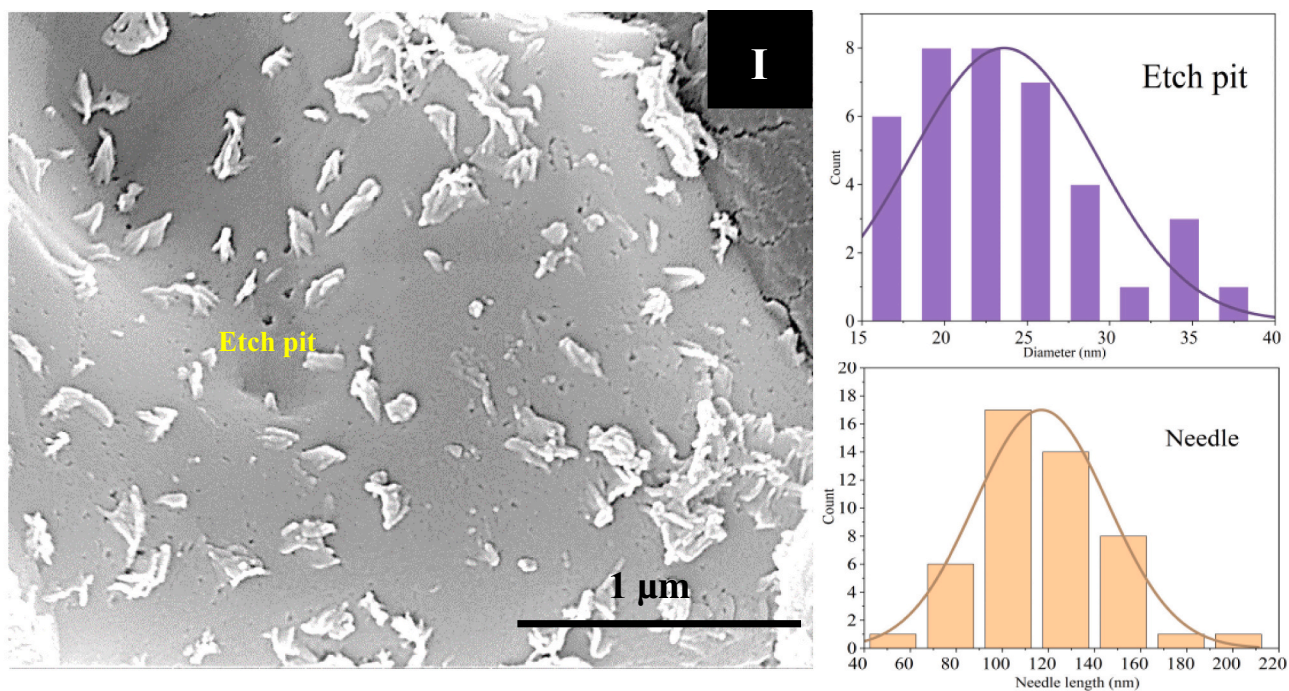


Fig. 8. SEM images of TC₃S hydrated in deionized water. The hydration was stopped at 4 h after water addition by freeze-drying. An image with a higher magnification was provided to give a clear picture of the particles on the surface (II). Nucleation of primary mono-flocs and dimer flocs were detected above or near the etch pit. C-S-H grows by nearly oriented attachment and block attachment. A layer of portlandite with a thickness of approximately 8–11 nm was detected between the undissolved surface and globule.

different from the treatment of samples in Fig. 5. The pristine feature of the surface is better preserved by freeze-drying than isopropanol exchange, as we can observe many etch pits on the surface of the particles. By counting 38 sites, the mean diameter (width) of the etch pits is about 24 nm. The length of C-S-H strips (clusters) is about 117 nm from counting 48 sites. The second image (Fig. 8II) with a higher magnification shows a clear feature of the particle surface. In the local region above the etch pits or near it, we can observe evidence for the nucleation of a primary mono floc (0), formation of a dimer floc (1), a single strip from the nearly oriented attachment (2) and the clusters from a strip attachment (3) or the single particle attaching to strips. This further proves that the precipitation of C-S-H starts from the nucleation of primary mono flocs that are poorly crystalline nanoparticles or colloidal, like the crystallization process of some other polymers or minerals [55,70]. The mono floc seems to be the intermediate C-S-H phase during the precipitation process as highlighted in the previous investigations [71,72]. Because it is thermodynamically metastable, it will aggregate into strips by the oriented attachment in a local region. With the increasing nucleation of mono floc and strips, the mono floc can also attach to the strip. Meanwhile, the strips may attach to each other to form a more stable cluster (block).

A linear gray level distribution in Fig. 8a-e indicates that a special layer exists between the precipitated C-S-H and undissolved surface. According to some experimental research on the dissolution of β -C₂S [73], there is an accumulation of Ca in the etch pit. This phenomenon may also occur in hydration of C₃S, so this layer would be portlandite that precipitates from the Ca ions absorbed on the colloidal surface in solution. A CH rim with a micron thickness was also detected between the hydration products and unhydrated mineral at 1 day [74]. In SEM images, the thickness of this layer is approximately 8–11 nm. Since the primary globule floc is the attachment of colloid [55,70], the double layer thickness of colloid may have some correlations with the precipitated layer. According to [75], the typical double-layer thickness of colloid at varying concentration can be estimated by:

$$\kappa^2 = \frac{F^2 \sum c_i z_i^2}{\epsilon_r \epsilon_0 R T} \quad (1)$$

where the reciprocal of κ is called the Debye length (namely, the double-layer thickness), F is Faraday's constant, R is the gas constant, T is the temperature in Kelvin, and ϵ_r and ϵ_0 are the relative permittivity and permittivity in a vacuum, respectively. c_i and z_i are the concentration and charge number of ions in solution, respectively. During early hydration of C₃S with deionized water, the main ions in the solution is Ca^{2+} and OH^- whose concentration is approximately 25 and 36 mmol/L respectively [76]. Under this molarity and with $\epsilon_r = 78.5$ (water) at 298 K, we can get a value of 2.07 nm for Debye length. It is smaller than the thickness of the layer in Fig. 8II. Given that both the surface of dissolved C₃S and nucleated C-S-H are colloidal structure, the stable distance between these two colloids is about 8–14 nm under the condition when the colloids have a charged surface (10–100 mV) in a solution with ion concentration in range of 10–100 mmol/L [77]. Because we did not stir the paste after the initial mixing, the layer between the strip and unhydrated C₃S probably precipitates by a quick accumulation of Ca ions between two colloidal surfaces during a sudden freeze drying.

Fig. 9 presents the surface of C₃S hydrated at 4 h in the presence of C₃A. Etch pits were also detected on the surface (Fig. 9a1). The mean diameter of etch pits is about 28 nm, which is a little larger than that of pure C₃S in Fig. 8. Learning from the dissolution theory regarding the saturation state of bulk solution [78], the low reaction plateau (low heat release in Fig. 5a before 4 h) is controlled by the step retreat. However,

the presence of etch pits in both Fig. 8 (pure C₃S) and Fig. 9a (C₃S with C₃A) indicates that this period is indeed controlled by the etch pit opening. In the IP, the transition happens from the step retreat to dislocation control (etch pit opening). To reveal the difference between the dissolution of C₃S with and without C₃A, we performed a further analysis based on the dissolution rate determining equation in [78].

$$|R_d| = \frac{A_1(1 - SI)|\ln(SI)|}{1 + A_2|\ln(SI)|} \quad (2)$$

$$SI = \frac{Q}{K_{sp}} \quad (3)$$

where A_1 and A_2 can be considered constants in this situation. R_d is the dissolution rate controlled by the etch pit opening. SI is the saturation index, Q is the ion product, and K_{sp} is the ion-product equilibrium constant. Based on Eq. (2), we can conclude that the dissolution rate of same C₃S particles with similar distribution of etch pit only relates to the saturation index of the solution. However, the previous articles [63,69] indicated that no significant difference was found between the main ions concentration in the pore solution of C₃S with and without C₃A under the IP. Hence, the big difference in heat flow at 4 h (Fig. 7a) can hardly be explained by rate controlling from the different dissolution rate of C₃S.

The nucleation and growth of the hydration products on the particle surface gives a reasonable explanation for the much lower heat release rate at 4 h. Fig. 9a2 shows that the needle length of C-S-H in the mixture system is about 94 nm, which is much shorter than this (116 nm) in pure C₃S. The diameters of the globule floc from C₃S with C₃A are even smaller than pure C₃S. Al ions in the solution induce the nucleation of the primary globule in a smaller size, but it suppresses the growth of strips from the attachment of primary particles. KH and KS can eliminate this inhibiting effect. The growth of C-S-H in KH and KS was much faster than it in deionized water, so the surface was covered by the hydration products as shown in Fig. 9b and c. The aluminates phase (stratlingite or ettringite) is hardly detected under SEM image. A comparison of the globule size in Fig. 9d shows that KH and KS can decrease the globule floc size to about 20 nm. It is worth noting that the presence of C₃A almost erased the difference between the effect from KH and KS on the floc size, which is found in pure C₃S hydration (Fig. 6). With this observation, it is obvious that the long DIP from pure C₃S with KS (Fig. 6b) is due to the nucleation of larger primary globule compared to KH. C₃A can weaken the effect from KS on the nucleation of globules, so it reduces the DIP of mixture system compared to the pure C₃S in KS (Fig. 7b).

4. Discussion

4.1. Ion species in the pore solution with respect to pH

The hydration of C₃S is a complex reaction process during which the dissolution of C₃S involves the precipitation of C-S-H and CH. The difference between the hydration evolution shown in Figs. 2 and 3 indicates that the pH impacts the precipitated phase in the products. The pH will greatly affect the ion species of Ca [79] as well as Si [80] in the solution. Fig. 10 presents the ion species in the pore solution of pure C₃S. Ca^{2+} decreases as the pH increases from 8 to 13.5 (Fig. 10a). In the meantime, CaOH^+ shows a sharp increase of about five orders of magnitude. The increasing pH makes Ca^{2+} transform into CaOH^+ , $\text{Ca}(\text{H}_3\text{SiO}_4)^+$, and $\text{Ca}(\text{H}_3\text{SiO}_4)\text{OH}$ when the value is lower than 10.3, but $\text{Ca}(\text{H}_3\text{SiO}_4)^+$ decreases dramatically after this critical value. The change in Si species in the solution is much more complex and the evolution of

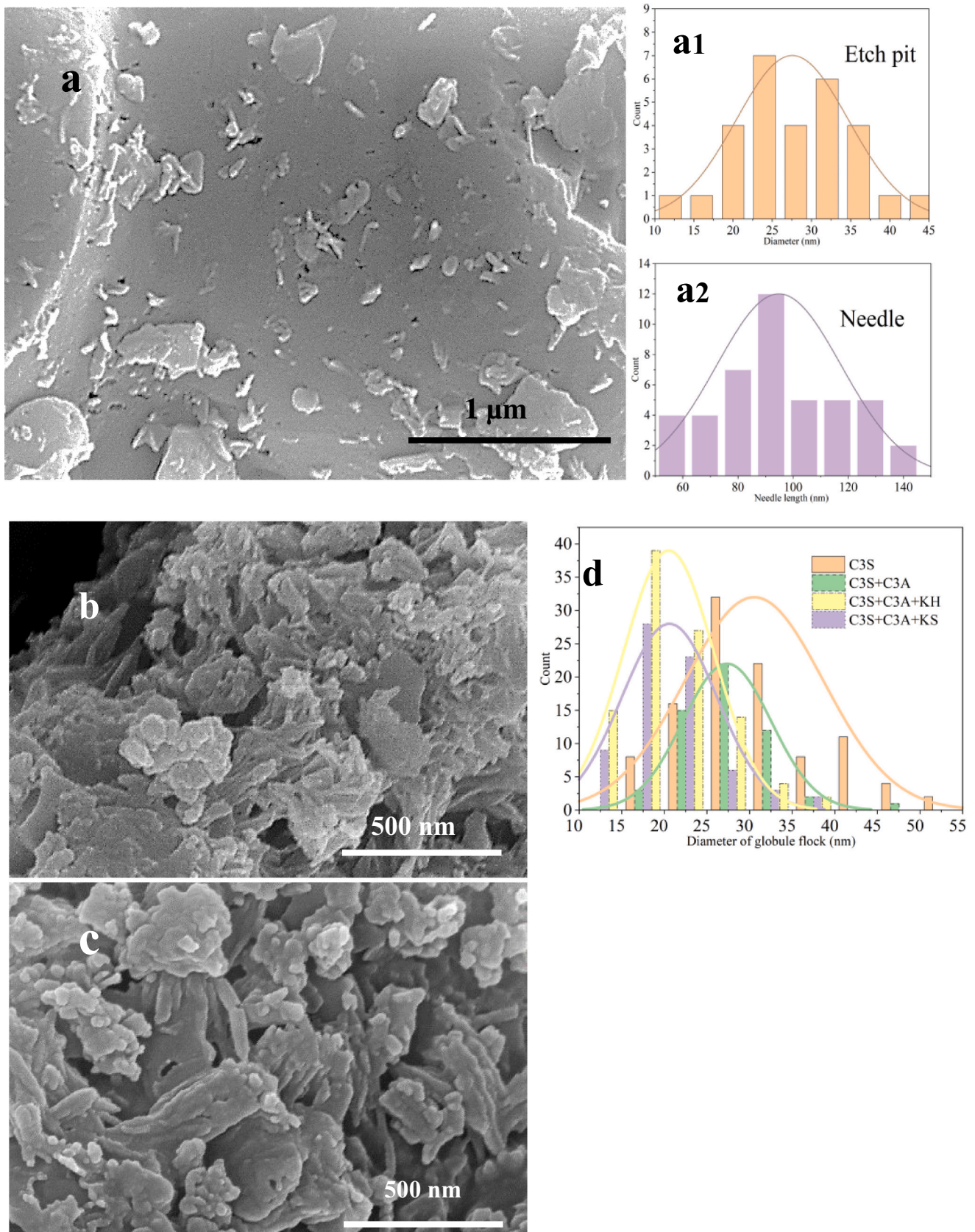


Fig. 9. SEM images of TC₃S hydrated with deionized water (a), KOH solution (b), and K₂SO₄ solution (c) in the presence of C₃A. The hydration was stopped at 4 h after water addition by freeze-drying. The diameter of the etch pit (a1) and needle length (a2) were counted for samples in deionized water. The diameter of the globule floc is summarized in d.

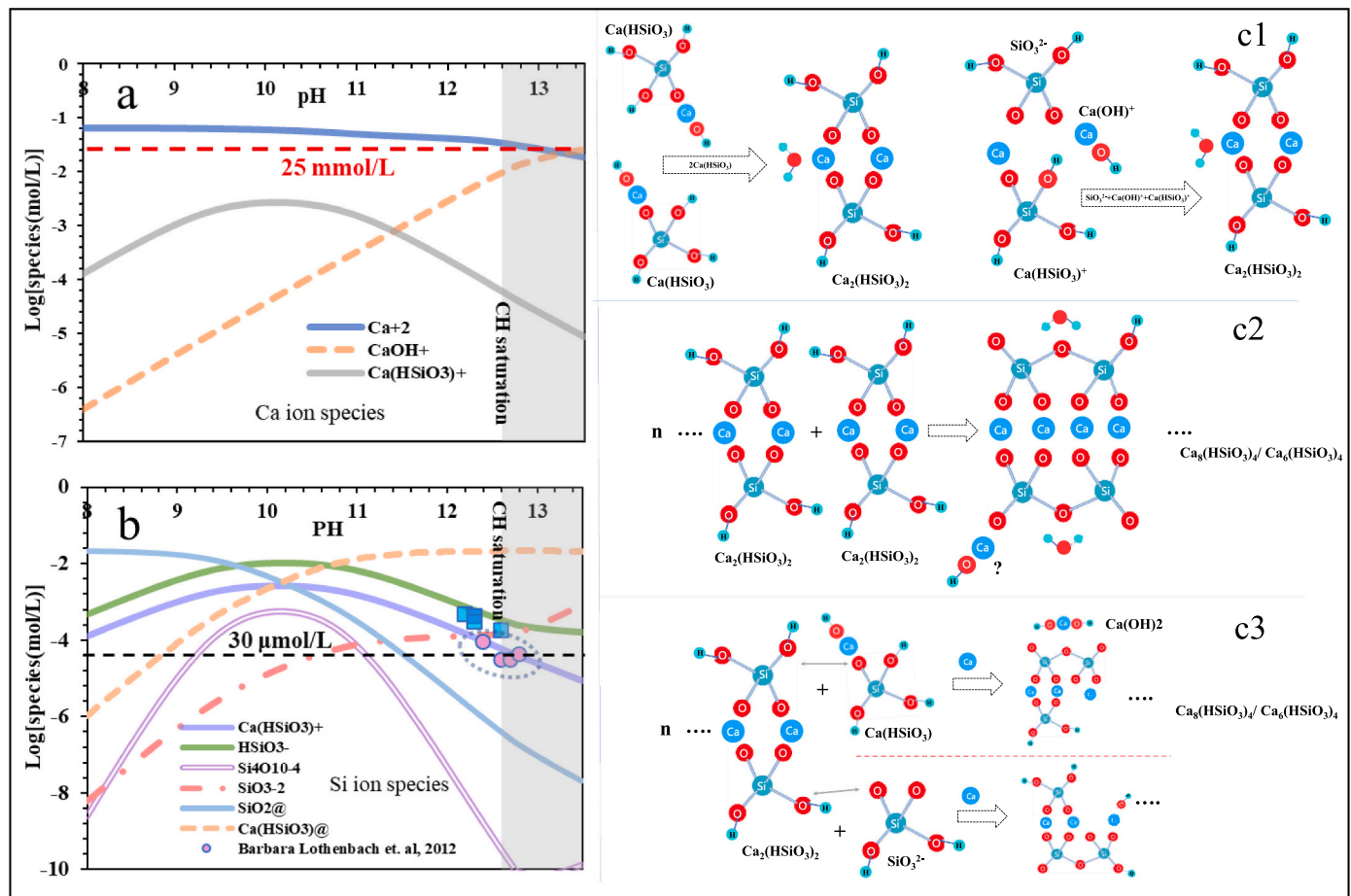


Fig. 10. Ca ion species (a) and Si ion species (b) in solution at different pH level from C_3S hydrated with deionized water (the results were simulated by GEMS, assuming it is without precipitation). The scatter data point is from reference [82] (the sphere is from the IP and the square is from the acceleration period). The c1 to c3 processes present the possible pathway to form the primary C-S-H structure.

some species in Fig. 10b is similar to the results in [80]. Because the pore solution of C_3S hydration is normally high alkaline ($pH > 11$), the thermodynamically stable species is comprised of $Ca(H_3SiO_4)OH$, $Ca(H_3SiO_4)^+$, $H_3SiO_4^-$, and $H_2SiO_4^{2-}$. The experimentally tested Si concentration in the pore solution during the IP is about $30 \mu\text{mol/L}$ at 25°C [24,69,76]. As shown in Fig. 10b, the tested value is close to the concentration of $Ca(H_3SiO_4)^+$, and it decreases with the increase in pH. Many previous papers showed that the Si concentration has a decreasing trend as hydration proceeds before the end of the IP [24,69,76,81]. It may come from the decrease of $Ca(H_3SiO_4)^+$ caused by an increase of pH during this period. The spherical dot data from [82] fits well with the simulation results. The square scatters in Fig. 10a are data from the acceleration period, which may imply a different equilibrium state between the stable C-S-H and solution instead of the unhydrated C_3S surface and solution. If we focus on the reaction of C_3S at low pH, $SiO_2@$ (H_4SiO_4) dominates in the solution when the pH is lower than 8. According to [83], neither Ca^{2+} nor $CaOH^+$ can react with H_4SiO_4 from the thermodynamic aspect. Therefore, in the reaction of C_3S with H_2SO_4 ($pH = 1$), Ca ions will precipitate into $CaSO_4$ (see in Fig. 2) and the H_4SiO_4 species precipitate as amorphous SiO_2 [84].

As Taylor highlighted in [85], a preliminary Ca—O layer must be formed as a basis before the polymerization of SiO_4 into Si_2O_7 . Fig. 10c1–3 illustrates the possible pathways for the formation of the primary C-S-H structure, and the reaction processes are summarized in Table 2. The possible polymerization process refers to the typical geopolymerisation of silicate [86]. The results from simulation based on density functional theory imply that the interaction between $CaOH^+$ and $H_2SiO_4^{2-}$ are the most favorable reaction in solution of pure C_3S [83].

Table 2

The possible reaction pathways for the C-S-H precipitation from the ionic complex in pure C_3S hydration.

Process	Reaction (use abbreviation from GEMS)	Bridge oxygen
c1	$2Ca(HSiO_3) \rightarrow Ca_2(HSiO_3)_2 + 2H_2O$ (left)	0
	$Ca(HSiO_3)^+ + SiO_3^{2-} + CaOH^+ \rightarrow Ca_2(HSiO_3)_2 + H_2O$ (right)	0
c2	(Preliminary complex structure) $Ca_{2n}(HSiO_3)_{2n} + Ca_2(HSiO_3)_2 \rightarrow Ca_{2n+2}(HSiO_3)_{2n}Si_2O_5 + 2H_2O$ $nCa_2(HSiO_3)_2 \rightarrow Ca_{2n}Si_{2n}O_{5n} + nH_2O$	2
c3	$Ca_{2n}(HSiO_3)_{2n} + Ca(HSiO_3) \rightarrow Ca_{2n+1}H_{2n-1}Si_{2n-1}O_{6n-4}Si_2O_5 + Ca(OH)_2$	1
	$Ca_{2n}(HSiO_3)_{2n} + SiO_3^{2-} + Ca^{2+} \rightarrow Ca_{2n+1}H_{2n-1}Si_{2n-1}O_{6n-2}Si_2O_5$	1

This is consistent with the thermodynamic simulation results by GEMS. Moreover, the interaction between Si species with $Al(OH)_4^-$ or Na^+ is highly possible as well, so the presence of these ions in solution will change the nucleation and growth of hydration products. Given that the c1 process is to build a good Ca—O layer basis for C-S-H, the $Ca(H_3SiO_4)OH$ species is critical for its nucleation and growth of it. As shown in Fig. 10b, a pH larger than 10.8 is a prerequisite to get enough $Ca(H_3SiO_4)OH$ species for a well-layered structure. This is consistent with XRD results from [87,88] in which C-S-H precipitated from pH less than 10.8 has few layer diffraction but the layer structure is evident for C-S-H precipitated from pH higher than that value. After a series of c1–3 reactions, the silanol exposed to the solution may deprotonate to form a

negative surface. As presented in [79], the $\text{Ca}(\text{H}_2\text{O})_6^{2+}$ and $\text{Ca}(\text{H}_2\text{O})_5(\text{OH})^+$ will be absorbed on the negative silanol site for the next step reaction.

4.2. Hydration of C_3S up to the end of the IP

After C_3S is mixed with the solutions, the reaction of C_3S starts with a superficial dissolution and is followed by nucleation and growth of the products in local regions near the surface. The near surface thermodynamic state can be classified into 5 regimes as shown in Fig. 11.

4.2.1. Stage I: fast dissolution

This is the initial stage after minerals contact with water. This stage has a high superficial undersaturation state for the dissolution of C_3S , so it has an ultra-fast dissolution rate. It results in a high heat release peak in the calorimetry test (see Figs. 4 and 7 before 30 min). According to the transition state theory [89,90], since the initial stage is far from equilibrium, the dissolution rate is only correlated to two terms: the concentration of the activated complex and the frequency of these complexes cross the energy barrier. It can be expressed by Eq. (4) [91], where R_d denotes the dissolution rate, R^+ is the forward reaction rate, k stands for a rate constant and the concentration of the activated species is presented as $[\text{AB}^*]$. AB^* is the interfacial complexes exposed to the solution which include $>\text{SiO}^-$, $>\text{SiOH}_2^+$, $>\text{SiOH}$, and $>\text{CaOH}^+$ for C_3S due to the moisture in air [61]. Each complex has its own reaction rate constant, so the number of selective sites where the most active complex stay has a great impact on the initial dissolution rate of the minerals.

$$R_d = R^+ = k[\text{AB}^*] \quad (4)$$

It is obvious that ionic O and Ca have the quickest dissolution rate [66,92]. The dissolution starts with a hydrolysis of ionic O and Ca to form OH^- , Ca^{2+} in solution, and CaOH^+ attached on the surface (Fig. 11). Consequently, the pH and Ca^{2+} in the bulk solution increase

evidently. Some ion species, like Al, in solution may absorb on the active sites to suppress the dissolution at a certain pH range (<12.5) [67]. Under this situation, the time to reach stage II and III will be delayed as shown in Fig. 7a.

4.2.2. Stage II: approaching dissolution equilibrium

As the quick initial dissolution proceeds, the increased pH and ion species in the solution augments the reverse reaction of the dissolution process. Under this condition, the thermodynamic state of the near surface region needs to be taken into account. Hence, the effective dissolution rate should be expressed by Eq. (5).

$$R_d = R^+ \left(1 - e^{\frac{\Delta G}{RT}}\right) \quad (5)$$

where R^+ is the forward reaction rate in Eq. (4), ΔG is the Gibbs free energy difference between reactants and products, R represents the gas constant, and T is the absolute temperature. The local thermodynamic state may be close to the bulk solution when the liquid to solid ratio is as high as 10,000 or 50,000 [47]; thus, the dissolution rate has a good correlation with the thermodynamic state of the bulk solution. This is because such a high ratio induces the initial pH of the solution to be much lower than 11. H_3SiO_4^- , H_4SiO_4 and Ca^{2+} dominate the ion species in solution, and most of them will have good mobility into the bulk solution so it can be detected by ICP-OES. When it comes to the actual hydration with a low liquid to solid ratio (<10), the thermodynamic state of the bulk solution is different from the near surface region as we discussed in Section 3.1. Distribution of the ion species can also help to understand the argument about the congruency of dissolution during hydration. The Ca/Si in the pore solution depends on the liquid to solid ratio [93]. When pure C_3S or cement hydrates with a normal water/solid ratio, the typical Ca/Si ratio from the bulk pore solution during the IP is approximately 833 (25 mmol/30 μmol shown in Fig. 10), referring to the results from ICP-OES [24,23,69,76,82]. However, the Ca/Si ratio in the

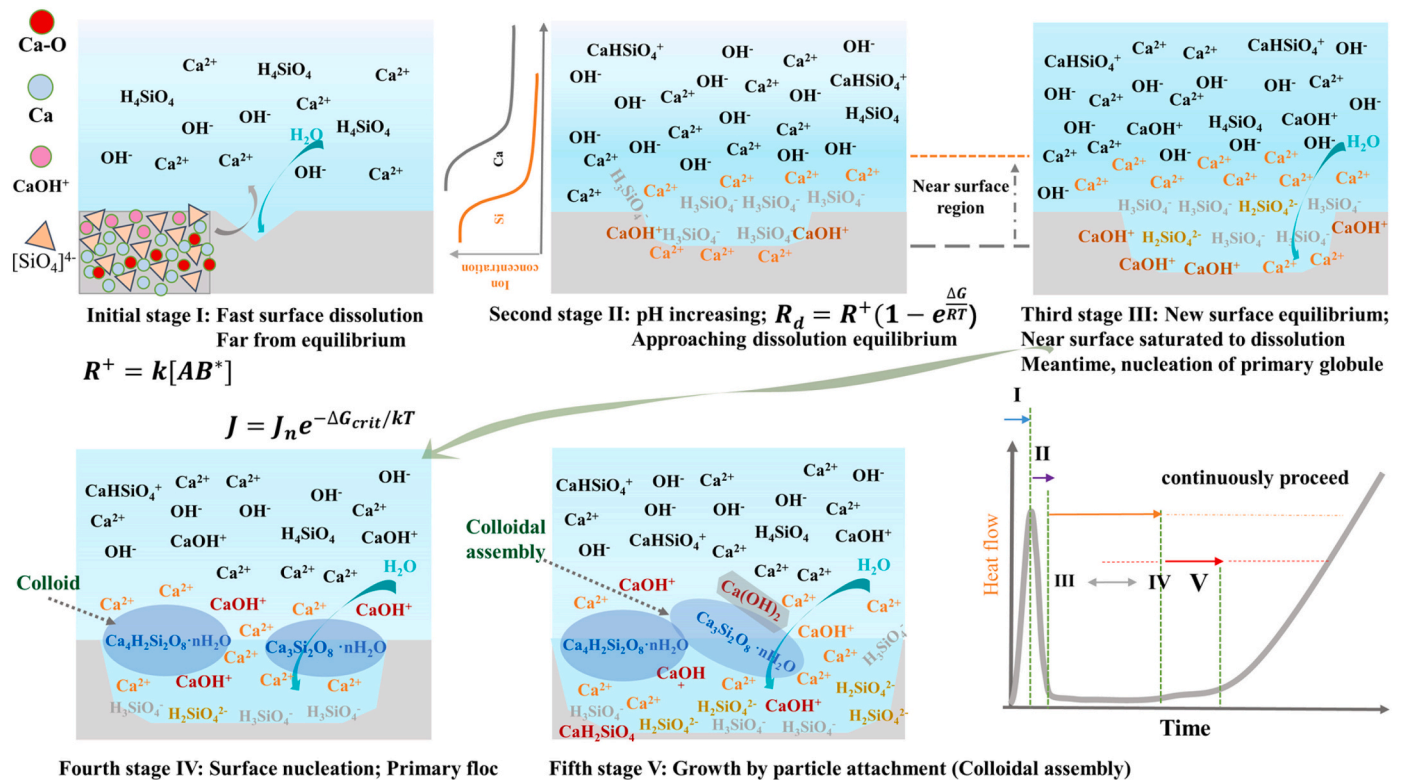


Fig. 11. Illustration of the hypothesis for hydration of C_3S up to the end of the low rate period. The ion species in black are ions far from the double layer with high mobility (that can be detected by filtering) and other colored notations of ions represent the surface absorbed species (hard to be detected in the pore solution). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

solution is close to 3 when water/solid ratio is very high [47]. This implies that the vast of number of Si ions on the surface can hardly move into the bulk solution whose pH is initially high due to the quick dissolution of ionic O and Ca in a limited content of water. Accumulation of $\text{Ca}(\text{H}_3\text{SiO}_4)\text{OH}$ on the selectively dissolved sites attracts cations (Ca^{2+} and CaOH^+) to form a cation layer. That is supported by the high positive zeta potential of hydrated C_3S and cement particles during the IP [94,95]. It may result in the formation of a locally concentrated region near the dissolution sites as shown in Fig. 11. The high local concentration of Si and Ca ions will build a near surface equilibrium with respect to dissolution even at a high water/solid ratio. Because it is a local equilibrium instead of a bulk equilibrium, the IP under a high w/c dissolution (100 or 200) will emerge at a similar time as under a normal w/c (0.5) (Fig. 2).

4.2.3. Stage III: new surface equilibrium

After a certain degree of dissolution, the near region comes to an equilibrium state with respect to dissolution of C_3S under static condition (without strong stirring). In the meantime, the high local concentration of Si and CaOH^+ ions will create an oversaturated state with respect to precipitation of primary C-S-H globules or CH. During the dissolution of minerals that is not involved with precipitation of new phases, it normally shows a low rate plateau in this period due to the step retreat [79]. Its low reaction plateau is controlled by the step retreat. However, the etch pit opening (see in Figs. 8 and 9) is the main dissolution process during the hydration of C_3S with the precipitation process in the IP (Fig. 7 at 4 h). The reaction rate in this period is controlled by the nucleation rate in the next stage instead of dissolution. Stage III and IV are two nearly concurrent stages during the hydration of TC_3S with water. However, the occurrence time of these two stages may be changed by the addition of admixtures.

4.2.4. Stage IV: surface nucleation

The primary C-S-H globules start to nucleate on the surface. The chemical structure of the globules could be with a Ca/Si ratio of 1.5, 2.0 [79], or even higher value because the deprotonation of silanol needs cations to neutralize the charge. The globule in solution will agglomerate into globule floc that is a colloidal structure as illustrated in Fig. 11 and shown in Figs. 8 and 9 in SEM image. The initial nucleation of the globule floc can be considered a classical nucleation process. The surface nucleation rate is given by [96–98]:

$$J = J_n e^{-\Delta G_{\text{crit}}/kT} \quad (6)$$

where J is the steady-state surface nucleation rate (number of nucleation events per surface area per second), ΔG_{crit} denotes the thermodynamic barrier to form a critically sized molecular cluster, and k represents the Boltzmann constant. J_n is a pre-exponential factor that can be considered a kinetic constant. The thermodynamic barrier is given with Eq. (7) by assuming a spherical nucleus:

$$\Delta G_{\text{crit}} = \frac{4\pi\gamma_{\text{sl}}r_{\text{crit}}^2}{3} \quad (7)$$

where γ_{sl} denotes the surface energy and r_{crit} is the critical radius of the nuclei. A certain number of nuclei should be formed to achieve a high enough probability of attachment between the primary nuclei. During the hydration of C_3S we can assume that the required density of nuclei for C-S-H growth by attachment is n . The DIP of nucleation can be expressed as:

$$t_{\text{ind}} = \frac{n}{J} = \frac{n}{J_n} e^{\frac{\Delta G_{\text{crit}}}{kT}} \quad (8)$$

A combination of Eqs. (7) and (8) results in Eq. (9),

$$\ln t_{\text{ind}} = \ln \frac{n}{J_n} + \frac{\Delta G_{\text{crit}}}{kT} = A + \frac{4\pi\gamma_{\text{sl}}r_{\text{crit}}^2}{3kT} \quad (9)$$

The DIP is from the end of stage II to IV. Fig. 12 shows a curve fitting between the duration of the induction period from hydration heat flow (Figs. 4 and 7) and the radius of globule flocs from SEM images (Figs. 5–6 and 8–9). The DIP has a good correlation with the globule size, especially in pure C_3S hydration stopped at 30 min with solvent exchange. The globule size of the hydration products stopped by freeze drying is much smaller than the products from solvent exchange, so the slope of the two fitted lines are significantly different. The triangle in Fig. 12 for pure C_3S deviates from the sample with C_3A , which implies the presence of Al will affect the kinetic of C-S-H nucleation.

4.2.5. Stage V: attachment to growth

This stage is dominated by growth of C-S-H through particle attachment, and the attachment of C-S-H is a colloidal assembly process similar to the other minerals [70]. The attachment happens on a selective orientation, so the morphology of C-S-H is strip like. It greatly consumes the Si and Ca ion species in the local region to reduce the near surface saturation state. Therefore, the dissolution of unreacted C_3S will have a sharp increase simultaneously. A growing number of attachment sites from pre-nucleated C-S-H increases the probability of later attachment, and this leads to an exponential increase in the hydration rate, resulting in an acceleration period.

The different stages may mix with each other during the hydration. The dashed line in Fig. 11 just represents the transition of the predominant reaction. For instance, the range with a red arrow noted with a “V” means that stage V dominates at this stage, but it is accompanied with all the other reactions happening at the same time.

4.3. Interpretation of factors affecting the DIP

The natural feature of raw materials has an impact on the DIP. C_3S with different particle sizes, polymorphisms and annealing treatments have the discrete density of defects on the surface. The defects have little effect on the time for the solution to reach a saturated state with respect to dissolution in the near surface zone. The doping may influence the dissolution rate at the initial water contacting, but the saturated state comes within a few minutes or even seconds after the C_3S contacts with water [47]. Afterwards the near surface layer will go into a new equilibrium condition with respect to precipitation of products, so the nucleation and growth of products take over the reaction process. Since the nucleation will preferentially start at the impurity site, the surface point defects or steps [99], these sites on the minerals surface accelerates the nucleation of primary flocs. These sites correspond to the etch pit or

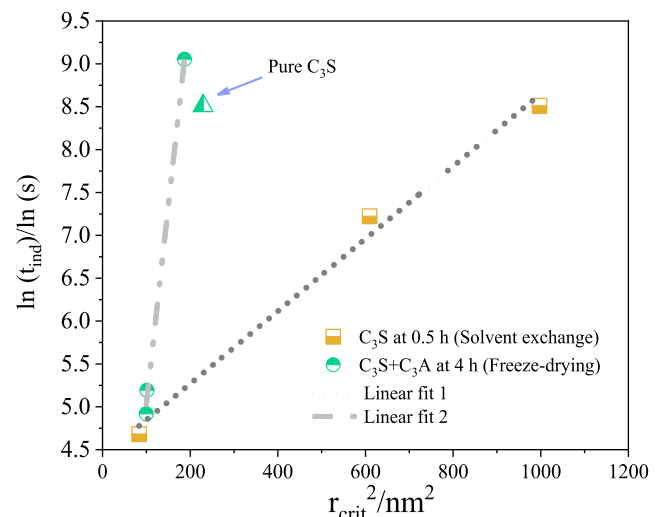


Fig. 12. The linear fitting data between $\ln(t_{\text{ind}})$ and r_{crit}^2 based on Eq. (9).

region near it during hydration of C_3S (see nucleation site in Fig. 7). The slower dissolution rate also results in a lower number of nucleation sites thus reducing the nucleation rate of primary C-S-H. A lower etch pit density elevates the time for stage III and IV to reach a sufficient density of primary particles for further particle attachment.

The pH value is a critical parameter to control the DIP. A high pH (≥ 13) will facilitate the precipitation of C-S-H at a low Ca and Si concentrations, so the hydration may directly come into stage V from some point at stage II. C-S-H grows in a condition where the dissolution of C_3S is still at a relatively high rate, so the heat release at the inflection point is much higher than the control sample, as shown in Fig. 4. A sufficiently high alkalinity even eliminates the IP [36]. It implies that hydration starts from stage I and goes straight to stage V. Some soluble inorganic salts [32] or nano seeds [31,33,34] can shorten the duration of stage III and IV, because they have an enhancing effect on the nucleation of primary globule flocs. While some soluble inorganic salts ($CuCl_2$, $CuSO_4$, $Pb(NO_3)_2$) have an incremental effect on the DIP [17,26] because the metallic hydroxides from these salts will precipitate under a much lower pH than portlandite, these salts consume hydroxides and keep a relatively lower alkalinity in solution to slow down the nucleation of primary C-S-H (stage IV) and portlandite. Al ions have an inhibiting effect on the dissolution of C_3S , but this effect just shows in the first peak, corresponding to a delay in the transition from stage II to III, as shown in Fig. 7a. Al ions change the kinetic of nucleation of C-S-H primary globules as well. The longer DIP induced by Al ions is mainly due to its suppression on the growth of C-S-H.

Fig. 13 demonstrates that the Ca/Si ratio measured from the pore solutions is far from the stoichiometric ratio with 3 in solid. Some organics increase the solubility of C-S-H and it is so evident on the Ca^{2+} concentration. This makes the solubility of C-S-H closer to and even higher than the equilibrium line of C_3S hydration. Hexitols or some other organics enforce prolonging effects on the IP but increase the Si

concentration in the bulk pore solution. The data dots for C_3S or white cement with retarding admixtures are higher than for the control sample, even being located on the upper part of the normal dissolution line (C_3S with C-S-H). The interaction between organic admixtures with Si ions will release more ions from the near region into the bulk solution, so the measured Si value was higher than the pure system. It modifies the double layer and will reduce the concentration of Si and Ca in the near surface region. This means that the precipitation of primary C-S-H on the surface with these admixtures requires a higher supersaturation state than in a solution without admixtures. When the dissolution of C_3S comes to stage II, the saturation state regarding precipitation in the near surface zone with the retarding organics is much lower than that in the plain system. Therefore, it has a lower nucleation rate at the end of stage II and requires a longer time to achieve a critical density of primary floc. Moreover, some organics will stabilize the primary flock, such as PCE [100]. It will hinder the attachment between primary particles, and consequently, the transition from stage IV to V will be prolonged.

4.4. Limitations and perspective for further investigation

The dissolving surface and precipitated products are analyzed based on the SEM images of the treated samples instead of in-situ measurement. Therefore, the hypothesis is proposed based on the assumptions: Firstly, the solvent exchange treatment by isopropanol has the same effect on the precipitated products of samples hydrating in different solutions; Secondly, the freeze-dry method preserves the pristine feature of the particles surface and the plating of Au has few effects on the sizes and number of etch pit.

The chemical composition of the layer structure between C-S-H and the unhydrated surface (Fig. 8) needs some direct evidence from the advanced equipment (such as HR-TEM [57]) with high resolution. The previous papers [69,76] concluded that the bulk pore solution reached an oversaturated state regarding the C-S-H during IP, so it implied a potential nucleation in the bulk solution. Although the nucleation on the surface defects or steps may be preferential, how does the homogeneous nucleation in pore solution contribute to the hydration process is lack of consideration in this hypothesis. It is better to include the homogenous nucleation model from [104] in the further investigation to complete the theory. The evidence for the nucleation of primary globules can hardly be detected under the SEM images, which may be due to the resolution limitations or the metastable state of it. According to the models from [54,104,105], the size of globule is about 3–4 nm, but we can only observe globule floc whose size is larger than 20 nm under SEM. We assumed that “n” is the sufficient density for the attachment of flocs to take over the hydration process. The investigation on determining this value is critical to prove this hypothesis.

5. Conclusions

The hydration of C_3S with a very high w/c is difficult to be explained by the dissolution theory with only with focus on the thermodynamic state of the bulk pore solution, because the dissolved percentage of C_3S detected from calorimetry and XRD test presents little differences between low (0.5) and high (200, 600) w/c. Therefore, more attentions should be paid to the nucleation of hydration products within the interfacial zone of the solid and solution.

From SEM images, the dissolution etch pit can be observed on the surface of C_3S particles whose hydration was stopped by free-drying near the end of IP. Al almost has no influence on the size of etch pit on C_3S at the end of IP. C-S-H precipitates on the etch pit or in region close to it. A nonclassical nucleation theory is better to explain the precipitation process of C-S-H during IP. It starts with nucleation of primary particles and then is followed by the growth from particle attachment. The attachment of C-S-H globule floc is a colloidal assembly process. A layer between the C-S-H floc and C_3S surface was detected, which probably is the precipitation of CH between the two colloidal

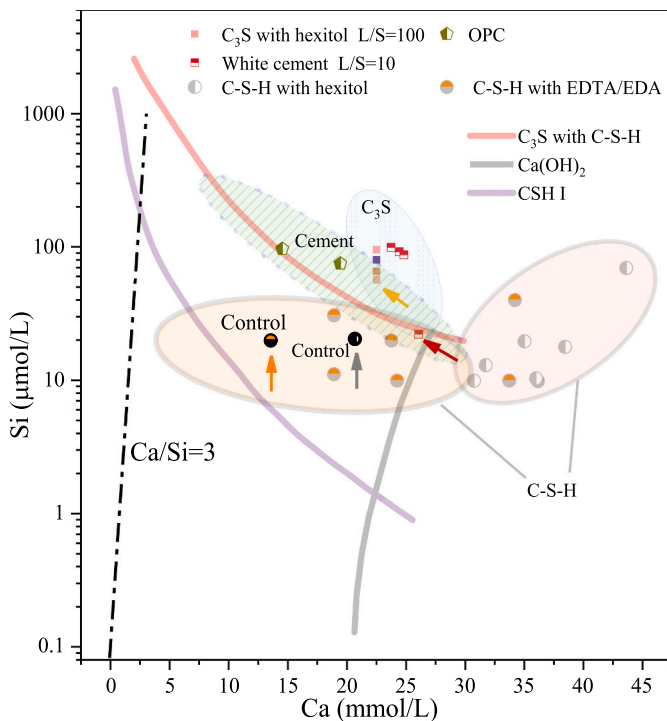


Fig. 13. Concentrations of silicon and calcium ions from the pore solution. The equilibrium lines of C_3S with C-S-H, CSH I and $Ca(OH)_2$ are adopted from [101]. Scatter data are from the pore solution of Portland cement during the IP [102], solution of C_3S [43]/white cement [38] with hexitols and C-S-H with the addition of organics [103]. Arrows point at the data dots from the control samples in the corresponding literature.

surfaces.

The increase in the heat release rate at the end of IP comes from the accelerating growth rate of C-S-H instead of dissolution of the etch pit. KOH and K₂SO₄ have an impact on the primary globule size and growth of strip C-S-H so that they change the DIP. Al ion inhibits the dissolution of C₃S at a very early age before the start of IP, and it also suppresses the growth of C-S-H to increase the DIP. The pH affects the Si and Ca ion species in the pore solution, which impacts both the dissolution of C₃S and the nucleation of primary particles.

Based on the dissolution and CPA theory, we suggest five stages in the early hydration process by focusing on the nucleation and growth of C-S-H within the local region, that is, Stage I: Fast dissolution, Stage II: Approaching dissolution equilibrium, Stage III: New surface equilibrium, Stage IV: Surface nucleation, and Stage V: Attachment to growth.

CRediT authorship contribution statement

Liming Huang: Conceptualization, Methodology, Software, Investigation, Data analysis, Writing-Original Draft, Writing-Review & Editing. Luping Tang: Writing-Review & Editing, Supervision, Project administration, Funding acquisition. Haitao Gu: Investigation, Resources. Zhen Li: Investigation, Resources. Zhenghong Yang: Review & Editing, Supervision, Project administration.

Declaration of competing interest

We declare no conflicts of interest.

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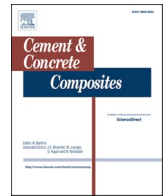
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Paper II

Real-time monitoring the electrical properties of pastes to map the hydration induced microstructure change in cement-based materials

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Real-time monitoring the electrical properties of pastes to map the hydration induced microstructure change in cement-based materials

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ABSTRACT

The effect of the supplementary materials (SCMs) on the moisture content and ion diffusivity at different hydration time is important for the service life modelling of modern concrete. This study designed a simple but valid method to monitor the microstructure change in pastes during hydration. A procedure easy to implement was proposed to detect the water content in pastes. The electrical conductivity of pore solution was evaluated by the evaporable water content in pastes and chemical composition in the binders. Results show that the electrical properties of pastes (conductivity, formation factor and its growth rate) can effectively indicate the hydration reactivity of binder, pore connectivity and volume of pore solution in the hardened pastes. The effect of water-binder ratio and SCMs on the structure of pastes are effectively indexed by the formation factor which is the conductivity of pore solution divided by that of paste. The inflection point of average growth rate of formation factor is a good index for the final setting of pastes. The relation between volume of evaporable water and formation factor is well demonstrated by the extended percolation theory. The real-time monitored electrical conductivity and formation factor of pastes can be used to calculate the chloride migration coefficient in hardened cement pastes.

1. Introduction

The moisture content and ion diffusivity in the cement-based materials change with the curing time due to the continuous hydration of binders. The hydration of binders is a complex process involving the dissolution of reactants and precipitation of products. The initial nucleation and growth of hydration products at the solid-liquid interface leads to the formation of clusters that eventually connect into an elastic network structure, resulting in the setting of paste due to the percolation of connection [1]. As hydration reaction continuously proceeds, the growth of products modifies the structure of the hardened cement-based materials. Because the desirable engineering characteristics of hardened concrete (strength, dimensional stability, and durability) depend on the microstructural features (i.e., the type, amount, and distribution of solids and voids) [2], a lot of models were proposed to simulate the microstructure development during hydration [3]. Despite of having some progresses, we are far away from reaching a complete simulation that allows engineers to perform a precise prediction on the performance

of concrete. To better understand the hydration process and provide data for simulation, a reliable in-situ test of hydration and microstructure development of concrete is of great significance. The use of supplementary cementitious materials (SCMs) are currently recognized as the main way to produce sustainable concrete [4,5]. Therefore, the anticipated mechanical performance and durability of modern concrete require a good knowledge about the hydration and microstructure evolution of both ordinary Portland cement (OPC) and the blended pastes.

There are many well-used methods to measure hydration rate and degree of cementitious materials, such as calorimetry, chemical shrinkage, chemically bonded water, X-ray diffraction and scanning electron microscope [6,7]. For the microstructure analysis, Monteiro et al. [8] had a detailed review to summarize the most advanced methods used in the research of cement-based materials. However, only a few of those methods can be applied as an in-situ measurement without any special treatment of samples. Moreover, the allowed dimension of samples is limited for the measurement by those methods.

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Low field proton NMR is a promising way to monitor the hydration [9] and structure evolution [10] of paste. However, the relaxation signals will be affected by paramagnetic matter (such as Fe) [11], so it is not a compatible method for the investigation of grey cement and the blended pastes.

Apart from all the above methods, the test of electrical conductivity was used in many previous studies [12–16] as a qualitative way to indicate the hydration and structure of the cement-based materials. The conductivity/resistivity of concrete was used as a viable index to study hydration and a good approach for designing the automated monitoring system in construction [17]. Karmazsin and Murat [18] designed an apparatus for a simultaneous test of the isothermal calorimetry and electrical resistance. Their results showed that the evolution of resistance was highly comparable with the calorimetry evolution during the hydration of calcium sulfate hemihydrate in a small cell. A similar setup was used to study the influence of chemical admixtures on the hydration of OPC [19], and the authors found that the increase in the electrical conductivity are in the same order as that in the heat liberation rate. Singh et al. [20] used conductivity test, combined with heat release and other analysis methods, to reveal the effect of citric acid on the hydration of OPC. They concluded that the ionic mobility and concentration of charge carriers were decreased by citric acid so that the hydration of cement was altered. The measurement of electrical conductivity was also frequently applied in the investigation of the blended system. Abo EI-Enein et al. [21] proposed several empirical equations to describe the correlations between water-binder ratio (w/b) or silica fume content and electrical conductivity. A similar empirical equation was correlated between conductivity of paste and kaolinite content [22]. The hydration of granulated slag blended with cement kiln dust or silica fume [23], and the rheological properties of pastes blended with silica fume were connected to the conductivity evolution with time [24]. Chrisp et al. [25] applied an auto-ranging impedance analyzer to test the conductivity of cover zone concrete blended with slag and fly ash. They used a normalized conductivity to indicate the effect of wetting and drying. McCarter [26] et al. used the same setup for monitoring the electrical response of alkali activated paste before 48 h and the conductivity of hardened concrete exposed at the marine environment. The normalized

conductivity based on the value at the initial time was defined to indicate the hydration of concrete with different binder types and w/b [27]. The evolution of conductivity was classified into four stages with respect to the dissolution and precipitation during the early hydration. However, some analysis of conductivity change based on pore solution concentration in Ref. [27] is contradictory to the tested ion concentration in pore solution in some published papers [28,29].

It is a challenging but meaningful work to find a quantitative relationship between the conductivity and hydration or other properties of cement-base materials. Conduction of electric current in cement paste includes two path ways: one is ionic conductivity through pore solution, which depends upon the temperature [15,30–32], type of ions and its concentration [33,34], and the connectivity between the high conductive solution; the other is electronic conduction through the gel-water and unreacted cement particles, particularly compounds of iron, aluminum and calcium [35]. By taking these factors into account, some empirical relations were proposed to correlate the conductivity with hydration time, porosity, hydration degree [36], mechanical performance (compressive strength [37,38]) and diffusivity [39,40]. Wilson et al. [41] found a general correlation between the effective chloride migration coefficient from their method and the bulk conductivity of pastes, but the white cement pastes deviated from the general line when the coefficient was correlated with inverse of formation factor or pore connectivity. Chidiac and Shafikhani [42] developed model based on the measured conductivity of concrete and the calculated conductivity of pore solution. Their model is effective in estimating the chloride migration coefficient in both OPC and the blended concrete.

The change of electrical conductivity of paste during hydration will be determined by the evolution of intrinsic factor as shown in Fig. 1. Hydration of minerals induces a change of phase assemblage and internal moisture, which in the meantime forms the structure of paste. As now popularly acknowledged [43], the availability of moisture and pore distribution in paste will, in turn, makes impact on the later age hydration. The volume and ionic concentration of pore solution was related to the phase assemblage and moisture content through thermodynamic laws. Besides the composition of paste, the connectivity of pore solution (similarly, pore connectivity) is the other factor that controls

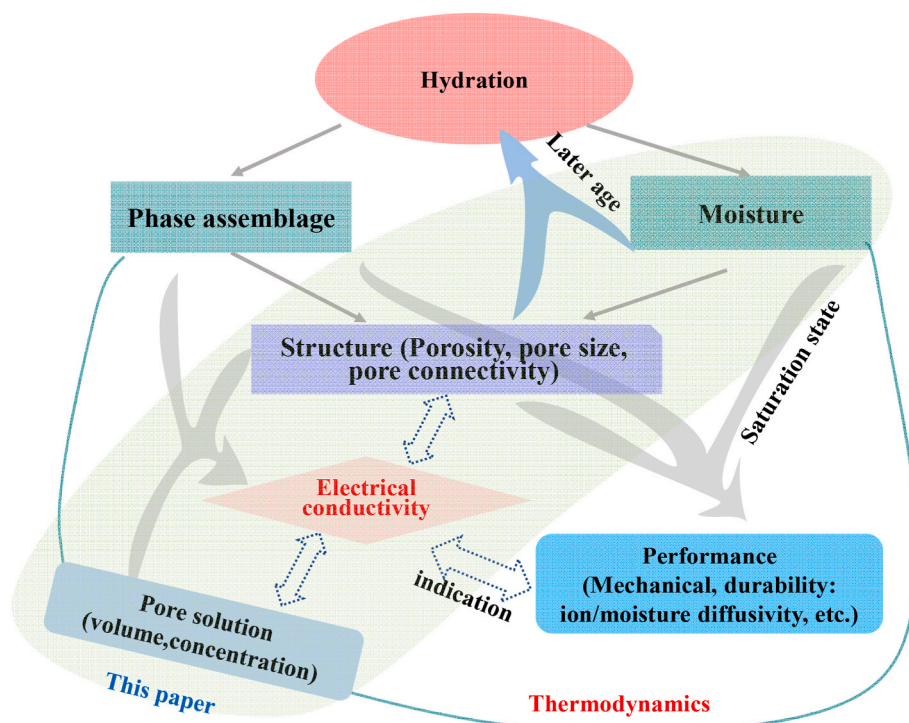


Fig. 1. The logical relationships between the electrical conductivity, hydration, and performance of paste.

the electrical conductivity in pastes. The mechanical performance and durability of cement-based materials are determined by its phase assemblage, microstructure, and the saturation state. These properties for one specific proportion can be qualitatively or empirically indicated by the conductivity, but it lacks a general description in both OPC and the blended pastes. A generally quantitative relationship is of great significance for not only the scientific research but also industrial application.

This paper presents an investigation on discovering how the electrical properties correlate with the hydration process, structure evolution and chloride migration in both OPC and the blended pastes. We designed a simple setup for an instantaneous conductivity monitoring, and then mainly focused on the deep understanding of the relationship between the conduction and structure of paste. A novel procedure was developed to detect the evaporable water content of paste so that the electrical conductivity of pore solution was calculated based on chemical composition of binder and volume of evaporable water. The formation factor was calculated to distinguish the effect of pore solution and structure on the conduction. Its growth rate was defined to indicate the setting and hydration reactivity of pastes. The electrical properties measured by the invented method were also correlated to the chloride migration coefficient. A good correlation has been found between formation factor and moisture content based on an extended percolation theory [44].

2. Experiments

2.1. Materials

The used cement is an ordinary Portland cement CEM I 52.5 R with a Blaine surface of 525 m²/kg. Three kinds of SCMs were considered, including slag Bremen (SL) with a Blaine surface of 420 m²/kg from Thomas cement AB, Fly ash (FA) from Cementa, and limestone from Nordkalk with a D₅₀ = 18 µm (LL). The chemical composition of each binder is shown in Table 1. The limestone has a calcite content ~89% and a relatively high SiO₂. Table 2 presents the mix design of 11 samples. In the binary systems, the replacement content of cement with SL and FA is the same as 35% by weight. In the ternary system, OPC was replaced with 35% SL and 16% LL. Pastes were mixed with three different w/b with 0.35, 0.45 and 0.55 respectively, except for the FA blended pastes with two ratios (0.35 and 0.45).

2.2. Procedures and methods

2.2.1. The electrical conductivity test

The electrical conductivity of paste was measured by a four-electrode method to minimize the effect from polarization. The electrodes were positioned in the Wenner configuration referring to Ref. [46] as shown

Table 1

Chemical composition of different binders (LOI: loss of ignition; δ_i : mole of chemical composition per gram binder).

Chemical Composition	CEM I 52.5 R		Slag		Fly ash		Limestone
	wt%	δ_i (mol/g)	wt%	δ_i (mol/g)	wt%	δ_i (mol/g)	wt%
CaO	62.2	1.11E-02	39.11	6.98E-03	5.1	9.11E-04	49.5
SiO ₂	19.6	3.06E-03	36.63	5.72E-03	54.6	8.53E-03	9.0
Al ₂ O ₃	4.5	4.41E-04	13.56	1.33E-03	22.4	2.20E-03	0.6
Fe ₂ O ₃	3	1.88E-04	0.49	3.06E-05	8.7	5.44E-04	0.3
SO ₃	3.5	4.38E-04	0.27	3.38E-05	0.8	1.00E-04	0.03
MgO	3.5	8.75E-04	8.52	2.13E-03	1.8	4.50E-04	–
K ₂ O	1.01	1.07E-04	0.57	6.06E-05	2.1	2.23E-04	0.3
Na ₂ O	0.27	4.35E-05	0.42	6.77E-05	1	1.61E-04	0.1
Cl	0.07	1.97E-05	0.009	2.54E-06	–	–	–
Sulfide	–	–	0.73 ×	–	–	–	–
LOI	2.5	–	–1.07	–	3.5	–	40.1

× Note: The sulfide in slag will be oxidized during the LOI test, so this induces an increase of weight. Although the hydration also makes oxidization of sulfide [45], we assume that its oxidization is rare due to the low hydration degree at early age.

Table 2

The mix proportion of samples (LOI_b: the normalized loss of ignition of binder system).

Samples	Binder	w/b	LOI _b
P035	OPC (SH P Slite CEM I 52.5 R)	0.35	2.5%
P045	OPC (SH P Slite CEM I 52.5 R)	0.45	
P055	OPC (SH P Slite CEM I 52.5 R)	0.55	
P135	65%OPC+35%FA	0.35	2.85%
P145	65%OPC+35%FA	0.45	
P235	65%OPC+35%SL	0.35	1.2%
P245	65%OPC+35%SL	0.45	
P255	65%OPC+35%SL	0.55	
P335	49%OPC+35%SL+16%LL	0.35	0.85%
P345	49%OPC+35%SL+16%LL	0.45	
P355	49%OPC+35%SL+16%LL	0.55	

in Fig. 2. The stainless screws were used as the electrodes and these are positioned in the middle line with a parallel distance of 25 mm to the bottom line, and the space between electrodes is 40 mm. A brief circuit diagram of the setup is presented in right of Fig. 2. The whole system was recorded and controlled by a datalogger. We used two relays (a and b) to control the power supply and one relay (c) to control the data collection. Besides during the time for instant test, the paired electrodes were connected to avoid polarization difference. The electrical conductivity of the samples was calculated as a semi-infinite slab with the voltage and current value. The whole setup was calibrated with the standard conductive solution (KCl) in the range of 0.015–74.97 mS/cm. In the first 24 h, the datalogger released an instant signal every 2 min to connect power system to provide a constant current (0.5–1 mA). Simultaneously, relay c created the connection for collecting the voltage between the two electrodes in the middle. It takes about 0.2 s to finish one instant test. The time interval was switched to 10 min from 1 day to 12 days. The data after long-term hydration was further collected at 28, 90 and 180 days.

The dry binder was homogenously mixed in a ceramic rotator with balls (D = 20–25 mm) at 12–20 rpm for 10 h. Firstly, water with 35% weight of binder was added into binder and then it was mixed with a slow rate by the planetary mixing machine for 60 s. Secondly, the rest of water was added up to the target w/b before a high rate stirring for 120 s. Afterwards, the pastes were poured into the small plastic boxes with four electrodes and a volume capacity of 1000 mL. The sample was sealed with the cap and put in the curing room with a constant temperature of 20 ± 1 °C. The data collection started at about 10 min after water addition.

2.2.2. Water distribution test

An easily implementing procedure was designed for the determination of water content in pastes (see Fig. 3). The pastes were mixed with the same procedure in section 2.2.1. Samples were casted in a Petri dish

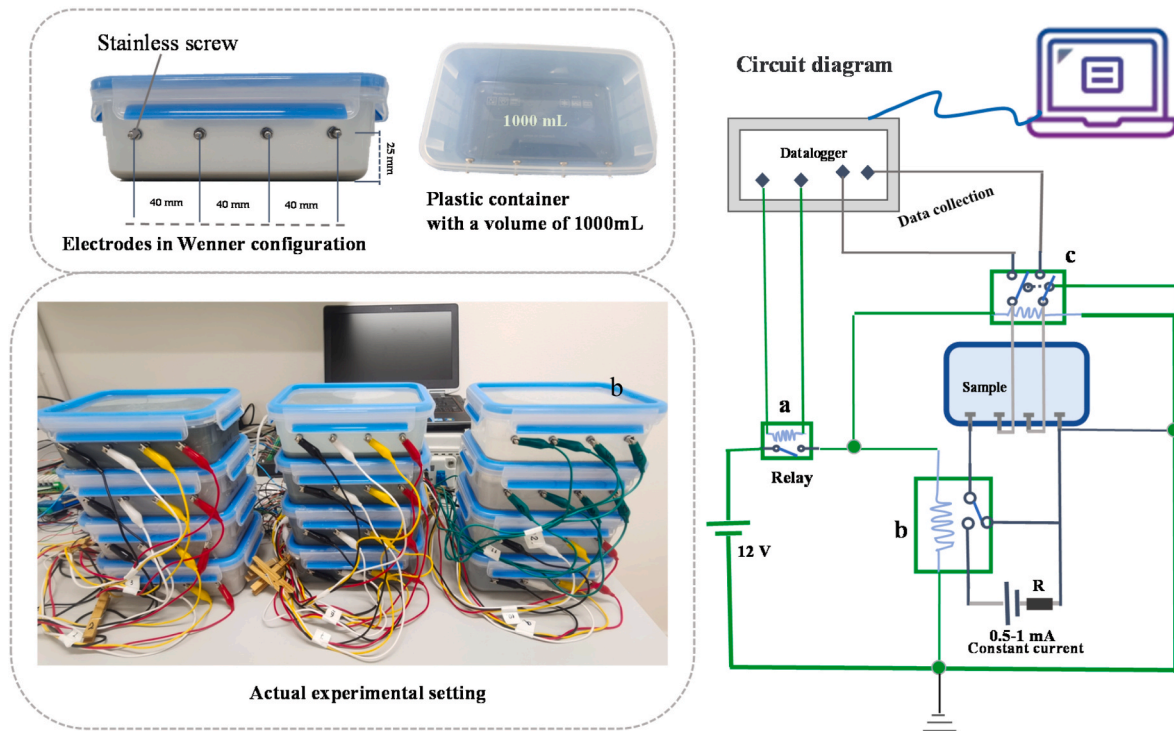


Fig. 2. A simple setup for monitoring the conductivity during hydration.

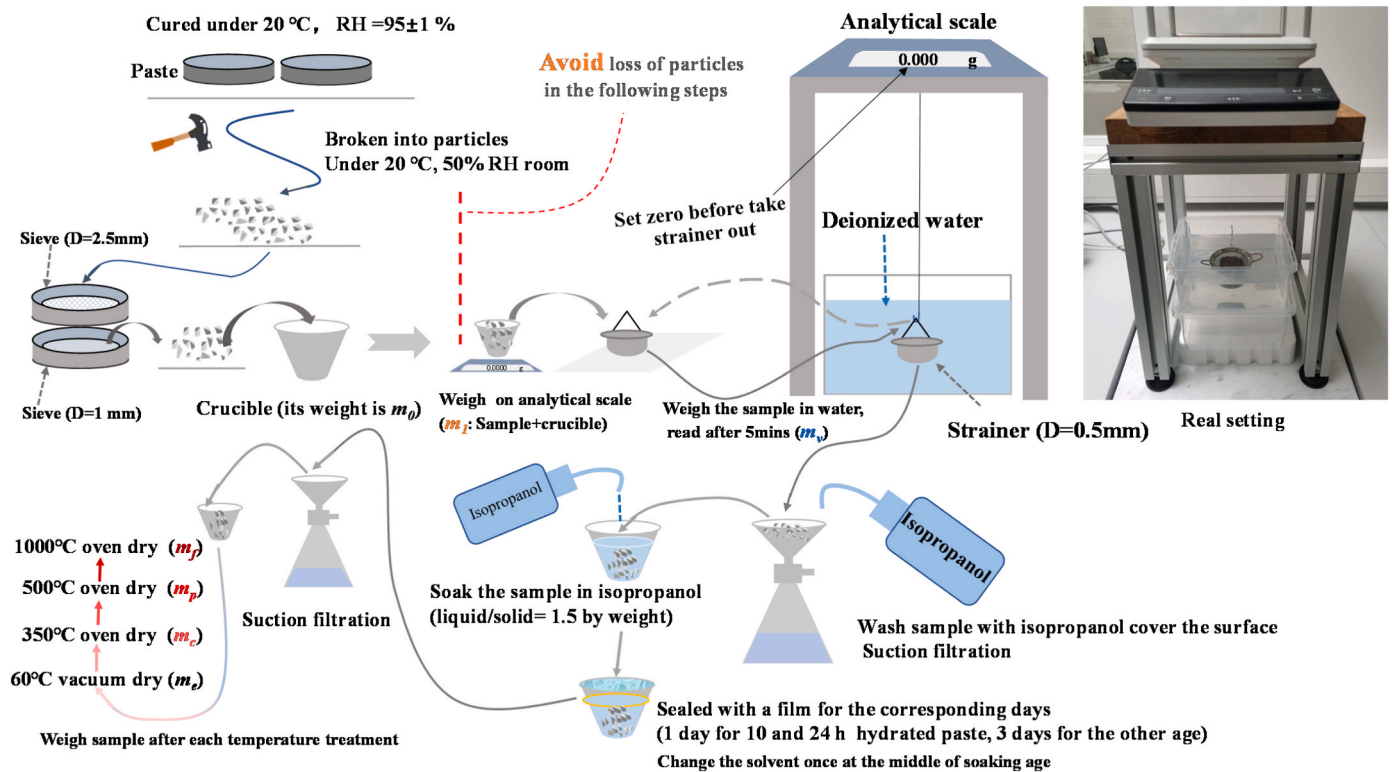


Fig. 3. The procedure for testing the water distribution in paste.

and cured in a box with $97 \pm 1\%$ RH at 20°C . The hardened pastes were broken into pieces after a series of curing times. Particles with size in a selective range ($D = 1\text{--}2.5\text{ mm}$) were collected for the treatment in the next step. To ensure the validity of data, the weight of particles should be $\geq 10\text{ g}$, and the accuracy of analytical balance is at least 0.001 g . The

mass of dry empty crucible was weighed and recorded as m_0 . The crucible containing particles was weighed and recorded as m_1 and then particles were transferred into a small strainer ($D = 0.05\text{ mm}$). The mass of particles immersed in water was weighed by the analytical balance that was zero set with holding of the strainer. Thereafter, the particles

were washed with isopropanol (IPA) before transferring back to the crucible. Samples were immersed with IPA with a liquid/solid ratio of 1.5 and sealed with a cling film. The procedure was finished within 30 min from water addition to the sealing. IPA exchange method is recommended as the preferred way for stopping the hydration and drying the paste [6]. Zhang and Scherer [50] asserted that the exchange duration need to be sufficient to reach ~99% IPA at the sample center. This exchange degree can be reached after 5-h immersing for sample with size of 1 mm. For a complete exchange of evaporable water, the immersing duration is at least 24 h for samples in this study (see Fig. 3). We changed the solvent once at the middle immersing age.

Samples were filtered, moved back to the crucible, and followed with a vacuum drying at 60 °C (V60) for 24 h. The mass of vacuum dried crucible with sample was weighed (m_e). Afterwards, the crucible was immediately put into a furnace with a temperature pre-heated to 105 °C. It was heated up to 350 °C with a rate of 5 °C/min and this temperature was maintained as constant for 2 h. After it was cooled down to 105 °C, it was moved out with the heat-resistant gloves and weighed on the analytical scale with an insulation layer between crucible and scale. The same step was repeated for the other temperatures, starting again at 105 °C to the target temperature (500 and 1000 °C, respectively) with a holding time of 2 h. The weight of crucible with sample at V60, 350, 500 and 1000 °C was recorded as m_c , m_p and m_f , respectively.

2.2.3. Setting time test

The setting of pastes was tested by a Vicat needle according to ASTM C191-08 under an environment temperature of 20 °C and relative humidity of 50%, except that pastes were mixed with the w/b of 0.35, 0.45 and 0.55 instead of w/b a for normal consistency. The fresh pastes were kept in a moist box with RH of 97% between the Vicat needle measurement intervals.

2.2.4. Chloride migration test

Pastes were casted into a rubber cylinder mould ($\phi_{in} = 50$ mm, $h = 110$ mm). After a sealed curing for 1 day, specimens were demoulded and moist cured until the age of 28, 90 and 180 days, respectively. Two samples with a thickness of 50 mm were cut from each specimen for the RCM test at the specified age. The test was performed according to NT BUILD 492 but without the vacuum saturation procedure because the specimens were moist cured before the test.

2.3. Determination of the evaporable and bound water content

With the weight from section 2.2.2, we can calculate the weight loss percent at the corresponding temperature ranges, so the evaporable water (Epw) percent with respect to binder (φ_{epw}) is stated as:

$$\varphi_{epw} = \frac{m_1 - m_e}{m_{ub}} \quad (1)$$

where m_{ub} is the mass of the mixed binder. Given that the carbonation of samples during early age can be neglected, the m_{ub} for paste without LL can be calculated by Eq. (2).

$$m_{ub} = (m_f - m_0) / (1 - LOI_b) \quad (2)$$

The weight loss at the temperature range of V60~350 °C, 350~500 °C and 500~1000 °C can be calculated by Eqs. (3)–(5), respectively.

$$\varphi_{\sim 350} = \frac{m_e - m_c}{m_{ub}} \quad (3)$$

$$\varphi_{350 \sim 500} = \frac{m_c - m_p}{m_{ub}} \quad (4)$$

$$\varphi_{500 \sim 1000} = \frac{m_p - m_f}{m_{ub}} - LOI_b \quad (5)$$

The CO₂ release from LL within the temperature range of 500~1000 °C needs to be subtracted for LL blended paste. Hence, the actual weight of binder is m_{ub}' by Eq. (6).

$$m_{ub}' = (m_f - m_0) / (1 - 44\% \times P_{lm} - LOI_b) \quad (6)$$

where P_{lm} is the replacement percentage of LL and this is 16% in this study. In addition, the weight loss from moisture between 500 and 1000 °C for LL blended is:

$$\varphi_{500 \sim 1000} = \frac{m_p - m_f}{m_{ub}'} - 44\% \times P_{lm} - LOI_b \quad (7)$$

Theoretically, according to the law of conservation of mass, we can get the mass balance Eq. (8). This can be used to check the accuracy of the test procedure.

$$\varphi_{epw} + \varphi_{\sim 350} + \varphi_{350 \sim 500} + \varphi_{500 \sim 1000} \equiv w/b \quad (8)$$

3. Results

3.1. Real-time conductivity of pastes with different w/b

The real-time monitored electrical conductivity of pastes is shown in Fig. 4. The evolution of electrical conductivity up to 400 days was classified into four regions by McCarter et al. [27] and the author had a detailed discussion on the relationship between the hydration process and conductivity evolution. Herein, some different explanations for the change of conductivity will be specified. Exemplifying with OPC paste with w/b = 0.35, The evolution of conductivity can be classified into four stages before 14 h (Fig. 4a).

