An Experimental Study of

CHANGES IN MICROSTRUCTURE OF CEMENT BASED MATERIALS WITH FLY ASH ON CHLORIDE INGRESS

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MASTER OF SCIENCE IN CIVIL ENGINEERING

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Summary

Present study investigates the differences in microstructure of cement based materials with fly ash on chloride ingress. Three separate mixtures with and without fly ash substitution were exposed to an accelerated chloride migration test (cf. NT BUILD 492). The tested mixtures included reference specimens of ordinary Portland cement and specimens with 23 and 35% of the binder substituted with fly ash. All specimens were cured for 28 days. Paste specimens were tested using X-ray Fluroscence (XRF), X-ray Diffraction (XRD), Thermogravimetric analysis (TGA), Dynamic vapor sorption (DVS) and a desiccator method. Cup test was performed on mortar specimens to investigate the vapor transport properties.

X-ray diffraction and thermogravimetric analysis indicate the formation of Friedel's salt from monocarbonate and chloride ions. The study shows that formation of Friedel's salt is decreasing with increasing fly ash content. The carbonate phases; calcite, hemicarbonate and monocarbonate are detected from XRD, but no clear correlation between varying fly ash content and carbonate phases could be established. The findings emphasizes the importance of considering fly ash blends as ternary systems, consisting of cement, fly ash and limestone filler, which introduces carbonate phases.

Small deviations between the pore volume distribution of the respective specimens were found based on the sorption isotherms. However, the tendency for all specimens is that chloride exposure refines the pores and thus results in larger volume of finer pores and less volume of bigger pores. This trend was slightly more pronounced for fly ash blends. Transport properties estimated from the cup test show that chloride exposure enhance transport properties of the specimens. The reference specimens made from ordinary Portland cement has a higher water vapor flow rate.

Resumé

Følgende studie beskæftiger sig med mikrostrukturelle ændringer af cement baserede materialer med flyveaske ved kloridindtrængning. Prøver med og uden flyveaske blev indledningsvist udsat for en accelereret klorid migrations test (jf. NT BUILD 492). Referenceprøver blev lavet med Portland cement og i flyveaskeprøverne er cementen substitueret med hhv. 23% og 35% flyveaske af den totale bindermasse. Forudgående for testning hærdede alle prøver i 28 dage. Pastaprøver blev testet med X-ray Fluroscens (XRF), Xray Diffraktion (XRD), Thermogravimetrisk analyse (TGA), dynamisk fugt sorption og en desikatormetode. Et kopforsøg blev foretaget på mørtelprøver for at undersøge fugttransportegenskaberne.

Resultaterne fra røntgendiffraktion og termogravimetrisk analyse viser at monocarbonat reagerer med kloridioner og danner Friedel's salt. Studiet viser at indeholdet af flyveaske reducerer mængden at dannet Friedel's salt. XRD bekræfter tilstedeværelsen af karbonatfaserne; hemikarbonat, monokarbonat og calcit, men der kan på baggrund af dette studie ikke etableres nogen klar sammenhæng mellem flyveaskeindhold og karbonatfaserne. Resultaterne understreger vigtigheden af at betragte pasta med flyveaske som tertiære systemer bestående af cement, flyveaske og kalkfiller. Kalkfiller introducerer karbonatfaserne.

Resultaterne fra sorptionsisotermerne viser kun en lille ændring i porerfordelingen for prøver med og uden flyveaske. Tendensen for samtlige prøver er, at klorideksponering raffinerer porerne, hvilket vil sige at de større porer bliver til flere mindre porer. Kopforsøget på mørtelprøver viser at klorideksponering øger vanddampspermeabilitetkoefficienten og at prøver med flyveaske har lavere koefficienter end referenceprøverne.

Preface

Present study was performed at the Department of Civil Engineering at the Technical University of Denmark. The project proceeded from August 2020 until January 2021. Small difficulties with the intended experimental program were encountered as a consequence of the partial lockdown caused by the COVID-19 pandemic. This thesis is submitted as the final project of the master's degree in civil engineering from the authors, Anne Sofie Hyldtoft Olsen and Rune Malthe Knudsen. The extent of this master thesis is 60 ECTS points equally distributed between the two mentioned students.

We would like to express our gratitude to Associate Professor Marianne Tange Hasholt at the Technical University of Denmark for letting us write our Master thesis with her proficient supervision. Thank you for technical guidance and for detailed and constructive comments throughout this project and throughout our time as students. We would also like to thank Associate Professors, Wolfgang Kunther and Kurt Kielsgaard Hansen for guidance regarding some of the experimental setups. We also wish to express our sincerest thanks to PhD student, Jennifer Anette Canul Polanco at the Technical University of Denmark for invaluable help and guidance beyond the expectable. The time Jennifer has invested in our project is gratefully appreciated. Furthermore, we would like to thank technicians and laboratory staff at the Department of Civil Engineering. During the project we have been in contact with a variety of different people, without whose support and advice this thesis would not have been possible.

Abbreviations

$AFm (C_4 A\bar{S}H_{12})$	$Ca_4Al_2O_6(SO_4)\cdot 14H_2O$ (Monosulfate).
$AFt (C_6 AS_3 H_{32})$	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$ (Ettringite).
C-S-H	Calcium Silicate Hydrate, 3CaO·2SiO ₂ ·4H ₂ O.
C_2S	Dicalcium Silicate, $2CaO \cdot SiO_2$ (Belite).
C_3A	Tricalcium Aluminate, $3CaO \cdot Al_2O_3$ (Aluminate).
C_3S	Tricalcium Silicate, 3CaO SiO ₂ (Alite).
C_4AF	Calcium Aluminoferrite, 4CaO·Al ₂ O ₃ ·Fe ₂ O ₃ (Ferrite).
CC	Calcium Carbonate, CaCO ₃ (Calcite).
CH	Calcium Hydroxide, Ca(OH) ₂ (Portlandite).
$C\bar{S}H_2$	Calcium Sulfate Dihydrate, CaSO ₄ ·2H ₂ O (Gypsum).
FA	Fly Ash.
FS	Friedel's Salt, $Ca_4Al_2Cl_2(OH)_{12} \cdot 4H_2O$.
Κ	Potassium oxide, K_2O .
Ν	Sodium oxide, Na ₂ O.
CBW	Chemically Bound Water.
CCN	Cement Chemical Notation.
DTG	Differential Thermogravimetry.
DVS	Dynamic Vapor Sorption.
LOI	Loss On Ignition.
OPC	Ordinary Portland Cement.
RH	Relative Humidity.
SCM	Supplementary Cementitious Materials.
TGA	Thermogravimetric Analysis.
w/b	Water-to-binder ratio.
w/c	Water-to-cement ratio.
VDD	
XKD NDD	X-Kay Diffraction.
XKF	X-Ray Fluorescence.

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1 Introduction

"We don't have plan B because there is no planet B. We have to work very hard, very seriously and urgently. This is what I am telling, not only as Secretary-General, but as a citizen of this world."

– UN Secretary-General, Ban Ki-moon

 \mathbf{E} ngineering is the activity of applying scientific knowledge to solve everyday problems. However, problems are perpetual and therefore the role of engineers are ever changing. In September 2015, a meeting was held in New York City. 193 nations stood united while facing the challenge of our generation. In unity they overlooked differences and agreed upon adopting the "Post-2015 development agenda" at the United Nations 68th General Assembly [I]. This agenda outlines 17 goals for sustainable development. The aim; is to protect, improve and preserve planet earth for future generations. In the agenda paper, the United Nations emphasize the importance of obtaining these goals without compromising human development and while reducing poverty. Consequently, success rely on green transition, through reducing anthropogenic CO₂-emissions, to diminish the harmful effects of global warming.

