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Hydration, pore structure, and related moisture properties of cement-based material – Experimental methods and laboratory measurements

Abstract

Cement-based materials, such as mortar and concrete, are the most employed construction materials in the world. Cement is an important component; it reacts with water to form a glue, called cement paste, which causes the material to harden. Today, cement production accounts for a significant portion of the world's annual carbon dioxide emissions. Replacing parts of cement with other materials that have cement-like properties, such as fly ash, can help reduce the climatic impact.

Fly ash is a residual product from coal-fired power plants that has previously landed on landfills. Replacing part of ordinary cement with fly ash changes the chemical composition and reactivity of the material. Knowledge of how these changes affect material properties is necessary to fabricate long-term durable structures with fly ash blended cement-based materials. This applies not least to the pore structure and related moisture properties because most processes that degrade cement-based materials are both penetrating and moisture dependent. The aim of this study was to contribute new data and knowledge in this area.

Unlike ordinary cement, fly ash has little ability to react directly with water. For fly ash to react with water, it depends on the reaction of cement with water. This causes cement-based materials with fly ash to cure more slowly during in the first days. However, this study shows that materials with fly ash have a lower degree of reaction and are more porous well-beyond the first days of curing. The latter part can be partly explained by the fact that the fly ash reaction binds less water than the cement reaction. Instead, fly ash uses part of the products formed by cement for its reaction.

Although the volume of pores increases with increasing fly ash replacement, this study shows that the material's ability to transport water in the vapour and liquid phase decreases. The porous structure in fly ash blended cement-based materials seems to be more heterogeneous and less connective than that in materials with only ordinary cement. This is of considerable practical importance because the ability to transport moisture controls the drying of the material; for example, the time required before moisture-sensitive flooring materials can be applied to a concrete surface.

Furthermore, the present study show that fly ash makes the curing and material properties more temperature sensitive. The reaction of fly ash is considerably delayed at low temperature. The effects are similar to those previously documented for ordinary cement during the first days but differ over longer time. For ordinary cement, low temperature leads to the formation of a more homogenous porous structure that allows the reactions to proceed for a longer amount of time. After a long time, materials with ordinary cement cured at low temperature seem to have the most well-developed properties. These long-term effects of low temperature are not observed as clearly for fly ash blended materials. The results highlight that it is especially important to protect structures with fly ash blended cement-based materials from low temperatures.

Finally, the laboratory work in this study involved some method development. A new measurement and evaluation routine was employed, to show that heat development can be measured from the reactions between cement (with and without fly ash) and water for up to a year after mixing. Previous studies have argued that this is not possible after the first few weeks of reaction. The results create new opportunities for researchers and the industry to study long-term reactions in cement-based materials. In this study, we also presented a new method for determining the amount of binder (e.g., cement and fly ash) in small samples of cement-based material. The method makes it possible to compare the measurement results for small samples of mortar or concrete obtained from a larger volume of material (i.e., with unknown compositions).

Key words: Cement, Mortar, Concrete, Hydration, Pore structure, Water vapour sorption, Moisture transport, Supplementary cementitious materials, Fly ash

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Table of Contents

Preface

The work leading to this thesis was performed at the Division of Building Materials, Lund University. SBUF (Development Fund of the Swedish Construction Industry), Skanska AB and Cementa AB are gratefully acknowledged for funding this project, and Nanocem for accepting this work as a partner project.

I would like to thank my supervisors, Peter Johansson, Lars Wadsö and Katja Fridh, without whose support and advice this thesis would not have been possible. A special thanks to Peter who acquired the funds for this project and encouraged me to go into research.

I would also like to acknowledge my colleagues, present and past, at the Division of Building Materials. Thank you for the interesting discussions, after-work activities and for letting me have my own spot in the lunchroom. Thanks also to my co-authors from other institutions, especially Mette Geiker and Daniel Jensen.

To my ever-supportive family and friends, thank you.

Lund, August 2020

Oskar Linderoth

Abstract

Cement-based materials, such as mortar and concrete, are the most employed construction materials in the world. Cement is an important component; it reacts with water to form a glue, called cement paste, which causes the material to harden. Today, cement production accounts for a significant portion of the world's annual carbon dioxide emissions. Replacing parts of cement with other materials that have cement-like properties, such as fly ash, can help reduce the climatic impact.

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properties. These long-term effects of low temperature are not observed as clearly for fly ash blended materials. The results highlight that it is especially important to protect structures with fly ash blended cement-based materials from low temperatures.

Finally, the laboratory work in this study involved some method development. A new measurement and evaluation routine was employed, to show that heat development can be measured from the reactions between cement (with and without fly ash) and water for up to a year after mixing. Previous studies have argued that this is not possible after the first few weeks of reaction. The results create new opportunities for researchers and the industry to study long-term reactions in cement-based materials. In this study, we also presented a new method for determining the amount of binder (e.g., cement and fly ash) in small samples of cement-based material. The method makes it possible to compare the measurement results for small samples of mortar or concrete obtained from a larger volume of material (i.e., with unknown compositions).

Sammanfattning

Cementbaserade material, såsom murbruk och betong, är världens mest använda byggnadsmaterial. Cement är en viktig delkomponent; det reagerar med vatten och bildar ett lim, kallad cementpasta, som får materialet att hårdna. Idag står cementproduktion för en betydande del av världens årliga koldioxidutsläpp. Genom att byta ut delar av cementet mot andra material med cement-lika egenskaper, till exempel flygaska, kan klimatpåverkan minskas.

Flygaska är en restprodukt från kolkraftverk som tidigare hamnat på deponi. När man ersätter delar av det vanliga cementet med flygaska förändras cementets kemiska sammansättning och reaktivitet. För att skapa långsiktigt hållbara konstruktioner med cementbaserade material krävs kunskap om hur dessa förändringar påverkar materialegenskaperna. Detta gäller inte minst porstrukturen och de relaterade fuktegenskaperna eftersom de flesta processer som bryter ner cement-baserade material är både inträngande och fuktberoende. Målet med denna studie var att bidra med ny data och kunskap inom detta område.

Till skillnad från vanligt cement har flygaskan liten förmåga att reagera direkt med vatten. Istället är flygaskan beroende av cementets reaktion med vatten för att själv reagera. Detta gör att cementbaserade material med flygaska härdar långsammare under de första dagarna. Emellertid visar denna studie att material med flygaska har en lägre reaktionsgrad och är mer porösa långt bortom de första dagarnas härdning. Det senare förklaras delvis av att flygaskareaktionen binder mindre vatten än cementreaktionen. Istället återanvänder flygaskan delar av de produkter cementet bildat för sin reaktion.

Även om volymen porer ökar med ökad inblandning av flygaska, visar denna studie att materialets förmåga at transportera vatten i ång- och vätskefas minskar. Den porösa strukturen i material med flygaskablandade cement tycks vara mer heterogen och mindre sammankopplad än i material med vanligt cement. Detta är av stor praktisk betydelse eftersom förmågan att transportera fukt styr uttorkningen av materialet; till exempel, den tid som krävs innan fuktkänsliga golvmaterial kan appliceras på en betongyta.

Vidare visar studiens mätningar att flygaska gör härdningen och materialegenskaperna mer temperaturkänsliga. Flygaskans reaktion fördröjs avsevärt vid låg temperatur. Effekterna liknar de som tidigare dokumenterats för vanligt cement under de första dagarna men skiljer sig åt över längre tid. För vanligt cement leder låg temperatur till bildandet av en mer homogen porös struktur som tillåter att reaktionerna förgår under en längre tid. Efter lång tid verkar material med vanligt cement härdat vid låg temperatur ha de mest välutvecklad egenskaperna. Dessa långtidseffekter av låg temperatur ses inte för material med flygaska. Resultaten belyser att det är särskilt viktigt att skydda konstruktioner med flygaskablandade cement mot låga temperaturer.

Slutligen, det laborativa arbetet i denna studie involverade viss metodutveckling. En ny mät- och utvärderingsrutin användes för att visa att värmeutveckling kan mätas från reaktionerna mellan cement (med och utan flygaska) och vatten i upp till ett år efter blandning. Tidigare studier har hävdat att detta inte är möjligt efter de första veckorna. Resultaten skapar nya möjligheter för forskare och industrin att studera långsiktiga reaktioner i cementbaserade material. Studien har också resulterat i en ny metod för att bestämma mängden bindemedel (till exempel, cement och flygaska) i små prover av cementbaserat material. Metoden gör det möjligt att jämföra mätresultat för små prover av murbruk eller betong erhållna från en större volym material (det vill säga, prov med okända sammansättningar).

Appended papers

This thesis is based on the following papers:

Paper I	Linderoth O, Johansson P, (2019), A method to determine binder content in small samples of cementitious material using hydrochloric acid and ICP-OES analysis. *Materials Today Communications, 20, 100538*
Paper II	Linderoth O, Johansson P, Wadsö L, (2020), Development of pore structure, moisture sorption and transport properties in fly ash blended cement-based materials. *Construction and Building Materials, 261, 120007*
Paper III	Linderoth O, Johansson P, Wadsö L, (2020) Effects of curing temperature on pore structure, moisture sorption, and transport in fly ash blended mortars (*Submitted)*
Paper IV	Linderoth O, Johansson P, (2020) Two methods to measure sorption isotherms for cement-based materials. *Accepted for the XXIV Nordic Concrete Research Symposium, Sandefjord, Norway 18-20th August 2021 (originally scheduled in August 2020)*
Paper V	Linderoth O, Wadsö L, Jansen D, (2020), Long-term cement hydration studies with isothermal calorimetry *(Manuscript)*
Paper VI	Geiker M, Danner T, Michel A, Bleda Revert A, Linderoth O, Hornbostel K, (2020), 25 years of field exposure of pre-cracked concrete beams; combined impact of spacers and cracks on reinforcement corrosion. *(Submitted)*

The authors contribution to the papers are as follows:

Paper I	OL planned and performed the experiments, analysed the data and wrote the manuscript. PJ contributed in planning the experiments and commented on the manuscript.
Paper II	OL planned and performed the experiments, analysed the data and wrote the manuscript. PJ and LW contributed in planning the experiments and commented on the manuscript.
Paper III	OL planned and performed the experiments, analysed the data and wrote the manuscript. PJ and LW contributed in planning the experiments and commented on the manuscript.
Paper IV	OL planned and performed the experiments, analysed the data and wrote the manuscript. PJ contributed in planning the experiments and commented on the manuscript.
Paper V	OL and LW prepared the specimens, planned and performed the isothermal calorimetry measurements, analysed the data, and wrote the manuscript. DJ performed the XRD-Rietveld and GEMS analyses, analysed that data and commented on the manuscript.
Paper VI	OL contributed in the sorption balance measurements, analysed that data, and commented on the manuscript.

Other publications

Publications related to the project but not appended to the thesis:

Linderoth O, Wadsö L (2016) Examining hydration kinetics obtained from different mixing procedures using isothermal calorimetry. *Proceedings of the International RILEM Conference Materials, Systems and Structures in Civil Engineering 2016 Segment on Fresh Concrete.* 22-24 August 2016, Technical University of Denmark, Lyngby, Denmark

Linderoth O, Johansson P (2017) Development of a laboratory method for assessing the cement content of an arbitrary samples of mortar or concrete. *Proceedings of the XXIII Nordic Concrete Research Symposium, Segment on Testing.* 21-23 August 2017, Aalborg, Denmark

Linderoth O (2018) Binding of moisture in fly ash blended Portland cement paste and mortar: Impact of replacement level and curing temperature. *Licentiate thesis*. 30 May 2018, Lund University, 64 p.

Linderoth O, Johansson P (2019) A comparative study of thermogravimetric analysis conducted on two different instruments. *Proceeding of the 15th International Congress on the Chemistry of Cement 2019.* 16-20 September 2019, Prague, Czech Republic

Wadsö L, Linderoth O, Kuratnyk T, Mayer A (2019) Studies of self-desiccation of hydrating binder systems by combined isothermal calorimetry and relative humidity measurements. *Proceeding of the 15th International Congress on the Chemistry of Cement 2019.* 16-20 September 2019, Prague, Czech Republic

Linderoth O, Johansson P (2019) Fuktegenskaper hos cementbundet material med flygaskainblandning. *Bygg och Teknik, 111, 7, p. 8-11*

Nomenclature

Symbols		
A	Surface area	m^2
B	Binder mass	kg
$Ca(OH)_2$	Calcium hydroxide	kg
d	Diameter	m
D_v	Moisture diffusion coefficient with vapour content as potential	$m^2 s^{-1}$
$\bar{D}_v$	Mean moisture diffusion coefficient with vapour content as potential	$m^2 s^{-1}$
k_p	Permeability coefficient	$kg\ m^{-1}$
m	Mass	kg
M_w	Molar volume of water	$m^3\ mol^{-1}$
P	Pore pressure	Pa
P_w	Pore water pressure	Pa
q_l	Liquid moisture flux	$kg\ m^{-2}\ s^{-1}$
q_m	Total moisture flux	$kg\ m^{-2}\ s^{-1}$
q_v	Vapour moisture flux	$kg\ m^{-2}\ s^{-1}$
R	Ideal gas constant	$J\ K^{-1}\ mol^{-1}$
t	Time	s
T	Temperature	K
v	Vapour content	$kg\ m^3$
W_e	Physically bound water	kg
W_n	Chemically bound water	kg
α	Degree of reaction/degree of hydration	-
γ_m	Surface tension of mercury	$J\ m^{-2}$
γ_w	Surface tension of water	$J\ m^{-2}$
θ	Contact angle between liquid and solid	-
μ	Dynamic viscosity	Pa s
φ	Relative humidity	-

Abbreviations

A	Al_2O_3
AFm ($C_4A\bar{S}H_{12}$)	Monosulfate
AFt ($C_4A\bar{S}_3H_{32}$)	Ettringite
C-S-H	Calcium silicate hydrate
C-A-S-H	Calcium aluminate silicate hydrate
C/S	Calcium to silicon ratio
C_2S	Dicalcium silicate (belite)
C_3S	Tricalcium silicate (alite)
C_3A	Tricalcium aluminate (aluminate)
C_4AF	Calcium ferro aluminate (ferrite)
C_4AH_{13}	Hydrogarnet
C	CaO
CH ($Ca(OH)_2$)	Calcium hydroxide
DVS	Dynamic vapour sorption
F	Fe_2O_3
FA	Fly ash
HD	High density
ICP-OES	Inductively coupled plasma optical emission spectroscopy
IGP	Inter-globule pore
IP	Inner product
ITZ	Interfacial transition zone
LD	Low density
LGP	Large gel pore
MIP	Mercury intrusion porosimetry
OP	Outer product
OPC	Ordinary Portland cement
RH	Relative humidity
S	SiO_2
SCM	Supplementary cementitious material
SEM	Scanning electron microscopy
SF	Silica fume
SGP	Small gel pores
Slag	Ground granulated blast furnace slag
TGA	Thermogravimetric analysis
wt%	Weight percent
w/c	Water-to-cement ratio
w/b	Water-to-binder ratio
XRD-Rietveld	X-ray diffraction with Rietveld analysis

1 Introduction

1.1 Background

Cement-based materials, mainly concrete, are the most commonly employed construction materials in the world [1, 2]. More than 1 m^3 of concrete per person is produced annually, resulting in billions of tonnes of material [3]. Concrete consists of a hydraulic binder, water, and aggregate. Because of its good strength, high durability, and easily available, low-cost, raw materials concrete has become a popular construction material.

Compared with many other construction materials, concrete has a low environmental impact; however, because it is produced in such large volumes, its contribution to the worldwide CO_2-emissions is significant [4]. Cement and concrete production are estimated to account for 5-8 % of the annual global man-made CO_2-emissions [3]. Approximately, 60% of these emissions are caused by calcination, the process in which limestone is heated to produce CaO, the main constituent in OPC. The other 40% originates from burning of fuels to heat the kiln [4].