The great increase of conductivity in stage I was not mentioned in Ref. [27]. This results from the fast increase in concentration of OH⁻, K⁺ or Na⁺ in pore solution mainly due to the quick dissolution of alkali metal ions after water addition. Samples with w/b of 0.45 have the highest conductivity in OPC pastes. The increase in w/b dilutes the K⁺ and Na⁺ concentration in pore solution, so P045 has a higher conductivity than P055. For the paste with w/b of 0.35, the connectivity of pore solution is the lowest. Although P035 has a higher alkali concentration, compared to P045, the electrical conductivity is lower. The blending of SCMs reduces the alkali concentration in the pore solution to decrease the initial conductivity. Lothenbach and Scrivener [47] ascribed the reduction in alkali concentration to three effects: dilution of OPC; consumption of portlandite leading to lower Ca concentration; increase of alkali uptake in C-A-S-H. The reduction effect only comes from the dilution effect since few products precipitate at early ages.

Stage II corresponds to the induction period. The concentration of Si ions increases during this period, but it has little influence on the conductivity. The concentration of Ca in this period is constant and even has a little reduction [28,48]. The slow growth of conductivity is due to the slow increase in pH and concentration of alkali ions to reach a critical supersaturation state of reactants. The w/b has few effects on the duration of this period, which is consistent with its effect on the heat release rate at this period [49]. At the end of this stage, the early hydration products (ettringite, C-S-H and portlandite) connects into a net structure for initial setting and results in the occurrence of stage III. The blending of FA, SL and LL prolongs the time from stage II to III. Because the reactivity of these SCMs is lower than cement, it takes more time to build the sufficient connections between particles.

Although the main conductive ions (OH⁻, Na⁺ and K⁺) have an increase during stage III [28,48], the conductivity of paste reduces due to the structure growth. The increase in w/b induces a longer stage III and this effect is more significant on blended system than OPC. The rapid growth of hydration products brings about the stage IV. The further fast growth of hydration products leads to the fill and blocking of pores in structure. Meanwhile, the consumption of free water reduces the volume of pore solution. These dual effects lead to a dramatic decrease in

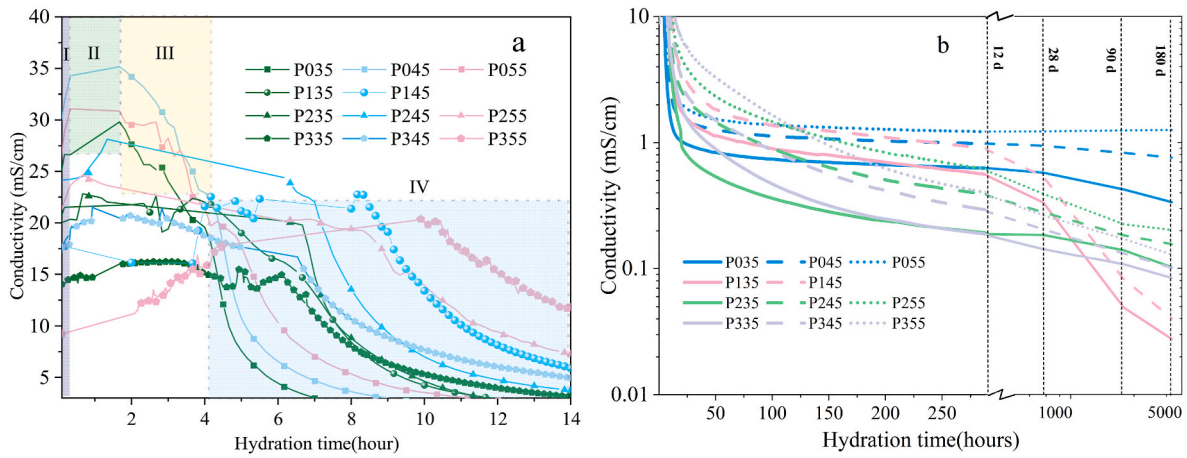


Fig. 4. Electrical conductivity of pastes during hydration: (a) detailed data before 14 h; (b) the measured data up to 180 days.

conductivity. The increase in w/b seems to have few effects on the decreasing rate of conductivity, but SCMs have impact on that rate. Fig. 4b shows that the conductivity of OPC paste falls into a rather stable stage with a very low decreasing rate. The conductivity of FA blended paste has the similar trend with a little higher decreasing rate at the stable stage compared with OPC from 10 h to 12 days. However, it has the most evident decrease from 12 to 180 days due to the pozzolanic hydration of FA. The conductivity of SL blended has a continuous decrease up to 180 days because of its high latent hydraulic reactivity. This trend was also found in many previous works [27,50,51], which confirmed again that the conduction test is an effective way to indicate the reactivity of SCMs.

3.2. Water distribution and hydration degree of pastes

Fig. 5a presents the weight loss of all pastes in different temperature ranges. According to Refs. [52,53], the solvent exchange by IPA starts with the replacement of the pore water, and then the water in small pores (interhydrate and interlayer) moves out under the concentration gradient. Therefore, the weight loss from vacuum dried at 60 °C includes not only the free water in pore solution but also the interlayer water, which is here classified as evaporable water (Epw). A clear tendency can be observed for all pastes, that is, a higher w/b results in a higher content of Epw at any hydration ages. The bound water or nonevaporable water (Nw) denotes the weight loss after the vacuum dried to oven dried at 1000 °C. It should be noted that, apart from dehydrolysis, the decarboxation [6,7,54] and LOI will induce a weight loss between 500 and 1000 °C. The LOI was subtracted in Eqs. (1)–(7). For the pastes with w/b

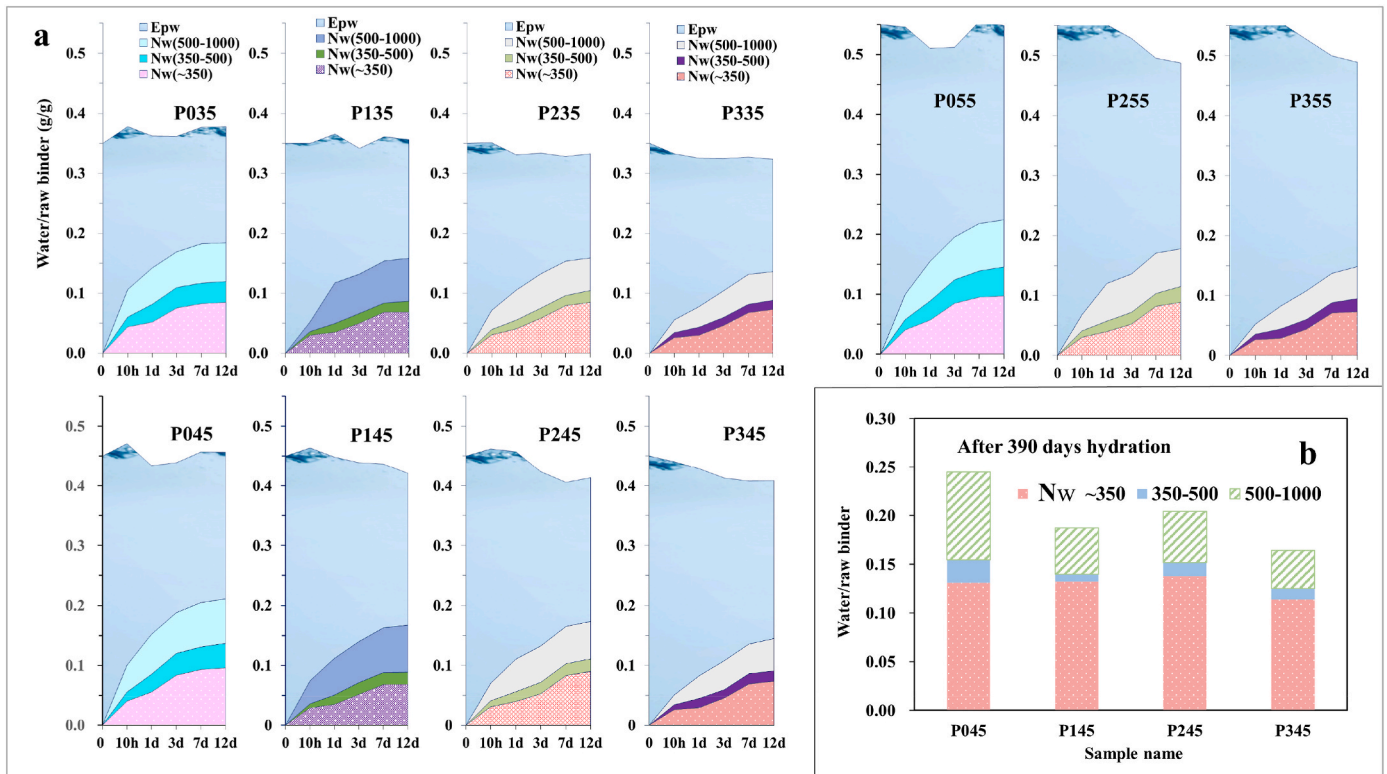


Fig. 5. Water distribution in pastes at different hydration times.

at 0.35 and 0.45, the ratio of final total water to raw binder in Fig. 5a is close to the w/b , so it implies that the carbonation is very weak.

OPC paste with $w/b = 0.35$ shows a slow growth in weight loss between V60 and 500 °C from 3 to 12 days. An increase of w/b to 0.45 and 0.55 augments the Nw of pastes after 1 day at all ranges, which confirms that the water availability is critical for the later age hydration. Nw of FA blended paste keeps rather stable after 7 days. FA blended pastes has a lower weight loss than OPC between V60 and 500 °C because a lower amount of OPC in binder generates less early-precipitated products (gypsum, ettringite, C-S-H, brucite and portlandite etc. [6,55]) whose dehydrolysis occurs up to 500 °C [6]. The blending of SCMs will accelerate the hydration of clinker [56], so Nw of FA pastes between 500 and 1000 °C is not even lower than OPC paste. According to the general results [7], The bound water (V60–950 °C) normalized to OPC increases with the increase in content of FA [57], so FA not only increases the hydration of OPC but also contributes to bound water in pastes by itself. A similar effect is observed in our results especially for water loss between 500 and 1000 °C. The w/b has a weaker effect on the bound water of FA blended than that of OPC paste.

The bound water of SL pastes between V60 and 500 is lower than that of OPC. Similarly, an enhancement effect on bound can be observed if we normalized the bound water to OPC content and this is consistent with Escalante-Garcia's investigation [58]. The weight loss of the SL blended paste is close to that of FA pastes with the same w/b between V60 and 1000 °C, but SL pastes have a higher content of Nw than FA pastes between V60 and 500 from 7 to 12 days. The ternary system with LL has the similar trend in the development of bound water as SL binary pastes. The main influence is that the replacement of LL induces a higher content of Epw than the other binder system.

It is controversial to use the weight loss up to 1000 °C as an index for the hydration degree of cement because it includes the loss of CO₂ and LOI. Nathan and Narayanan [59] proposed a model to distinguish the enhancing effect from SCMs, but they did not take the decarbonation into account. In the R3 method developed by François Avet et al. [60], a good correlation was found between bound water at 110–400 °C and cumulative heat release from calcined clay blended pastes. The authors chose 400 °C as the upper temperature based on the initial decomposition of portlandite. However, the lowest decomposition temperature of

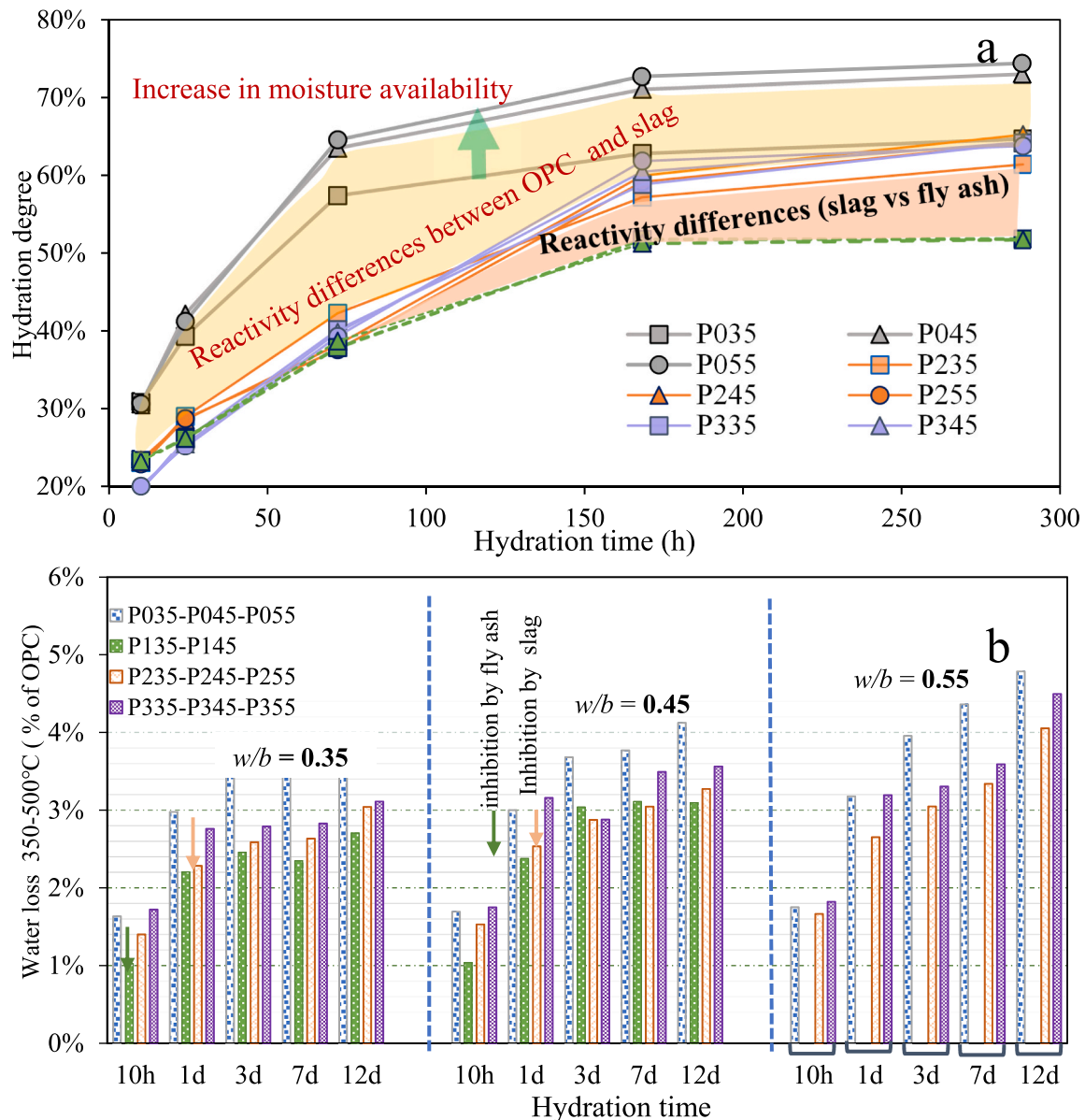


Fig. 6. Hydration degree (a) and the normalized water loss between 350 and 500 °C (dehydrolysis of portlandite) (b) at different hydration times.

portlandite is about 350 °C [61]. Therefore, we used the weight loss between V60 and 350 °C to indicate hydration degree of binders (α):

$$\alpha = \frac{\Delta w_t^{350}}{\Delta w_{390d}^{350}} \quad (9)$$

where Δw_t^{350} is the weight loss between V60 to 350 °C from paste at the corresponding time (t) and Δw_{390d}^{350} is the weight loss in the same range from pastes cured in moisture condition for 390 days.

Fig. 5b shows Nw in the well-hydrated paste (particles with $D < 1$ mm curing under moisture condition for 390 days at 20 °C). The bound water in OPC, FA blended, SL blended, and ternary pastes is 0.245, 0.188, 0.204 and 0.164 g/g binder, respectively. P045, P145 and P245 have the similar content of Nw at V60-350 °C, and P345 has the lowest Nw at this range after 390 days. The differences in reactivity of OPC, FA and SL can be effectively distinguished by the hydration degree evolution (see Fig. 6a). SL and FA show different reactivities evidently after 3 days and the gap increases with hydration time, while the difference between OPC and SL decreases from 3 to 12 days. An increase of w/b from 0.35 to 0.45 enforces a significant enhancement in hydration of OPC after 1 day. w/b has weak effect on the hydration degree of the blended pastes before 12 days. The water loss between 350 and 500 °C was normalized to OPC content and presented in Fig. 6b. This part of water is typically ascribed to the decomposition of portlandite. An increase in w/b facilitates the precipitation of portlandite especially after 3 days. Although FA has a much lower reactivity than SL, it has a greater inhibition on the precipitation of portlandite than SL. Blending of LL increases the portlandite content compared with SL binary pastes. Adu-Amankwah et al. [62] reported the same effect from LL on content of portlandite, and they claimed that it was because a less calcium is needed to form the calcium-rich AFm phases as more Al is bound in the C-S-H of LL ternary paste.

3.3. Electrical conductivity of pore solution

Pore solution is the main conductive component in the paste and the ionic conductivity of solution depends on species of ions and the concentration of them. The concentration of the highly soluble alkalis can be calculated with the evaporable water content from the last section. The volume of Epw (V_{epw}) can be calculated as:

$$V_{epw} = \frac{m_{epw}}{\rho_{epw}} = m_b \times \varphi_{epw} \quad (10)$$

where m_{epw} (g) is the mass of Epw, ρ_{epw} is the density of water (1 g/cm³) and m_b is the mass of binder in paste.

The concentration of K^+ and Na^+ in pore solution can be calculated by Eq. (11), based on two assumptions: firstly, the alkalis are dissolved completely within the first few minutes after water mixing; secondly, the solvent exchanged water including interlayer water is classified as conductive “pore solution”. The latter assumption is reasonable because Lothenbach and Nonat [61] proposed that part of alkalis absorbed in the interlayer space.

$$C_i = \frac{m_b \times \delta_{ic}}{V_{epw}} = \frac{\delta_{ic}}{\varphi_{epw}} \quad (11)$$

where C_i denotes the concentration of alkalis, i represents K^+ or Na^+ , and δ_{ic} is the mole concentration of chemical composition in binder as presented in Table 1. For the SL blended paste, we use the effective mole concentration ($\delta_{iblanded}$) and it needs to be modified by Eq. (12) [63], because the alkalis in SL is not as soluble as those in OPC.

$$\delta_{iblanded} = \left(1 - 1.8 \times \left(\frac{m_s}{m_b}\right)^2\right) * \left(\delta_{is} \times \frac{m_s}{m_b} + \delta_{ic} \times \frac{m_c}{m_b}\right) \quad (12)$$

where m_s and m_c represents the weight of SCMs and cement in paste,

respectively. δ_{is} is the mole concentration of alkalis in SCMs. K_2O and Na_2O in FA are hardly soluble during the early hydration, so the contribution of alkalis from FA is negligible ($m_s = 0$). In addition to K^+ and Na^+ , the high conductive ions in pore solution comprise OH^- , Ca^{2+} , SO_4^{2-} and Cl^- . The concentration of sulfate can be roughly approximated by Eq. (13) according to Ref. [64] where the value of α is 0.06 L/mol. Because of the low content of Cl in binder (see Table 1), its concentration in pore solution is negligible. The Ca^{2+} concentration was assumed to be constant as 25 mmol/L which is close to the typical saturated value during early hydration [28]. OH^- concentration was then calculated from charge balance by Eq. (14):

$$c_{SO_4^{2-}} \approx \alpha(c_{K^+} + c_{Na^+})^2 \quad (13)$$

$$c_{OH^-} = c_{K^+} + c_{Na^+} + 2c_{Ca^{2+}} - 2c_{SO_4^{2-}} \quad (14)$$

The electrolyte conductivity of pore solution (σ_{ps}) can be expressed as a sum of molar conductivity of each ion species (i) [65]:

$$\sigma_{ps} = \sum_i z_i \lambda_i c_i \quad (15)$$

where z_i and c_i are the valence and molarity of “i” species, respectively. λ_i is the equivalent conductivity that is related to the ionic strength (I_M) and conductivity coefficients (G_i) for the high concentration of ions in pore solution as [33]:

$$\lambda_i = \frac{\lambda_i^0}{1 + G_i \times I_M^{1/2}} \quad (16)$$

λ_i^0 is the equivalent conductivity of ionic species at infinite dilution. This value for the relevant ions at 20 °C was obtained from the literature [66] by interpolation. G_i of specific ions refers to the value in Ref. [33]. The I_M has the following definition:

$$I_M = \frac{1}{2} \sum_i z_i^2 c_i \quad (17)$$

Electrical conductivity of pore solution was calculated by Eq.(10)–(17) based on the chemical composition in Table 1 and Epw content at corresponding hydration time (in Fig. 5). By substituting the concentration of ions in the squeezed pore solution from Refs. [29,67] into Eq. (15)–(17), we calculated conductivity of pore solution of corresponding mix from literatures. The evolution of conductivity was fitted by Hill function, and the optimized parameters and function expressions are presented in Table 3.

Fig. 7a shows the calculated conductivity and fitted line of 11 samples. Electrical conductivity of pore solution decreases as the increase in w/b because a higher w/b introduces more evaporable water into paste to lower concentration of alkali ions. Blending of SCMs lowers the conductivity of pore solution, and this is consistent with the data calculated based on the squeezed pore solution in published papers (see Fig. 7b). Shi [68] also found that the blending of SCMs would reduce the conductivity of pore solution. Although the FA used in Ref. [67] has a high alkali content (3.9% K_2O and 0.9% Na_2O), the concentrations of K^+ , Na^+ and OH^- in the FA blended pastes are similar with that in pastes with an identical replacement of quartz. This confirms our assumption that alkalis in FA are hardly dissolvable. The measured conductivity before 2 h (see Fig. 4) is lower than the calculated conductivity of pore solution at early ages because the presence of cement particles breaks the connectivity of pore solution. The chemical composition of OPC in this study is highly similar to that of OPC used in Ref. [67], so the calculated conductivity evolution of P055, based on chemical composition and Epw, is close to that of OPC with $w/b = 0.5$ from the squeezed pore solution (see light blue hexagon in Fig. 7a and dashed line sphere in Fig. 7b from 4 to 288 h. The main contribution to the conductivity of pore solution comes from the OH^- which accounts for around 70% (see Fig. 7b). Electrical conductivity of pore solution keeps almost constant until it has a sharp increase after about 6 h. The fitted lines in Fig. 7a

Table 3

The fitting results of pore solution conductivity depending on time by Hill function.

Sample	Expression ($\sigma_{ps}(t)$)	End value(mS/cm)	R ²
P035	$\sigma_{ps} = 95.6 + (165.9 - 95.6) \times \tau^{1.86} / (\tau^{1.86} + 144.4)$	165.9	0.998
P045	$\sigma_{ps} = 76.9 + (131.3 - 76.9) \times \tau^{2.25} / (\tau^{2.25} + 512.0)$	131.3	0.998
P055	$\sigma_{ps} = 65.2 + (102.9 - 65.2) \times \tau^{2.38} / (\tau^{2.38} + 503.0)$	102.9	0.987
P135	$\sigma_{ps} = 63.1 + (104.4 - 63.1) \times \tau^{1.5} / (\tau^{1.5} + 108.8)$	104.4	0.996
P145	$\sigma_{ps} = 51.6 + (96.0 - 51.6) \times \tau^{0.75} / (\tau^{0.75} + 27.0)$	96.0	0.995
P235	$\sigma_{ps} = 75.2 + (149.6 - 75.2) \times \tau^{0.96} / (\tau^{0.96} + 31.4)$	149.6	0.990
P245	$\sigma_{ps} = 61.7 + (114.5 - 61.7) \times \tau^{1.13} / (\tau^{1.13} + 116.9)$	114.5	0.992
P255	$\sigma_{ps} = 52.4 + (111.6 - 52.4) \times \tau^{0.75} / (\tau^{0.75} + 60.3)$	111.6	0.96
P335	$\sigma_{ps} = 61.4 + (133.3 - 61.4) \times \tau^{0.60} / (\tau^{0.60} + 16.7)$	133.3	0.998
P345	$\sigma_{ps} = 50.6 + (86.9 - 50.6) \times \tau^{0.88} / (\tau^{0.88} + 35.8)$	86.9	0.995
P355	$\sigma_{ps} = 43.8 + (78.0 - 43.8) \times \tau^{0.86} / (\tau^{0.86} + 84.9)$	78.0	0.994

show the same trend as the evolution of value calculated from the squeezed pore solution in Fig. 7b. These suggest that Eq. (10)–(17) can effectively quantify the specific conductivity of pore solution with no need for extracting the solution from paste and the further test evolving with any expensive equipment (ICP-OES, IC, AAS [28]).

3.4. Real-time evolution of microstructure

3.4.1. Real-time formation factor

The formation factor (F) was initially defined by Archie [69] as a fundamental property to relate the resistivity of sandstone with its permeability or porosity. Because the hardened cement-based materials has the similar porous nature as sandstone, F is widely used in pastes or concrete by the definition with Eq. (18) [70,71]:

$$F = \frac{R_p(t)}{R_{ps}(t)} = \frac{\sigma_{ps}(t)}{\sigma_p(t)} \quad (18)$$

where $R_p(t)$ and $\sigma_p(t)$ is the resistivity and conductivity of the saturated cement-based materials, respectively. $R_{ps}(t)$ and $\sigma_{ps}(t)$ is the resistivity and conductivity of bulk pore solution respectively. t is the curing age.

Fig. 8 presents the evolution of F in pastes up to 180 days. F initially

keeps near constant for a certain time (~ 2 –9 h), and the duration of this period varies due to the blending of SCMs and different w/b (see Fig. 8a). The initial F are larger than 1 and it generally decreases with the increase of w/b . It is followed with a sharply increasing stage after the constant period. The similar declining point was found in the ultrasound test due to the percolation of solid at the setting time [1,72]. The effect of w/b on the F is magnified by the hydration in the fast growth period. The ratio of F in pastes with $w/b = 0.35$ to pastes with $w/b = 0.45$ is 1.90, 2.57, 3.90 and 2.05 for OPC, FA, SL and ternary system, respectively. F of P035 and P045 keep increasing with a slow rate from 12 to 180 days, but that of P055 shows an interesting decrease from 28 to 180 days. The FA blended pastes have the highest increase in F compared with other pastes from 12 to 180 days so that they have the highest value at 180 days among pastes with the same w/b . F of the SL blended pastes shows an evident increase after 12 days, but its growth rate is much lower than the FA pastes. The differences in F of SL binary pastes and ternary pastes with the same w/b is negligible after 28 days.

Fig. 8b illustrates the comparison of F of pastes with $w/b = 0.35$. OPC paste has the highest F at early age, but F of SL blended paste exceeds that of OPC after 36 h. LL reduces the growth rate of F in the first 36 h, but F of ternary pastes climbs up to exceed that of OPC at 110 h. The P135 has the lowest F because of the low reactivity of FA at early age. With an increase of w/b to 0.45, the difference between OPC and SL blended paste is magnified in the first 24 h. F of P245 and P345 exceeds that of P045 at 110 and 140 h respectively, which is much longer than this time for paste with w/b of 0.35 (36 and 110 h, respectively). An increment of w/b to 0.55, furthermore, intensifies the inhibition effect of SL and LL on the growth rate of F in the first 24 h. P255 and P355 exceed the P055 at the same time of 175 h.

F also relates to the ion diffusivity and pore connectivity as this equation [70,73]:

$$F = \frac{1}{\Phi\beta} \quad (19)$$

Φ is the porosity and β is the index of pore connectivity. Herein, the water porosity was used to calculate the pore solution connectivity, and it is defined as:

$$\Phi_e = \frac{V_{epw}}{V_p} = \frac{m_1 - m_e}{m_1 - m_0 - m_v} \quad (20)$$

V_p is the volume of the hardened paste. With the data of water distribution (Fig. 5) and F , the pore solution connectivity (β) was calculated (see Fig. 8c–d). An increment in w/b increases this value in pastes. As hydration proceeds, the β decreases dramatically from water addition to 24 h. Although the volume of Epw in SL blended systems (see Fig. 5 P235/245, P335/P345) is higher than that in OPC pastes with identical w/b , β of the SL blended pastes is lower than OPC. This results in a higher

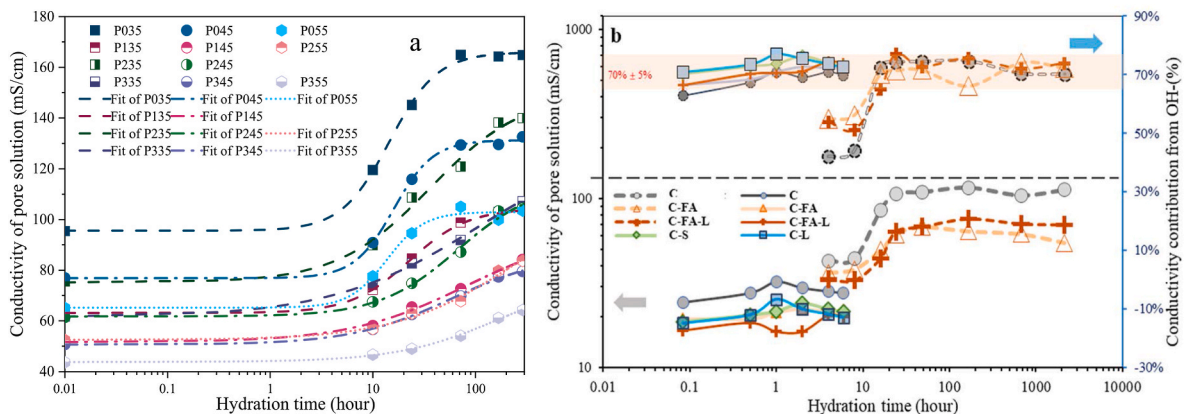


Fig. 7. Calculated conductivity of pore solution. (a)- the values in this paper. (b)- the conductivity value calculated based on the tested concentration of squeezed pore solution from literatures (solid line from Ref. [29] with $w/b = 0.75$, dash line from Ref. [67] with $w/b = 0.5$, C: OPC; FA: FA; S: SL; L: LL).

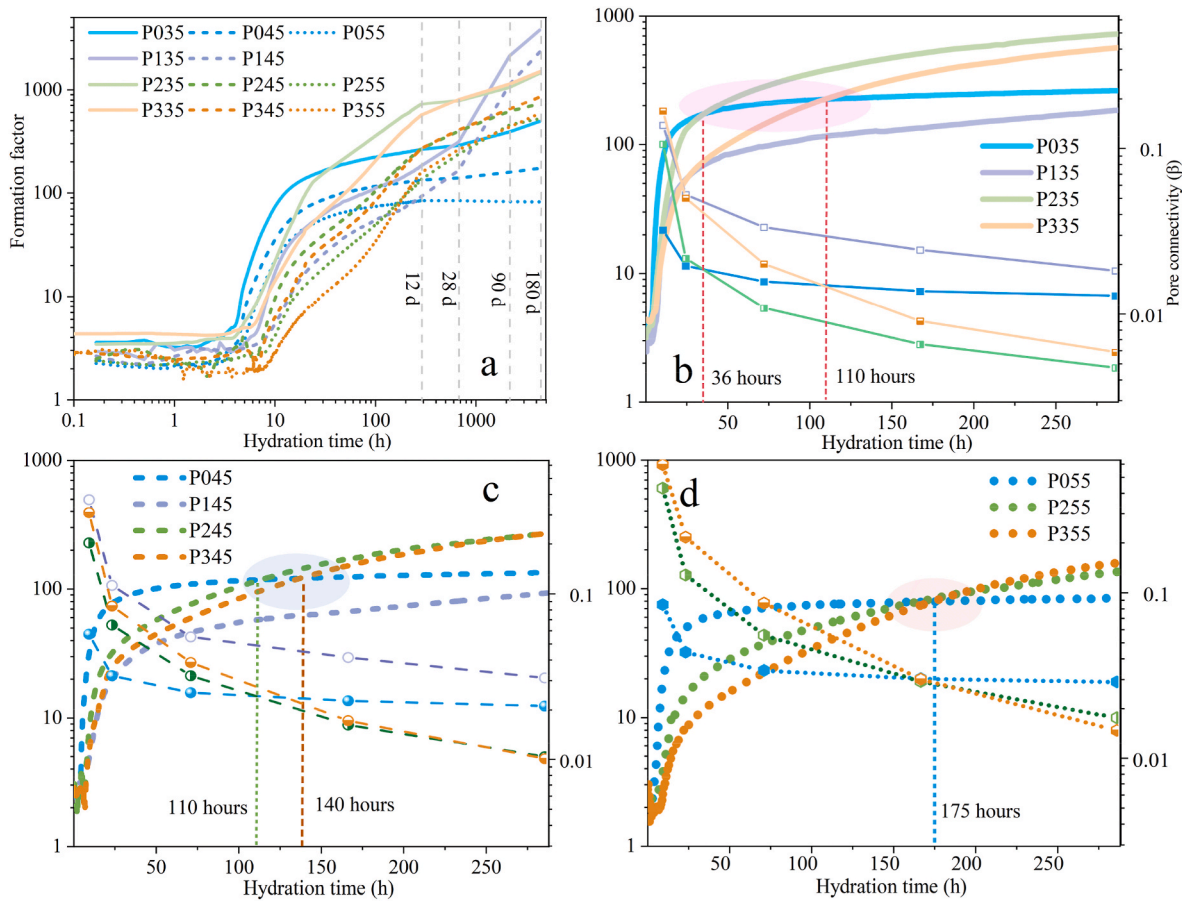


Fig. 8. Evolution of formation factor and pore solution connectivity with hydration time.

F of SL blended paste. It implies that the differences in F between various binder systems mainly derive from discrepancies in β .

3.4.2. Average growth rate of F

For a further detail analysis of the growth rate of formation factor, the average growth rate of F ($a-F$) is defined as:

$$a-F = \frac{F(t)}{t} \quad (21)$$

where $F(t)$ is the F at hydration time t . The $a-F$ of pastes is presented in Fig. 9. The shape of $a-F$ curve is similar with the typical shape of heat release rate curve. By referring to the category based on the heat release [43], the evolution of $a-F$ of OPC paste can be classified into three periods as well. It includes “to the end of low-rate period” (period I), “accelerate period” (period II) and “deceleration period” (period III). For the blended paste, one more peak occurs after the main peak and it belongs to the fourth period (period IV).

Period I: $a-F$ has a sharp decrease in the beginning. It reaches the lowest value that keeps almost constant for a period. The hydration of OPC in this period involves the dissolution of minerals, the precipitation of ettringite and nucleation of C–S–H [74]. However, these reactions have few effects on the volume and connectivity pore solution, so F is almost constant at this period (see Fig. 8a). Dividing F with time gets a sharp decline in $a-F$. The continuous precipitation of ettringite and C–S–H gradually strengthens the connectivity between particles. This reduces the connectivity of pore solution, so the F may have a slow linear-like growth leading to a constant $a-F$. An increase in w/b increases the duration of period I and decreases $a-F$ at the end of this period. Blending of SCMs reduces $a-F$ and prolongs this period. We define the inflection point of $a-F$ as the end of period I (see dash line in Fig. 9c and

d), the duration of period I was presented in Table 4.

Period II: $a-F$ has a sharp increase in this period. The hydration goes into period with a rapid growth of hydration products (ettringite, C–S–H and portlandite [74,75]) after the low $a-F$ period. It increases the connectivity between the solid particles to block the connection of pore solution. Meanwhile, the water transfer from free water to chemically bound to reduce the content of Epw, thus also decreasing the connectivity of pore solution. $a-F$ is an effective index for demonstrating the hydration reactivity of binders with the same w/b . Fig. 9 a and b show that OPC has the highest $a-F$ in period II due to its higher reactivity compared with SCMs (FA, SL and LL). Although the hydration degree of FA and SL blended paste has few differences in the first 24 h (Fig. 6a), $a-F$ of SL blended is much higher than FA. It implies that the interaction and links between the unhydrated particles is not only controlled by the precipitation of products on surface but also double layers structure between solid and pore solution. The dissolution of FA is typically lower than SL [76], so there is fewer specifically absorbed anions (K^+ , Na^+ or Ca^{2+}) and secondary water [77] on FA surface than SL. Moreover, the absolute zeta potential of FA is much higher than SL and cement in $Ca(OH)_2$ solution [77], so it means that the stable distance between the FA and other particles are larger than that of SL and other particles. This weakens the connection between solids to bring a higher connectivity of pore solution.

Period III: $a-F$ shows a decreasing trend after the period II, and this is due to a reduction in the growth rate of hydration products as well as the water consuming rate. The main peak of $a-F$ of OPC pastes is at 12.6, 14 and 14 h for w/b of 0.35, 0.45 and 0.55, respectively (see Fig. 9a and b), which is close to the main peak of heat release rate (12–14 h for OPC [43]) form OPC pastes. The blending of SCMs delays the main peak to 16–20 h and this interval is also close to the time for the main peak of

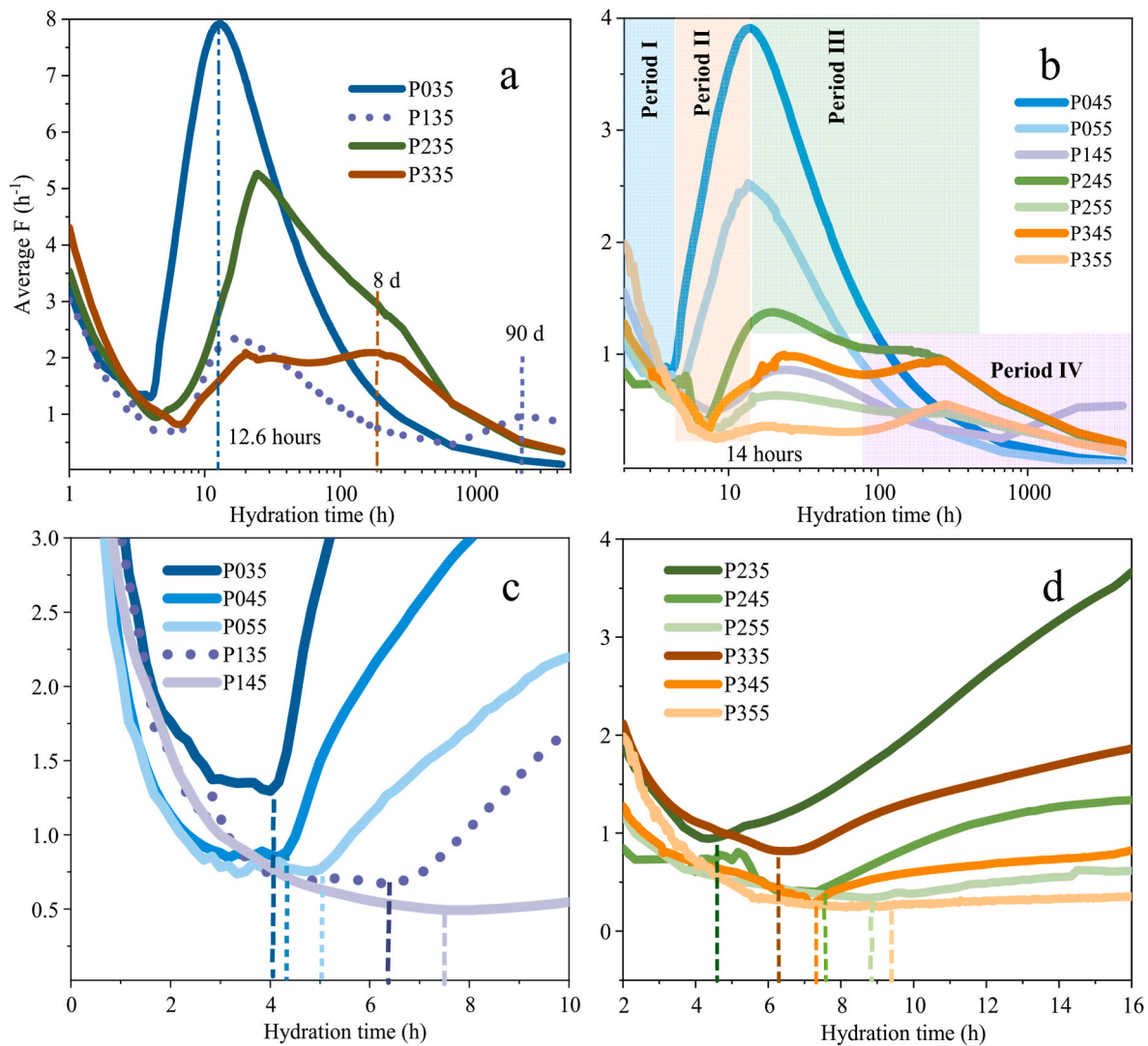


Fig. 9. Evolution of $a-F$ of pastes with hydration time.

Table 4
Setting time and inflection points of $a-F$ from fresh pastes.

Sample	Time/h		
	Initial setting	Final setting	Inflection point of $a-F$
P035	2.82	4.37	4.07
P045	3.62	5.02	4.38
P055	4.14	6.80	5.04
P135	4.06	6.65	6.35
P145	4.85	7.17	7.30
P235	2.99	5.72	4.60
P245	4.20	7.92	7.50
P255	4.49	9.50	8.80
P335	3.08	6.12	6.25
P345	4.13	7.97	7.33
P355	5.82	10.23	9.30

heat release in OPC with SL and FA [78]. An increase in w/b has minor influences on the main peak position especially from 0.45 to 0.55. SCMs decrease the declining rate of $a-F$ and they even induce one more peak. Interestingly, the inhibiting effect on the precipitation of portlandite from FA is higher than that from SL (Fig. 6b), but the $a-F$ of FA paste is much lower than that for SL pastes. This may be owing to the phenomenon that FA absorbs Ca^{2+} on its surface during the dissolution process [50,79,80], and these Ca ions would not necessarily precipitates

as portlandite or C-S-H.

Period IV: This period corresponds to one new peak during the deceleration of $a-F$. Because the latent hydraulic reactivity has been activated after 3 days, the reaction of SL induces a further breaking of the pore connectivity, namely refining the pore size. This latent hydraulic reactivity can be observed from the increment in the differences between the normalized portlandite content in OPC and SL blended paste (see Fig. 6b). The time for the second peak of $a-F$ in P235, P245 and P255 is about 8–12 days, and this period corresponds to a quick increase in the reaction degree of SL according to Ref. [80]. The reaction of FA is normally activated much later than 10 days [7,80], so the second peak of FA blended pastes occur at about 90 days in this study. An increase in w/b seems to delay the occurrence of this peak.

3.4.3. Setting time

Fig. 10 shows the penetration depth in fresh pastes tested by the Vicat needle. The initial and final setting time were determined referring to ASTM C191-08 standard and the results are presented in Table 4. An increase in w/b prolongs both the initial and final setting time. This delaying effect is more evident on final setting than initial setting. Penetration depth of ternary pastes fluctuate under all w/b conditions (Fig. 10a). The blending of SCMs inhibits the decreasing rate of the penetration depth (see Fig. 10b–d), and FA has the strongest inhibiting effect. Lootens et al. [81] found the analytical correlation between the

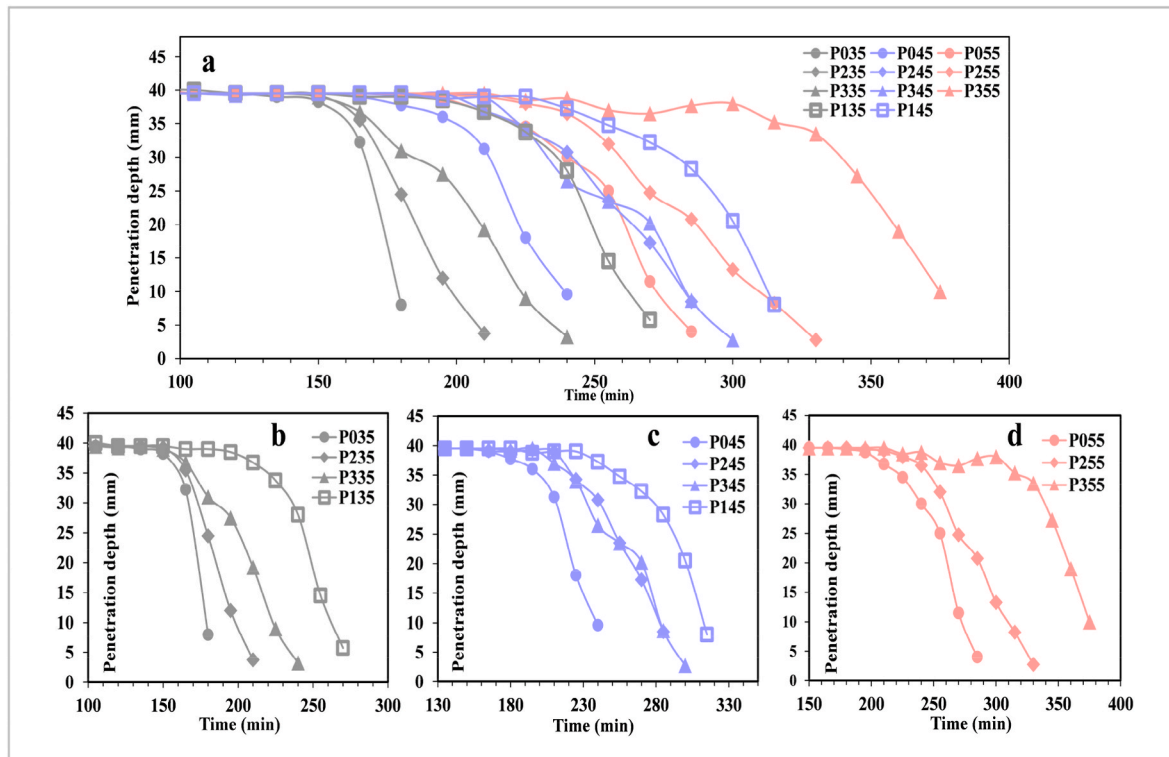


Fig. 10. Penetration depth of Vicat needle in pastes at different hydration times.

penetration depth and yield stress of materials. A penetration depth of 25 mm from a needle used in ASTM C191-08 can be associated to a yield stress of order 40 kPa. The spherical shape of FA mitigates the inter-particle surface friction [82]. Moreover, the higher absolute zeta potential of FA leads to a larger distance between particles compared to SL. Therefore, FA paste needs a longer time to gain the enough density of hydration products to reach the yield stress for setting than SL blended paste. The dilution effect from SL also induces pastes to take a longer time to gain the critical yield stress for the initial setting than the plain pastes. Table 4 illustrates that both initial and final setting have a positive correlation with inflection point of α -F. It will be further detailed in the discussion part.

3.4.4. Time-dependency of chloride migration coefficient and F

The proper evaluation of chloride migration coefficient is important for service life modelling. Chloride migration coefficient is a time-dependent parameter that decreases with the curing time following an empirical power function [83–86], owing to the continuous hydration of binder. Table 5 shows the chloride migration coefficient of pastes tested by rapid chloride migration (D_{RCM}) at different curing time. D_{RCM} of pastes show an unsurprising decrease with the curing time except for P055. D_{RCM} increases with the increase in w/b , but the w/b has a weak influence on D_{RCM} of SL binary paste at 180 days. The blending of SCMs decreases the chloride migration in pastes, and this effect is more evident in pastes with longer hydration time and higher w/b . D_{RCM} of P055 shows an interesting increase with hydration time after 28 days.

The similar deviation was detected in some previous investigations [84, 85] as well. OPC based concrete might have a higher chloride migration coefficient at later age when the w/b is rather high (>0.5).

Eq. (19) indicates that the inverse of F ($1/F$) correlates to the pore connectivity and porosity, so the evolution of $1/F$ was used to compare with D_{RCM} . Fig. 11a shows that a minor increase in the $1/F$ can also be observed in P055 after from 28 to 90 days. This implies the increase in D_{RCM} is due to the changes of structure in hardened pastes. The dependency of D_{RCM} on time is similar with the dependency of $1/F$ on time in OPC and FA blended pastes (see Fig. 11 a and b). The effect from w/b on the D_{RCM} is close to its effect on $1/F$ in these two binder systems. Both the D_{RCM} and $1/F$ in the slag blended pastes show a declining trend with the increase in curing time, but the decreasing rate of D_{RCM} is much higher than that of $1/F$ especially for pastes with w/b of 0.35 and 0.45. Because the $1/F$ is measured from pastes under the sealed curing, the hydration rate of pastes with w/b of 0.35 and 0.45 is limited due to the lack of liquid water at later age, thus leading to the slow decrease of $1/F$ after 90 days. However, D_{RCM} was tested from samples under the water curing so the later-age hydration is higher than the sealed samples. This causes a higher decrease in D_{RCM} of the water curing samples than that in $1/F$ of the sealed curing samples (see Fig. 11 c and d).

Table 5

The D_{RCM} of pastes cured to 28, 90 and 180 days.

Time/days	Chloride migration coefficient ($\times 10^{-12} \text{ m}^2/\text{s}$)										
	P035	P045	P055	P135	P145	P235	P245	P255	P335	P345	P355
28	8.02	15.56	21.08	8.90	11.35	5.12	5.82	7.29	5.79	5.39	6.40
90	5.84	11.67	26.28	2.27	3.67	3.17	3.85	4.52	2.70	3.64	3.81
180	3.52	10.46	26.15	0.84	1.51	2.50	2.60	2.91	1.76	1.94	3.71

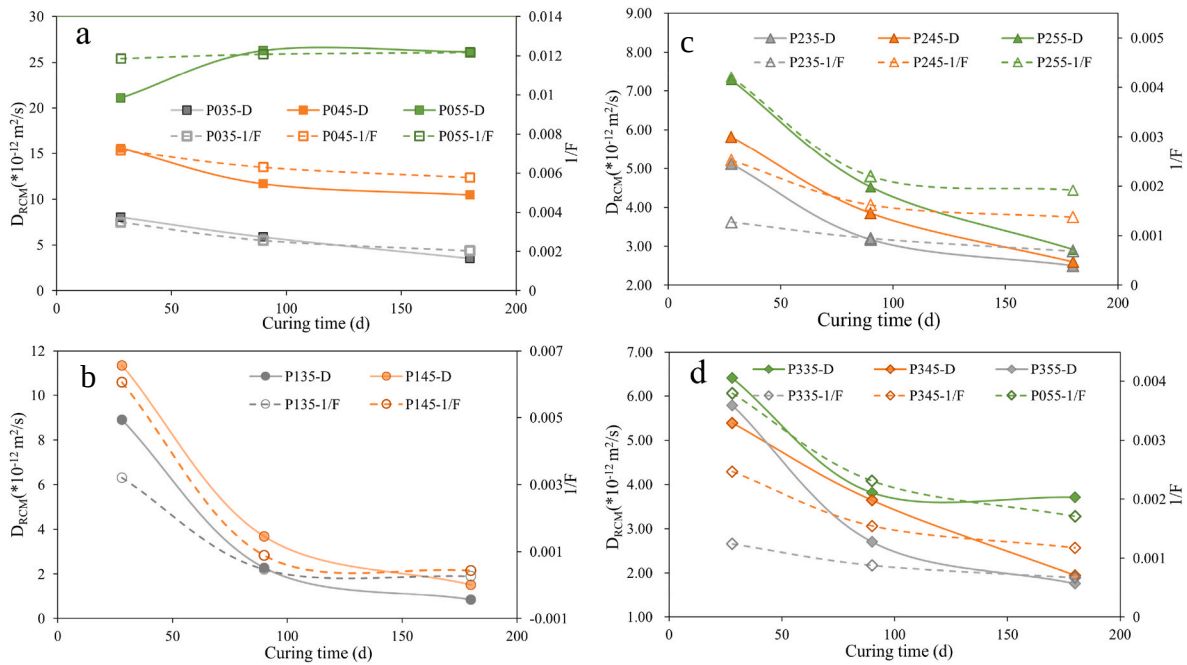


Fig. 11. The evolution of chloride migration coefficient (solid scatters) and inverse of F (the hollow scatters) with hydration time: a- OPC pastes; b- The FA blended pastes; c- The slag blended pastes; d- The ternary pastes.

4. Discussion

4.1. Correlation between setting time and formation factor

The setting of cement-based materials has been indicated by many test methods [87], and the change of electrical properties is one of the major index [88]. It can be observed that the decreasing rate of penetration correlates to the growth rate of F with the comparison between Figs. 9 and 10. The inflection time of $a-F$ is positively related to the setting time as shown in Table 4. Setting of cement paste is generally understood as a percolation process in which intersection of hydration products on particles surface leads to the formation of clusters, and which eventually join into a continuous elastic network [1]. In OPC with normal aluminates content, the setting of cement is mainly controlled by a formation of sufficient C-S-H on particles surface [89,90]. The increasing precipitation of C-S-H from period I to II (in Fig. 9) results in the percolation of the links built by the overlapping of C-S-H on the surfaces of particles.

Many previous researches [91–93] noticed a reduction of conductivity of paste during setting, however, lack of building any mathematic relation between electrical properties and setting time. The $a-F$ in this paper represents the structure building rate, so the change of it is effective to indicate the setting of pastes. Fig. 12 shows that the inflection point of $a-F$ has a good linear correlation with the final setting time regardless of types of binder or w/b . The linear correlation is not so general between the inflection point and initial setting time for all pastes, but the correlation is good in pastes within the same binder system (Fig. 12 arrow line). This may be due to the differences in particles size distribution (or surface nature of the particles in solution) between cement and SCMs. Moreover, it should also be noted that in the standard test (ASTM C191-08, Vicat) the points for initial setting are arbitrary chosen. Generally, the change of $a-F$ during hydration is a good index for setting of pastes.

4.2. Percolation theory understanding the relation between Ep_w and formation factor

Water plays a critical role during the hydration process. It works not

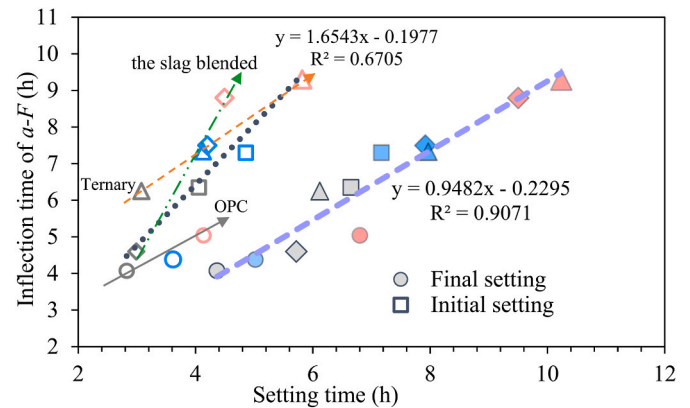


Fig. 12. Correlations between setting time and inflection point of $a-F$. OPC, FA blended, SL blended and ternary paste are presented with circle, square, rhombus and triangle respectively. The grey, blue and rose color correspond to w/b of 0.35, 0.45 and 0.55 respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

only as a “porter” to carry the ions out of raw minerals into solution but also as a key component to build the chemical structure of hydration products. Pore solution is also the main basis of current transmitting through the cement-based materials. The electrical conductivity of paste is affected by many intrinsic factors during hydration as shown in Fig. 1. To simplify the system at the specific hydration degree, the composition in pastes can be classified into two main phases: the insulative (dry solid) and conductive component (liquid solutions). Archie [69] found a power function relation between the volume percentage of conductive saline (Φ) and the formation factor F of gas sand, and it was further stated as the general form [94]:

$$\frac{\sigma_p}{\sigma_{ps}} = 1 / F = a^* \phi^n \quad (22)$$

where a is non-uniform constant, n is the shape factor. After an extension

of the percolation theory of networks to the continuum cases [95,96], the conductivity shows a general relation as a formula similar to Archies' law:

$$\sigma_p = a * \sigma_{ps} * (\varphi - \varphi_c)^m \quad (23)$$

After the substitution of conductivity with F , we get:

$$F = 1 / a * (\varphi - \varphi_c)^{-m} \quad (24)$$

herein, we assume that the conductive component includes the ions in the pore water and the layer water, hence φ is the volume of Epw (φ_e). φ_c is the critical value for the percolation of conductive component. m is the shape factor as in Archies' law and a is a constant. Fig. 13 demonstrates the raw data and the regressed curve, and Table 6 shows the optimum parameters. F correlates perfectly with Epw through the general percolation theory with respect to different binder type (see Fig. 13a and R^2 in Table 6).

Binder types have impact on the shape factor and threshold for percolation, so a general fitting with all binder types is not so good with $R^2 = 0.74$. The single-shaped particle system has a lower shape factor than the system with a complex shape mixing, such as the sand and chalk with a value of 1.6 but the calcium montmorillonite with 3.28 [94]. FA has a uniform spherical shape, so it will reduce the shape complexity of binder particles resulting in the lowest shape factor ($m = 1.52$). LL has the granular shape like sand so that it reduces the shape factor. Comparing to OPC, the higher m value in the SL blended paste indicates that SL binder system has a more complex shape combination than the others.

The values of percolation threshold for solution in OPC, FA, SL and ternary blended pastes are 0.157, 0.242, 0.223 and 0.256, respectively. This means that plain OPC paste needs the lowest volume of solution to have a percolation, which in turn implies that it has the highest pore connectivity compared to the blended system. Gui et al. [39] found that FA and SL refined the pore structure to decrease the pore connectivity in pastes, thus reducing the gas permeability. The refinement effect from SL and FA also increase the chloride resistivity (see Table 5 and in Refs. [96,97]). According to lattice model for percolation [98], the site threshold values for face centered cubic and body centered cubic is 0.198 and 0.245 respectively. Therefore, it implies that the blending of SL and FA may refine the pores spatial packing state, which is worthy of consideration for the future modelling.

4.3. The relationship between D_{RCM} and electrical properties

The relationship between electrical properties and chloride migration coefficient were discussed in some previous publications [40,99,

Table 6
The regressed parameters based on Eq. 24

Sample	Expression	a	φ_c	m	R^2
P0	$F = 1/0.246 \times (\varphi_e - 0.157)^{-2.11}$	0.246	0.157	2.11	0.98
P1	$F = 1/0.498 \times (\varphi_e - 0.242)^{-1.52}$	0.498	0.242	1.52	0.93
P2	$F = 1/0.806 \times (\varphi_e - 0.223)^{-2.35}$	0.806	0.223	2.35	0.99
P3	$F = 1/0.578 \times (\varphi_e - 0.256)^{-1.82}$	0.578	0.256	1.82	0.97
PA	$F = 1/0.129 \times (\varphi_e - 0.279)^{-0.98}$	0.129	0.279	0.98	0.74

100]. Tong and Gjörv [99] empirically found a quadratic relation between the electrical conductivity and chloride migration coefficient. However, some investigations [40,100] also reported a linear correlation between these two parameters. Theoretically, the diffusivity of ions in the porous materials correlates to F and electrical conductivity as Eq. (25) [70,73]. D_p and D_{ps} are the diffusivity of the ions in paste and bulk pore solution, respectively.

$$D_p = \frac{D_{ps}\sigma_p}{\sigma_{ps}} = \frac{D_{ps}}{F} \quad (25)$$

Fig. 14 presents the correlations between the electrical properties and D_{RCM} in this study. It shows a linear relationship between the electrical conductivity and D_{RCM} in pastes. A better linear correlation is detected between D_{RCM} and $1/F$ with a $R^2 = 0.98$ in Fig. 14b compared with $R^2 = 0.96$ in Fig. 14a. The difference value between the regressed and the measured D_{RCM} is presented in Fig. 14c. It shows that the residual in regression based on $1/F$ is apparently smaller than that in the regression based on electrical conductivity. The correlation between the D_{RCM} and σ_p is not quite linear because of the effect from conductivity of pore solution as presented in Eq. (25). Moreover, the conductivity of pore solution is largely influenced by the saturation degree according [101] and as shown in Fig. 7. The chloride migration is mainly controlled by pore structure instead of concentration of pore solution. The slope of the regression line between the D_{RCM} and $1/F$ is $2.037 \times 10^{-9} \text{ m}^2/\text{s}$, and this value is very close to the coefficient of chloride migration in the dilute solution ($2.03 \times 10^{-9} \text{ m}^2/\text{s}$ [102]). Therefore, the real-time monitored electrical properties are effective to indicate the chloride migration coefficient in hardened cement pastes especially based on the $1/F$. This parameter can be used to calculate the chloride migration coefficient in pastes, including the effect from the SCMs and hydration time (see Figs. 11 and 14).

5. Conclusions

A simple conductivity test setup was designed for a real-time monitoring of the hydration and microstructure evolution of pastes with various w/b and binder systems. It can be used as an in-situ test and even

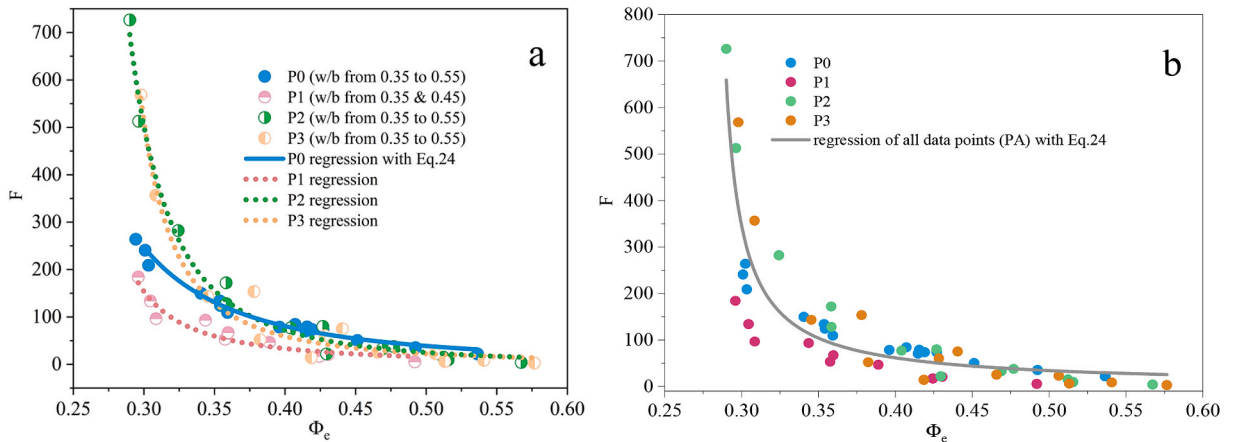


Fig. 13. Relationship between the Epw and F . P0, P1, P2 and P3 correspond to OPC, FA, SL and ternary blended pastes, respectively. a-data with respect to binder type; b-the regression result regardless of binder type.

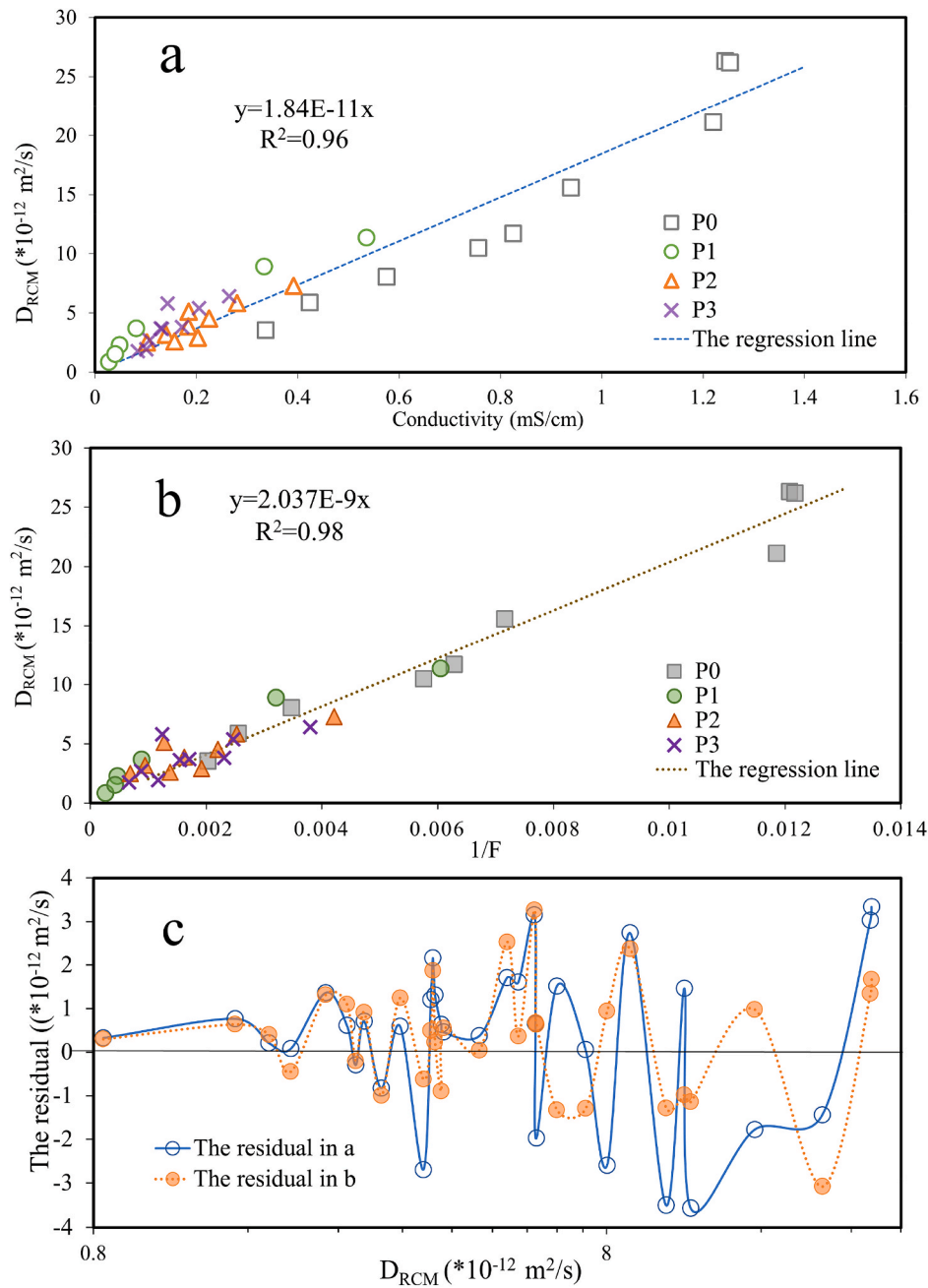


Fig. 14. The regression of chloride migration coefficient and electrical properties in pastes: a- Conductivity and D_{RCM} ; b- D_{RCM} and $1/F$; c-the differences between the regression line and measured data.

for the on-site monitoring in large scale. The distribution of E_{pw} and N_w can be easily determined with the procedure proposed in this paper. Water content from the developed procedure gives data for calculating the conductivity of pore solution based on the chemical composition of binders, without any needs for squeezing the pore solution out of the paste. With the measured conductivity of paste and calculated conductivity of pore solution, the real-time F and $a-F$ was defined for a deep analysis of hydration process and pore structure.

The evolution of conductivity closely relates to the chemical reaction process. The differences in F of pastes with various binders are mainly derived from the pore connectivity. $a-F$ is an effective index for indicating the structure development rate in pastes. The shape of $a-F$ curve is similar with that of heat release, so it contains a first peak, a main peak and the later stable period in OPC pastes. Another peak shows in the hydration of paste blended with SL and FA due to the latent hydraulic

reaction of SL and pozzolanic reaction of FA. The evolution of $a-F$ in the blended pastes was correspondingly classified into four periods. The rapid growth of C-S-H induces an inflection point of $a-F$ from period I into II, which can perfectly indicate the final setting time.

The w/b impacts the electrical conductivity, F , and $a-F$ of pastes. An increase in w/b lowers the alkali concentration in pore solution, leading to a lower electrical conductivity. However, it increases the connectivity of pore solution to reduce F . An increment in w/b also reduces $a-F$ of pastes, and the $a-F$ can effectively indicate the reactivity of different binders under the same w/b condition. Dilution effects from SCMs reduce the initial conductivity of paste mainly due to the lower alkali concentration in pore solution. SL has a weaker reduction in the conductivity of pore solution than FA and LL. Blending of SL refines the pore structure at early age, so the SL blended paste has a higher $a-F$ than OPC after about 4 days. FA reduces F and $a-F$ in the first 12 days due to its low

reactivity at early age, but the effect of its pozzolanic reaction shows after 28 days. LL increases the connectivity of pore solution. However, its filling effect on pore structure is effective after a certain hydration age.

The relation between volume of Epw and F can be well demonstrated by an extended percolation theory. This enables an in-situ evaluation of Epw through conductivity test. The real-time monitored electrical conductivity and $1/F$ can be used to estimate the chloride migration coefficient in hardened cement pastes. This study provides both useful methods and theoretical basis for the prediction and simulation of moisture content and ions (e.g. chloride) ingress in cement-based materials with a continuous long-term hydration during its service life.

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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Paper III

Using water vapour and N₂ isotherms to unveil effects of SCMs on nanopores and evaluate hydration degree

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Using water vapour and N₂ isotherms to unveil effects of SCMs on nanopores and evaluate hydration degree

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ABSTRACT

Nanopores are critical for the durability of cement-based materials, but the refinement of these pores by SCMs is yet to have a clear understanding. This paper studied effects of the water–binder ratio, SCMs and the drying on the distribution of nanopores using water vapour and N₂ sorption isotherms. Results show that data of water vapour sorption can be used for a practical evaluation of the hydration degree of SCMs with thermodynamic simulation. Fly ash increases the volume of large gel and capillary pores. It lowers the difference between the sorption of water vapour and N₂. Slag evidently refines the nanopores by increasing the volume of ink-bottle gel pores with an interlayer-size neck. A higher w/b produces more large pores to reduce the effect of drying. Removal of water induces contraction of interlayer and reduces gel pores volume, which causes large difference between sorption of water vapour and N₂.