 CO_2 -emissions originate from a variety of sources, and the construction industry is one of the main contributors. Nonetheless, awareness has in recent years focused on the production and consumption of cement and cement based materials. The cement industry is anticipated to be responsible for 6-8% of the total anthropogenic CO_2 -emission [2]. Henceforth, the nations of the world placed the civil engineer in an essential position on that September day in 2015. A position where the civil engineer has the responsibility to act and to include the sustainable development goals at the essence of all work. The CO_2 -emissions are problematic and emphasize the importance of solutions that contribute to reduce the carbon footprint associated with cement production [3], [2]. Supplementary cementitious materials present such a solution as they reduce the needed quantity of cement. Research indicates that replacing part of the cement with supplementary cementitious materials as binder can reduce CO_2 -emission with up to 30-40%, without compromising the performance of the concrete [2].

Understanding the properties of supplementary cementitious materials in concrete is important to ensure durability. The aim of the present thesis is to uncover new information regarding fly ash, which is a well known and recognized supplementary cementitious material [4], in order to reduce the environmental impact of concrete. The Post-2015 development agenda outlines 17 goals which are not all of relevance for this study. The work can be related to the sustainable development goals 9 and 11.

- 9th Build resilient infrastructure, promote sustainable industrialization and foster innovation
- $11^{\rm th}$ Make cities inclusive, safe, resilient and sustainable

Fly ash was first proposed in combination with cement in 1914 and has since seen increasing usage all over the world **5**. The material is a bi-product from coal fired power plant, that would otherwise have to be deposited, if not utilized in concrete. The use of fly ash in concrete thus reduces cement consumption and prevent the deposition of potential harmful powder. Replacing cement with fly ash in concrete does however impose new challenges regarding durability. The effect of substitution of fly ash has been studied since it was first proposed, but there are still

gaps in the knowledge about its influence on concrete structures. Especially understanding the relation between microstructure and transport properties is important to predict the behavior of the concrete. The availability of fly ash might decrease as countries switch coal based energy with sustainable sources. However, although fly ash might be an admixture that in the future will belong to the past, the importance of understanding its effects is of high concern in order to gain knowledge about good candidates for supplementary cementitious materials in the future.

This master thesis builds upon a series of previous studies conducted at the Technical University of Denmark. These studies have prompted questions and pointed to problems with high volume fly ash concrete in combination with chloride ingress. The problem with chloride in concrete is an important issue, because the presence of chlorides is inevitable in coastal regions and in cold weather climates where deicers are used to secure roads. Structures not durable to chloride ingress in these areas will have a shorter lifetime on the expense of the climate and the economy.

Chloride ingress in concrete is known not only as a damage mechanism but also as a microstructural altering process **[6]**. Understanding how chloride ions change the microstructure and alter the transport properties is the single most important factor in predicting servicelife for reinforced concrete structures **[7]**. Thus, great value can be transferred if optimization of concrete in this regard can be accomplished. The presence of chloride ions in the pore solution breaks down the passive film that protects the reinforcement bars. This process can cause severe corrosion. Corrosion is a problem because it causes a significant reduction in shear strength and compromise the integrity of the structure. Chlorides in concrete can be present in two ways, either as free ions in the pore solution or as bound ions in the paste matrix. However, the extensive pozzolan reaction in high volume fly ash concretes seems to alter certain features. Especially changes in the chloride ion binding can alter the transport properties **[6]**.

Hasholt et al. (2019) Showed that concrete with high fly ash content had reduced frost resistance compared to the reference ordinary Portland cement specimens. The strength was in the same range and the fly ash blends had a sufficient air content to be classified as frost resistant. This raises concern about the frost resistance of high-volume fly ash blends in chloride exposed environments. The paper concluded that the findings point towards a changed chemical reaction with chlorides when fly ash is present. The study also found that a concrete surface exposed to chloride changed density and permeability. It was suggested that this changed density and permeability would lead to a changed resistance of the exposed specimen. This hypothesis was confirmed by Olsen (2020) D. Here, specimens with 50 % fly ash substitution in the binder performed worse in the accelerated freeze-thaw test even though the compressive strength of the specimens was higher. This further supports that chemical reactions where chlorides take part might influence the frost resistance of fly ash blended specimens.

Wolter (2020) [10] observed that the quantity of Friedel's salt in chloride exposed specimens with and without fly ash was approximately the same. One of the hypotheses in her study was: that if Friedel's salt is formed from monosulfate, the excess sulfate ions would be bound as ettringite. Thus, it was expected that a higher amount of ettringite could be detected in chloride exposed specimens. This hypothesis was not confirmed and especially chloride binding in fly ash blends was concluded to be a topic for further research. The study also found that the ordinary Portland cement specimens after chloride exposure contained more calcium carbonate than specimens without chloride exposure and specimens made with fly ash substitution.

The objective of the present thesis is to examine the microstructure of cement based materials with fly ash before and after chloride ingress. The study is conducted based on the findings of the above mentioned studies. However, accepted and proposed theory on the subject is likewise important to develop a hypothesis and plan the experimental work. Henceforth, the exact hypothesis of this study will be developed in *Section* 3 after the theory section.

2 Theory

"You never get something for nothing."

– Lecturer in concrete technology at DTU

The following chapter concerns the hydration and transport properties of cement based materials, that will be the base for further work in this thesis. In some places in this thesis, cement chemical notation is used to describe chemical compounds and chemical reactions. The Cement Chemical Notation (CCN) used is presented in Table 1.

 Table 1: Cement chemical notation (CCN)
 11, 12.

CCN		A	F	H	K	N	Ē	Ī
Chemical formula	\mid CaO \mid SiO ₂	Al ₂ O ₃	$\rm Fe_2O_3$	H ₂ O	K ₂ O	Na ₂ O	CO_2	SO_3

2.1 Ordinary Portland Cement

Ordinary Portland Cement (OPC) is produced from natural materials with a high content of Calcium Carbonate (CC) such as limestone, chalk, seashells, etc. [4]. During the manufacturing of OPC, the material is transformed into various compounds of calcium. These compounds are called clinker minerals. The four main cement clinker minerals of interest are; alite (C₃S), belite (C₂S), aluminate (C₃A), and ferrite (C₄AF). In the present report the clinker minerals will be called by their cement chemical notation presented here in parenthesis or by their clinker mineral nickname; alite, belite, aluminate, and ferrite. Their exact chemical composition and chemical names can be seen under *Abbreviations*.

When anhydrous Portland cement is mixed with water, the clinker minerals react and form various solid phases [4, 13]. The composition of hydration products depends on the clinker composition of the cement. As an example, the composition of the four clinker mineral in Aalborg Portland Rapid Cement is presented in Table [2].

	C_3S	C_2S	C ₃ A	C_4AF
Content in Rapid Cement [%]	53	20	8	12

 Table 2: Clinker mineral composition in Aalborg Portland Rapid cement 14.

As it can be seen from Table 2, the clinker minerals account for 93% of the content in cement according to "Cement og Beton Håndbogen" 14. In the declaration of performance for Aalborg Portland Rapid Cement 15 it says, that the clinker mineral content account for minimum 95% and up to 100% of the cement. The remaining 0-5% is a combination of added limestone filler and up to 4% SO₃, which is a designation of the gypsum content ($C\bar{S}H_2$). Furthermore, some sodium oxide (N) and potassium oxide (K) may be present in small quantities as a bi-product from the clinker mineral production.

2.1.1 Alite

Alite (C_3S) is the most important clinker mineral in Portland cements [16]. Alite reacts with water and forms the major hydration products: Calcium Silicate Hydrate (C-S-H) and Calcium Hydroxide (CH), where C-S-H is the main contributor to the strength of cement paste [4] (cf. Section [2.3] Hydration Products). The hydration reaction of alite is shown in Eq. (1).

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \tag{1}$$

From stoichiometric calculations, it can be found that alite produces 39 % CH and 61 % C-S-H based on the mass-% [4]. It has been shown that about 70 % of the alite has reacted within the first 28 days and practically all of it has reacted within the first year of hydration [16]. Hence, it is commonly said that alite contributes both to early and late strength development but is essential for the early age strength [17].

2.1.2 Belite

Belite (C₂S) forms similar hydration products as alite, but the difference in the two clinker minerals should be found in their reaction rate and the chemical stoichiometric equations. The reaction is shown in Eq. (2).