The future demand for cement and concrete is expected to increase, not the least in newly industrialised countries such as China and India [1]. Along with the increasing awareness of climate change, this fact puts pressure on the cement industry to reduce their emissions and produce more sustainable materials. A similar pressure for change was observed in the 1970s following the energy crisis, which ultimately led to a significant reduction in the kiln-fuel consumption [5]. Today, most major cement producers have reduced their energy consumption by optimising the production process and increasing the use of non-fossil fuels, thereby making Portland cement production among the most efficient industrial thermal processes in the world [4]. According to Gartner [5], any further significant improvements in energy efficiency in the near future are unlikely.

Supplementary cementitious material (SCM), such as ground granulated blast furnace slag (slag) and fly ash (FA), are used to replace part of the ordinary Portland cement (OPC) to reduce the environmental impact of the binder. Both these SCMs are waste products from other industries, slag from steel production, and FA from the burning of coal in coal-fired power plants. Because they do not require calcination, the partial replacement of OPC by SCMs results in a significant reduction of CO_2-emissions. Although SCMs seem to be the most promising solution to further reduce emissions, they also change the chemistry of the binder, e.g., resulting in microstructural changes, which may alter important material properties. Despite the increasing interest recently, more research on cement-based materials with SCM-blended binders is still needed [6-8].

This thesis focusses on the hydration (the reactions between binder and water), pore structure, and related moisture properties of FA blended cement-based materials. The introduction of FA, with a different chemical and physical composition than the OPC [6, 7], changes the rate of hydration and properties of the hydration products. Thus, the development of the pore structure and related moisture properties changes. Knowledge regarding these properties is important to predict, e.g., the drying, shrinkage, and service life of cement-based materials. The aim of this work was to further the understanding of these properties by combining knowledge from previous studies with new knowledge from laboratory measurements.

1.2 Aim and research questions

The aim of this thesis is to further the knowledge of how partial FA replacement and curing temperature affects hydration, pore structure, and the related moisture properties of cement-based materials. To achieve this, the following research questions are formulated:

1. How does partial FA replacement affect hydration?
2. How does curing temperature affect the FA reaction?
3. How does FA replacement and curing temperature affect the pore structure?
4. How is moisture sorption and moisture transport in desorption affected by FA replacement and curing temperature?
5. What features of the pore structure govern its moisture transport ability?

1.3 Limitations

Some important limitations of this work are as follows:

- The project is experimental, and modelling or development of models is not included.
- There are many types of OPC and FA. Here, combinations of a finely ground OPC and a siliceous FA have been tested.
- Moisture sorption and moisture transport are studied in desorption; absorption and hysteresis is not investigated.
- Only moisture in the hygroscopic relative humidity range is considered.
- Samples are cured under sealed conditions at different temperatures, but mixing and measuring are conducted at 20°C.
- Only isothermal conditions are studied.

1.4 Materials

The laboratory measurements in this project were conducted on samples of cement paste and mortar with combinations of OPC (CEM I 52.5 R) and siliceous FA (class F, ASTM C618) as binder. The following combinations of OPC and FA were primarily tested: 100-0, 85-15, 65-35, and 30-70 wt% OPC to FA, which are referred to as OPC, 15FA, 35FA, and 70FA, respectively. Except for 70FA, which is rather extreme, these binders can be used in most building construction applications with a cement-based material. Other combinations occur exceptionally, for example, in *Paper II*, where cement pastes with 0-70 wt% FA replacement (in steps of 10 wt%) were applied to sequentially measure the early heat of hydration. For mortars, a siliceous sand (EN 196-1) with particle sizes of 0-2 mm was used as aggregate. Further details on the materials, mix compositions, and preparation procedures are given in the appended *Papers I-V*.

Paper VI is the only exception were the abovementioned materials are not used. In *Paper VI*, the author's contribution was limited to the sorption balance measurements on concretes with partial FA (20 wt%) and silica fume (SF; 4 wt%) or only SF (4, 12 wt%) replacement, as part of a larger study. Further details on these materials are provided in the paper.

1.5 Methods

The experimental methods used in the project are listed in Table 1. The table also shows properties studied by each method, in which of the appended papers the methods are used, and where in the thesis further details are given.

Table 1
Methods used in the project, the properties studied by each method, the papers in which each method is used, and where in the thesis further information is found.

Method	Properties studied	Paper	Thesis
Isothermal calorimetry	Heat of hydration, degree of hydration	II, V	2.3.1
Mercury intrusion porosimetry (MIP)	Pore structure	III	2.5.1
Thermogravimetric analysis (TGA)	Chemically bound water	III	3.1.1
Sorption balance	Physically bound water, pore structure	II, III, IV, VI	3.2.2
Desiccator method	Physically bound water, pore structure	IV	3.2.2
Cup test	Moisture transport	II, III	3.3.1
Inductively coupled plasma optical emission spectroscopy (ICP-OES)	Binder content	I	-
X-ray diffraction with Rietveld analysis (XRD-Rietveld)	Phase composition, degree of hydration	V	-

2 Hydration of cement-based materials

This chapter provides an overview of the underlying chemical reactions and mechanisms that give rise to hardened cement paste and its associated properties. The first section presents the chemical reactions that occur as Portland cement is mixed with water. In the second section, the most commonly used SCMs are presented, especially FA, because it is used in this work. The third section describes the hydration process. The fourth section details the hydration products, especially the main hydrate phase, calcium silicate hydrate (C-S-H). The fifth and final section describes the porous structure caused by hydration and the growth of the cement paste.

2.1 Ordinary Portland cement

When anhydrous OPC comes in contact with water, its particles immediately start to dissolve, marking the start of a series of reactions referred to as hydration. Hydration is a complex process because OPC consists of several clinker minerals that react at different rates, forming different hydrates. The four main clinker minerals are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and calcium aluminoferrite (C_4AF). Comprehensive reviews on the chemistry of cement and cement hydration have been given in previous studies (e.g., [9, 10]). Additionally, several review articles on the mechanisms of cement hydration have been published recently, not only for OPC but also for blended cements [6, 11-14].

Typical OPC contains more than 50% of C_3S and lower amounts of C_2S, C_3A, and C_4AF. Calcium silicates (C_3S and C_2S) are responsible for the formation of C-S-H and calcium hydroxide (CH), the two major hydrates of OPC. These hydrates make up the majority of a porous cement paste that binds the aggregates together, giving the material its strength. C_3S is the most important for the first month's strength development, whereas C_2S contributes to the strength at a later age. The stoichiometric reactions of C_SS and C_2S are given in Eqs. 1-2. As C-S-H does not have a univocal chemical composition, Eqs. 1-2 have intentionally been written with x and y rather than numerical coefficients.

$$\mathrm{C_3S + (3 - x + y)H \rightarrow C_xSH_y + (3 - x)CH} \qquad (1)$$

$$\mathrm{C_2S + (2 - x + y)H \rightarrow C_xSH_y + (2 - x)CH} \qquad (2)$$

C_3A may react in different ways based on the surrounding circumstances. When it is in contact with only water, the reaction is very rapid and may cause premature setting of the material. Premature setting limits the workability and deteriorates important material properties such as the compressive strength. Therefore, sulphate in the form of gypsum is added to cement. Gypsum decelerates the C_3A reaction, giving it a rate pattern similar to that of C_3S [15], and forming ettringite in the process (Eq. 3). When the system runs out of gypsum, the remaining C_3A reacts with ettringite to from monosulfate (Eq. 4). If all the ettringite is consumed and C_3A is still left, it may react with CH from the silicate reactions to form a hydrogarnet phase (e.g., through Eq. 5). Hydrogarnets have a range of compositions, of which C_4AH_{13} is the most common.

$$\mathrm{C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}_3H_{32}} \qquad (3)$$

$$\mathrm{2C_3A + C_6A\bar{S}_3H_{32} + 4H \rightarrow 3C_4A\bar{S}H_{12}} \qquad (4)$$

$$\mathrm{C_3A + CH + 12H \rightarrow C_4AH_{13}} \qquad (5)$$

The second aluminate phase, C_4AF, reacts similarly to C_3A, but at a slower rate, thereby forming ettringite, monosulfate, and hydrogarnet, where some of the A is substituted by F. However, when it contains F, the reaction products are no longer pure ettringite and monosulfate, despite the structural similarities. A strict cement chemist would thus call them AFt and AFm instead, where the t and m represent the number of sulphate ions: three and one, respectively. In OPC, C_3A and C_4AF are mixed such that no F-free products exist. For stringency, the terms AFt and AFm are therefore used for all products throughout this thesis.

2.2 Supplementary cementitious materials

SCMs are mainly used to replace a part of the OPC for environmental reasons. Therefore, the SCMs need to possess some hydraulic properties. Taylor [9] stated that the ability of a substance to act as a hydraulic binder mainly depends on two factors:

- It should react with water to a sufficient extent.
- When reacting with water, it must yield solid products of very low solubility and with a microstructure that gives rise to the requisite mechanical strength, volume stability, and other necessary properties.

Two materials that fulfil Taylor's criteria are slag and FA, which are also the most commonly used SCMs in modern cements. Both slag and FA are by-products from other industries that would otherwise end up on landfill: slag from steel works and FA from coal-fired electric power plants. These SCMs are environmentally favourable because they require no additional clinkering processes, but both originate from CO_2-heavy industries. However, at present, none of these emissions are assigned to the cement manufacturers.

According to the European cement association [16], the average clinker content of European cements was 73.7% in 2018; this number is expected to decrease in the coming years. The increasing use of SCMs makes it more important to understand their effect on the hydration and properties of cement-based materials. Numerous studies have focussed on blended cements and cement-based materials in the last decades (two recent and comprehensive examples are [6, 7]). Despite this, the understanding of SCMs in cement and cement-based materials is still incomplete.

Like OPC, slag and FA consist to a large proportion of calcium, silicon, and aluminium oxides. The calcium content is especially important because it governs the ability of the material to react spontaneously with water, i.e., its hydraulic potential. Figure 1 shows two ternary diagrams of CaO-SiO_2-Al_2O_3: a) compositions of OPC, slag, and FA and b) composition of the most common hydration products.

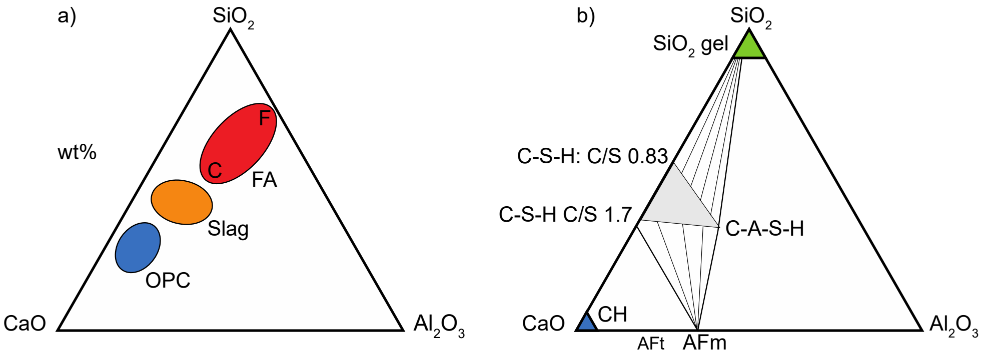

Figure 1
Two CaO-Al$_2$O$_3$-SiO$_2$ ternary diagrams: a) OPC, slag and FA (class C and F, ASTM 618-15), and b) the most common hydration products. Adapted from [6].

As seen in Fig. 1a, slag and FA contain less calcium than OPC but more aluminium and silicon. Slag is a latent-hydraulic material, which means it can react directly with water under certain conditions. FA is considered a pozzolanic material and has little ability to react directly with water; instead, it reacts with CH formed by the OPC to produce C-S-H through Eq. 6. This reaction is known as the pozzolanic reaction, and includes, apart from CH, amorphous silicon from the FA.

$$3\mathrm{CH} + 2\mathrm{S} \rightarrow 3\mathrm{C} - 2\mathrm{S} - 3\mathrm{H} \qquad (6)$$

Apart from the CH content, the onset of the pozzolanic reaction highly depends on the alkalinity of the pore solution. The alkalinity builds up over the first days of reaction and then triggers the dissolution of amorphous silicon [6]. This means that little SCM reactions are likely to occur in the first days. The onset of reaction also depends on the type of SCM and then mainly on its hydraulic potential. As seen in Fig. 1b, the hydrate composition changes with the chemical composition of the binder. C-S-H is the main hydrate phase of both the OPC and the pozzolanic reaction; however, C-S-H formed by OPC and SCMs may have different properties. This is further discussed in Section 2.4.1 on C-S-H.

2.2.1 Fly ash

The first study on the use of FA in cement is possibly that of Davis et al. [17], published in 1937. The burning of coal for power generation began in the 1920s. However, before society became aware of the consequences of air pollution, the residual particles were released into the atmosphere. This soon changed, and plants were fitted with equipment that prevented particle pollution, resulting in large amounts of FA residue [18]. FA consists of spherical particles of different sizes, as shown in Fig. 2.

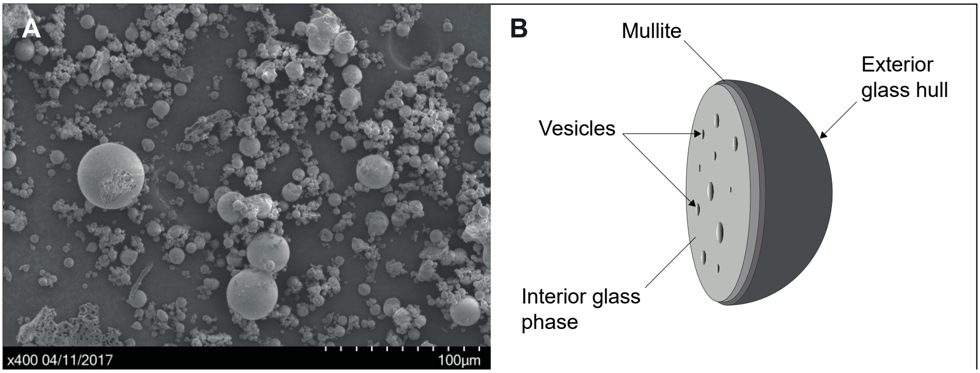

Figure 2
A) Clusters of FA particles captured with scanning electron microscopy (SEM), and B) illustration of a single fly ash particle in cross-section

The particles are formed while the FA is suspended in exhaust gases that are rapidly cooled. The rapid cooling means few minerals have the time to crystallise. Instead, FA particles consist mostly of amorphous glassy phases. One exception is mullite, a crystalline phase which consists of aluminium-silicon. The crystalline phases are typically inert, and thus, they lower the ultimate degree of FA reaction. According to Neville [19], the glassy phases in FA are only dissolved once the pH exceeds 13.2. This partially explains why FA depends on the OPC reaction to react itself.

2.3 The hydration process

2.3.1 Isothermal calorimetry

Isothermal calorimetry is a common method to study cement hydration. It measures heat production and can be used to quantify both the very early reactions (first hour or hours) [20], the onset of the main reactions [21], and the main hydration peak [22]. It is also useful because most properties of cement-based materials are related to the heat production. For example, mortar strength development is approximately linearly related to the produced heat [23]. Calorimetry data are also used as input for models of hydration kinetics because the measured thermal power is a continuous result that has a strong connection to the hydration reactions [24, 25]. The degree of hydration can be defined as the ratio of produced heat to the heat produced at full hydration [25]. Isothermal calorimetry was used in *Paper II* to study the effects of FA replacement on the first week of reaction. It was also used in *Paper V* to study the long-term cement hydration up to one year after mixing.

The following sections present example results with isothermal calorimetry from appended *Papers II* and *V*, but there are also results that are only shown here in the main part of the thesis (Figures 4 and 5). For these measurements, 3-g samples of cement paste (w/b 0.45) were cast in 20 mL plastic vials. Solids were added to the vials standing on an analytical balance with a 0.01-g resolution; water was then added using a pipette. The vials were sealed with plastic screw caps and placed in a holder on a vortex mixer (Stuart SA8, Bibby Scientific, UK) set to 1600 rpm for 60 s. After mixing, the vials were placed in an isothermal calorimeter (TAM Air, Thermometric; now TA instruments, USA), set to 20 °C (see also *Paper II*, where the same procedure was used).