1. Introduction

Hardened cement-based materials have a porous structure with a wide range of pore sizes from about 5 Å [1] up to the millimeter level (induced by the entrained/entrapped air). Pores of different sizes play different roles in determining the performance of concrete, including the mechanical properties, dimensional stability and durability [2]. The mesoscale pores, mainly existing in calcium silicate hydrate (C-S-H), control the durability such as shrinkage and creep [3], as well as moisture transport in the unsaturated matrix [4]. The complexity of the mesoscale structure of C-S-H is the main obstacle to get a fundamental breakthrough in a general description of the composition–structure–property relationships from the molecular building block view [5]. Therefore, a credible characterization of the nanopores is significant for the assessment of concrete performance, and for a further understanding of the correlation between structure and properties.

To reach the goal of reducing emissions in the cement industry, increasing amounts and diversity of supplementary cementitious materials (SCMs) are used in modern concretes. It is well known that SCMs influence the properties, e.g. the mass transport in cement-based materials [6,7]. However, there are still many gaps in correlating the microstructure of hardened cement-based material with its transport properties, especially for mixtures with the addition of SCMs. It has been found in our previous investigation [4] that slag and fly ash induce a large reduction in the chloride migration and moisture transport in unsaturated paste, without having much effect on the total porosity. The main differences seem to occur in the connectivity of nanosized pores. A clear picture of nanopores in non-dried blended pastes will facilitate the understanding of how SCMs impact the durability properties which are related to the refined pore structure.

Many methods have been applied in the characterization of the nanoscale structure of cement-based materials, covering adsorption

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isotherms of N₂ [8] and water vapour [9–11], small-angle X-ray scattering [12,13], small-angle neutron scattering [14], low-field proton NMR [15–17], and mercury intrusion porosimetry [18]. A treatment to remove the water in the materials is required in most of these measurements. Currently, there is no such method that can remove the non-bound water without damage to the structure of the C-S-H. During the process of water removal (drying process), the mesoscale pore structure [19,20] and the chemical structure after a certain extreme drying [15] will be altered due to the change of forces and interactions in the matrix. For measuring the mesoscale pores, the most widely-used methods are the sorption isotherms of N₂ and water vapour (static or dynamic [11,21]). Several publications reported effects of different drying methods on the pore structure by N₂ adsorption [8,22]. Water vapour sorption has been considered as the most suitable approach to reveal the microstructure of the cement-based materials in a full scale [9]. The specific surface area (SSA) measured by water vapour sorption is generally larger than that by N₂ sorption by a factor, in some drying conditions, of up to 10 times or more [23–27]. Odler [26] explained that the lower SSA by N₂, compared to water vapour, is mainly due to the extremely limited accessibility of nitrogen molecules into the small pores, but there was no clear indication about the critical pore size that is accessible for N₂. Jennings and Thomas [28] discussed the publication by Odler [26] to stress that a part of the pores in low density (LD) C-S-H is hard for N₂ to access as well. However, they had a consensus that the ratio of high density (HD) C-S-H and LD C-S-H would influence the difference in SSA by these two methods. The incorporation of SCMs will modify the structure of the main hydration products, including the ratio of these two C-S-H [29]. One part of this paper aims to have a comprehensive assessment of effects of SCMs on the differences in the measured pore structure by water vapour and N₂ sorption.

The amount of HD and LD C-S-H, which most possibly relates to the inner and outer products [30,31], depends on the hydration degree of the cement and SCMs. Hydration degree is an important index of cement-based materials, which correlates to not only the mechanical performance but also the durability of concretes. For Portland cement, the degree of hydration can be assessed by the consumption of crystal mineral in clinker, which can be calculated by Rietveld analysis of X-ray diffraction data [32]. However, it is much more complicated when the binders contain amorphous SCMs phases. Scrivener et al. [33] summarised most of the methods applied for measuring the hydration degree of SCMs, and all the methods with a good rating require either access to advanced equipment (such as NMR) or a highly professional skill in the data analysis (PONKCS method). This paper will propose an easy-to-perform method to determine the hydration degree of SCMs at later ages by using water vapour sorption data to calculate the C-S-H content [11,34] and simulation by GEMs software (an open access source).

The effect of SCMs on the nanopores of hardened pastes has been investigated in this study. Pore structure information was analysed in detail based on the data from dynamic water vapour sorption (DVS) and nitrogen sorption isotherms (NS). The pore size distribution (PSD) in hardened pastes was calculated by the Barrett–Joyner–Halenda (BJH) model with the data from DVS and NS. The content of C-S-H was determined from the DVS data, and thermogravimetric analysis (TGA) was applied to determine the portlandite content. The hydration degree of SCMs has been evaluated by the C-S-H and portlandite content coupled with GEMs simulation. Finally, a comprehensive discussion is presented to understand the underlying mechanism of the differences in water vapour and N₂ sorption equilibrium process. The advantages and limitations of the proposed method for the hydration degree evaluation are addressed in the discussion part as well.

2. Materials and methods

2.1. Preparation of samples

Cement (CEM I 52.5 R) with a Blaine surface of 525 m²/kg was used

in this investigation. Two different kinds of SCMs (ground granulated blast furnace slag and fly ash) and limestone were used to replace part of Portland cement to produce the blended pastes. Detailed information on the slag (SL), fly ash (FA) and limestone (LL) powder is described in [35]. Table 1 presents the mass proportions of the 11 samples. The pure CEM I (noted as P0) was used as the reference binder. CEM I was partially replaced by 35 % FA (noted as P1) or SL (noted as P2) to obtain a binary binder system. A ternary system (noted as P3) was made by replacing cement with 35 % SL and 16 % LL. P0, P2 and P3 were mixed with water–binder ratios (*w/b*) of 0.35, 0.45 and 0.55, respectively. P1 was mixed with a *w/b* of 0.35 and 0.45. The procedure for mixing is described in detail in [36].

Samples were cast in zip bags (150 mm × 200 mm). In order to easily crush the hardened pastes into small particles, the fresh pastes were rolled into a plate shape with a thickness of about 1 mm before the bags were sealed. All samples were taken out and crushed into small particles with a diameter of about 1 mm after a sealed curing for 1 week. Afterwards, the particles were cured in water for 6 months in a sealed box (1 l), and the mass of the curing water was controlled (about 15 % of particles mass) to provide enough moisture but avoid too much leaching. A part of each sample was then conditioned under 11 % relative humidity (controlled by the saturated LiCl solution) for 1 year. The temperature of the curing and mixing environment was constant at 20 ± 1 °C.

2.2. Dynamic water vapour sorption isotherm

The 6-month wet cured samples were used to measure the vapour desorption isotherms. The dynamic vapour sorption isotherm was performed in a gravimetric water vapour sorption instrument, DVS (Advantage, Surface Measurements Systems, UK). In this, the mass of small samples is continuously recorded during their exposure to different relative humidity (RH) conditions. Samples of 40–60 mg were exposed to an RH-sequence (95 %–90 %–80 %–70 %–50 %–40 %–35 %–30 %–20 %–10 %–0 %) at 20 °C. Each RH step required a duration of 30–60 h to reach the criterion of mass loss rate lower than 0.0001 %/min. For each mix, we measured at least two samples and the results are an average of parallel measurements.

2.3. Nitrogen sorption

A BET instrument (TriStar3000, Micromeritics) was used to measure the nitrogen sorption isotherm of samples that were dried under 11 % RH for 1 year. Before the sorption measurement, samples had been outgassed for 4 h with a continuous N₂ gas flow at 60 °C for a fast water removal [22]. Adsorption isotherms were measured over the pressure range of 0.01–0.982 P/P₀ with an equilibrium interval of 10 s for each step at 77 K. Each sample has been repeated at least once, and the final value is an average of parallel tests.

Table 1
Mix proportions of 11 different samples by weight percentage.

Samples	Binders				<i>w/b</i>
	Cement	Fly ash	Slag	Limestone	
P035	100 %	–	–	–	0.35
P045					0.45
P055					0.55
P135	65 %	35 %	–	–	0.35
P145					0.45
P235	65 %	–	35 %	–	0.35
P245					0.45
P255					0.55
P335	49 %	–	35 %	16 %	0.35
P345					0.45
P355					0.55

2.4. Thermogravimetric analysis

The weight loss due to the decomposition of portlandite was measured by a thermogravimetric and differential thermal analysis instrument (SDT Q600, TA Instruments) with a Stanton Redcroft STA 780 simultaneous thermal analyser. Powder samples (dried at 11 % RH for 1 year) were heated at a rate of 10 °C/min under a continuous nitrogen flow (100 cm³/min) from 20 °C to 1000 °C.

2.5. Thermodynamic simulation

Thermodynamic modelling was performed using an open access software-free Gibbs Energy Minimization program GEM-Selektor v3.7. The simulation was based on the cement database Cemdata18 [37] combined with the PSI-GEMS thermodynamic database [38]. The effects of different SCMs on the phase assemblage of products were analysed by assuming that clinker has a hydration degree with 92.2 % after a 6-month water curing at 20 °C (based on portlandite content by TGA). This value is very close to the value reported in [39] with similar clinker composition and curing condition.

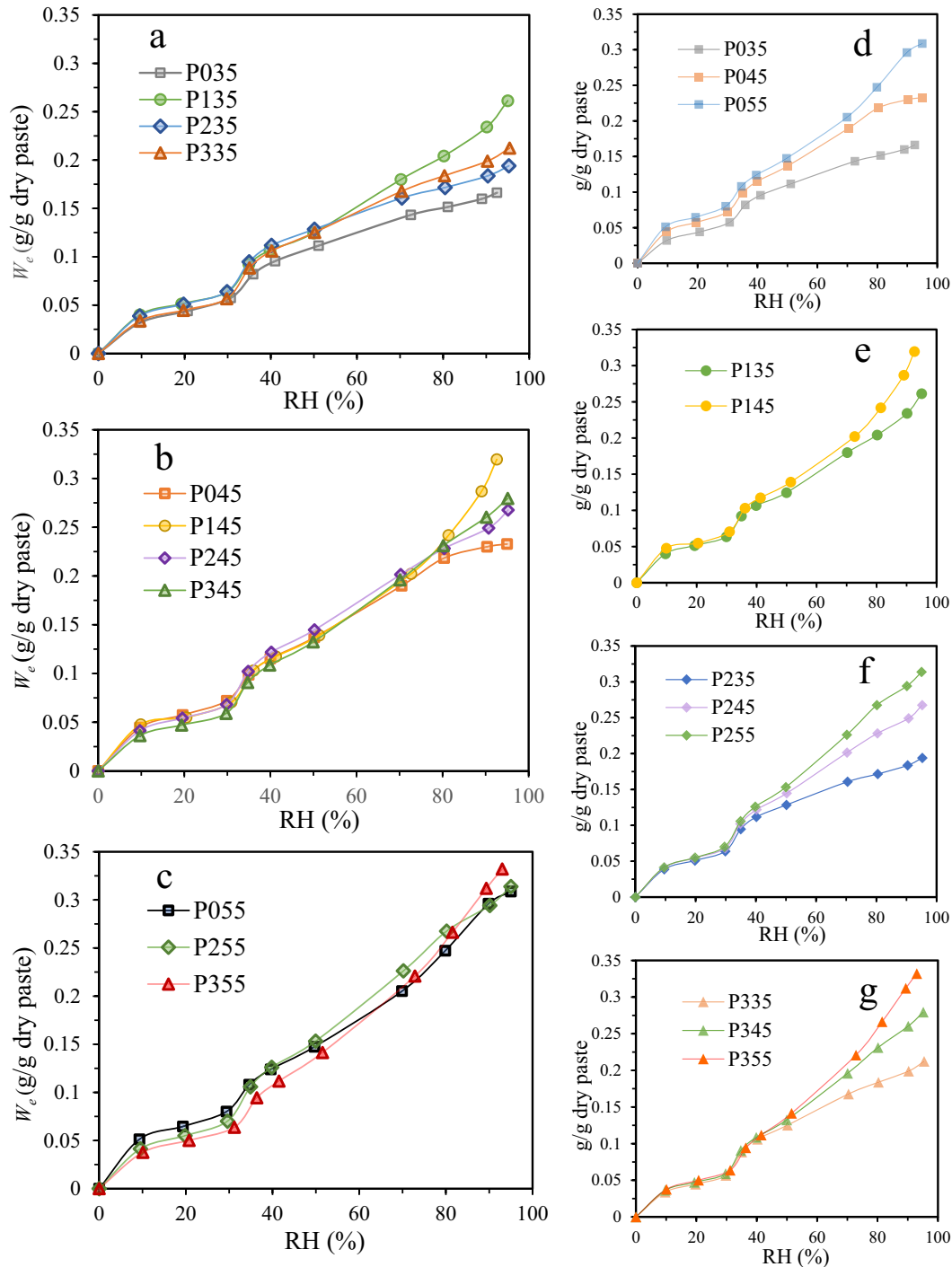


Fig. 1. Water vapour desorption isotherms of all the 11 samples measured at 20 °C. Plots in a, b and c are comparisons between different binder systems with the same w/b. Plots in d, e, f, and g are comparison between different w/b ratios with the same binder system.

3. Results

3.1. Water vapour desorption isotherms

Water vapour desorption and adsorption isotherms were used for modelling moisture transport, understanding the mechanism of drying shrinkage [40,41], and microstructural changes during the drying process [9]. Fig. 1 shows the water vapour desorption isotherms of hardened cement-based pastes (hcps). With the same w/b of 0.35, the replacement with SCMs increases the moisture content (W_e) in the hcps under all RH conditions. Due to the refinement effect of SCMs, both the vapour diffusion and total moisture transport coefficient of the blended pastes will be much lower than that of CEM I paste [36]. These dual effects induce a longer drying time for the modern concretes (blended with SCMs) than for the ordinary cement concretes, something which deserves special attention for the application of SCMs in buildings.

When pastes were mixed with the w/b of 0.45, the blending of 35 % FA seemed to have a minor effect on the moisture content below 70 % RH. This is consistent with the findings in [42], where the paste was cured under a sealed condition for 6 months. At RHs above 70 %, the blended pastes contain more moisture than the CEM I paste, and the differences between the blended pastes and CEM I pastes increase as the RH gets higher.

An increase in w/b to 0.55 reduces the difference between the moisture content in the SL blended pastes (P2 and P3) and that in the CEM I paste (P0) (see Fig. 1c) at RH above 70 %. The ternary paste (P355) has the lowest moisture content in RH below 35 %. Fig. 1d shows that an increase in w/b induces moisture content in CEM I pastes at all RH conditions. However, the increase in moisture content of the blended pastes mainly occurs at RH above 40 % as the w/b increases. Olsson et al. [43] reported a similar phenomenon in well-hydrated (water curing for 4 years) slag blended pastes.

Moisture capacity (φ) has been defined as the derivative of the moisture content with respect to RH [44]. It is an important parameter to describe and model the moisture transport in cement-based materials. The average moisture capacity ($\bar{\varphi}$) in certain RH intervals is calculated by Eq. (1). W_{ei} and W_{ej} correspond to the moisture content in hcps at RH_i and RH_j , respectively.

$$\bar{\varphi} = \frac{W_{ei} - W_{ej}}{RH_i - RH_j} \quad (1)$$

Fig. 2 presents the comparison of the average moisture capacity of different hcps. For pastes with w/b of 0.35 and 0.45, the difference in moisture capacity occurs in the RH intervals of 30 %–36 % and at RHs above 50 %. In general, the blending of SCMs will increase the moisture capacity in these ranges, and FA presents the largest increase. The sudden drop of moisture content from RH of 36 % to 30 % has been explained as the occurrence of cavitation during the drying process [45,46]. The cavitation-induced moisture capacity is higher in the blended pastes than in the CEM I pastes at all w/b mixtures. This is due to the refinement of the pore structure, which will be discussed in a later section. A further replacement of cement by LL increases the moisture capacity of pastes with all w/b at RHs above 60 %, compared with the binary SL blended pastes.

3.2. The specific surface area by BET method

SSA of the wet and dried pastes was calculated from the water vapour desorption and N_2 adsorption data, respectively, based on the BET theory [47]. The adsorption data up to P/P_0 of 32 % were used for the regression based on Eq. (A) in [47], which works well to describe a unimolecular adsorbed layer. A detailed illustration of the calculation process can be found in a publication by Belie et al. [11].

Table 2 shows the SSA from water vapour desorption (S_w), N_2 adsorption (S_N) and the ratio between them (S_w/S_N). It is evident that an increase of w/b from 0.35 to 0.55 causes an increment in both S_w and S_N

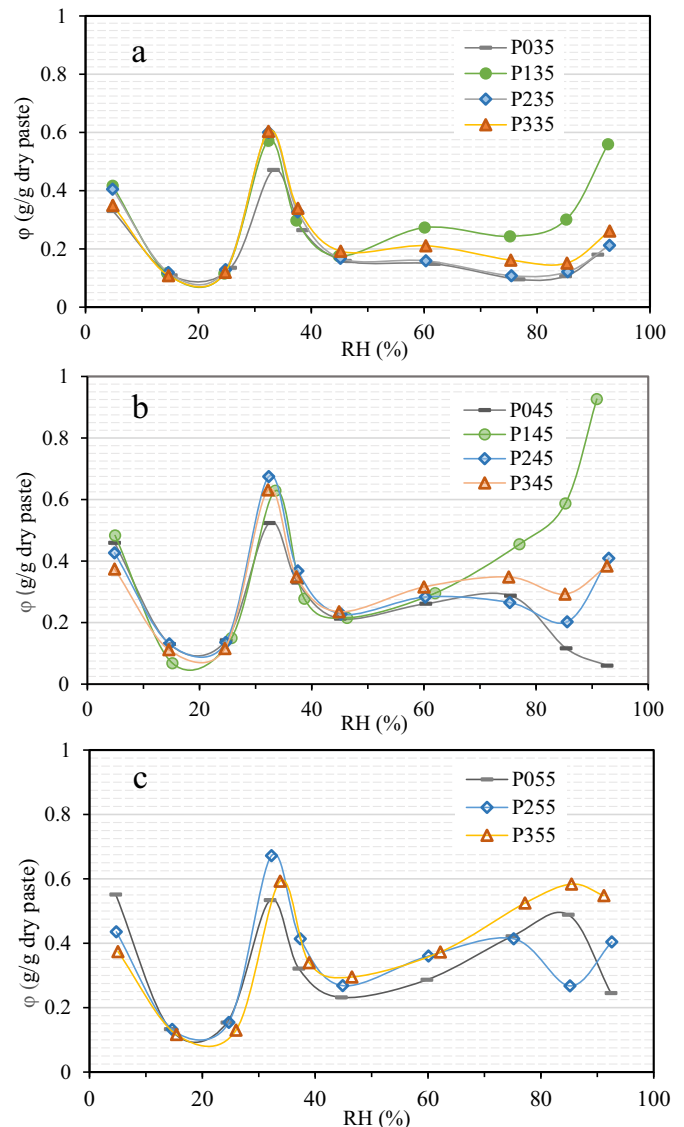


Fig. 2. The average moisture capacity at different RH intervals: a – w/b of 0.35; b – w/b of 0.45; c – w/b of 0.55. Note that the x-coordinate is the average value of the two ends of the RH interval.

Table 2

The surface area of hcp based on water vapour desorption and N_2 adsorption by BET method.

Samples	Specific surface area (m^2/g)		S_w/S_N
	N_2 adsorption	Water vapour desorption	
P035	15.2 (± 0.5)	162.6	10.7 (± 0.4)
P045	21.9 (± 0.2)	200.3	9.1 (± 0.1)
P055	25.6 (± 0.3)	221.5	8.7 (± 0.1)
P135	18.5 (± 0.6)	183.3	9.9 (± 0.3)
P145	25.0 (± 1.5)	218.4	8.7 (± 0.5)
P235	14.6 (± 0.6)	160.1	10.9 (± 0.4)
P245	17.4 (± 1.3)	192.0	11.1 (± 0.8)
P255	22.0 (± 0.7)	218.9	9.9 (± 0.3)
P335	14.1 (± 1.7)	160.1	11.5 (± 1.4)
P345	19.4 (± 1.3)	187.1	9.7 (± 0.6)
P355	23.7 (± 0.4)	216.9	9.1 (± 0.2)

of all binder systems. It should be noted that S_N is rather lower than the typical value of hardened cement-based materials due to long conditioning time and 60 °C drying. The blending of SL shows a slight

reduction in both S_w and S_N , and the difference is very small when the deviation is considered. A further blending of LL weakly increases the S_N , but it slightly decreases the S_w of hcp with w/b of 0.45 and 0.55. FA binary pastes have a higher SSA than the CEM I paste with the same w/b . The S_w of wet pastes is in the range of 8–13 times higher than S_N of the dried pastes. The blending of FA seems to decrease this difference, but SL increases it of hcp with w/b of 0.45 and 0.55.

A large difference in the S_w and S_N of cement-based materials has been found in many of the previous investigations [11,23,25–27,48–50]. A similar phenomenon was also reported in montmorillonite [51], for which the ratio between S_w and S_N reached as much as 15 due to the swelling of the basal space during wetting (or contraction during drying) of natural montmorillonite [52]. There is no such difference in the S_w and S_N of building materials with other binders such as gypsum, lime or autoclaved lime and silica [24,53]. C-S-H, as the main hydration product of Portland cement-based materials, has a similar structure to that of clay (such as montmorillonite), so it is sensitive to the water content [20]. During the drying treatment of samples for the N_2 sorption test, the interlayer space will be narrowed due to the removal of water [54–56].

Moreover, a long drying process also induces a polymerisation of silicon chains and changes the chemical structure [57,58]. After the nanosized space has contracted to some level or been blocked by chain connections, it is inaccessible for the N_2 molecule. Even though some

part of the small layer space is thermodynamically accessible for N_2 , its diffusion rate is rather lower than that of water vapour. The large difference (water vapour at 20 °C and N_2 at –196 °C) in the temperature of the measuring environment will affect the equilibrium time, but it may not be the main factor. A further detailed discussion will be given in Section 4.1, which is different from some statements in [11,27].

Fig. 3 shows a typical comparison of the sorption of water vapour in wet hcp and N_2 in long-time dried hcp, exemplified with P0 and P1. An increase in w/b induces a higher adsorption of N_2 , but it induces minor effects on the water vapour desorption of the blended pastes (P1, also see P2 and P3 in Fig. 1). Within the pressure interval (P/P_0 below 32 %), where the data are used for SSA calculation, the adsorption of water molecules in hcp is >10 times higher than that of N_2 molecules in the dried hcp. However, the surface area occupied by a single N_2 molecule is only about 1.4 times as large as that by a single water molecule (0.162 nm² for N_2 and 0.114 nm² for H_2O [27]). Therefore, the difference between S_w and S_N is caused by a much lower adsorption of N_2 in the dried pastes than that of water vapour in wet pastes. When C-S-H was dried at RH of 11 %, about 0.7 mol H_2O would be added to the C-S-H structure at the D-dry condition (1.7CaO·SiO₂·[1.3–1.5]H₂O) [59,60], so we can deduce that the adsorbed water in C-S-H under 11 % RH is about 3.84×10^{-3} mol/g dried mass. The magnitude of this value is in a good match with the adsorption of water vapour in Fig. 3a. The water sorption in

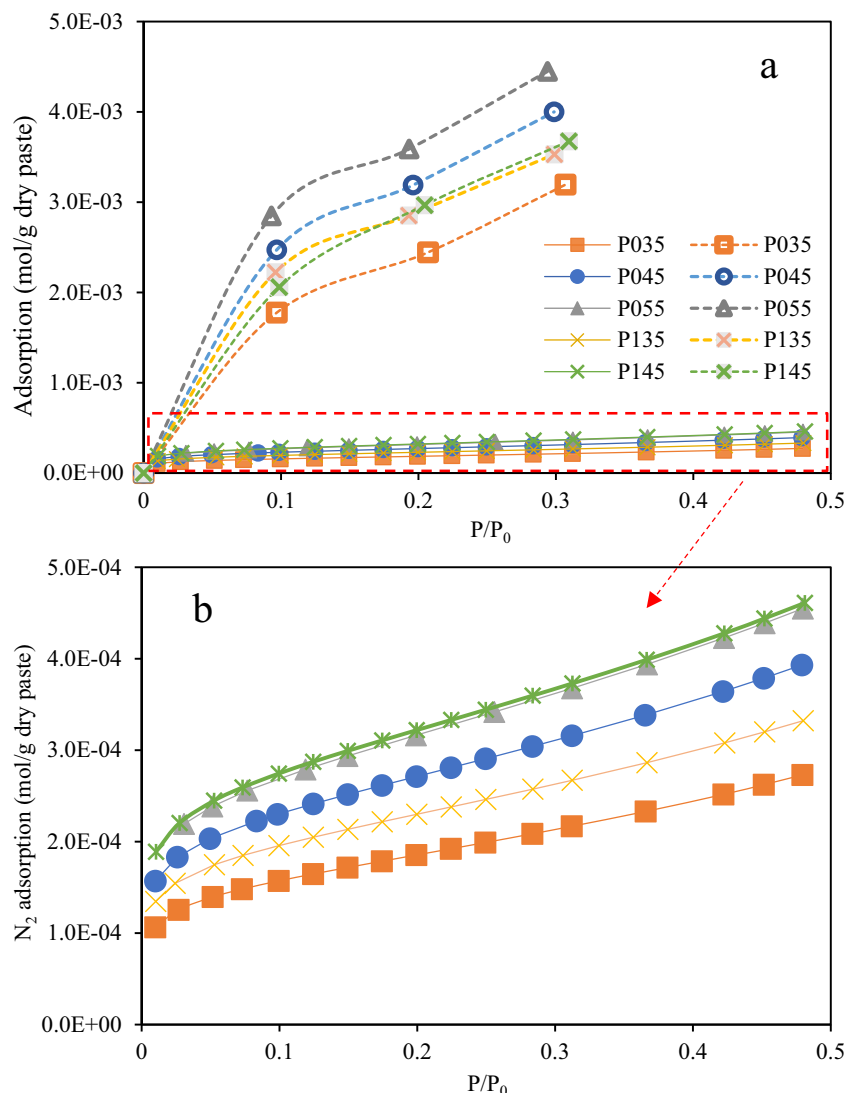


Fig. 3. Typical comparison of the sorption of water vapour and N_2 in hcps: dashed line – water vapour desorption; solid line – N_2 adsorption.

hcps is lower because some other hydration products also contribute to the weight of dried hcps other than C-S-H. Provided that N_2 could penetrate the layer space of the C-S-H, the adsorbed amount should be of the same order as the water vapour. However, the amount of adsorption indicates that almost no N_2 penetrates the interlayer space of C-S-H.

3.3. Pore size distribution by the BJH method

3.3.1. Effect of ions in pore solution on PSD by DVS

The BJH method was first proposed by Barrett, Joyner and Halenda [61] to calculate the pore size distribution in porous substances based on N_2 isotherms. This model was also widely applied for the determination of PSD in cement-based materials using water vapour desorption data [10,11,41]. Although the pore shape in hcps is more complex than the assumed cylinder shape in this method, and cavitation occurs during the desorption process [45,46] (corresponding to one peak in Fig. 4), the calculated results provide meaningful information for a comparative investigation such as this study.

The Kelvin equation Eq. (2) has been used in the BJH method to describe the correlation between the relative humidity (equilibrium gas pressure P/P_0) and the radius of the condensed liquid in the cylinder pores (r_k).

$$\ln RH_k = -\frac{2\gamma V}{r_k RT} \cos \theta \quad (2)$$

where RH_k is the relative humidity value that results from the curvature effects of the menisci at liquid/vapour interfaces. γ is the liquid surface tension (7.28×10^{-2} N/m at 20 °C), V is the molar volume of liquid (1.798×10^{-2} l/mol for water), R is the gas constant (8.314 J/K/mol), T is the absolute temperature of the sample and θ is the contact angle between the liquid and pore wall (assumed to be 0).

However, the equilibrium pressure at the plane surface (p_s) of the solution will be influenced by the ions in the solution. The correlation between the ion concentration and relative humidity at the plane surface (RH_s) is empirically expressed by Raoult's law [62,63], as shown in Eq. (3). n_w is the moles of water in the solution and n_i is the total moles of ions in the solution. Therefore, the observed relative humidity value (RH_o) is a combination of curvature and ion effects, which can be described as Eq. (4).

$$RH_s = \frac{p_s}{p_0} = \frac{n_w}{n_w + n_i} \quad (3)$$

$$RH_o = RH_k RH_s \quad (4)$$

The ion concentration in the pore solution was calculated with the chemical composition and water content, which has been previously illustrated in [35]. Herein, we subtracted the alkali ions in the C-S-H by taking the adsorption coefficient of 1.2 % for Na and 2 % for K [64], respectively. The C-S-H content was determined based on the water content at 20 % RH, which will be described in Section 3.4.1. Water content decreases with the lowering of RH, and Raoult's law is only valid for dilute solutions. Therefore, to simplify the analysis we use the water content in naturally saturated pastes (under the sealed curing) to calculate the ion concentrations.

The previous studies [10,11,41] ignored the effect of ions on the RH_s of the pore solution, and they used the observed RH_o as RH_k . Fig. 4 shows the comparison of the calculated PSD with the RH_s of the pore solution and pure water. The ions in the pore solution seem to have a weak effect on the calculated pore width and volume of pores with diameter < 10 nm. However, the omission of ion effects will severely underestimate the size and volume of capillary pores (width > 20 nm). Therefore, it is necessary to include the effect of ions on the RH_s of the pore solution during the calculation of the PSD by using the BJH method on water vapour desorption isotherms.

3.3.2. Comparison of pore size from DVS and NS

On the pore surfaces, there is a physically adsorbed layer of molecules with a statistical thickness t [48,61]. The radius of an open cylinder pore (r_p) is a sum of r_k and t ($r_p = r_k + t$). The correlation between the statistical thickness of the water film and RH in hcp was first reported by Hagymassy et al. [48]. Badmann [65] introduced Eq. (5) to describe the correlation by using two parameters K_1 and K_2 . These two parameters are dependent on the composition of the materials. Therefore, we used a trial-error method to adjust the constants for different binder systems. The optimum parameters are obtained by getting a good match between

Table 3

The coefficient of the t -curves for different binder systems, representing a w/b of 0.35.

Coefficients	P035	P135	P235	P335
K_1	3.51	2.86	3.20	2.55
K_2	-1.89	-2.10	-2.50	-2.00

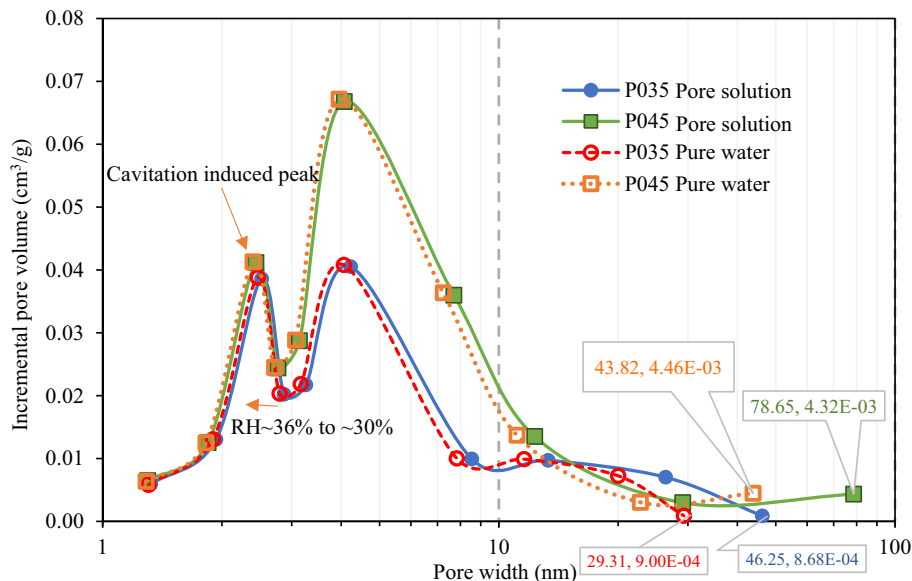


Fig. 4. The effect of ions in pore solution on the calculated PSD of hcps.

the measured and calculated total pore volume. Table 3 presents the optimum parameters for 4 different binder systems with all w/b (exemplified by a w/b of 0.35). Fig. 5 shows the t -curves of the different binder systems. It seems that the CEM I paste has the highest thickness of water films at RHs below 50 %, and the SL binary paste increases to be higher than CEM I paste at RH above 50 %. The ternary pastes have the thinnest water film. However, the differences between binder systems is minor, which is consistent with the reported value in [48].

$$t(RH) = K_1 + K_2(\ln(-\ln(RH))) \quad (5)$$

Fig. 6 shows the PSD by analysing the water vapour and N_2 sorption data with the BJH method. The calculated pore widths (diameter of open cylinder pores) are in a range of 1–90 nm, so the pore structure at mesoscale can be effectively indicated by the water vapour desorption data. According to the classification by Jennings in [9], the moisture below 25 % RH corresponds to the water in the interlayer space. The calculated pore width (including the t thickness) is approximately 1.66 nm at ~20 % RH. Referring to the definition in Jennings' colloidal model [66], the moisture in spaces of this dimension includes the water in the interlayer space, intraglobular pores (to 1 nm) and small gel pores (1–3 nm). Without consideration of the water film (t thickness), the pore width filled at ~20 % RH is about 1.2 nm. The 1H NMR results from Muller et al. [67] indicated that there is no distinguishing signal between the water in the interlayer space and intraglobular pores, so they classified the pore space up to 1 nm as interlayer space. Therefore, we classified the moisture up to 20 % RH as water in the interlayer space in this study (see Fig. 6a).

Moisture desorption between 20 % and 40 % RH induces a peak in the incremental volume of pores with sizes between 1.66 and 3.3 nm. The moisture change in the range of 25 %–50 % has been designated as water in SGP or in HD C-S-H [9]. However, a sudden drop between 36 % and 30 % RH is due to the cavitation in larger pores during the drying process. The capillary tension in ink-bottle pores with small necks increases to a very large value, with which pressure cavitation (homogeneous nucleation of bubbles of vapour) could occur. This phenomenon is commonly observed in the N_2 [68] and water vapour desorption [45,46] curve of materials with the complex mesoscale pores. Maruyama et al. [45] found no cavitation in pores smaller than 5 nm (6.4 nm including the t thickness) during the desorption of cement-based materials at 20 °C. Thommes et al. [69] reported that the cavitation occurs in pores wider than 8.5 nm during N_2 desorption of mesoporous silicas, and it shows no dependence on the pore shape, pore size or the neck size (at least for necks smaller than 2.6 nm). Rastogi et al. [46] stated that cavitation occurred in the gel pores (in a range of 2–8 nm) of the inner product. Based on these findings, we suggest that the moisture loss from

40 % to 20 % RH is the water in SGP and the ink-bottle LGP connected with the interlayer space. It is meaningless to designate the volume at this interval to pores with a specific size, but it is significant for understanding the refinement effect of SCMs by comparing the volume of ink-bottle gel pores from different binder systems.

The moisture loss from 80 % to 40 % corresponds to the water in pores with a diameter of 12.3–3.3 nm, so it can be classified as the volume of the open LGP pores. Moisture in RH of 97 %–80 % is water in capillary pores with a diameter larger than 12.3 nm. This part of the water is closely related to the w/b [41], so it can be used to estimate the original w/b of the hcp [9].

Fig. 6a–c indicate that the blending of SCMs slightly reduces the volume of interlayer space in hcp within all the w/b . Both SL and FA increase the value of the cavitation-induced peaks, which implies a refining of the LGP to reduce the connectivity. The difference between binary and CEM I hcp becomes larger at higher w/b . This reveals a more evident refinement effect from SL and FA, resulting in a larger reducing effect on the moisture and chloride transport [7,35,36,43]. The volume of open LGP pores (3.3–12.3 nm) is increased by the blending of SL and FA, and this effect is significant on hcp with a w/b of 0.35. The dilution effect of SCMs will induce a higher effective water-to-cement ratio in the blended hcp than in the CEM I hcp, so it will increase the hydration degree of clinker in the binder systems [70,71]. Moreover, the further hydration of FA and SL generates more content of C-S-H, so the volume of LGP is higher in the binary hcp than in CEM I hcp. A further replacement of CEM I by LL reduces the C-S-H content and thus decreases the LGP compared to SL binary hcp. The dilution effect also induces an increase in the volume of capillary pores (12.3–80 nm), and FA has the largest increasing effect on capillary pores in hcp with w/b of 0.35 and 0.45.

Fig. 6d–g presents the comparison between the PSD by water vapour and by N_2 sorption of hcp. It shows that the N_2 sorption measurement of hcp dried at 60 °C with N_2 can only detect the LGP and capillary pores. The detected volume of LGP by N_2 sorption is much lower than that by water vapour sorption. The vacuum or high-temperature drying method induces severe damage of the layer structure of C-S-H, so it results in the contraction of the interlayer space and coarsening of some of the gel pores [16,20,72]. In CEM I and ternary hcps, we can observe an evident increase in capillary pores resulting from the coarsening of the gel during the drying treatment in this study.

A mild drying method such as D-drying [8] or a careful solvent exchange treatment [19,22] can minimise the effect of drying on the structure of the hcp to obtain a higher SSA from the N_2 sorption test. Zhang and Scherer [22] reported that the isopropanol replacement method was the best way to preserve the microstructure, and a high SSA (~88 m²/g for OPC pastes with w/b of 0.5) could be measured by N_2 sorption of hcp by this drying method. However, the volume of pores with diameter below 4 nm is far smaller than 0.02 ml/g and this value shows no difference at different curing ages (see Fig. 5 in [22]). Although the hcp was treated with the optimum drying method, the interlayer space and a large part of the gel pores have not been measured by the N_2 sorption. The significant difference in PSD by water vapour sorption and by N_2 sorption (see Fig. 6d) is due to not only the effect of drying but also the difference in accessibility of water and N_2 molecules into the small nanosized channels. This will be discussed further in the final section. The volumes of capillary pores in all binder systems, from both water vapour and N_2 sorption measurement, increase as the w/b increases from 0.35 to 0.55. However, the increase of w/b from 0.35 to 0.45 in CEM I pastes induces a minor increase in the capillary pores, and it mainly increases the volume of LGP.

3.4. Determination of hydration products and hydration degree of SCMs

3.4.1. Determination of the amount of hydration products

As stated in the previous section, the moisture under 20–25 % RH mainly corresponds to the water in the interlayer space of C-S-H.

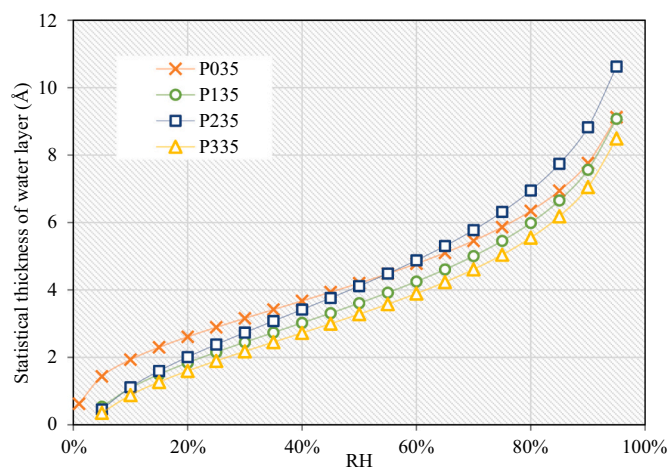


Fig. 5. Statistical t -curves of the adsorbed water film for different binder systems.

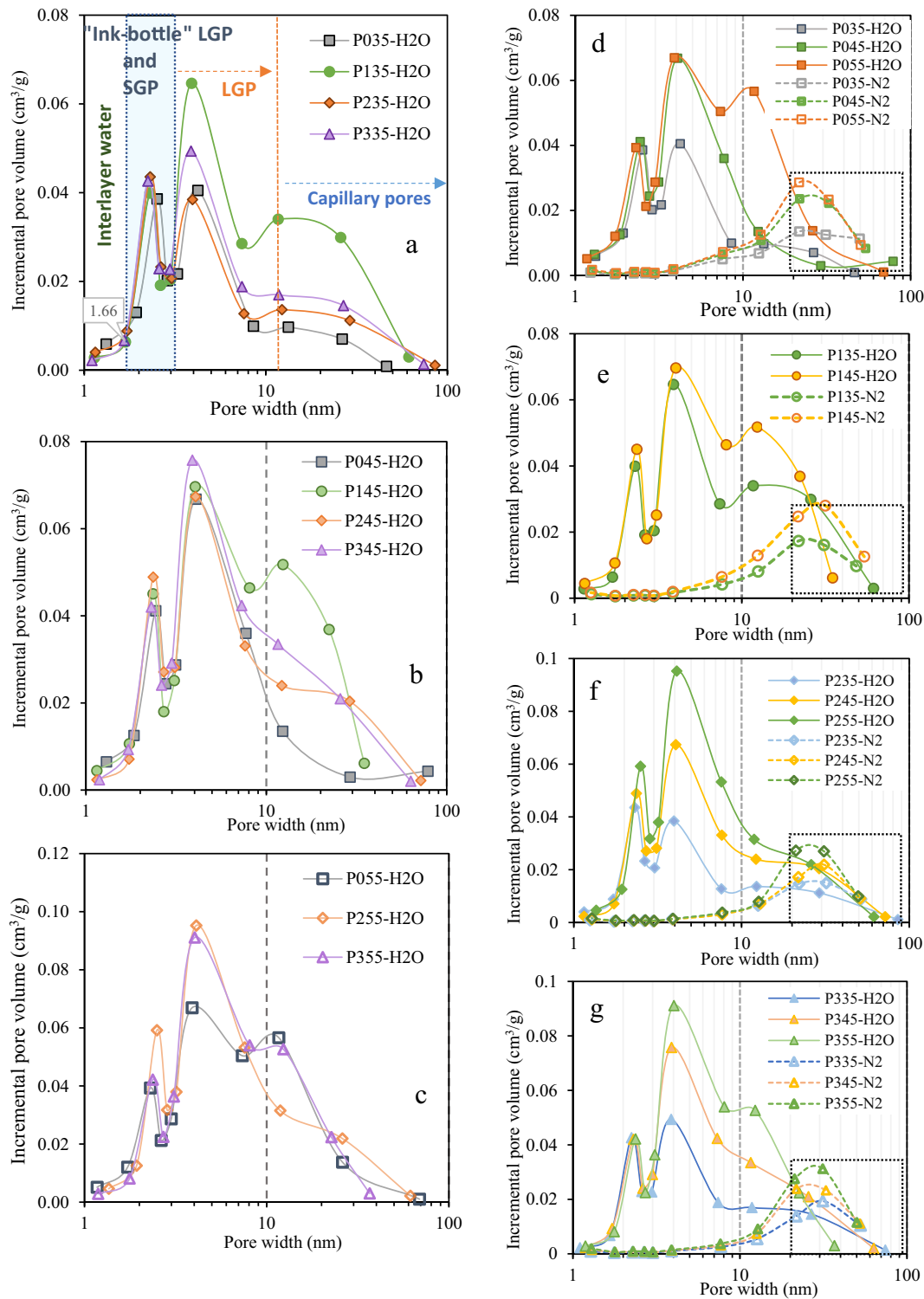


Fig. 6. The PSD in hcp calculated by BJH method from water vapour desorption ($P^{***}\text{-H}_2\text{O}$) and N_2 sorption isotherm ($P^{***}\text{-N}_2$). Graphs a, b and c are the comparison in different binder systems with w/b of 0.35, 0.45 and 0.55, respectively. Graphs d, e, f, and g are the comparison in pastes with the same binder system but different w/b .

Bonnaud et al. [73] performed a molecule dynamic simulation to reveal the thermodynamics of water confined in the interlayer space, and they found that the interlayer water started to dry at about 20 % RH. This part of the evaporable water is assigned as structural water because its drying will induce irreversible deformation [9]. Due to the unique mesoporous structure of C-S-H, its SSA is at least an order of magnitude greater than any other hydration products [34]. The vast majority of the moisture in

hcp is adsorbed in the interlayer space of C-S-H when RH is below the condensation point in the gel pores. Based on the commonly used atomic structure of $1.65\text{CaO}\cdot\text{SiO}_2\cdot 1.75\text{H}_2\text{O}$ from [74] or $1.69\text{CaO}\cdot\text{SiO}_2\cdot 1.80\text{H}_2\text{O}$ from [75], the evaporable water (dried at $\sim 0\%$ RH) in the C-S-H structure is approximately $7.3 \times 10^{-3} \text{ mol/g}$ (or 0.131 g/g) dried C-S-H with about 0.55 mol chemically bound water attached to Ca or Si atoms [76]. This value is close to the experimentally

measured value (0.1 g/g) in [34] and very close to the value used in [11,41] for calculation of the C-S-H content. if we assume that SCMs have minor effect on the evaporable water in interlayer of C-S-H, Eq. (6) can be used to estimate the C-S-H content in all hcps in this study.

$$W_{CSH} = \frac{n_{e,20}}{\bar{n}_{w,CSH}} \quad (6)$$

where $n_{e,20}$ (mol/g) is the amount of water adsorbed in hcp at 20 % RH (partially shown in Fig. 3 and calculated from Fig. 1), $\bar{n}_{w,CSH}$ is the amount of evaporable water in C-S-H with respect to the dried weight (7.3×10^{-3} mol/g), and W_{CSH} is the weight of C-S-H in the dried hcp.

The amount of portlandite was detected by TGA for assessing the feasibility of evaluating the hydration degree of SCMs by water vapour sorption data. The mass loss in the temperature range of 350–500 °C (m_L) was used to calculate the content of portlandite (W_p) in the dried hcp. M_p and M_w are the molar mass of portlandite and water, respectively. m_{dp} is the weight of the hcp dried at 11 % RH.

$$W_p = \frac{m_L}{m_{dp}} \frac{M_p}{M_w} \quad (7)$$

Fig. 7a shows the calculated C-S-H content in the hcps. P035 has the lowest C-S-H content with a value of 0.351 g/g, due to the limited availability of water in large pores for later age hydration. A w/b of 0.45 provides more water for hydration to induce a significant increase in the amount of C-S-H (to about 0.477 g/g). An increase of w/b from 0.45 to 0.55 can enhance the later hydration to produce the highest content of C-S-H in CEM I hcp among all the mixtures, but this effect is much

weaker than the change due to the increase of w/b from 0.35 to 0.45. This is consistent with the volume of LGP in Fig. 6d, and it implies that the addition of water in CEM I pastes with w/b higher than 0.42 (the critical value for reaching full hydration [77]) has minor effects on the hydration degree at later ages. For hcp with w/b of 0.35, the blended hcps have higher amounts of C-S-H due to the dilution effect of SCMs to increase the effective water to cement ratio. With w/b of 0.45 and 0.55, the blended hcps have lower amounts of C-S-H than the CEM I hcp. The increase in w/b of the blended hcps has a much weaker effect in terms of increasing the C-S-H content compared with CEM I hcp.

Fig. 7b shows that CEM I hcp with w/b of 0.55 has the highest portlandite content with 0.22 g/g, which is about 92.2 % of amount in a fully hydrated CEM I calculated by GEMs (23.87 %). The blending of FA and SL will reduce the portlandite content mainly due to the pozzolanic reaction of FA and latent hydraulic hydration of SL [78], so the previous publication reported that portlandite content in the blended hcp can be used to calculate the hydration degree of SCMs [33]. The increase in w/b facilitates the consumption of portlandite.

3.4.2. The evolution of hydration products by GEMs simulation

Thermodynamic simulations have been widely applied to reveal the effect of SCMs on the hydration and phase assemblage in the hcps. De Weerd et al. [79] performed such a simulation to understand the effect of limestone on the phase assemblage and volume change of hcp. Schöler et al. [80] applied this method in a quaternary binder system with slag, fly ash and limestone. Lothenbach and Zajac [81] conducted a review on the application of thermodynamic modelling on the blended hcp, and

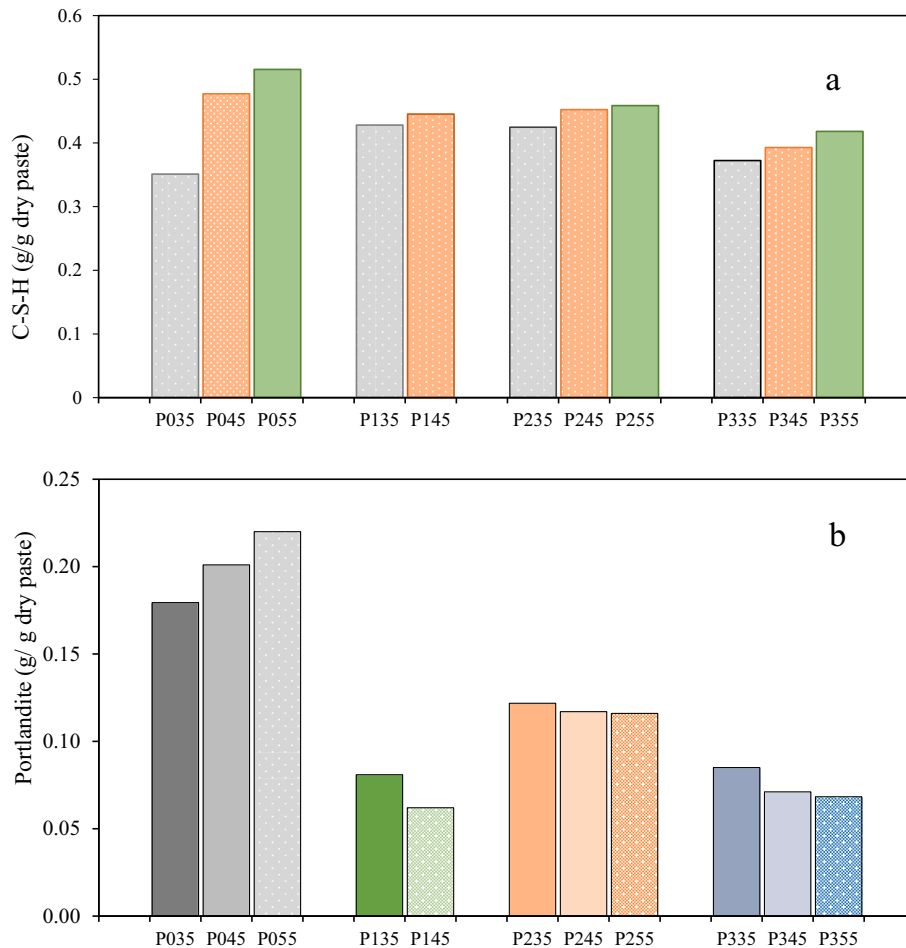


Fig. 7. Amounts of the two main hydration products in hcp: a – the content of C-S-H in hcp calculated by water vapour desorption data; b – the content of portlandite in hcp determined by thermogravimetric analysis.

emphasised that the corresponding models and approaches had achieved a mature level. The increasing availability of thermodynamic data is continuously improving the reliability of thermodynamic calculations on cement-based systems.

Fig. 8 shows the evolution of hydration phases in the hcp with the increase in hydration degree of SCMs (SL and FA). It should be noted that the hydration degree of CEM I has been assumed to be 92.2 %, which is calculated by dividing the measured content of portlandite in P055 (22.0 % by TGA) with portlandite content in the full-hydrated paste (23.87 % by GEMs). For the blended hcp, the lowest effective water-to-cement ratio is 0.53, so it would be reasonable to make such an assumption for clinker in the blended pastes.

The key point for performing a good thermodynamic simulation is to use an accurate database, and to identify the right phases in the hydration products. The presence of Fe and Al in the binder system will form the Fe-siliceous hydrogarnet (Si-hydrogarnet) [82]. The limited amount of limestone in cement (see the composition of CEM I in [35]) will induce the formation of hemicarboaluminate (Hc) and monocarboaluminate (Mc) [79,83]. The blending of limestone will stabilise the Mc, so there is no Hc in the ternary SL system at a later age [84] (also see Fig. 8c). The amount of ettringite, monosulfate (AFm), Hc and Mc is a complex equilibrium related to the amount of calcium aluminate, sulfate, and calcite in the binder system. When the hydration products have an Al/Si ratio higher than 0.1, strätlingite will be present in addition to C-A-S-H [85]. However, strätlingite would form only after all the portlandite has been consumed by the pozzolanic reaction of fly ash [83], and this is not likely to occur in the actual hydration situation.

After taking all these phase formation mechanisms into consideration, the simulation results are reliable for the evaluation of the phases content. The attention is focused on the amount of the two main hydration products, C-S-H and portlandite. For the FA binary hcp, portlandite will decrease due to the consumption by the pozzolanic reaction of FA. In the meantime, the amount of C-S-H will increase with the hydration degree before a complete consumption of FA. Theoretically, a hydration degree of 38 % (13.26 % of FA in the binder system) will consume all portlandite in P145. Above this hydration degree, the content of C-S-H will decrease due to the formation of strätlingite. In the SL blended hcp, the amount of C-S-H shows a gradual increase, while that of portlandite shows an opposite trend, as the hydration degree of SL increases to 1.

3.4.3. Hydration degree of SCMs

With the results in Fig. 8, the amount of C-S-H and portlandite in the dried hcp can be calculated by using Eq. (8). W_{phase} (g/g) is the mass fraction of hydration products, m_{phase} (g) is the weight of hydration products, m_{wp} (g) is the total weight of hcp, and m_{ps} (g) is the weight of the pore solution.

$$W_{phase} = \frac{m_{phase}}{m_{wp} - m_{ps}} \quad (8)$$

Fig. 9 shows the relationship between the hydration degree of SCMs and the amounts of the main hydration products per gram of dried hcp. According to this linear correlation, we can calculate the hydration degree of SCMs by the measured amount of C-S-H or portlandite (see Fig. 7). For the FA binary system, portlandite has not been completely consumed by pozzolanic reaction of FA (see Fig. 7) due to its limited hydration degree. Therefore, the data below a hydration degree of 35 % are used to perform the regression of FA binary hcp.

Fig. 10 shows the hydration degree of FA and SL based on the calculated C-S-H content from DVS and the measured portlandite content from TGA, respectively. A generally good match can be observed between the hydration degree assessed by the C-S-H and portlandite content. This confirms that the estimation of the C-S-H content by water vapour desorption is reliable for assessing the hydration degree. The calculated hydration degree of FA is in a range of 20 %–30 %, and this range matches the previously reported data [33,78,86] for hcp blended

with 35 % FA with a similar curing condition. The determined hydration degree of SL is about 40 %–52 % for binary hcp and 43 %–59 % for ternary hcp. These values are very close to the measured hydration degree of SL blended hcp with the w/b of 0.42 reported in [87], and some minor differences are probably mainly due to the differences in the composition and fineness of the cement or SL. As the w/b increases, the increase in hydration of FA and SL at later ages can be effectively identified by this determination method. Although the increase of w/b from 0.45 to 0.55 has minor effects on the hydration of CEM I, its effect on increasing the hydration of SCMs is evident. This means that the hydration of SCMs at a later age is more sensitive to the availability of moisture in pores compared to cement clinker.

4. Discussion

4.1. Origin of the differences in microstructure measured by water vapour and N_2 sorption

There is a large difference in pore structure of hcp detected by water vapour and N_2 sorption (see Table 2 and Fig. 6). This phenomenon has also been reported in many previous investigations [11,23,25–27,48–50]. However, the underlying mechanism for such a big difference is still not clearly identified. The temperature for the water vapour sorption experiments (normally 20–25 °C) is much higher than that for N_2 sorption (about –196 °C). However, the coefficient of thermal expansion is about $11 \times 10^{-6}/^{\circ}\text{C}$ for dried concrete [88], so the maximum thermal strain is 0.15–0.2 % after cooling down to –196 °C [89]. This value is considerably lower than the magnitude of difference in the SSA and volume of mesopores by these two methods. Therefore, we can deduce that the effect from thermal strain is negligible.

The microstructure of C-S-H is very sensitive to the moisture content [20]. The drying of the surface water in the electrical double layer will reduce the repulsive force between globules to drive the globules somewhat closer [20,66]. This induces the contraction of SGP and coarsening of LGP (see Fig. 6 and illustration in Fig. 11). Drying treatment also results in a reduction of the hydration and osmotic repulsion forces with the decrease in water films [90]. Therefore, the layer distance will decrease to increase the repulsion for creating a new balance between the attraction and repulsion. Change of colloidal distance reduces the connectivity of the gel pores and the accessible volume for N_2 . Furthermore, drying also induces new chemical bonds between globules or at the end of globules [91]. All these effects contribute to the difference in the PSD from water vapour and N_2 sorption, thereby causing an irreversible change of structure in hcp.

The equilibrium state of the sorption measurement impacts the obtained results. A typical C-S-H structure with Ca/Si of 1.65 in [74,75] has a basal space of about 11.8 Å. The free space in the interlayer is about 5 Å [1] in wet C-S-H, and the diameter of the C-S-H globules is about 3–4 nm [66,92]. Ideally, the diffusion at these dimensions may be dominated by Knudsen diffusion because Knudsen number ($=3/0.25$) is larger than 10 [93]. The kinetic diameters of N_2 and H_2O are 0.364 nm and 0.265 nm for this diffusion process [94], respectively. The severe drying will induce a collapse of the interlayer space by up to about 25 % (a contraction by 0.25 nm) [54–56]. The free layer distance is reduced to about 0.3 nm which is smaller than the kinetic diameters of N_2 . This explains why interlayer space is inaccessible for the N_2 , and this also means that N_2 cannot get access to the gel pores with an interlayer space neck (see Fig. 11). However, water can re-enter most of the interlayer [9] and hydrate the counterions to induce swelling of the interlayer space [20,52,95].

A mild drying method may make it possible to get a SSA by N_2 of about 100 m²/g for hcp at later ages [22,96], which is much closer to the SSA by water vapour compared with the large difference shown in Table 2. However, the difference in the PSD measured by water vapour and N_2 sorption still exists. Therefore, apart from finding methods to minimise the effect of drying, the reliability of N_2 sorption measurement

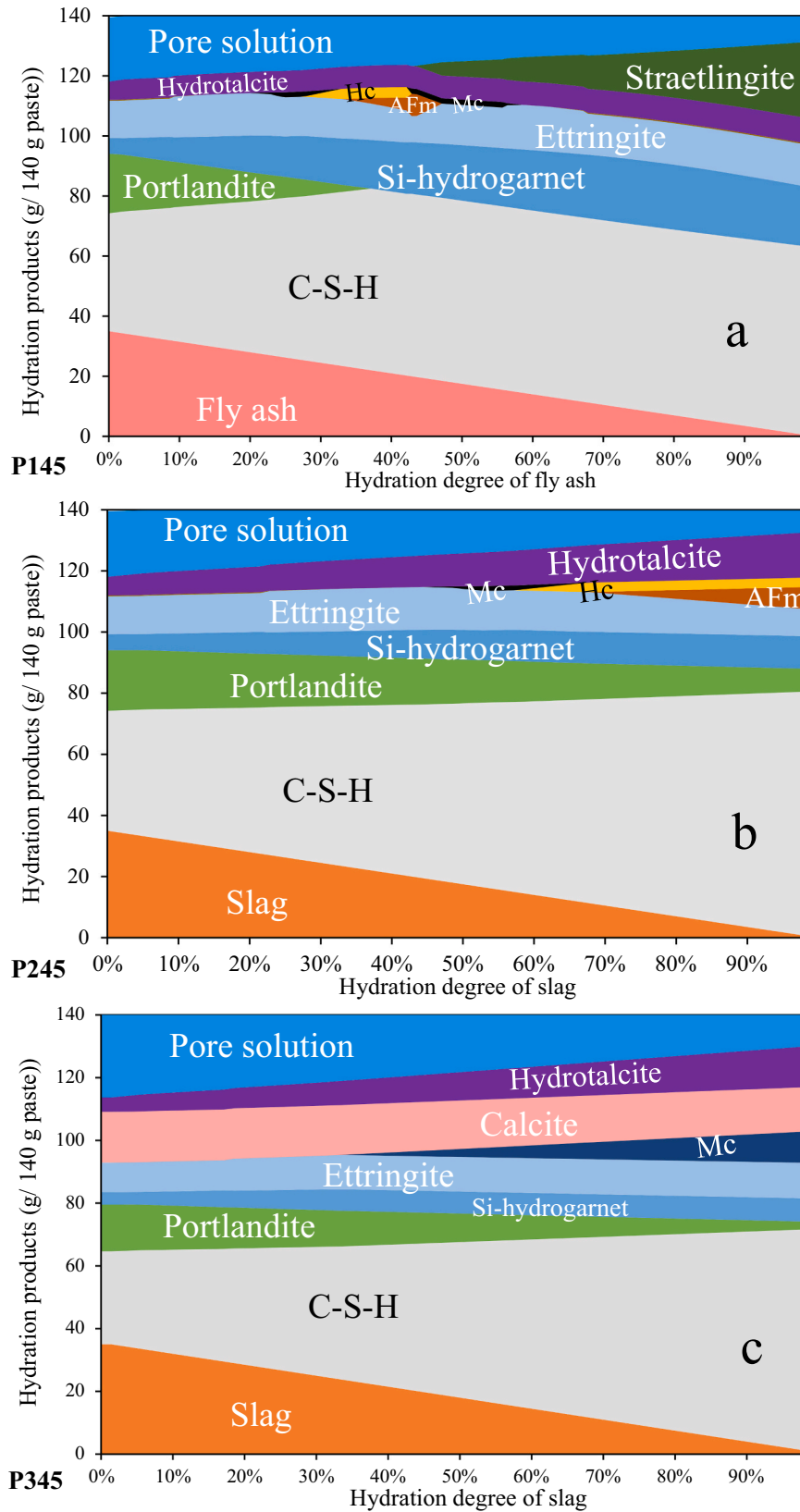


Fig. 8. Phase assemblage of hydration products with the increase in hydration degree of SCMs: a – FA blended binary system; b – SL blended binary system; c – SL and LL ternary system.

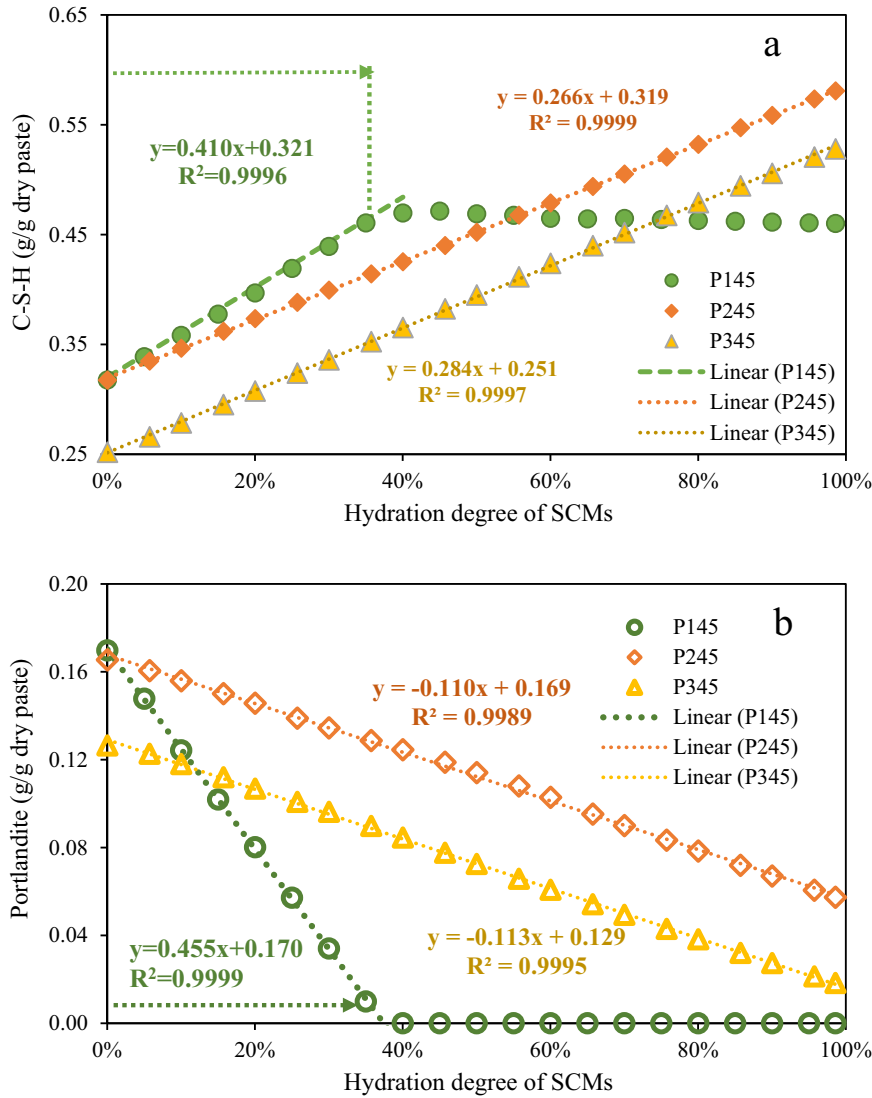


Fig. 9. The relationship between the amount of the main hydration products and hydration degree of SCMs: a – C-S-H; b – portlandite.

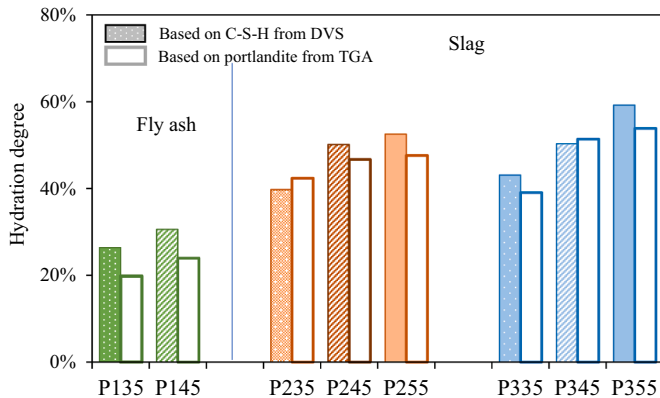


Fig. 10. Hydration degree of FA and SL in the blended hcp after a 6-month water curing.

can be increased by means of improving the equilibrium, such as adjusting the equilibrium time and decreasing the particle size of the sample [97].

4.2. The effect of SCMs

The replacement with SCMs (slag and fly ash) increases the volume of ink-bottle gel pores with small necks (see Fig. 6). Moreover, the hydration products of the SL blended pastes include some Mg-Al layered double hydroxide (LDH) [98] with a layer space filled with water but inaccessible for N_2 after drying. The adsorbed amount of water in LDH is significant because the content of evaporable water is about 40 % with respect to its dry weight [99,100]. These effects will induce a larger difference between the mesoscale pore structure of hcp measured by water vapour and that by N_2 sorption. Therefore, we can observe a higher difference in sorption of water vapour and N_2 in the SL hcp compared with CEM I hcp with w/b of 0.45 and 0.55.

The chemical composition of fly ash is rich in Al_2O_3 but lacks CaO. Blending of it will incorporate Al into the structure of C-S-H to increase the layer space [85,101]. Meanwhile, it will reduce the Ca/Si ratio markedly, so it results in reduction of counterions in the interlayer space (mainly Ca). The SSA of the well-crystallised 11 Å tobermorite (basal space of ~11 Å, Ca/Si of 1) measured by water vapour [101] is similar to the SSA measured by N_2 , with a value of about 76–78 m^2/g [102]. This implies that the contraction of the interlayer space in C-S-H is mainly due to the dehydration of counterions. The decrease in the interlayer Ca will reduce the contraction level of the interlayer space. Furthermore,

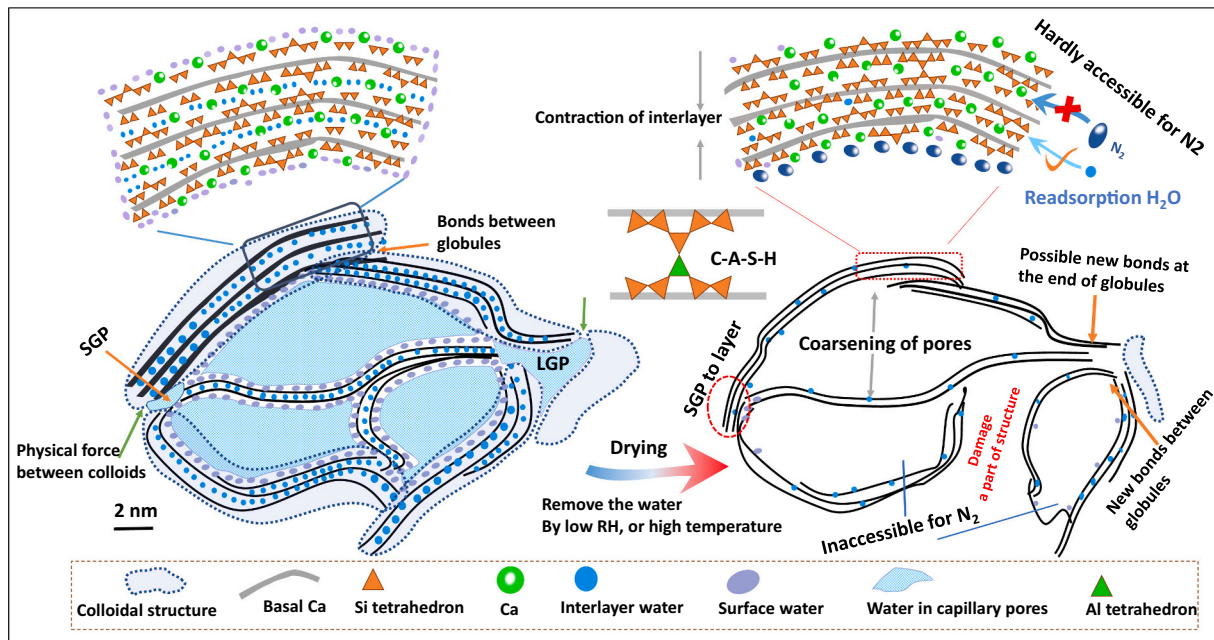


Fig. 11. Illustration of the effect of drying on the C-S-H structure and sorption difference in water vapour and N_2 .

incorporation of Al will induce some cross-connection between layers by Al ions (see Fig. 11), improving the crystallinity of the structure [103], which will also lower the contraction of the layers due to drying.