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH \tag{2}$$

Belite produces 18% CH and 82% C-S-H based on the mass-% [4]. Hence, one could be tempted to think that belite is a larger strength contributor than alite. This is also true if looking at the ultimate strength of cement paste, but the reaction rate of belite is much slower than for alite. Within 28 days of hydration only approx. 30% of belite has reacted and after 1 year about 90% [16]. The strength development for the four clinker minerals is shown in Figure [1].



Figure 1: Strength development of cement paste 17.

From Figure 1 it can be seen that alite is the largest contributor to the strength of cement paste in the time frame relevant for construction (typically up to 28 days). Even though hydrated belite forms more C-S-H, the hydration time is also an important parameter to take into considerations. Hence, you never get something for nothing. Alite and belite supplement each other and are both important for strength development. Hydrated belite also contributes to the durability of hardened cement paste 4. Since CH can be dissolved in acidic environments, the low content of CH formed from the hydration of belite makes the cement paste less vulnerable to acidic and sulfate waters. This will be elaborated in *Section* 2.3 Hydration Products.

2.1.3 Aluminate

Aluminate (C₃A) can form different reaction products depending on the environment of the hydration **18**. The reaction of aluminate and water is extremely fast and the reaction products; C₃AH₆, C₄AH₁₉, and C₂AH₈ cause flash set without the required strength properties **4**. For this reason gypsum is added in cement. The presence of sulphate ions slows down the reaction, and results in a reaction with a overall pattern similar to that of alite **19**.

Hydration of aluminate with water and gypsum is a multi-step reaction, where aluminate first reacts with gypsum to form ettringite ($C_6A\bar{S}_3H_{32}$). The second reaction takes place when gypsum is used up. Then aluminate reacts with ettringite formed from the first step and forms monosulfate ($C_4A\bar{S}H_{12}$). If there is still more aluminate present and all the ettringite has been used up, a third reaction between the produced CH from the silicate reactions and aluminate may take place. The product of the third reaction is a hydrogarnet phase which has different possible compositions [18]. The most common is C_4AH_{13} which also is the one shown here. The three steps of the hydration of aluminate are shown in Eq. (3)-(5).

Step 1:
$$C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}_3H_{32}$$
 (3)

Step 2:
$$2C_3A + C_6A\bar{S}_3H_{32} + 4H \to 3C_4A\bar{S}H_{12}$$
 (4)

(Step 3:)
$$C_3A + CH + 12 H \rightarrow C_4AH_{13}$$
(5)

As shown in Figure 1 aluminate has a positive effect on early age strength development. The full hydration of aluminate takes several months depending on the temperature and water to binder ratio 20. A variety of different theories explaining the mechanism of retardation of aluminate by gypsum exist 4 [18] [20]. This is still an ongoing investigation, but the bottom line is, that gypsum is added to avoid quick and flash set. It should also be mentioned, that sulfate ions have an accelerating effect on the silicates, and therefore an upper limit of gypsum is a necessity for the cement composition. The optimum gypsum content of cement is determined from a test where maximum strength and minimum shrinkage is the main aim [4].

2.1.4 Ferrite

The fourth clinker mineral in cement is ferrite (C_4AF). Its hydration reaction is similar to the reaction of C_3A , but the reaction rate of C_4AF , when gypsum is present, is slower than for C_3A [20]. The first step of the reaction of ferrite with water and gypsum forms ettringite, but also portlandite (CH), iron hydroxide, and possibly (FH₃) are formed. The difference between the first step reaction of ferrite compared to aluminate is that some of the A are substituted by F, which means that the formed ettringite is no longer on its pure form. Ettringite formed from ferrite hydration is therefore called AFt to allow for this disparity which is shown in Eq. (6). The same goes for the formed monosulfate in the step 2 reaction whereas monosulfate will be entitled AFm shown in Eq. (7). As for aluminate, ferrite does also have the possibility of forming a hydrogarnet phase shown in Eq. (8).

Step 1:
$$C_4AF + 3C\bar{S}H_2 + 30H \rightarrow \overbrace{C_6(A,F)\bar{S}_3H_{32}}^{AFt} + CH + (FH_3)$$
 (6)

Step 2:
$$2C_4AF + C_6(A, F)\bar{S}_3H_{32} + 12H \rightarrow 3C_4(A, F)\bar{S}H_{12} + 2CH + (2FH_3)$$
 (7)

AFm

(Step 3):
$$C_3AF + CH + 15 H \to C_4(A, F)H_{13} + (FH_3)$$
 (8)

2.2 Fly Ash

Supplementary Cementitious Materials (SCM) appear increasingly inevitable as the cement industry advance towards a more sustainable future. Commonly used SCMs include Fly Ash (FA) that is a bi-product from burning pulverized coal. Even as FAs availability is decreasing due to the sustainable transition, it is important to understand its properties, so that knowledge might be transferred to other SCMs.

Fly ash is a fine powder with a particle size in the range of 1-100 µm [21]. Figure 2 illustrates a cluster of fly ash in which spherical, glassy particles are present. The particles are formed under high temperatures inside a coal furnace, followed by rapid cooling as the suspended particles are carried away by exhaust gasses. The solid particles also have a hollow counterpart called cenospheres. Chemically FA consists primarily of amorphous alumio-silicate and varying calcium content. FA might also include a small amount of unburned coal and different metals.



Figure 2: The solid fly ash particle (Left picture taken from 22). (1) Mulite. (2) Exterior glass hull. (3) Vessiles. (4) Interior glass matrix.

Because of the variation in the composition and properties of fly ash, it is necessary to distinguish between different types. In the Western world, the classification of fly ash is primarily carried out in compliance with EN 450 [23] or ASTM C618 [24]. The two major categories in ASTM C618 is class F and C, whereas the hardening properties are the most significant difference. Class C has both pozzolanic and cementitious properties, where class F only has pozzolanic properties. Similarly, the European standard sets a series of criteria for fly ash to ensure quality. Here, the classification in different categories is based on loss on ignition (cf. Section [4.5]). EN 450 does not cover high calcium FAs but requires free and reactive CaO to be below 1.5% and 10%, respectively. Hence, EN 450 conforming fly ashes generally correspond to ASTM Class F.

Due to the calcium oxide requirement in EN 450 [23] the FA can be assumed to contribute to the cement paste as a pure pozzolan reactive. The pozzolan reaction, in which FA reacts with hydration products, is complex due to the unpurified nature of industrial bi-products. Nevertheless, the reaction can be simplified to alumio-silicate and calcium reacting with CH to produce C-S-H and calcium-aluminate hydrates. The reactions are generally slower, thus causing slower strength development. The reaction uses CH from the cement hydration, which would otherwise be vulnerable to depletion during moisture exposure. The reaction can be simplified to Eq. [9] [4].

$$Pozzolan + CH \xrightarrow{Slow} C-S-H$$
(9)

The slower nature of the pozzolan reaction contributes by altering certain features. Firstly, slow reactions lead to slower strength development and heat liberation in the paste. Secondly, the reaction is lime consuming (i.e. consuming CH in the process) which improves durability in acidic environments. Thirdly, the reactions products fill up capillary spaces which refine porosity and improve strength [4]. Table [3] gives an indication of likely outcomes with increasing FA content in the binder. Many of the mentioned properties are interconnected and highly time dependent because of the slower pozzolan reaction.

Table 3: Commonly achieved outcomes with increasing fly ash content in the binder. The table is based on fly ashes that conform to EN 450 or class F fly ash in accordance with ASTM C618 [5, 18, 25, 26].

Input	Outcome				
		Pore tortuosity	-		
	Increase \uparrow	Setting time	-		
		Refined porosity			
	Decrease ↓	Permeability	1		
Increased for ash content		Conductivity	(1)		
increased by ash content		Heat of hydration	2		
		Strength development rate	-		
		Risk of bleeding	-		
		Pore solution pH	3		

- (1) The porosity, permeability, and connectivity of high volume fly ash concrete are highly dependent on the age from casting. At early age, the features may be opposite with high fly ash substitution.
- (2) Due to the slower nature of the pozzolan reaction, the heat of hydration will also be lowered, but it should also be mentioned that the pozzolan reaction is also more vulnerable to temperature differences and is likely to happen very slow at low temperatures.
- (3) Pastes with 40, 50 and 60% fly ash were tested and compared to a OPC-reference. The pore solution was found to drop from pH 13.9 to 12 for 21 days old paste with 60% FA [26].