2.3.2 Early age

Hydration is a dissolution-precipitation process; the clinker minerals are transformed into solid hydrates through the passage of ions in solution. The reactions of OPC and SCMs were previously described in Sections 2.1 and 2.2. As soon as OPC grains come into contact with water, they begin to dissolve, releasing heat and ions as chemical bonds in the clinker phases are broken. The mixing water then becomes a pore solution, containing various ions. The composition of the pore solution depends on the solubility of the OPC clinker minerals. C3A and gypsum are both very soluble and thus dissolve the fastest. The main clinker mineral, C3S, is also soluble and contributes significantly to early dissolution [26, 27]. The rapid early dissolution continues until the pore solution becomes saturated or even supersaturated with ions, at which point, hydrates begin to precipitate close to the dissolving grain surfaces [28].

Figure 3 shows the heat production rate (or thermal power) of a typical OPC paste during the first 48 h. The curve provides an overview of the early hydration process divided into five stages. The dissolution process described thus far occurs within the first hour, marked as (1) in Fig. 3.

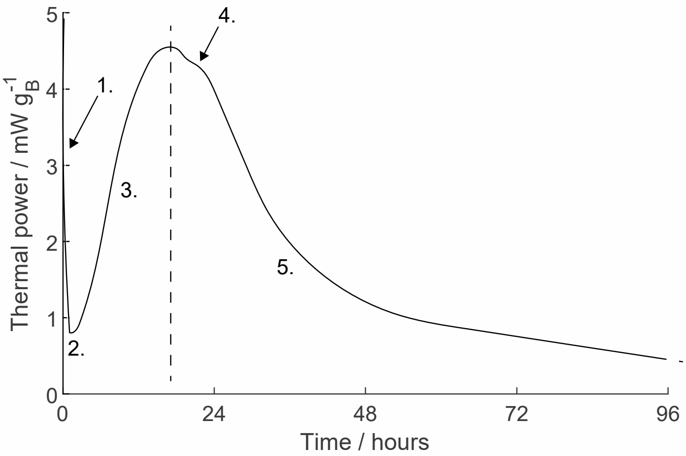

Figure 3
Schematic heat evolution curve of an OPC in the first 48 h at 20 °C. Numbers 1-5 denotes different stages of hydration, as explained in the text.

Saturation of the pore solution causes a slowdown of dissolution and thus lower thermal power, which is known as the induction period (2). The induction period is a period of low reaction, during which only minor amounts of AFt and C-S-H, for example, are precipitated [29]. Thomas et al. [30] showed that this period is not a true induction period but that it occurs because the size and number of regions in which hydrates grow are still small. Taking place before the material has set, the induction period is of major importance in civil engineering because it allows the concrete to be transported without loss of workability.

What influences the induction period is not entirely clear; and the same can be said regarding the onset of the acceleration period (3). According to Kumar et al. [26], the acceleration could be triggered by a sudden precipitation of CH. The following rapid reaction is generally attributed to the nucleation and growth of C-S-H [11, 12, 31] or more specifically C-S-H needles [32]. The C-S-H precipitation begins at the cement and aggregate surfaces and grows into the spaces between to form a cement paste along with the other hydrates. The precipitation of hydrates results in the consumption of ions that allows the continued dissolution of clinker minerals and thus further occurrence of the reaction. Soon after the onset of acceleration, the rapid formation of hydrates causes the material to set, drastically lowering the workability.

Simultaneous with the acceleration period, ions from C_3A and gypsum precipitate to form AFt phases. When all gypsum is depleted, the remaining C_3A dissolves rapidly, causing a second peak of heat release (4) [11]. If the cement is properly balanced with respect to sulphate, the sulphate depletion peak occurs after the main peak. A second and third peak related to C_3A and gypsum have been reported [33], where the second peak was attributed to the transformation of AFt to more stable AFm phases.

Period (5) in Fig. 3 is known as the deceleration period. The mechanisms that cause the main hydration peak and thus the reaction to enter the deceleration period are not entirely clear. Previously, this was attributed to the onset of a diffusion-controlled process; because the layer of hydrates thickens, it becomes harder for water to pass through, thus hindering further reaction. However, this theory has been questioned in recent reviews [11-13] because the measured results do not agree with the expectations of a diffusion-controlled reaction. For example, Berodier [34] found that C-S-H was homogenously distributed on all particle surfaces. Had diffusion been the rate-limiting step, aggregate surfaces close to cement grains would have had more hydration products, but this was not observed.

There does not seem to be a consensus regarding the mechanisms that cause the reaction to transition from acceleration (3) to deceleration (5); however, recent studies agree that it is related to a decrease in the growth rate of C-S-H. Bazzoni et al. [32] stated that changes in the growth mechanism of C-S-H could cause the deceleration; Dittrich et al. [29] showed that the peak of the main reaction coincides with the slowdown in C-S-H formation; and the recent needle model presented by Ouzia and Scrivener [35] showed that the main peak of reaction coincides with the time at which most of the grain surfaces are covered with C-S-H needles, and the needles grow the fastest. In a subsequent review, Scrivener et al. [13] concluded that the acceleration and decelerations periods should be considered a single episode as there is no sudden change of mechanism.

The early hydration process largely depends on the binder’s chemical composition and physical properties. The latter includes, e.g., the particle size distribution; finely ground binders react faster than binders consisting of coarse particles. Figure 4 shows the thermal power of cement pastes (w/b 0.45) with two differently ground OPCs, which have similar chemical compositions.

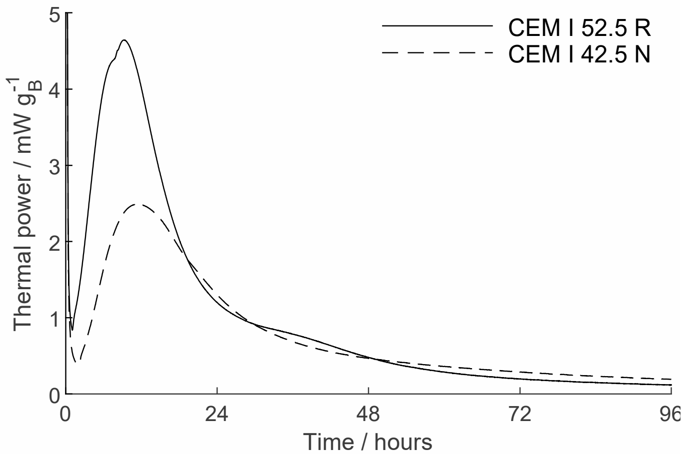

Figure 4
Thermal power of cement pastes (w/b 0.45) made with two differently ground OPCs during the first four days, measured by isothermal calorimetry at 20 °C: a finely ground CEM I 52.5 R (520 m^3 kg^{-1}) and a coarser CEM I 42.5 N (330 m^3 kg^{-1}) which have a similar chemical composition.

Other factors that affect the rate of hydration include the mixing method and ambient temperature conditions. The effects of mixing intensity — i.e., mixing speed, duration, and presence of aggregates — on hydration were studied by Han and Ferron [36] and Juilland et al. [27]. They reported that by increasing the mixing intensity, the initial dissolution is enhanced, which shortens the induction period and increases the slope and peak of the acceleration period. Juilland et al. [27] attributed the enhanced dissolution to a more efficient transport of ions away from the dissolving grain surfaces. Consequently, this leads to an increased formation of C-S-H nuclei, which has an accelerating effect on the rate of precipitation during the acceleration period. It is clear that the effect of the mixing method should not be overlooked, because it may affect both the short and long term hydration.

The temperature conditions during mixing and curing affect the rate of hydration and thereby the development of most material properties. Like increased mixing intensity, elevated temperature accelerates the dissolution, which shortens the induction period [37]. On the contrary, low temperature means that the early reactions become severely retarded. Figure 5 shows the thermal power of OPC pastes measured at 5 or 20 °C.

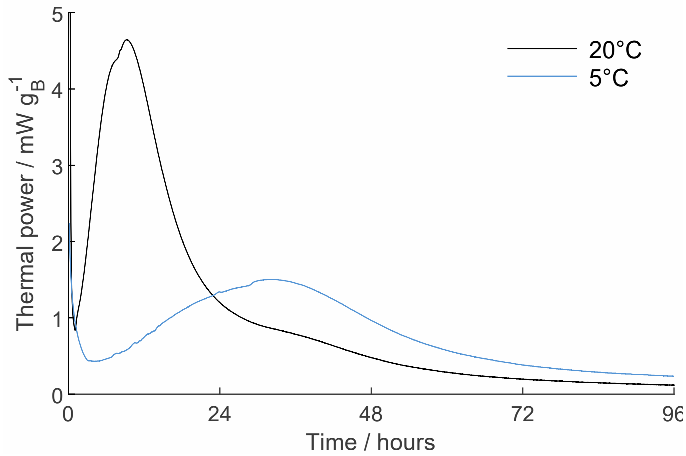

Figure 5
Heat production rate of cement pastes (w/b 0.45) with OPC during the first four days, measured with isothermal calorimetry at 5 or 20 °C

SCMs (to a varying degree) depend on the OPC reaction to react themselves (cf. section 2.2). Because they require an alkaline environment to dissolve and CH to react with, little SCM reactions are likely to take place in the first days. Partial replacement of the OPC with SCMs therefore results in a prolonged induction period and a lower heat production rate in the first days as the OPC reaction is diluted [38, 39]. These effects are seen in Figures 6a-d (from *Paper II*) where the thermal power and cumulative heat generated by cement pastes with OPC and varying FA replacement for the first four or seven days are presented.

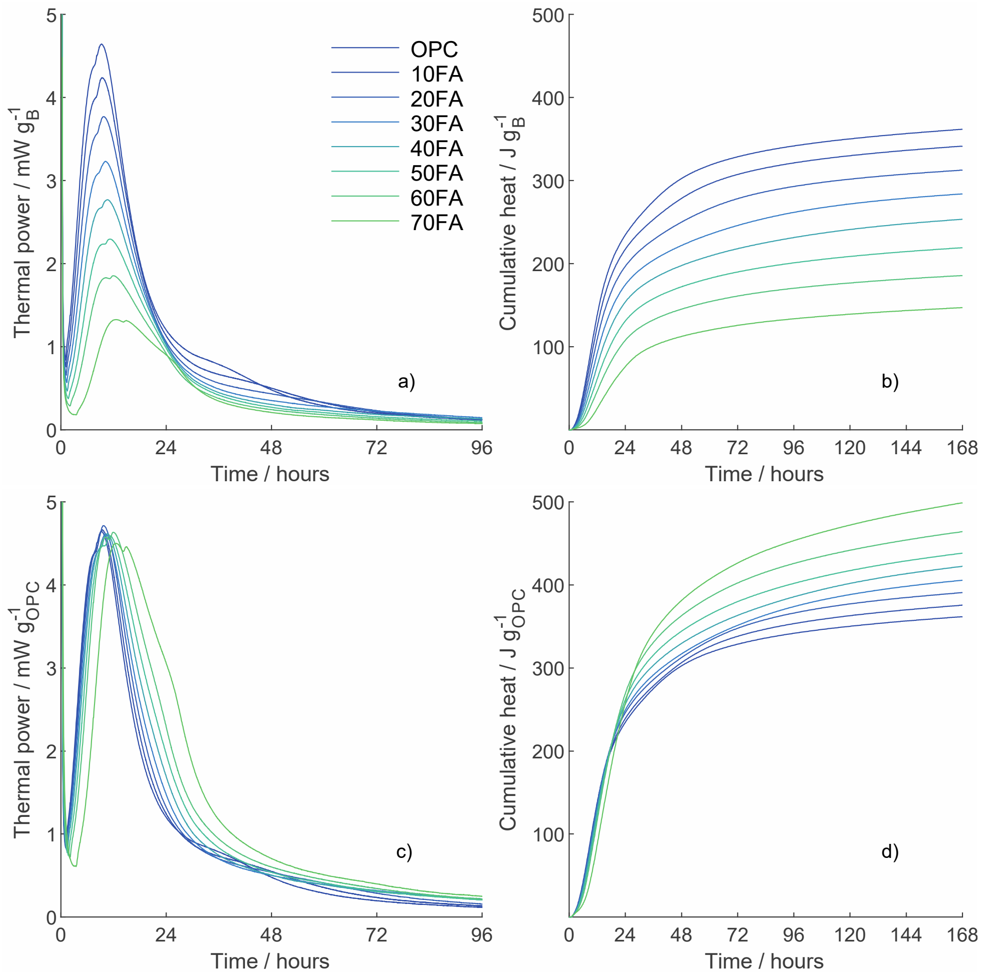

Figure 6
From Paper II: a) heat production rate (thermal power) and b) cumulative heat release per gram of B; in c) thermal power and d) cumulative heat per gram of OPC. Results for cement pastes (w/b 0.45) with increasing FA replacement, measured at 20 °C by isothermal calorimetry.

Figures 6a-d show that increasing FA replacement dilutes the binder reaction in the first days, as manifested by a delayed onset of acceleration, a lower peak of main reaction, and less cumulative heat. However, by presenting the results per gram of OPC, as shown in Figures 6c-d, it is seen that the presence of FA accelerates the OPC reaction. This is known as the filler effect [40, 41]; the additional surfaces provided by the FA particles serve as nucleation sites for the OPC hydrates. Furthermore, the effective w/c ratio is increased because there is more space and water available for the OPC reaction. Berodier and Scrivener [41] showed that this effect not only promotes the early OPC reaction but also leads to a more homogenous distribution of hydrates that could favour the reactions at a later age.

The mechanisms behind the early cement hydration are a complex combination of multiple factors. More detailed descriptions and discussions of these mechanisms are beyond the scope of this thesis. Instead, the reader is referred to any of the extensive reviews written on this topic in recent years, for example, references [11, 13, 15].

2.3.3 Later age

For most cementitious binders, the rate of reaction decreases dramatically after the first day (cf. Figures 3-6) [42, 43]. However, provided there is water, anhydrous material and space for hydrates to precipitate, the reactions may proceed for weeks, months or even years at a lower rate. Lack of space is considered the main reason why hydration eventually ceases [12, 13, 44, 45]. It arises either as the remaining spaces for hydrates to precipitate in are depleted on water (e.g., at low w/b) or as they are refined below a critical size required for precipitation (e.g., at high w/b). Although the hydration after the first weeks is responsible for a considerable part of the development of material properties, comparatively little is known about the reaction kinetics and mechanisms at this time.

In OPC, C_3S and C_3A dissolve the fastest and their reactions are nearly completed after the first days or week. Hydration thereafter will be mainly of C_2S and C_4AF [42, 46]. Most SCM reactions also take place at this time; as described in Section 2.2 (cf. Eq. 6), the most common SCMs react with CH (formed by the OPC) and some water to produce C-S-H. Therefore, their reactions can only start once a part of the OPC has reacted. In cement pastes with partial slag or FA replacement, Berodier and Scrivener [47] showed that slag exhibited a significant reaction after a few days and affected material properties within the first week, whereas FA reacted slower and had little impact in the first weeks. Similar observations for FA were reported by De Weerdt et al. [48]. From their results it is also evident that the FA reaction is very temperature sensitive; after six months of curing at 5 °C, only approximately 10-15% of the FA had reacted, compared to approximately 30-35% at 20 and 40 °C.

Few studies have investigated the kinetics and mechanisms of long-term hydration. According to Scrivener et al. [12], this is mainly due to a lack of experimental methods that can provide good precision data at that time. One exception is XRD-Rietveld; however, it is a time consuming and rather operator dependent method [49]. Another potential method is isothermal calorimetry. In most studies, the use of calorimetry is limited to the first weeks or the first month. Scrivener et al. [12] stated that (referring to the study of Berodier [34] who measured for 28 days), "beyond this point, the rate of heat evolution is so low that significant errors can arise in the cumulative heat evolution data due to small fluctuation in the base line, etc.".