SCMs increase the volume of LGP and capillary pores (see Fig. 6). This reduces the contribution from the gel pores in the SSA of hcp, so it reduces the effect from SGP and the interlayer after drying. The increase in w/b increases the percentage of LGP and capillary pores as well. Therefore, we can observe the decrease in S_w/S_N not only after blending of FA but also with the increase in w/b .

4.3. Advantages and limitations in the proposed method

Compared with the previous methods for determining the hydration degree [33], the approach proposed in this paper is easy to perform without the use of advanced equipment if we use the saturated salt solutions for RH control. Furthermore, we can obtain a good indication of the pore size distribution by water vapour sorption. The evaluation of hydration degree of SCMs can be performed as simple as follow:

- Measuring the weight of samples after an equilibrium at 20 %–25 % RH.
- Afterwards, drying the samples under ~ 0 % RH or vacuum dry at room temperature (23–25 °C) to a constant weight.
- Using the moisture loss from 25 % to 0 % RH to calculate the content of C-S-H with Eq. (6).
- Performing a thermodynamic modelling to get the hydration products in the system with the increase in consumption of SCMs, and with a certain amount of hydrated clinker.
- Based on the correlation between hydration degree and C-S-H amount in thermodynamic modelling, we can feed the data in step c to obtain a practical hydration degree of SCMs.

However, if some SCMs have large influences on the hydration of clinker, a method needs to be coupled to evaluate the hydration degree of the cement clinker. This would benefit from further research on developing practical method to measure the unreacted clinker, such as extraction or selective dissolution. This method is strongly dependent on the database for thermodynamic modelling. We did not perform an accurate assessment of the effect of SCMs on the actual Ca/Si of the C-S-H. Slag and fly ash will reduce the Ca/Si in C-(A)-S-H to reduce the water

content in the interlayers. Ignoring this change leads to the underestimation of hydration degree due to the lower calculated C-S-H content based on water vapour sorption. This point will be improved because much research is ongoing to continuously enrich the thermodynamic database [37,81].

5. Conclusions

Dynamic vapour sorption and N_2 sorption isotherms have been used to investigate the effects of the water–binder ratio and SCMs on the mesoscale pore structure of cement-based materials. A novel approach is proposed for an effective evaluation of the hydration degree of SCMs based on water vapour sorption and thermodynamic modelling. Finally, a holistic discussion has been carried out to understand the large difference in the pore structure measured by water vapour and N_2 sorption.

SCMs markedly increase the moisture capacity of hcp at RHs above 50 % due to their effect of increasing the volume of large gel pores and capillary pores. Cavitation will occur during the desorption of water vapour at RH between 36 % and 30 %, which will induce an overestimation of the volume of the small capillary pores. However, the increase in the cavitation-induced value reveals part of the refinement effect of the SCMs. It is essential to include the effect of ions on the equilibrium pressure of water vapour on a plane surface when the BJH model is applied to calculate the pore size distribution. Replacement of CEM I by slag and fly ash increases the volume of both small and large gel pores, and this effect is most evident at the lowest w/b (0.35 in this study). The dilution effect from SCMs provides essential extra water for reaching full hydration of the clinker. The estimated content of C-S-H in hcp reveals that the increase in w/b clearly promotes the hydration of SCMs at later ages.

Coupled with the thermodynamic simulation by GEMs, the amount of C-S-H calculated from water vapour desorption can be used to perform an effective evaluation of the hydration degree of SCMs. This method can be easily operated without use of expensive equipment, and a reasonable hydration degree of SCMs can be obtained as long as a reliable thermodynamic data are available for the binders being investigated. Steps for how to perform this method are illustrated in final section.

A large difference can be observed between the pore structure of hcp measured by water vapour sorption and N_2 sorption. This is mainly

derived from the effect of drying on the C-S-H structure and differences in diffusion kinetics. A severe drying treatment will induce a large contraction of C-S-H so that the interlayer channels are inaccessible for N₂. The underlying mechanism of the drying effect is illustrated by the colloidal globule model of C-S-H, and the effect of SCMs on the difference between water vapour and N₂ sorption has been comprehensively discussed.

CRedit authorship contribution statement

Liming Huang: Conceptualization, Methodology, Investigation, Data analysis, Writing-Original Draft, Writing-Review & Editing. **Luping Tang:** Methodology, Writing-Review & Editing, Supervision, Project administration, Funding acquisition. **Lars Wadsö:** Investigation, Writing-Review & Editing. **Ingemar Löfgren:** Investigation, Writing-Review & Editing. **Nilla Olsson:** Investigation, Project administration. **Zhenghong Yang:** Review & Editing, Supervision, Project administration.

Declaration of competing interest

We declare that there are no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Paper IV

Distribution and dynamics of water in the blended pastes unraveled by thermoporometry and dielectric properties

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Distribution and dynamics of water in the blended pastes unraveled by thermoporometry and dielectric properties

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ABSTRACT

Water distribution in hardened paste and its dynamics determine many properties related to durability. Moisture distribution was determined by thermoporometry and the vacuum drying. Dynamics of confined water were measured by broadband dielectric spectroscopy. Water in pores < 2.4 nm cannot form tetrahedral ice structure due to the geometrical constraints. The volume of unfrozen water (in interlayer and gel pores) decreases after the drying at all relative humidity levels. A server coarsening of gel pores occurs with drying between 75 % and 55 % RH. Fly ash, slag and limestone have limited effects on relaxation processes of silanol hydroxyl groups and interlayer water. However, they slow down the dynamics of water in small gel pores, due to stronger interactions between the water and the solid interface. This study clarifies the microstructural changes during the drying and the sensitivity of water dynamics to the chemical environment in C-S-H of blended pastes.

Keywords: Moisture distribution; Dielectric relaxation; Water dynamics; SCMs; C-S-H

1 Introduction

Water, one of the main ingredients for concrete production, is greatly involved in the reaction of cementitious materials. It has the function of a “carrier” to dissolve ions from mineral surfaces to form a solution which builds itself into the chemical structure of hydration products. Furthermore, it also plays a critical role in determining deterioration of cement-based materials by controlling transport properties [1,2] and corrosion reactions [3]. In addition, freeze-thaw induced damages [4,5] and alkali-silica reaction [6] are rather sensitive to the water confined in the porous matrix. Therefore, it is of great interest, both from scientific and practical perspectives, to have a clear understanding of the moisture distribution in the porous structure at different relative humidity (RH) conditions and how this affects water dynamics in nanopores of cement-based materials.

Supplementary cementitious materials (SCMs) are utilized in cement-based materials to reach the goal of reducing CO₂ emissions from the construction sector [7,8]. Incorporation of SCMs impacts the microstructure of hardened cement-based materials (hcp). Our previous investigation identified the effects of typical SCMs (fly ash, slag and limestone) on nanopore structure by water vapour desorption isotherms [9]. However, the sorption isotherm is the total moisture content in pores smaller than a critical value, and it cannot be used to characterize the detailed distribution of water in hcp at a specific relative humidity. Low-field nuclear magnetic resonance is widely used as a nondestructive method to quantify the spatial distribution of water in porous materials and the microstructure of calcium silicate hydrate (C-S-H) [10–13], but the application of this technique is limited to the investigation of white cement and some other selected materials. Because the presence of paramagnetic matter (such as Fe and Mn) increases the surface relaxation of water [14], which will interfere the quantitative description of geometry effects, it can hardly be used in detecting the pore size distribution of pastes with Portland cement and typical SCMs.

One alternative method to detect the water distribution under geometrical confinement is low-temperature differential scanning calorimetry (LT-DSC). Brun et al. [15] proposed a method, based on LT-DSC, defined as thermoporometry, to calculate the size of pores filled with a liquid by studying the thermodynamics of liquid-solid phase transformations in porous materials. Provided a nearly saturated condition, thermoporometry was well applied to investigate the pore size distribution of calcium sulfoaluminate cement pastes [16,17] and Portland cement mortar [18]. However, it has been found that extremely confined water can avoid crystallization at any temperature, given that the pore size (width < ~2 nm) is too small for water molecules to form a tetrahedral ice structure [19]. The interlayer space and small gel pores in C-S-H present this kind of size restriction. Water in such parts helps to understand the structure of C-S-H [11,20] and corresponds to the irreversible shrinkage [21]. A recent study named the interlayer space (< 1.4 nm) as rigid gel pores because their size and volume had few changes during the first drying and wetting [22]. The moisture distribution in hcp under different RH is a complex problem since the volume of nanosized pores show dynamical changes during the drying process. There was a debate about whether the volume of gel pores would be largely increased by drying under 85 % RH [23,24], in which the different criteria for classification of gel pores also elevated the contradiction in understanding the dynamic process. The concept of gel pores in hcp was originally proposed by T.C. Powers and T.L. Brownyard [25]. They classified the pores with the width < 2.7 nm as gel pores, which part of the pores is inside the gel-like products and is rather stable due to its size being lower than the limitation of nucleation of hydration products. H.M. Jennings [26,27] assigned the pores from

1 to 12 nm as gel pores based on a colloidal model of C-S-H. Different classifications were also proposed based on dynamics of water by proton nuclear magnetic resonance varying in the intervals between 1.5 and 5 nm [11,20,28]. LT-DSC may help to resolve some part of the puzzle about how moisture redistributes in gel pores during drying and thereby improving the understanding of the C-S-H structure.

The behavior of water in hcp at low temperatures, practically, determines the potential frost damage of cement-based materials. The phase transition of freezable water to ice induce hydraulic pressure by expelling the unfrozen water [29]. Moreover, a continuous cooling causes the cryo-suction process that drives the liquid towards the frozen sites [30]. These water migration processes are intimately related to the distribution of freezable and unfrozen water in the porous matrix as well as the dynamics of water confined in the nanosized pores. Confined water has distinguishing structural and dynamical properties that differs from bulk water [19,31,32]. Broadband dielectric spectroscopy (BDS) has been widely used in the investigation of water dynamics confined in C-S-H at low temperatures. However, the understanding of the dynamical behavior and the local confining condition of water in C-S-H are different in several papers. Cervený et al. reported [33] three relaxation processes of water in C-S-H gel that were assigned to be chemical bound water, water in small pore < 1 nm and large gel pore water, respectively. Garcia-Lodeiro et al. [34] also detected three relaxation processes but their interpretations of the three processes are somewhat different. Goracci et al. [35] found four relaxation processes, each one corresponding to different confining conditions, and they assigned processes 3 and 4 to water in small gel pores and large gel pores, respectively, by referring to Jennings's colloidal model [27]. A comparison between the relaxations in synthetic tobermorite and xonotlite provided a more detailed description of the fastest relaxation processes of water in calcium silicate hydrate systems [36]. Overall, there is a lack of a general and comprehensive understanding of water dynamic confined in hcp, and it is short of investigations of how SCMs influence the distribution and dynamics of water.

This study used LT-DSC to quantitatively describe the distribution of water confined in different pores after drying at various equilibrium conditions. Insights will be provided for the distribution of water in capillary pores and gel pores in relation to freezable and unfrozen (supercooled) water. BDS was used to investigate the dynamics of water confined in the hcp. Different relaxation processes will be shown to correspond to local chemical environments of the C-S-H microstructure, and we provide a comprehensive understanding of how the water dynamics is affected by its local environment. The effect of SCMs on the distribution of water confined in pores, as well as the dynamics of water, is elucidated for improving the

understanding of how the microstructure in the blended pastes and the drying process are related to water dynamics.

2 Materials and methods

2.1 Preparation of samples

Detailed information of materials and mixing procedure can be found in a previous publication [2]. Table 1 shows the binder mix in this paper. Portland cement (CEM I 52.5 R) was used as reference (noted as P045). Binary systems were made by replacing cement with 35 % siliceous fly ash (P145) and 35 % slag (P245), respectively. In the ternary system (P345), cement was replaced by 35 % slag and 16 % limestone. All the binder systems were mixed with a water to binder ratio of 0.45. After one week of sealed curing, the samples were crushed into particles smaller than 1 μm and then water cured for two months. Afterwards, particles were moved into conditioning boxes with four different RHs (97.6 %, 75.5 %, 54.4% and 33 %) controlled by saturated salt solutions at 20 °C [37]. Portlandite was put on the top layer of each conditioning box as absorbent of CO_2 to avoid carbonation of pastes. All the measurements were operated for samples after 1.5 years of conditioning. The total evaporable water content in the hardened pastes was measured by vacuum drying of particles at 25 °C for 1 week.

Table 1 Binder mix of each sample

Sample name	P045	P145	P245	P345
Mix by weight	100 % CEM I	65 % CEM I+35% fly ash	65 % CEM I+35% slag	49 % CEM I+35% slag+16 % limestone

2.2 Low temperature differential scanning calorimetry

LT-DSC measurements of powder samples were performed using the TA instrument DSC Q2000. Samples with a weight of about 20 mg were put in hermetical sealed aluminum pans. The samples were firstly cooled from 20 °C to -60 °C with a rate of 2 °C/min, and then equilibrated for 5 min before reheated to 20 °C with the same rate. Samples conditioned at 97 % RH were measured with a second cycle using the same protocol. To better compare the signals of the different binder systems, a normalization was done to obtain a similar starting point of all curves for better comparison. A mimic pore solution was made by adding 150 mmol/L KCl and 50 mmol/L NaCl into the extracted pore solution of CEM I paste with a water-binder-ratio of 1, and it was then measured with the same temperature procedure for evaluating the heat of fusion of the pore water in hcp.

2.3 Broadband dielectric spectroscopy

The well-conditioned particles were ground to a powder prior to testing. The complex dielectric permittivity of the powder samples was measured by a broadband dielectric spectrometer

(Novocontrol Alpha-N) in the frequency range 10^{-2} – 10^6 Hz. Isothermal frequency scans were performed at temperatures from -147.15 to 26.85 °C (130–300 K) with an increment of 5 °C (K). The sample temperature was controlled with a deviation lower than ± 0.1 K. Parallel gold-plated electrodes with a diameter of 10 mm were used to tightly hold the powder samples (about 0.5 g). The thickness of each sample was ~ 0.2 mm.

3 Results and discussion

3.1 Thermoporometry analysis of LT-DSC

According to the thermodynamic properties of water-ice phase transformation, the relationship between pore size and solidification temperature can be described by the Gibbs-Thomson equation [15,18]

$$r_p = \frac{A}{\Delta T_s} + \delta \quad \dots\dots\dots (1)$$

where r_p (nm) is the radius of the cylinder pore, ΔT_s (°C) is undercooling compared to the melting point of bulk ice crystals. A is a constant determined by the surface energy between water and cement-based material. δ is a constant related to the layer thickness of unfrozen water and the pore shape. The shape of the pores is normally assumed to be cylindrical. Parameters A and δ have been taken as 64.67 and 0.57 for the freezing process, and 32.33 and 0.69 for the melting process [18].

Based on a comprehensive consideration of the baseline for LT-DSC and the differences in the heat capacity of the different phases (liquid, ice crystals and porous body), the amount of ice formation at different temperatures can be calculated by Eq. (2) [18].

$$m_c(T + n\Delta T) = m_c(T) + \sum_1^n \frac{\Delta T}{2} \left[\frac{Q(T+n\Delta T - \Delta T) - Q_0}{qh_f} + \frac{Q(T+n\Delta T) - Q_0}{qh_f} \right] \exp \left[\frac{\Delta T(C_{pC} - C_{pL})}{h_f} \right] \quad \dots\dots (2)$$

where $m_c(T)$ is the ice mass at temperature T with respect to the original sample weight, ΔT is the temperature interval (selected to be 0.02 °C in this study), h_f (J/g) is the heat of fusion for pore water, $Q(T)$ (W/g) is the heat flow into the sample, Q_0 (W/g) is the heat flow of baseline, q (°C/s) is the heating rate, C_{pL} (J/g/°C) is the heat capacity of the pore liquid and C_{pC} (J/g) is the heat capacity of ice crystals. The heat of fusion of the pore solution was obtained by measuring the DSC curve of the mimic pore solution, as described in section 2.2. The heat capacity of the pore liquid and the ice as a function of temperature is described by Eq. (3) and (4), respectively. The temperature dependence of the density of ice (ρ_i) is given by Eq. (5) [15].

$$C_{pC} = 2.114(1 + 3.737 \times 10^{-3}T) \quad \dots\dots\dots (3)$$

$$C_{pL} = 4.222(1 - 5.4 \times 10^{-4}T) \quad \dots\dots\dots (4)$$

$$\rho_i \approx 0.9167 - 2.053 \times 10^{-4}T - 1.357 \times 10^{-6}T^2 \dots\dots\dots (5)$$

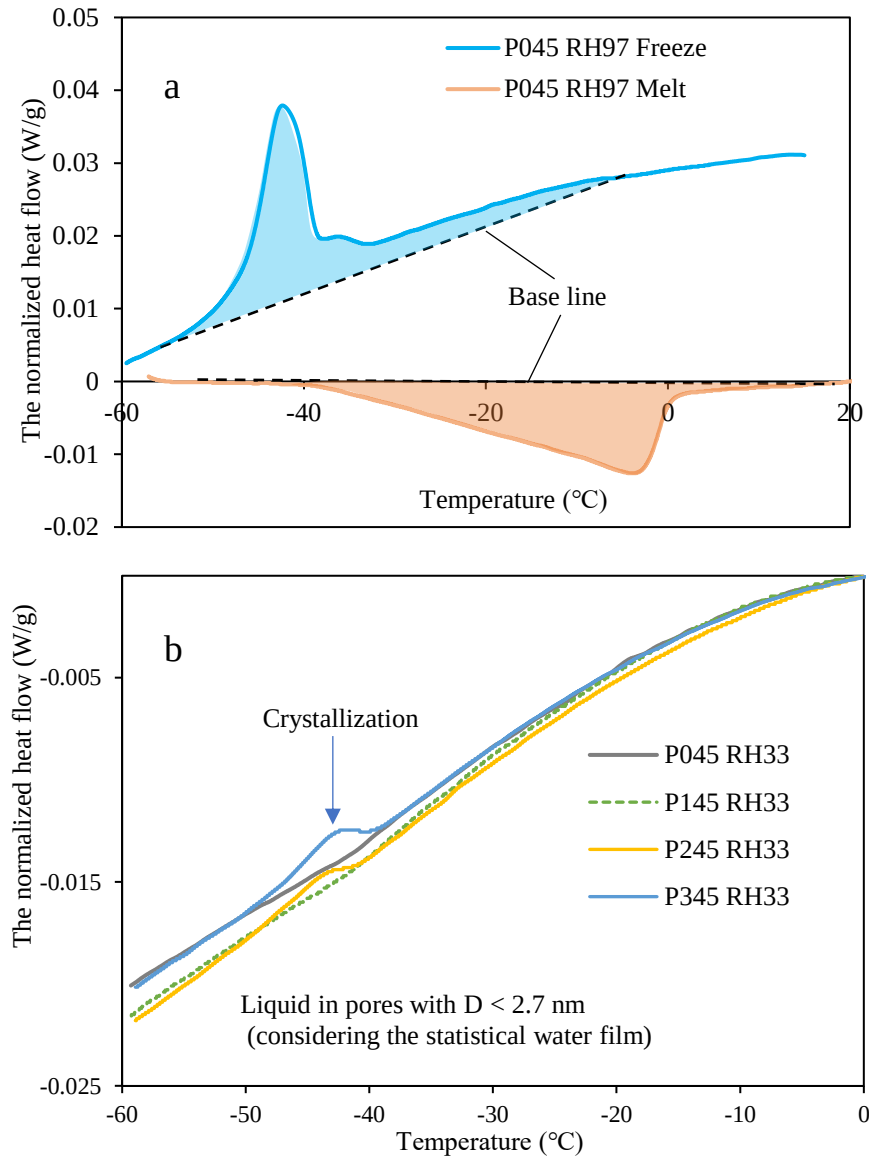


Fig. 1 Typical low temperature DSC curves of cement-based materials, exemplifying with CEM I paste conditioned under RH of 97 % (a) and pastes conditioned under RH of 33 % (b). In (a), the upper curve shows the results of cooling and the lower the heating curve. In (b), the results of cooling.

As shown in Fig. 1a, the baseline of LT-DSC, on cooling, is described by a straight line from the freezing start to about -55 °C. The baseline of the heating curve, i.e., showing the the melting process, is horizontal and normalized to be about 0 W/g. A significant hysteresis can be observed in the freezing-melting curve of hcp. The average melting temperature is considerably higher than the average freezing temperature, which is in agreement with the freezing and melting of water in many other porous media [38]. This is mainly because of a geometrical hindrance effect from the pore shape, making crystallization more difficult. The attractive potential from the pore walls also induces a compression effect, so the competition between the hindrance and compression results in a non-monotonic correlation between the

freezing temperature and the pore diameter [39]. An extreme confinement (pore diameters less than about 2 nm) will even inhibit the water molecules from forming ice crystals [19]. Sun and Scherer [18] concluded that there was no freezing in pores with a width smaller than 4.5 nm. Bager and Sellevold [40] reported that no ice was formed in hardened cement paste equilibrated at RH of 33 and 11 %. No exothermic peak was detected in white cement paste at 33 % RH [41] as well. Fig. 1b shows no indication on crystallization of water in P045 and P145 at RH of 33 %, but crystallization is detected in the slag blended pastes (P245 and P345) equilibrated at the same RH. This interesting result may be induced by the refined ink-bottle shape of pores with small necks [9]. During the drying process, it may be difficult to dry the inner parts of these pores. It may also due to the expelling of water from interlayer or small nanosized pores to larger pores during the cooling process, which is similar to the freezing process of montmorillonite [42]. Further experiments are needed for an in-deep understanding of this phenomenon.

Fig. 2a shows the calculated distribution of ice volume in cement paste under different RHs using Eq. (2). Due to the low amount of crystallization in hcp in equilibrium with 33 % RH, the curves of these samples are not presented. As expected, the volume of ice in hcp decreases as it is dried at lower RHs. The hysteresis of the freezing and melting process is observed under all RHs. After the calculation of the cylinder pore width with Eq. (1), the hysteresis in freezing and melting data is more evident based on the difference in the lowest pore width for the formation of ice crystal. The freezing curves seems to imply that the critical pore width is about 4 nm, so it seems to imply that no ice formation in pores smaller than this value. However, a crystallization peak was detected in silica nanopores with diameters of 3 nm [43]. Molecule dynamic modelling also indicated that the critical size for the nucleation of ice is with a gyration radii of 1 nm [44]. The pore size based on the melting curve has a critical value of 2.4 nm, so it is obvious that curves during melting are more reasonable for evaluation of the water distribution inside hcp. The hysteresis becomes weaker in hcp conditioned at lower RHs.

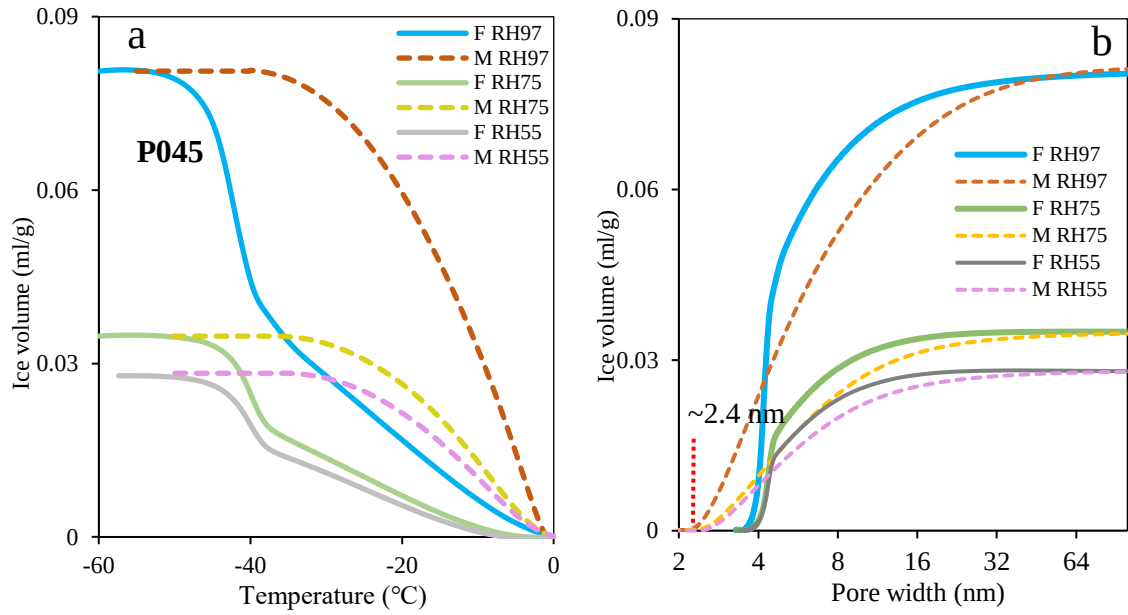


Fig. 2 The calculated ice volume in P045 conditioned with RH of 97 %, 75 % and 55 % using Eq. (3) (a) and the corresponding ice volume in nanopores based on Eq. (1) (b) with respect to freezing (noted as F) and melting (noted as M) process.

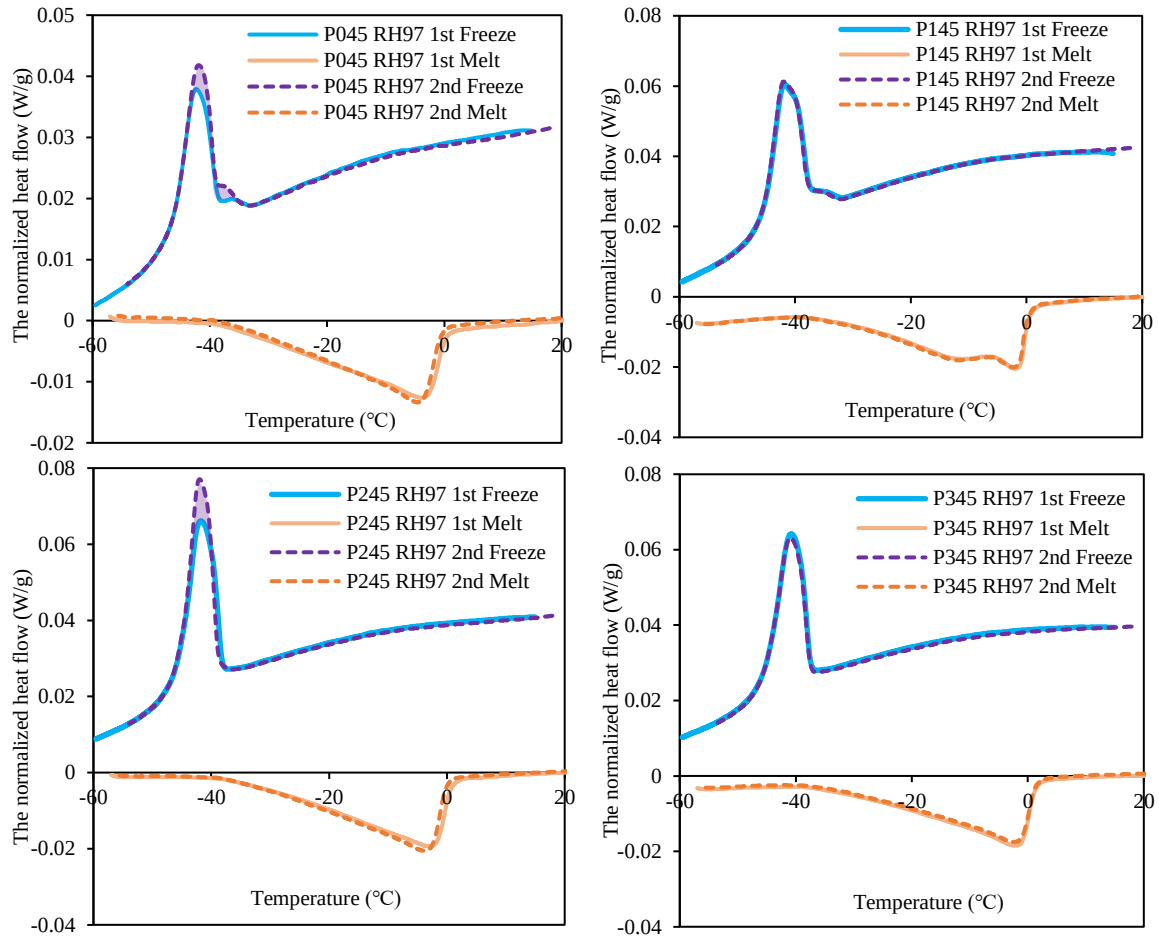


Fig. 3 Effect of cyclic freezing and melting experience on the DSC curves of hcps.

An exposure of cement-based materials to low temperatures will change the microstructure of the matrix [45], which impacts the mechanical performance [5]. To assess the effect of the rather quick LT-DSC measurement on the distribution of water, a second freezing-melting scan was performed immediately after the first. Fig. 3 shows that the second LT-DSC scan is almost identical to the first one for P145 and P345, indicating a reversible behavior of the distribution of water in those materials. However, the first freeze-thaw cycle induces an increase in the freezable water content in P045 and P245, as clearly seen from the increase of the crystallization enthalpy in the second scan. This is probably due to the expelling of interlayer water into gel pores during the freezing. P045 and P245 have a higher C-S-H content than the other two in a well-hydrated condition [9]. Moreover, incorporation of Al in the C-S-H structure will stabilize the layer structure [46] to mitigate the effect of drying as well as freezing. The combination of these effects causes the difference in the moisture redistribution in hcp under the freeze- thaw process, However, also for P045 and P245 the LT-DSC results show that there are generally only weak irreversible effects on the moisture distribution.

3.2 Effect of SCMs on the moisture distribution during the first drying

Supplementary cementitious materials impact the phase assemblage of hydration products, change the size and total volume of pores, as well as influence the durability of these materials [47]. Fig. 4 presents a comparison of the ice formation in the different binder systems, based on both freezing and melting data. The distribution of freezable water in the pores is important since it determines the frost performance of the cement-based materials [5,48,49]. During the drying process, water confined in pores of different sizes would also influence the diffusion of moisture [2] and the shrinkage in hcp [50].

Compared to the pore size distribution calculated using water vapour sorption data, Fig. 4 presents clearer information about the distribution of moisture at each RH. The fly ash blended paste has the highest ice content at 97 % RH. Most of the differences occur for the water confined in pore sizes from 4 to about 8 nm, which can be observed in both the freezing and melting curves. The melting curves show that slag binary paste seems to have somewhat lower content of water confined in pores from 3 to 8 nm, but a higher water content in pores larger than 8 nm, compared to the fly ash blended paste. The CEM I paste has the lowest ice formation in all ranges of pores. These findings are somehow consistent with the measured moisture content by water vapour isotherms [9] and the pore size distribution in the same mixes with different curing conditions [2]. A further replacement of CEM I with limestone reduces the freezable water content compared to the binary slag paste.

The initial ice formation temperature of paste at 97 % RH is lower than that temperature of paste at 75%, and a drying from 97% to 75% RH results in a clear reduction in the volume of ice formed in pastes. This phenomenon was observed not only in cement-based materials [40] but also for water in porous silica materials [43]. Fly ash blended paste has a much lower content of ice than the slag blended pastes at 75 % RH. This implies that a large part of the freezable water dried in the fly ash paste from 97 % RH to 75 % RH, resulting in the fly ash blended paste with a similar amount of ice as the CEM I paste. Several publications reported that an appropriate amount of fly ash mixed into concrete can effectively improve the freeze-thaw durability [48,51]. The freeze-thaw performance is actually directly related to the volume of freezable water in hcp, so the saturation condition is a critical factor for a given mix [49]. Therefore, it is important to consider the saturation conditions in correspondence to service environment when investigating the effect of fly ash or slag [52,53] on freeze-thaw properties. When exposed at a moderate water-saturation environment (such as XF1 and XF2 in EN 206-1), the paste with 35 % fly ash may have the best freeze-thaw resistance at a RH of 75 % due to its low amount of freezable water and high amount of air-filled pore volume. While exposed to a high water-saturation environment (such as XF3 and XF4 in EN 206-1), it may have the worst frost performance due to its high volume of freezable water at 97 % RH.

At RH of 55 %, the distribution of freezable water in the fly ash blended paste is almost the same as that of the CEM I paste. At the same RH, slag blended pastes have formed a much higher amount of ice than the other two binder systems. This can be explained by the effect of slag on the pore structure, which increases the volume of pores in range from 4 to 10 nm (noted as gel pores in [54]). However, it is apparent that the drying process is not just emptying water from larger to smaller pores. Rather, water in all size ranges of pores is affected by drying, and this will be detailed in next section.

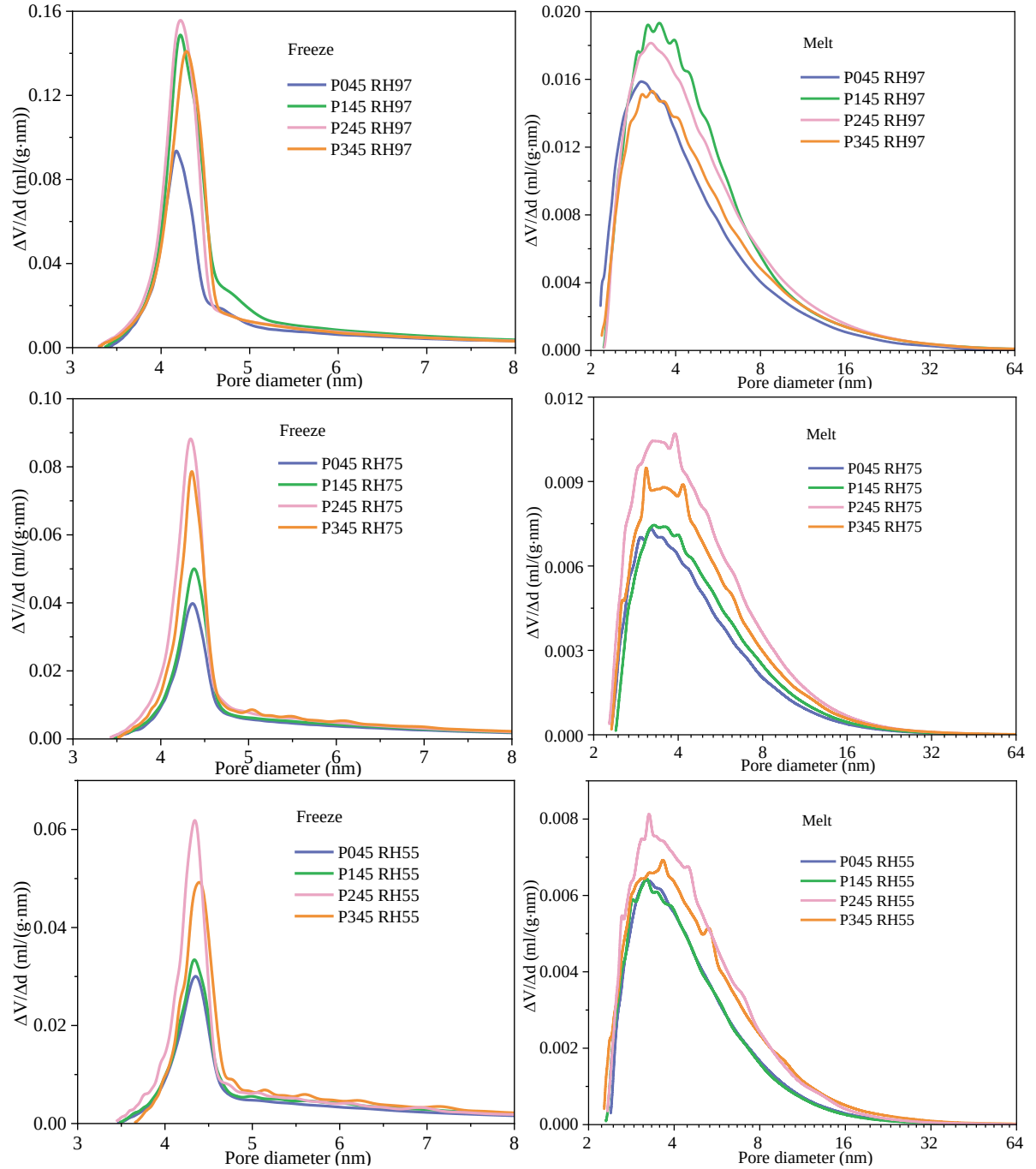


Fig. 4 Comparison of the calculated distribution of ice in all pastes conditioned at RH of 97 %, 75 % and 55 %. The distributions are obtained from both the freezing (left panels) and melting process (right panels).

3.3 Distribution of water under different RHs

Drying of cement-based materials causes microstructure change of the main hydration products, such as contraction of layer and coarsening of capillary pores [9,55,56]. This dynamical change of the structure may induce an anomalous evolution of moisture redistribution, thereby increasing the portion of water in small pores while drying the large pores [57]. Fig. 5 demonstrates the contents of freezable and unfrozen (supercooled) water in the cement-based pastes at different RHs after the first drying process. Water in pores with a diameter smaller

than about 2.4–2.7 nm cannot form ice crystals [19,43,44,58], so water in such confinements is not giving rise to any crystallization or melting peaks in the LT-DSC data. This unfrozen part of the water was calculated by subtracting the volume of freezable water from the total evaporable water content measured by vacuum drying.

Compared with samples at a RH of 97 %, drying to 75 % RH mainly decreases the freezable water content in hcp. The unfrozen water content shows a minor decrease, which keeps almost constant in P045, P145 and P245. Referring to the definition by H.M. Jennings [27], the water in interlayer and small gel pores (SGP) show few changes, and the main drying occurs in large gel pores and capillary pores. However, the criteria for classification of gel pores vary in different references as shown in Table 2. According to T.C. Powers and T.L. Brownyard [25], the unfrozen water is exactly the water in gel pores, whereas in classification based on other publications it includes both water in interlayer space and gel pores [11,20,28,57,59]. It has been a heated discussion about whether the drying of cement-based materials induces an increase in the content of “interlayer water” at a RH of ~80 % [23,24,57]. The “interlayer water” in the previously discussed papers is based on proton NMR relaxation measurements, and referred to water in pores < ~3 nm [13,20]. This part of the water accounts for most of the evaporable water in hcp at a RH of 80 %. It is an extreme confinement, and therefore it is expected to be of the same amount as the unfrozen water. According to the distribution of unfrozen water, the drying at a RH of 75 % presents no increase in volume of water under such a confinement in both CEM I and the blended pastes.

Table 2 Summary of the criteria for classification of gel pores in representing publications.

References	Assigned interval for gel pores
T.C. Powers and T.L. Brownyard [25]	< 2.7 nm
I. O. Yaman et al. [59]	0.5 to 4 nm
H.M. Jennings [27]	1 to 3 nm (SGP) and 3 to 12 nm (LGP)
P.J. McDonald et al. [28]	1.5 to 4.1 nm
A.C.A. Muller et al. [13,20]	3 to 5 nm
A. Valori et al. [11]	2 to 5 nm
Ippei Maruyama et al. [24]	1.87 to 3.4 nm, $\sim 5.35 \pm 0.63$ nm

It is interesting that the hcp dried at a RH of 55 % has a much lower content of unfrozen water than those dried at a RH of 75 %. It seems that the amount of freezable water shows a very small reductions from 75 % to 55 % RH, especially in the blended pastes. A drying down to 55 % RH causes a contraction of the layer distance in C-S-H [57,60,61], and decreases the statistical thickness of the surface water layer [9]. Moreover, the water removal process induces a movement of some C-S-H sheets, which results in a coarsening of gel pores [23,56,62].

Together, these effects give rise to that the volume of freezable water at 55 % RH is similar to that at 75 %. This implies that the coarsening of gel pores evidently occurs during the drying within this RH interval. Provided that pores in hcp show no dynamical changes, the drying at 75 % and 55 % RH corresponds to empty open pores with a diameter larger than ≈ 8 nm and ≈ 4 nm, respectively, according to the Kelvin equation. H.M. Jennings et al. [63] hypothesized that water in this range is closely related to the structure of low-density C-S-H, and the rearrangements of microstructure within this RH range was associated with irreversible shrinkage. Therefore, the redistribution of this part of water is significant to understand the correlation between microstructure change of C-S-H and properties of cement-based materials. An equilibrium at 33 % RH dries out vast majority of the freezable water, but it causes a slight increase in the amount of unfrozen water in the blended hcp compared with the hcp at a RH of 55 %. This can be ascribed to the transformation of some gel pores into the interlayer spaces [57]. Drying at 33 % RH may also induce the piling of C-S-H [64] to form more surface area for absorbing unfrozen water.

Fig. 6 illustrates the detailed distribution of evaporable water in hcp during the first drying. The water distribution has been classified into four intervals: < 2.7 nm, 2.7–10 nm, 10–20 nm and > 20 nm, and the amounts of evaporable water in these ranges were obtained by combining data of the melting curve in Fig. 4 with the amount of unfrozen water in Fig. 5. The data of P045 and P145 show that the amount of water confined in interlayer and gel pores change during the drying at any RH condition. It is again confirmed that the water in interlayer and small gel pores (< 2.7 nm) never shows an increase during the first drying process under equilibrium. Water in capillary pores is almost completely dried out at 75 % RH. In addition, there is a loss of more than half of the water in large gel pores (2.7–10 nm) [27], also named interhydrate spaces [13,20]. At a RH of 55%, only a small fraction of the water contained within these pores is lost, in contrast to a RH of 75%. The main loss is detected for water in interlayer and small gel pores (< 2.7 nm). A drying at 33 % RH completely removes the water in large gel pores (> 2.7 nm). A minor increase in the amount of unfrozen water can be understood as a result of C-S-H sheets movement.

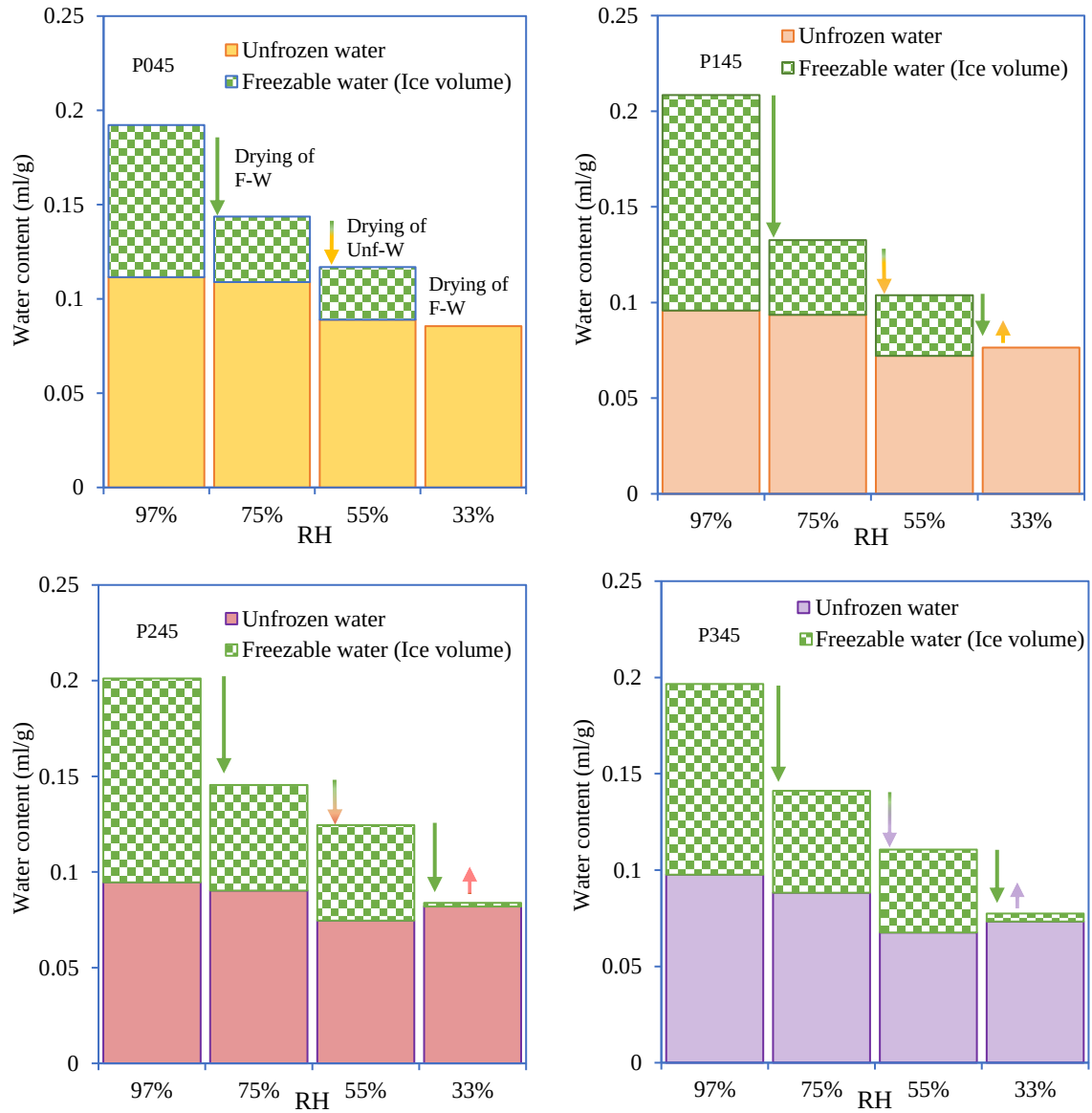


Fig. 5 Moisture distribution in hcps during the desorption process indicated by the reduction of freezable water (F-W) and unfrozen water (Unf-W).

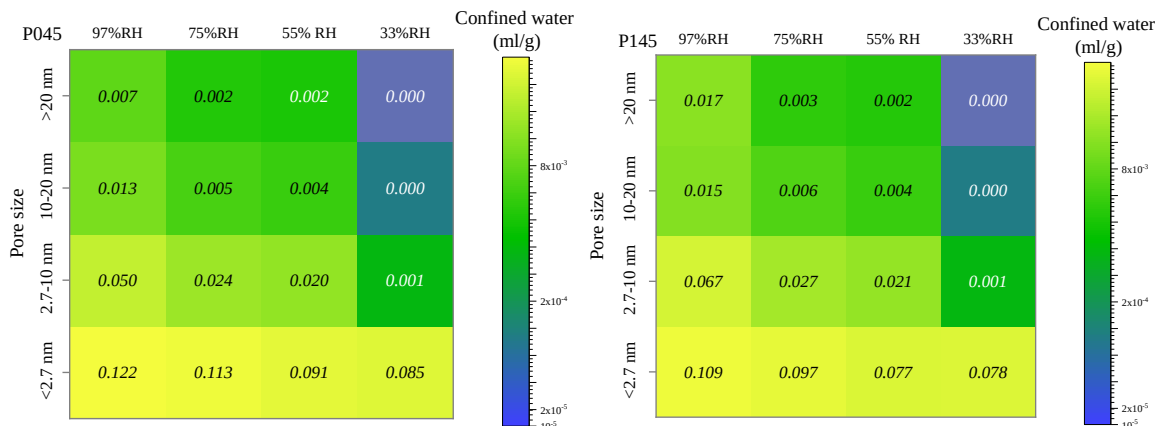


Fig. 6 Moisture distribution in hcps during the desorption process indicated by the reduction of freezable and unfrozen water, exemplified by P045 and P145.

3.4 Dynamic of the confined water in hardened paste

Electric polarizability of water in nanosized regions relates to the local chemical environment, which determines the strength of water-mediated intermolecular forces. It affects various properties of a material, such as surface hydration, ion solvation, molecular transport through nanopores and chemical reactions [65,66]. The frequency-dependent dielectric response of water in hcp is influenced by the confinement condition as well as the temperature of the material [33,67,68]. A spatial confinement on a nanoscale alters the molecular dynamics of water by affecting dipolar rotations and reorientations. Fig. 7 shows how the dielectric permittivity depends on the frequency and temperature in a BDS measurement. Five relaxation processes (R1 to R5) can be detected for hcp at a RH of 97 %.

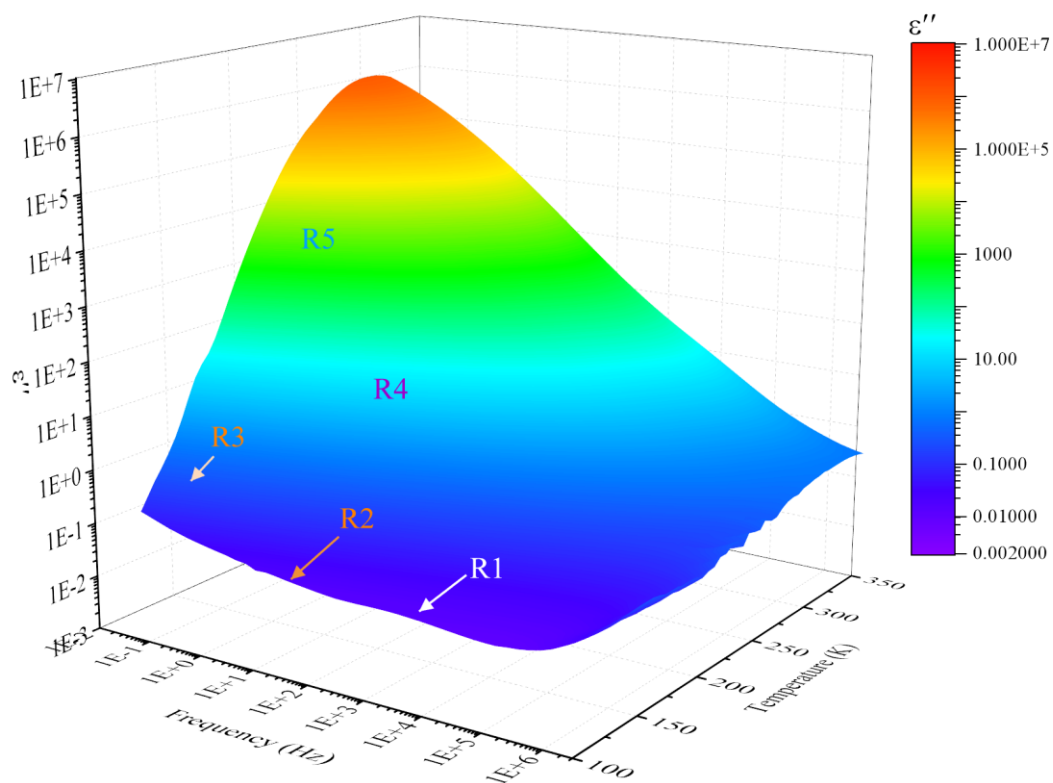


Fig. 7 Typical three-dimensional temperature and frequency dependences of the dielectric permittivity ϵ'' of hcp heated from 130 K to 350 K (exemplified by P045).

Because the dielectric processes have a symmetric shape, the Cole-Cole function [69] has been applied to fit the imaginary part of the dielectric permittivity at the different temperatures, as shown in Eq. (7).

$$\epsilon^* = \epsilon_{\infty} + \frac{\Delta\epsilon}{1+(i\omega\tau)^{\alpha}} \dots\dots\dots (7)$$

where $0 < \alpha \leq 1$ leads to a symmetrical broadening for the relaxation function, compared to a Debye relaxation (which corresponds to a single exponential relaxation in time domain). $\Delta\epsilon$ is

the relaxation strength, and ε_∞ is the dielectric constant at “infinite frequency”. ω is the angular frequency, ε^* is the complex dielectric permittivity, and τ is a generalized relaxation time.

As an example, Fig. 8a presents the fitting results of the P045 sample at three selected temperatures. Fig. 8b to 8d demonstrate the temperature dependence of the relaxation time, broadening parameter, and relaxation strength of each relaxation process. The relaxation process 1 (R1) is fastest and has the lowest activation energy. This process was found even in C-S-H dried at 120 °C [33], and it was hypothesized to arise from rotation/reorientation of hydroxyl groups bound to the structure. Musumeci et al. [36] performed a comparative study of xonotlite and tobermorite to distinguish the dynamics of Ca-OH and Si-OH environments, and showed that hydroxyl groups bound to the Ca atom have a faster dynamics and lower activation energy than those bound to Si. According to this, the R1 process in Fig. 8b has the characteristics of hydroxyl in Si-OH environment. The broadening parameter of R1 stays almost constant from 130 to 170 K, while its relaxation strength shows a minor increase after 150 K.

Relaxation process 2 (R2) was also reported in many previous investigations of water confined in synthetic C-S-H and Portland cement pastes [33,35,36,70]. This is the second fastest process and it is due to the strong local interactions of water with surface groups and charge compensating cations. The local chemical environment of water molecules consists of solvation/hydration water close to the hydroxyl groups and near the charge compensating cations (Ca or Na). Vasilyeva et al. [71] claimed that this process was not observed in glass materials, so it was assumed that R2 reflected the water molecules near hydrated cations located in the interlayer of clay materials. However, this process has been found in silica matrices MCM-41 [72,73] and in tobermorite [36] where there are no interlayer cations existing. Therefore, a more reasonable interpretation is that R2 is due to the dynamics of water molecules hydrating the silanol groups [74] or water confined in small pores less than 1 nm [33]. This process is very sensitive to the local environment, which indicates that the presence of different cations will impact its dynamics.

Relaxation process 3 (R3) has a broadening parameter of about 0.5, and its relaxation strength ranges from 0.5 to 4 (see the values for other samples in the Supplementary Information, SI). This process is considered to be an “universal” relaxation process of confined water, as it is present in all kinds of confinements [19]. In fact, it is even present in amorphous bulk ice (or supercooled bulk water) [75], which indicates that it is an intrinsic local relaxation of water molecules and not substantially affected by interactions with surfaces or types of molecules or ions. However, this relaxation process is somewhat affected by a reduction in the number of

hydrogen bonds between the water molecules, particularly in the case of hydrophilic host materials [76]. Water confined in pores from 1 to about 2.4 nm is inhibited to form a network structure of tetrahedrons by building four hydrogen bonds for each molecule, but these molecules may form small clusters connected by more than single hydrogen bond [33]. Fig. 9 presents a comparison of the dynamics of water in fly ash blended paste (P145) in equilibrium at 97 % and 33 % RH, together with data of bulk ice relaxation from Refs. [77,78] for comparison and a better understanding of the different types of water in hcp. R3 in hcp is close to the dynamics of ice in tri-propylene glycol solution [78]. At low temperatures, the ice is also occupying a large volume of the pores in hcp at a RH of 97 %, so R3 may also include the relaxation of crystalline ice. However, it is not only due to the relaxation of ice as it is also observed in the hcp at a RH of 33 %, in which there is almost no water crystallization, as measured by LT-DSC (see Fig. 1 and Fig. 5). R3 in P145 at a RH of 33 % is slower than that at a RH of 97 %, and it is located between R4 and R3 in hcp at a RH of 97 %. Thus, the “universal” process R3 most likely becomes slower with drying at lower RH due to a stronger interaction with the pore surfaces. R1 is slower at a RH of 33 %, compared to 97%, while R2 is more or less unaffected. Both R1 and R2 are probably due to local reorientations of water molecules which take part of the structure in C-S-H, and therefore these dynamical processes are not substantially affected by the total water content in the samples.

Relaxation process 4 (R4) is not detected in P145 at a RH of 33 %, which implies that this process is very sensitive to the moisture content. It was once assigned to the relaxation of water in large gel pores (3–12 nm) [35]. However, most of the water in these pores will crystallize to form ice and liquid water may exist only above a temperature of about -50 °C (see melting curve in Fig. 1 and 3). It is apparent that R4 is observed at the temperatures lower than the melting temperature and the relaxation strength remains almost constant at temperatures above the melting (see Fig. 8). Instead, it is more likely due to a Maxwell–Wagner process, which is related to interfacial polarization between liquid and solid faces [73]. The broadening factor of a uniform Maxwell-Wagner process is 1. However, this process in hcp has a broadening factor in range from 0.65 to 0.75, which implies a wide range of pore size distribution. The saddle-like temperature dependence of the relaxation time at higher temperatures ($1000/T$ in the range 3–4) is ascribed to the loss of evaporable water in the matrix. This somehow can explain why R4 is missing for samples at a RH of 33 %, since the drying of water in gel pores will decrease the interfacial area between liquid and solid and instead increase the area of the air-solid interface. Relaxation process 5 (R5) is the slowest process and it occurs in the dielectric spectrum at temperatures above the onset of melting obtained by LT-DSC. Furthermore, its relaxation strength is anomalously high (see Fig. 8 and figures in SI). A similar relaxation in

clay materials was explained to be due to the percolation of diffusing charge carriers in connected pores [71]. However, a further investigation is needed for better understanding this relaxation process, and it will not be further considered in this study since it is unlikely related to water dynamics.

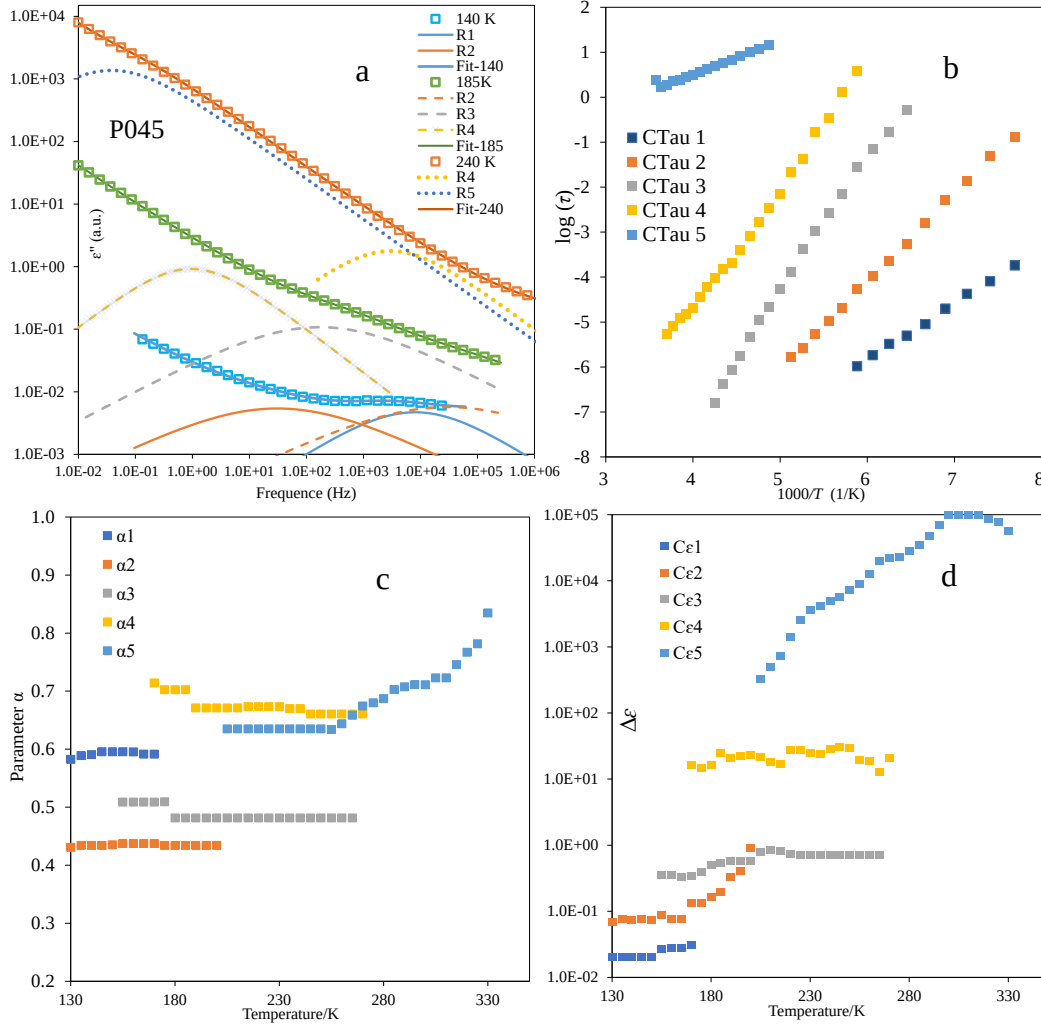


Fig. 8 Display of the general fitting of relaxation data of P045 with RH of 97 %: Graph a – Match between the fitted line and the measured results; Graph b – The generalized relaxation time at different temperatures; Graph c – Broadening parameter α at different temperatures; Graph d – Strength of dielectric relaxation.

The relaxation times of the different relaxation processes obviously depend on the temperature. Two common equations are used to describe the temperature dependence. The first one is the Arrhenius equation [79], and it is given by:

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right) \dots\dots\dots (8)$$

where τ_0 is the pre-exponential time constant, E_a is the activation energy of the relaxation process, and k_B is Boltzmann constant. The Arrhenius temperature dependence is typical for more local and non-cooperative relaxation processes, often denoted as β -relaxations.

The second equation is called the Vogel-Fulcher-Tammann (VFT) equation [31,80], and it is given by:

$$\tau = \tau_0 \exp\left(\frac{DT_0}{T-T_0}\right) \dots\dots\dots (9)$$

where D is a parameter related to the fragility (how much the temperature dependence deviates from an Arrhenius dependence), and T_0 is the temperature at which the dynamics of the system diverge to an infinitely slow relaxation time. The VFT temperature dependence is typically observed for cooperative relaxation processes as the viscosity related structural relaxation, commonly denoted as the α -relaxation.

Fig. 9 shows that the dynamics of structural water (R1 and R2) is a β -process with an Arrhenius dependence. The supercooled water confined in the gel pores seems to have a VFT dependence at relatively high temperatures. This fragile-to-strong crossover (from VFT to Arrhenius) is commonly occurring for supercooled water confined in a hydrophilic porous matrix [19,32]. R4 also has an Arrhenius dependence in the temperature range below 250 K. All the fitting results for the relaxation processes with an Arrhenius behavior are presented in Table 3, which will be further discussed in next section.

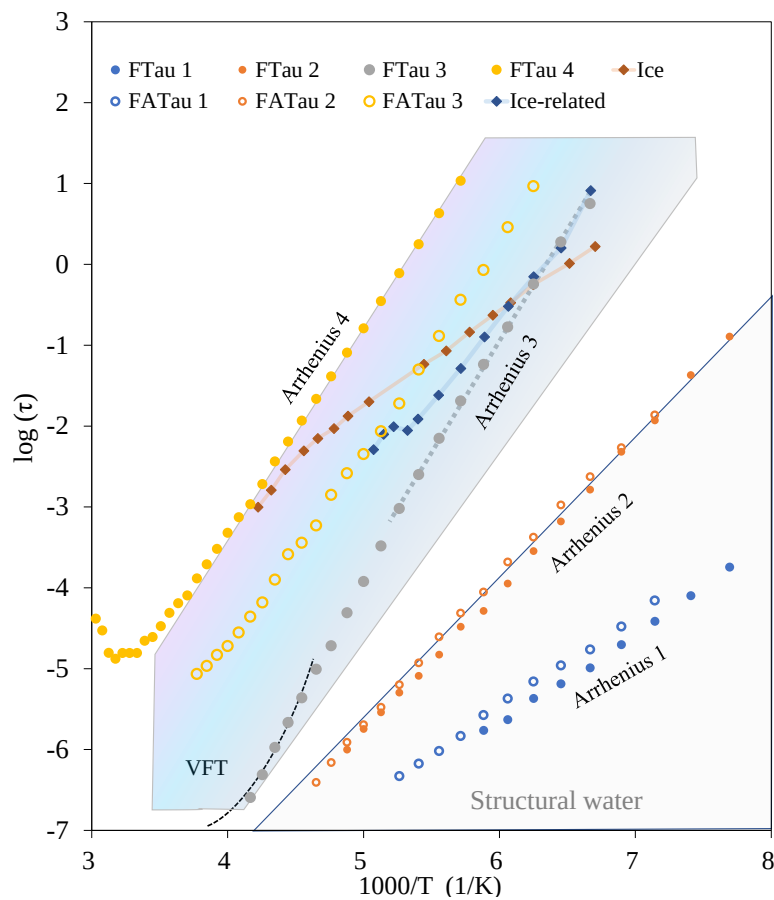


Fig. 9 Comparison between the relaxation times of P145 at a RH of 97 % (FTau*) and 33 % (FATau*). Data of an ice relaxation is adopted from, ice l_h [77] and an ice-related relaxation in frozen tri-propylene glycol solution [78] are shown for comparison.

3.5 Effect of SCMs on the water-related relaxation processes

[Fig. 10](#) presents a comparison of the relaxation times of the water-related processes in hcps with different binder systems. Blending of SCMs has small effects on the broadening parameter (see SI) and the relaxation time of the structural water, but it changes the relaxation strength of R1 and R2. The blended hcps have a much higher relaxation strength than the CEM I paste for R1 (see [Fig. S1](#)). It is well recognized that the blending of slag and fly ash will reduce the Ca/Si ratio of C-S-H [81,82]. The structure of C-S-H with a lower Ca/Si ratio has a higher content of OH attached to the Si atoms [83]. Furthermore, both fly ash and slag will increase the amount of Al incorporated in the structure [84], which may increase the layer distance of the calcium aluminosilicate hydrate. These dual effects induce a larger number of water molecules attached to the silanol groups, thus resulting in the highest relaxation strength of R2 among the four binder systems below 160 K. Garcia-Lodeiro et al. [34] also reported that decalcification of C-S-H had almost no effects on the relaxation time of these two processes but changed the relaxation strength of each process. The fly ash blended paste dried at 33 % RH has a much lower relaxation strength than that at 97 % RH for both R2 and R1 (see [Fig. S2](#) in SI), but their relaxation times are almost the same. This confirms that a change of the interlayer water content has minor effects on the dynamics (relaxation times) of R1 and R2.

The CEM I paste has the fastest R3 and R4 relaxations among the hcps. A high concentration of Na^+ and OH^- will attract water to form a hydration shell, which weakens the hydrogen bonds of these water molecules and even decreases the average number of hydrogen bonds for the water molecules [85]. The concentration of alkali ions and the pH of the pore solution is determined by the composition of binders and the solubility of ions. For the binders used in this study, the CEM I paste has the highest concentration of alkali ions [86], so this may be the reason for its fastest water dynamics. The Maxwell–Wagner process, also called interfacial relaxation, originates from the existence of free charge carriers inside the system. These carriers migrate under the applied electrical field and accumulate at the interfaces in the system to induce polarization [87]. SCMs will impact the surface structure for water adsorption [9] as well as the concentration of ions. Therefore, both the relaxation time and strength of R4 are altered by the blending of SCMs. Blending of SCMs will make R4 slower, and as shown in [Fig. 10](#), this effect is most pronounced for fly ash. The relaxation strength of R3 is not necessarily determined by the amount of water molecules in pores between 1 and 2.4 nm, because it is a result of the hydrogen bond relaxation [76,88], and therefore proportional to the total number of hydrogen bonds. This may explain why the CEM I paste has the lowest strength of R3 (see the SI), although it has the highest amount of unfrozen water (see [Fig. 5](#)).

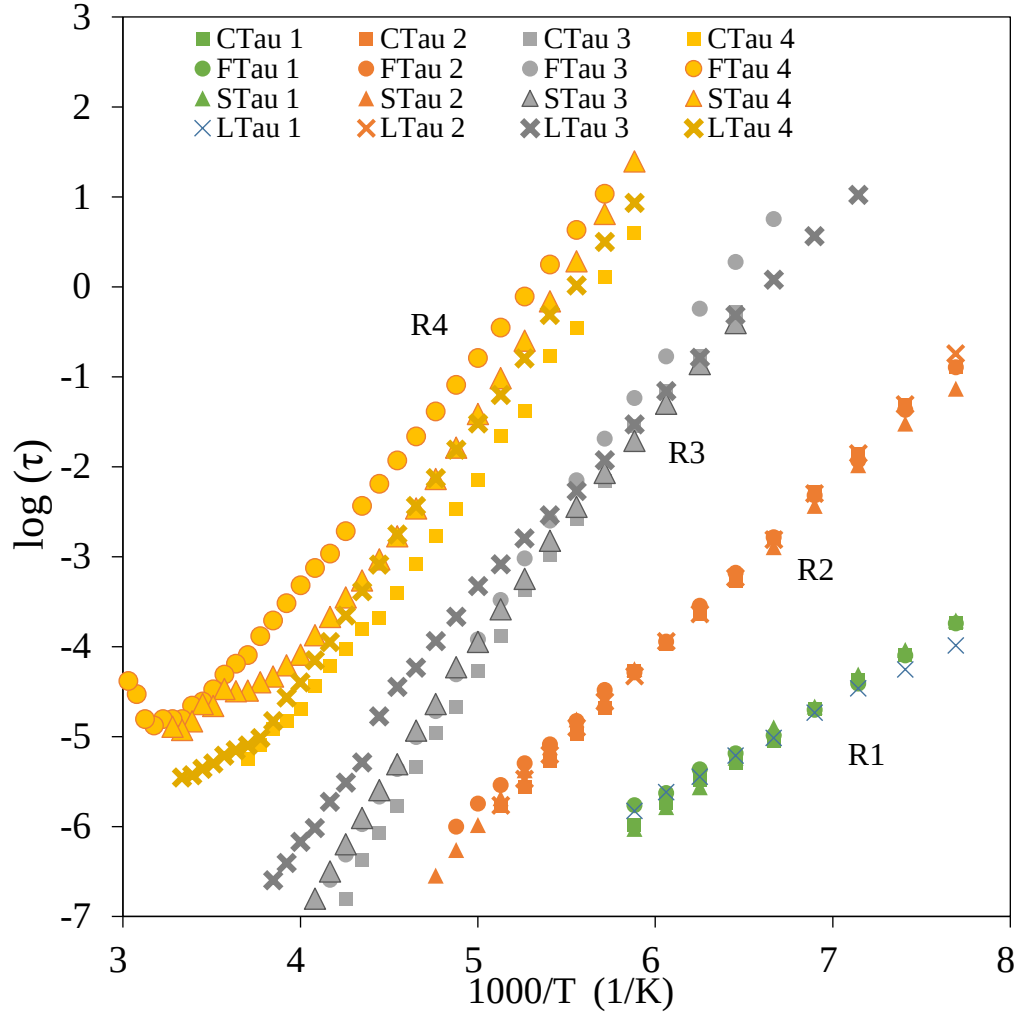


Fig. 10 Comparisons of the relaxation times of processes in hcpS at a RH of 97 %, including CEM I paste (CTau*), the fly ash blended paste (FTau*), the slag binary pastes (STau*) and the ternary paste (LTau*).