The pore distribution is important regarding transport properties. Research has found that the development and refinement of pores in fly ash paste is highly time dependent. Manmohan et al. (1981) [27] found that the pore distribution changes when comparing OPC-paste and FA-paste at 28 days and 1 year of age. They showed that the porosity is higher for the 30 % FA blended paste after 28 days, but after 90 days the opposite is observed, except for the very fine pores.

The changes in microstructure are important for the transport properties concerning ingress of chloride and other substances. Research conducted with rapid chloride penetration test (cf. ASTM C1202 [28]) have shown that chloride permeability of a 56 % FA-concrete being nearly double that of a OPC concrete at 28 days. The trend was found to reverse around 180 days of age. This tendency is likely due to the slower nature of the pozzolan reaction. However, altering cement chemistry due to the presence of fly ash regarding chloride ingress and chloride binding is not yet completely understood [5].

2.3 Hydration Products

Ions from dissolved OPC and FA form a series of hydrates (cf. Section 2.2 and 2.1) [IS]. Hydration of OPC can be considered a binary system consisting of the clinker mineral part and the limestone filler part. FA introduces a third part and hence, FA blended pastes can be described as ternary system. The primary hydration products; C-S-H and portlandite (CH) are accompanied by smaller amounts of ettringite (AFt ($C_6AS_3H_{32}$)) and monosulfate (AFm (C_4ASH_{12})) as described in Section 2.1. The limestone filler part contributes mainly with monocarbonate and the FA part forms additionally C-S-H.

2.3.1 Calcium Silicate Hydrate (C-S-H)

Calcium Silicate Hydrate (C-S-H) is the main solid phase in hydrated OPC-paste making up 50-60 % of solid volume **[4]**. C-S-H has a non-definite stoichiometry and is by definition the name of any amorphous or poorly crystalline calcium silicate hydrate **[16]**. The dashes in its name indicate the non-definite stoichiometry. C-S-H is the primary contributor to the long-term strength and durability of the paste, hence the value of its presence **[4]**.

C-S-H is an amorphous gel, that binds aggregates and cement paste together in a strong matrix. During the hydration process, the main amount of mixing water is bound as C-S-H. The nature of this compound contributes greatly to the pore structure and transport properties [18]. The amorphous properties of C-S-H also give good abilities to absorb and bind ions. This process is in general described as very important for chloride ion binding in cement paste [6].

The growth of C-S-H is still an ongoing investigation, where the old protective membrane theory battles the dissolution theory [29, 30, 31]. However, there is consensus about how C-S-H is formed with an inner product and outer product. The formation of C-S-H will be explained briefly in the present section.



Figure 3: Formation of C-S-H. (1) Anhydrous cement grain. (2) Outer product of C-S-H precipitation on the cement grain surface. (3) Outer precipitation of C-S-H in needle shape covering the surface. (4) Inner product of C-S-H formation [18, [29].

In Figure 3 an anhydrous cement grain (1) reacting with water is shown. The dissolved ions in the solution will start to form clusters in the original water filled spaces on the surface of the cement grain, hence the name, outer product (2). This happens within the first hours of reaction and causes the setting of the paste [18]. At some point the cement grain will be covered by outer products (3) and the reaction rate will become slower [31]. Finally, inner products will start to grow in the boundary layer between un-reacted cement and outer products (4). Some minerals (i.e. Mg, Fe, and Si) will not migrate as easily through outer products, hence the Ca/Si ratio of inner products and will be generated at a lower rate than outer products. Despite the initial differences of inner and outer products, it has been shown that over time, the two products will be very similar and C-S-H will behave more like a homogeneous gel with the same porosity.

2.3.2 Calcium Hydroxide (CH)

Calcium Hydroxide (CH), also called Portlandite, occupies up to 20-25% of the solid volume in hardened Portland cement [4]. CH is a hydration product of alite, belite, and ferrite and has a definite stoichiometry that structures in layers and form hard crystals with a hexagonal-prism morphology [4, 16, 18]. Despite the definite structure, CH typically appears in different sizes and shapes dependeing on the space available [32, 18]. It has been shown that CH grows as prisms without the spatial constraints [33]. A representation of CH is shown in Figure [4].



Figure 4: CH formation in available spaces.

Larger CH crystals are non-beneficial since they possess less adhesion capacity due to lower surface area and tend to form oriented structures [4]. CH contributes limited to the mechanical properties but has a large impact on the durability of the material. The durability is altered by lowered alkalinity which depends on the concentration of Na⁺, K⁺ and OH⁻. The high alkalinity of cement paste is mainly obtained from CH [4] [18]. Furthermore, CH is prone to depletion if not consumed elsewhere [34]. Fortunately, CH is a vital component in the pozzolan reaction (cf. Section [2,2]).

2.3.3 AFm and AFt phases

The calcium sulfoaluminate hydrates, such as ettringite and monosulfate typically makes up 15-20% of the solid volume in hardened Portland cement paste [4]. AFm and AFt phases are formed by the reactions of C_3A and C_4AF . These phases is commonly considered not to affect the mechanical properties of concrete [4] [18]. However, in regard to chloride ingress, these phases are very important as they are the primary contributors to the formation of Friedel's salt.

As preliminary outlined in Section 2.1.4, the naming of AFm and AFt takes the disparity between the content of A or F into account, but in the terms, AFm and AFt lies also the different anions (e.g. sulfate, carbonate, aluminosilicate, and chloride) that could be bound in the phase 35. The m and t respectively indicate whether it is a Al₂O₃-Fe₂O₃-mono or tri phase 35, 36.

Eq. (3) and (6) show that ettringite is formed from the hydration of aluminate phases (C_3A and C_4AF). Ettringite is typically the first hydrate to crystallize and the precipitation of ettringite contributes to stiffening, setting and early strength development [4]. Ettringite is formed in the original water filled spaces [32]. After sulfate depletion, the remaining unhydrated aluminate phases will react with ettringite and start to form AFm-phases instead where the increased aluminate ions in the solution can be bound.

A common representation of the AFm-phases is $[Ca_2(Al, Fe)(OH)_6]\cdot X\cdot xH_2O$ where X equals the exchangeable anion and x denotes the affiliated amount of water molecules [35], 36]. The most common AFm phases in concrete are monosulfate and monocarbonate which is usually produced from the AFt phase if calcite is present [37]. If chloride is present some AFm phases can form Friedel's salt, which will be elaborated in Section [2.7.7]. As shown in the reaction equation for aluminate and ferrite (cf. Eq. [4]) and [7]), it is commonly accepted that aluminates and ferrites second step reaction forms monosulfate. However, most cements have an added content of limestone filler, and studies have shown that the presence of limestone filler seems to favor the formation of monocarbonate rather than monosulfate [38].

2.4 Pore Structure

The pore structure of cement based materials comprises a complex network of interconnected pores. The pore system is among the most essential concrete characteristics as it governs moisture transport and sorption along with freeze-thaw durability. Shortly after casting, the formation of pores initiates as the hydration products start to develop and creates interlocked spaces between the solids [4, 39, 18].

The largest pores, called entrapped air voids, can be formed already during casting. These pores do not participate in the moisture transport, since they tend to remain air filled. Their size is in the range of millimeters [4], and they weaken the structure in relation to strength. The entrapped air voids do not promote the transport properties and will not be further refined during hydration [18]. The beneficial pores in concrete are smaller. Entrained air bubbles are usually in the size range of 50-200 µm [4] and these pores are crucial for the freeze-thaw durability. However, since they are also empty, they do not influence the transport properties.

The essential pores for the transport of moisture are even smaller and filled with water. When the paste starts to hydrate, the spaces not filled by solid material will be water filled, and these spaces are called the capillary pores. The capillary pores vary in shape and size in the range of $0.01-5 \,\mu\text{m}$ [4]. The size and shape of these pores depends on the original distance and location of the anhydrous components and the degree of hydration. The transport of moisture and ions (e.g. chloride ions) mainly happens in these pores. Transport of ions can happen in two ways, either through water flow or ionic movement in still water due to diffusion or migration [40].