The aim of *Paper V* was to investigate the time for which thermal power of hydration can be assessed with isothermal calorimetry. Measurements were conducted for one year, using a new measurement and evaluation routine, which is described in the paper. The sample were cement pastes with OPC or OPC with partial FA replacement as binder. After one year, XRD-Rietveld analyses were conducted on the samples with OPC. These and the calorimetric results were used to determine the degree of hydration by different methods; and the results showed good agreement. Figures 7a-d show the heat of hydration as a function of time for cement pastes (w/b 0.45) with increasing FA replacement measured with isothermal calorimetry.

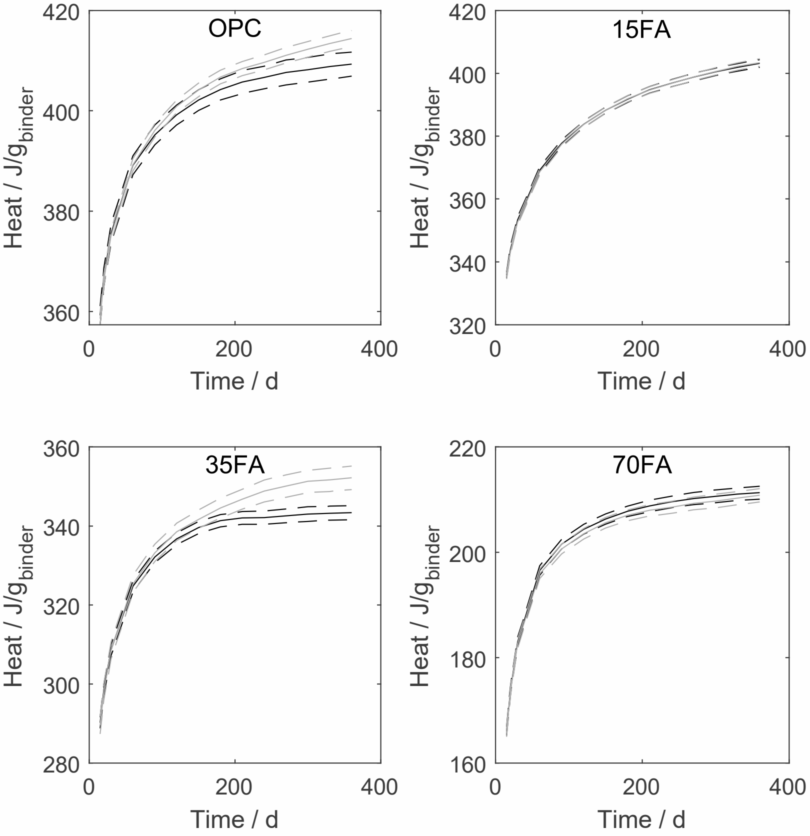

Figure 7
From Paper V: Calculated mean heats (solid lines) with one standard deviation (dashed lines) for duplicate measurements on cement pastes (w/b 0.45) with a) OPC, b) 15FA, c) 35FA, and d) 70FA as binder

These results show that the heat produced at one year decreases with increasing FA replacement, but that measurable reactions still continue in all systems. Duplicate results generally follow each other well, except for OPC and 35FA, for which the differences are probably because the baselines for the lowest results are wrong. The FA blended pastes were not compared with XRD-Rietveld because the essentially amorphous FA cannot be quantified by this method.

2.4 Hydration products

Hydrates form as ions from the dissolving OPC and SCM particles precipitate. Together the hydrates constitute a hardened cement paste. The cement paste is the adhesive that binds the aggregates in concrete together, and therefore, it is responsible for most engineering properties of cement-based materials. Because of the extensive studies by Powers et al. during the 1930-60s — especially their seminal publication in 1948 [50] — the properties of hardened Portland cement paste are well documented. Their work was recently revisited in two publications by Brouwers [51, 52]. However, the understanding of the individual hydrate phases, their growth mechanisms, and microstructural properties is still incomplete (and topics of discussion [11-13, 15]). The picture is further complicated by the increasing use of SCMs.

The first subsection below focusses on C-S-H because it is the main hydrate phase of both the OPC and the pozzolanic reaction, and therefore, occupies a majority of the paste volume. Consequently, C-S-H is the most important phase for the microstructural development and thus for the binding and transport of moisture, all of which are properties in focus of this thesis. The second subsection gives a brief presentation regarding the other major hydrate phases.

2.4.1 C-S-H

C-S-H is not only the most abundant hydration product but it is also responsible for many important properties of the cement paste, and thus for the material as a whole. It is not a very strong, or stable phase; however, C-S-H forms a continuous gel that binds the cement and aggregate grains together, giving the material its strength. Other hydration products, for example, CH form strong individual solid crystals, but do not contribute much to the materials strength.

As the main hydrate, C-S-H is the phase in which a large part of the mixing water is chemically bound. Additionally, the C-S-H gel has a large intrinsic porosity consisting of fine gel pores that contribute significantly to the physical binding of moisture. The importance of C-S-H for the pore structure and the related moisture sorption and transport properties are further discussed in Chapter 3. This section focusses mainly on the formation and growth of C-S-H. Figure 8 illustrates the nanostructure of a single C-S-H layer (or sheet), in which water is chemically bound.

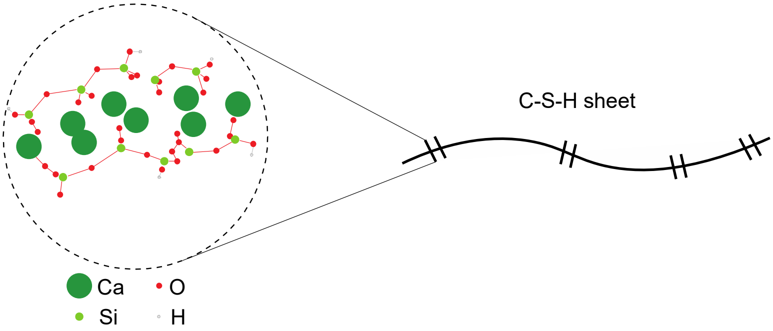

Figure 8
Schematic illustration showing the nanostructure of a single C-S-H sheet. Adapted from [53]

C-S-H is a complex phase that, despite thorough investigations (see, e.g., [54-57]), is still not completely understood. Mainly because of its varying stoichiometry and morphological structure. Taylor [9] described the formation of two different types of C-S-H: outer (OP) and inner product (IP). In recent reviews on cement hydration, Scrivener el al. [12, 13] used the same nomenclature. Tennis and Jennings [58] also identified two types of types of C-S-H — low (LD) and high density (HD). Their definitions are similar to those of OP and IP. In this thesis, the former nomenclature (OP and IP) is used. The two types are morphologically different, which means that their shapes and microscopic structures are not the same, whereas their chemical compositions are similar. Figure 9 shows schematic illustrations of OP and IP C-S-H growth on a dissolving OPC grain surface.

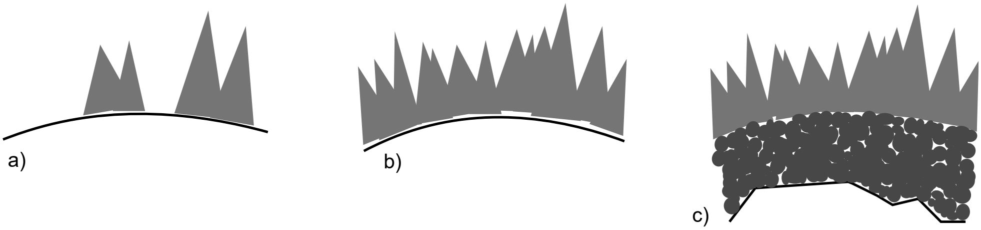

Figure 9
Growth of C-S-H: a) OP C-S-H precipitation on grain surfaces during the first hours, b) OP C-S-H needles cover the whole grain surface, coinciding roughly with the main peak of hydration, and c) growth of IP C-S-H in the space between the dissolving grain and the OP C-S-H. Adapted from [59].

Bazzoni [32, 59] proposed a C-S-H growth mechanisms according to which OP C-S-H is formed as needles shooting from the grain surfaces in the first hours (Fig. 9a). Rapid formation of OP C-S-H during the acceleration period causes setting of the material and the formation of a pore structure because the initially continuous water phase between the solids is divided into pores by the growing cement paste (Fig. 10)

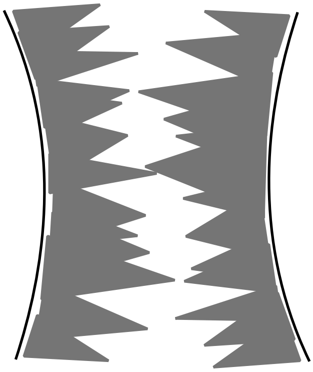

Figure 10
Schematic illustration showing the early formation of pores as C-S-H needles from two adjacent grains meet.

The rapid growth of OP C-S-H continues until the grain surfaces are completely covered with hydrates (Fig. 9b), which seems to coincide with the main peak of the hydration [35]. Beyond this time, a denser IP is formed in the spaces between the dissolving cement grains and the rim of OP (Fig. 9c). OP C-S-H continues to form in the remaining outer spaces, however, at a lower rate. Although initially different, recent studies showed that the C-S-H gel becomes increasingly homogenous as hydration proceeds. Gallucci et al. [60] observed that in one-year old cement pastes, there were hardly any differences between the OP and IP C-S-H. Muller et al. [61] presented evidence that the C-S-H densifies with time because the number of gel pores intrinsic to the C-S-H no longer increases at later age. Several models have been suggested to describe the microstructural build-up of C-S-H, [50, 55, 56, 62, 63]; three recognised models are presented in Section 2.5.

Similar to the rate of reaction, the growth and microstructure of C-S-H have proven to be sensitive to, e.g., temperature, relative humidity (RH), and the chemical composition of the binder [6, 64-66]. In the 1940s, Powers and Brownyard [50] reported that gels prepared at low temperature were structurally different from those prepared at high temperature. More recently, Gallucci et al. [60] reported that the apparent density of C-S-H increased by up to 25% as the temperature was raised from 5 to 60 °C. However, their results were questioned by Gajewicz-Jaromin et al. [67] who found that the increase was considerably smaller. Regardless, it appears that an increase in the C-S-H density with temperature means that less water is chemically bound (per hydrate) and that the fraction of coarse pores increases as the cement paste occupies less space. Similar effects of temperature were also reported previously [68, 69]. According to Thomas and Jennings [70], C-S-H densifies not only with further hydration and elevated temperature but also through chemical ageing. This process is slow under normal conditions but is significantly accelerated by elevated temperatures and drying. Microstructural alterations of the C-S-H could explain the detrimental effects of, e.g., elevated temperature on the long-term compressive strength of concrete with OPC (see, e.g. reference [71]). Interestingly, the effect is not as pronounced for materials with blended cements, as reported by De Weerdt et al. [48]. Similar observations were made in *Paper III,* in which the effects of curing temperature on pore structure and related moisture properties were investigated on mortars with OPC and varying fly ash replacement.

Alterations of the C-S-H (and thus of the pore structure) by drying are problematic because many microstructural measurements require hydration to be stopped or the physically bound water to be removed from the pore structure. The extent of these microstructural alterations has been discussed in detail, e.g., in terms of whether they are reversible, and below which RH they occur [65, 72-76]. What is clear is that the choice of drying technique should be carefully considered depending on the material property that needs to be studied. This is especially important if the delicate C-S-H microstructure is to be preserved. The impact of some established drying techniques for the results of microstructural measurements have been compared in, e.g., [77, 78].

C-S-H is the main hydrate phase also of most SCM reactions. However, C-S-H formed by OPC and SCMs has different properties. Most notably, the calcium to silica ratio (C/S) of C-S-H formed by SCMs is lower than that of C-S-H formed by OPC. This is because most SCMs contain less calcium than OPC. Many SCMs also have a higher alumina content than OPC which leads to an increased incorporation of aluminium in the C-S-H (and the formation of the so-called C-A-S-H gel, cf. Fig. 1b) [79]. According to Richardson [80], these changes of the C-S-H affect its morphology. He states that OPC forms C-S-H with a fibrillar structure, which becomes more foil-like with increasing SCM replacement. Furthermore, the foil-like C-S-H more efficiently fills space, which could explain the improved durability of materials with blended cements compared to OPC. Lothenbach et al. [6] report that the differences between OPC and SCM C-S-H are hardly distinguishable, and that they should even out with time.

2.4.2 Other hydrates

CH is the second product that is formed from the calcium silicate reactions (Eqs. 1-2). It is a crystalline phase of plate-like crystals with a wide range of sizes, mainly determined by the available space. Most CH is formed as small crystals intimately mixed with the C-S-H. CH has negligible impact on the mechanical properties but is important for material durability because it is a major source of alkalinity. Furthermore, it is vital for the pozzolanic reaction (Eq. 6), in which it is consumed to form C-S-H. CH is a very soluble phase and may therefore be lost through leaching. High SCM replacements and leaching that lower the CH content could increase the risk of durability issues, such as reinforcement corrosion.

Other phases worth mentioning are AFm and AFt which are formed by the alumina and ferrite reactions (cf. Eqs. 3-4). Similar to CH, they normally do not affect the mechanical properties. The two groups however have very different morphologies: AFm forms as plate-like crystals similar to CH, whereas AFt is formed as distinct rods.

2.5 Pore structure

The porous structure of cement-based materials is very complex, but of vital importance for their durability because it governs the sorption and transport of moisture [81, 82]. Pores start to form shortly after the mixing of binder and water as hydrates precipitate in the space between the solids. The largest pores are air voids and compaction pores formed by entrapment of air during mixing. These pores are in the size ranges of millimetres or even centimetres and thus are visible to the naked eye. Because of their sizes, these pores generally remain air-filled throughout the hydration process and therefore are not refined.

As hydrates precipitate, shrinkage occurs as the hydrate volume becomes smaller than the combined volume of mixing water and binder. This is known as chemical shrinkage and may cause micro-cracks in the cement paste. Because of hydration and chemical shrinkage, a part of the porosity may also be depleted on water, thereby lowering the RH. This drying (without evaporation to the ambient) is called self-desiccation. Figure 11 illustrates concrete in cross-section.

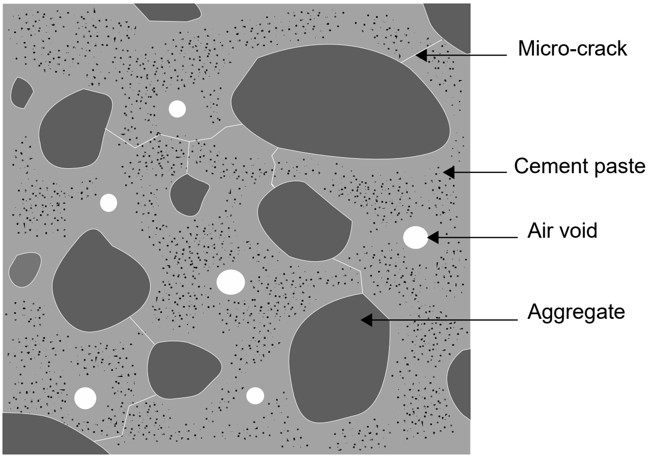

Figure 11
Illustration of concrete in cross-section

The pore structure that is most relevant for the mechanical properties, moisture properties, and durability of the material is not observed in Fig. 11. These pores and spaces are in the size range of micrometres to nanometres and therefore are not visible except for when observed through a microscope. Several models have been suggested to describe this pore structure; three of the most recognised models are those of Powers and Brownyard [50], Feldman and Sereda [62, 63], and Jennings [55, 56]. The former two models are illustrated in Fig. 12.