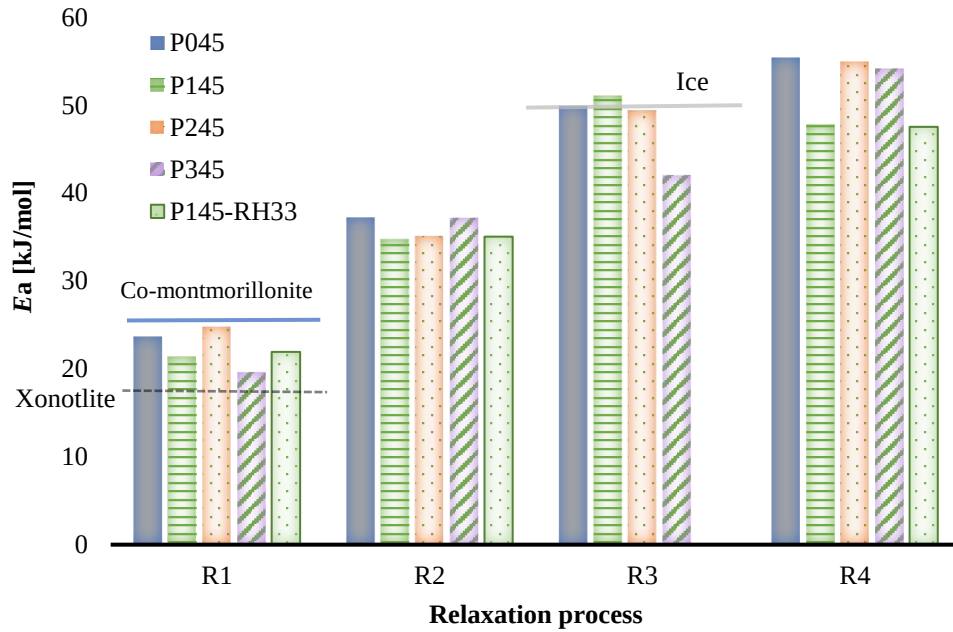


Fig. 11 Activation energies (E_a) of the different water related relaxation processes in hcpS.

Table 3 shows a comparison of fitting parameters obtained by using Arrhenius equation to describe the temperature dependence of the relaxation processes, and Fig. 11 presents a comparison of the regressed activation energies. The activation energy of R1 is in a range of 19.65–24.85 kJ/mol. Those values are higher than the activation energy of the Si-OH relaxation in xonotlite (17.28 kJ/mol or 0.18 eV) [36] but lower than the activation energy of the a similar relaxation in Co-montmorillonite (25 kJ/mol) [71]. The addition of fly ash and limestone does not have any significant influence on the activation energy of R1, although there is a slight increase in $\log(\tau_0)$. Similarly, drying P145 at 33 % RH has little effect on the activation energy and $\log(\tau_0)$ of the structural water, compared to the paste conditioned at 97 % RH. The activation energy of R2 remains relatively constant across all binder systems, ranging from 34.79 to 37.42 kJ/mol. The characteristics of R2 are quite similar to process 2 in synthetic C-S-H [34] and tobermorite [36]. The activation energy of R3 is close to the activation energy of glassy bulk water, also called amorphous ice, (45 kJ/mol [76]) but lower than the activation energy of the hexagonal crystal ice (ice I_h) (~ 50 kJ/mol [77,89]). Fly ash slightly increases the activation energy of R3, probably due to the lower ion concentration in the pore solution. The effect of slag on this process is mainly present at high temperatures, in the non-Arrhenius regime, but at lower temperatures P245 has a similar activation energy and $\log(\tau_0)$ as P045. Replacement of CEM I with limestone and slag reduces the activation energy. Fly ash causes a lower activation energy of R4 compared to the CEM I paste. Slag has a small effect on the activation energy of R4, but it increases $\log(\tau_0)$.

Table 3 Fit parameters by using the Arrhenius equation to describe the temperature dependences of the water related relaxation processes in hcpS at a RH of 97% and P145 at a RH of 33%

Mix ID	Relaxation	slope (k)	$\log(\tau_0)$	R^2	E_a (kJ/mol)
P045	R1	1.237	-13.25	0.998	23.67
	R2	1.946	-15.78	0.999	37.24
	R3	2.607	-17.02	0.996	49.90
	R4	2.896	-16.52	0.997	55.42
P145	R1	1.119	-12.39	0.998	21.41
	R2	1.818	-14.89	0.999	34.79
	R3	2.671	-16.97	0.998	51.11
	R4	2.500	-13.29	0.999	47.84
P245	R1	1.297	-13.63	0.997	24.82
	R2	1.836	-15.11	0.998	35.13
	R3	2.582	-16.91	0.996	49.41
	R4	2.870	-15.68	0.996	54.92
P345	R1	1.027	-11.85	0.998	19.65
	R2	1.944	-15.73	1	37.20
	R3	2.196	-14.50	0.994	42.02
	R4	2.831	-15.68	0.999	54.17
P145RH33	R1	1.146	-12.36	0.998	21.93
	R2	1.832	-14.85	0.999	35.06
	R3	2.484	-14.68	0.998	47.53

4 General discussion

4.1 Structure of the unfrozen water in interlayer and gel pores

The term "water" typically refers to a liquid phase; however, at temperatures below the glass transition temperature (which value is still debated, see in Ref. [76]), glassy water can exist. Despite being a solid, its structure displays a disordered arrangement similar to that of the liquid state [90], and as seen in this and other papers it also exhibits comprehensive local dynamics, as even crystalline ice phases do. Since bulk water instantaneously undergoes crystallization to ice below approximately 235 K, water in confined geometries has been employed as a model to reveal the structural and dynamical properties of bulk water in the deeply supercooled regime [19]. The potential correlation between supercooled confined water, glassy water, and amorphous bulk ice has been thoroughly discussed in various studies [76,91,32]. Fig. 12 illustrates the heat capacity of CEM I and fly ash paste during the cooling process from room temperature to -150 °C. There is no signal for any glass transition of unfrozen water in hcp at 33 % RH, in consistency with all types of confined water [91]. Only concentrated bulk aqueous solutions exhibit a glassy transition, resulting in a significant reduction of the heat capacity between -100 and -145 °C, as shown in Fig. 12 for some solutions [92,93].

It has been discovered that unfrozen water in C-S-H exhibits reactivity. A substantial portion of the water present in the pore space of the C-S-H gel dissociates to form Ca-OH and Si-OH groups [94]. The hydroxyl groups present in these structures exhibits the fast R1 relaxation. Water in disconnected small pores shows an ice-like behavior, causing a hydraulic increase in the C-S-H shear strength.

The structure of water confined in C-S-H nanoslits with a size $< \sim 2.5$ nm is largely affected by the hydrophilic surface. According to molecular dynamics simulations [95], the hydrophilicity of the C-S-H nanopore space is due to nonbridging oxygen atoms on disordered silicate chains. These serve as hydrogen-bond acceptors, directing hydrogen atoms of interfacial water molecules towards calcium-silicate layers. The water in this space has a distinct multirange structure: a distorted tetrahedral arrangement within 2.7 Å and a disordered arrangement resembling similar to dense fluids within 4.2 Å [95]. Such water structure results in the second fastest relaxation of water, R2. The activation energy of supercooled water confined in small gel pores indicates the dynamics of water clusters with a reduced number of hydrogen bonds [33]. According to modelling results the average number of hydrogen bonds in bulk water is approximately 3.6 per water molecule. However, for water molecules confined in C-S-H the average number of hydrogen bonds is typically as low as 2.34 [95].

The absence of a glass transition in confined water may be attributed to the limited volume, preventing cooperative rearrangements of water molecules into an ice-like tetrahedral network structure [91]. The suggested glassy structure of water in C-S-H layer [95] is expected to have the observed Arrhenius temperature dependent dynamics at low temperatures, while the crossover to a VFT behaviour at about 225 K (see Fig. 10) [33,96] suggests that the dynamics becomes more fluid-like and cooperative in character above that temperature.

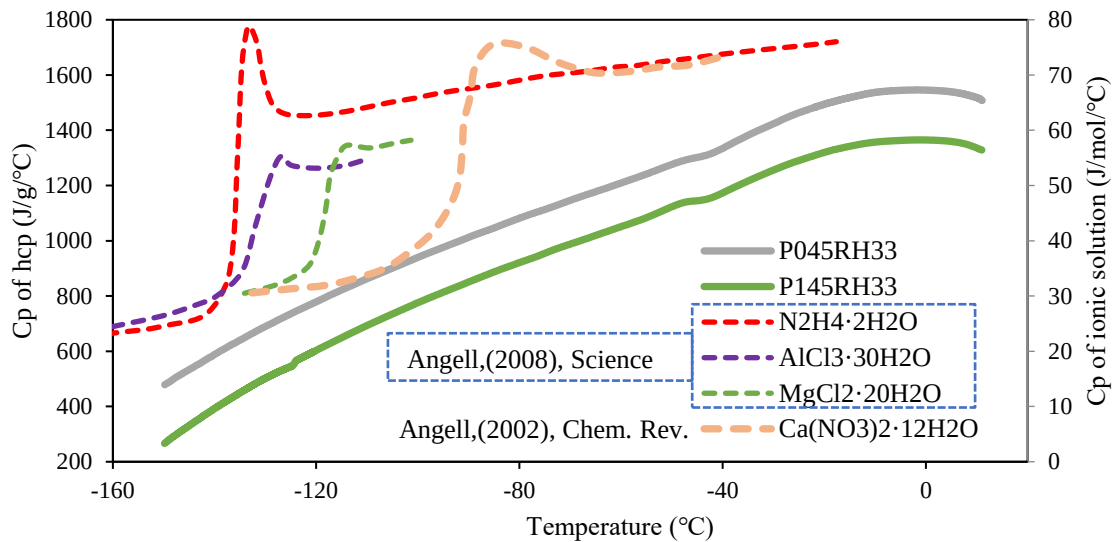


Fig. 12 Heat capacity of P045 and P145 at a RH of 33 % compared to the heat capacity of concentrated aqueous solutions reported in published papers [92,93].

4.2 Effect of SCMs on the water dynamics and distribution

Blending of SCMs modifies the pore size distribution in hcps so the moisture capacity becomes different from CEM I pastes [2]. Fly ash results in the highest moisture content among hcps at 97 % RH. The disparities are mainly observed for the liquid confined within pores in large gel pores (a size range of approximately 4 to 8 nm). The binary paste with slag has a slightly smaller volume of water confined in the gel pores, but a larger volume of water in capillary pores (>8 nm) compared to the paste blended with fly ash. In all pore size ranges, the CEM I paste exhibits the least ice formation. These results align with the outcomes of water vapour desorption [9]. When cement is partially replaced by limestone, the amount of freezable water decreases even further compared to slag binary paste.

SCMs increase the amount of frozen water but reduce the amount of unfrozen water. Drying conducted at 75% RH showed no increase of water confined in small gel pores (< 2.4 nm) in both CEM I and blended pastes. The main loss occurs in the volume of unfrozen water during the drying between 75% and 50% RH, which can be attributed to coarsening of gel pores leading to a redistribution of water. The slag has the smallest reduction of unfrozen water, but

it presents the largest increase in unfrozen water during a drying from 50 % to 33 %, which may be due to its unstable structure during the drying at low RH.

Three kinds of relaxation dynamics have been detected for the unfrozen water in hcps. The impact of SCMs on the relaxation time of structural water is found to be very limited in this study. In addition, it is well acknowledged that blending slag and fly ash modifies the structure of C-S-H [81,82], and reduces the Ca/Si ratio to increase the number of H atoms attached to the nonbridging oxygens [83]. Therefore, the blended pastes have a higher relaxation strength of R1 compared with CEM I pastes. Furthermore, fly ash largely elevates the quantity of the incorporated Al in the structure [84], potentially increasing the layer distance of calcium aluminosilicate hydrate. These two effects result in the highest number of water molecules attached to the silanol group, thus leading to the highest relaxation strength of R2 among the four binder systems below 160 K.

It has been observed that SCMs have a significant impact on the relaxation properties of water molecules in gel pores, changing the relaxation time and strength of R3. This can be attributed to the lower concentration of alkali ions in the pore solution of SCMs blended pastes compared to CEM I, which attracts water molecules to form a hydration shell and thereby reducing the average number of hydrogen bonds between those and neighboring water molecules [85]. Furthermore, the blending of SCMs can also affect the surface absorption of water near the pore walls [9] and the concentration of ions, leading to changes in the relaxation time and strength of R4. Therefore, it is important to consider the impact of SCMs on the relaxation properties of water molecules and its relation to the transport of ions when designing cementitious materials.

4.3 Limitations

An exposure to low-temperature enforces effects on the microstructure of the layered materials [42] as well as the C-S-H [45]. Although Fig. 3 shows that only few irreversible effects were observed during the fast DSC scan procedure, an understanding of how the reversible change impacts the moisture distribution will determine the reliability in assessing the moisture distribution in hcps by the thermoporometry method. This study used thermoporometry to perform a comparative investigation between different binder systems. Therefore, it is worth noting that the discussion is partially based on the assumption that the influence of low temperatures on the microstructure is similar across mixes with different binders. One additional point to consider is that relaxation process R3 encompasses both the dynamics of unfrozen water and ice. It is challenging to distinguish these two processes in the dielectric

relaxation curve. A combination of other methods, such as quasi-elastic neutron scattering and NMR, may be helpful for a further investigation of the nature of the water dynamics [97].

5 Conclusions

Moisture in hardened cement-based paste would redistribute due to the dynamic microstructural change during the drying process. Blending of SCMs impacts the moisture redistribution and the dynamics of water confined in nanoscale pores to alter the performance of cement-based materials. The main findings in this study can be summarized as below.

During the fast low-temperature differential scanning calorimetry measurement, there are almost no irreversible changes of water distribution in the fly ash and ternary pastes. Thermoporometry works well in characterizing moisture distribution in cement-based materials at various RH conditions. The melting curve is better than the freezing curve for evaluation of water distribution in hcp. It enables to measure the water confined in pores larger than ~ 2.4 nm. No matter freezing down to any temperature, water in pores smaller than the critical value, including the interlayer and a part of gel pores in C-S-H, will not form a tetrahedral ice structure due to the limited number of hydrogen bonds. However, this part of water can be measured by a combination of the LT-DSC and vacuum drying test.

SCMs influence not only the moisture distribution in hcp equilibrated at 97 % RH, but also the redistribution of water during a serial drying down to 33 % RH. It is confirmed that the fly ash binary paste contains the highest moisture content among all mixes, and its moisture loss during a drying at 75 % RH is the largest. The amount of unfrozen water in hcps is reduced by the SCMs, but the slag blended pastes have a higher volume of freezable water compared with CEM I paste equilibrated at the same RH. The presence of limestone in ternary pastes has a reducing effect on the freezable water content potentially to improve the frost performance of concretes.

A drying at 75 % RH lowers the part of the unfrozen water in both CEM I and the blended pastes compared to that at 97 % RH. This figures out some puzzles in the discussion of dynamical pore structure changes during the first drying between different publications [23,24,57]. This study confirms that the drying process has no increasing effect on volume of pores < 2.7 nm, at least not at equilibrium conditions. The sever coarsening of gel pores occurs during the drying between 75% and 55 % RH, which results in the phenomenon that the volume of unfrozen water has a considerable loss during this interval. A drying at 33 % RH causes an increase in the volume of unfrozen water due to the microstructure change of the C-S-H gel.

Five dynamical relaxation processes have been detected, and four of which are related to the water dynamics. The two fastest processes are dynamical behavior of the structural water in C-S-H, corresponding the hydroxyl in Si-OH (R1) and water confined in the interlayer space (R2). SCMs have few effects on relaxation time of these two processes. The third fastest process (R3) is ascribed to the relaxation of water molecules with reduced hydrogen bonds and mixed with the ice relaxation and is altered by the SCMs, which probably is due to the dilution effect on ion concentration in the pore solution. The fourth process (R4) derives from the interfacial polarization between the liquid and solid, and SCMs slow down this process. These results would update the understanding of change C-S-H microstructure during the drying process and the mechanism of how SCMs affect the water and ion transport in the nanosized channels.

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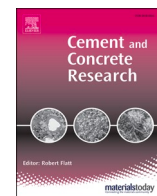
Paper V

Moisture and ion transport properties in blended pastes and their relation to the refined pore structure

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Moisture and ion transport properties in blended pastes and their relation to the refined pore structure

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ABSTRACT

This paper presents a study of the moisture transport properties in blended pastes measured by a new procedure and setup. The dependence of moisture transport coefficient on relative humidity (RH) is confirmed. The differences in the moisture dependency may be due to discrepancies in the critical RH for the percolation of liquid. Fly ash and slag increase the percentage of mesopores or “ink-bottle” pores with a mesoscale neck and they strongly reduce the pore connectivity in pastes. These effects cause the evident reduction in the moisture and chloride diffusivity. The additional replacement with limestone filler has little effect on the pore connectivity. The formation factor controls the moisture transport at the high RH interval, but the volume of small pores (middle capillary and mesopores) is the major determinant at a low RH interval. The relationship between water-binder ratio, pore structure and moisture transport or chloride migration coefficient is discussed.

1. Introduction

Moisture content and transport properties in cement-based materials are essential parameters during the construction and long-term use of concrete structures. The humidity conditions in concrete substrate before applying a covering material is directly related to the risk of moisture damage and mould growth [1]. Moreover, these properties of cement-based materials make an impact on the transport of CO₂, O₂ and chloride ions in concrete, which determines the deterioration process of reinforced concrete structures [2,3]. Reliable moisture transport parameters are critical for not only ensuring the appropriate construction schedule but also the accurate prediction of the service life of concrete structures.

The transport of condensable vapors through a microporous substance is a complex process that involves vapor diffusion, surface diffusion, condensation, evaporation, and flow of liquid and depends on the RH in materials [4]. The condensation and evaporation rates may be negligible compared to the diffusion process [5], but the volume of pores with the condensed liquid determines the connectivity of empty pores that influences the diffusion process. The condensed volume of water

(namely, the moisture content) relates not only to the microstructure in cement-based material but also to the ion concentration in pore solution [6]. The blending of supplementary cementitious materials (SCMs) is efficient in reducing CO₂ emissions in the cement industry [7], so an increasing amount of fly ash, slag, limestone, and calcined clay has been blended into cement to produce more sustainable concrete. SCMs modify the microstructure [8–10] and the pore solution in cement-based materials [11], leading to different moisture and ion transport properties compared to the ordinary Portland cement (OPC) concrete. The lack of knowledge about the moisture fixation and transport performance in sustainable concrete has caused some clients and contractors to worry about the application of the blended cement in constructions [12].

Many papers investigated the reduction effect of SCMs on the chloride migration in cement-based materials from the experimental investigation or modeling aspect [13–18]. However, there were a limited number of papers that studied the effect of SCMs on the moisture transport performance. Baroghel-Bouny [2] found that the apparent moisture diffusion coefficient of concrete with 8 %–10 % silica fume is lower than the reference concrete when the water saturation degree is larger than 50 %. Saeidpour and Wadsö [19] used a modified cup

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method to investigate the difference between the vapor diffusion coefficient of the blended mortar in adsorption and desorption processes. Their results indicated that both silica fume and slag induced a one order of magnitude reduction in the vapor transport coefficient in both adsorption and desorption processes. They ascribed this effect to the higher amount of gel pores and lower volume of capillary pores in the blended system. The same reduction effects from silica fume and slag were also reported in the investigation by Olsson et al. [20], and this effect is more evident at higher RH levels. The authors tried to correlate the difference in the moisture diffusion rate with the difference in the structure of C-S-H in the hydration products, but no plausible correlation was concluded. The high moisture resistance in the blended system may mainly come from its refinement of the pore structure. This was also mentioned in the discussion part of other published papers [19–21], but which parameter relating to the pore structure should be used to correlate with vapor diffusion has not been clearly established. There are many parameters to describe the pore structure in cement-based materials: porosity, pore size distribution, pore connectivity, tortuosity, the critical entry pore size (CP) and formation factor (*FF*). The decrease of CP was raised as the reason for forcing the vapor transport through the smaller pores in the blended mortar than in OPC [20,21] because Berodier and Scrivener [9] found that slag reduced the CP of pastes cured in water for 28 days. However, paste with fly ash normally has a similar and even larger CP compared to OPC paste before 90 days [9,22]. It indicates that the decrease in CP can hardly explain the much lower vapor diffusion in the fly ash blended mortar than OPC.

Some numerical simulations were performed to predict the vapor diffusion or relative permeabilities of OPC concrete based on the pore size distribution [23] or pore network [24]. However, these models may not fit for the blended system because of the minor differences in the pore size distribution and the huge differences in moisture transport properties especially at high RH compared to OPC. Therefore, it is of great significance to find some comprehensive parameters that can effectively indicate the vapor transport performance. The *FF* is one of the comprehensive parameters, and it is closely related to the mass transport inside the porous materials. As Eq. (1) shows, it is correlated to both porosity (Φ) and pore connectivity (β) [25,26], which also has a relation with ionic conductivity and the ion transport properties as highlighted in [27].

$$FF = \frac{\sigma_{ps}}{\sigma_p} = \frac{D_{ps}}{D_p} = \frac{1}{\Phi\beta} \quad (1)$$

where σ_{ps} is the electrical conductivity of pore solution and σ_p is the electrical conductivity of paste. D_{ps} and D_p are the diffusivity of the ions in the bulk pore solution and paste, respectively.

This paper aims to reveal the relationship between the moisture or chloride ion transport properties measured in laboratory and the pore structure parameters in both the OPC and blended pastes, so that the engineers and scientists can better predict the drying process and service life of the concrete. There are several methods to determine the moisture transport properties in porous materials based on steady-state conditions (constant flux through the samples, such as the cup method [28]) or non-steady-state conditions (such as semi-infinite drying [2]). The cup method takes a long time (>5 months) to get the equilibrium for a constant flux, which also strongly depends on the sample dimensions. The semi-infinite drying method may be much faster than the cup method, but it relies heavily on the initial humidity control of the sample [29]. In certain RH intervals, the vapor diffusion coefficient (D_v) from the cup method may be comparable with the value calculated by using the moisture content and the moisture transport coefficient (D_w) from the semi-infinite drying method [30,31]. Saeidpour and Wadsö [32] used small samples of cement paste and found that an unsteady-state method could not give a result that was evaluated by methods based on Fick's law due to the anomalous diffusion. This also indicates that results from the steady-state and unsteady-state method will be difficult

to compare (at least for small samples).

A new procedure and setup for the moisture diffusion test of pastes are described in this paper. It enables to measure both D_v and D_w of the same sample in one procedure. The chloride migration coefficient was measured by the rapid chloride migration method (RCM) [33]. The pore size distribution in hardened pastes was measured by the mercury intrusion porosimeter (MIP). The refinement effect of SCMs on the pore structure in pastes is discussed by the interpretation of different parameters. The differences in moisture and chloride transport in pastes blended with different SCMs are comprehensively compared to the pore structure parameters in the final part of the discussion.

2. Materials and methods

2.1. Materials

OPC is CEM I 52.5 R with a Blaine surface of 525 m²/kg. OPC was mixed with three different SCMs (slag, fly ash and limestone). Slag (SL) with a Blaine surface of 420 m²/kg was obtained from Thomas Cement AB company. Fly ash (FA) was from Cementa, and limestone with $D_{50} = 18 \mu\text{m}$ (LL) was supplied by Nordkalk.

Table 1 shows the chemical composition of all binders. Table 2 presents the mix proportions of the 11 samples. In the binary systems, OPC was replaced with 35 % FA (P1) or SL (P2). OPC was replaced with 35 % slag and 16 % limestone to obtain a ternary system (P3). Pastes were mixed with three different water-binder ratios (*w/b*) of 0.35, 0.45 and 0.55, respectively, except for P1 with only two *w/b* (0.35 and 0.45).

2.2. Methods

2.2.1. Preparation of pastes

The pastes were homogeneously mixed in the planetary mixer whose stirring rate can be continuously adjusted. For a good homogeneity of mixing, 100 stainless steel balls (16 mm diameter) were added in the bowl. The speed of the agitator was controlled with about 75 rpm and 7 rotations per revolution to avoid bouncing of the balls. OPC paste (P0) with *w/b* = 0.35 was mixed for 1 min after the addition of all the deionized water in the bowl with OPC. A rubber scraper was used to move the materials adhering on the wall and in the bottom to the middle. Afterwards the paste was mixed for another 2 min. The pastes with *w/b* = 0.45 were firstly mixed with the amount of water equal to *w/b* = 0.35 for 1 min. Afterwards, the slurry was scraped with the rubber scraper as described above. Then, the remaining amount of water was added and mixed for another 1 min. After a second scraping, the paste was mixed for another 2 min. The pastes with *w/b* = 0.55 were firstly mixed with the amount of water equal to *w/b* = 0.35 for 1 min. After the first scraping, the water was added up to *w/b* = 0.45 followed a 1 min mixing and a second scraping. Finally, the rest of the water was added and mixed for 1 min. After the third scraping, the paste was mixed for another 2 min. The paste was taken out to cast in the polypropylene tubes shown in Fig. 1. For the blended pastes, an extra 1 min pre-mix of

Table 1
Chemical composition of different binders (*LOI*: loss of ignition).

Chemical Composition (wt%)	CEM I 52.5 R	Slag	Fly ash	Limestone
CaO	62.20	39.11	5.10	49.50
SiO ₂	19.60	36.63	54.62	9.00
Al ₂ O ₃	4.50	13.56	22.41	0.60
Fe ₂ O ₃	3.00	0.49	8.68	0.30
SO ₃	3.50	0.27	0.80	0.03
MgO	3.50	8.52	1.79	–
K ₂ O	1.01	0.57	2.10	0.30
Na ₂ O	0.27	0.42	1.00	0.10
Cl	0.07	0.01	–	–
Sulfide	–	0.73	–	–
<i>LOI</i>	2.50	–1.07	3.50	40.17

Table 2

The mix proportion of the 11 different samples.

Samples	w/b	-	Binders (by weight)			
			CEM I 52.5 R	Fly ash	Slag	Limestone
P035	0.35	100 %				
P045	0.45					
P055	0.55					
P135	0.35	65 %		35 %		
P145	0.45					
P235	0.35					
P245	0.45	65 %			35 %	
P255	0.55					
P335	0.35					
P345	0.45	49 %			35 %	16 %
P355	0.55					

the dry binder was performed before adding the water. Afterwards, the blended pastes were mixed by following the same protocol as the OPC pastes. To avoid inhomogeneity caused by bleeding, the sealed tubes with fresh paste were put on the rotator with a speed of 12 rpm for 24 h. Finally, the samples were stored in the curing room with a constant temperature of 20 °C for 390 days.

2.2.2. Procedures and setup for the moisture diffusion test

After curing for 390 days, the tubes were wet cut from the top with a constant water flow using an electric diamond saw. Firstly, we cut a thin layer from the surface (~3 mm) to make an even surface. Afterwards, three discs with a thickness of about 7 mm were cut for the vapor diffusion measurement (shown in Fig. 1). The actual thickness (h) and diameter (D) of the discs were measured at 4 different places to take an average value. The rest of the sample was used to do the semi-infinite drying measurement. Both the discs and the rest of samples were conditioned under RH = 97.6 % for 14 days. Before the discs were mildly pressed in the tubes with the saturated salt solution for different RH control, a layer of watertight tape (double side, Stokvis VST397F1210) was adhered around the side of the disc. The head and tail of the tape were connected without any gap or overlapping (a “slash” shape in Fig. 1). Two dummy disc samples (engineering plastic, acetal

copolymer) were used to check the leakage of the sealing tapes at each RH intervals. The tape was adhered around the side of the dummy samples, and then the dummy sample was mounted in the tubes.

After the sample was mounted into the tubes, the distance between the solution surface and disc (L) was measured. The RH in the tubes and conditioning box was controlled by use of the saturated salt solutions: NaCl (75.5 %), KCl (85.1 %) and K₂SO₄ (97.6 %) at 20 °C [34]. Vapor diffusion in the pastes was measured under 4 different RH intervals, 97.6–75.5 % (RH97-75), 85.1–75.5 % (RH85-75), 97.6–50 % (RH97-50) and 75.5–50 % (RH75-50). The semi-infinite drying was conducted under two different RH conditions (75.5 % in the box and 50 % in the climate room). To avoid any leakage from the edge of the tubes, a thin circle of watertight adhesive (LOCTITE® 60 Seconds Universal glue) was applied around the edge. All the tubes were weighed at a sequence of conditioning times. We took 3 parallel measurements and some of the original data is presented in Fig. S1 and S2 (Supplementary information).

2.2.3. Moisture content test

Pastes were also crushed into particles (<2 mm) and then conditioned in the box with different RH controls (97.6 %, 75.5 % and 50 %, respectively). Calcium hydroxide was put in the climate box as a sacrifice to absorb CO₂. The RH in the conditioning box was monitored by the RH sensors (testo 174H). After 1 year conditioning, the particles were used to measure the evaporable water content by vacuum drying at 60 °C for 3 days.

2.2.4. Rapid chloride migration test

Pastes were mixed by following the same protocols described in Section 2.1, and then a rubber cylinder mould (inner diameter of 50 mm, height of 110 mm) was used to cast the samples. After the sealed curing for 1 day, samples were demoulded and put into a moist curing for 28 days and 90 days. At the specified age, two samples with a thickness of 50 mm were cut from each specimen for the RCM test. The test was performed according to NT BUILD 492 but without the vacuum saturation procedure because the specimens were moist cured before the test.

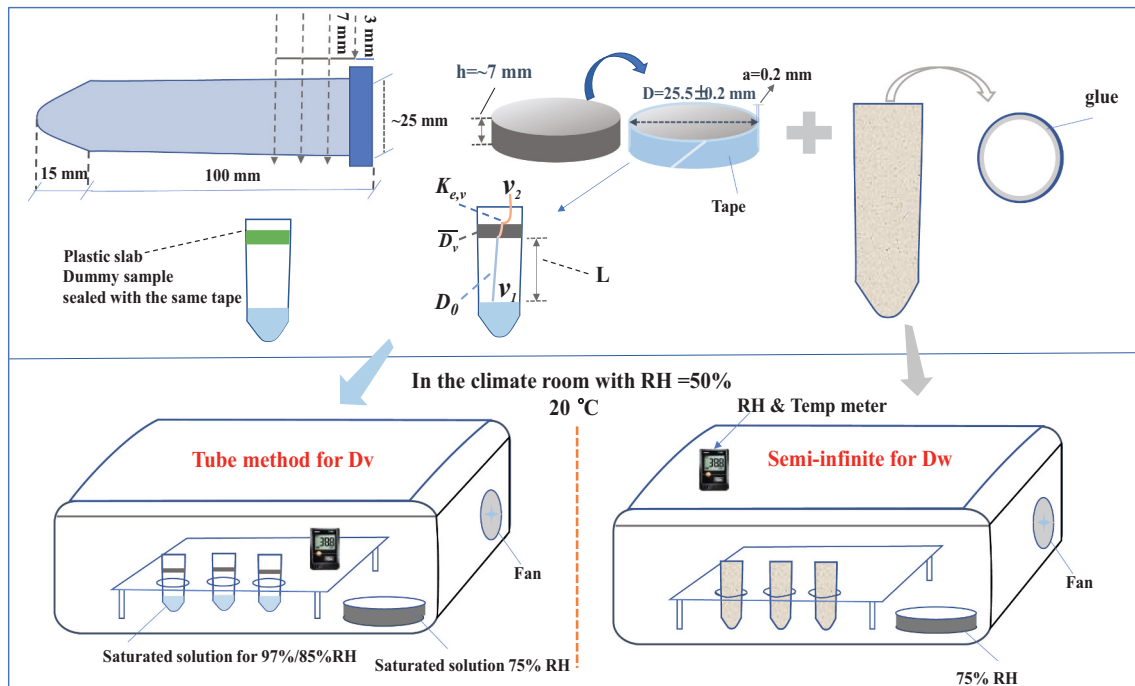


Fig. 1. A sketch of the new method for measuring the moisture diffusivity of pastes.

2.2.5. Electrical conductivity

The electrical conductivity of the pastes was tested by Wenner's four electrodes method which was detailly described in one previous paper [35]. The conductivity data at 28, 90, and 365 days were collected. The conductivity of the pore solution was calculated according to the empirical function in [35].

2.2.6. MIP measurement

After crushing, the pieces of 3–8 mm size were selected by sieving. Afterwards, the hydration of the samples was stopped by immersing the pieces into isopropanol for 3 days, which duration is appropriate for a full solvent exchange [36]. The pieces were then dried with continuous pumping under vacuum at 40 °C for 3 days. The pore size was measured by a MicroActive AutoPore V 9600 Version 2.03 machine. The pressure was initiated at 0.003 Pa and increased up to 250 MPa, which allows for the intrusion of pore entries from 373 μm initially down to about 6 nm (contact angle of 138°).

2.2.7. Calculation of the moisture transport properties

The related abbreviations are summarized in Table 3. During the semi-infinite drying process, the moisture content was considered as the driving force for moisture transport in this non-steady-state conditions. The one-dimensional diffusion can be described by Fick's second law as Eq. (2).

$$\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial x^2} \quad (2)$$

The distribution of moisture content inside pastes is an analytical solution of the above equation with the boundary condition: $C = C_1$; $x = 0$; $t > 0$, and the initial condition: $C = C_0$; $x > 0$; $t = 0$. Hence, its distribution inside the paste follows Eq. (3) [30,37].

$$\frac{(C - C_1)}{(C_0 - C_1)} = \operatorname{erf} \frac{x}{2\sqrt{D_w t}} \quad (3)$$

where C_0 and C_1 (kg/m³) are the initial moisture content in the pastes (moisture content at RH = 97 % in this paper) and moisture content on the drying surface (moisture content at RH = 50 % or 75 %), respectively. The “ x ” is the distance from the surface to the inside position where the moisture content is C . D_w (m²/s) is the moisture transport coefficient and t (s) is the duration of the drying time. The loss of

diffusing substance from the semi-infinite medium is given by

$$\left(D_w \frac{\partial C}{\partial x} \right)_{x=0} = \frac{D_w (C_0 - C_1)}{\sqrt{\pi D_w t}} \quad (4)$$

An integral of Eq. (4) from zero time to t can get:

$$M_t = 2(C_0 - C_1) \sqrt{\frac{D_w t}{\pi}} = k_w \sqrt{t} \quad (5)$$

M_t (kg/m²) is the moisture loss of the samples drying to time t . Furthermore, we can get the drying coefficient k_w by the regression of moisture loss (M_t) and $\sqrt{t}$ (see Fig. S3 in supplementary information). Thereafter, the total moisture transport coefficient D_w can be obtained by Eq. (6).

$$D_w = \frac{\pi k_w^2}{4(C_0 - C_1)^2} \quad (6)$$

The vapor diffusion coefficient $D_{v,s}$ (m²/s) during semi-infinite drying was defined as [38]:

$$D_{v,s} = \frac{D_w \cdot dW}{v_s \cdot d\phi} \quad (7)$$

where $dW/d\phi$ is the moisture capacity of the pastes (data shown in Table S1 and S2 in supplementary information). Herein, the average moisture capacity was used as shown in Eq. (8). W_1 and W_2 are the moisture content in cement pastes conditioned under ϕ_1 and ϕ_2 , respectively. It is calculated by Eq. (9).

$$\frac{dW}{d\phi} = \frac{W_2 - W_1}{\phi_2 - \phi_1} \quad (8)$$

$$W_i = \frac{m_i - m_0}{\frac{m_0}{\rho_0}} = \frac{\rho_0(m_i - m_0)}{m_0} \quad (9)$$

where m_i is the weight of the pastes conditioned at RH = ϕ_i , m_0 is the weight of the pastes vacuum dried at 60 °C and ρ_0 is the bulk density of the vacuum dried pastes.

Generally, the vapor diffusion through the disc samples obeys Fick's first law

$$j_{v,t_i} = \frac{\Delta v}{D_{v,t_i} h} \quad (10)$$

where j_v , t_i is the vapor flux during the diffusion from time t_{i-1} to t_i . t_i corresponds to the latest time weighing the tubes, Δv (kg/m³) is the difference in the vapor content between the upper and lower surfaces of the specimens and h (m) is the thickness of disc. The leakage of dummy sample, Δm_{dt} (kg), was included in the calculation of the vapor flux from t_{i-1} to t_i , j_v , t_i , so it can be calculated by Eq. (11).

$$j_{vt} = \frac{\Delta m_{st} - \Delta m_{dt}}{\Delta A t} \quad (11)$$

where $\overline{D_{v,t_i}}$ (m²/s) is the average vapor diffusion coefficient between t_{i-1} and t_i and Δm_{st} (kg) is the weight loss of tubes with discs of pastes from t_{i-1} to t_i . The surface vapor content is not so easy to measure, but the vapor content on the surface of the saturated salt solution and in the climate box (room) can be calculated by

$$v_i = v_s^* \phi_i \quad (12)$$

where v_i is the moisture content in air at the corresponding RH and v_s is the saturation moisture content in air (17.28 g/m³ at 20 °C). Therefore, considering the surface moisture resistance ($K_{e,v}$) and moisture transport in tube air, the mass flux from the saturated salt solution to the climate box reads

Table 3
Abbreviations of the terminology.

Abbreviation	Meaning of it
CP	The critical entry pore size
FF	Formation factor
Φ	Porosity
β	Pore connectivity
σ_{ps}	The electrical conductivity of pore solution
σ_p	The electrical conductivity of paste
D_{ps}	The diffusivity of ions in pore solution
D_p	The diffusivity of ions in paste
D_v	The vapor diffusion coefficient
$\overline{D_v}$	The average vapor diffusion coefficient
D_w	The moisture transport coefficient
C_0	The initial moisture content in pastes before drying
C_1	Moisture content on the drying surface
k_w	Drying coefficient
$D_{v,s}$	The vapor diffusion coefficient during semi-infinite drying
W_i	Water content in paste conditioned at relative humidity of ϕ_i
v_i	Moisture content in air at relative humidity of ϕ_i
$K_{e,v}$	The surface moisture resistance
j_v, t_i	Water vapor flux at the time interval t_{i-1} to t_i
D_0	The diffusion coefficient of water vapor in air
D_s	The moisture diffusion coefficient in the saturated paste
D_{v0}	The moisture diffusion coefficient in the dry paste (0 % RH)
ϕ_c	The critical relative humidity for percolation of liquid in paste
D_{RCM}	The chloride migration coefficient tested by RCM

$$j_{v,t_i} = \frac{v_2 - v_1}{\frac{h}{D_{v,t_i}} + \frac{L}{D_0} + \frac{1}{K_{ev}}} \quad (13)$$

The K_{ev} is approximately 0.007 m/s [19] for the discs with the similar size in this investigation. With the weight loss change (see Fig. S2 in supplementary information) substituting into Eq. (11), we can use Eqs. (12) and (13) to calculate the average vapor diffusion coefficient from the tube method.

3. Results

3.1. Semi-infinite drying diffusivity (D_w and $D_{v,s}$)

Fig. 2 shows the moisture diffusion coefficient (D_w) and vapor diffusion coefficient ($D_{v,s}$) determined by the semi-infinite drying method. All the pastes dried at 75 % RH have a lower D_w than those dried at 50 % RH. The D_w , which was also called the apparent moisture diffusion coefficient in [2,39], was found to be moisture dependent in cement-based materials. It decreased as the saturation degree increased from zero and reached the minimum value at some middle degree (0.5–0.8). After the percolation of liquid was reached at this critical value, D_w increased with the saturation degree. The specific value of this critical saturation degree might be related to the structure of the hydration products, such as the volume of high density (HD) C-S-H [2]. The blending of FA and SL in pastes increases the volume of HD C-S-H [40].

Their D_w has a larger difference at 50 % and 75 % RH compared to OPC pastes (see Fig. 2a), and this effect is similar to that of silica fume [2].

The pastes with a higher w/b show a higher D_w . The blending of SCMs presents a significant reduction in the D_w during both 50 % and 75 % RH drying. To obtain a normalized value, the transport coefficients of the blended pastes have been calculated by dividing them with these coefficients of the OPC pastes with the same w/b . The normalized factor of D_w at 75 % RH is in the range of 0.05–0.18 (see Fig. 2c), and the factor shows a decreasing trend as w/b increases, except for the ternary paste. The ternary paste shows the lowest D_w among the pastes with $w/b = 0.35$. When w/b is 0.45 and 0.55, the SL binary pastes have the lowest value compared to the other pastes. The further replacement of OPC by LL increases the moisture transport coefficient. While drying at RH = 50 %, the blended pastes present a higher normalized factor compared to 75 % RH. The factors of FA or SL binary pastes stay in a range of 0.18–0.27, and the FA blended paste with $w/b = 0.45$ has the lowest factor. A further blending of LL increases the factor of D_w to a range of 0.38–0.54, which is almost twice the factor of the SL binary paste.

$D_{v,s}$ and its normalized factor are presented in Fig. 2b and d, respectively. The drying RH has the similar effect on $D_{v,s}$ as on D_w , but the discrepancy in $D_{v,s}$ at the different RH is smaller than that in D_w . This phenomenon is more evident in the blended paste mainly due to the higher moisture capacity ($dW/d\rho$) in blended pastes compared to OPC (see Table S1 and S2 in supplementary information). Some published papers [20,41] also found that the blended pastes (SL/silica fume) had a

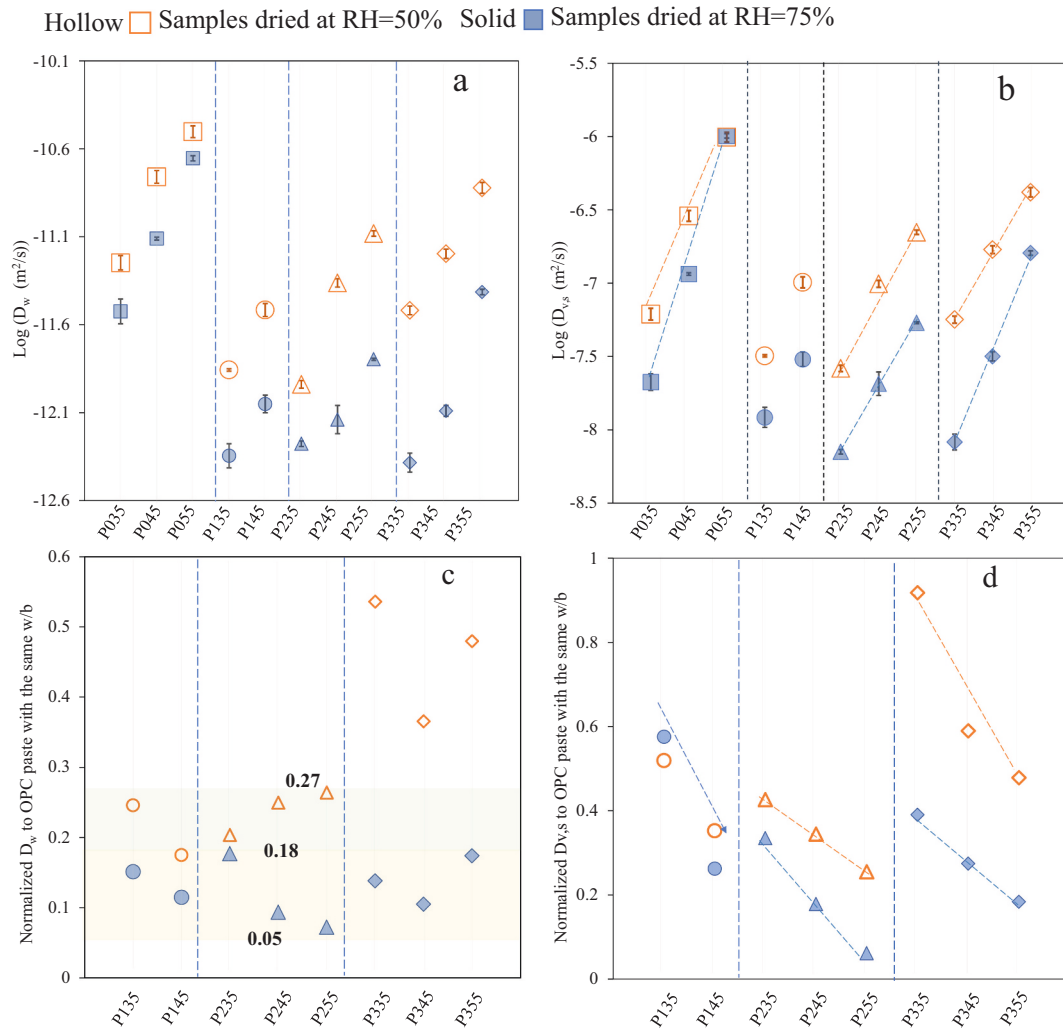


Fig. 2. The D_w and $D_{v,s}$ of pastes during drying at RH = 50 % and 75 % (20 °C): a - D_w of all pastes; b - $D_{v,s}$ of all pastes; c - D_w of the blended pastes normalized to the OPC pastes with the same w/b ; d - $D_{v,s}$ of the blended pastes normalized to the OPC pastes with the same w/b .

higher moisture capacity than OPC at RH higher than 50 %. The logarithm of $D_{v,s}$ shows an almost linear increasing trend with respect to w/b . The SL binary pastes have the lowest normalized factor with a range of 0.06–0.33 in 50 % RH and 0.25–0.43 in 75 % RH compared to the other pastes with the same w/b . The normalized factors of the FA pastes stay in 0.26–0.58. The factors of ternary pastes are around 0.18–0.39 at 50 % RH, which is a little higher than SL binary pastes. It increases greatly up to 0.92 (close to OPC) in P3 with w/b of 0.35 when drying at 75 %. As the w/b increases to 0.55, this value decreases to 0.47. The decreasing trend of the normalized factor with w/b can be observed in all the blended pastes. It means that the reducing effect of SCMs on vapor diffusion will be magnified at a higher w/b . The higher w/b produces more water in capillary pores for the later age hydration of SCMs [42], so that the pore refinement effect from hydration is more evident resulting in a lower normalized factor of $D_{v,s}$.

3.2. Vapor diffusion coefficient in different RH intervals

A long time is required to reach an equilibrium of the moisture content in cement-based materials for applying Eq. (8). The measurement on the steady-state flux through discs is a more popular method to determine the vapor diffusivity in cement-based materials than the semi-infinite drying method. We referred to the ASTM E96/E96M-13 [28] standard and created the tube setup for the D_v test (Fig. 1). Fig. 3 provides some typical data during the experimental process. Both the temperature and RH were controlled well with a stable value (Fig. 3a). The effect of leakage from dummy samples was evaluated by normalizing the difference in D_v with and without consideration of leakage to D_v value. Fig. 3b presents the typical results, illustrated with P035 at four intervals, and it shows that the leakage induces a 4 % deviation in the stable state D_v value (after about 180 days). It should be noted that all the “ D_v ” values in the figures are the average diffusion coefficient at a certain RH interval (namely, $\bar{D}_v$). Fig. 3c shows the evolution of $\bar{D}_{v,t}$ for pastes with $w/b = 0.35$ in two RH intervals. The samples, including those that are not shown in Fig. 3c, reached a steady state flux after 32 days except P035 in 97.6 %–75.5 % intervals. $\bar{D}_v$ of P035RH97–75 continued to increase until 183 days, and this phenomenon exists in all the three parallel tubes (see the decreasing slope of the weight loss in

Fig. S2-a in supplementary information).

The $\bar{D}_v$ at about 182 days is plotted in Fig. 4 as the indication of the steady-state diffusion coefficient. The increase in the RH intervals tend to increase the deviation within the 3 parallel tests, which is consistent with the results of the cup methods in [19]. However, the deviation level in the tube method is lower than in the cup method. It is due to not only the better sealing of tube method but also the differences in mixtures and disc size compared to the test in [19]. Overall, the tube method for measuring the vapor diffusivity is at least as valid as the traditional cup methods.

Fig. 4a illustrates the $\bar{D}_v$ of pastes with w/b of 0.35 in four different RH intervals. The FA binary paste (P135) has the lowest $\bar{D}_v$ with a value of only half of that in P035 when the RH interval is lower than 80 % (85 % to 75 %). In RH75–50, the SL binary paste has the highest $\bar{D}_v$. The discrepancy in coefficient value between the blended pastes and OPC pastes increases after this RH interval because the $\bar{D}_v$ in OPC pastes has an evident increase after this RH but the $\bar{D}_v$ in the blended pastes seems to be moisture independent with only minor changes in the four RH intervals. This is consistent with the results reported in the previous investigations [19–21]. However, if we analyze the details of the diffusion coefficient of the blended pastes in different RH intervals, we can see that it is not completely RH independent. With a $w/b = 0.35$, the $\bar{D}_v$ of the ternary paste decreases slightly as the RH intervals increase, and that of the SL binary paste has an increase after RH85–75. The decreasing trend in $\bar{D}_v$ is still observed in the FA and ternary pastes with w/b of 0.45 (Fig. 4b) as the RH goes to a higher level. The reduction effect from SCMs on the vapor diffusion is more evident at the higher w/b (from Fig. 4a to c) in RH intervals higher than 62.8 % (75.5 % to 50 %). For instance, the $\bar{D}_v$ of SL blended paste normalized to OPC paste is 0.52, 0.29 and 0.14 for w/b of 0.35, 0.45 and 0.55, respectively, which is similar to the findings in the semi-infinite drying test ($D_{v,s}$). The further blending of LL increases the moisture diffusion in pastes below the RH interval of 97.6 %–50 %, but the differences in the SL binary and ternary pastes are negligible after this interval. The logarithm of $\bar{D}_v$ almost has a linear correlation with w/b . A change in w/b from 0.35 to 0.55 brings an increase in the coefficient of SL blended and OPC pastes with a factor about 2.5 and 10, respectively (Fig. 4d). It is much lower than the increase in $D_{v,s}$ from semi-infinite drying test (Fig. 3b). A further comparison between $D_{v,s}$

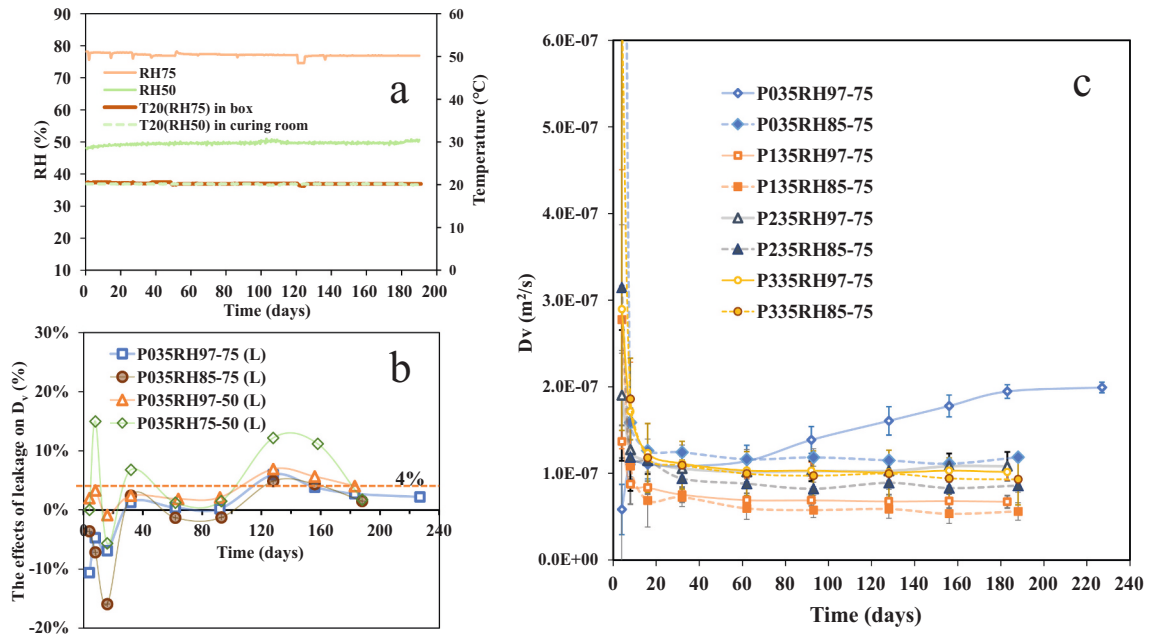


Fig. 3. Some typical data during the vapor diffusion coefficient test. a - the conditioning temperature and RH monitored by testo 174H sensor. b - the effect of leakage normalized to the value of D_v . c - the typical evolution of vapor diffusion coefficient versus time. Note that D_v in the figure is $\bar{D}_v$ in the text.

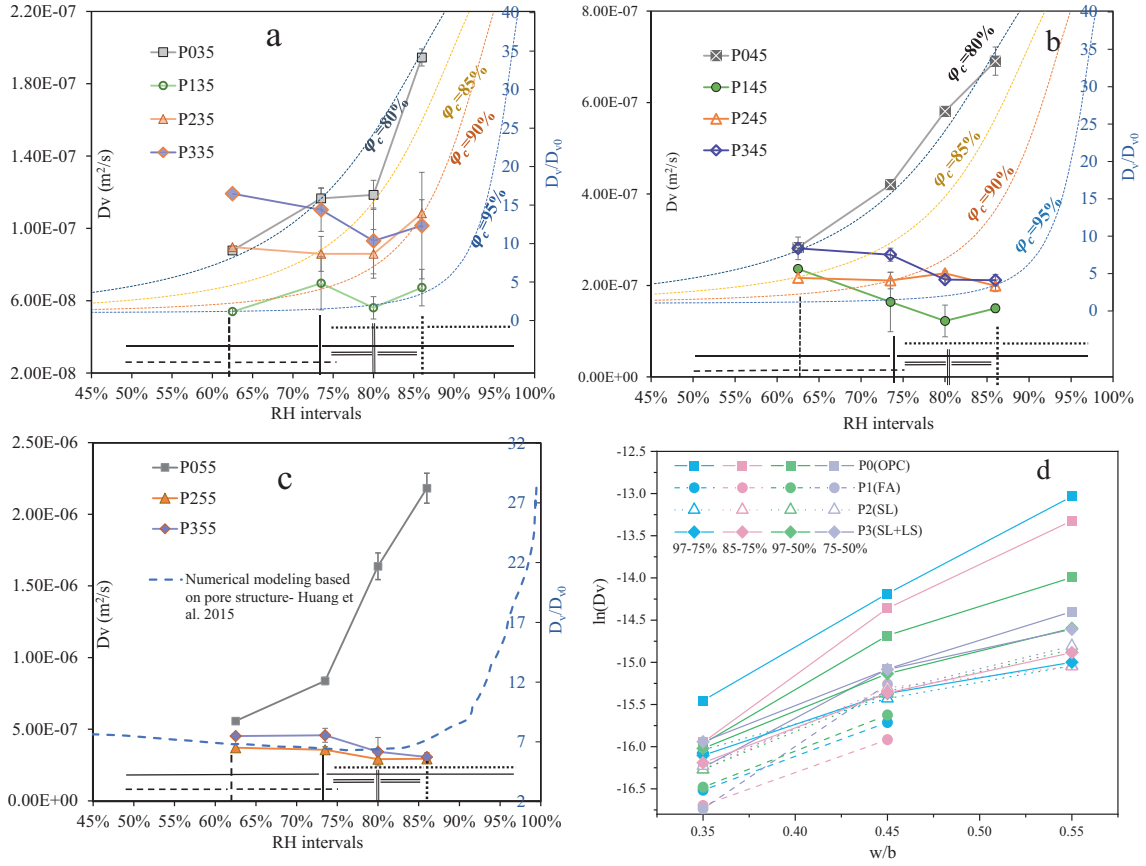


Fig. 4. $\overline{D}_v$ of all the pastes in 4 RH intervals. a - pastes with $w/b = 0.35$; b - pastes with $w/b = 0.45$; c - pastes with $w/b = 0.55$; d - comparison between different w/b . The evolution of D_v/D_{v0} calculated with Eq. (14) is also plotted in a and b with 4 different critical RH ($\varphi_c = 80\%$, 85% , 90% , and 95%). A typical numerical modeling result is adopted in c from [23].

and $\overline{D}_v$ will be discussed in the last section.

Some publications focused on the relationship between the vapor diffusion coefficient and the RH or saturation condition in cement-based materials. For the blended mortar, the vapor transport properties seemed to show a minimal dependence on the RH when the data of OPC and blended mortar were plotted in the same figure [20]. However, there is an increase in $\overline{D}_v$ when RH goes to a rather high level (97.6 % to 94.6 %) in both adsorption and desorption process as presented in different figures in [19]. The modelled results [4,23] indicate that the D_v of the condensable vapor in porous concrete is apparently dependent on the RH or saturation condition. Because the pores will be gradually filled by the liquid from small to large size as the RH increases, the free path for the vapor diffusion will be blocked by liquid and the moisture transports with a mix of vapor diffusion and liquid flow.

The non-saturated pore walls are covered with an adsorbed water layer, whereas the empty pores are filled with a dry air and water vapor gas mixture [43]. As described in detail by Baroghel-Bouny [2], the moisture transport in cement-based materials involves the transport of both the gas (vapor) and liquid phase under non-saturated conditions when the pore volume is only partially filled with the liquid phase. Depending on the considered material and on its saturation state, either process can be prominent. Before the liquid phase reaches a contiguous connection (percolation) at the critical RH condition (φ_c), the vapor diffusion dominates the moisture transport process. Otherwise, the Darcian moisture transport of the liquid phase is prominent, and in this case, particularly high values of the transport coefficients are expected. Therefore, the results from the cup method will overestimate the vapor diffusion at the high RH interval due to the mixing of liquid flow; this phenomenon is evident in OPC pastes (see Fig. 4).

An empirical formula was proposed by Bazant and Najjar [43] to describe the dependence of the moisture transport coefficient on RH, which was modified into Eq. (14) by Sakata [44].

$$\frac{D_v}{D_{v0}} = 1 + \frac{\frac{D_s}{D_{v0}} - 1}{1 + \left(\frac{1-\varphi}{1-\varphi_c}\right)^n} + (\varphi - 1) \frac{\frac{D_s}{D_{v0}} - 1}{1 + \left(\frac{1}{1-\varphi_c}\right)^n} \quad (14)$$

where D_v , D_s , and D_{v0} are the vapor diffusion coefficients in the cement-based materials with $\text{RH} = \varphi$, 1, and 0, respectively. Actually, D_s is the transport coefficient of the liquid calculated based on the gradient of the vapor content. The n is an empirical exponent constant. The results of this formula were in good agreement with the simulation results based on a pore network model in [4] involving both the vapor diffusion and liquid flow. Eq. (14) was used to explain the difference in the dependence of $\overline{D}_v$ on RH condition. $D_s/D_{v0} = 50$ was selected as the typical value for the OPC-based concrete with w/b of about 0.45 based on both experimental results and simulations [4,19,20,23]. $n = 2$ was used as a general value according to the previous analysis based on the extended percolation theory in [35]. Fig. 4a and b include the evolution of D_v/D_{v0} in pastes with different critical percolation points ($\varphi_c = 80\%$, 85% , 90% and 95%). It shows that the tendency of OPC pastes is really close to the modelled evolution at $\varphi_c = 80\%$ – 85% , and that of the blended pastes is similar with the modelled results at $\varphi_c = 95\%$. This means that the percolation of the liquid in OPC pastes occurs under a much lower saturation state than that of the blended pastes, which is consistent with our previous results [35]. It implies that the different percolation point of the liquid in pastes may be the main reason for the large discrepancy in dependence of the $\overline{D}_v$ on RH for different binder systems. Based on the

modeling investigation [23], the mild decrease in $\bar{D}_v$ with the elevated RH may be due to the blocking of the vapor transport without boosting of the liquid flow (Fig. 4c).

3.3. Chloride migration coefficient

The chloride migration coefficient is another important mass transport parameter in cement-based materials that is related to the durability of reinforcement concrete. Fig. 5 demonstrates the migration coefficient tested by the RCM method (D_{RCM}) at curing ages of 28 and 90 days. In both OPC and binary pastes, the trend is, as expected, that the D_{RCM} increases as the w/b increases. However, the influence from w/b is much weaker in the ternary system with a replacement of OPC by 51 % SCMs compared to the others.

The blending of SCMs evidently reduces the D_{RCM} of pastes with w/b higher than 0.45 at 28 and 90 days. With a $w/b = 0.35$, the FA blended paste has a higher D_{RCM} than OPC with a normalized value of about 1.1 at 28 days, but the normalized value descends to 0.39 at 90 days (see Fig. 5b). The normalized value of P235 and P335 is about 0.7 at 28 days, which is close to the value of P145. The reducing effect of SCMs on D_{RCM} becomes more significant in pastes with a higher w/b . This phenomenon is similar to the findings on moisture transport (Fig. 2d and 4). Pastes have a lower D_{RCM} at 90 days than at 28 days except for OPC with $w/b = 0.55$ (P055). The chloride migration coefficient is a time-dependent parameter that will decrease with the curing time following an empirical power function [13,45–47] due to the continuous hydration. However, an interesting deviation similar to P055 was detected in the previous investigations [46,47] as well. The OPC based concrete might have a higher chloride migration coefficient at later age when the w/b is rather high (> 0.5). Because of the increase in the hydration degree of

SCMs, the normalized value decreases from 28 to 90 days and the value of FA binary pastes has the most evident change. The blended pastes have the normalized value at a much lower value range at 90 days (from 0.5 to 0.1) than at 28 days (from 1.1 to 0.3).

3.4. Structure of pastes

3.4.1. Pore structure by MIP

The MIP measurement was used to investigate the pore structure in hardened cement-based materials. Pore size measured by MIP refers to the threshold diameter corresponding to the intruded pressure rather than a real size, which will underestimate the size of big pores within the “ink-bottle” shape [48,49]. Therefore, it should be noted that the pore size in this text represents not only the diameter of cylinder pores but also the neck of “ink-bottle” pores that influence the transport properties as well. However, it can provide the threshold diameters and intrudable pore space as the comparative indices for the pore information in cement-based materials [22,48]. Fig. 6 presents the differential pore size distribution of pastes and the detailed comparison between different categories. The intrudable pore volume has been classified into three ranges: mesopores (4.5–50 nm), middle capillary pores (50–100 nm) and large capillary pores (>100 nm) [50]. The percentage of the intruded pore volume in these three ranges is illustrated in Fig. 7. The CP is the inflection point on the curve of intruded volume versus pore size, such as the pore size corresponding the peak value in the $dV/d\log(D)$ curve [22].

Fig. 6a and b show that the blending of FA decreases the CP of pastes with w/b of 0.35 and 0.45 under the sealed curing condition after 390 days. However, SL brings an increase in the CP of pastes with w/b of 0.35 and 0.45 under the seal curing. Therefore, the much lower $\bar{D}_v$ (Figs. 2 and 4) of the blended pastes can hardly be ascribed to the reduction in the CP that was mentioned as the main factor controlling the moisture transport in [20,21]. SL could decrease the CP of pastes at later age when the pastes were cured in water [9]. Water curing provides sufficient water in the big capillary pores so that the precipitation of the hydration products can fill these pores during later hydration of SL. However, during the sealed curing (without the water supply), the inner RH of the pastes is no >95 % after 7 days even with the dilution effect from 50 % SCMs [51]. According to Kelvin's equation, liquid water can only be accessible in pores with a diameter smaller than 70 nm in 95 % RH at 20 °C when the effect from alkali ions has been taken into account [6]. Consequently, the filling effect from the hydrates produced by the later age hydration of FA and SL can only occur in the mesopores and middle capillary pores under the sealed curing condition (as in this study). This may explain why in Fig. 6, the volume of the pores with a size (or neck size) < 100 nm in the blended pastes is significantly lower than that in OPC, whilst there still exists a certain amount of large capillary pores (> 100 nm) in the blended pastes, especially for those with w/b of 0.35 and 0.45. It might also be the reason for the differences in the effects of SL on the CP between the water curing in [9] and the sealed curing in this study. Although the total porosity (6 nm–373 μm) in FA binary pastes is higher than that in OPC pastes, the main differences are in the volume of intrudable pores smaller than 100 nm. In both conditions with w/b of 0.35 and 0.45, the FA blended pastes have the similar large capillary pore volume but a much higher mesopores volume compared to OPC (see Fig. 7). The volume of the middle capillary pores decreases after the blending of FA due to its secondary hydration at the later ages, and this effect is prominent in pastes with w/b of 0.45 (Fig. 6b and Fig. 7).

The total porosity (6 nm–373 μm) of SL binary pastes with w/b of 0.35 and 0.45 is close to that of OPC with the same w/b , but the increase in the volume of mesopores pores with meso-neck occurs after the blending of SL. A reduction in the percentage of middle and large capillary pores can be observed in SL binary pastes with w/b of 0.45 and 0.55 compared to OPC pastes (Fig. 7). It should be noted that this unnecessarily implies a high reduction effect in the actual size of the pore,

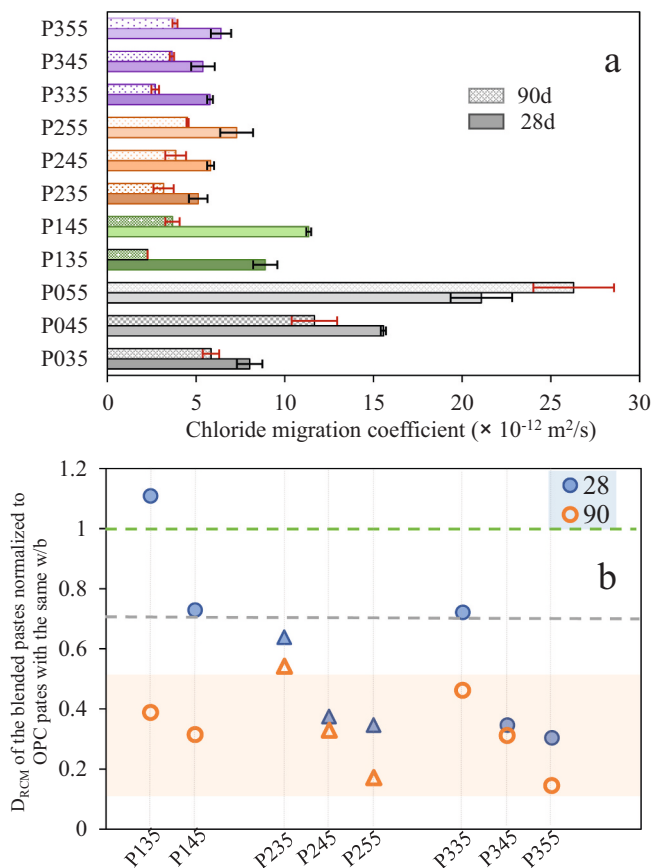


Fig. 5. Chloride migration coefficient of pastes tested by RCM. a - the original value; b - the value of blended pastes normalized to OPC with the same w/b .

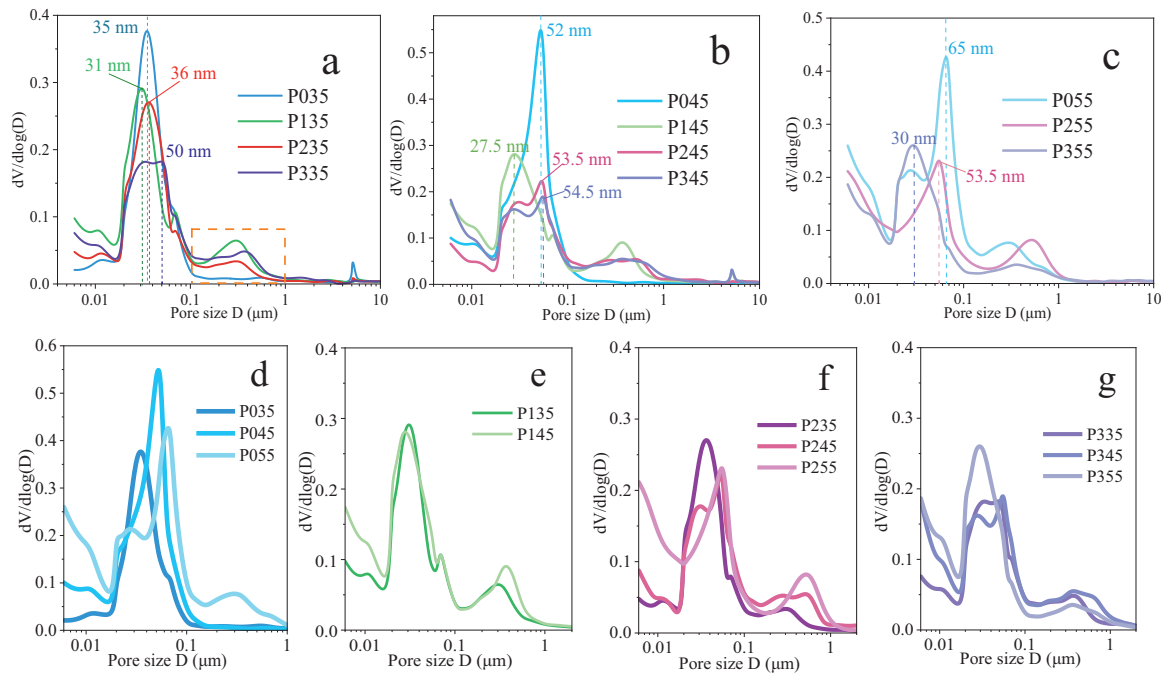


Fig. 6. Pore size distribution of pastes measured by MIP: the comparison between pastes with w/b of 0.35 (a), 0.45 (b), and 0.55 (c); comparison between different w/b for OPC (d), the FA blended (e), the slag binary (f), and ternary (g) pastes.

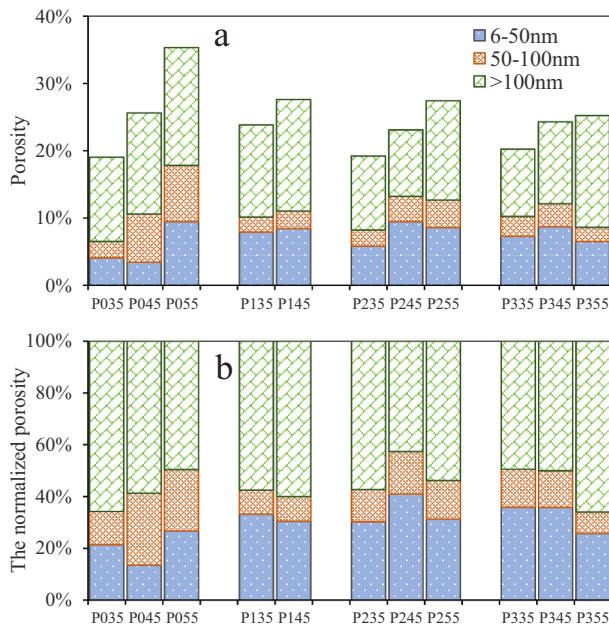


Fig. 7. Intrudable pore size distribution of pastes tested by MIP: a - original value; b - the percentage of the intruded pore volume normalized to 1.

since it may also result from an increase in the percentage of “ink-bottle” pores with small necks. Moreover, the latent hydraulic reaction of SL may happen on the local surface of large capillary pores to produce hydrotalcite-like phase, C-A-S-H gel and Ca—Al layered double hydroxide phase [52], resulting in a reduction in the pore sizes as well as the pore volume. Although the LL in ternary pastes alters the phase composition in the hydration products [53], its effect on the pore structure is very weak in pastes with w/b of 0.35 and 0.45. The dilution effect of LL introduces a higher effective water to hydraulic binder (OPC and SL) ratio, so it increases the percentage of mesopores in the ternary

paste compared to the SL binary paste with w/b of 0.35. With the w/b of 0.55, the CP in the SL binary pastes is slightly lower than that of OPC (Fig. 6c). A further replacement of LL increases the volume of the large capillary pores but decreases the CP from 53.5 nm in binary pastes to 30 nm in ternary pastes.