Additionally to the capillary pores are the interlayer spaces. The interlayer spaces are even smaller and do not have a large effect on the strength nor permeability. Figure 5 illustrates a possible visualization of the pore system for cement paste. The large areas between C-S-H gel can be considered capillary pores while the C-S-H spikes themselves can overlap and form interlayer spaces.



Figure 5: Pore structure.

However, when aggregates are added into the mix, a zone binding the aggregates to the paste is formed. This zone is called the Interfacial Transition Zone (ITZ), and its composition is different than for pure paste. ITZ has a higher porosity and a lower content C-S-H [4]. Nevertheless, this zone will not be extensively examined in this thesis but is of interest for the transport properties. A study carried out by Linderoth (2020) [18] found that the ITZ zone should have little effect on the sorption properties. This theory was supported by Neville (2011) [11].

Blending FA into the binder changes the pore system. FA is known to increase the tortuosity of the pore system. This is due to the fact that C-S-H formed by the pozzolan reaction is different from C-S-H formed by OPC. Hence, it is expected that increasing FA in the binder will refine the pore structure and reduce the connectivity **TS**.

2.5 Water in Cement Paste

Classification of water in cement paste is typically based on the degree of ease with which it can be removed from the system [4, [11]. Sorption isotherm is the relation between water content and relative humidity under isothermal conditions. In desorption, the relative humidity determines which pores that will be emptied. Smaller and smaller pores are emptied as the RH is lowered.

The easiest water to remove from the system is the capillary water. The capillary water is present as free water in the capillary pores. This water is not affected by the attractive force from the solid surface of the hydration products [4]. Contrary to the capillary water is the adsorbed water that is under the influence of attractive forces from the solid products. The adsorbed water, close to the solid surface, requires lower RH to remove from the system. A large part of the adsorbed water is lost when hydrated cement paste is dried to 30% RH.

As shown in Figure 5 the overlapping of C-S-H spikes forms interlayer spaces. These spaces are filled with water called interlayer water. This water is difficult to remove but it is possible if the paste is dried below 11 % RH. The C-S-H gel shrinks considerably if this water is removed 4.

Lastly, is the chemically bound water. Water is chemically bound in cement paste as a result of the hydration process in which the clinker minerals react with water particles. Water is often present in excess amounts, so it is often not a constraint for the reaction itself. It is generally excepted that the chemically bound water is non-evaporable and that it can only be removed by heating [4, 11]. Even though the chemically bound water is mainly removed by temperature increases, Linderoth (2020) [18] suggests that low RH can also effect part of the C-S-H, AFm and AFt phases. Hence, it is difficult to distinguish between which type of water, that is removed at the different RHs. The estimation of chemically bound water depends on the degree of hydration and the method used to remove the evaporable water (cf. Section [4.2]) [18].

Adding fly ash to the paste will affect the amount of chemically bound water especially the content at early age, as the pozzolan reaction is slow and does not bind much water except for the water bound in CH. The present project analyzes 28 days old pastes. It is therefore expected, to see less bound water in the FA paste specimens.

2.6 Moisture Transport

Moisture transport can be defined as the process in which water passes through the pore structure **[18]**. The process can be roughly divided into two; Liquid water transport because of pressure difference, described by Darcy's law, and water vapor transport because of difference in vapor content, described by Fick's law **[41]**, **[18]**. The dominant transport process is determined by the moisture conditions. This concept is shown on Figure **[6] [18]**.



Figure 6: Possible moisture transport scenarios. (1) Pure liquid flow, (2) Pure vapor transport and (3) Combination of water flow and vapor transport **18**.

Figure **6** outlines possible transport mechanisms in the pore structures. The exact mechanism is difficult to assess as the different connectivity and tortuosity is likely to affect the transport. However, it is likely a combination of liquid transport and vapor diffusion (cf. Figure **6**) **[18]**. Despite this, it is generally accepted to only apply Fick's law when assessing the transport, since the boundary conditions for a traditional situation often rely on vapor pressure only **[41]**.

Investigation of moisture transport becomes increasingly interesting for FA blends. Sorption isotherms only asses the pore distribution but do not give information about the connectivity and tortuosity. FA blends are known to have less connectivity and larger tortuosity, which influence the transport properties. The pozzolan reaction of FA does not significantly fill pore volume but rather refine it. The exact reason for this is still to be fully understood **[18]**.

2.7 Chloride Ingress

Chloride ingress is essential for predicting the service life of reinforced concrete [7]. Free chloride ions can break down the protective films at reinforcement bars, which can cause corrosion of the reinforcement bars [4]. Chloride-induced corrosion is a recognized durability problem for reinforced concrete exposed to deicers and seawater [6]. Dissolved chloride ions in these areas are likely to penetrate the concrete, thus shortening the service life [42] [7] [6]. The main transport mechanisms of chlorides are diffusion, capillary suction, permeation, and migration [7]. Diffusion is induced by the concentration gradient, capillary suction due to the capillary action, permeation is induced by the pressure gradient and migration happens due to an electrical potential gradient [43].

Another important factor in chloride transport is the binding process in which ions are bound in the cementitious material. Binding reduces the number of free ions in the pore solution and alters the transport properties. Hence, understanding chloride binding is important for service life predictions, and precise modeling can potentially save money **6**.

2.7.1 Chloride binding

Free Cl⁻-ions in the pore solution are accompanied by chloride binding products. Literature suggests three main binding products: Absorption of Cl⁻ in the C-S-H phase, the formation of Friedel's salt $(Ca_4Al_2(OH)_{12}Cl_2 \cdot 4H_2O)$, and to some extent the formation of Kuzel's salt $(Ca_4Al_2(OH)_{12}Cl(SO_4)_{1/2} \cdot 5H_2O)$ [6]. The formation of Kuzel's salt is rarely observed, unlike Friedel's salt that seems inevitable.

Friedel's salt can theoretically be formed through several reactions. The most recognized is the transformation of monosulfate as seen in Eq. (10). This reaction causes smaller solid volume and thus increased porosity [10]. It can be seen in Eq. (10) how sulfate ions $(SO_4^{2^-})$ are released into the pore solution. The free sulfate ions will react with more monosulfate if portlandite $(Ca(OH)_2)$ is present and form ettringite $(Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26 H_2O)$.

$$\underbrace{\operatorname{Ca_4Al_2SO_4(OH)_{12} \cdot 6H_2O}_{\text{Friedel's salt}} + 2\text{Cl}^- \rightarrow \underbrace{\operatorname{Ca_4Al_2(OH)_{12}Cl_2 \cdot 4H_2O}_{\text{Friedel's salt}} + \text{SO_4}^{2-} + 2\text{H}_2O \qquad (10)}_{\text{Friedel's salt}}$$

The addition of limestone filler in OPC (i.e. up to 5% Aalborg Portland Rapid cement) also introduces monocarbonate. The willingness of monocarbonate to bind chlorides is disputed, but multiple articles point to the difficulties of incorporation Cl^- in monocarbonate phases [44, 6]. Ipavac et al. (2013) [44] found decreasing chloride binding with increasing limestone filler and attributed it to these difficulties. Shi et al. (2017) [45] did, however, find evidence for the phenomenon by thermogravimetric analysis. The possible reaction would look like Eq. ([11]).

$$\underbrace{\overbrace{\text{Ca}_4\text{Al}_2\text{CO}_3(\text{OH})_{12}\cdot5\text{H}_2\text{O}}^{\text{Monocarbonate}} + 2\text{Cl}^- \rightarrow \underbrace{\overbrace{\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{Cl}_2\cdot4\text{H}_2\text{O}}^{\text{Friedel's salt}} + \text{CO}_3^{2-} + \text{H}_2\text{O}}_{(11)}$$

The free carbonate ions (CO_3^{2-}) could be problematic as they can initiate carbonation of the paste. It is also likely that Friedel's salt can be formed from strätlingite like phases $(Ca_4Al_2SiO_2(OH)_{10}\cdot 3H_2O)$ which would produce free SiO_2^{2-} [45]. Another interesting yet non-understood phase is mullite $(3Al_2O_{32}SiO_2)$. Mulite comes from fly ash and together with Cl⁻ and calcium it is likely to produce Friedel's salt.