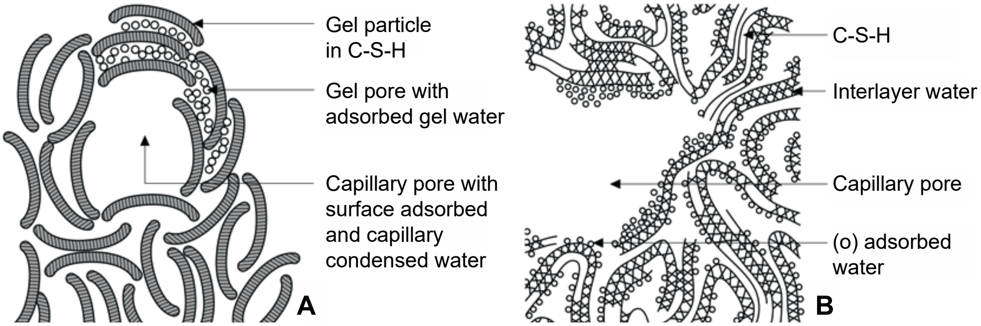

Figure 12
A) Powers and Brownyards model of the microstructure, and B) the model by Feldman and Sereda. Adapted from [83]

The main difference between these models is the description of the fine cement paste structure. Powers and Brownyard [50] describe this as consisting of small gel pores, without distinguishing between C-S-H, CH, or other hydrate phases. Between the gel particles are fine gel pores with adsorbed water (or gel water). Capillary pores form as spaces between the cement grains are encapsulated by the growing cement gel and contain capillary condensed water. As the capillary condensed water only exist in pores above around 45% RH (according to the Kelvin equation [84]), this RH marks the transition (in desorption) from capillary to gel pores. This RH corresponds to pores of approximately 2.7 nm in diameter (assuming cylindrical pores and normal room temperature).

Feldman and Sereda [62, 63] described C-S-H as consisting of irregular arrays of single layers that come together randomly to form interlayer spaces. The interlayer water is only lost upon strong drying, starting at approximately 30% RH, but is the most pronounced below about 11% RH (at normal room temperature). They describe this drying as reversible because water may re-enter the interlayers upon re-saturation. The absorbed water is found on the C-S-H surfaces, but in contrast to Powers and Brownyard [50], they do not distinguish any gel pores. Instead, all the spaces that are not filled with hydrates are considered to be capillary pores.

The most recent (and well-accepted) models of this pore structure is that of Jennings [55, 56]. His first model, CM-I, was published in 2000 but was modified into CM-II in 2008. The CM-II model is illustrated in Fig. 13.

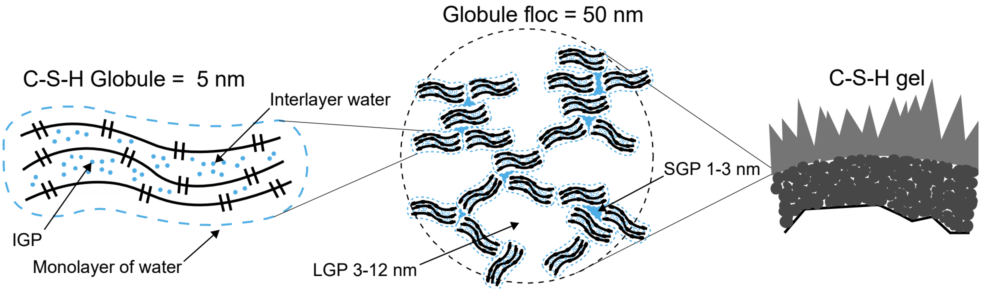

Figure 13
Schematic presentation of the CM-II model. Partially adapted from [55]

In the CM-II model, C-S-H is described as consisting of small globules, of approximately 5 nm in size. The globules exhibit a layered structure with interlayer spaces and inter-globule pores (IGP). These spaces are smaller than 1 nm in size. A layer of adsorbed water covers the globule surfaces in their saturated state. Multiple globules are packed together to form globule flocs. Small gel pores (SGP; 1-3 nm in diameter) are formed between globules and large gel pores (LGP; 3-12 nm in diameter) between globule flocs. Pores larger than 12 nm are considered capillary pores, i.e., not intrinsic to the C-S-H gel. This division was recently modified by the findings of Muller et al. [61] who found that the pore volume corresponding to LGPs decreased with time. They suggested that part of the LGPs (although similar in size) are not intrinsic to the C-S-H but are formed between hydrates as so-called inter-hydrate spaces. Similar observations were later made by Berodier and Scrivener [47]. However, they found (for cement pastes cured under water) that the capillary pore volume continued to decrease until all the pores reached a size of approximately 8-10 nm. Below this size, the pores were smaller than the critical size required for precipitation.

Powers and Brownyard [50] marked the transition from capillary to gel pores by the presence of capillary condensed water. As per the definition of Jennings [55], gel pores are spaces smaller than 12 nm (or 8-10 nm if the findings of Muller et al. [61] and Berodier and Scrivener [47] are considered). The definition of Jennings does not depend on the presence of capillary pore water but rather on how the pores were formed; capillary pores are residuals of the continuous water phase, whereas gel pores are intrinsic to the C-S-H. This means that, as hydration proceeds, the capillary pores are refined and decrease in volume, whereas the gel porosity increases. Figure 14 illustrates the capillary and inter-hydrate pore structure close to an aggregate surface in a cement-based material.

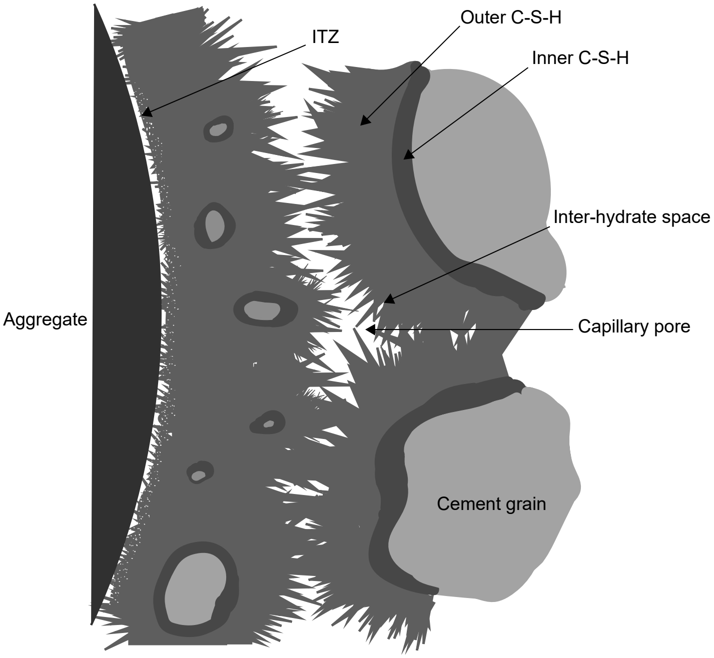

Figure 14
Illustration of the capillary and inter-hydrate pore structure in cement paste close to the aggregate surface

In addition to the abovementioned porosity, previous studies have reported that a porous interfacial transition zone (ITZ) is formed between aggregate surfaces and the bulk cement paste [85, 86]. The ITZ is formed as the packing of cement grains against much larger aggregates result in a predominance of small cement grains close to the aggregate surface. Scrivener et al. [86] found that although the ITZ has an impact on transport properties, it is counteracted and outweighed by other effects. Baroghel-Bouny [74] showed that this zone should have little impact on the moisture sorption in the hygroscopic range as the voids in which the moisture equilibrium processes take place then are much smaller than those in the ITZ. The effect of aggregates on the pore structure is discussed in *Paper II*, the measurements of which indicate that they have little impact on the moisture sorption. Table 2 summarises the types of pores and approximate pore size (capillary pores and smaller) as interpreted from the references mentioned in this section.

Table 2
Division of pores in cement-based materials according to their diameter, assuming cylindrical pores (mostly from [55])

Porosity	Approximate sizes
Capillary pores	>12 nm
Inter-hydrate spaces	8-12 nm
Large gel pores	3-8 nm
Small gel pores	1-3 nm
Interlayer water	>1 nm

Characterisation of the pore structure and related moisture properties (moisture sorption and transport) was the main focus in appended *Papers II-IV*. In *Paper III,* MIP measurements were used to provide additional information regarding the pore structure. This method is described in the next section, along with example results from *Paper III.*

2.5.1 Mercury intrusion porosimetry

MIP is a common technique to characterise the pore structure of cement-based materials [87-90]. The method is based on the intrusion of non-wetting mercury to the pore structure under increasing pressure; it can capture a wide range of pores, from around 2 mm to approximately 4 nm in diameter. The results can be used to estimate the pore volume, pore size distribution and critical pore entry diameter. The latter is interpreted as the smallest diameter which is geometrically continuous throughout the sample and is thereby related to the permeability [91]. The Washburn equation (Eq. 7; [92]) describes the relationship between pore pressure and pore sizes:

$$P = \frac{\gamma_m \cos\theta}{d} \tag{7}$$

where P (Pa) is the pressure, γ_m (J m^{-2}) is the surface tension of mercury, θ is the contact angle between mercury and the pore surface, and d (m) is the pore diameter. The results vary depending on the contact angle assumed between mercury and the pore surface [90]. Furthermore, the calculation assumes that all pores are cylindrical, which for cement-based materials is not true because pores can assume any shape.

When interpreting MIP results, it should also be noted that mercury only intrudes the open porosity and that many large pores are only accessible through smaller openings. The latter is known as the ink-bottle effect (Fig. 15) and may cause an overestimation of small pores and an underestimation of large pores; pore size distributions derived from MIP measurements should thus rather be seen as pore entry size distributions.

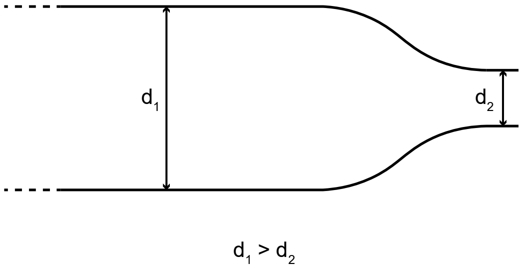

Figure 15
Illustration of an ink-bottle pore, where d_1 and d_2 are diameters.

According to Espinosa and Franke [93], harsh drying and chemical ageing of cement-based materials lead to the formation of additional ink-bottles. SCMs seem to have a similar effect because their reactions refine pore openings more than they lower the total pore volume (see for example reference [47]).

In *Paper III*, MIP measurements were conducted on mortars with varying FA replacement that had been cured at different temperatures for one year. The results can supplement the moisture sorption and moisture transport measurements on the same material by providing information regarding mainly the critical pore entry diameters. The total pore volumes were not evaluated from the measurements because the binder content of the samples was not known. The results are shown here in Fig. 16.

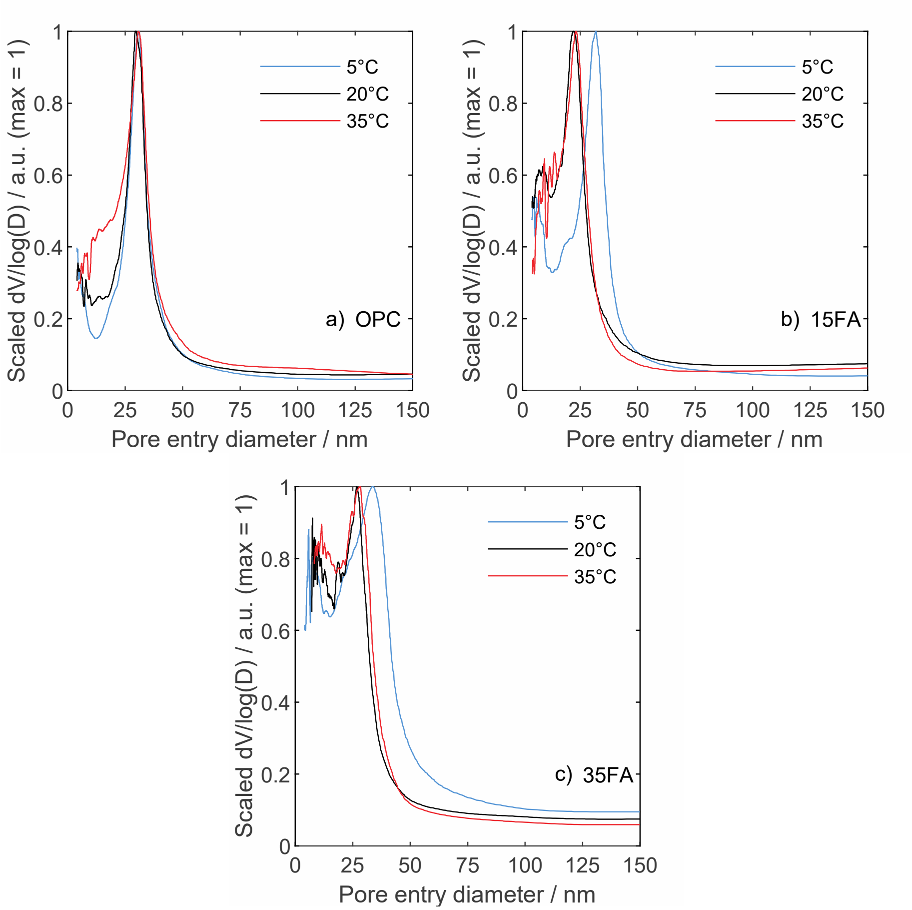

Figure 16
From Paper III: scaled MIP derivative curves for mortars with a) OPC, b) 15FA and c) 35FA as binders after one year of curing under sealed conditions at 5 (blue), 20 (black) or 35 °C (red)

Figures 16a-c show that the temperature effect changes with increasing FA replacement. The FA reaction is sensitive to low temperature, as is indicated by a larger critical pore entry diameter (horizontal position of the main peak in the curves). Furthermore, the FA reaction seems to increase the heterogeneity of the pore structure because with increasing FA replacement, a larger fraction of mercury intrudes pores smaller than the critical pore entry diameter.

3 Water in cement-based materials

Water added during the mixing of cement-based materials is either chemically bound in the hydrated phases or physically bound in the pores of the hardened cement paste. Water can also be added or lost when the material comes in contact with the atmosphere, for example, as water vapour evaporates or as rain water is absorbed.

Partial dehydration of the physically bound water is often necessary during construction to prevent the degradation of wood, flooring-materials, or adhesives that are in contact with or in close proximity to a concrete surface. Other deteriorating processes such as chloride penetration, carbonation, and freeze-thaw scaling are also moisture dependent [81]. Consequently, the moisture properties of cement-based materials need to be understood and the corresponding data need to be collected. Collected data can be used in computational models to predict, for example, the drying, shrinkage, and service life of cement-based materials.

This chapter details the binding and transport of moisture in cement-based materials. The first section focusses on the chemically bound water, the second section on the physically bound water, and the third and final section deals with moisture transport.

3.1 Chemically bound water

The amount of water added during the mixing of cement-based material is often an excess compared to what is theoretically required to reach full hydration. It is traditionally assumed (i.e., according to Powers and Brownyard [50]) that OPC binds approximately 0.25 g g^{-1} (water per cement) at complete reaction. Furthermore, that by determining the chemically bound water content it is possible to calculate the degree of hydration (α) using Eq. 8.

$$\alpha = \frac{W_\mathrm{n}}{0.25B} \tag{8}$$

where W_n (g) is the chemically bound water content and B (g) is the binder content.

However, the chemically bound water content has been shown to vary not only with the degree of reaction but also depending on how the physically bound water was removed from the pore structure prior to analysis [94]. Powers and Brownyard [50] used oven drying (at 105 °C) to dry their samples. This is a harsh drying method that destroys part of the AFt and C-S-H, for example, leading to an underestimation of the chemically bound water content. Moreover, moderns OPCs are more reactive than those used in the 1940s and probably bind more water at full hydration (regardless of the drying method). This means that depending on the type of OPC and drying method, more or less water may be bound at full hydration than the 0.25 g g^{-1} reported by Powers and Brownyard [50].

Another complicating factor is that the chemically bound water content per reaction (for both OPC and SCMs) seems to vary with the curing temperature [48, 60] (see also *Paper III*). Because of this, chemically bound water is not a suitable measure to determine the degree of reaction (e.g., with Eq. 8) unless these variations are accounted for.

In addition, note that the maximal chemically bound water (per g of cement) does not equal the minimal w/c ratio required for complete hydration. As mentioned in Chapter 2, the formation of hydrates results in a chemical shrinkage that may deplete part of the porosity on water, causing the material to self-desiccate (lower its RH without drying to the ambient). With decreasing RH, there are fewer water-filled pores that are large enough for hydrates to precipitate. This lowers the rate of reaction, and at around 80% RH, hydration virtually ceases.