Pastes with the higher w/b have a higher total porosity (see Fig. 7). The change in w/b from 0.35 to 0.45 causes an evident increase in the CP of OPC pastes from about 35 to 53 nm, and OPC with w/b of 0.55 has a CP up to 65 nm. The effect of w/b on the CP in the blended pastes is more complex than the effect on OPC. The increase in w/b even decreases the CP in the FA blended pastes, and the same trend can be observed in the ternary pastes. The volume of large capillary pores typically increases with the increase in w/b in all binder systems, but the changes in mesopores and middle capillary pores is dependent on the binder type.

3.4.2. Pore structure parameters from electrical conductivity

As shown in Eq. (1), the pore structure parameter related to the mass transport process can be detected by the electrical conductivity of the paste and its pore solution. However, the conductivity of the actual pore solution is difficult to experimentally measure. Rajabipour and Weiss [54], and Wilson et al. [27] used the solution extracted from the hardened pastes to measure the electrical conductivity of the pore solution. The problem with this method is that it neglects the conductivity of ions accumulated in the diffusion layer between the solid surface and the solution. The superficially trapped ions may be difficult to be extracted by squeezing of the pore solution [55]. Omitting of the surface conduction would underestimate the FF in the porous structure as mentioned in [54,56], and it is very significant when the conductivity of electrolyte (pore solution) is not so high (<5 S/m) [57]. An alternative way to determine the ionic conductivity of pore solution is to calculate the value based on the concentration of highly conductive ions in the pore solution derived from the degree of hydration, binder chemical composition, and alkalis binding to the cement hydration products [58]. It seems to be more plausible to take all the highly dissolvable alkalis into account, which roughly includes the conductivity of ions trapped in the diffusion layer.

Table 4 presents the measured values of the electrical conductivity of

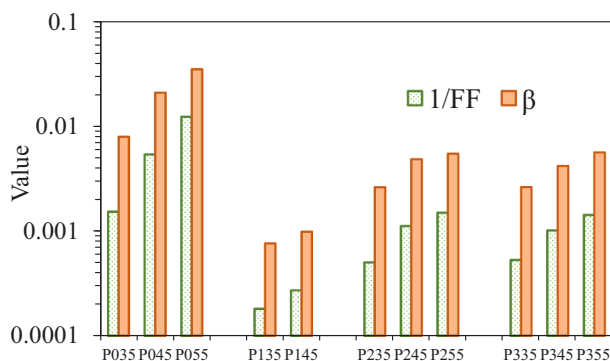
Table 4

The measured electrical conductivity of pastes, the calculated conductivity of the pore solution, the inverse of FF , porosity by MIP and pore connectivity in pastes at about 1 year (390 days).

Sample	Electrical conductivity (mS/cm)		1/FF	ϕ	β
	Paste	Pore solution			
P035	0.251	165.9	1.52E-03	0.19	7.84E-03
P045	0.701	131.3	5.34E-03	0.26	2.07E-02
P055	1.249	102.9	1.21E-02	0.35	3.45E-02
P135	0.019	104.4	1.78E-04	0.24	7.48E-04
P145	0.026	96.0	2.71E-04	0.28	9.82E-04
P235	0.075	149.6	4.98E-04	0.19	2.60E-03
P245	0.128	114.5	1.12E-03	0.23	4.85E-03
P255	0.167	111.6	1.50E-03	0.27	5.46E-03
P335	0.070	133.3	5.26E-04	0.20	2.60E-03
P345	0.085	86.9	9.75E-04	0.24	4.01E-03
P355	0.111	78.0	1.42E-03	0.25	5.60E-03

the pastes, the conductivity of the pore solution, the inverse of FF (1/FF), porosity and pore connectivity. The conductivity of the pore solution was calculated by the empirical function in [35], which involves the chemical composition of the binder and the degree of hydration (evaporable water content) at the corresponding hydration time. The calculated conductivity of the pore solution in pastes ranges from 165 to 78 mS/cm. Apparently, the blending of SCMs decreases the conductivity of pore solution mainly due to the lower content of dissolvable alkali in SCMs compared to OPC [59] and the dilution effect of SCMs leading to an increased effective w/b . The increase in w/b from 0.35 to 0.55 in the OPC paste induces the highest increase in the 1/FF, with a factor of about 8 times compared to the blended pastes and with the maximum factor about 3 times in the SL binary pastes.

Fig. 8 shows that the pore connectivity (β) is the same as 1/FF in terms of its tendency to change with respect to the change in w/b and the binder types. A significant increase in both 1/FF and β can be observed as the w/b increases. The blending of FA has a huge reduction effect on the 1/FF with a factor of about 1/8.5 and 1/20 in the paste with w/b of 0.35 and 0.45 normalized to OPC, respectively (see Table 4 and Fig. 8). SL induces a normalized factor of about 1/3, 1/5, and 1/8 in the 1/FF of pastes with w/b of 0.35, 0.45, and 0.55, respectively, compared to OPC with the same w/b . The ternary pastes with LL (P3-series) have a similar 1/FF or β as the SL (P2-series) binary pastes. Table 5 presents the 1/FF of pastes at 28, 90 and 365 days, which was calculated based on the data in Table S3 (see supplementary information). 1/FF decreases as the hydration proceeds from 28 to 90 days due to the structural growth of the hydration products and the consumption of evaporable water. This change is more evident in the blended pastes compared to OPC, especially in the FA blended pastes in which the secondary hydration of FA occurs at the later ages [35,42].

**Fig. 8.** The inverse of FF and pore connectivity of pastes cured for 1 year.**Table 5**

The calculated inverse of FF of pastes at 28, 90 and 365 days.

Sample	1/FF		
	28 days	90 days	365 days
P035	3.09E-03	2.46E-03	1.52E-03
P045	6.88E-03	6.21E-03	5.34E-03
P055	1.19E-02	1.21E-02	1.21E-02
P135	2.97E-03	5.41E-04	1.78E-04
P145	5.65E-03	1.01E-03	2.71E-04
P235	1.28E-03	9.07E-04	4.98E-04
P245	2.41E-03	1.65E-03	1.12E-03
P255	3.73E-03	2.22E-03	1.50E-03
P335	1.44E-03	8.87E-04	5.26E-04
P345	2.34E-03	1.58E-03	9.75E-04
P355	3.51E-03	2.27E-03	1.42E-03

4. Discussion

4.1. The refinement effect of SCM on the pore structure

SCMs have an impact on the pore structure in cement-based materials. Their refinement effect on the CP in pastes depends on the curing conditions. The water curing condition supplies abundant water for the later hydration to precipitate the hydration products in the large capillary pores, so that the latent hydraulic reaction of SL can decrease the CP in pastes [9]. When the pastes are cured under the sealed condition, SL presents no such effect on the CP as shown in Fig. 6, due to the lack of water in the large capillary pores. Nonetheless, SL decreases the percentage of large capillary pores and increases the percentage of mesopores or pores with mesoscale neck in the pastes with w/b of 0.35 and 0.45. It can even reduce the total porosity (6 nm–373 μ m) in pastes with w/b of 0.55 (see Fig. 7). Therefore, it can induce a significant reduction in the 1/FF and β of the blended pastes (see Fig. 8). FA has an evident reduction effect on the CP in the hardened paste at a later age (after 390 days curing), but this effect is weak before 90 days even under a water curing condition [9,22]. It increases the percentage of mesopores or “ink-bottle” pores with a mesopore size neck, which shows an increase in the volume of mesopores in the MIP test (see Fig. 7 and results in [22]). Moreover, the unreacted FA may also act as an impermeable “aggregate” as shown in the SEM images in [9,60]. The combined effects contribute to the increase in the tortuosity and decrease in the pore connectivity (see Fig. 8). A further blending of LL in slag pastes seems to have no significant influence on the pore size distribution, so that the SL binary and ternary pastes with the same w/b have minor differences between their 1/FF and β . A higher w/b provides more water accessible for the later age hydration so that the refinement effect from SCMs becomes more evident at higher w/b (see Figs. 6–8), thus resulting in an increase in the reduction effect on the moisture or chloride transport coefficient (see Fig. 2d, 4, and 5b).

The transport of moisture and ions in the cement-based materials is not only related to the pore structure but also the chemical structure of the hydration products. However, there still exists many undetectable details in the pore structure, such as the volume percentage of stagnant pores (dead-end pores) in which the mass transport rate will be much slower than the connected pores [61]. The increase in number of stagnant pores may be detectable under SEM [9,60] within a very small region (micrometer size), but the bulk data at macroscale size is not measurable by any method at present. The increase in the dead-end pores or the decrease in the pore connectivity may be due to the formation of foil-like C-A-S-H in the blended pastes [52,62]. The strengthened interfacial hydrogen bond and indirect adsorption of Cl ions in C-A-S-H slows the water and chloride transport in the nanometer channel compared to C-S-H [63]. A detailed discussion of chemical structure of hydration products and the mass transport properties is beyond the scope of this paper.

4.2. Correlation between moisture transport during semi-infinite drying, tube test and porosity

The previous investigation [64] found that the CP had a correlation with water permeability and the chloride migration coefficient. However, this paper shows that only the $\bar{D}_v$ of OPC pastes increases with the increase in the CP. The correlation between $\bar{D}_v$ and CP is, more or less, arbitrary without any clear correlation in the blended pastes (see Fig. S4 in supplementary information).

The correlation between porosity and conductivity of sedimentary rocks was empirically described by Archie's law [65,66]. The relationship between the FF and porosity of the hardened cementitious materials was discovered [26,67], as shown in the following equation.

$$\frac{1}{FF} = a^* \phi^n \quad (15)$$

where a is a non-uniform constant, n is the shape factor and ϕ is the volume of the conductive saline solution that corresponds to the volume of pores filled with water at 97.6 % RH. Eqs. (16) and (17) can be obtained by substituting Eq. (15) into Eq. (1). Herein, we extend the D_p and D_0 to moisture transport coefficient in the saturated cement-based materials (as liquid) and in the air (as vapor), respectively.

$$\frac{D_p}{D_0} = a^* \phi^n \quad (16)$$

$$\log D_p = \log a D_0 + n \log \phi \quad (17)$$

Fig. 9 shows the correlation between the logarithm of the drying constant (k_w) and the volume of pores with liquid at 97.6 % RH. The average value of k_w for each sample was calculated from data in Table S1 and S3 (Supplementary information). The critical Kelvin's diameter for the condensation of vapor into pore water is about 150 nm at 97.6 % RH [6]. Therefore, the porosity of pores smaller than 150 nm (from data in Fig. 7) is plotted in Fig. 9. There are only two samples that deviate from the regression line (see the circled markers in Fig. 9). This may be due to the fact the percentage of ink-bottle pores in P145 and P255 is much higher than that in the other samples, as mentioned in the previous section. Apart from the two points, a good linear regression can be observed between $\log(k_w)$ and $\log(\phi)$ for the sample drying at both 50 % and 75 % RH, which is consistent with the formula in Eq. (16). Because of the big difference in the moisture capacity as well as in the pore solution concentration, there is no general correlation between the porosity and D_w or $D_{v,s}$, as shown in Fig. S5-a and S5-b (in supplementary information). It is apparent that the OPC with w/b of 0.35 has the lowest porosity (see Fig. 7), but the D_w or $D_{v,s}$ is the highest among the pastes

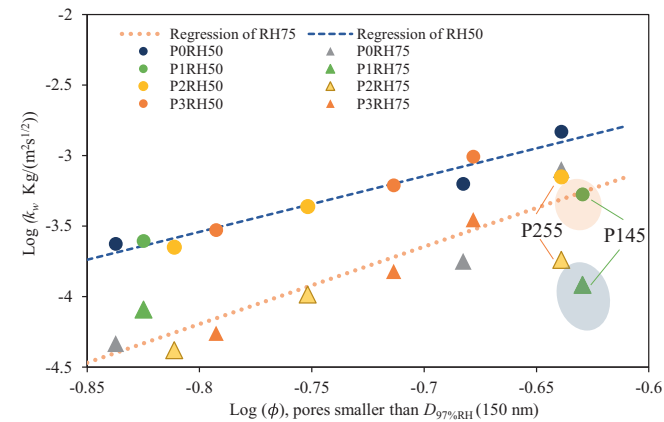


Fig. 9. The correlation between the drying constant (k_w) and the volume of pores with diameter smaller than the critical Kelvin diameter at 97.6 % RH (150 nm).

with the same w/b (see Fig. 2). SCMs have a significant reduction effect on the pore connectivity in pastes (see Fig. 8) and also modify the structure of hydration products (C-A-S-H) [52,60,63,68]. Their effects on both refining pore structure and chemical structure result in a much slower moisture transport in the blended paste than in OPC pastes even with a lower porosity.

It seems that the $\log(\phi)$ has a better linear correlation with the logarithm of the average vapor diffusion coefficient ($\bar{D}_v$) in RH97-50 or RH75-50 than in RH97-75 or RH87-75 (see Fig. S5-c and d in supplementary information). There are much more data deviating from the general linear line in Fig. S5-c than in Fig. S5-d (Supplementary information). This may be due to the fact that the high RH moisture induces a large percentage of pores filled with liquid, which causes the moisture transport process to be strongly mixed with the liquid flow and its blocking effect on vapor diffusion [4]. Consequently, the connectivity of pores determines the moisture transport process instead of the porosity.

Fig. 10 presents the correlation between $\bar{D}_v$ from the steady-state vapor diffusion test (Fig. 4) and $D_{v,s}$ from the semi-infinite drying test (Fig. 2). The value of $\bar{D}_v$ in the RH97-50 is close to the value of $D_{v,s}$ during drying at 50 % RH (linear slope of 0.92 and $R^2 = 0.96$). However, the difference in D_v and $D_{v,s}$ is more evident at the high RH condition (see Fig. 10b). Due to the data point on the upper right corner (from P055), the R^2 value of data in Fig. 10b is similar with that in Fig. 10a, but it is obvious that the confidence level is very low in correlation at 75 % RH. The correlation also becomes weaker in the blended pastes (see the enlarged part), and the slope becomes much higher compared to the data in Fig. 10a. In one report from Nilsson [30], the $\bar{D}_v$ in the RH interval of 85–60 % is comparable with $D_{v,s}$ during drying at 50 % RH, which is consistent with our result in Fig. 10a. However, the difference between $\bar{D}_v$ and $D_{v,s}$ largely increases at the high moisture level (>75 %). According to the previous investigations [32,69,70], this is mainly due

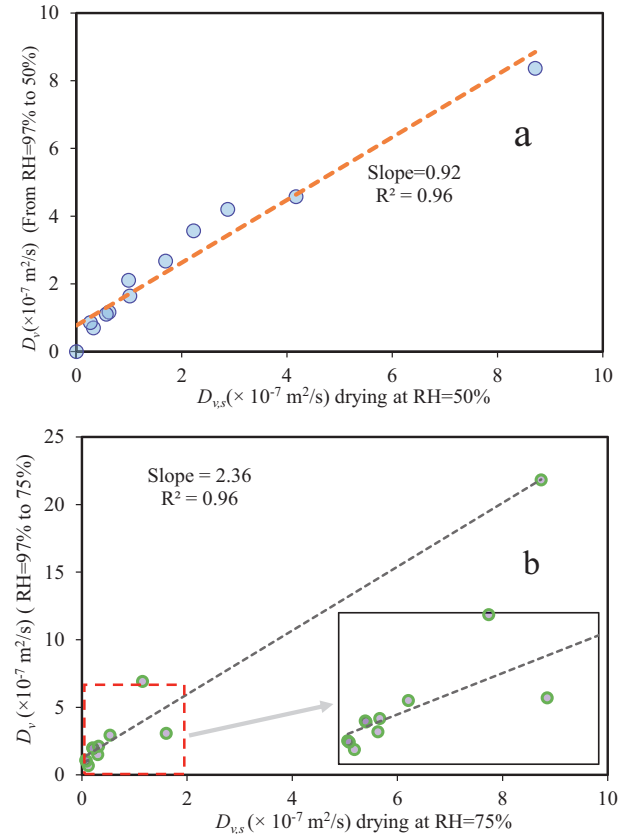


Fig. 10. The correlation between the average vapor diffusion coefficient (D_v) and $D_{v,s}$ from semi-infinite drying at 50 % RH (a) and 75 % RH (b).

to the contraction of C-S-H gel during drying, resulting in the anomalous transport phenomenon. Fick's law can not describe the whole drying process under this kind of non-steady state.

4.3. Correlation between $\bar{D}_v$ and FF

The moisture transport in cement-based materials also relates to the FF and the pore connectivity. Moradillo et al. [71] found that the water adsorption rate correlated to the FF , and it was a linear relationship between the initial rate of water absorption and the reciprocal of the square root of the FF . The $\bar{D}_v$ of cement-based materials is moisture dependent [19,20], owing to the fact that the liquid will gradually occupy the pores in the structure with the increase in the RH. The increasing RH or saturation condition mixes the vapor diffusion with the liquid flow during the moisture transport process [4,23]. Therefore, the correlation between $\bar{D}_v$ in different RH intervals and $1/FF$ is separately plotted in Fig. 11a-f.

According to the analysis in the previous section, the $\bar{D}_v$ at a high RH interval is determined by the pore connectivity instead of the porosity. A good linear correlation between $\bar{D}_v$ in RH97-75 with $1/FF$ (see Fig. 11a) confirms this conclusion. The enlarged plot in Fig. 11b shows that this linear correlation is general in both OPC and the blended pastes with $R^2 = 0.985$. Because the pore connectivity determines the moisture transport process, the vapor diffusivity of the blended pastes is much lower than OPC pastes at the high RH interval. Although they have a similar porosity (see Fig. 7), the β or $1/FF$ of the blended pastes is much smaller than that of OPC pastes (see Fig. 8).

Fig. 11c indicates that the correlation between the $1/FF$ and $\bar{D}_v$ still exists in RH85-75, but the correlation in the blended pastes deviates from the general trend with a higher slope than the general line as shown in Fig. 11d. The critical RH (φ_c) for the percolation of the liquid in the

blended pastes is much higher than that for OPC (see Fig. 4) due to the difference in pore structure and alkali concentration in the pore solution [35,58]. Therefore, the condition of RH85-75 is sufficiently higher than φ_c for the percolation of the liquid in OPC pastes but it does not reach the level of percolation of liquid in the blended pastes. As the RH intervals decrease, the connectivity of the liquid phase in the pores evidently decreases so that the moisture transport process turns to be mainly determined by the porosity in pastes (see Fig. S5-c in supplementary information). Consequently, the $\bar{D}_v$ of the blended pastes is close to that of the OPC pastes with the same w/b in RH75-50 (see Fig. 4), even though the $1/FF$ or β of the blended pastes is much lower than that of the OPC paste. The slope of the blended samples in Fig. 11d-f increases, as the major determinant of $\bar{D}_v$ transitions from the pore connectivity to the porosity with the decrease of RH. FA pastes with w/b of 0.45 deviates from the fitting line of the blended pastes due to its much lower pore connectivity compared with the SL blended pastes with the same w/b .

4.4. Chloride migration coefficient and FF

The chloride migration coefficient in the paste correlates to the pore structure parameter FF and the migration coefficient in the pore solution as shown in Eq. (1). Wilson et al. [27] presented a detailed discussion on the relationship between the effective chloride migration coefficient (D_{eff}) and the electrical properties of pastes, such as the electrical conductivity of pore solution and pastes, FF , or the pore connectivity. They found a general correlation between D_{eff} from their method and the bulk conductivity of pastes. The data of white cement pastes deviated from the general line when D_{eff} was correlated with $1/FF$ or the pore connectivity. It should be noted that in their study, the conductivity of pore solution was measured by extracting the pore solution from pastes. As mentioned in Section 3.4.2, the conductivity of the extracted pore

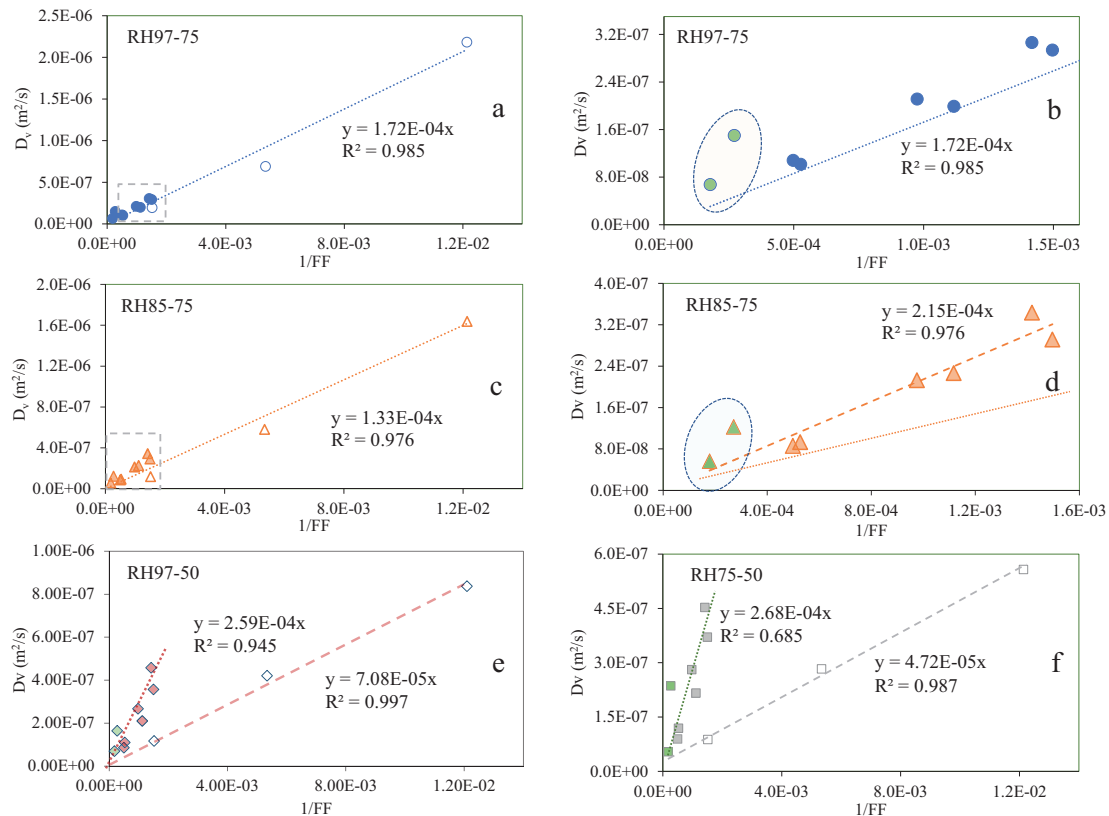


Fig. 11. The correlation between the average vapor diffusion coefficient and $1/FF$: a and b - $\bar{D}_v$ in RH97-75; c and d - $\bar{D}_v$ in RH85-75; e - RH97-50; f - RH75-50. The hollow markers are the data of the OPC pastes, the solid markers are the data of the blended pastes, and the green markers are the data of the FA blended pastes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

solution neglected the surface conductivity, which would impact the calculation of FF when the conductivity of the pore solution is low (<5 S/m, such as in LC_3 or white cement pastes) [54,56,57]. Moreover, avoiding the carbonation of the extracted pore solution during the whole experimental process is critical for measuring a correct conductivity value for the pore solution because the OH^- (pH) in the pore solution contributes $>70\%$ to the ionic conductivity [35].

Chidiac and Shafikhani [58] developed an effective model to estimate the chloride migration coefficient based on the measured conductivity of concrete and the calculated conductivity of pore solution derived from the binder chemical composition and the hydration degree. Provided that we neglect the binding capacity of the hydration products during the non-steady-state migration of chloride under the applied electric field, Eq. (18) can be used to estimate the D_{RCM} based on FF . D_{ps} is the chloride migration coefficient in the bulk pore solution, which was often assumed to be 2.03×10^{-9} (m²/s) [13], but it could be smaller than this value due to the interaction with other ions in the pore solution.

$$D_{RCM} = \frac{D_{ps}}{FF} \quad (18)$$

Fig. 12 presents the relationship between the measured D_{RCM} (from Fig. 5a) and the $1/FF$ (from Table 5). In general, the D_{RCM} of all the pastes is located close to the modelled line (dash line in Fig. 12a), but the pastes with w/b of 0.35 deviate from the modelled line when we focus on the low D_{RCM} region (see Fig. 12b). Because the sealed curing pastes were used to measure the conductivity, the pastes with w/b of 0.35 are far from the saturation state under this curing condition. However, the D_{RCM} was tested under the nearly saturated condition which might result in a deeper chloride penetration depth or a higher value of D_{RCM} . The conductivity and chloride migration coefficient in [58] was normalized

to the mortar volume and adopted in Fig. 12b. Both the data at 84 days and 1 year stay close to the modelled line. Therefore, the pore connectivity or FF should be a key controlling factor for the chloride migration in the OPC based materials.

5. Conclusions

A novel setup and procedure are proposed in this work, which enables to obtain the data of moisture transport coefficients, including k_w , D_w , $D_{v,ss}$, and $\bar{D}_v$, within one test procedure. The moisture transport coefficient is dependent on the RH condition due to the condensation of the liquid phase in the pores. SCMs alter not only the moisture transport coefficient at certain RH but also its dependence on the RH condition. The effects of SCMs on the moisture transport properties can mainly be ascribed to their refinement of the pore structure.

$\bar{D}_v$ of OPC pastes presents an increasing trend as the RH increases due to the gradual condensation of water in the porous structure. The ϕ_c for the percolation of the liquid in cement-based materials is determined by the pore structure and pore solution concentration. The blended pastes have a more complex pore structure and lower alkali ions in the pore solution than OPC pastes; hence the blended pastes require a much higher critical RH for the percolation of the liquid than OPC pastes. It results in a relatively stable $\bar{D}_v$ of the blended pastes in the RH intervals lower than 85 %. An increase in w/b augments the reduction effect of SCMs on the moisture transport and chloride ion migration coefficient in the pastes.

FA lowers the CP of pastes after curing for 390 days, but SL has no reduction effect on the CP of the pastes under the sealed curing condition because of the low accessibility of liquid water in large capillary pores. The blending of FA induces an increase in the total porosity but does not increase the volume of the large capillary pores. SL decreases the percentage of large capillary pores and increases the percentage of mesopores or “ink-bottle” pores with a mesoscale neck. Both FA and SL have a large reduction effect on the pore connectivity in the pastes after long-term curing. A further blending of LL has a similar effect but not as big as the SL blended pastes on the pore connectivity in the hardened pastes after about 1 year. The higher w/b provides more water for the later age hydration of FA and SL, so that their refinement effects become more evident.

$D_{v,s}$ is close to $\bar{D}_v$ at the low RH condition ($\sim 50\%$), but the difference between them will largely increase at a high RH. Both the FF and porosity of small pores (middle capillary and mesopores) are important parameters that determine the moisture transport properties in the cement-based materials. FF is the major determinant for the moisture transport process at a high RH interval, and the porosity of small pores is the major determinant at a low RH interval.

A highly simplified model was proposed with only one measurable parameter FF of pastes for the correlation to the chloride migration coefficient. This model can generally estimate the D_{RCM} of both pastes and mortars. Regarding the performance concretes, the blending of SCMs has an impact on pore structure in the interfacial transition zone. Some more detailed investigations are needed to apply the data in this paper into the blended concretes.

CRediT authorship contribution statement

Liming Huang: Conceptualization, Methodology, Investigation, Data analysis, Writing-Original Draft, Writing-Review & Editing. Luping Tang: Methodology, Writing-Review & Editing, Supervision, Project administration, Funding acquisition. Ingemar Löfgren: Investigation, Writing-Review & Editing. Nilla Olsson: Investigation, Project administration. Zhenghong Yang: Review & Editing, Supervision, Project administration. Yongqiang Li: Investigation, Resources.

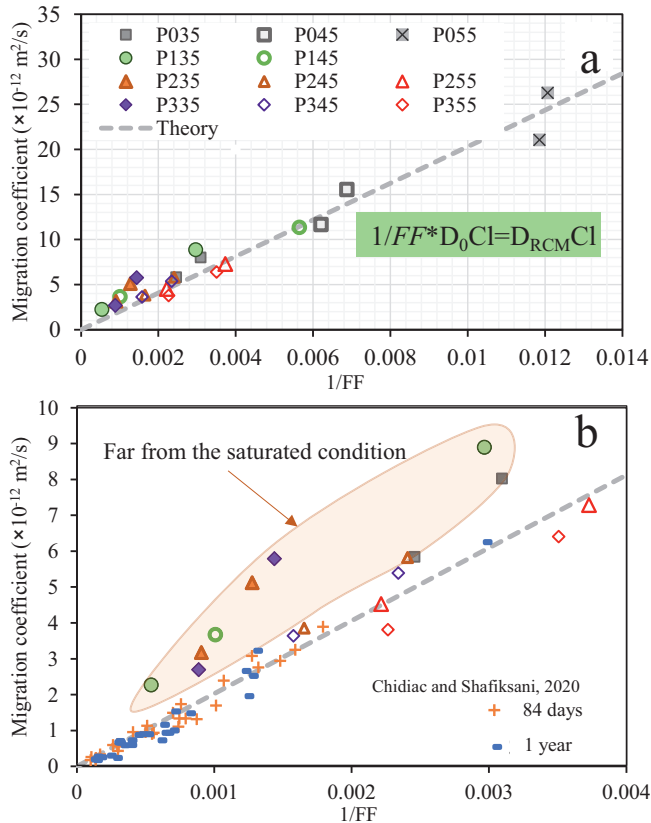


Fig. 12. The correlation between the chloride migration coefficient and $1/FF$: a - data in this paper at the curing time of 28 and 90 days; b - data in [58] was used and adopted after some normalizations.

Declaration of competing interest

We declare no conflicts of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cemconres.2022.106949>.

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Paper VI

Long-term performance of reinforced concrete under a de-icing road environment

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Long-term performance of reinforced concrete under a de-icing road environment

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ABSTRACT

In the middle of 1990, over 30 different mixes of concretes with eight different binders and water-binder ratios of 0.3 to 0.75 were exposed to a highway environment with a heavy de-icing salt spread for the examination of long-term performance, including chloride penetration, reinforcement corrosion and frost attack. This paper presents the results from this long-term study regarding chloride penetration and reinforcement corrosion. The results show that the chloride penetration in concretes under a de-icing salt road environment is much weaker than that in concretes under marine splash environment in Sweden. The estimated critical chloride content for the corrosion initiation is about 0.3 % by mass of binder for rebars with uncracked concrete cover. Considering the chloride redistribution in the surface zone, ClinConc model has been modified so that it can present a better description of the chloride profiles in the concretes at such an exposure site.

1. Introduction

The corrosion of reinforcing steel induced by chloride and frost damage are major challenges for the service life of reinforced concrete structures exposed to a de-icing salt environment. To design sustainable, economical, and safe concrete structures, models are needed for the description of chloride transport in concrete exposed to such an environment. Moreover, models are also significant to evaluate the residual service life for existing reinforced structures. They are applied to assess the starting time of reinforcement corrosion, internal frost damage or frost scaling. These models should be robust, credible, and based on the physical/chemical principle, which should also be validated with long-term results from the reinforced concrete structures installed in fields. The measured results can serve as input parameters in performance-based approach for offering rational designs, allowing innovation in concrete construction, and providing efficient means for assessing of the as-built structure [1].

Investigations of the frost resistance and corrosion of reinforcement steel induced by chloride have been initiated since the 1980's in Sweden. Many findings are well-known and popularly cited in current studies. These influential achievements include Tuutti's conceptual model for predicting service life of reinforced concretes [2], the slab-test for rating

the surface scaling [3] and internal damage [4] due to the frost attack, the frost and service life model by Fagerlund [5,6] and Petersson [7], the evaluation of the chloride penetration by the RCM (Rapid Chloride Migration) test [8,9], and the ClinConc model for predicting chloride penetration [9,10]. During the last decade, the ageing effect (hydration, drying and carbonation) on the salt-frost resistance of concrete was investigated by Utgenannt [11]. Fridh [12] performed experimental studies of the destruction mechanisms for the internal damages due to the frost attack. Tang and Utgenannt [13] reported the penetration of chloride into concrete after a 10-year exposure in the road environment. Li [14] carried out experimental investigations on the freeze-thaw induced chloride penetration into concretes. In the past years, Tang et al. [15] summarized different models for the prediction of resistance of chloride penetration into concrete and they also tried to use the field data to verify these models. Boubitsas et al. [16] reported the field data of chloride penetration into concretes with various binder types after an exposure of 20 years in a Swedish marine environment. Their findings regarding chloride penetration in concretes exposed to marine environments, especially those in the splash and atmospheric zones, could also be useful for understanding the chloride penetration in concretes under road environments exposed to de-icing salt due to the similarity in ageing processes.

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Among the research in other countries, only a few literatures reported the corrosion resistance performance of the reinforced concrete under a de-icing salt environment. Polder and Hug [17] measured the penetration of chloride from de-icing salt in one bridge in Netherlands after a long-term service (30 years). Gode and Paeglitis [18] conducted an evaluation of the chloride migration in bridge piers under de-icing salt environment to predict the remaining service life. Some models were also developed to evaluate the chloride penetration under this environment with the consideration of carbonation [19] and cracking [20]. Although there are some ongoing projects in this area, problems still exist in the practical application of the experimental results in service life models for reinforced concrete structures under the road environments. It is mainly due to the lack of sufficient data from concrete with various binder types and proportions after a long-term exposure. An effective model for prediction of chloride penetration based on the field data is also needed under this special environment.

A series of reinforced concrete specimens have been exposed to de-icing salts at the field site by a highway Rv40 between Gothenburg and Borås in Sweden since the winter of 1996–1997. The severe cold weather in the winter needed an intensive use of de-icing salts on road for defrosting. Chloride penetration profiles in these concrete specimens were measured after an exposure for 1, 2, 5, 10, and 20 winters. Corrosion conditions of the embedded rebars in the specimens were examined after an exposure of 10 and 20 winters. These measured data

from exposure sites would function as the useful information about long-term performance of concretes served under the de-icing salts environment. With these data we can have the opportunity to validate various models for service life prediction. This paper presents the findings from this long-term study about the chloride penetration and corrosion of reinforcement. The ClinConc model [10] has been modified to present a better prediction of chloride penetration in concretes with different proportions after a long-term exposure to the de-icing road environment.

2. Experimental information

2.1. Concrete specimens

Concretes with 33 types of mixing proportion were designed for the long-term exposure experiments in the field site. The different mix proportions are presented in Table 1. The detailed information of the raw materials and properties of concrete were published in a previous report [21] and some fresh properties were presented in [22]. Concretes were cast with various water-binder ratios from 0.3 up to 0.75, and with eight types of binder system. Some concretes were added with air entraining agent (AEA) in a range of 0.008–0.04 % by mass of binder. Two types of concrete component were produced at the laboratory and then moved to the exposure site after a moist curing for 35 to 70 days in

Table 1
Mixture proportions of concretes exposed at the Highway 40 field site.

Types of binder	w/b	Binder kg/m ³	Fine kg/m ³	Coarse kg/m ³	AEA ^a mass %	Sp ^b mass %	Air vol%	28-day strength ^c MPa
Anl ^d	0.40	420	886.4	851.6	0.028	0.97	4.8	65.4
	0.50	380	890.2	821.8	0.012		4.5	50.8
	0.30	500	833.5	978.5		3.25	1.3	100.6
	0.35	450	880.3	953.7		2.27	0.9	91.3
	0.50	380	938.6	866.4			1.3	54.8
Anl + 5%SF ^e	0.75	260	1007.4	791.6	0.012		4.5	30
	0.40	420	860	860	0.04	1.2	4.7	78.1
	0.50	380	865.5	831.5	0.022		4.4	58.2
	0.30	500	806	985.1	0	1.7	1.2	119.7
	0.35	450	846.5	954.5	0	1.5	1.1	103.5
Fin Std ^f	0.50	380	905.8	870.2	0	0	0.9	62.6
	0.40	420	863	863	0.02	1.2	4.9	48.8
	0.50	380	885	817	0.008	0	4.5	42.1
Slite Std ^g	0.30	540	767.7	938.3	0	3.6	2.5	66.9
	0.50	390	915.2	844.8	0	0	1.2	47.4
	0.40	420	880.3	845.7	0.027	1.7	4.9	60.7
Fin Rpd ^h + 44%SL ⁱ	0.50	390	874.1	806.9	0.01	0	4.4	46
	0.30	520	799.9	939.1	0	3.8	2.3	85.7
	0.50	410	892.3	823.7	0	0	1.4	59.9
Fin Rpd	0.40	420	858	858	0.027	1.15	4.5	55
	0.50	370	891.8	823.2	0.01	0	4.7	41.5
	0.30	540	761.9	931.2	0.01	3.8	1.6	82
Anl + 10%SF	0.40	420	863	863	0.027	2	4.7	57.6
	0.50	380	885	817	0.013	0	4.9	43.4
	0.30	540	767.7	938.3	0	4.15	2.4	66.5
P Kalk C ^j	0.40	420	851.5	851.5	0.08	1.42	4.8	81.4
	0.30	500	796.5	973.5	0	2.1	0.5	126.9
	0.35	450	844.1	951.9	0	1.7	0.9	112.7
P Kalk C ^j	0.40	420	880.3	845.7	0.03	1.7	4.8	68.9
	0.50	390	874.1	806.9	0.014	0	4.7	51.8
	0.30	530	781.2	954.8	0	3.6	2.2	98.5
P Kalk C ^j	0.35	470	851	922	0	2.62	1.8	86.3
	0.50	400	903.8	834.2	0	0	1.2	60.9

^a AEA – Air entraining agent, supplied by Cementa L17, percentage by mass of binder.

^b Sp – Super-plasticizer, purchased from Cementa Melcrete, percentage by mass of binder.

^c Compressive strength tested according to SS 13 72 10.

^d Anl – Swedish structural cement (Anlångningscement, CEM I 42,5 N - SR 3 MH/LA).

^e SF – Silica fume (Elkem Microsilica, Norway).

^f Fin Std – Finnish standard Portland cement blended with 15–18 % slag (CEM II/A-S).

^g Slite Std – Ordinary Portland cement in Sweden, made in Slite (CEM I 52.5 N).

^h Fin Rpd – Finnish rapid Portland cement blended with 10–15 % limestone filler (CEM II/A-LL 42.5R).

ⁱ SL – Finnish ground granulated blast-furnace (ggbf) slag.

^j P Kalk C – Swedish Portland cement blended with 10–15 % limestone filler (CEM II/A-LL).

the laboratory, including one plain concrete specimen with a size of $400 \times 300 \times 300$ mm and the other reinforced concrete beams with a size of $1200 \times 300 \times 300$ mm. The plain concretes were used for the test of chloride profiles. The reinforced concrete beams were designed for the investigation of corrosion resistance of rebars in concretes under pre-cracked and uncracked conditions. Ribbed rebars with diameter of 12 mm were bended at the ends for placing them at the specific position. The end of rebars were coated with epoxy, and the length of the exposed part of rebars was about 480 mm (see Fig. 1). There are mainly two different setups of the rebars with a cover thickness of 15 mm and 30 mm, respectively. Some rebars were also embedded in concrete with a cover thickness of 60 mm above the set of bars with a cover thickness of 30 mm. A copper wire was soldered on one of the ends of rebar. The other end of the copper wire was connected to a plinth in a nearby electronic box for electrochemical measurement. The detailed information of the setting of reinforcements in concretes can be found in the report [23] and there is a manual for how the rebars were cast in each specimen [24].

2.2. Field exposure conditions

The field exposure site has been established in the autumn of 1996 at the highway 40, which locates outside Borås in Sweden. As shown in Fig. 2, specimens were mounted in steel frames at the road level and then were put upon the gravel layer. To ensure the traffic safety, the exposure site was separated from the road by a guard rail. A part of the guard rail kept open (below the height of 0.45 m) to ensure the specimens fully exposed to the splashing water from the traffic. The distance between the exposure surface and safe line of road is about 2.7 m. The specimens were exposed to many winters with low temperature, moist environment, and de-icing salts. This kind of climate corresponds to the exposure class equal to XD3/XF4 according to EN 206-1. Fig. 2 also shows the sampling position for the measurement of chloride profiles. The air temperature at a weather station close to the exposure site was about 10°C as a monthly average. The detailed condition of the exposure site can be found in the report [13].

3. Experimental methods for testing chloride penetration profiles and rebar corrosion

3.1. Measurement of chloride penetration profiles

After an exposure of about 1, 5, 10 and 20 winters, the concrete blocks were taken to the laboratory for sampling. Concrete cores with diameter of 100 mm, from the middle height of the vertical exposure surface, were collected for the measurement of chloride profiles (see Fig. 2). The samples were taken at a certain depth by a diamond tool on a

lathe step by step from the surface of exposure. The sampling depth was measured with an accuracy of 0.5 mm by a caliper. The samples were dried at 105°C immediately after the grinding. Afterwards the dried samples were stored in a desiccator until the analysis for chloride content.

The total chloride content in each sample was analyzed by means of potentiometric titration principally based on AASHTO T260 with acid extraction.

3.2. Measurement of reinforcement corrosion

After exposed for 10 and 20 winters, the corrosion level of the rebars in the reinforced concrete beams were estimated by the use of one handheld instrument RapiCor, which is based on the galvanostatic pulse technique, as described in [13,25,26]. This instrument measures three parameters: the corrosion rate; the half-cell potential of a rebar inside the concrete and the ohmic resistivity of the concrete cover. These parameters were utilized for the assessment of the corrosion condition. The main parameter from this instrument is corrosion rate, integrating with the resistivity and half-cell potential as the complementary parameters for assessing the level of corrosion or corrosion index. Table 2 shows the criteria of corrosion index used in this study. The green, yellow, orange and red color present the corrosion of steel bar with a level of negligible, low, moderate and high, respectively.

After a nondestructive measurement of corrosion on the concrete surfaces, some of the beams containing suspiciously corroded rebars were selected for destructively examination of corrosion condition. These beams were firstly sawn at the position where one end of rebar laid in the transvers section to the cross-section of the exposed rebar. Then the RapiCor instrument was used again to measure the corrosion with the sure connection to the rebar (to check if there was any misleading result from the measurement by connection of the soldered cable). The rebars were collected by means of sawing and splitting from each concrete beam. The actual condition of corrosion in each rebar was examined by a visual observation as well.

3.3. Measurement of carbonation depths

For some selected types of concrete, the carbonation depths on the split surfaces were measured by using the colorimetric method with 1 % phenolphthalein solution. It should be noted that no systematic measurement of carbonation depths was planned in the research program, but just occasionally carried out on some types of concrete for destructive tests, such as those after removal of rebars or on the small specimens for testing frost attack.

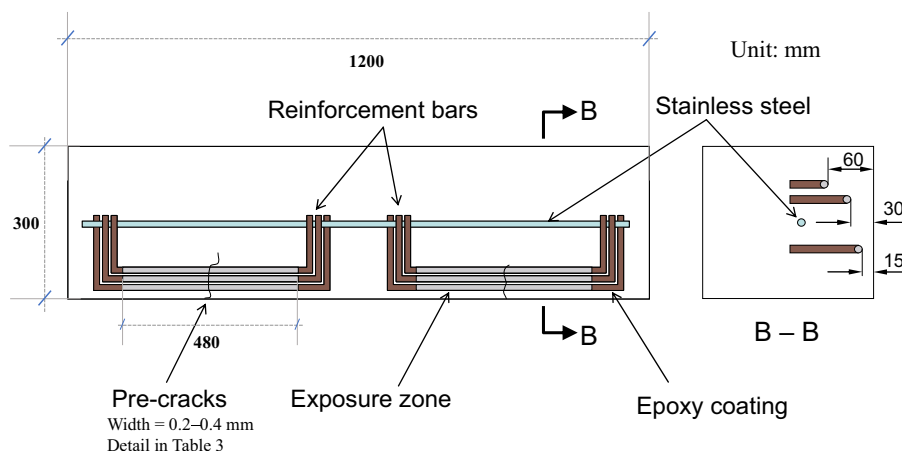


Fig. 1. Arrangement of rebars in the reinforced beams exposed to the Rv40 field site [17].

Notes: 1) There was no rebar located at the level with a cover thickness of 60 mm in most of the beams. 2) Each rebar was soldered with a copper wire which connected the rebar to the plinth in a box outside the specimen for the measurement of corrosion by the electrochemical method.

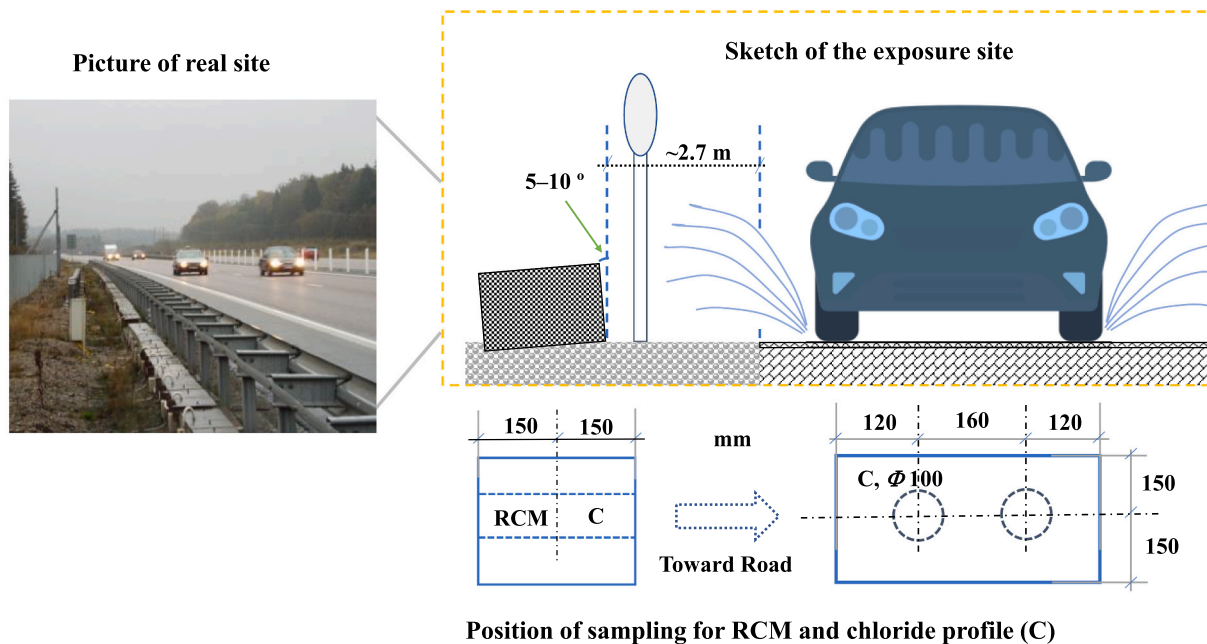


Fig. 2. Placement of specimens at the Rv40 field site for exposure.

Table 2
Criteria for different indexes of reinforcement corrosion.

Corrosion Index	Corrosion level	Corrosion rate $\mu\text{A}/\text{cm}^2$	Resistivity $\Omega\cdot\text{m}$	Half-cell potential $\text{mV}_{(\text{CSE})}$
1	Negligible	<0.1	-	-
		0.1~0.5	> 10	> -200
2	Low	0.1~0.5	< 10	< -200
		0.5~1	> 10	> -200
3	Moderate	0.5~1	< 10	< -200
		>1	> 10	> -200
4	High	>1	< 10	< -200

4. Performance of concrete and reinforcement

4.1. Resistance to chloride penetration

4.1.1. Effect of binder types

Fig. 3 presents the comparison of chloride penetration profiles in concrete with five different types of commercial cements after exposed for 20 winters. It is difficult to find a general tendency in the chloride content at the specific depth with different types of cements, so there is no absolute ranking of the resistance to chloride penetration for different commercial cements with different w/b . For the concretes with $w/b \leq 0.4$, the Fin Rpd cement has the lowest chloride contents in most of the depths. An increase in w/b generally induces a deeper chloride penetration into the concretes.

The effect of mineral additions (silica fume and slag) on the chloride penetration is shown in Fig. 4. It seems that a replacement of Swedish structural cement by 5 % silica fume has no significant effect on chloride penetration after 20 years exposure, but its effect on reducing chloride content becomes clear when it is replaced with 10 % silica fume. For concretes with $w/b = 0.3$, the blending of 44 % slag has minor effects on chloride penetration. This is mainly because of the limited hydration degree of slag and clinker. According to Powers's model [27], a full hydration of typical Portland cement requires at least a w/b of 0.36, so

slag in concretes with w/b of 0.3 has a low accessibility to water at later age to limit its refinement effect on the pore structure. Yio et al. [28] reported that the slag blended pastes with w/b of 0.3 had a higher gas transport coefficient than the plain paste. A recent study also found that slag had a much weaker effect on chloride migration coefficient of pastes with w/b of 0.35 than those with w/b of 0.45 at 6 months [29]. Therefore, when the concretes are mixed with w/b of 0.4–0.5, the reducing effect from slag is much clearer especially in the depth larger than 20 mm. This mainly derives from the effect of slag on refining the pore structure, such as reducing the pore connectivity [30], and changing the chloride binding capacity [31,32].

4.1.2. Effect of w/b and the entrained air

Fig. 5 presents the chloride penetration profiles in concretes mixed with different w/b , and with/without entrained air after an exposure of 20 winters. It is evident that a decrease in w/b enforces concretes with a higher resistance to chloride penetration. This phenomenon is more obvious in concretes with w/b larger than or equal to 0.40, but there is one exception in the concrete with the binder noted as Fin Rpd + 44%SL. In this mix the chloride penetration profile is quite similar in concretes with w/b of 0.40 and 0.50.

The effect of AEA on chloride penetration in the concretes with w/b of 0.5 is shown in Fig. 6. For the concretes mixed with Anl and Anl + 5 %

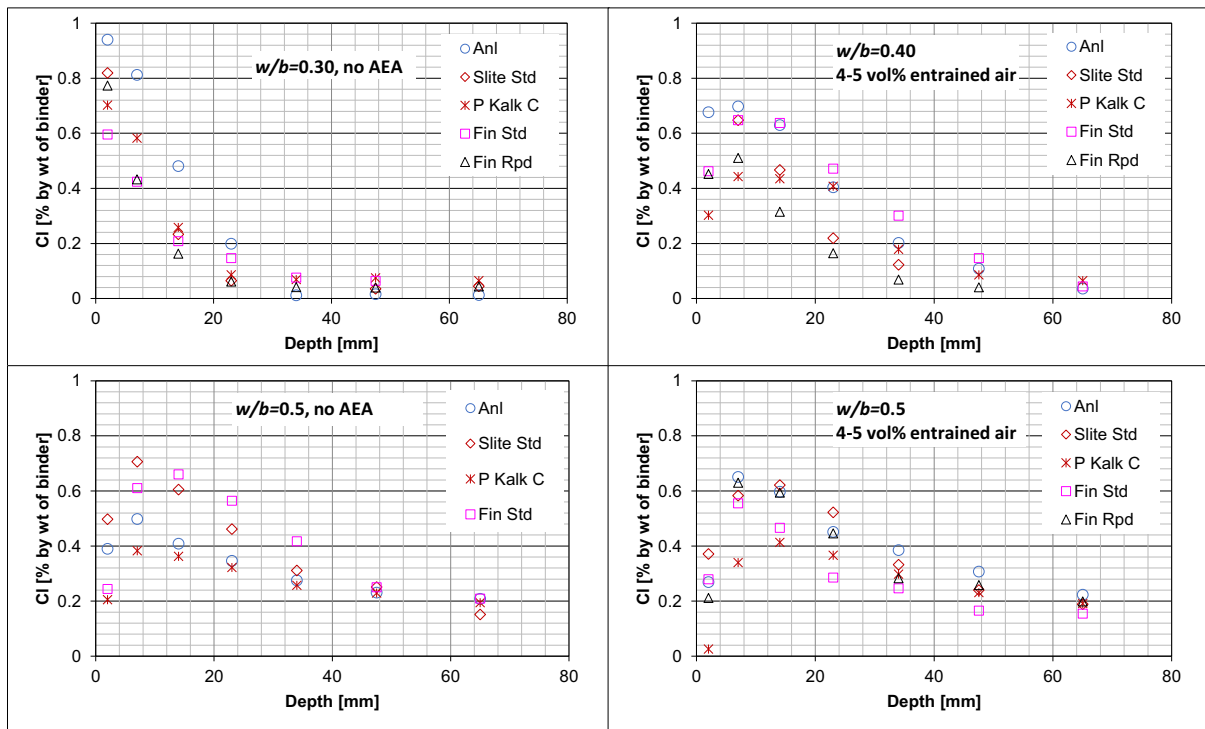


Fig. 3. Comparison of chloride penetration profiles in concretes cast with different types of commercial cements.

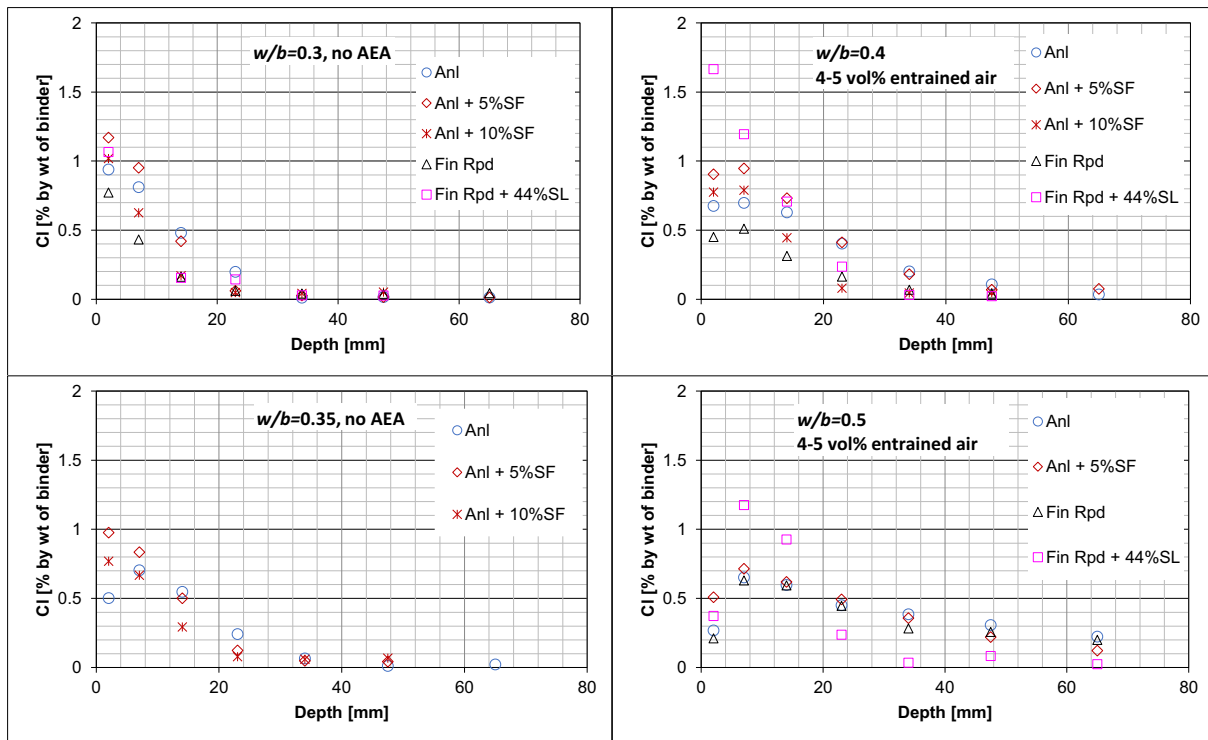


Fig. 4. Comparison of chloride penetration profiles in concretes with the addition of different supplementary cementitious materials.

SF (see Fig. 6, left side), the introduction of entrained air void induces a higher chloride content from the surface and to the depth at about 60 mm. In the deeper place up to 120 mm, the chloride content in concretes with AEA stays close to that in concrete without entrained air. However, the entrained void seems to have little influence on the resistance to chloride penetration in concrete mixed with Slite Std or P Kalk C cement

(see the right side in Fig. 6). Therefore, it is obvious that the effect of AEA on chloride penetration in cement-based materials depends on the types of binders.

4.1.3. The influence of different exposure durations

The chloride penetrations in two mixes of concrete with w/b of 0.4

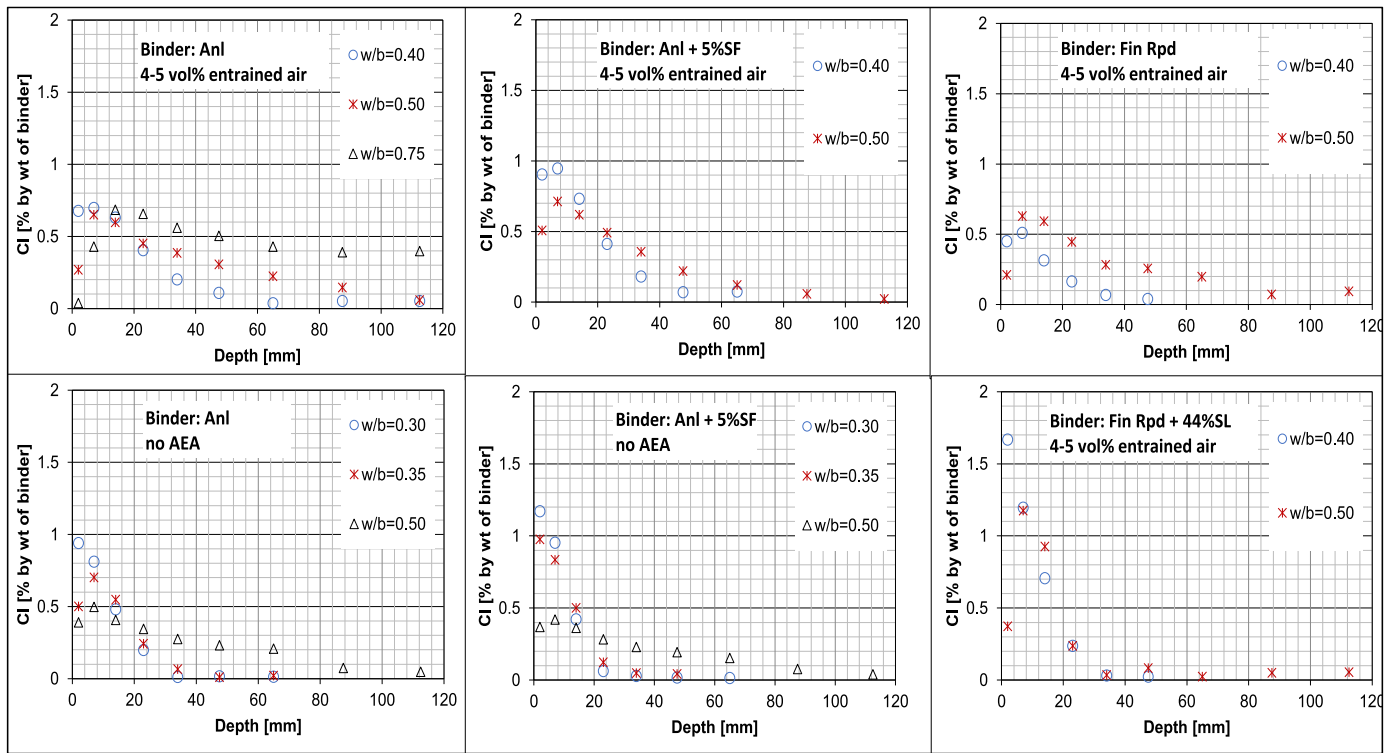


Fig. 5. Chloride profiles in concretes with different w/b , binder types and AEA contents.

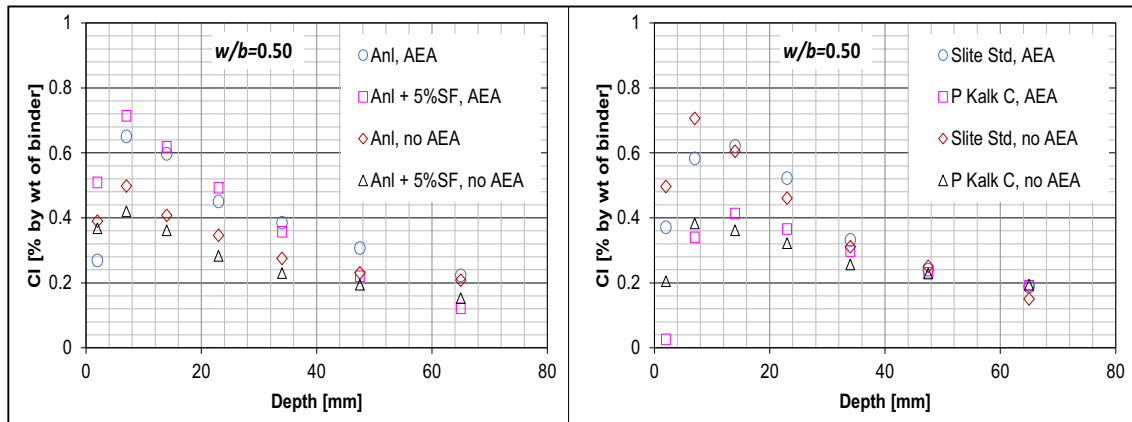


Fig. 6. Chloride profiles in concretes with and without AEA after 20 winters exposure.

are compared in Fig. 7 to focus on the effect of different exposure durations. The chloride profiles in concretes with Swedish structural cement (Anl) are similar in different exposure durations from 1 to 10 winters, and the value is evidently lower than that of concretes after an exposure of 20 winters. An interesting phenomenon has been observed in concrete with Swedish structural cement replaced with 5 % SF. The chloride content in the depth of 0–20 mm was unexpectedly higher in concretes with a shorter exposure duration. After four winters from 1996 to 2000, a new technique was used for spreading the de-icing salts and the average dosage was reduced to a half of the previous winters [13], so this may result in a lower free chloride concentration in pore solution. However, the free chloride in pore solution accounts for <10 % of total chloride content, and the main contribution is from bound/absorbed chloride in solid phase (AFm and C-S-H) [33]. Therefore, this interesting difference may result from phases change after a long-term interaction and leaching, such as decomposition of chloride-containing AFm, leaching of portlandite and decalcification in C-S-H [33,34]. Moreover,

the carbonation in the near surface zone is also one of the main factors. Carbonation will induce a decrease in the pH of pore solution, this process may increase the Cl binding when the pH lowers from 13 to 12 and the binding capacity would decrease when the pH decreases after 12 [35]. Hence, the surface zone could have a higher chloride content at 5 years than later age due to the limited carbonation.

Fig. 8 shows the comparison of chloride penetrations in all concretes with $w/b \leq 0.4$ after exposure of 10 and 20 winters. The chloride penetration depths in concretes after an exposure of 20 winters are generally deeper than those in concretes after an exposure of 10 winters. However, the minor differences in concretes with w/b of 0.3 indicate that for these types of concretes the penetration under the road environment is rather slow after the 10-winter exposure.

4.1.4. Effect of the exposure environment

The chloride profiles in concretes with Anl cement exposed to marine environment have been reported in a previous study [16] after a 20-

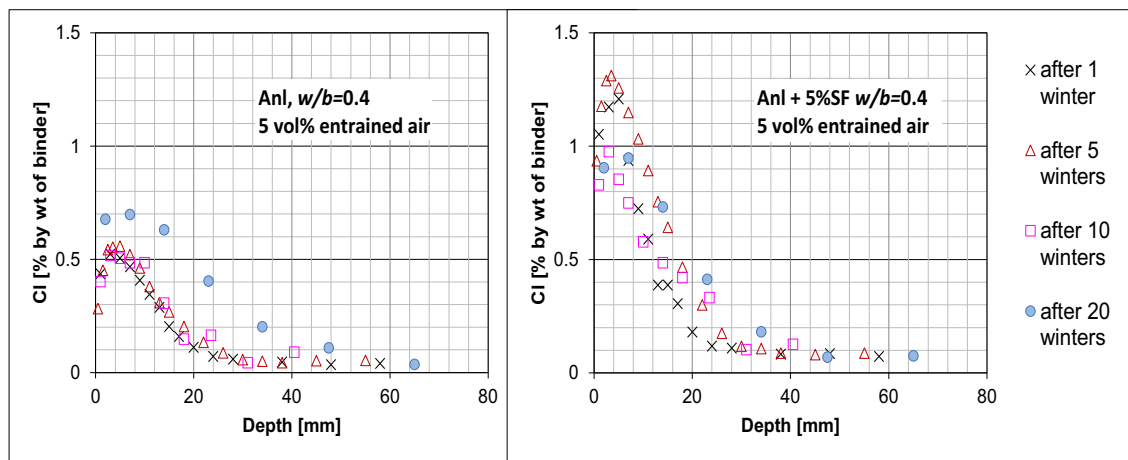


Fig. 7. Chloride profiles in two selected types of concretes after the exposure of different durations.

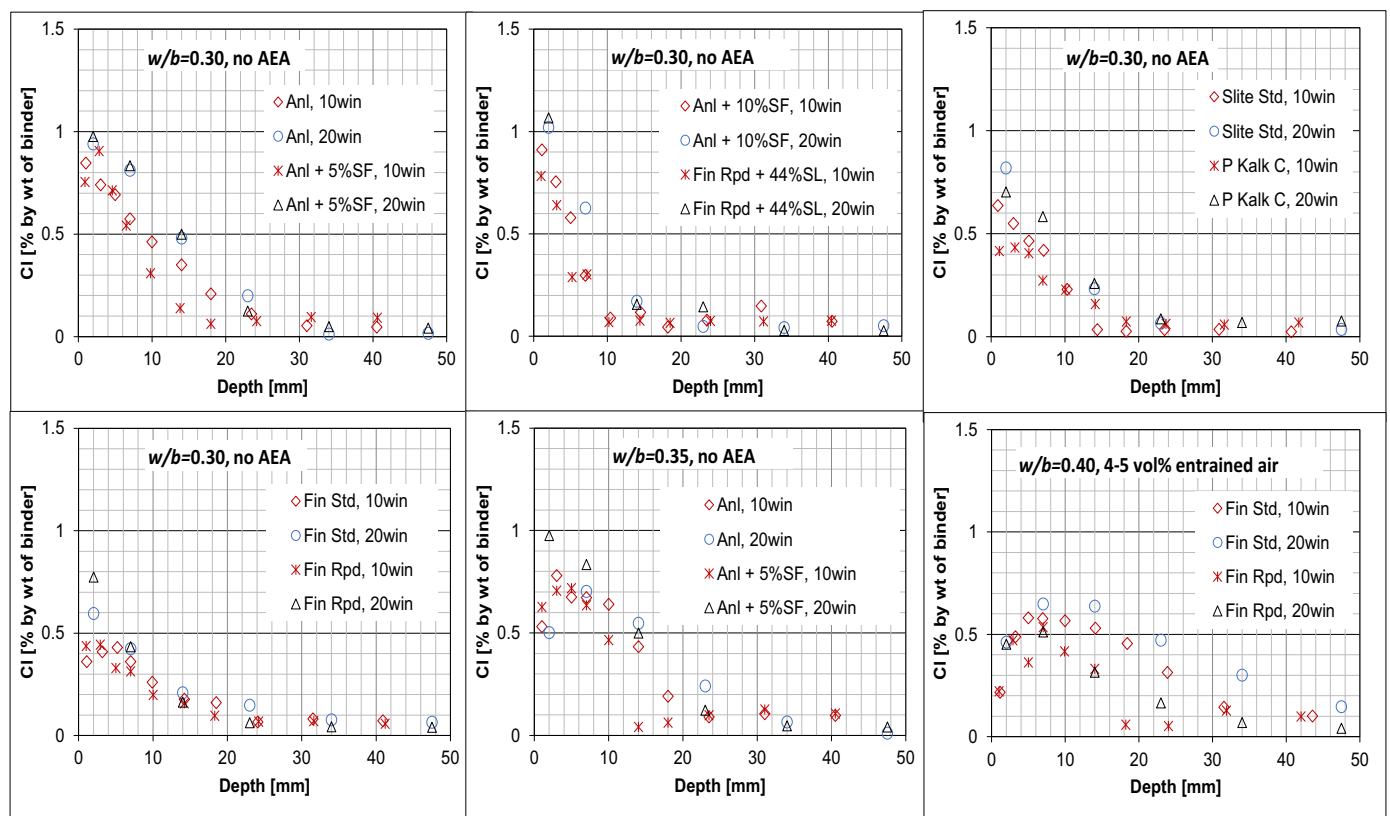


Fig. 8. Chloride profiles in different concretes after an exposure of 10 and 20 winters (win = winter).

year-exposure along Swedish western coast. Fig. 9 presents the comparisons of chloride penetration profiles in four similar concretes exposed to different environments (marine atmospheric, marine splash and de-icing salt road). Apparently, an exposure in the marine environment, especially in splash zone, induced a higher chloride content than that in the road environment in all depths. After an exposure of 20 winters/years, the chloride penetration in concrete with Swedish structural cement (Anl) and w/b of 0.35 is severer in marine atmospheric environment than that in road environment. For the concretes with 5 % SF, the difference in chloride profiles between marine atmospheric and road environment is less than that of concretes with plain Swedish structural cement. However, it is worth to note that the concretes with w/b of 0.35 at the highway site were not mixed with any AEA but this

was used in the mixes exposed at the marine site. The chloride ingress process is moisture dependent as well. A higher moisture content induces a larger chloride migration [36], so the marine environment induces a severer ingress of Cl than road environment. Leaching would cause the coarsening of microstructure to induce a peaking phenomenon in concretes at marine exposure [34,37]. Moreover, splashing zone has a much higher frequencies wet-dry cycles to induce severer leaching and precipitation on the surface zone. This results in a more evident phase change of products and microstructure changes compared to atmospheric zone and road environment, so we can observe a much higher ingress and peak of chloride content.