Literature regarding chloride ingress in high volume fly ash concrete and quantification of how chloride is bound are sparse. However, studies have been carried out. Thomas et al. (2011) [46] examined different SCMs, including FA, and found that SCMs significantly alter the chloride binding capacity of cement paste. Included in this study were specimens with 25 % FA substitution in the binder and with w/b = 0.5. They found that fly ash blends showed increased binding of chlorides, but they were not able to establish a relationship between alumina content and the binding capacity. The lack of correlation was attributed to the fact that aluminate-silicate crystals like mullite (cf. Figure 2) might not be able to react with Cl^- ions. The study also suggests that if free chlorides are lost through leaching a portion of the bound chlorides is likely released. However, part of the binding is irreversible.

It is generally recognized that fly ash reduces the permeability of concrete through a refinement of the pore structure. The refinement of pores contributes to lower migration rate and penetration depth [5]. Jain et al. (2009) [25] proposed that the tortuosity altering nature of FA will influence the ingress process. This alteration might also influence the binding process. Curing age is likewise an important factor. FA pastes have been found to cause higher chloride ingress at early age due to the slow pozzolan reaction [47].

The other important binding process is the absorption of Cl⁻ into the C-S-H phase. This is recognized to make up a considerable portion of the total binding. However, the effect on the gel itself is not properly understood. The absorption could cause transport altering properties in the paste. Also, the formation of extra C-S-H in FA blends can increase binding capacity as the gel can absorb more chlorides [46] [25]. In general terms, it can be expected that the amount of bound chlorides increases in FA blends.

3 Hypothesis

"If we knew what it was we were doing, it would not be called research, would it?"

- Albert Einstein

I n continuation of the findings obtained by studies of Hasholt et al. (2019) [8], Wolter (2020) [10], and Olsen (2020) [9] (cf. Section [1]), the scope of this study is to further investigate how chlorides are bound in cement paste. Furthermore, investigating how the substitution of fly ash in the binder alters the transport properties and microstructure of the paste in comparison with cement paste without fly ash.

The hydration reactions of OPC and the pozzolanic reaction of fly ash, both form the main solid phase of the binder; C-S-H. However, fly ash has a different chemical composition than OPC, and the pozzolanic reaction uses CH to form C-S-H. Fly ash blended pastes will consequently also have a different composition and properties, but how these differences will manifest if the specimens are exposed to chlorides is not well understood. An important piece in the puzzle is the understanding of how chloride is bound in OPC and FA blends. The changed chemical composition is one thing that might shed some light on the issue. A more physical approach is to look directly at the differences in transport properties. Based on previous findings and the generally accepted theory within this topic, the following hypotheses of this study are established.

- 1. When cement paste is exposed to chlorides, free chlorides react with monocarbonate and form Friedel's salt, whereby carbonate ions are released. The carbonate ions take part in new reactions. It is the reaction of the carbonate ions that are different, depending on if fly ash is present in substantial amounts.
- 2. Chloride ingress will alter the microstructure of hardened paste differently, depending on whether the specimen contains fly ash or not.

In this project, the hypotheses will be investigated by using the following test methods. The rapid chloride migration test NT BUILD 492 [48] will be used for chloride exposure. In addition, the current during the NT BUILD 492 test will be logged continuously throughout the experiment, to see how the resistance of the specimens progresses. Hydration of the specimens will be stopped prior to some of the experiments to obtain results comparable to the literature of different samples at the same age. Compounds in paste samples and anhydrous compounds will be estimated using fluorescent X-ray and phases in paste samples and anhydrous compounds will be estimated using X-ray diffraction. The thermogravimetric analysis will also be used to identify different phases and to identify the amount of chemically bound water. Two different methods to obtain sorption isotherms will be executed to obtain knowledge about the pore structure, and the moisture transport properties will be examined by a cup test.

The theory behind each used method will be explained in Section $\frac{1}{4}$ and the actual materials used and methods performed will be elaborated in Section $\frac{5}{5}$.

4 Methodologies

"Before anything else, preparation is the key to success" – Alexander Graham Bell

The methods performed and the materials used will be explained in *Chapter*. The intended purpose of this chapter is to provide additional background knowledge about the methods. The relevant equations will be shown, and the choice of methods will be argued.

4.1 Chloride Ingress

A variety of test methods for chloride ingress exist. The methods are divided into; long- and short-term methods. Different tests have both advantages and disadvantages, and the choice of method should be based on the experimental situation [49]. Long-term methods are time consuming but imitate natural conditions well. Short-term methods are widely used because of the reduced duration. The two commonly used short-term methods are ASTM c1202: Rapid chloride permeability test [28] and NT BUILD 492: Rapid migration test [48]. Both use an electric field to migrate chloride ions into the specimens and they are both widely used in the literature [25, 5, 47]. In the Nordic countries, there is a tradition of using NT BUILD 492 [48].

NT BUILD 492 [48] states that results should be expressed in means of the non-steady-state migration coefficients, D_{nssm} [$\cdot 10^{-12}$ m²/s]. This coefficient is used to assess the migration when chloride diffusion is caused by an external electrical field and can be calculated with Eq. (12).

$$D_{nssm} = \frac{0.0239 \cdot (273 + T) \cdot L}{(U-2) \cdot t} \cdot \left(x_d - 0.0238 \sqrt{\frac{(273 + T) \cdot L \cdot x_d}{U-2}} \right)$$
(12)

Where, T [°C] is the average temperature of the initial and final temperature of the analyte solution, L [mm] is the thickness of the sample, U [V] is the applied voltage, t [hr] is the test duration, and x_d [mm] is the measured penetration depth [48]. Higher coefficients mean that the chlorides migrate more easily through the sample. The measured current, I [A] can be converted into resistance by Ohm's law. Furthermore, the resistance R [Ω /mm] can be normalized with the length of the specimen [9], as shown in Eq. (13).

$$R = \frac{U}{I}/L \tag{13}$$

Chloride concentration in the ingress zone decreases gradually from the exposed surface. In Figure 7 by Tang et al. (1995) 50 a comparison of the theoretical and experiment ingress zone is shown. The experimental ingress zone shown in Figure 7 is obtained from a study made by Andrade et al. (1994) 51. A detectable limit of Cl^- is estimated from a study by Otsuki et al. (1993) 52. Otsuki et al. found that the color change of 0.1 M gNO_3 happens when Cl^- content is above 0.15% by weight of cement. The limit is converted to suitable measures from the relevant cement content in the study, and with the assumption that the concrete density is 2400 kg/m^3 . The detectable limit is shown together with the theoretical and experiment ingress zone in Figure 7.



Figure 7: Theoretical and experimental Cl^- distribution 50 and estimated detectable limit.

The examination of the color change of 0.1 M AgNO_3 , finds that concrete specimens exposed to NT BUILD 492 48 would have a chloride content of 0.01875% by mass of concrete.

4.2 Arresting Hydration

When studying hydrated paste one of the most important parameters affecting its microstructure is the pretreatment and preparation of the sample [53]. The two largest concerns are how the sample is cured and how the hydration process is stopped. In the following, the main focus will be on how hydration is stopped since curing is more well regulated by the DS/EN standards.

A variety of different methods such as oven drying, freeze drying, and solvent exchange methods can be used to stop the hydration. Zhang et al. (2011) [54] conducted a study to compare the different methods for arresting hydration of paste. They found isopropanol exchange followed by ambient drying was the best known method to preserve the microstructure with minimal effect on the composition of paste. However, they also emphasize that there is no known drying procedure, that will inhibit any chemical and/or physical effect.