For the OPC used at that time, Powers and Brownyard [50] predicted a practical minimal w/c ratio (required for full hydration) of 0.42. Recapitulating their work, Brouwers [51] found that this value was approximately 0.39 for modern OPC. However, even at these w/c ratios it takes a very long time to reach full hydration, as the microstructure grows dense, thereby limiting the reaction kinetics [47]. Although they never reach full hydration, cement-based materials are often made with lower w/c ratios than the predicted minimum for other purposes not the least to achieve a rapid self-desiccation.

Partial replacement of OPC with SCMs affects the maximal content of chemically bound water as well as the content at early age. Most SCMs react more slowly and bind less water per reaction (other than that inherent to the CH) than OPC [48, 95]. The latter means that Eq. 8 is not suitable for calculating the degree of reaction for blended cements. The effects of fly ash replacement and curing temperature on the chemically bound water and CH contents were investigated in *Paper III*. The results are shown in Fig. 17 (Section 3.1.1).

3.1.1 Thermogravimetric analysis

TGA is a common technique for determining chemically bound water and CH contents in cement-based materials to follow hydration [42, 96, 97]. It can also be used to study the effect of different treatments and exposures on hydrated phase assemblage [98, 99]. The technique is based on the principle that hydrated phases decompose sequentially as the temperature increases, thus releasing water and carbon dioxide that result in mass loss.

It is often the case that multiple phases decompose within a similar temperature range, making their individual contributions to the mass loss hard to differentiate. However, some hydrates can be quantified: CH decomposes between approximately 380-550 °C; this interval is only shared with minor amounts of C-S-H and hydrotalcite. Calcium carbonate is the only phase that decomposes between approximately 600-750 °C [100]. The content of chemically bound water is generally derived from the mass loss up to 550-600 °C, that is, before calcium carbonate starts to decompose.

Figures 17a-d show the chemically bound water and CH content in mortars with OPC and 35FA cured at 5, 20, or 35 °C from *Paper III*. Analyses were conducted at different times, ranging from three days to six months after mixing.

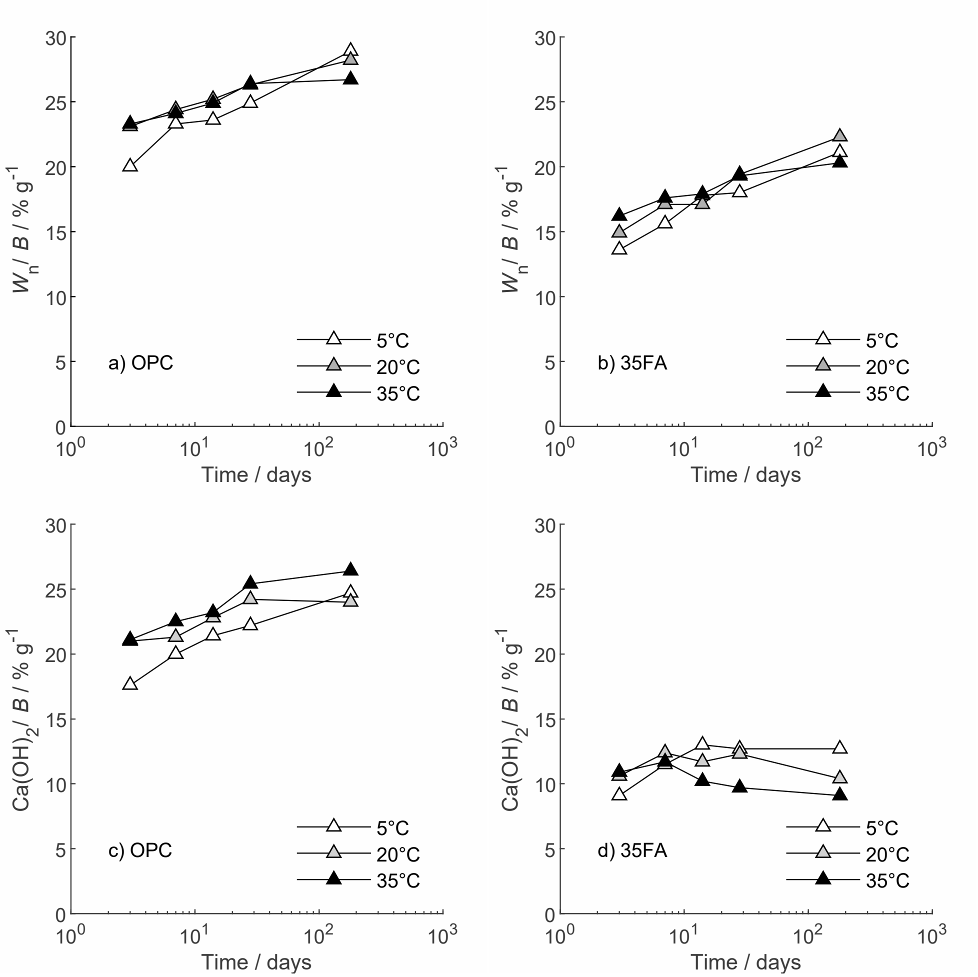

Figure 17
From Paper III: Chemically bound water (W_n) (a-b) and CH (here, it is given as $Ca(OH)_2$) (c-d) contents per gram of binder (B) in mortars (w/b 0.45) made with OPC or 35FA as binder, cured at 5, 20, or 35 °C under sealed conditions. Analyses were performed at different times, ranging from three days to 6 months after mixing.

Figures 17a-d show that a large part of hydration takes place in the first days, as the content of chemically bound water only increases slightly up to six months. Furthermore, FA replacement reduces the content of chemically bound water (W_n) and CH ($Ca(OH)_2$). This could be because of that FA reacts more slowly, has a lower degree of reaction and binds less water per reaction than OPC [7, 48, 95, 101]. The latter is explained by the pozzolanic reaction (Eq. 6) whereby amorphous silicon from the FA reacts with CH (produced by the OPC) and some water to form C-S-H. Thus, less 'new' water is bound chemically per FA reaction.

The results also show the effect of curing temperature. Low temperature delays the reactions at an early age, as can be seen by the lower contents of chemically bound water and CH with both binders. However, for OPC, there is an inversion effect so that the highest tested temperature gives the lowest chemically bound water and CH content at six months (Fig. 17a). This is probably caused by a variation in the chemically bound water content per reaction with temperature [48], which also affects the microstructural build-up [60]. The effect is not seen for 35FA, which could probably be because the temperature has a reversed effect on the FA reaction at later age (compared to the OPC). The decrease in the CH content can be used to indicate the FA reaction (Fig. 17d), which suggests that elevated temperatures accelerate the FA reaction but that it is severely delayed by a low temperature.

3.2 Physically bound water

The mixing water which is not chemically bound in hydrates or evaporates to the atmosphere, is physically bound in the pore structure of the material. The physically bound water is present mainly as adsorbed or capillary condensed water (capillary water). In addition, free water (bulk water) may exist near saturation. Figure 18 illustrates water in a cement-based material during drying from a water saturated state.

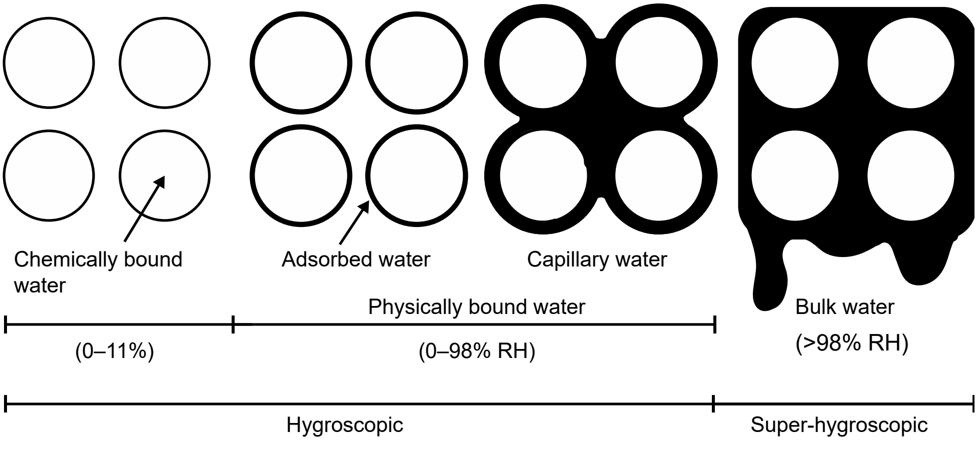

Figure 18
Principle illustration of water in, on, and around solids in a cement-based material. Additionally, the approximate RH-intervals in which the water is lost upon drying are given.

Bulk water fills air pores and micro-cracks close to saturation, e.g., if the material is immersed in water for a long time. Below approximately 98% RH and to around 45%

RH, water is bound in capillary pores, inter-hydrate spaces, and large gel pores by a combination of capillary condensation and adsorption. Below 45% RH, adsorption is the primary binding mechanism. However, at low RH, it is difficult to distinguish between the physically and chemically bound water. Even if most of the chemically bound water is only lost upon heating, some hydrates decompose also upon strong drying, e.g., parts of the C-S-H, AFm, and AFt phases. According to Feldman and Ramachandran [72, 73], a significant loss of chemically bound water occurs as the RH falls below 11%, but some loss is apparent at approximately 30%. Any removal of chemically bound water will cause permanent damage to the pore structure. Microstructural alterations also occur as physically bound water evaporates; for example, in capillary pores, inter-hydrate spaces, and gel pores that contain capillary condensed water because negative pressures are generated in the retained water, which promotes a consolidation of the structure. According to Jennings et al. [76], these changes are reversible in the capillary pores but cause irreversible shrinkage in the gel pores.

Below 45% RH, adsorbed water exists in small gel pores and the C-S-H interlayer spaces. Feldman and Sereda [63] found that complete removal of water from the interlayers collapses the C-S-H structure, but that if given enough time, the structure is restored upon re-saturation (Fig. 19). Jennings et al. [76] state that although water may re-enter these spaces over the entire RH-range, complete saturation is unlikely even at very long timescales. Upon severe drying, water may not be able to re-enter the structure at all as bonds form between the collapsed layers. Wu et al. [65] reported that alterations at low RH are reversed as the sample is re-saturated, and that the permanent changes reported in other studies are caused by long-term exposure to low RH because it promotes the chemical ageing of C-S-H.

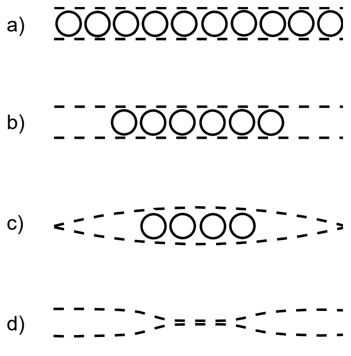

Figure 19
Principle illustration of water exiting the interlayer spaces of C-S-H upon drying. Adapted from [63]

Regardless of whether the microstructural alterations caused by drying are temporary or permanent, they increase the volume of inter-hydrate spaces and capillary pores because the C-S-H consolidates and thereby occupies less space. Changes in the pore structure caused by drying and wetting are interesting because most cement-based materials are exposed to variable moisture conditions during their service life. For example, microstructural rearrangements can be expected in cement-based materials exposed to an indoor environment (typically low RH). This should be considered in the design and evaluation of, e.g., moisture sorption and moisture transport measurements, which aim to describe these properties in real building constructions with cement-based materials.

3.2.1 Sorption

The relation between physically bound water and RH under isothermal conditions can be described with sorption isotherms. The first sorption isotherms for cement-based materials were presented by Powers and Brownyard [50] more than 70 years ago. They conducted measurements on concrete with OPC (of the type used at that time). Since then, sorption isotherms have been measured for a wide range of cement-based materials [74, 88, 102-112]. Sorption measurements are also an important part of the appended *Papers II-IV*.

The shape of the sorption isotherms depends on the initial moisture state of the material. Isotherms can be measured during absorption or during desorption, that is, going from a dry to a saturated state or vice versa. However, the desorption branch of the isotherm is always above the absorption branch. These direction dependent differences are known as sorption hysteresis, and curves between the two branches are called scanning isotherms. Hysteresis at low RH is probably caused by a combination of permanent loss of chemically bound water and microstructural rearrangements as water moves in and out of gel pores and interlayer spaces. At higher RH, hysteresis is normally attributed to capillary condensation, as filling and emptying of a pore take place at different RH because of the ink-bottle effect [93] (cf. Fig. 15, section 2.5.1). Sorption hysteresis and absorption are not discussed further as it goes beyond the scope of the thesis. Our focus here is mainly on the desorption branch of the isotherm.

In desorption, smaller and smaller pores are emptied. The desorption branch of the sorption isotherm thus reflects both the pore volume and pore size distribution of the material. However, the latter is rather a distribution of the pore entry sizes because many pores are only connected to their ends though smaller openings. The Kelvin equation (Eq. 9; [84]) can be used to relate pore sizes to RH under the following assumptions: all pores are cylindrical; there is no layer of adsorbed water on the pore surfaces; and there are water meniscuses. In reality, pores can assume any shape, there is always adsorbed water, and meniscuses are only maintained down to about 45% RH (at 20°C). The calculated pore sizes should thus be seen as mere estimates. The Kelvin equation is given as follows:

$$d = \frac{-4\gamma_{\mathrm{w}} M_{\mathrm{w}} \cos\theta}{RT \ln(\varphi)} \tag{9}$$

where d is the Kelvin diameter (or pore diameter in m), γ_{w} is the surface tension of water (0.0728 J m^{-2}), M_{w} is the molar volume of water (17.98×10^{-6} m^3 mol^{-1}), θ is the contact angle, R is the gas constant (8.314 J mol^{-1} K^{-1}), φ is the RH (Pa Pa^{-1}), and T is the absolute temperature (293.15 K). Using the Kelvin equation and values above, Fig. 20 shows the approximate relationship between pore diameter and RH.

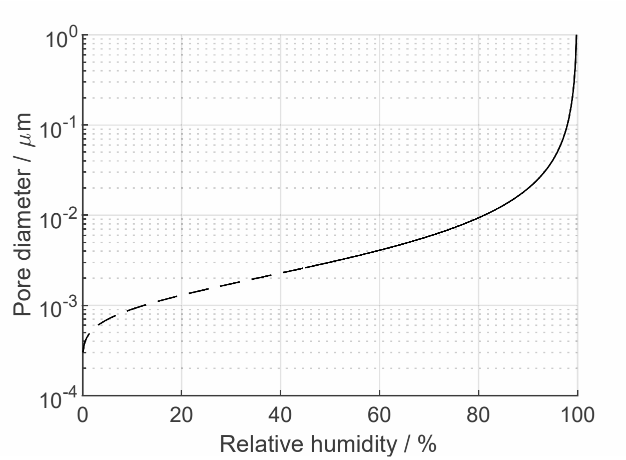

Figure 20
The approximate pore diameters calculated using the Kelvin Equation as a function of RH. The curve is dashed below 45% as the assumptions on which the Kelvin equation are based on are not valid in this region (also in Paper II)

As discussed in the previous chapter, pores are typically divided into different categories by their size (see for example references [55, 56, 113]). Saeidpour and Wadsö [102] interpreted the findings of Muller et al. [113] to divide the desorption isotherm into four parts corresponding to different RH-ranges. Their division is also used here (including *Papers II, III*) but with a slight modification; the largest gel pores (corresponding to 80-70% RH) are separated from the other gel pores (70-30%).

≥ 90%	Capillary pores
90-80%	Inter-hydrate spaces
80-70%	Large gel pores
70-30%	Gel pores
30-0%	Water in C-S-H interlayers

3.2.2 Desiccators and sorption balance

The two most common methods to measure water vapour sorption isotherms for cement-based materials are the desiccator method (e.g., in [106, 108] and sorption balance (first described in [114], see also [88, 102, 105]). The latter is also known as dynamic vapour sorption (DVS). With both methods, the moisture content at different RH can be determined from the difference in mass compared to a dry state. With the desiccator method, samples are conditioned to the mass equilibrium with different RH using saturated salt solutions. In a sorption balance, the mass of small samples is continuously measured during exposure to a predefined sequence of RHs, the desired RH is then obtained by a mixture of water vapour saturated and dry nitrogen gas.