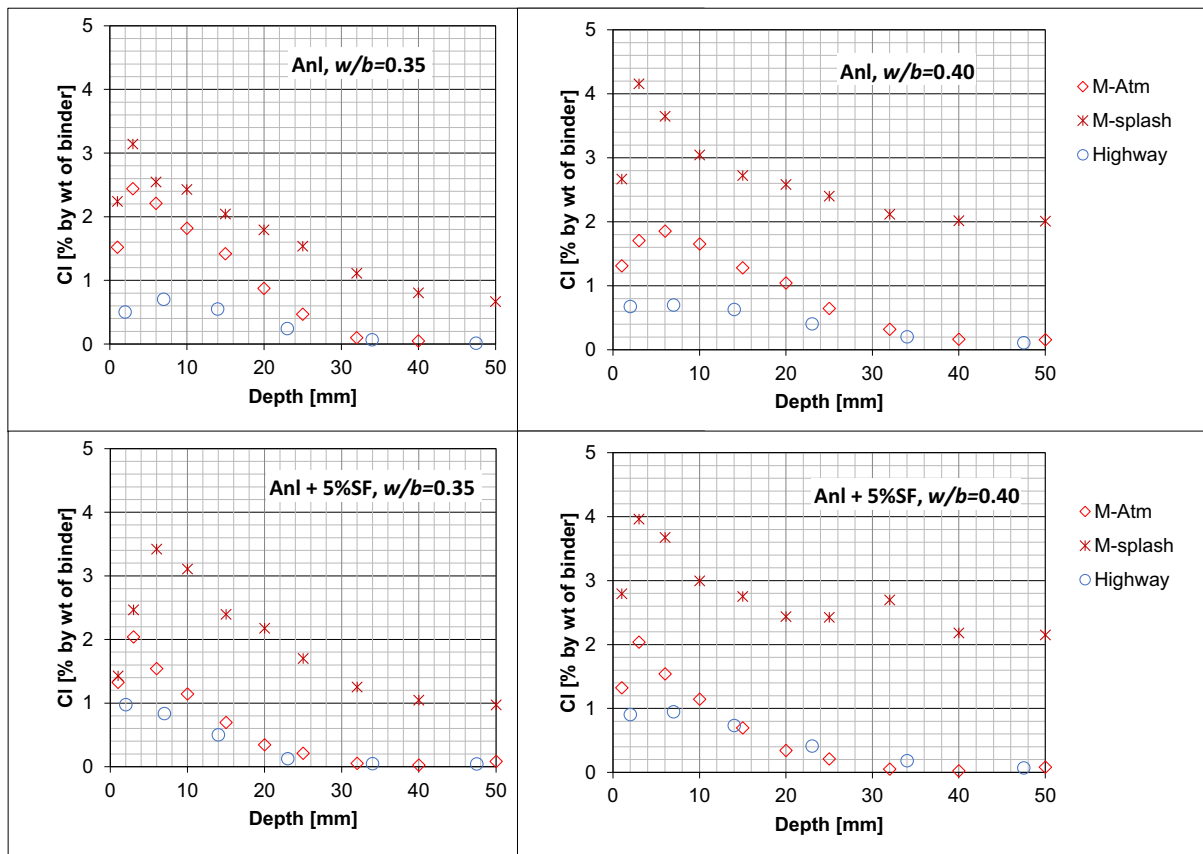


Fig. 9. Chloride penetration profiles in concretes after an exposure of 20 winters/years under the M-Atm (marine atmospheric), M-splash (marine splash) and highway (de-icing road) environments.

4.2. Resistance to reinforcement corrosion

It has been proven through several destructive examinations that the measured corrosion index by the handheld instrument RapiCor were in reasonable agreement with the visual observation [25,38,39]. Because the rebars with 15 mm cover thickness in the lower part of the beam that was covered by the snow for a longer period than the rebars with 30 mm cover, these rebars revealed less corrosion than those with 30 mm cover. The chloride penetration profiles were sampled at the same level as the rebars with 30 mm cover. Therefore, we summarize the measured corrosion indexes for the rebars with 30 mm cover only (see Table 3). Fig. 10 shows a typical comparison between the visual examination and the RapiCor measured corrosion state of reinforcement.

Table 3 shows that a low corrosion (index 2) occurred in five types of uncracked concrete with w/b of 0.40–0.50 after 20 winters. Moderate to high corrosion (indexes 3–4) occurred only in four different uncracked concretes with w/b larger than or equal to 0.50. The blending of slag and silica fume can significantly inhibit the corrosion of rebar in concrete with the same w/b . It was expected that corrosion occurred more in types of pre-cracked concrete. From two occasional measurements of corrosion, it is difficult to know the actual initiation of corrosion. However, if we take corrosion index 2 (low corrosion) as the near initiation, we can roughly estimate a critical chloride content for the initiation of corrosion at the depth with about 0.3 % by mass of binder for most of rebars in uncracked concrete. For the rebar in concrete with Fid Rpd cement and w/b of 0.5, a moderate corrosion occurred even at the depth with chloride content of 0.1 % of binder by mass. This rebar was released for visual examination and rust stains were indeed observed [13]. No good explanation can be given for this observation from current investigations. It seems that the critical chloride content of corrosion of rebars is lower in the pre-cracked concrete cover than that

in the uncracked. However, a further investigation is needed for drawing a clear conclusion.

4.3. Resistance to carbonation

As mentioned in Section 3.3, the carbonation depths were measured only in some selected types of concrete. The measured results are listed in Table 3 in the column after the corrosion index of rebars in the uncracked concrete. It is obvious that the carbonation only occurs in a thin layer close to surface. For the concretes with $w/b \leq 0.5$, the carbonation depth is <3 mm after 20 winters. Even for concretes with w/b of 0.75, the carbonation depth is only 3–6 mm after 10 winters. From data in a parallel project for frost attack, the concrete with CEM III/B (slag content 66–80 %) and w/b 0.5, the carbonation depth was 5–6 mm after 20 winters [40]. Therefore, it can be concluded that all the types of concrete in this study should have a good resistance to carbonation under the de-icing salt road environment.

The composition at the surface after 20-year was altered due to carbonation [41]. Some investigations ascribe the peak phenomenon to the carbonation induced phase and microstructure change [35,37]. Carbonation is one the factor for peak of chloride content, but it can be observed that the influential depth of carbonation is much lower than the peak position. Therefore, leaching of hydration products and interaction between de-icing salts and concrete make large contributions in the formation of peaks as well.

5. Modelling of the chloride penetration

According to the previous publications [13,15], the ClinConc model performed a better prediction of the chloride penetration in concretes exposed to the de-icing environment among three different kinds of

Table 3

Corrosion indexes of steel bars with 30 mm cover in concrete beams after an exposure for 20 winters.

Binder	Uncracked					Pre-cracked	
	w/b	air vol %	Cl%-binder at the rebar	Corrosion Index	Carbonation depth [mm]	Crack [mm]	Corrosion Index
Anl	0.40	4.8	0.3	2	1-2	0.2	2
	0.50	4.5	0.3	2	1-2	0.2	1
	0.30	1.3	0.1	1		0.2	2
	0.35	0.9	0.1	1		0.3	1
	0.50	1.3	0.3	3		0.3	3
	0.75	4.5	0.9	4	3-6	0.2	4
Anl + 5% SF	0.40	4.7	0.3	1		0.2	1
	0.50	4.4	0.15	1		0.4	1
	0.30	1.2	0.1	1		0.2	1
	0.35	1.1	0.1	1	1-2	0.4	1
	0.50	0.9	0.3	1	2-3	0.3	2
Fin Std	0.40	4.9	0.15	1	0-1	0.4	1
	0.50	4.5	0.3	1		0.3	2
	0.30	2.5	0.1	1		0.3	1
	0.50	1.2	0.5	4		0.4	3
Slite Std	0.40	4.9	0.1	1		0.2	2
	0.50	4.4	0.4	1		0.4	1
	0.30	2.3	0.1	1		0.4	1
	0.50	1.4	0.4	2		0.4	2
Fin Rpd + 44%SL	0.40	4.5	0.1	1		0.4	1
	0.50	4.7	0.2	1		0.3	1
	0.30	1.6	0.1	1		0.4	1
Fin Rpd	0.40	4.7	0.1	1		0.4	2
	0.50	4.9	0.1	3	0-1	0.4	3
	0.30	2.4	0.1	1		0.3	1
Anl + 10%SF	0.40	4.8	0.1	1		0.4	1
	0.30	0.5	0.1	1		0.2	1
	0.35	0.9	0.1	1		0.2	2
P Kalk C	0.40	4.8	0.1	2		0.2	2
	0.50	4.7	0.1	1		0.4	1
	0.30	2.2	0.1	1		0.2	3
	0.35	1.8	0.1	1		0.2	1
	0.50	1.2	0.3	2		0.3	3

Note: Italic values were measured after exposed for 10 winters.

models including the simplest model based on Fick's law, the probabilistic model DuraCrete and the mechanism-based model ClinConc. Kim et al. [42] reported that it also worked well in the prediction of chloride profiles in concretes under different marine exposure environments. Therefore, the ClinConc model will be used as the basic model for a further modification. A more detailed information of this model has been described in [7].

5.1. The main input data

The main input parameter in ClinConc model is the chloride migration coefficient of concrete at the age of 6 months, measured by the RCM test according to the Nordtest standard NT BUILD 492. Because the RCM test was not standardized in 1997, the coefficients were not tested

at the ages of 6 months. Therefore, the migration coefficient by RCM from some previous studies were adopted to obtain some empirical equations by regressions. Fig. 11 show that the relationship between chloride migration coefficient and w/b follows a power function.

$$D_{RCM} = A \left(\frac{w}{b} \right)^B \quad (1)$$

where constants A and B depend on binder type and dosage of AEA. The regression equations in Fig. 11 were used for estimating the chloride migration coefficient in the relevant types of concrete.

5.2. Other input data

When the de-icing salt is splashed on the concrete surface, the

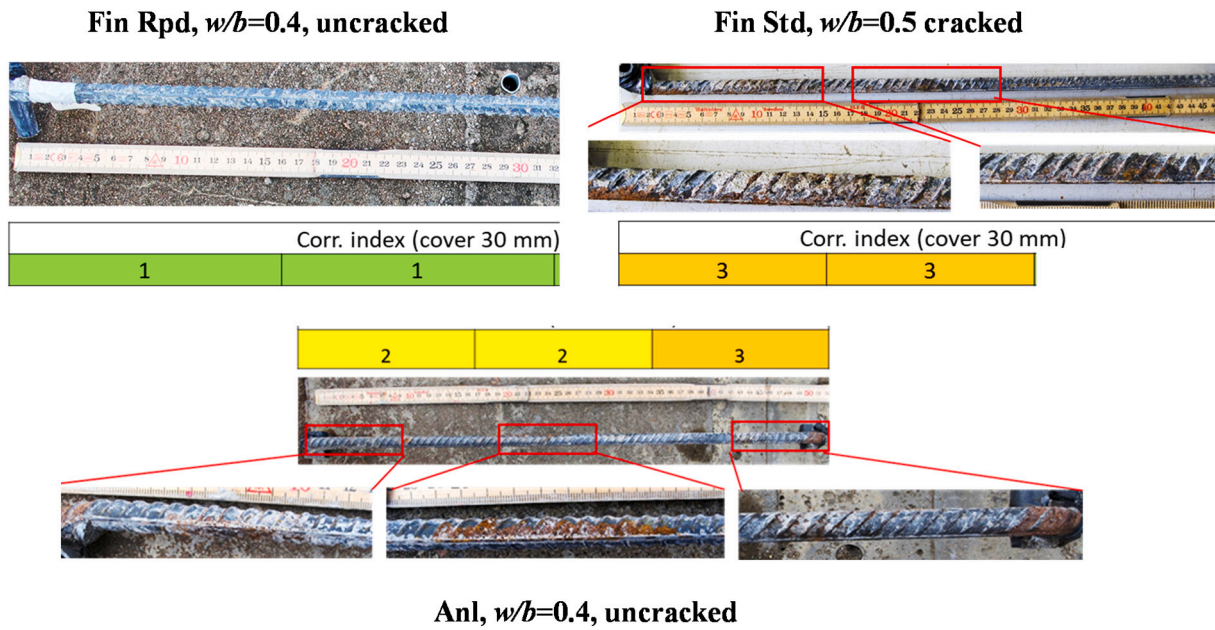
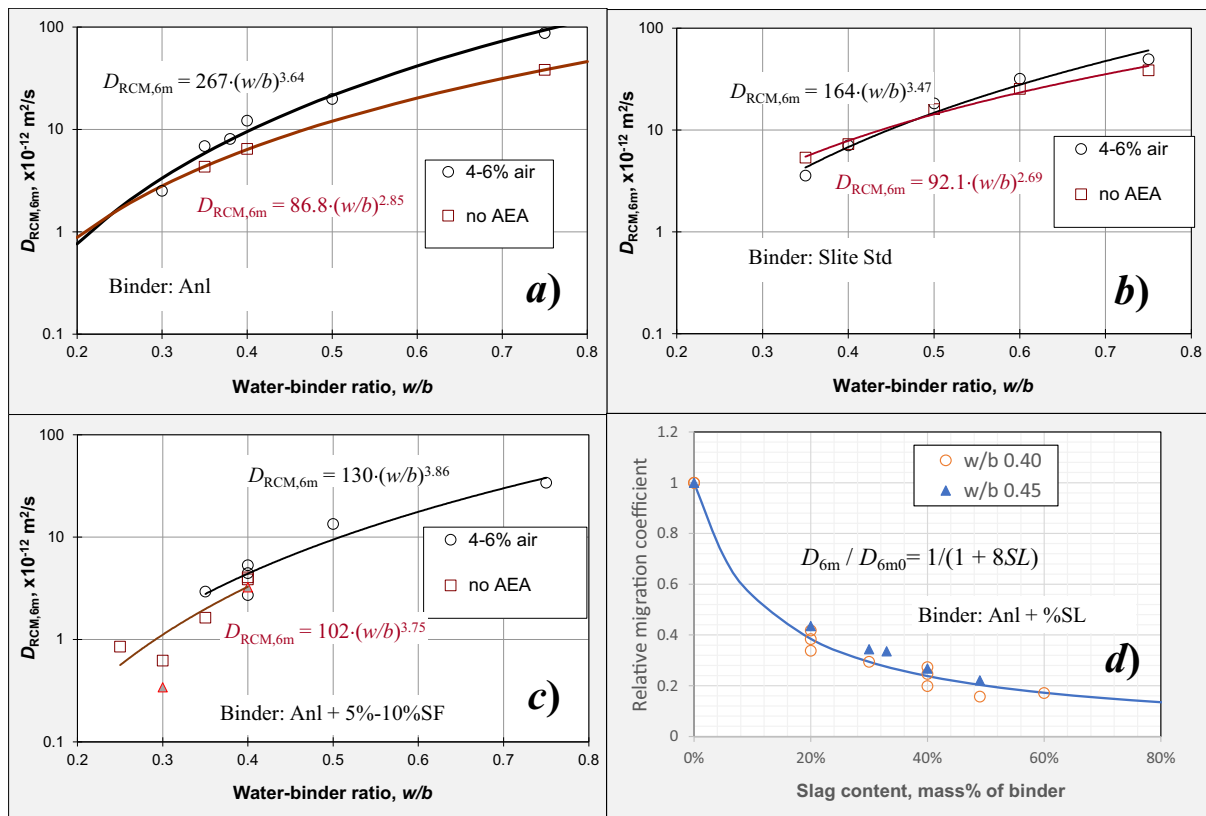


Fig. 10. Comparison between RapiCor measured corrosion and visual examination.

Fig. 11. Relationship between D_{RCM} and w/b or D_{RCM} and slag content: in a) to c) the data were adopted from [43], and the data in d) were adopted from [44].

chloride penetration occurs during the whole year, even though the surface concentration may dramatically change from saturated concentration (as unmelt de-icing salt) to zero (after heavy raining or road washing). It is difficult to know the actual variation of chloride concentration on the surface of concrete. Therefore, the environmental data were adopted with the chloride concentration of 1.5 g/l and the mean annual temperature of 10 °C which has been used in our previous

simulation for concretes under road environment [13,15]. The initial chloride concentration in each concrete has been estimated by the evaporable water content with the chloride content of 15 mg/l in mixing water. The initial alkali content in cement and slag was calculated by the data from manufacturers. The age factor for chloride binding has been taken as 1/3 of the value under submerged environment. The expansion factor and the age factor due to drying were not taken into

consideration. Some other parameters in the model use the same value as those described in [10] or [15]. More detail of input parameters can be found in Table A1.

5.3. Simulation by the previous ClinConc model

By adopting the input data presented in 5.1 and 5.2 into ClinConc model, we get the modelled data in Fig. 12 to compare with the measured profiles. The modelled penetration depths seem to fairly agree with the measured chloride ingress. However, there are large differences between the predicted profiles and the measured data, especially in concretes with high w/b (≥ 0.4). A peak occurs near surface zone in most of the chloride penetrations in concretes with w/b larger than or equal to 0.35, and this results from the drying-wetting cycles [45], carbonation and interaction of de-icing salts on concrete surface exposed to the road environment. Therefore, it is difficult to make an accurate prediction on the total chloride content by models based on the Fick's law.

A further modification is needed for the previous ClinConc model so that the modelled profiles become closer to the measured value. The fair match between the modelled chloride penetration front and the measured one implies that the predicted free chloride content in the deeper part of concrete is reasonably correct. Thus, the abnormal shape of chloride penetration profiles may be because of the change in the binding behavior in the lower depth of penetration. The distance from surface to the peak point is designated as x_{peak} in our modification. The value of x_{peak} were collected from the measured chloride content and presented in Fig. 13. The correlations between x_{peak} and w/b can be expressed by a logarithmic function as shown in the formulation of Eq. (2). The values of parameter, α and β , of different binders are shown in Table 4.

$$x_{\text{peak}} = \alpha_p \ln\left(\frac{w}{b}\right) + \beta_p \quad (2)$$

5.4. Further modification of ClinConc model

The peak phenomenon of chloride profile in concretes was often attributed to effect of drying-wetting cycles on pore solution in some literatures [45–47]. However, we strongly believe that both carbonation and calcium redistribution or leaching play a critical role in the chloride binding behavior of pastes. It has been proven that, after carbonation, the chloride binding capacity dramatically decreased due to the changes in the pore structure [48,49], pore solution [19,50], phase assemblage [50–52] and moisture condition [49,53]. However, as shown in Section 4.3, the carbonation depth for most of types of concrete in this study is < 3 mm, which is markedly less than the peak depth. Therefore, the lower chloride content in the near surface zone may only partially be attributed to the effect carbonation on the surface. The Monte Carlo simulation was performed in this study to reveal the dissolving behavior of portlandite ($\text{Ca}(\text{OH})_2$) in solutions with various chloride concentrations. The saturation index (SI) of portlandite is calculated according to the formula.

$$SI = \log\left(\frac{Q}{K}\right) \quad (3)$$

where Q is the ion activity product, and K is the equilibrium constant of ion product. The dissolution of portlandite has been predicted by a simple calculation based on the saturation index. Fig. 14 shows that the SI of portlandite will decrease as the increase in concentration of NaCl . Therefore, as the chloride content increases during its penetration into concrete, more portlandite will dissolve into solution due to the decrease in the saturation degree of pore solution. Moreover, calcium ions in the near surface zone will be washed by the rain or splashed water, so it induces the inner Ca ions move to the surface. This process will cause the change of the pore structure and the chloride binding capacity of pastes in the near surface zone. However, the combining effect of carbonation and leaching is difficult to be quantified by theoretical model or

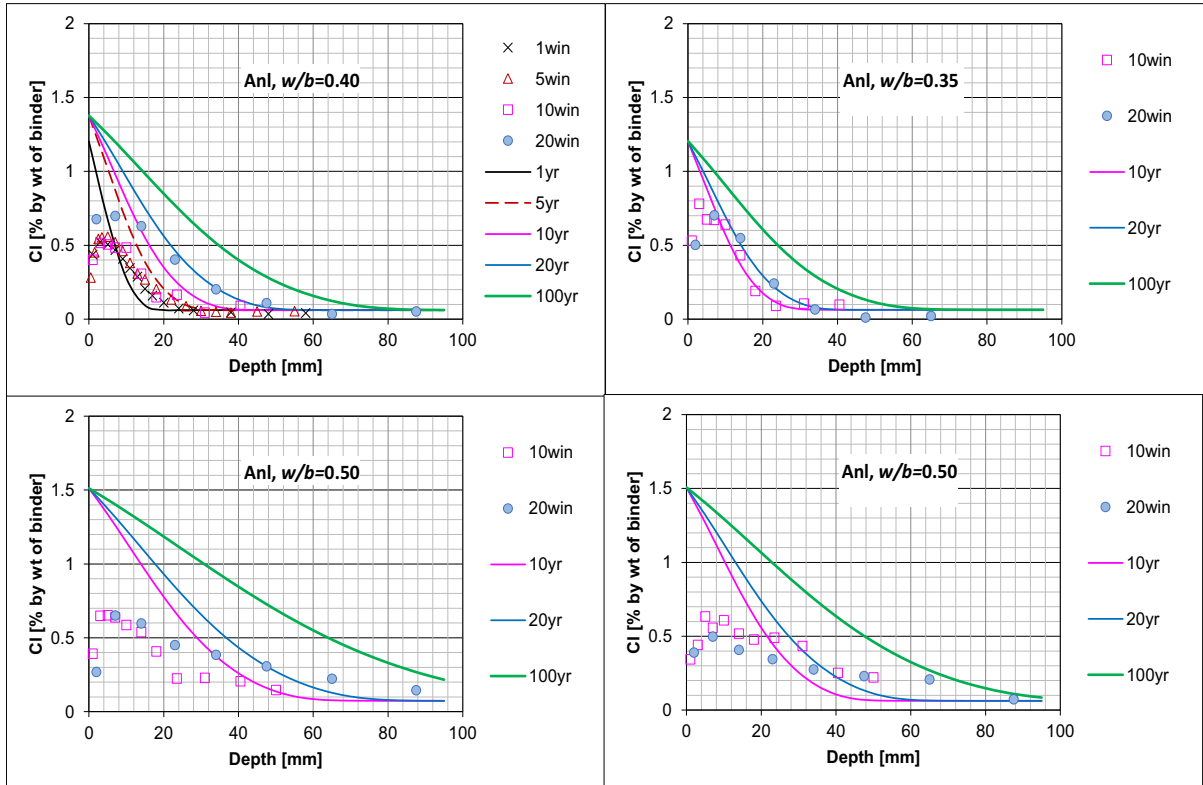


Fig. 12. Comparison of some of the measured (marks, win = winter) and predicted (lines, yr = year) chloride profiles in concrete by the previous ClinConc model.

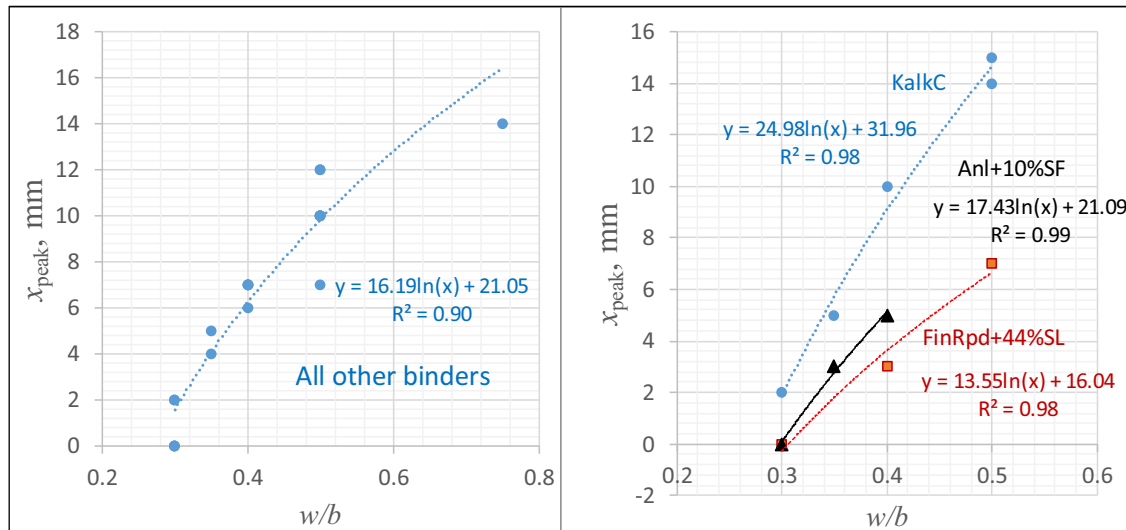


Fig. 13. Correlations between x_{peak} and w/b in concretes with different binders.

Table 4

Parameters for the calculation of peak position in Eq. (2).

Binder	α_p	β_p
Anl, Slite Std, Anl + 5%SF, Fin Std, Fin Rpt	16.2	21
Fin Rpt + 44%SL	13.6	16
Anl + 10%SF	17.4	21
P Kalk C	25.0	32

experimental method. Hence, two empirical equations (see Eq. (4)) are proposed to describe the redistribution of bound chloride content in the near surface zone of concretes exposed to the road environment.

$$f_{red} = \begin{cases} \left[1 - k_1 \cdot c_f \cdot \frac{(x_{peak} - x)}{x_{peak}} \cdot \sqrt{\frac{w}{b} - b_0} \right] \cdot k_2 \cdot \sqrt{\frac{w}{b} - b_0} & x \leq x_{peak} \\ k_2 \cdot \sqrt{\frac{w}{b} - b_0} & x > x_{peak} \end{cases} \quad (4)$$

where f_{red} is the redistribution factor of the bound chloride applied in ClinConc model, and c_f is the concentration of free chloride predicted using the ClinConc model. The parameters b_0 , k_1 and k_2 are constants and their values for different binders are shown in Table 5.

A “trial-and-error” approach was applied to obtain constant values in Eq. (4), and Table 5 presents parameters for different binder systems. Some interesting information can be observed about the long-term behavior of binders. The k_1 constant indicates the degree of reduction in the chloride binding capacity on the surface zone. This value of binders containing slag or limestone is higher than that of other binders, which indicates a larger reduction in the chloride binding, and this may be because of a weaker resistance to leaching and a larger change in compositions due to leaching, carbonation, and interaction of de-icing salts with hydration products. The constant k_2 means the general extent of decrease in the chloride binding capacity near the concrete surface zone. The binder with limestone (P Kalk C) has the lowest value, and this may be due to the weak interaction between limestone and chloride ions. The constant b_0 indicates a critical w/b with which value

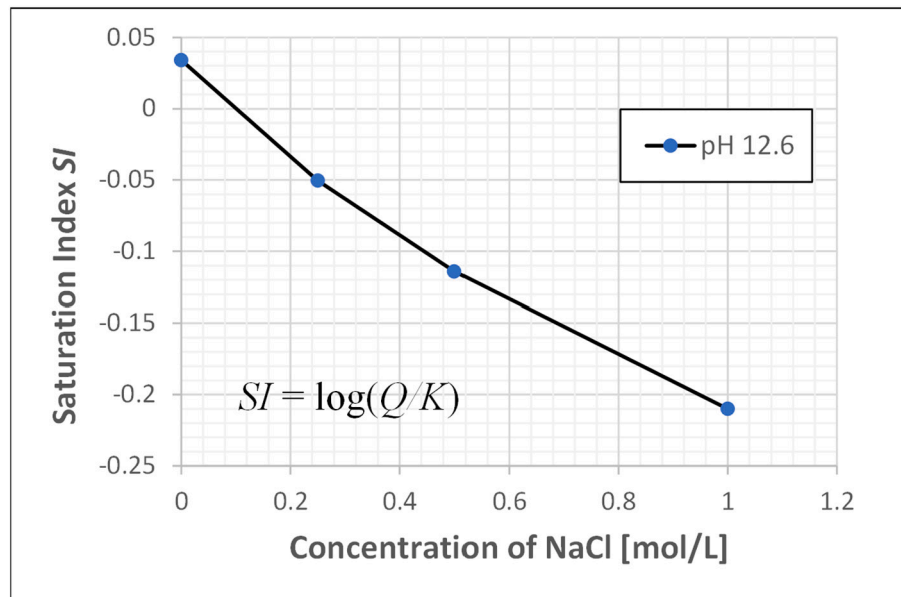


Fig. 14. Saturation index of portlandite in solution with different concentration of sodium chloride.

Table 5

Value of constants applied in the calculation of chloride redistribution factor in Eq. (4).

Binder types	b_0	k_1	k_2
Anl, Fin Rpt, Slite Std	0.3	1	1
Anl + 5 %–10%SF	0.35	1	1
Fin Std	0.3	1.5	1
Fin Rpt + 44%SL	0.4	2	1
P Kalk C	0.3	2	0.75

the surface of concrete has no significant decrease in the binding capacity of chloride. The blending of SF (5 %–10 %) and slag (44 %) will bring an increase in this value, which results from the finer microstructures and a less diffusible matrix compared with other binders.

Fig. 15 illustrates more detailed difference between ClinConc and the modification. The predicted results of Swedish structural cement are shown in Fig. 16, and those for the other types of binders are shown in Figs. A1 to A4 in the Appendix. From these figures, it can be observed that the modelling of this modified ClinConc model have a good match with the measured chloride profile in majority of concretes with different binders and various w/b . Apparently, the modified ClinConc model performs reasonably well in the most cases including the description of chloride contents and front of penetration.

Consequently, it enables to perform the modified prediction of chloride penetration in concretes under the de-icing salt environment in the following way:

1. Calculate free and bound chloride content in concretes by the use of the ClinConc model as previously described in [15];
2. Calculate the redistribution factor of chloride by Eq. (4), and then recalculate the bound chloride profiles by multiplying the factors;
3. Finally, the total chloride profiles in concretes are calculated by the modified values as previously described in [15].

6. Concluding remarks

The long-term performance of many concrete blocks has been

investigated by means of both experiments and modelling. These concretes were exposed to the de-icing salt environment around a highway in Sweden up to 20 years. Based on the electrochemical measurement and the visual examination of the rebars in concrete beams, the corrosion condition is well assessed after exposed to a de-icing salt road environment. The following conclusions can be drawn based on the experimental and modelling results.

- The performance of five types of the commercial cements regarding resistance to chloride penetration are heavily dependent on the w/b . For $w/b \leq 0.4$, Finnish rapid cement (Fin Rpd) concrete presents the best resistance to chloride penetration among these cements. The blending of silica fume and slag improves the long-term performance of concretes. The replacement of cements by both 10 % silica fume and 44 % slag can reduce chloride penetration at all investigated ages.
- The threshold content of chloride in concretes with w/b 0.5 is about 0.3 % of binder by mass. For concretes with $w/b \leq 0.4$, the penetration chloride content at depth of 30 mm is generally lower than this threshold value after an identical exposure duration. With the uncracked concrete cover, the rebars started to corrosion at the critical chloride content of approximately 0.3 % of binder mass. A lower critical chloride concentration seems to be detected for the initiation corrosion of rebars in concretes with the pre-cracked concrete cover.
- The chloride penetration in concretes exposed to the de-icing salt in a Swedish road environment is much slower than that in concretes exposed to the Swedish marine splash zone as well as atmosphere zone after 20 years.
- The results of long-term exposure in this study demonstrated again that the corrosion assessment by RapiCor instrument, a non-destructive measurement device, is in a good agreement with the findings from the visual examination.
- Generally, The ClinConc model presents a reasonably good prediction of the penetration front of chloride into bulk concrete, but it has a poor prediction on the chloride content near the surface zone. Therefore, it has been modified by taking the redistribution of bound

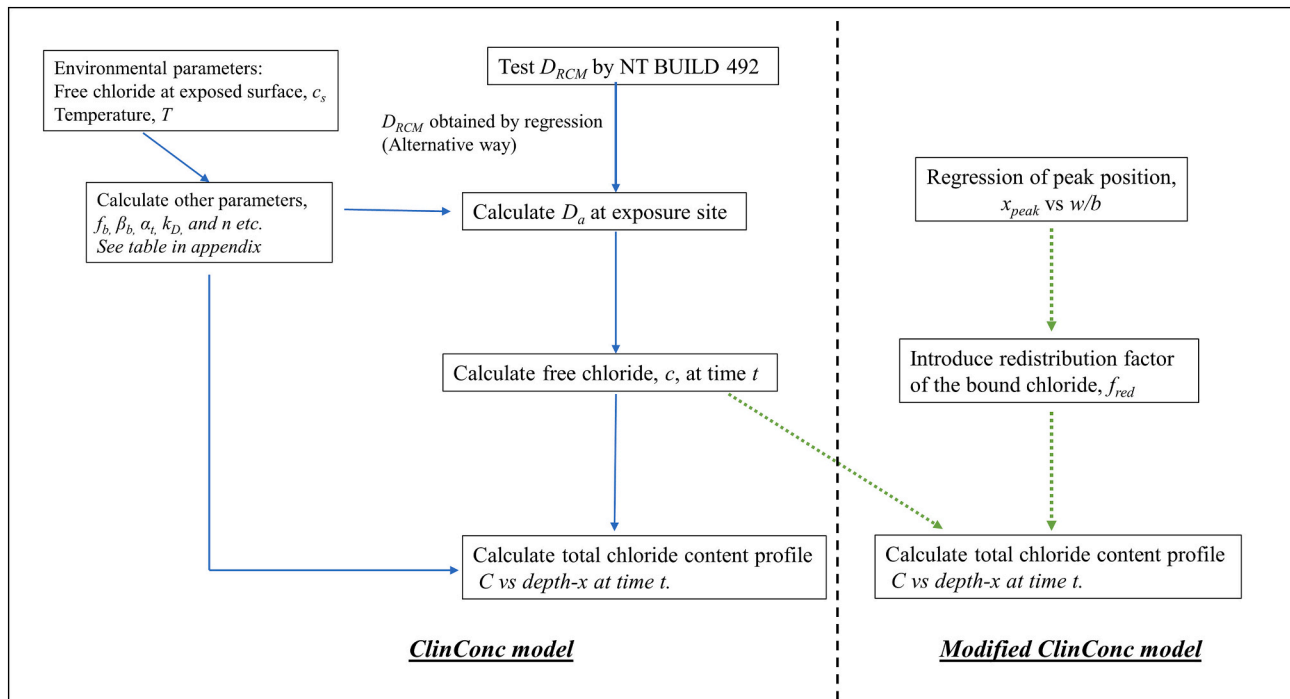


Fig. 15. Flow chart about the operation of ClinConc and the modification of it.

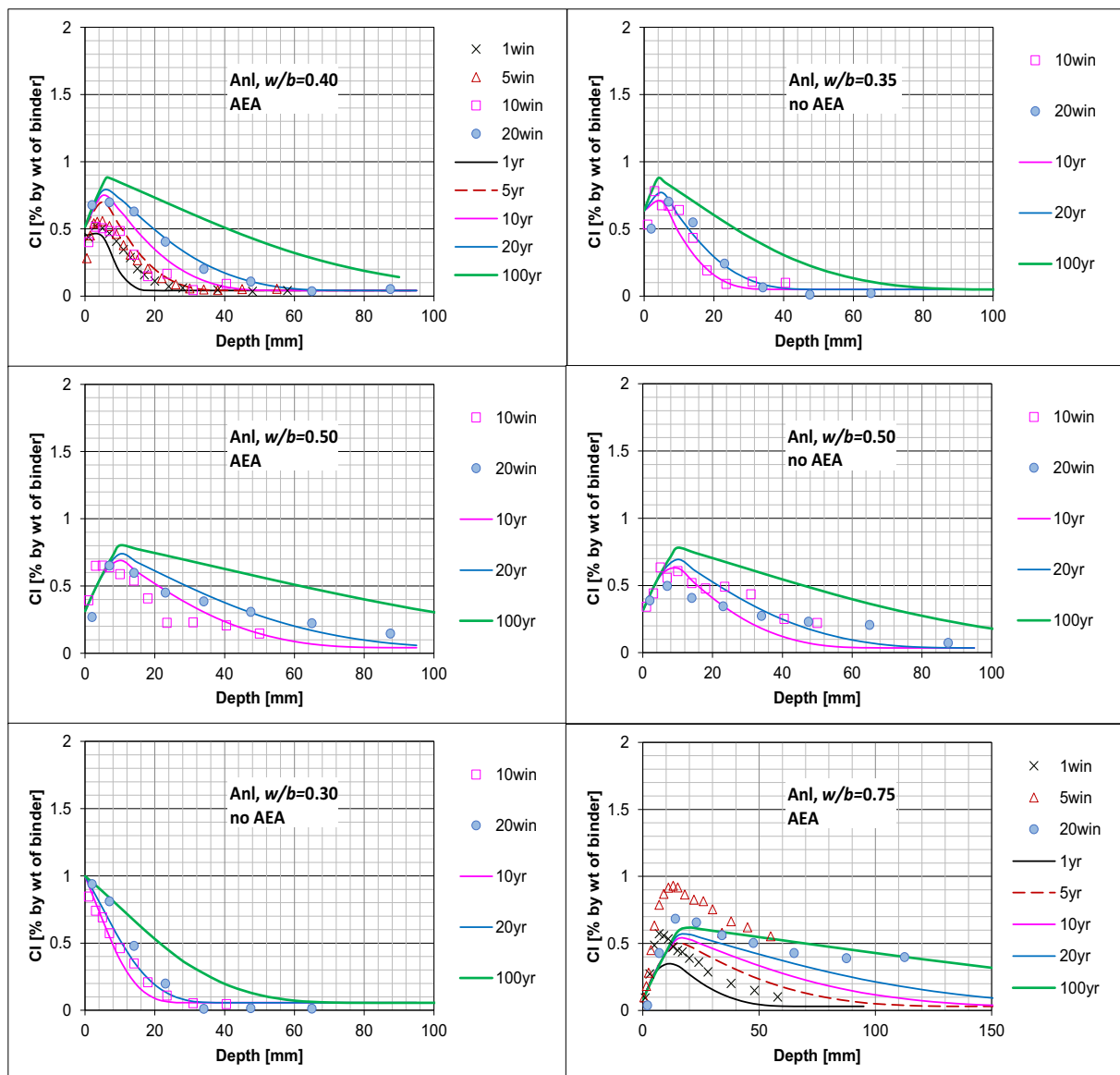


Fig. 16. Comparison of the measured (marks, win = winter) and predicted (lines, yr = year) chloride penetration profiles in concretes with Anl cement.

chloride into consideration. The modified model performs very well in the description of the chloride penetration profiles in all depth, proving by a good match between the measured and modelled chloride content.

CRediT authorship contribution statement

Luping Tang: Conceptualization, Methodology, Investigation, Data analysis, Writing-Original Draft, Revision & Project administration. *Dimitrios Boubitsas*: Methodology, Investigation, Data analysis, Writing-Original Draft & Revision. *Liming Huang*: Methodology, Investigation, Data analysis, Writing-Original Draft, Writing-Revision & Editing.

Declaration of competing interest

We declare that there are no known competing financial interests or

personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A

The chloride penetration profiles predicted by the modified ClinConc model for the other types of binders are shown in Figs. A1 to A4.

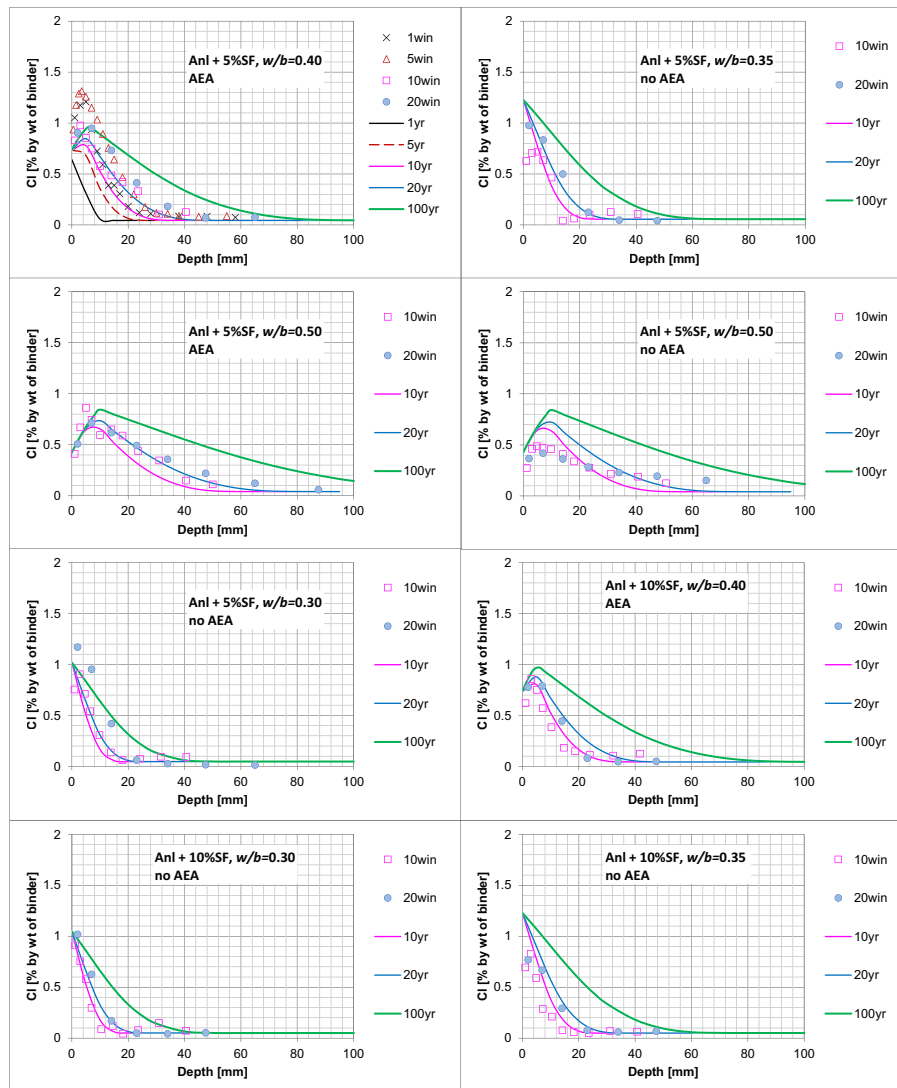


Fig. A1. Comparison of the measured (marks, win = winter) and predicted (lines, yr = year) chloride penetration profiles in concretes with the binder Anl + 5 %–10%SF.

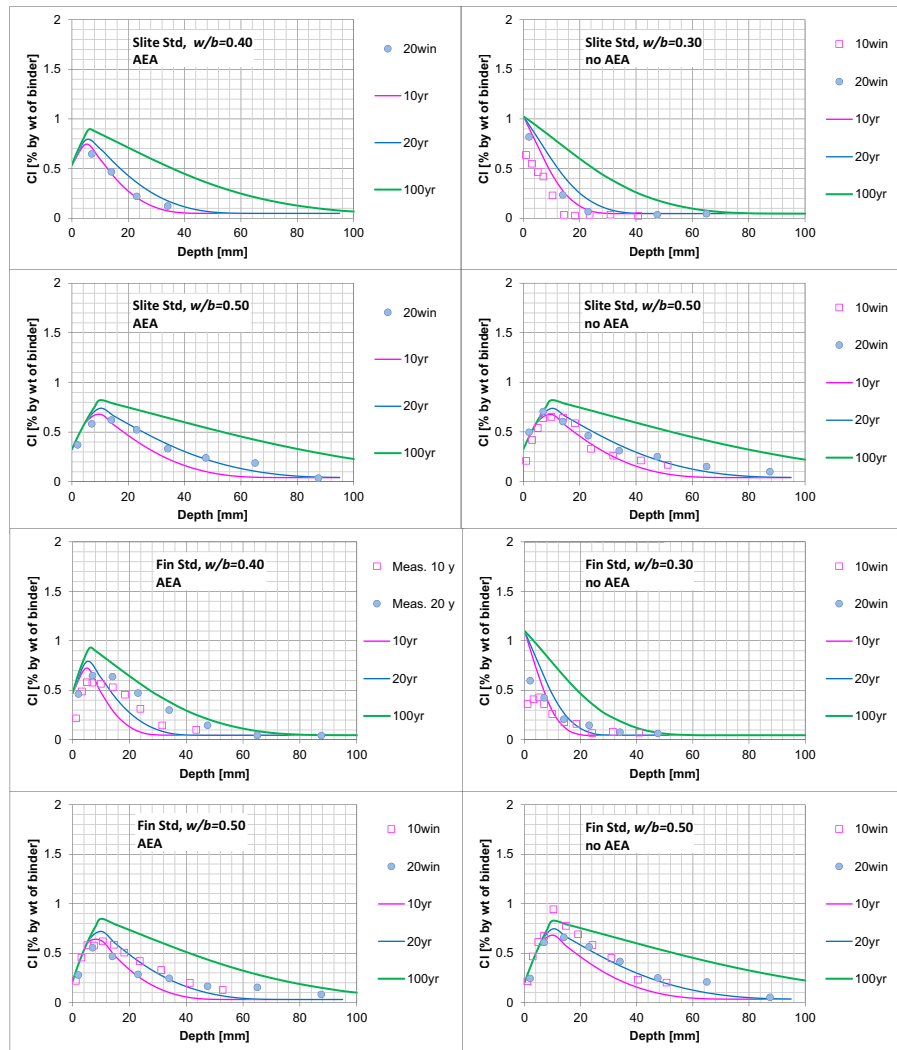


Fig. A2. Comparison of the measured (marks, win = winter) and predicted (lines, yr = year) chloride penetration profiles in concretes with the binders Slite Std and Fin Std.

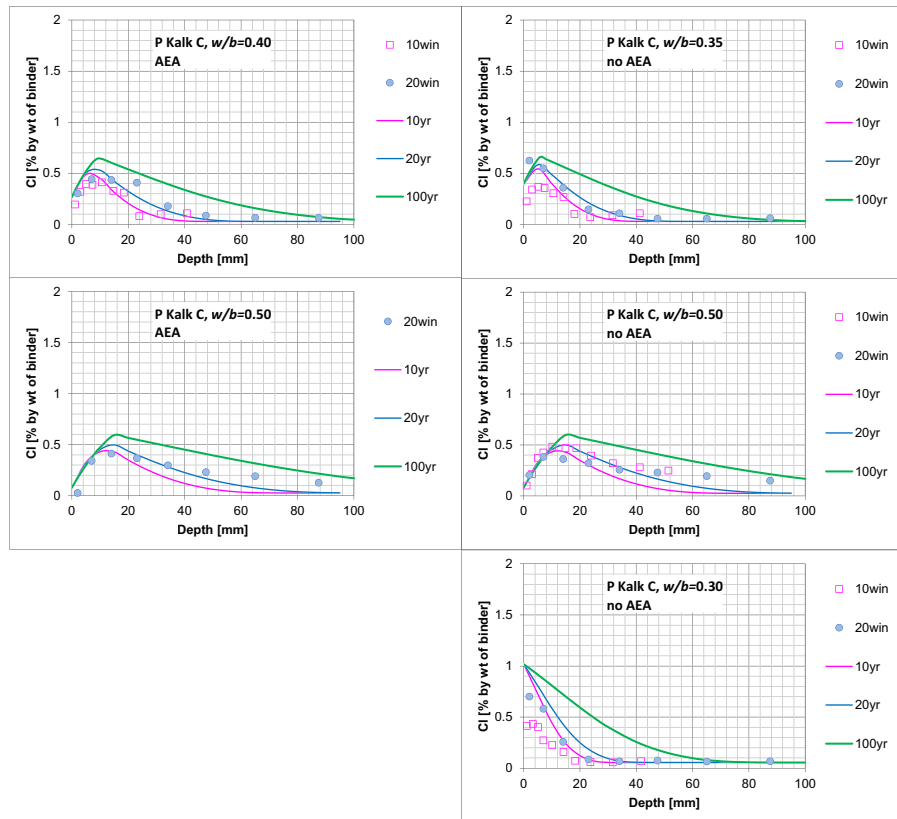


Fig. A3. Comparison of the measured (marks, win = winter) and predicted (lines, yr = year) chloride penetration profiles in concretes with the binder P Kalk C.

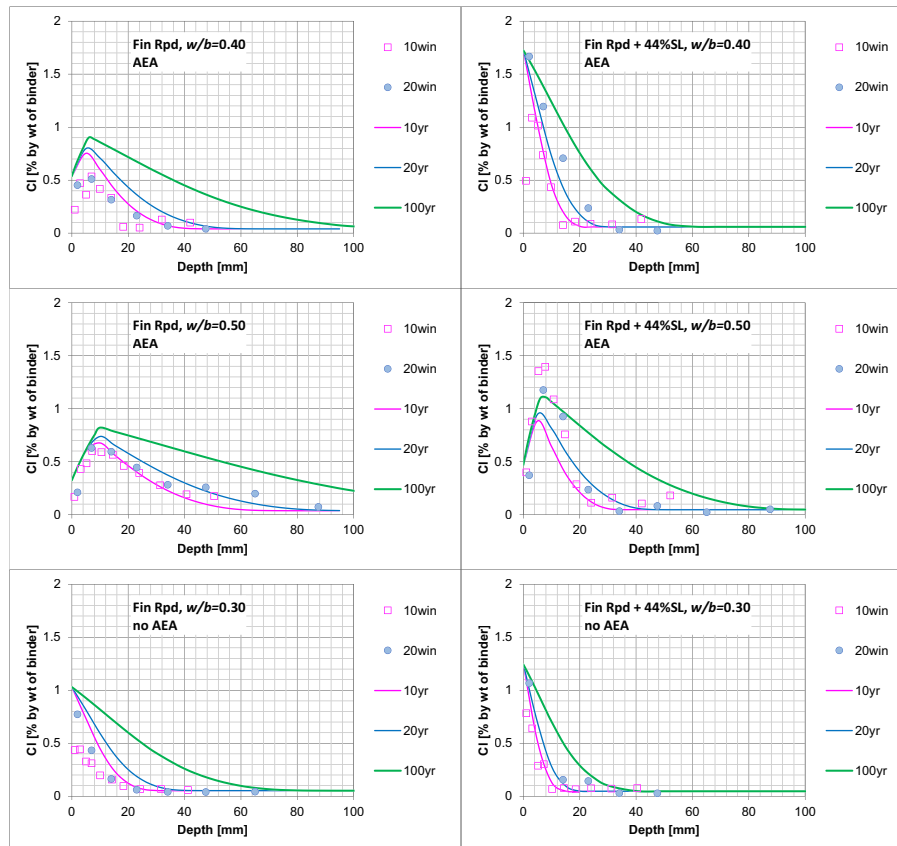


Fig. A4. Comparison of the measured (marks, win = winter) and predicted (lines, yr = year) chloride penetration profiles in concretes with the binders Fin Rpd and Fin Rpd + 44%SL.

Table A1
Parameters applied in ClinConc model for simulation of chloride profile of concretes in Table 3.

Binder type	Binder kg/m ³	$D_{RCM, 6m}$	Binding factor f_b	Binding exponent β_b	Time-dependent binding a_t	k_D	Age factor n	Gel quantity $W_{gel,6m}$, kg/m ³	Pore volume $V_{pore,6m}$	c [OH ⁻] mol/L
100%Anl	420	9.51	3.6	0.38	0.120	1	0.093	390.1	0.10	0.61
	380	21.42	3.6	0.38	0.073	1	0.066	404	0.12	0.44
	500	2.81	3.6	0.38	0.167	1	0.118	309.4	0.09	0.77
	450	4.36	3.6	0.38	0.143	1	0.105	351.2	0.10	0.65
	380	12.04	3.6	0.38	0.073	1	0.066	402.8	0.12	0.45
95%Anl + 5%SF	260	93.7	3.6	0.38	0.120	1	0.093	312.7	0.14	0.26
	420	3.78	3.6	0.38	0.127	1	0.096	384.5	0.11	0.56
	380	8.95	3.6	0.38	0.073	1	0.066	396.4	0.14	0.42
	500	1.12	3.6	0.38	0.173	1	0.121	309.3	0.11	0.70
	450	1.99	3.6	0.38	0.150	1	0.109	349.1	0.12	0.59
100%FinStd	380	7.58	3.6	0.38	0.073	1	0.066	398.4	0.14	0.40
	420	3.41	4.04	0.36	0.120	1	0.093	371.4	0.12	1.41
	540	1.81	4.04	0.36	0.167	1	0.118	317.8	0.12	1.84
	390	14.27	3.6	0.38	0.073	1	0.066	417.6	0.14	1.21
100%SliteStd	420	6.82	3.6	0.38	0.120	1	0.093	391.6	0.10	1.33
	390	14.8	3.6	0.38	0.073	1	0.066	416.8	0.13	0.97
	520	3.61	3.6	0.38	0.167	1	0.118	323.4	0.10	1.66
	410	14.27	3.6	0.38	0.073	1	0.066	438.1	0.14	0.97
56%FinRpd + 44%SL	420	1.5	5.16	0.32	0.120	1	0.093	322.4	0.18	0.95
	370	3.25	5.15	0.32	0.073	1	0.066	319.3	0.19	0.78
	540	0.79	5.15	0.32	0.167	1	0.118	277.9	0.17	1.24
100%Fin Rpd	420	6.82	3.6	0.38	0.120	1	0.093	392.4	0.11	1.89
	380	14.8	3.6	0.38	0.073	1	0.066	404	0.12	1.47
	540	3.61	3.6	0.38	0.167	1	0.118	335.5	0.11	2.43
90%Anl + 10%SF	420	3.78	3.6	0.38	0.133	1	0.1	377.4	0.12	0.52
	500	1.12	3.6	0.38	0.180	1	0.124	311.6	0.13	0.60
	450	1.99	3.6	0.38	0.157	1	0.112	344.4	0.12	0.56
P Kalk C	420	6.82	3.6	0.38	0.120	1	0.093	392	0.11	1.18
	390	14.8	3.6	0.38	0.073	1	0.066	415.5	0.13	0.89
	530	3.61	3.6	0.38	0.167	1	0.118	328.3	0.10	1.55
	470	5.47	3.6	0.38	0.143	1	0.105	367.3	0.11	1.32
	400	14.27	3.6	0.38	0.073	1	0.066	428.3	0.14	0.85

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Paper VII

Non-destructive test system to monitor hydration and strength development of low CO₂ concrete

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Non-destructive test system to monitor hydration and strength development of low CO₂ concrete

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ABSTRACT

Application of supplementary cementitious materials for production of low CO₂ concrete affects the reaction kinetics, meaning deviation in early hardening properties such as setting time and the strength development. As traditional methods are developed for concrete with ordinary Portland cement, this different early-age behavior is of concern. Non-destructive monitoring of concrete performance is very useful for facilitating use of low CO₂ binders. This paper presents a new technique to monitor the electrical conductivity and temperature at different depths of hydrating concrete. Data of conductivity monitoring system are compared with widely-used methods (ultrasonic pulse velocity and isothermal calorimetry). Results show that indices from monitoring system can replicate the hydration evolution, setting time and compressive strength of low CO₂ concrete. Electrical conductivity of concrete is very sensitive to mineral reactions and consistent with evolution of heat release. Linear correlations are found for penetration resistance in relation to ultrasonic velocity, formation factor and maturity, respectively. The effect of binder type and water-to-binder ratio on hardening is highly temperature-dependent. The proposed approach enables to include all these factors in characterizing the hardening process onsite. It is shown that formation factor performs better than ultrasonic pulse velocity in indicating the solid network percolation during the setting process. Formation factor from test system is also a good parameter for quantitative description of compressive strength development, which is independent of the binder types, mixture proportions and curing ages.

Keywords: SCMs; Non-destructive test; Formation factor; Setting; Compressive strength.

1 Introduction

On the way toward carbon neutrality, many kinds of approaches are tried to reduce CO₂ emissions in construction sector. The utilization of supplementary cementitious materials (SCMs) is currently acknowledged as the primary approach to minimize the cement consumption which leads to lower emissions generated due to cement production [1,2]. An incorporation of SCMs makes impact on both the fresh properties (such as, workability, plastic viscosity and yield strength) and the hardening properties (such as setting time and the strength development) [3]. Effects on these properties on the performance of concretes at the constructing sites are critical for the practical use of alternative binders. Diversity of SCMs results in

difficulties in controlling and predicting the performance of low CO₂ concrete.

During the hydration process, a transition of concrete from fluid to hardened state governs the construction progress, which may impact both the quality and cost of a concrete structures. For instance, hardening process, in terms of setting time and attainment of specific strength levels affects decisions in terms of the right time for demoulding and for the further construction procedures such as measures to prevent thermal cracks or heat curing requirements for casting in cold seasons. Moreover, it is also very important for the digital fabrication (3D printing), as Reiter et al. [4] stated that evolution of specific yield stress of concrete is of significance as otherwise the self-weights of the structure can be destructive. The Vicat apparatus is one of representative traditional methods to detect the hardening properties of paste which is specified in many standards, including EN 196-3 and ASTM C191-08. For the hardening of concrete, a similar method to measure the penetration resistance is proposed in ASTM C403/C403M – 05. However, these traditional methods for quality control are operated off-site and are time-consuming due to the need of following specified operational manuals. These methods are therefore not adequate for the quality control of a fast or automated construction [5]. It is also well-known that hardening is sensitive to temperature changes so the traditional methods need to control the temperature and humidity of the environment. However, these conditions are different from the actual field site, especially during the construction of some massive concrete structures [6]. Therefore, a reliable non-destructive testing method with possibility for automated frequent on-site monitoring as well as digital fabrication with good efficiency and reliable quality, would be very helpful to mitigate the noted challenges in handling construction with the use of SCMs.

Although there are many non-destructive methods to assess the mechanical performance [7,8] or to identify problems of concrete structure, such as grouting faults [9] or cracks [10], only few of them can be used to obtain time-resolved hardening properties of concrete. Gu et al. [11] embedded piezoelectric transducers into the concrete specimen as actuators and sensors to detect the harmonic response amplitude and related the value to the strength development from 1 day up to 1 month. Tawie and Lee [12] verified the feasibility of piezoceramic sensing technique to monitor the strength development by an empirical correlation to resonant frequency shift. Voigt et al. [13] compared ultrasonic wave reflection and maturity methods on monitoring the strength of Portland cement mortar by relating them to the compressive strength up to 7 days. However, these investigations did not consider the hardening process before final setting. Shimizu [14] found that the conductivity shown a sudden drop during the setting, and Calleja [15] also reported that the conductivity change can reflect the setting of hydraulic materials. However, there was no quantitative description between setting time and evolution of conductivity. The setting of oil well cement has been monitored by ultrasonic pulse velocity (UPV) [16], and the theoretical analysis on setting time was further reported by Scherer et al.

[17] in relation to the percolation of hydration products during hydration process. However, it seemed that the percolation point occurred earlier than the initial setting time, and there was no further discussion on the correlation to final setting point or mechanical performance after final setting. Proton nuclear magnetic resonance relaxometry was applied as an indicator for setting of pastes in correlation to water depletion during cement hydration [18], and it seems to be promising as a nondestructive method in lab research but impractical for onsite application. Poursaei and Weiss [19] used an electrical impedance spectrometer to build an automated electrical monitoring system to monitor the evolution of electrical conductivity of cement paste. The impedance spectroscopy test system in the cited investigation cannot fulfil an onsite use due to the complex setting and expensive price of machine. Moreover, that investigation only provided a concept to illustrate the possibility of using electrical conductivity to monitor performance, but it did not describe any performance index of concrete.

Our previous investigation found that an electrical conductivity monitoring system is very promising to map the hydration induced microstructure change of the blended pastes [20]. A linear correlation has been identified between inflection time of electrical conductivity and setting time. Herein, we additionally upgraded the monitoring system with sensor arrays, including the ability of determining temperature, and which can be easily implemented within onsite construction. Detailed comparison analysis is given in this paper to demonstrate the credibility of the method to replicate the evolution of hydration in early and later hydration stages through monitoring evolution of conductivity and temperature. The comparisons of temperature and electrical properties are made with:

1. development of penetration resistance before final setting as well as the compressive strength development up to 28 days.
2. monitored evolution of UPV in hydrating low CO₂ concrete.
3. measured heat of hydration with isothermal calorimetry of two concrete mixes for revealing the mechanisms of hydration and hardening.

Additionally, the quantitative correlation between setting time, compressive strength and formation factor is discussed from a physical/chemical-mechanism perspective. It verifies that the upgraded system with sensor arrays enables to monitor the setting process and strength development of concretes with various types of binder, through monitoring temperature and electrical properties from cradle to long-term service.

2 Experimental procedures

2.1 Non-destructive monitoring system

2.1.1 Electrical conductivity and temperature

The electrical conductivity of concrete was measured by a four-electrode method to minimize the effect of polarization. The arrangement of electrodes at each row was referred to the Wenner configuration [21] (see 4 blue electrodes in [Figure 1](#)). This set-up is an upgraded version based on our previous system [20]. The old version is rather simple with 4 electrodes, so it can only measure small samples and without the consideration of temperature effect. In this updated array sensors, one more sensor is added in each row to measure the temperature, and these sensors have been calibrated with an accuracy of ± 0.2 °C. Multilayer sensors are assembled on a carrier board, which enables the system to measure temperature and electrical conductivity at different depths of large concrete specimens. The invented device for control and data recording has a dimension with 15×20×50 cm, which is portable for onsite test. The measurement at each depth was finished individually from the top to the bottom. The controlling programs of this system was also improved to avoid the mutual influence of different layers, and to minimize the influence of electrode polarization. It takes about 0.1 seconds to finish one instant measurement. In the first 24 h, the datalogger recorded the data at 5 mins intervals. The time interval was switched to 10 mins from 1 day to 7 days. The data at later hydration ages were collected at 14 and 28 days.

A major improvement in this method is that the effect of temperature on electrical conductivity of concrete has been considered in this study. The activation energy ($E_a=13.375$ kJ/mol) was determined by Arrhenius equation, Eq. (1), using the measured conductivity of the mimic pore solutions conditioned between 3 and 70 °C. The A is a pre-exponential constant, R is the gas constant (8.314 J / K mol), and T (K) is the absolute temperature of sample.

$$\sigma = A \cdot e^{\frac{E_a}{RT}} \quad (1)$$

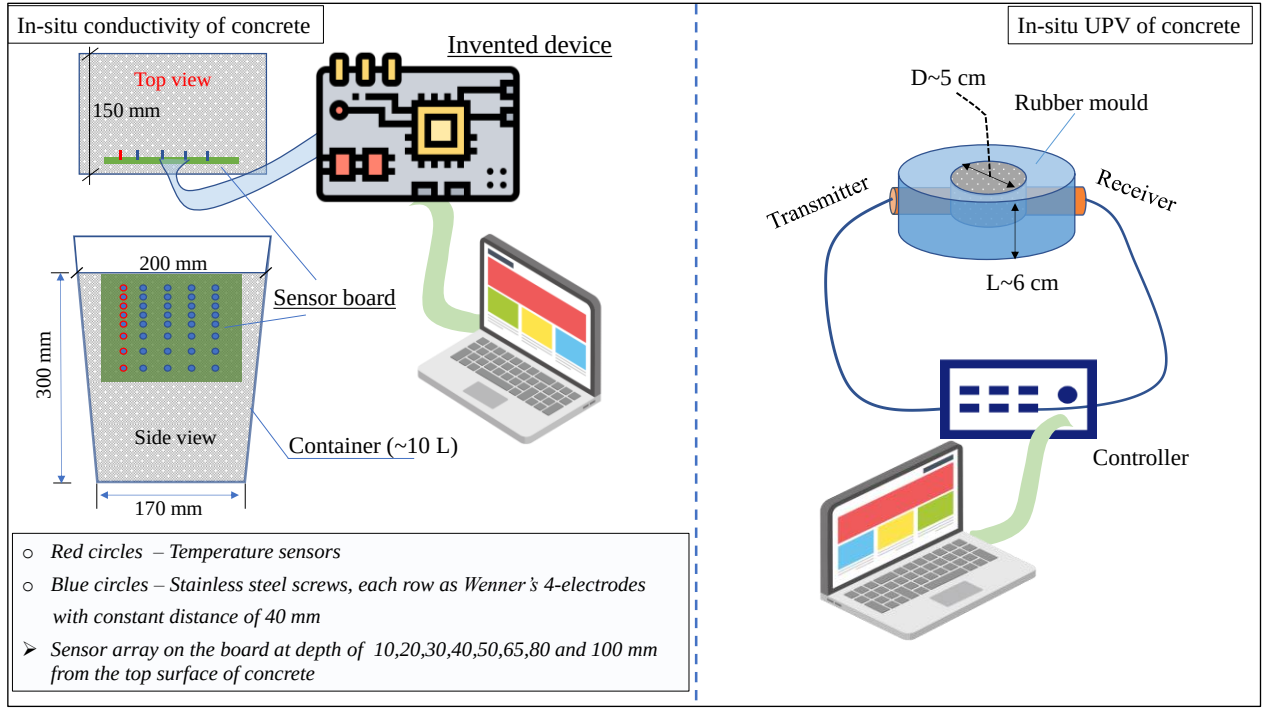


Figure 1 Setup for monitoring the conductivity and UPV in concrete during hydration

The calculation of electrical conductivity by Wenner's method is based on the use of semi-infinite boundary. However, the actual size of concrete in practical application does not always satisfy this semi-infinite boundary condition, especially for the upper rows of the sensors. To investigate the effect of size on the calculated electrical conductivity, numerical modelling was carried out using COMSOL Multiphysics with a geometry similar with the container (see Figure 2). The simulation was conducted using the AC/DC mode, which encompassed the electric current conservation equation. Moreover, all surfaces of the geometry were set as insulative boundaries in order to achieve accurate results. The matrix was assigned a constant electrical conductivity of 0.1 mS/cm, and the input constant current from A to B was set to 0.1 mA. The simulated potential difference between V_2 and V_1 was used to calculate the electrical conductivity by Wenner's method. The dimension factor (γ) was evaluated by dividing the obtained conductivity with the calculated one. Fig 2 shows that γ is about 1.96 at the first row and decreases with depth. From these simulated results the relationship between γ and the depth of sensors (x) can be established. All these simulated values have been validated with the standard solutions (KCl) which are very close to the experimental value (see the comparison of simulated and experimental results in Figure 2).

After considering effects of both temperature and dimension on electrical conductivity, the conductivity of hydrating concretes at each depth can be calculated by Eq. (2). The result of each sample in this study is the average value from second to eighth row.

$$\sigma_c = \frac{I}{2\pi\Delta Vd} \cdot \gamma \cdot e^{\frac{Ea}{R} \left(\frac{1}{273.15+T} - \frac{1}{298.15} \right)} \quad (2)$$

where σ_c is electrical conductivity of concretes normalized to 25 °C, I is the applied constant current between

the outer two electrodes, ΔV is potential difference between the two middle electrodes, d is the distance between Wenner's electrodes and γ is the dimension factor at different depths.

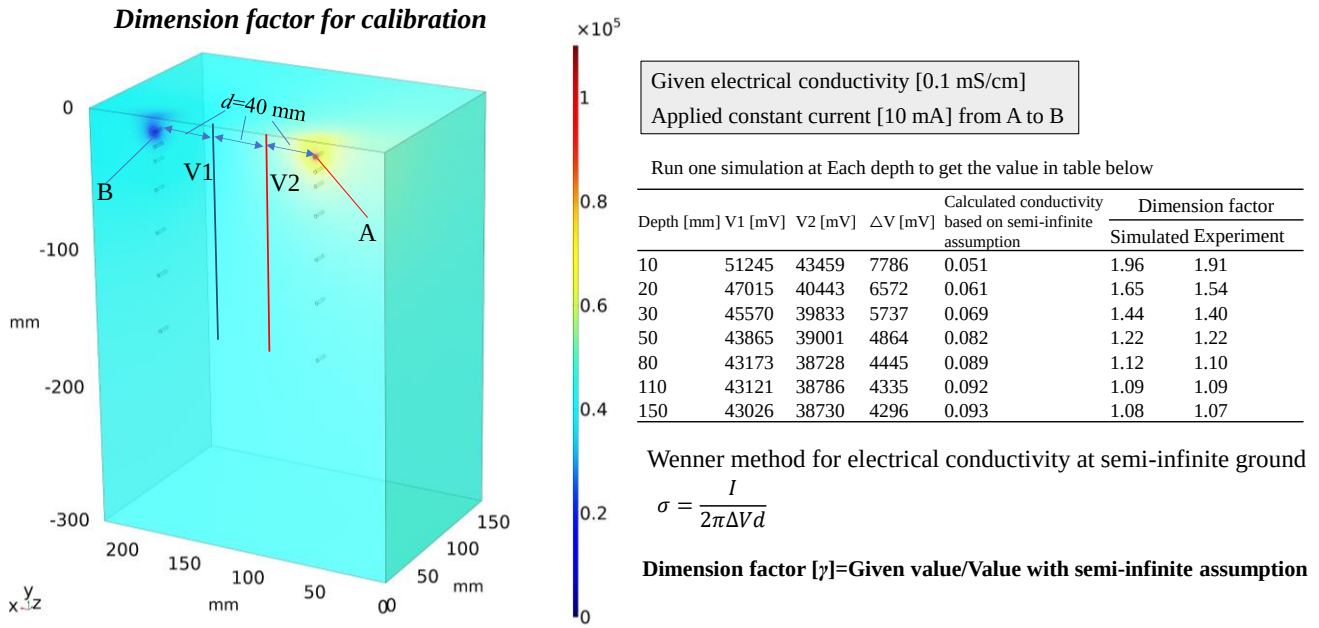


Figure 2 Dimension factor based on numerical simulation and comparison with experimental results.

2.1.2 Ultrasonic pulse velocity

The setup for monitoring UPV (IP-8 Ultrasonic Measuring System from Ultratest GmbH) is shown in [Figure 1 \(right side\)](#). It consists of two channels with acoustic emission system, a controller and a computer. A transmitter and a receiver are positioned in the silicon mould directly opposite to each other, with an insertion into the inner empty cylinder featuring a protrusion of approximately 3 mm. This is done to ensure a firm connection to the fresh concrete while maintaining a measurement distance of 60 mm between the transmitter and the receiver. The ultrasonic pulse was set with a frequency of 25 kHz, and the velocity in the hydrating concretes normally varies from 100 m/s to 5000 m/s at about 20 °C. The concrete samples were cast into mould with a mild vibration right after mixing, and it was then connected to the controller under the automatic control of computer. The interval for recording the ultrasonic waves is constant with 2 or 5 min. Each sample had three parallel measurements, and the result is presented as an average value of these measurements.