The advantage of solvent exchange is that it preserves the chemically bound water in the hydrates, preserves the microstructure, and removes soluble ions from the pore solution [55]. Solvent exchange, preferable with isopropanol, is the suggested pretreatment for XRD, MIP, and TGA, but for TGA it is best followed by a replacement of isopropanol with diethyl ether, due to lower boiling point and therefore minimizing the amount of organics absorbed to the hydrates [55]. After stopped hydration, the desired analysis should be performed as quickly as possible to avoid part of the hydrates being destroyed [55].

4.3 X-Ray Fluorescence

X-Ray Fluorescence analysis (XRF) gives an indication of the chemical composition of the sample. The technique uses X-rays to bombard the compounds' inner shells, thereby removing an electron. Electron shell theory then ascribes that an electron from the other shell will jump to fill the missing spot, and in the processes, it emits a unique signal. The signal can be detected and compared to existing data to determine bulk composition [56]. The limitation of XRF is that it only gives the chemical composition of the analyzed sample and not the mineral phases. Moreover, most XRF-instruments have limited ability to detect the first 11 elements in the periodic system. For geologic samples, where metals are usually present in their oxidized state, this will cause the total detectable mass to be lower than 100 % mainly due to the absence of detectable oxygen. Some XRF-instruments use a configuration with a quantification algorithm that takes this into account by stoichiometric calculations of the oxides. Others only give the output of the detected compounds, hence the analyst must convert the detected element to its oxidized compound manually.

4.4 X-Ray Diffraction

X-Ray Diffraction (XRD) is one of the most prominent techniques for analyzing crystalline materials like cement. The method utilizes that crystalline structures diffract X-rays in different angles and hence produces a sample diffractogram 57.

The first step of XRD analysis is phase identification. Here, an obtained diffractogram from the anhydrous powder sample is compared to a database, to identify known phases. The position of peaks can be related to the symmetry and unit cell size of each phase. Different intensities in a complex diffractogram are relatable to the mass percentage of each phase. This mass percentage can be estimated with the Rietveld method.

Rietveld uses the least square method to reduce the difference between the measured diffractogram and the calculated diffraction profile. This can be illustrated in a difference plot which is a representative of the precision of the fit. Parameters, like the goodness of fit and the weightedprofile R-factor, are likewise indications of the precision. However, no threshold values exist, and the visual fit is still an important part of the Rietveld analysis [58]. Especially when it comes to confirming that all peaks are identified. In a Rietveld analysis the intensity at location i, is summed over the p phases in the mixture, and k presents the plane indices (h,k,l). The method can be described with Eq. (14) as done by Saoüt et. al. (2010) [58].

$$y_{ci} = \sum_{p} \left[S_p \sum_{K} p_K L_K \left| F_K \right|^2 \Phi\left(\Theta_{iK}\right) P_K \right] + y_{cbi}$$
(14)

Where, y_{ci} is the calculated intensity of the i^{th} step, S_p is the scale factor, p_K is the multiplicity factor, L_K is the Lorentz and polarization factor, F_K is the structure factor, Φ is the profile function, P_K is the preferred orientation function and y_{cbi} is the calculated intensity of the i^{th} step of the background 58. Eq. (14) is minimized using least square refinement by Eq. (15).

$$\sum_{i} \frac{(y_i - y_{ci})^2}{y_i} \tag{15}$$

The amorphous content of a specimen can be determined using the external standard method, also known as the G-factor method. A well defined crystalline material (e.g. corundum) can be used to establish the amorphous content for refinement of other samples. Afterwards, the G-factor can be calculated with (16).

$$G = \frac{S_s \rho_s V_s^2 \mu_s}{C_s} \tag{16}$$

Where, S_s is the scale factor of the standard, ρ_s is the density of the unit cell, V_s is the unit cell Volume, μ_s is the Mass Attenuation Coefficient (MAC) and C_s is the standards crystalline percentage. The G-factor can be used to rescale the crystalline percentage with Eq. (17).

$$w_j = \frac{S_j \rho_j V_j^2 \mu_j}{G} \tag{17}$$

Where the j subscript stands for the phase to be rescaled. The rescaled weight percentage also needs to be adjusted for the bound water. This approach will be the same as for TGA results and will be explained in Section 4.5.

4.5 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) can be used to determined the chemically bound water in cementitious paste. It is also possible to determine certain phases based on the temperature zone in which they release H_2O or CO_2 [13]. TGA is done by placing the sample in a chamber and gradually raising the temperature while measuring the mass loss under a constant flow of nitrogen.

The mass loss as a function of temperature is called the TG-curve, and from this graph, the total amount of CBW can be determined as the specimens total mass loss at 600°C. In this temperature range phases decompose into H₂O. For temperatures above 600°C it is expected that phases decompose into CO₂.

Differential Thermogravimetry (DTG) is the derivative of TGA. The peaks of a DTG graph at different temperatures can be assigned to different thermal reactions of respective minerals and hydrates **53**. Dehydration, decarbonation, and oxidation are generally associated with a mass change, that can be seen on a DTG-curve. This is a powerful tool to see how small changes in a cementitious system (e.g. chloride exposure or substitution of SCM) will affect the composition of solids. In Figure 8 the DTG curve of typical solids for cementitious systems is shown **53**.



Figure 8: DTG of typical solids for cementitious systems from Lothenbach et al. 53.

It is shown at which temperature the respective phases decompose. For example, portlandite dehydroxylates $(Ca(OH)_2 \rightarrow CaO+H_2O)$ at approx. 460 °C and main water loss of ettringite is around 100 °C. The AFm phases (monosulfate, monocarbonate, Friedel's salt, and strätlingite) have a layered structure with loosely bound water which typically can be seen on the DTG as several peaks. On Figure 9 the DTG curves for the AFm phases are shown separately 53. From Figure 9 it can be seen that the main peaks of monocarbonate and monosulfate are very similar, and care should be taken when trying to distinguish between the two phases.

Even though the peaks shown in Figure 9 and 8 look definite for each of the phases they represent, one could imagine that when all or some of these peaks are present in a cementitious paste sample, the demarcation of each phase becomes more difficult, and therefore care should be taken if trying to quantify each phase. Lothenbach et al. (2016) 53 suggest that quantification is limited to gypsum, portlandite, and calcite.



Figure 9: DTG of AFm phases from Lothenbach et al. 53

As shown on Figure S portlandite decomposes between 400 and 500 °C. The mass loss (ML_{TGA:400-500}) in this temperature range is due to the evaporation of water, which can be used to calculate the amount of portlandite present. This can be done from Eq. (18) where the molar masses of portlandite ($M_{Ca(OH)_2}=74$ g/mol) and water ($M_{H_2O}=18$ g/mol) are used [53].

$$m_{\rm Ca(OH)_2} = M L_{\rm TGA:400-500} \cdot \frac{M_{\rm Ca(OH)_2}}{M_{\rm H_2O}}$$
 (18)

In the same way the amount of calcite (CaCO₃) can also be estimated from the DTG curve. CaCO₃ decomposes to CaO and CO₃ above 600 °C. The mass loss above 600 °C (ML_{TGA:>600}) can together with the molar mass of CaCO₃ ($M_{CaCO_3}=100 \text{ g/mol}$) and CO₂ ($M_{CO_2}=44 \text{ g/mol}$) give an estimation of the (CaCO₃) content shown in Eq. (19).

$$m_{\rm CaCO_3} = M L_{\rm TGA:>600} \cdot \frac{M_{\rm CaCO_3}}{M_{\rm CO_2}} \tag{19}$$

Furthermore, several studies have used TGA and DTG to determine the amount of Friedel's salt [6, 45]. In Figure 9 it can be seen that Friedel's salt (FS) have three peaks. The peak around 230-380 °C corresponds to the mass loss of the main water layer [6]. Due to the crystal structure of FS there are 6 water molecules in the main water layer, hence a factor 6 is introduced in the calculation of the amount of FS, shown in Eq. (20). Additionally, a baseline made from a non-chloride exposed sample is introduced when determining the mass loss due to FS ($M_{\rm TGA:FS}$). In Eq. (20) the molar masses of FS ($M_{\rm FS}$ =561.3 g/mol) and water ($M_{\rm H_2O}$ =18 g/mol) are used.