Both the desiccator method and sorption balance were used in *Paper IV*. The aim was to compare the methods by determining desorption isotherms on samples of the same mortar. The results are presented here in Fig. 21. The differences are considerable, up to 10% RH at some moisture contents. A similar study was conducted by Johannesson and Janz [115], however, on samples of porous glass and sandstone. They observed that the methods agreed well, suggesting that the differences reported here are material-dependent.

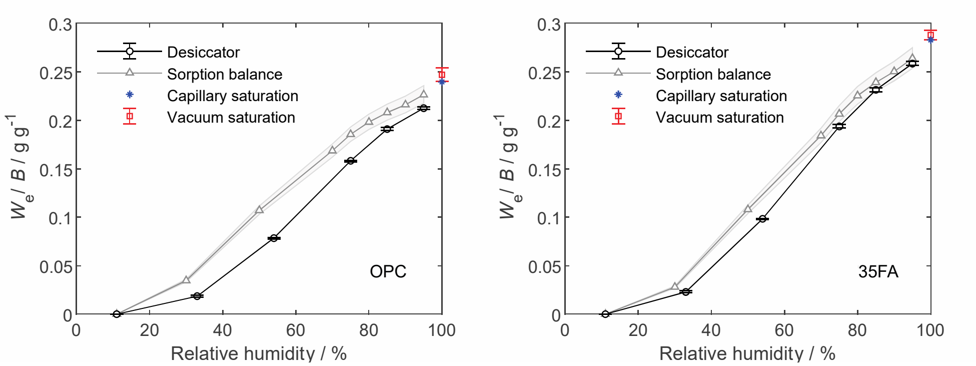

Figure 21
From Paper IV: Desorption isotherms of mortars (w/b 0.45) with OPC (left) and 35FA (35 wt% FA replacement) (right) as binder; determined by the desiccator method (circles) and with a sorption balance (triangles) after two years of sealed curing at 20 °C. Moisture contents at capillary (asterisk) and vacuum saturation (square) are also given. Error bars show the max and min values of six observations with the desiccator method. The shaded area around the sorption balance results shows the calculated uncertainty related to the binder content. The results are given as physically bound water (W_e) per gram of binder (B), as a function of RH

One difference between the methods is the time duration. In Paper IV, a complete desorption isotherm was measured in two weeks in the sorption balance, whereas it took several months using the desiccator method. Because of the shorter measurement time, mass equilibrium is generally not achieved at all RHs in the sorption balance. To counter this, most studies use curve fitting and extrapolation with exponential functions to estimate the mass at infinite time at each step (see, e.g., [102, 103, 116] or *Paper II*). Although this will probably improve results, it is then assumed that sorption follows an exponential path towards equilibrium. However, in desorption, this does not seem to be the case other than at high and very low RHs. At intermediate RHs, sorption kinetics are very slow after an initial transient period. This is referred to as anomalous or non-Fickian sorption [106, 117] (i.e. one that does not follow Fick's law of diffusion [118]). de Burgh and Foster [106] observed that the non-Fickian sorption became increasingly prominent in desorption until a maximum was reached at 35% RH (at 23 °C). They attribute this to time-dependent microstructural rearrangements as the capillary condensed water leaves the pores. The remaining saturated spaces then experience forces that encourage consolidation. If the mechanical response of the pore structure is delayed, this appears as a slow mass decay. Similar observations were also made by Maruyama et al. [119].

At low RH (where there is only adsorbed water), sorption kinetics become Fickian again (cf. Fig. 11 in [106]). Similar observations were made when evaluating results from desiccator measurements for *Paper IV*; examples are given here in Figs. 22a-b.

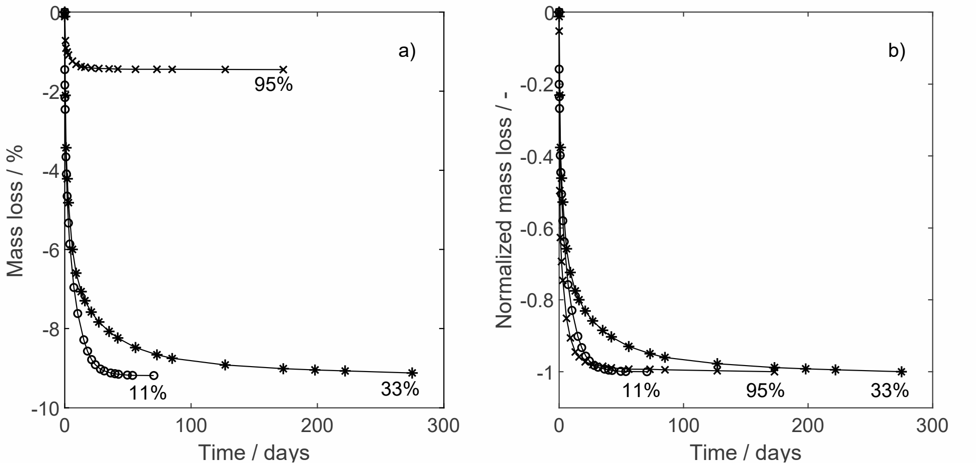

Figure 22
With data from Paper IV: a) mass loss versus time and b) normalised mass loss versus time plots for mortar samples with 35FA as binder, conditioned with the desiccator method. Three RHs are shown, 95% (cross), 33% (asterisk), and 11% (circles). The 11%-samples had previously been dried to the mass equilibrium with 95% RH

Another major difference between the two methods is the sample size; in *Paper IV,* this difference was approximately a factor 1000. However, as observed by both de Burgh and Foster [106] and Maruyama et al. [119], the sample size mainly affected the initial transient phase and not the subsequent non-Fickian behaviour.

Non-Fickian behaviour is also observed in absorption (see, e.g., [104]). This suggests that the microstructural alterations that occur in desorption are reversible to some extent. The idea that partially reversible microstructural rearrangements can explain the non-Fickian sorption kinetics was further evidenced in a recent study by McDonald et al. [120]. They described it as caused by a dynamic porosity that changes the pore size distribution in both absorption and desorption.

Because non-Fickian sorption occurs on a rather long time scale, it might not be captured by the comparatively rapid sorption balance measurement. This can possibly explain the differences between the results from the sorption balance and the desiccator method (Fig. 21 and *Paper IV*). The results highlight that the choice of the sorption method is of decisive importance, e.g., if the data are to be used in computational models to predict drying of cement-based material, then a 10% difference in RH probably represents several months of drying.

According to the author’s opinion, both methods can be used to measure sorption isotherms, and which method is most suitable depends on the pore structure to be represented. In some cases, it may be sufficient to end each step before the mass versus time curve shows non-Fickian behaviour because then, the results could be more representative of the original (never-dried) pore structure. However, most cement-based materials are exposed to lower RH during their service life. Thus, if the results are to mimic the pore structure near the surface of a cement-based material, the non-Fickian sorption should probably be included. Regardless, the same method should be used if results for materials with different binders, for example, are to be compared. Most sorption measurements in this thesis (see, e.g., *Papers II* and *III*) have been conducted with sorption balances. The main purpose was to study the effects of FA replacement and curing temperature on the pore structure of samples cured under sealed conditions (i.e., without drying to the ambient).

3.2.3 Example sorption results

In *Paper II*, desorption isotherms were determined with sorption balances at different times, ranging from three days to six months, to follow the development of pore structure in cement paste with OPC, 15FA, and 35FA as the binder. The results are shown here in Figures 23a-d.

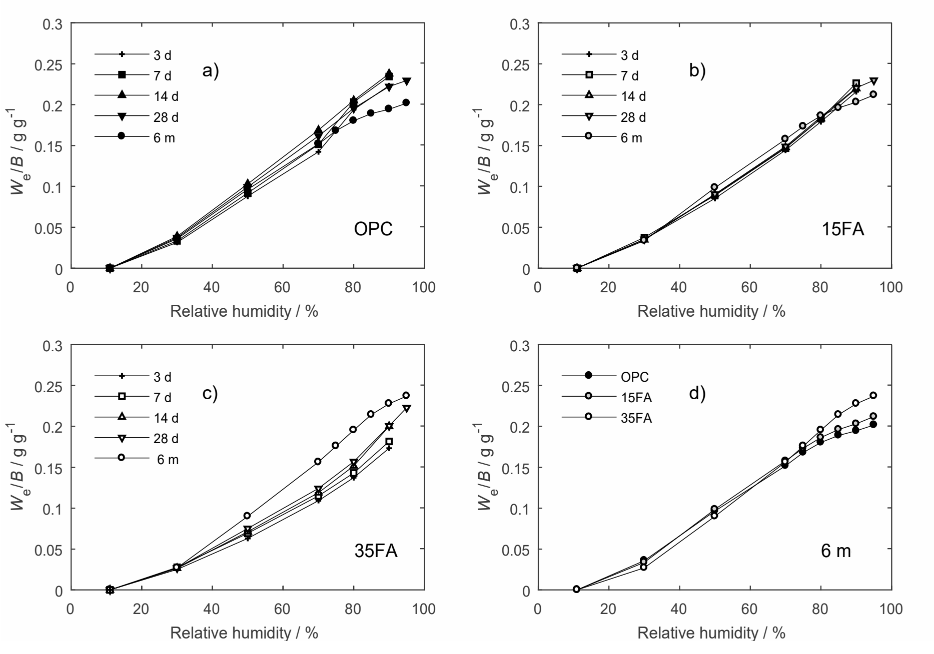

Figure 23
From Paper II: Desorption isotherms of cement paste (w/b 0.45) made with a) OPC, b) 15FA, and c) 35FA as binder, measured with sorption balances. Measurements were conducted at different times, ranging from three days to six months of sealed curing at 20 °C. d) The results after six months are compared. The results are given as physically bound water (W_e) per gram of binder (B), as a function of RH

Figures 23a-d show that FA replacement reduces the early reactivity of the binder, thus resulting in a less developed pore structure in the first month. The desorption isotherms of the FA containing materials are lower than those of the material with OPC. Furthermore, the isotherms are steeper in the high RH-range, indicating a larger fraction of coarse porosity with more pores emptying above 95% RH.

Between 28 days and six months the pore structures of all tested materials are markedly refined; however, the refinement is the most pronounced in the FA blended materials. This is evident from the results in Figures 24a-b (also from *Paper II*) which present results from Figures 23a-d after 28 days and six months as bars dividing the moisture content into different RH intervals. In Fig. 24b, the moisture content has been normalised by the moisture content at 95% RH. This makes it possible to compare only the shape of the desorption isotherms, that is, the pore size distributions.

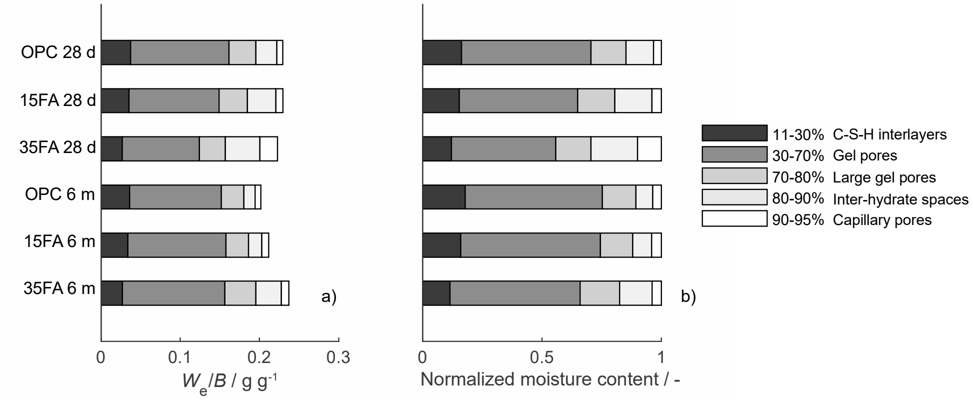

Figure 24
From Paper II: Desorption isotherms after 28 days and six months obtained from Figures 23a-d presented as a) bars dividing the moisture content into different RH-intervals and b) bars normalised by the moisture content at 95% RH

Figures 24a-b further indicate that long-term FA reactions considerably alter the pore structure. The FA reaction does not fill pore volume but refines porosity. Possible reasons for this are that solid CH crystals are consumed by the FA to form finely porous C-S-H; furthermore, FA binds less water chemically per reaction (other than that inherent to the CH) than OPC [48, 95]. Moreover, the degree of FA reaction is much lower than that of OPC, even after several months of reaction. In addition, the maximal degree of FA reaction is limited as FA normally contain considerable amounts of inert material in the form of crystalline phases (the FA used in *Papers I-V* contains approximately 30 wt% of inert material).

In *Paper VI*, the desorption isotherms were determined for 25-year-old concretes made with OPC and 4 or 12 wt% SF (referred to here as 4SF and 12SF) or with 4 wt% SF plus 20 wt% FA (4SF-20FA). The measurements were conducted with sorption balances as part of a larger study focusing on the reinforcement corrosion in pre-cracked concrete beams exposed to marine environments. Samples were taken from the beam cores; the material can therefore be assumed to have had limited contact with the atmosphere. The results are interesting as they show the pore structure of extremely well-hydrated materials. The isotherms are presented here in Fig. 25 (redrawn with data from *Paper VI*).

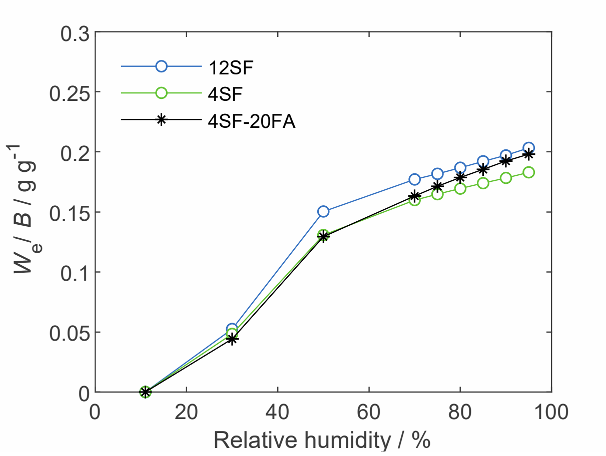

Figure 25
Data from Paper VI: Desorption isotherms of concretes (w/b 0.4) with 4SF, 12SF, or 20FA as binder measured with sorption balances. Samples were taken from the cores of concrete beams submerged for 25 years in seawater. The results are given as physically bound water (W_e) per gram of binder (B), as a function of RH

As seen in Fig. 25, the upper half of the isotherms is very flat. This indicates that the inter-hydrate spaces and capillary pores have been refined. In theory, if these pores remain water-filled and in contact with the remaining anhydrous material, the upper part of the isotherm should become almost horizontal with time, as all the pores that are not intrinsic to the C-S-H can then be refined to the critical minimum size required for precipitation of hydrates [47].

In *Paper III*, the effects of curing temperature on the pore structure were investigated for mortars with OPC, 15FA and 35FA as the binder. The main results are shown in Fig. 26.