2.2 Materials

Binders in this study include ordinary Portland cement CEM I 52.5 R with a Blaine surface of 525 m²/kg, fly ash (FA) from Cementa, and slag with a Blaine surface of 420 m²/kg from Thomas cement. Limestone powder from Nordkalk with a D_{50} =18 μ m (LL) was used as well. The chemical composition of each binder has been shown in the previous paper [20]. [Table 1](#) presents the mix design of 4 kinds of concretes. In the binary systems, the replacement content of cement with SL and FA is 35 % by weight. In the ternary systems, Portland cement was replaced with 35% SL and 16 % LL. The slag binary concretes were mixed with water

to binder ratio (w/b) of 0.45 (C245) and 0.55 (C255), respectively. The fly ash blended concrete was mixed with w/b of 0.45 (C145) and the ternary concrete was mixed with w/b of 0.38 (C338). Aggregates used in C145 and C255 consist of siliceous sand and stone with size distribution ratio of 85.2% : 14.8% (1-4 mm : 4-10 mm), which has a bulk density of $1.74 \times 10^3 \text{ kg/m}^3$ and a close packing density of $1.96 \times 10^3 \text{ kg/m}^3$. the aggregate C245 and C338 were cast using the sand with a density of $2.66 \times 10^3 \text{ kg/m}^3$ from Eurosand and stone with a density of $2.85 \times 10^3 \text{ kg/m}^3$ from Skanska. Superplasticizer (PCE) was Master Glenium 5118 (with 17.5 % dry substance) from Master Builder Solutions.

Table 1 The mixture proportions of concretes (kg/m^3)

Mix ID	Cement	Slag	Fly ash	Limestone	Water	PCE	Sand (<4 mm)	Coarse aggregate (4-10mm)
C145	286		154		201	3.2	1411	246
C245	280	151			194	3.0	954	795
C255	247	133			209	2.7	1449	256
C338	242	173		79	187	4.0	953	780

2.3 Procedures and Methods

2.3.1 Casting of concrete

Ingredients of concrete were mixed in a self-falling mixer with capacity of 50 L. Firstly, water and binder were mixed for 2 minutes. Subsequently, the aggregates were gradually added into the mixer, and mixing continued for another 5 minutes. The fresh concretes were then cast in a container as shown in [Figure 1 \(left side\)](#). The board with array sensors was fixed in the container before casting. After filling (with little vibration if needed) to a certain height (10 mm higher than the first row of sensors), the top of the container was sealed to avoid moisture loss. C145 and C255 were cast and cured in climate temperature of $22 \pm 1 \text{ }^\circ\text{C}$ while the production and curing temperature for C245 and C338 were $19 \pm 1 \text{ }^\circ\text{C}$.

2.3.2 Conductivity of pore solution

The electrical conductivity of pore solution is acquired from data in previous investigation of pastes with the same cementitious materials. It is assumed that the aggregates are rather stable (for the monitored time), so they do not alter pore solution conductivity and the hydration process. The calculation of pore solution conductivity has been illustrated in detail in [20], which was mainly based on two assumptions: firstly, the alkalis have a fast dissolution within the first few minutes after water mixing; secondly, the solvent exchanged interlayer water of C-S-H is classified as conductive “pore solution”.

2.3.3 Strength development

The hardening process of concrete was monitored by a traditional standard (ASTM C 403/C 403M – 05) with the penetration resistance (strength) test on the mortar part of concrete mixture. After 24 h, concrete cubes were cured in water until the targeted ages. The compressive strength of concrete samples was measured at 12 h, 24 h, 3 d, 7 d, 14 d and 28 d, respectively according to standard EN 12390-3:2019. It should be noted that the size of C145 and C255 sample is 100×100×100 mm³, but that of C338 and C245 is 150×150×150 mm³. Therefore, the strength values of C145 and C255 were normalized by a dimension factor of 0.93 for a better comparison according to [22].

2.3.4 Isothermal calorimetry

The heat of hydration for C245 was measured by I-Cal 2000 Isothermal Calorimeter (Calmetrix company), which is capable to measure isothermal heat flow of concretes. It is equipped with 2 sample cells with a capacity of 450 ml. Cells are well isolated from each other by a wide air gap, so it ensures unparalleled precision and stability by eliminating any cross-influence. The temperature was set to 20 °C with a stability of ± 0.001 °C. Two duplicate measurements were performed simultaneously to obtain an average value for presentation as a result.

3 Results and discussion

3.1 Real-time monitored data from the upgraded technique

3.1.1 Electrical properties

Figure 3 shows the real-time monitored electrical properties of hydrating concretes. The formation factor (F) of concrete samples is calculated by Eq. (3), where σ_{ps} is the electrical conductivity of pore solution according to [20] and σ_c is the monitored electrical conductivity of concrete. The assumption here is that the aggregate does not interact with the pore solution and consequently does not affect the hydration reactions. It should also be noted that σ_{ps} of C338 is obtained as a multiplicative function of conductivity of paste with w/b of 0.35 and a dilution factor ($0.38/0.35=1.09$).

$$F = \frac{\sigma_{ps}}{\sigma_c} \quad (3)$$

It can be observed from Figure 3a that evolution of electrical conductivity observed in pastes [20] exhibits a similar trend compared to the electrical conductivity of hydrating concrete. The improved measurement system presented in this study shows to be more effective than the previous version in monitoring hydration before final setting time happens, as it is capable of obtaining a more stable and consistent data line by

eliminating polarization effects. In the first 1.8 h, a fast increase in conductivity is caused by a continuous dissolution of clinker [23] and dissolution of slag [24], which results in an increase in pH and alkali. Calcium concentration in pore solution reaches a supersaturated state with respect to portlandite [25]. After this period, the precipitation of hydration products (portlandite and C-S-H) transforms from being dominated by nucleation to growth [26] to a state in which connections are built between mineral particles. This will reduce the electrical conductivity. In the period from 4 h to 20 h, a peak occurs in all samples. The time for this peak coincides with the second reaction of aluminates in presence of sulfates, which will be later discussed in section 3.3.2. The accelerated dissolution of aluminate and formation of ettringite [27] may reduce the sulfate ion concentration in pore solution so it requires release of hydroxide ions to balance the charge. This results in a minor increase of conductivity (see C255 in [Figure 3a](#)). The peak for C145 and C255 is observed at approximately 8 hours, whereas for C245 and C338 it occurs around 12 hours. As pointed out in section 2.2.1, C145 and C255 were cast in a higher environmental temperature compared to C245 and C338. As the peak time of both silicate and aluminate reaction is sensitive to curing temperatures [28,29], the occurrence of the aluminate peak is slower at lower temperature. Conductivity of C245 has the highest value in the first 10 h, whereas the remaining three mixtures have a similar value when considering the deviation observed in parallel tests.

The dissolution of alkalis in fly ash (siliceous fly ash) is much lower than the slag so C145 has a lower alkali concentration and pH than C245 at the same w/b . In the period prior to setting, the variation in conductivity of binary concretes is primarily attributable to differences in the concentration of conductive ions present in the pore solution. This is evident from the fact that the initial formation factors, which are approximately 15, are nearly identical for the binary concretes, as depicted in [Figure 3b](#). The ternary concrete has the highest formation factor over hydration time up to 168 h. This can be ascribed to the lowest effective water to binder ratio, thus introducing the lowest water porosity in concrete matrix. Moreover, the fine limestone can accelerate the hydration [30] and promote an earlier volume-filling hydration process, leading to a denser structure [31]. Its effect is more evident after 32 h according to the increasing difference between C245 and C338. Although the formation factor of C255 is below C145 before 86 h due to a higher w/b , it grows higher than that of fly ash binary concrete as slag consumes in the hydration process much earlier than fly ash [32].

The effect of aggregate on the electrical properties is evaluated by dividing formation factor of concrete with that of pastes with same w/b , and this also equals to the ratio between conductivity of pastes and concretes. [Figure 3c](#) shows that incorporation of aggregates will induce a difference factor between formation factor of concrete and pastes with a value between 2–7. This difference factor before setting time seems to have a close value to the ratio between the value of solid to water volume ratios in concrete and that of paste. During

the hardening process from 6 h to 16 h, the factor has an increase to a peak point and then significantly decrease to values similar with the ratio of water volume fraction in pastes and that of concretes. This implies that the main influential factor shifts from volume of solid to volume of liquid after the generation of solid networks [33] during the hardening process.

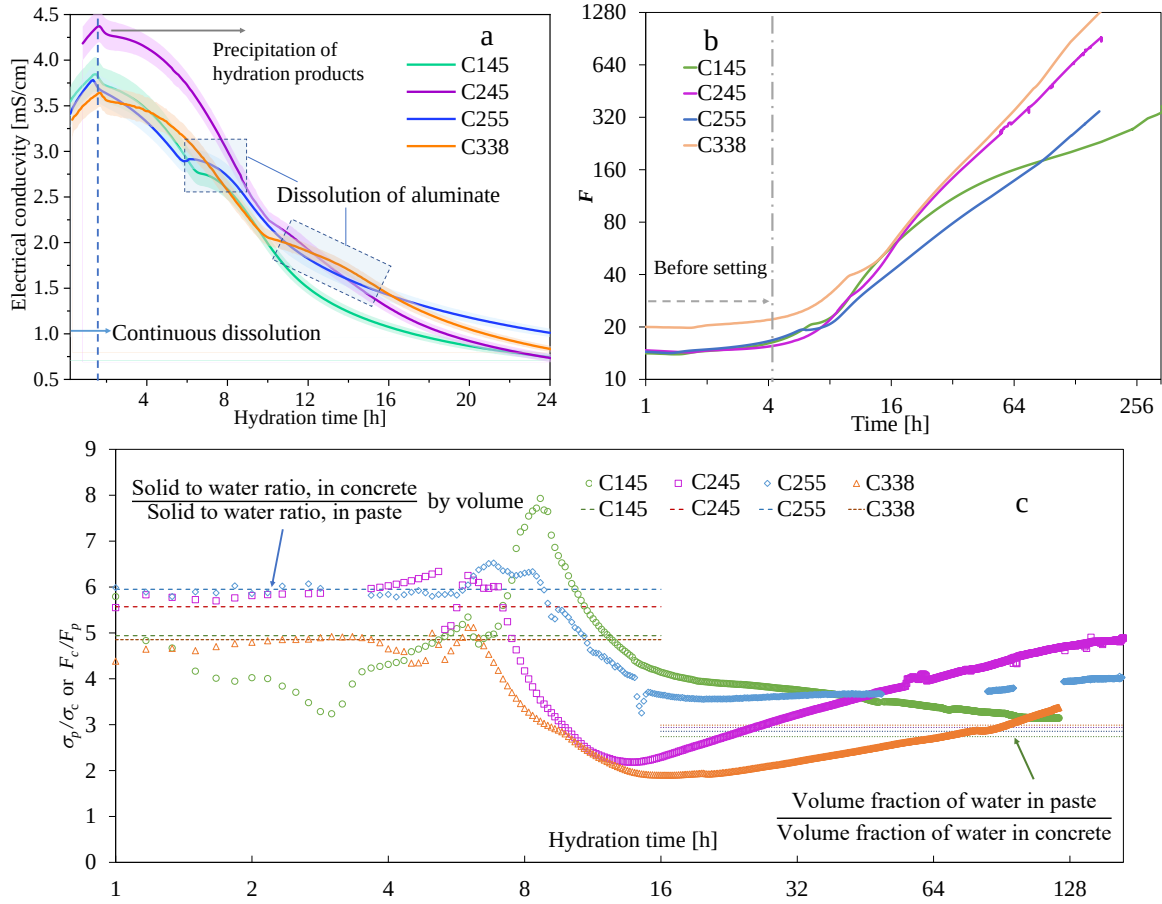


Figure 3 Real-time monitored electrical properties of concrete: a – evolution of electrical conductivity in the first 24 h; b – the calculated formation factor of concrete; c – the ratio between electrical conductivity of paste and concrete.

3.1.2 Temperature evolution and maturity

Temperature has a significant effect on the hydration and hardening process of cement-based materials. The temperature of concrete will be affected by two aspects: the environmental temperature and the heat release from the hydration reaction. The latter factor makes major contributions in massive concretes. In state of the art research of cement-based materials, an isothermal method is being majorly used to investigate the hydration process and assess hydration degree [34]. However, this kind of isothermal condition is far from the practical onsite conditions. One advantage of the updated measuring system is to include temperature sensors on the sensor panel, to enable monitoring the temperature regime.

Figure 4a illustrates the temperature profiles of low carbon concretes exposed to the laboratory environment (22 ± 1 °C or 19 ± 1 °C). For the assessment of onsite performance of concretes, an index called maturity [35]

was defined for assessing the hydration and hardening of concrete. The correlation between maturity and strength (or shrinkage and setting) has been established in many previous investigations [36–39]. Therefore, some nondestructive devices were produced to measure maturity index which through its relation to strength can be utilized for assessing the onsite performance of individual concrete mixture. Maturity index (M) of low carbon concretes in this study, have been calculated by Eq. (4) according to Nurse-Saul maturity function.

$$M = \sum_0^t (\bar{T} - T_0) \Delta t \quad (4)$$

where $\bar{T}$ is the average temperature of concretes during the time interval Δt , t is the elapsed time and T_0 is datum temperature for calculation. To evaluate the thermal effect of hydration, the datum temperature is assumed to be -10 °C. The temperature difference (dT) between the inner (at depth of 100 mm) and surface layer (at depth of 10 mm) was evaluated to check the thermal effect of hydration.

The temperatures of the concrete mixes were approximately 1–2 °C higher than the room temperature at starting point (about 12 min after water mixing) (see Figure 4a). It stays almost constant at the first 4 h due to the low rate of reaction during the induction period. After this period, the temperature reaches a peak due to the hydration heat release. It starts to decrease after the peak because the heat release rate slows down and becomes lower than heat dissipation. Figure 4b shows that C245 has the maximum temperature difference (about 1.4 °C) between inner part and surface of concrete with the dimensions shown in Figure 1. The maximum temperature difference for C145, C255 and C338 is 1.2, 0.9 and 0.2 °C, respectively. There are fluctuations and occasional negative values in the temperature difference of C338 due to variations in environmental temperature. Figure 4c demonstrates that the temperature profile in C245 exposed to the lab environment is very close to the heat flow with isothermal calorimetry at 20 °C. Due to the heat dissipation, the time for temperature growth (~4h) is however after the (~2 h) induction period. An important coincidence is that the peak temperature time is interestingly simultaneous with the time of aluminate reaction peak. Maturity of C338 is lowest due to the lowest content of cementitious binder and environmental temperature. C245 has a lower maturity than C145 in the first day due to a lower curing temperature, but maturity of C245 grows faster after 4 h because slag involves greatly into hydration after that time due to its faster and higher reactivity than fly ash in that time period [32,40]. This also explains the higher dT in Figure 4b. C255 has a higher initial maturity than C245, but maturity of C245 becomes close to C255 after 7 days.

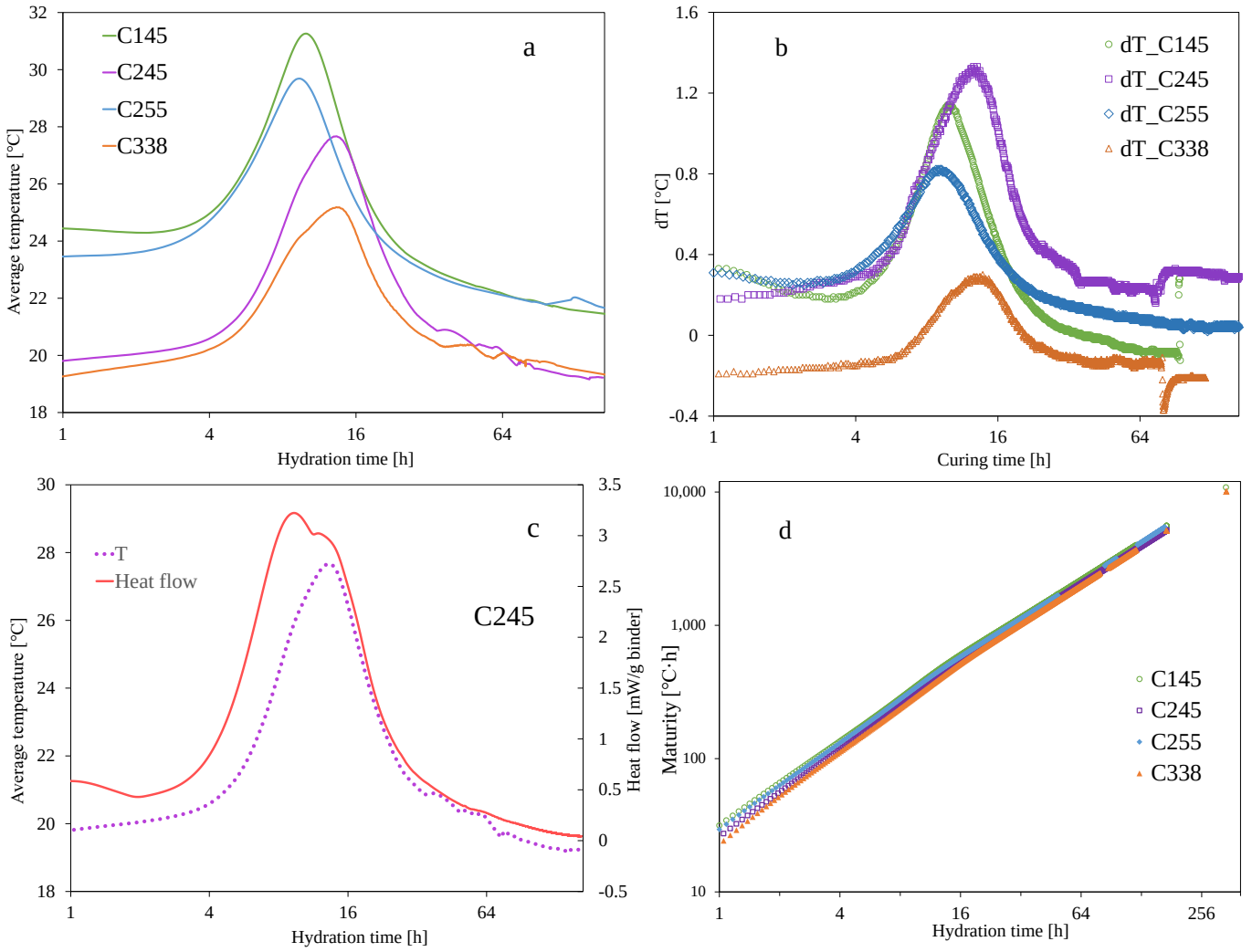


Figure 4 Monitored temperature evolution and heat release of concretes: a – temperature up to 128 h: b – temperature difference at depth of 100 mm and 10 mm: c – comparison between isothermal calorimetry and temperature evolution of C245: d – maturity of concretes up to 14 days.

3.2 Evolution of UPV

Ultrasonic wave velocities in porous materials is determined by the volume fraction of liquid and solid phase [41]. During the hydration of cementitious materials, the changes in connectivity of produced solid materials also makes impact on the velocity. Hydration induces an increase in rigidity of concrete mix to increase wave speed, so many investigations have applied measurement of UPV to indicate the hardening process of cement-based materials [16,33,42,43]. This study used a setup to monitor the evolution of UPV in hardening process of low carbon concrete. This serves to compare with function of the invented device for measuring the electrical properties.

Figure 5a shows that UPV of concrete keeps almost constant before 2 h because there is little consumption of free water during this period, which corresponds to the induction time of cement hydration. UPV of the suspension state is dominated by the volume fraction of solid. The ratio between solid and liquid in C145, C245, C255 and C338 is 10.3, 11.1, 9.8 and 11.7, respectively. Consequently, a similar sequence of UPV can

be detected in these concretes at the initial stage. Some minor observed differences in the sequence may be caused due to effect of temperature. After 2 h the precipitation of hydration products builds connection between particles to induce an increase in UPV. The growth of particle connection in C145 grows faster than C255 due to the lower w/b [20], so UPV of C145 becomes higher than C255 after 4 h. The square of UPV (v^2) is linearly correlated to elasticity of materials, which is determined by the dynamic Young's modulus and dynamic Poisson's ratio [44]. Therefore, the change rate of elasticity can be indicated by the value of dv^2/dt (see Figure 5b). It shows that C145 and C338 have a similar tendency of change rate, and this is consistent with decrease in the connectivity of pore solution as in [20]. As the concrete hardens, the precipitation of hydration products is decreased both in amounts and kinetics, resulting in a decrease in the growth rate of dynamic Young's modulus. From 2 h to 8 h, C255 has the lowest dv^2/dt due to its highest w/b . This can also be attributed to the lower growth rate of solid networks resulting from the dispersed distribution of the precipitated hydration products on particle surface [26,31]. Due to the aluminate reaction from 12 to 18 h in C245 and C338, there is an evident increase in the growth rate of elasticity. The higher peaks in Figure 5b implies that the dynamic Young's modulus of C338 increases at a faster rate than C245, which is caused by an accelerating of hydration by fine limestone power after 4 h.

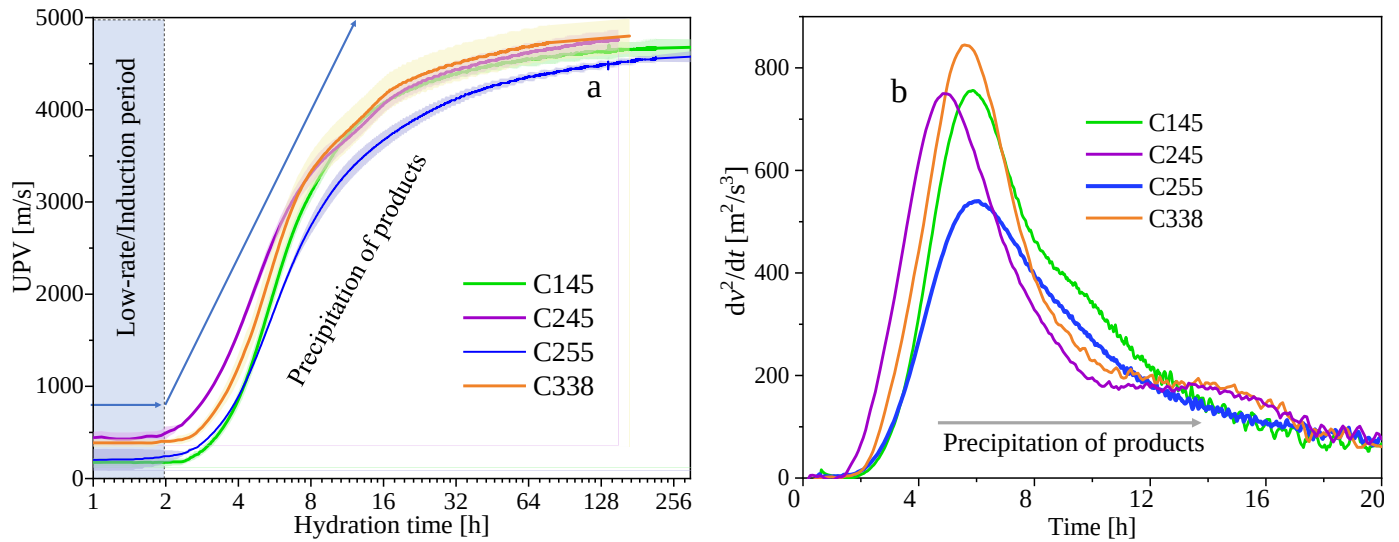


Figure 5 Monitored UPV in hydrating concrete (a) and dv^2/dt (b).

3.3 Properties of setting process

3.3.1 Development of penetration resistance

The penetration resistance was measured by the traditional method (ASTM C403) to assess the initial hardening process of low carbon concrete. As binders dissolve after water mixing, the nucleation and growth of hydration products cause the formation of clusters which eventually connects into an elastic structural network [33]. During this period, both the UPV and formation factor present a significant increase after the solid network percolation is reached. Therefore, it is evident that UPV and electrical properties (resistivity

and formation factor) can indicate the hydration induced structural formation and elastic property [45].

Generally, the evolution of penetration resistance has a similar time-dependent tendency to the evolution of both UPV and formation factor (see Figure 6). According to the definition of initial and final setting point in ASTM C403, the development of penetration resistance can be classified into two regions with the initial setting strength (3.5 MPa) as the critical point. During this period, the determining parameter affecting the of stress has found to be the interparticle or C-S-H internetwork distance [46], which is affected by the fineness of the particles, w/b and reactivity of binders [47]. For pastes cured under the same condition, we have observed that an increase in w/b decreases the resistance to needle penetration [20]. However, Figure 6 shows that although C245 has a higher value in both UPV and formation factor, the development of penetration resistance is slower compared with C255 in the first 5 h. This is mainly due to the impact of temperature on the hydration and setting [48,49], which is also indicated by the lower maturity in Figure 4. To evaluate the effect of temperature on hydration of low carbon concrete, the equivalent curing age (t_e) of concrete was calculated by Eq. (5) [35].

$$t_e = \sum_0^t e^{-\frac{E}{R}(\frac{1}{T} - \frac{1}{T_r})} \Delta t \quad (5)$$

where E is apparent activation energy of hydration (30 kJ/mol for C145 and C255; 44 kJ/mol for C338 and C245 [50]). T_r is the absolute reference temperature (298.15 K).

The equivalent curing age of samples is presented on the upper coordinate axis in Figure 6. It shows that the development of penetration resistance in C245 and C255 is quite similar before the initial setting, in terms of the equivalent curing age. However, after this time the growth of strength in C245 (with average of 11.1 MPa/h) is much faster than C255 (with average of 6.7 MPa/h), and it is consistent with the evolution of UPV (see Figure 5). The fine limestone can provide nucleation sites for hydration products so it can accelerate the hydration [51]. Moreover, the lower w/b also induces a shorter particle distance, so these dual effects result in the fastest development of penetration resistance in C338 between all the mixes with respect to equivalent curing age. For the fly ash binary system, aluminate ion dissolved from fly ash may hinder the hydration of silicates due to its binding on the surface sites [52]. Therefore, C145 has a slower hardening process than C245 especially after the initial setting. Slag has a faster hydration rate than fly ash. In addition, the surface charge and precipitation rate of hydration product on SCMs particle surface is also an important factor controlling the hardening process [53,54]. Temperature is a critical factor for the initial percolation of solid links. After initial setting, penetration resistance is determined by the reactivity potential of the binder and the liquid volume.

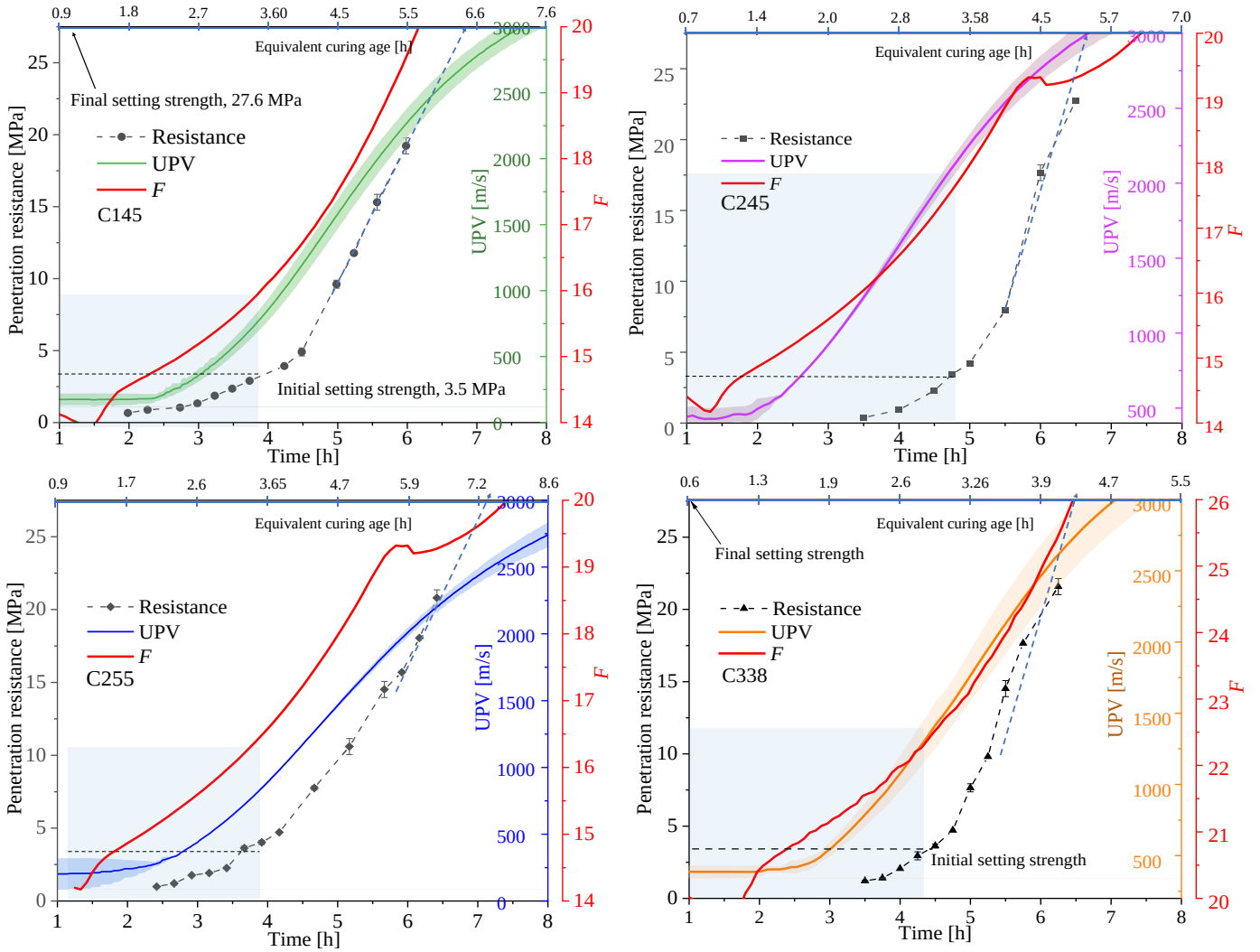


Figure 6 Evolution of penetration resistance of concretes compared with the UPV and formation factor

Figure 7 demonstrates a detailed comparison between hydration heat release, electrical conductivity, UPV, formation factor and penetration resistance with the slag blended concrete as an example. In the first place, the comparison between the evolution of heat flow and conductivity is considered. As the heat flow reaches the lowest value at about 2 h, the change rate of electrical conductivity ($\Delta\sigma/\Delta t$) declines from a positive to a negative value. This means that the dissolution rate of conductive ions largely decreases. Moreover, the reduction in the distance between particles result in the decrease in the connectivity of pore solution [20,55], starting to induce a decrease in conductivity. An intriguing increment in the rate change of stress ($\Delta\sigma/\Delta t$) is discernible between 2 and 3 hours, which can be attributed to an elevation in pH during the process of C-S-H growth [23]. After entering the acceleration period of alite hydration, $\Delta\sigma/\Delta t$ shows a sharp decrease. The peak time of the lowest $\Delta\sigma/\Delta t$ is very close to peak of heat flow from the alite hydration. The minor difference is mainly due to a higher temperature in the mixtures cured in a laboratory climate condition in comparison with (see Figure 4) the samples analyzed in an isothermal temperature (20 °C). After the alite hydration peak, a further dissolution of C_3A and the accelerated formation of ettringite will induce an aluminate peak [56]. During this period $\Delta\sigma/\Delta t$ increases due to the fact that the further dissolution of minerals and the sulfate

consumption cause an increase in concentration of hydroxide ions. The aluminate peak also can be clearly detected by the electrical conductivity change. The precipitation rate of hydration products gradually decreases as the hydration goes into the deceleration period, so both the heat flow and $\Delta\sigma/\Delta t$ enter a very stable stage. After the induction period, an increase in penetration resistance is observed, as well as in ultrasonic pulse velocity (UPV) and formation factor. The hydration heat release has a very low value at both the initial setting and final setting point with about 9 J/g and 20 J/g binder. These values account for less than 5 % of a complete hydration of this binder system (typical heat with 460–470 J/g [57]). The increases in UPV and formation factor are also rather minor compared to the values after 7 days (see Figure 3). A detailed correlation between penetration resistance and these values will be presented in the next section.

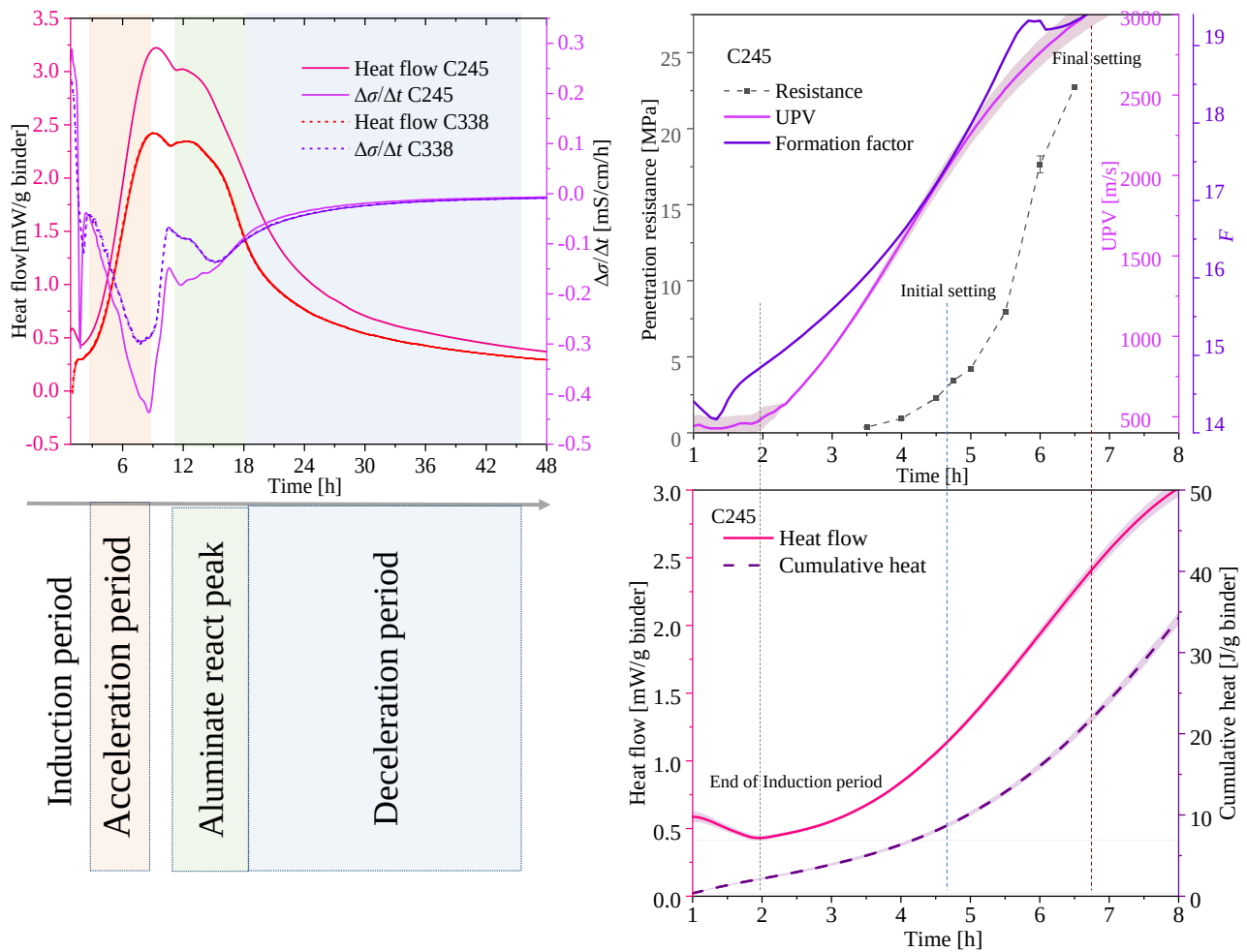


Figure 7 Detailed comparison between evolution of isothermal calorimetry and electrical conductivity (left side), and its relation to the formation factor, UPV and penetration resistance of C245 (right side).

3.3.2 Penetration resistance in relation to UPV, formation factor and maturity

The discrepancy in the development of penetration resistance is noticeable before and after the initial setting, as observed in the preceding section. Kolawole et al. [58] applied a shear rheo-viscoelasticity approach to test the properties of concrete mixtures from water mixing up to sometime after final setting. They classified the response of mix into 3 kinds of states: (1) plastic state; (2) semi-plastic state; and (3) solid state. These

terms are originally defined in soil mechanics by Atterberg, which is called Atterberg limits [59,60] by relating state of soils to its moisture content. When penetration resistance is plotted against with UPV, formation factor and maturity, the correlations can be classified into two regions: plastic state before ~ 4.9 MPa and semi-solid (plastic) state between 4.9 MPa and 27.6 MPa. [Figure 8](#) shows the correlation in two different states and Table 3 shows the results of regression in these two regions separately. According to the R^2 value, a linear correlation can be observed in the relationship between penetration resistance and all these three monitored properties, respectively. The slope of the linear line at semi-solid state (k_2) is much lower than that of plastic state (k_1). It is interesting that the critical value is slightly higher than the initial setting strength (3.5 MPa) according to the definition in ASTM C403.

During the plastic state, the penetration resistance is actually determined by the development of the yield stress of the cement-based mixture [61]. Only a few of the binders have been dissolved to form C-S-H and other hydrates during this period (see low heat in [Figure 7](#)). Therefore, the stress-strain performance of the fresh mix is partially controlled by C-S-H links and mainly by non-contact colloidal interactions between cement particles [62]. An increase in the network links will increase the elasticity to transform the mechanical properties of matrix from the plastic to elastic state [63], and the semi-solid state is an intermediate state in between. This implies that the density of C-S-H and charging state of the particle surfaces are critical for mechanical response during the hardening process. The differences in slope at two states are more evident in C245 and C338 than that in C145 and C255. The slope of the regression line of C245 and C338 at semi-solid state is only 1/3 to 1/7 of these slopes in plastic state whereas the ratio is about 1/2 to 1/4 for C145 and C255. As mentioned in the previous section, these differences can be ascribed to discrepancies in the reactivity of binders and w/b . However, further investigations are warranted to elucidate the underlying mechanism responsible for the considerably lower increase in UPV and formation factor compared to that in penetration resistance at the semi-solid state.

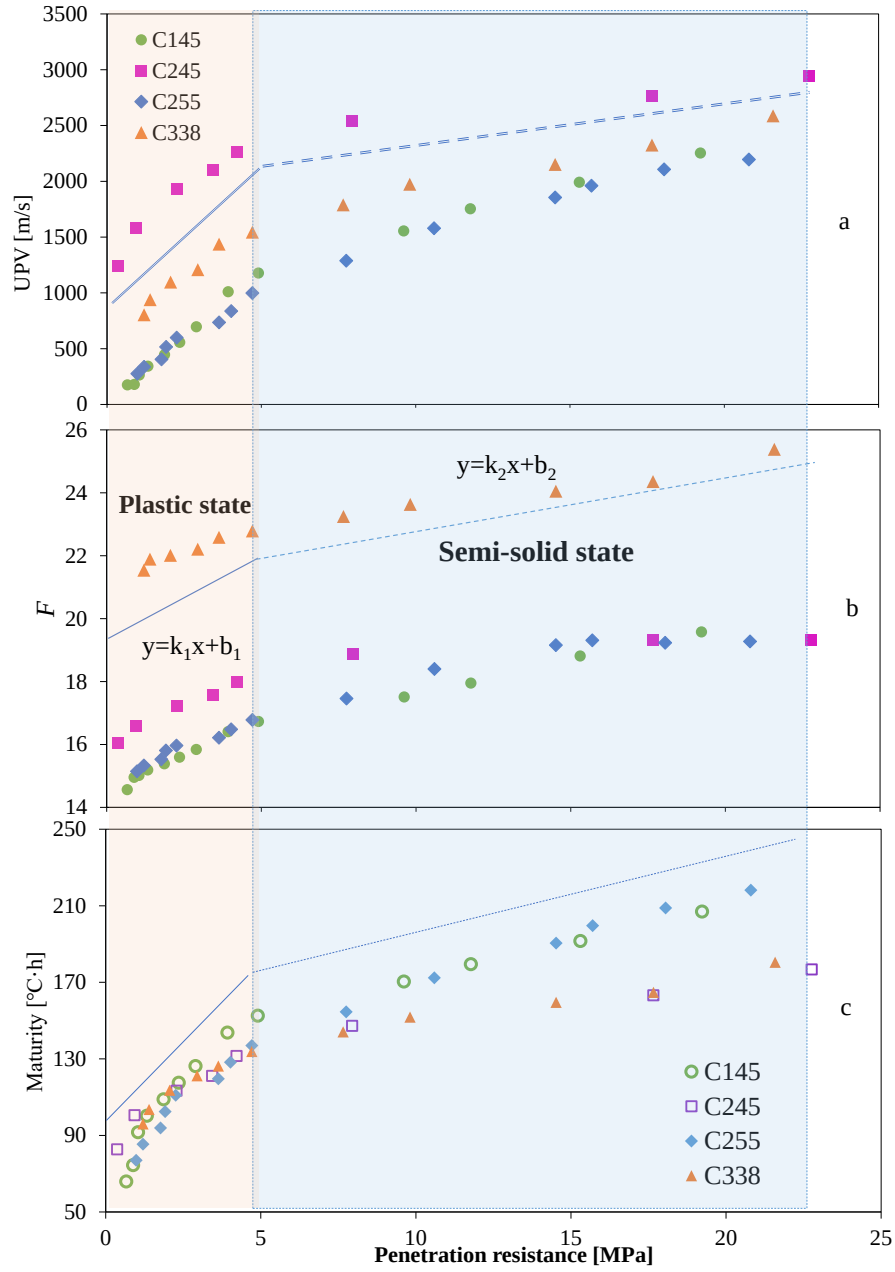


Figure 8 Quantitative correlation between penetration resistance and UPV, formation factor or maturity.

Table 2 Regressed parameters between penetration resistance and indices at plastic state and semi-solid state.

Mix ID	Parameters	Plastic state (k_1, b_1)			Semi-solid state (k_2, b_2)		
		Relation to UPV	Relation to F	Relation to maturity	Relation to UPV	Relation to F	Relation to maturity
C145	k	245.78	0.48	19.3	75.27	0.2	4
	b	3.4	14.5	66	831	15.6	131.1
	R^2	1	0.98	0.93	1	1	0.99
C245	k	247.2	0.47	11.31	33.73	0.07	2.26
	b	1268.5	16	84.5	2182.9	18	125
	R^2	0.95	0.98	0.94	0.95	0.78	0.97
C255	k	181.22	0.4	14.78	76.38	0.17	5.15
	b	124	14.9	69	706.8	16.3	115.3
	R^2	0.98	0.96	0.95	0.98	0.87	0.99
C338	k	204.82	0.32	10.15	58.16	0.14	2.53
	b	627.3	21.3	88.8	1325.4	22.1	123.8
	R^2	0.96	0.95	0.95	0.98	0.97	0.98

3.4 Setting, UPV and electrical properties

The percolation theory of consolidation has been extensively applied to understand the mechanics of soil during its drying process [63]. Although Pellenq and Damme [46] highlighted that the setting of cement-based materials was different from soil hardening due to its “wetting” instead of “drying”, the underlying physics of setting is similar to soil drying due to the formation of solid networks and interactions towards a percolation point for transition of plastic to elastic state.

Percolation theory based on hardcore/soft-shell model was used to establish a quantitative description of elastic modulus with a certain function during hydration [17]. According to this model, the evolution of UPV from about 4 to 9 h can be described by Eq. (6) with exponent parameter of 2, which is consistent with the experimental results reported in [64].

$$\sqrt{v^2 - v_0^2} = C(t - t_0) \quad (6)$$

where v is the acoustic velocity at curing time t , v_0 is the velocity in the suspension before percolation (herein the UPV of concrete at the initial time is used), C is a free parameter as constant, and t_0 is the time for the percolation of solid network. The evolution of electrical properties during the setting process of cementitious material has the similar tendency as UPV regarding the percolation of solid networks between particles [64]. Correlation between formation factor and evaporable water content has been well described by the percolation theory with a exponent parameter around 2 [20]. Therefore, Eq (6) is modified by replacing the acoustic velocity with formation factor to obtain (7).

$$\sqrt{F^2 - F_0^2} = h(t - t_0) \quad (7)$$

where F is the formation factor at curing time t , F_0 is the formation factor at few minutes after water addition, and h is a free parameter constant.

Figure 9 shows the regression results by using Eq. (6) and (7) in a certain time interval to describe correlation between UPV, formation factor and curing time. The regression part in formation factor was selected within a time interval with a good linear region before the second inflection (see Figure 9a). The final hardening from semi-solid to a solid state can be indicated by inflection point of growth rate of formation factor ($a-F$), which is calculated by dividing formation factor with time [20]. UPV was analyzed in the same way to get the inflection time of growth rate of UPV ($a-UPV$) (Figure 9c and d).

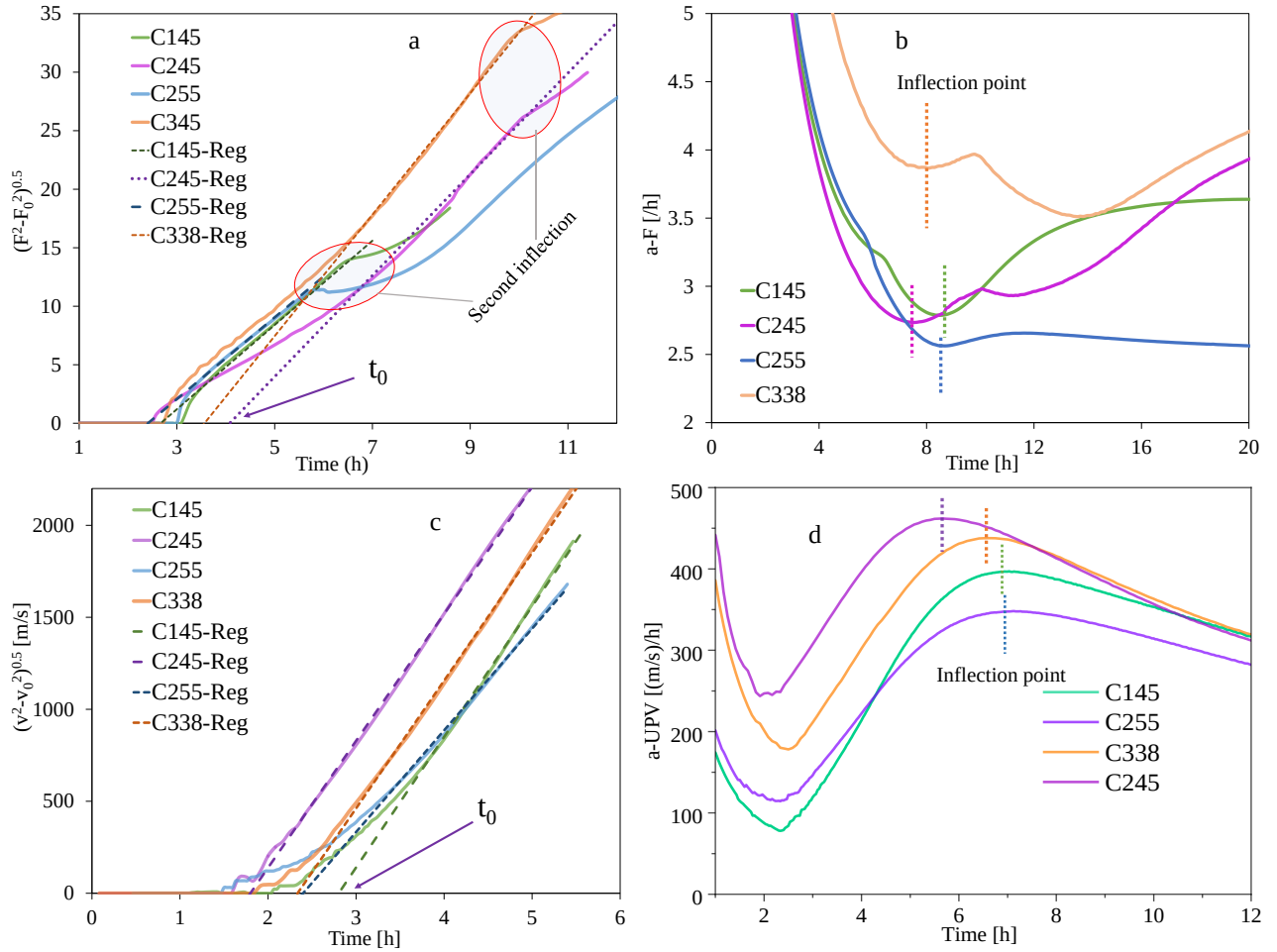


Figure 9 Setting time assessment of concrete based on the UPV and formation factor inflection time.

Table 3 summarizes the regression function, critical time and the setting time of all concrete samples. Figure 10 presents the correlation between critical time and setting time. Critical time of formation factor can well describe both initial setting and final setting point of low carbon concrete mixtures with a linear correlation regardless of the influence of temperatures. The flection time of $a-UPV$ can have a similar indication on final setting time as formation factor, but the critical time of UPV change seems to have a bad correlation to the initial setting time.

Table 3 Correlation between inflection point, regression function and setting time

Sample	Regression in selected zone		Critical time [h]				Setting time [h]	
	Eq. (6)	Eq. (7)	t_0 of UPV	t_0 of F	Peak of $a-UPV$	Inflection time of $a-F$	Initial setting	Final setting
C145	$y=710x-1990$	$y=3.60x-9.64$	2.80	2.68	7.00	8.48	3.81	6.82
C245	$y = 690x-1242$	$y=4.32x-17.64$	1.80	4.08	5.67	7.33	4.83	6.56
C255	$y = 553x-1326$	$y=3.49x-8.42$	2.40	2.41	7.25	8.58	3.73	6.97
C338	$y = 694x-1622$	$y=5.19x-18.50$	2.34	3.56	6.64	7.72	4.41	6.31

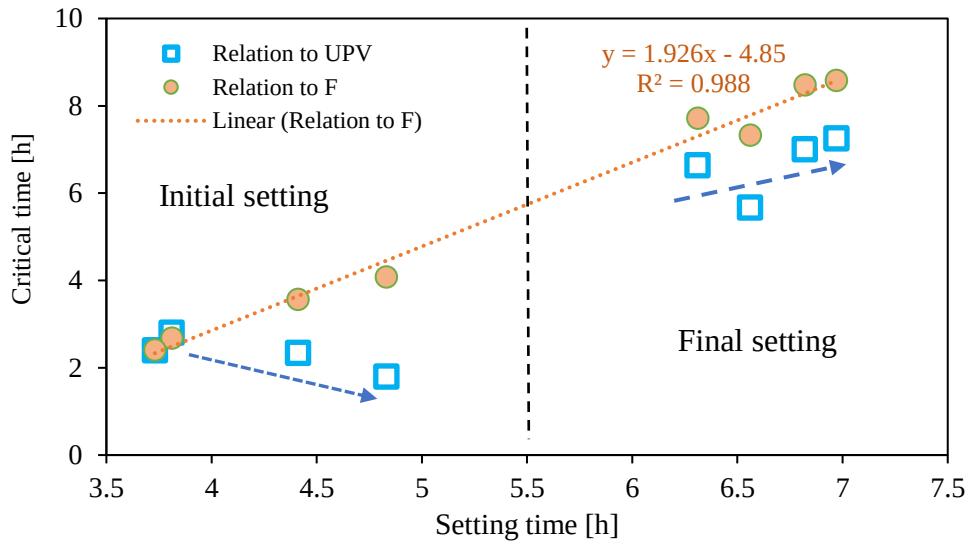


Figure 10 Correlation between setting time and critical time of monitored properties.

3.5 After final setting

3.5.1 Compressive strength development

The compressive strength of concrete was tested after final setting to reveal the development of mechanical performance during the hardening process (see Figure 11). Fly ash binary concrete (C145) has the highest compressive strength at 12 h with a value of 5.9 MPa, and slag blended concretes have a very similar strength varying from 4.0 to 4.6 MPa at this curing time. The reason behind C145 having this strength value may be ascribed to its cementitious content which is highest among all the mixtures or probably due to the curing temperature effect (see the highest maturity in Figure 4). The strength development from 24 to 168 h is determined by the w/b and the reactivity of the SCMs. A lower w/b induces a higher compressive strength at this period. Given the same w/b , slag blended concrete develops faster so it has a higher strength than the fly ash concrete. This is because slag involves earlier in hydration compared to fly ash [40,65]. Despite with a higher w/b , compressive strength of C255 seems higher than C145 after 336 h due to expected higher reactivity of slag compared to fly ash in early ages. Compared with C245, a higher strength development in C338 after 24 h is not only due to the lower w/b but also the chemical effect of limestone. The chemical interaction on the surface of limestone alters reaction kinetics and phase assemblage. The fine limestone enables nucleation of C-S-H on the surface of calcite and promotes the formation of other phases, such as carboaluminates. Therefore, the addition of an appropriate amount of fine limestone can enhance early strength development [31,66].

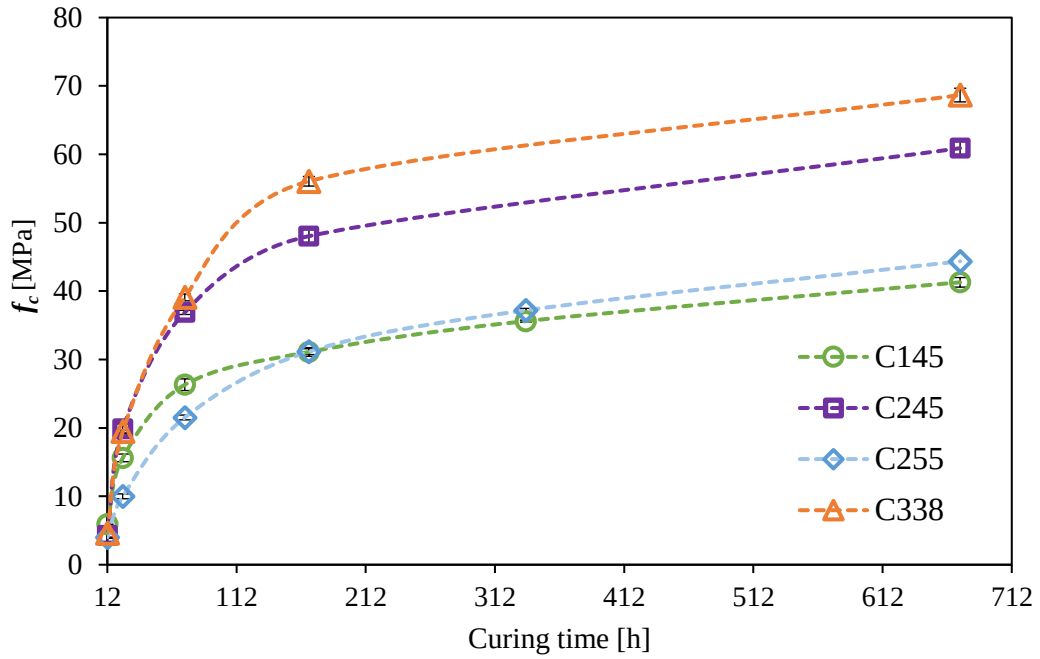


Figure 11 Development of compressive strength with error bar of low carbon concrete after final setting.

3.5.2 Correlation between compressive strength, formation factor, UPV and maturity

Electrical conductivity of cement-based materials at certain temperature is determined by the porosity, ion concentration and connectivity of pore solution [20]. The use of formation factor can eliminate the effect of ion concentration in pore solution, so it directly relates to water porosity according to Archie's law [67] as Eq. (8).

$$F = a(\Phi)^{-m} \quad (8)$$

where parameter “ a ” is non-uniform constant, “ m ” is the shape factor (with an average value of 2 for binders in this study) and Φ is the volume fraction of pores filled with a conductive solution.

This equation describes the volume of pores filled with a conductive liquid, so it may exclude the empty pores and air void in the non-saturated concrete matrix. However, the samples in this study are sealed cured so the matrix is naturally in a saturated condition with limited proportion of empty air voids. It should however be emphasized that in practical utilization, the saturation degree of the matrix should be taken into consideration.

The mechanical performance of porous materials is closely determined by pore structures inside the matrix. Many empirical functions were proposed to describe the correlation between the porosity and compressive strength of concretes [68,69]. One typical expression is a logarithmic function reported by Schiller [70]:

$$f_c = K \ln(\Phi_0/\Phi) \quad (9)$$

where f_c is the compressive strength, K is the constant parameter, and Φ_0 is porosity at which the strength practically vanishes. After substituting Eq (8) into Eq (9), we can obtain a logarithmic function for describing the correlation between formation factor and compressive strength as Eq. (10).

$$f_c = K \left(\ln \Phi_0 - \frac{\ln a}{m} \right) + \frac{K}{m} \ln F \quad (10)$$

Figure 12a shows that compressive strength of low carbon concretes has a linear correlation with $\ln F$ having a $R^2=0.99$. This quantitative description presents an opportunity for in-situ monitoring of the strength development of low carbon concretes with different SCMs. It is independent on the curing age as well as the binder types. For comparison, the correlation between compressive strength and electrical conductivity of concretes (σ_c) is illustrated in Figure 12b. Although the R^2 is rather high with 0.96, Figure 12d illustrates that its deviation is much higher than the relation to formation factor. The primary reason for this phenomenon is the influence of the ionic conductivity of the pore solution on the electrical conductivity of the concrete.

For a more scientific description of the relationship between strength and pore size based on physical principles, Luping [71] proposed a model using Griffith's theory to include the average pore radii. Furthermore, Kumar and Bhattacharjee [72] simplified the correlation between porosity and compressive strength as Eq. (11)

$$f_c = \sqrt{\frac{E_0 T_0}{\pi} \frac{1-\Phi}{\sqrt{r_m}}} \quad (11)$$

where E_0 , T_0 and r_m are the modulus of elasticity, specific surface energy of solid and the mean distribution radius, respectively. With the porosity from Eq. (8), we can rewrite Eq (12) for correlating the strength to formation factor and pore radius.

$$f_c = \frac{K_2}{\sqrt{r_m}} \left[1 - \left(\frac{F}{a} \right)^{-\frac{1}{m}} \right] \quad (12)$$

where K_2 is a constant including intrinsic properties of solid (E_0 , T_0). For a consolidation packing, the critical radii in porous materials is related to the formation factor as Eq. (13) [73]: Therefore, we can get the correlation between formation factor and strength as Eq (14).

$$r_m \propto \frac{1}{\sqrt{F}} \quad (13)$$

$$f_c \propto K_2 \cdot F^{\frac{1}{4}} \cdot \left[1 - \left(\frac{F}{a} \right)^{-\frac{1}{m}} \right] \quad (14)$$

Figure 12c shows the regression between $F^{-1/m}$ ($m = 2$) and compressive strength, and it is very reliable with

$R^2=0.99$. We can additionally derive the quantitative expression between formation factor and compressive strength as Eq (15). This expression is also independent on curing time or binder types.

$$f_c = F^{\frac{1}{4}} \times \left(10.76 - 52.57 F^{-\frac{1}{2}} \right) = 10.76 F^{\frac{1}{4}} - 52.57 F^{-\frac{1}{4}} \quad (15)$$

Hereto, two quantitative descriptions of the compressive strength in relation to formation factor have been proposed. Eq. (10) is an empirical correlation, but it is straight forward and simple, so it can be easily used in practice. Correlation in Eq (14) is deduced by following the physical principle. It is more suitable for scientific understanding but not so easy to be used in practice.

In previous investigations, the compressive strength was widely correlated to UPV [7,9,45,74–77] or maturity of concrete mixtures [13,35,37,39,78]. For highlighting the advantage of the formation factor, the correlations between compressive strength with maturity and UPV have been regressed in [Figure 13](#). It is obvious that the correlation between maturity and strength is largely dependent on the binder types and w/b . The general correlation for all mixtures leads to a very weak exponential function with a R^2 of 0.78. Many empirical expressions have been reported for correlation between UPV and strength as summarized in one review paper [77]. The results in this study can be regressed with an exponential expression as Eq. (16). In which A and B are constant parameters.

$$f_c = A \cdot e^{B \cdot v} \quad (16)$$

Although the R^2 is 0.96, the data points of C145 and C255 deviate largely from the regression line. In summary, the correlation between formation factor and strength is the best among three indices, which can be applied on-site to monitor the hydration induced strength development of low carbon concretes regardless of the mixture proportions.

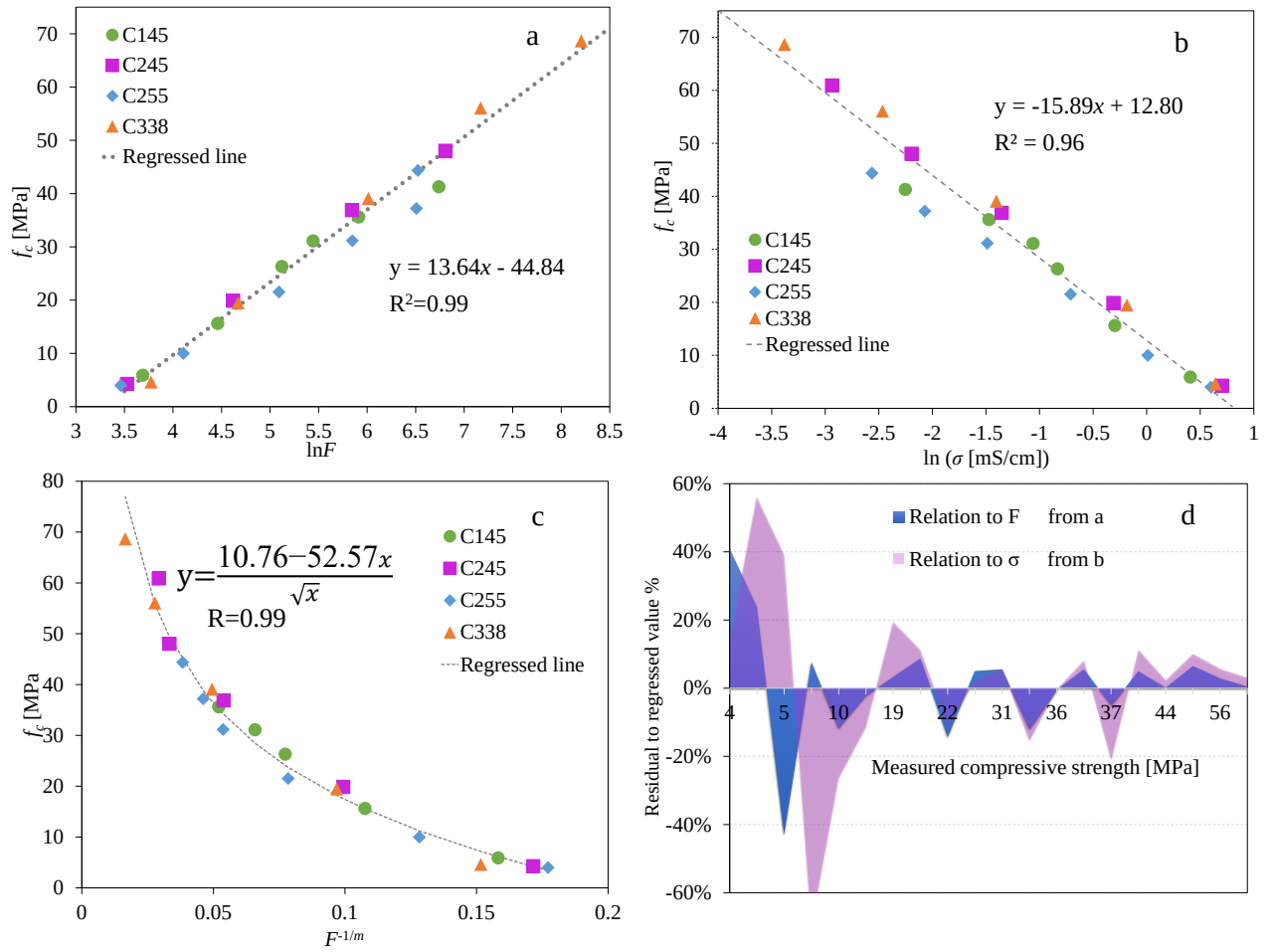


Figure 12 Quantitative correlations between compressive strength and electrical properties in different functions

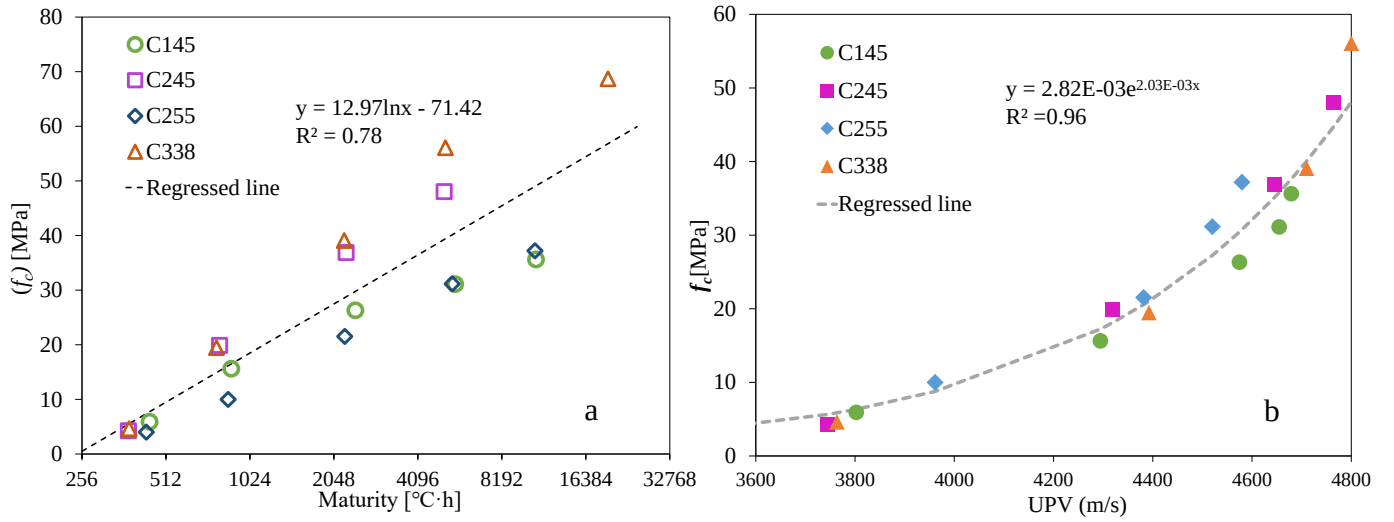


Figure 13 Quantitative correlations between compressive strength and maturity and UPV

4 Conclusions

A reliable non-destructive monitoring approach is essential for promoting the application of various SCMs in the concretes no matter for on-site construction or automated fabrication. In this study an improved automated monitoring device for profiling the electrical conductivity of the concrete with incorporation of SCMs is presented. The incorporated temperature sensors allow to simultaneously record the inner temperature at different depth, which is also very useful for normalizing the electrical conductivity to a reference temperature. The credibility of the method is ensured by comparing the monitored data with parameters obtained from several traditional methods used for testing the hydration, setting time, and compressive strength of concretes.

The presented non-destructive test system can effectively measure the electrical conductivity of hydrating low carbon concretes at different depths by automatic control to avoid polarization and cross-layer interference. Monitored conductivity profiles in time indicates that this parameter is affected by evolution of the hydration reactions. It can reflect the reaction states of alite and aluminates, which is confirmed by comparisons made with isothermal calorimetry measurements. The shape of temperature evolution in the concretes exposed to lab environment is similar with the shape of the heat flow from calorimetry test.

The monitored ultrasonic pulse velocity is a reliable indicator for the hydration and initial setting process of low CO₂ concretes, but its value is dependent on the mixture proportion of concrete especially on the aggregate content. Both formation factor and UPV are good indices to reflect on the evolution of the hardening process before final setting. The mechanical response of hydrating concretes changes a lot after the initial setting, and it can be classified into plastic and semi-solid state with a critical penetration resistance of 4.9 MPa. At each state, a very good linear correlation has been established for penetration resistance in relation to UPV, formation factor and maturity, respectively. The evolution of UPV and formation factor will encounter a sudden change during the hardening process, which can be explained by the percolation theory. The inflection time of formation factor correlates linearly to the initial and final setting time of concrete. SCMs and *w/b* impact the hardening process of concrete, but this is heavily dependent on the temperature history. The presented approach and developed device in this study, can include all these factors for onsite monitoring.

Although all indices (including electrical conductivity, formation factor, maturity and UPV) indicate the compressive strength development of low CO₂ concrete with variations in mix design, the formation factor is concluded to the best representing indicator since it seems to be independent of the binder types, mixing proportion and curing ages.

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Popular science summary:

Concrete is the essential material for the construction of many structures, so it is the second most used material in the world after water. Cement, being the primary material in the production of concrete, poses a significant challenge to achieving carbon neutrality in the construction sector, due to the emissions generated during its manufacturing process. Nowadays, the most feasible and mature way to reduce emissions from cement production is to replace it partially by supplementary cementitious materials (SCMs). The use of SCMs reduces the amount of cement needed in concrete, which in turn reduces CO₂ emission during cement production and decreases the overall carbon footprint of concrete.

Examples of SCMs include fly ash, slag and limestone powder. Some of them are industrial by-products that would otherwise be disposed of in landfills, but instead can be used to create stronger and more durable concrete. Although benefits of using SCMs in concrete extend beyond just reducing the carbon footprint, the use of diverse SCMs induce difficulties in controlling and predicting the performance of concrete. When using traditional methods to predict the right time for laying or finishing concrete containing SCMs, the inaccurate predictions will result in humidity-related issues such as cracking and mould growth, causing a threat to human health and safety. Therefore, a comprehensive understanding of the properties of the blended concrete is needed to establish appropriate models for better control the performance.

This dissertation has conducted an in-depth study on exploring the impact of SCMs and related additives on hydration of cementitious materials and microstructure change, and their relationship to transport processes. A device was designed to continuously monitor the effect of SCMs on hydration-induced structure change, and it was subsequently upgraded to monitor the hardening process of concrete containing SCMs. The work in this dissertation contributes to promote the high-quality use of SCMs in sustainable concretes.

Liming Huang