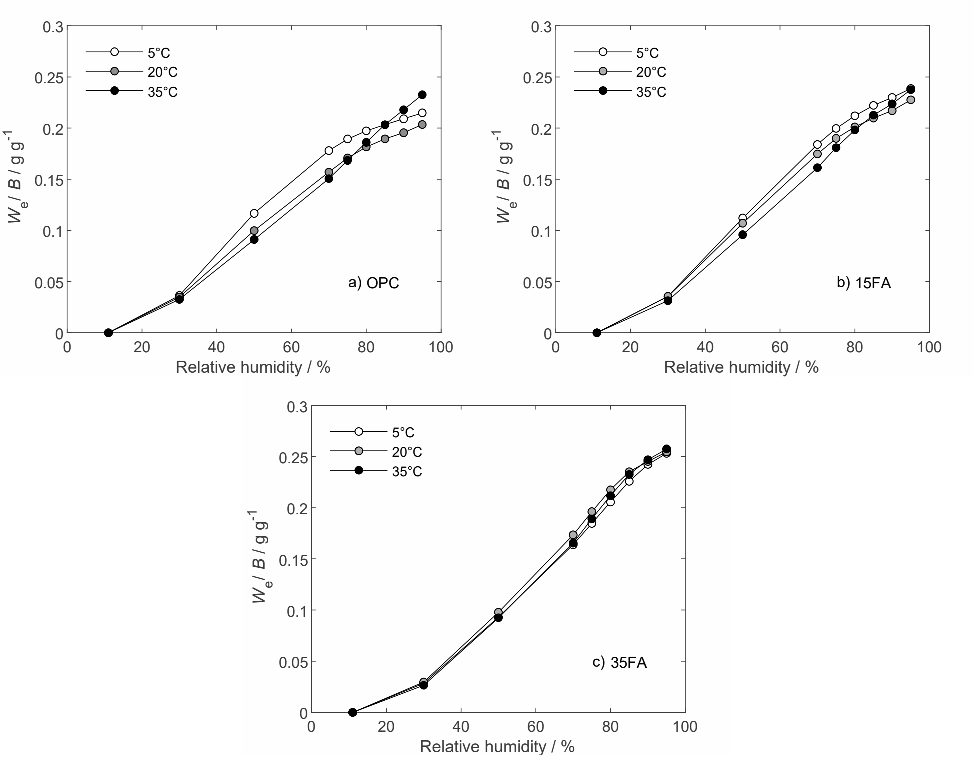

Figure 26
From Paper III: Desorption isotherms of mortars (w/b 0.45) made with a) OPC, b) 15FA, and c) 35FA as binder; after one year of sealed curing at 5, 20, or 35 °C. The results are given as physically bound water (W_e) per gram of binder (B) as a function of RH

It has long been known that temperature affects the properties of cement-based materials; in the 1940s Powers and Brownyard [50] noted that materials prepared at low temperature were structurally different from those prepared at higher temperature. Figures 26a-c show that the differences in pore volume and pore size distribution decrease with increasing FA replacement. A probable explanation is that temperature has a large effect on the FA reaction. Unlike OPC, the degree of FA reaction varies significantly with temperature also at later ages [48]. The FA reaction is accelerated by elevated temperature, but is severely limited by low temperature. The effect of the FA on the pore structure is thereby reversed compared to that of C-S-H. The density of C-S-H increases with temperature; thus, it binds less water and occupy less space [60]. In addition, this leads to a larger fraction of coarse pores and a more heterogeneous pore structure. Differences in C-S-H density can probably explain the results for OPC in Fig. 26a, whereas the effect of temperature on the FA reaction probably explain why the differences due to temperature decrease with increasing FA replacement (Figs. 26b-c).

3.3 Moisture transport

Transport of moisture in cement-based materials occurs as liquid water flow or as water vapour diffuse through the pore structure. Liquid flow is caused by a difference in pore water pressure, whereas vapour diffusion is driven by a difference in vapour content. The moisture conditions determine which of the mechanisms is the dominant one, as illustrated in Fig. 27.

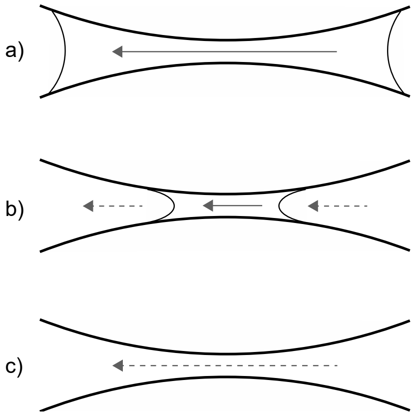

Figure 27
Moisture transport scenarios: a) only liquid flow, b) a combination liquid flow and diffusion, and c) only diffusion.

Near water saturation, most of the pores are water-filled, and liquid phase flow is the main transport mechanism. Moisture transport can then be described using Darcy's law (Eq. 10; [121]):

$$q_\mathrm{l} = -\frac{k_\mathrm{p}}{\mu}\frac{\Delta P_\mathrm{w}}{\Delta x} \qquad (10)$$

where q_l (g m^{-2} s^{-1}) is the liquid moisture flux, k_p (g m^{-1}) is the permeability coefficient, μ (Pa s) is the dynamic viscosity, ΔP_w (Pa) is the difference in pore water pressure, and Δx (m) is the distance.

Below saturation, a part of the porosity no longer contains capillary condensed water. Moisture transport is then a combination of liquid phase flow and vapour diffusion (as in Fig. 27b). At low RH, there is only adsorbed water, wherein diffusion is the main transport mechanism (Fig. 27c). Diffusion is described by Fick's first law, with vapour content as the potential (Eq. 11; [118]):

$$q_v = -D_v \frac{\Delta v}{\Delta x} \tag{11}$$

where q_v (g m^{-2} s^{-1}) is the vapour moisture flux, D_v (m^{2} s^{-1}) is the diffusion coefficient, and Δv (g m^{-3}) is the difference in vapour content over a distance Δx (m).

In most cement-based materials, the moisture transport is a combination of liquid flow and vapour diffusion (similar to the scenario in Fig. 27b). The contribution of each mechanism to the total moisture transport is, however, hard to quantify as the pore structure is a complex network of pores in a wide range of shapes and sizes. Moisture transport properties have been investigated in several studies using numerous experimental methods (see for example references [103, 108, 109, 122-124]). Most methods only measure the total moisture transport, and the results are typically given as diffusion coefficients calculated by Fick's first law with vapour content as the potential (see also appended *Papers II* and *III*).

Water vapour sorption isotherms provide information regarding the pore volume and size distribution; however, they give little information regarding pore connectivity and the tortuosity of the pore structure. The latter can be described as the difference between the distance A-B and the distance a water molecule needs to travel to get from A to B. These features seem to be particularly important for the moisture transport ability [91]. Recent studies suggest that are both the connectivity and tortuosity are affected by partial SCM replacement of the OPC [103, 123, 125]. *Papers II* and *III*, show that FA replacement decelerates the moisture transport and decreases its moisture dependence (see also Fig. 28 below). Simultaneously, sorption measurements show that the FA blended materials have a larger pore volume than the OPC reference. This suggests that the FA reaction does not fill the pore volume but refines porosity. Furthermore, that pore volume is less important for moisture transport than the pore size distribution, pore connectivity, and pore structure tortuosity. This was further evidenced by MIP measurements, indicating that the FA reaction refines pore openings and increases the heterogeneity of the pore entry size distribution (see *Paper III* and Fig. 16, section 2.5.1).

Exactly why FA has this effect on moisture transport remains to be explicitly shown. A possible reason is that C-S-H formed by the pozzolanic reaction has a different morphology than that formed by OPC, which decreases moisture permeability. Another reason could be that the SCM reactions are delayed compared to the OPC.

Thus, their reaction products mostly precipitate in an already formed pore structure which could increase its heterogeneity. Yet another possible reason is that the pozzolanic reaction replaces solid CH crystals with finely porous C-S-H. More research is required in this area.

3.3.1 Cup tests

The most common method to study moisture transport is probably the cup test [103, 123]. It is also the preferred method in appended *Papers II* and *III*. Cup tests measure the steady-state diffusion; samples are placed between two constant RHs until the rate of mass change reaches a constant value. Upon steady-state flow, the moisture flux can be calculated using the rate of mass change and Eq. 12:

$$q_m = \frac{\Delta m}{A \Delta t} \tag{12}$$

where q_m (g m^{-2} s^{-1}) is the total moisture flux, A (m^2) is the samples surface area, and $\Delta m / \Delta t$ (g s^{-1}) is the mass change rate.

Fick's first law with vapour content as potential (Eq. 11) can be used to calculate the diffusion coefficient. However, in this case, it is the mean diffusion coefficient over the tested RH-interval (that is, the difference between the inside and outside of the cup). Equation 11 is then rewritten as Eq. 13:

$$q_\mathrm{m}(\varphi_1, \varphi_2) = -\overline{D}_v \frac{\Delta v}{\Delta x} \tag{13}$$

where $\overline{D}_v$ (m^2 s^{-1}) is the mean diffusion coefficient between two RHs, φ_1 and φ_2 (Pa Pa^{-1}). More detailed descriptions of the cup method setup and the subsequent evaluation are given in Saeidpour and Wadsö [123] and in *Papers II* and *III*.

In *Paper III*, cup tests were performed on mortars with OPC, 15FA, and 35FA as the binder and cured for one year at different temperatures. The results are reproduced here in Figures 28a-c.

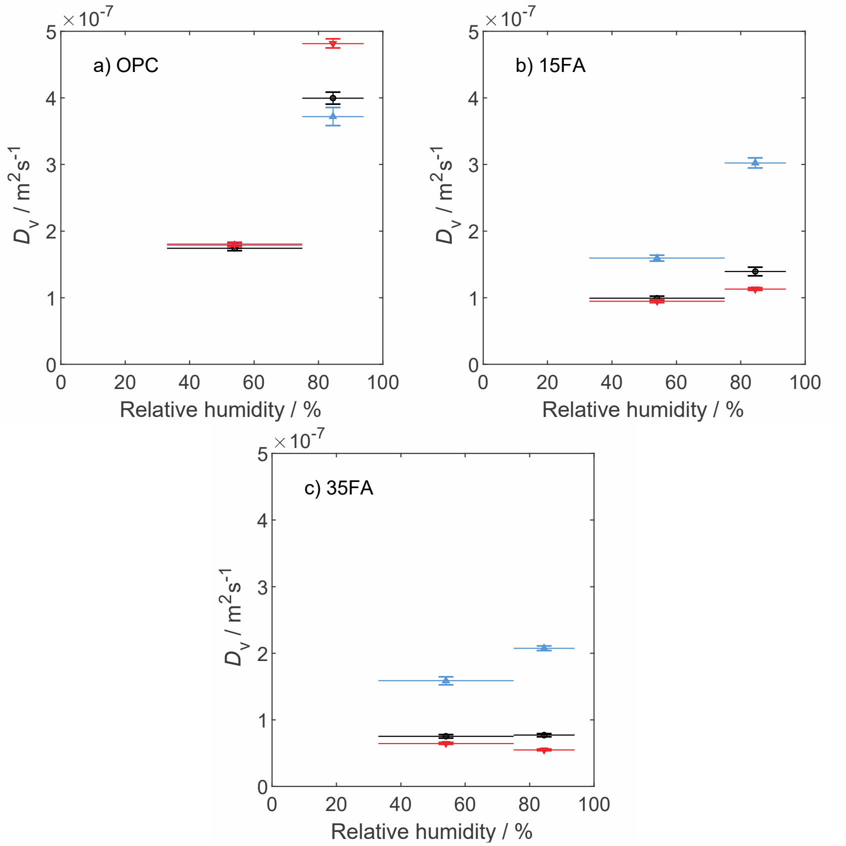

Figure 28
From Paper III: Diffusion coefficients of mortars (w/b 0.45) made with a) OPC, b) 15FA and c) 35FA as binder. Measured in desorption and for two RH-intervals: 33-75% and 75-95%. The material was cured for one year at 5°C (blue downward pointing triangles), 20 °C (black circles) or 35 °C (red upward pointing triangles). Error bars show the standard deviation of six (OPC, 15FA at 20 °C) or three (OPC, 15FA at 5, 35 °C and 35FA at 5, 20 and 35 °C) samples

Figures 28a-c show that FA replacement slows down the moisture transport and decreases its moisture dependence. The former is seen by lower diffusion coefficients, and the latter by a smaller difference between the diffusion coefficients for the same material in the two RH-intervals. Furthermore, the results show that the curing temperature affects moisture transport and that the effect changes as OPC is increasingly replaced with FA. For 15FA and 35FA, a low curing temperature results in diffusion coefficients that are approximately a factor two higher compared to normal or elevated temperature. A probable explanation for this difference is that low temperature limits the FA reaction [48]. Regardless of the curing temperature, FA replacement results in a 2 to 8 times lower diffusion coefficient compared to the material with only OPC, with the largest difference seen after curing at 35 °C.

4 Concluding remarks

Replacing part of the OPC with SCMs, such as FA, is considered the most promising solution for further reducing the carbon footprint of cement-based materials. However, the introduction of SCMs not only affects the carbon footprint but also important material properties, which is highlighted in the present thesis. For sustainable building constructions with cement-based materials, it is important not only to reduce emissions but also to maximise their durability and service life. One objective of this work was to further the knowledge regarding how FA affects pore structure and the related moisture properties (sorption and transport) of cement-based materials. These are crucial features for the durability and service life because most deteriorating processes that affect cement-based materials are both penetrating and moisture dependent.

4.1 Fly ash replacement and curing temperature

FA reacts slower than OPC. This means that with increasing replacement, the material properties are less developed at an early age. One example is a larger, coarser, and probably more permeable porosity (*Paper II*). The latter is indicated but not explicitly shown in this thesis, because the available methods to measure moisture transport (or moisture permeability) are not useful at the early age due to their long measurement times.

The differences in pore volume and pore size distribution between materials with and without FA replacement decrease with time. However, some differences, particularly in pore volume, remain even after 1.5 years of curing. The FA reaction does not fill pore volume (as much as that of OPC) but refines porosity and lowers the permeability (*Paper II*). The latter is seen as lower moisture diffusion coefficients at one year with increasing FA replacement. Together with measurements of pore entry sizes (*Paper III*), this indicates that the FA reaction affects the cement paste morphology, such that the pore connectivity decreases and the pore structure tortuosity increases; furthermore, these features seem to be more important for the permeability of the pore structure than pore volume.

The FA reaction is more temperature sensitive than that of OPC (*Paper III*). Unlike OPC, the differences in the degree of FA reaction due to temperature do not even out with time. The FA reaction seems to be particularly limited by low temperatures. This indicates that it becomes all the more important, with increasing FA replacement, to protect the material from low temperatures, particularly at an early age, for adequate material properties to develop.

4.2 Long-term hydration

Compared with the first days or week, little is known regarding long-term hydration mechanisms mainly because few methods can provide good precision data at this age. However, as shown in the present work, an ordinary isothermal calorimeter can be used to measure the thermal power of hydration for at least one year (*Paper V*). The results provide new opportunities for researchers and the industry to study long-term reactions in cement-based materials.

4.3 Towards computational models of drying

Partial drying of cement-based materials is often required at the construction stage to prevent degradation of adhesives and flooring-materials applied to their surface. For cement-based materials in contact with the atmosphere, drying is a combination of self-desiccation and evaporation processes (although the latter mainly affects the material close to the surface). The time for sufficient drying is typically estimated by measuring the relative humidity of the material with relative humidity sensors.

A method to model drying could be to determine water vapour desorption isotherms (the relationship between physically bound water and relative humidity), chemically bound water content, and moisture diffusion coefficients (in the relevant relative humidity range). However, as highlighted by the present work, these material features vary, e.g., with the binder composition, age, and curing temperature (*Paper II* and *III*). Furthermore, there is probably a gradient in pore structure from the material's surface to its centre which varies with the ambient conditions (*Paper IV*). This gradient likely affects not only the sorption of moisture but also moisture transport. In short, any model that aims to predict the drying of cement-based materials in this way with any accuracy will rapidly become very complex.

5 Future research

Based on the findings in this thesis, here are some suggestions for future research:

- Variations in the pore structure (and thus related moisture properties) with the distance from a surface in contact with the atmosphere should be investigated. This is important for the development of computational models that aim to predict, for example, drying of cement-based materials.
- Chemically and physically bound water contents can theoretically be used to calculate self-desiccation. However, for such calculations to be useful, best practice routines to determine these contents need to be developed.
- The role of aggregates for moisture transport in cement-based materials should be investigated further. If their effect can be quantified, moisture transport measurements (for example, cup tests) could be performed on cement paste rather than on concrete. This would shorten the time duration of the measurements and would thus allow moisture transport properties to be determined at an earlier age.
- Methods to measure moisture transport at an early age (e.g., in the first month) should be developed because the established methods are of limited use due to their long time durations.
- The relationship between moisture transport and other material properties should be investigated. From this study (as well as previous studies) it seems that pore connectivity and pore structure tortuosity have a greater impact on moisture transport than pore volume and pore size distribution. A method that potentially reflects these properties is mercury intrusion porosimetry; furthermore, it is a rapid method that can be used from an early age.

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