$$m_{\rm FS} = \rm ML_{TGA:FS} \cdot \frac{M_{\rm FS}}{6 \cdot M_{\rm H_2O}}$$
(20)

Sample mass of the solid fraction is changing during hydration. Therefore, the results from Eq. (18), (19) and (20) need to be normalized with Eq. (21) so they are expressed as g per 100 g paste. It is normalized with the total mass loss from 0-600 °C based on the TGA and w/b.

$$m_{\text{norm}} = \frac{m}{ML_{\text{TGA:>600}} \cdot (1 + \text{w/b})}$$
(21)

It should be mentioned, that there are many factors that could influence the result from TGA. Some of the important factors are the heating rate, the amount of solid, gas flow rate, and the pretreatment of the sample. Therefore, it is commonly not a good idea, to compare peak intensities and mass estimations of different phases obtained in one laboratory with results obtained elsewhere. When doing TGA, a golden rule is to do the same procedure in an almost neurotic way. Lothenbach et al. (2016) **53** suggest a heating rate of 10-20 °C/min and a purging gas rate of 30-50 ml/min. When analyzing anhydrous compounds a sample mass of 20 mg is suggested. For paste samples with more phases, a sample mass above 50 mg is recommended.

TGA is also used to determine the Loss on Ignition (LOI) of anhydrous components. LOI is the mass loss percentage when a cementitious material is heated to 950 °C [59, 60]. Low LOI is a part of the specification for the cement to avert too high amounts of carbonate minerals e.g. limestone filler (CaCO₃). Water also contributes to higher LOI as it can be bound in for example gypsum (CaSO₄·2H₂O) and released when heated. If free lime (f-CaO) in cement is exposed to moisture prior to intentional hydration it can hydrate to form Ca(OH)₂, which may absorb CO₂ and form CaCO. This will also lead to higher LOI.

4.6 Sorption Isotherm

Water vapor sorption isotherms is an acknowledged method for studying the pore structure of cement based materials [61]. Through sorption isotherm one is able to determine the water as a function of (RH). The most common two methods are the desiccator method and the sorption balance. The difference in the two methods is both the equipment and the time required, but the principle of the two methods is the same. However, a study by Linderoth (2020) [61] found a substantial difference of up to 10% between the two methods. The difference was pronounced within the range of 50-30% RH.

Saturated salt solutions have the ability to provide air of definite relative humidities, which is the principle of the desiccator method describe in DS/EN ISO 12571 [62]. When the saturated salt solution is placed in a desiccator, the RH of the air is determined by which salt that is used. Having more desiccators with samples from the same specimen inside exposed to different relative humidities and weighing their mass until equilibrium is obtained, is the basics of the desiccator method. The method is time consuming and, as the RH for each salt is also sensitive to the temperature, the test setup should be done in a climate chamber at a known temperature.

A Dynamic Vapor Sorption (DVS) balance is another well accepted method to determine the sorption isotherm. The benefits of this method is that it is less time consuming and able to determine both a desorption isotherm and an adsorption isotherm graph. However, care should be taken by interpreting the results of an adsorption isotherm, since drying from a prior desorption measurement will alter the structure and composition of the tested sample.

The DVS equipment gradually increases or decreases the RH inside a chamber where a sample is placed, and the mass is then monitored continuously for the different RHs. The beneficial shorter measurement time of the DVS also comes with a downside. Due to this, the mass equilibrium of the sample is generally not achieved for all RHs. To consider this, an exponential curve fitting could be done. However, it should be mentioned that the exponential trend is only applicable for very high and low RHs. For the intermediate RHs complete sorption kinetics are slower and does not follow an exponential trend **[IS]**.

4.7 Cup Test

Based on the assumption that the transport mechanism is solely based on Fick's first law, it can be examined through a cup test. The cup test investigates moisture transport properties and can be an important supplement to the sorption isotherms. The test method is often used and exist in many different forms [41] [63] [64] [65].

In this thesis the experiment is based on the setup described by Hansen (2015) [65] and DS/EN ISO 12572 [63] (cf. Section [5.8]). The final mass change rate for each successive weighing is calculated as the average of the last 5 measurements with Eq. (22) and (23). The cup test can be considered in equilibrium when each of the 5 measurements is within $\pm 5\%$ of G.

$$G = \frac{\sum_{n=1}^{5} \frac{(m_2 - m_1)}{(t_2 - t_1)}}{5} \tag{22}$$

$$g = \frac{G}{A} \tag{23}$$

Where, G [kg/s] is the average mass change rate, m_1 and m_2 are the masses at the given time t_1 and t_2 in respectively [kg] and [s], A [m²] is the exposed surface area of the sample, and g [kg/(m² · s)] is the water vapor flow rate. Due to the nature of the experiment (cf. Section 5.8), the water vapor flow rate needs to be corrected for masked edges with Eq. (24) and (25).

$$g_{me} = \frac{4 \cdot d}{\pi \cdot S} \cdot \ln\left(\frac{2}{1 + \exp\left(\frac{-2\pi \cdot b}{d}\right)}\right) \cdot g \tag{24}$$

$$g_{corr} = g - g_{me} \tag{25}$$

Where, g_{me} [kg/(m² · s)] is the flow rate from masked edged, d [m] is the specimen thickness, S [m] is the hydraulic diameter of the cup opening, b [m] is the width of the masked edges and g_{corr} is the corrected water vapor flow rate. The corrected g is used in Eq. (26) to calculate a new G for further calculations.

$$G_{corr} = g_{corr} \cdot A \tag{26}$$

The water vapor pressure difference across the specimen is calculated with Eq. (27) and (28).

$$p_s = e^{23.5771 - \frac{4042.9}{T - 37.58}} \tag{27}$$

$$\Delta p = \left(\frac{RH_1}{100} \cdot p_s\right) - \left(\frac{RH_2}{100} \cdot p_s\right) \tag{28}$$

Where, p_s [Pa] is the saturation vapor pressure, T [K] is the average measured temperature, RH_1 and RH_2 is the relative humidities on the two sides of the specimen [%] and Δp [Pa] is the water vapor pressure difference across the specimen. The water vapor permeance can be calculated and corrected for the air layer below the specimen. This is done with Eq. (29).

$$W_{corr} = \frac{1}{\frac{A \cdot \Delta p}{G_{corr}} - \frac{d_s}{\delta_s}}$$
(29)

Where, W_{corr} [kg/(m²sPa)] is the the water vapor permeance for the sample alone, d_s [m] is the thickness of the air layer and δ_s is the water vapor permeability coefficient for stagnant air in this thesis assumed to be $195 \cdot 10^{-12}$ kg/(m · s · Pa). The water vapor permeability coefficient for the material can be found with Eq. (30).

$$\delta = W_{corr} \cdot d \tag{30}$$

Finally, the water vapor flow rate can be calculated by using Fick's first law for a one dimensional diffusion, as shown in Eq. (31).

$$g_{total} = \delta \cdot \frac{\Delta p}{d} \tag{31}$$

5 Materials and Methods

"Explaining your work in a concrete way is an achievement within itself."

– Anne Sofie Hyldtoft Olsen

A variety of tests were performed to examine the difference of using pure Ordinary Portland Cement (OPC) and Fly Ash (FA) substitution in the binder. Three different pastes and two mortar mixtures were cast. Reference specimens were cast only with OPC as binder and are named OPC. The specimens with fly ash substitution are named FAXX, where XX is the percentage of fly ash in the binder (cf. Section 5.1). Some specimens were also exposed to chlorides. As will be described later in Section 5.2 the specimens were cut to obtain a nonchloride exposed part (I), and a part that has been exposed to chlorides (II) in a chloride migration test. An overview of the different tests and naming is shown in Table 4.

Table 4: Overview of different test performed on respective specimens. *Cup test was performed on mortar samples (cf. Section 5.8).

ID	$Stored in Ca(OH)_2$	Migration test	XRF	XRD	TG_A	Sorption isotherm: Desiccator	Sorption isothern: DVS	dIW	$C_{up} t_{est} \star$
Paste samples									
OPC (\mathbf{I})	×		×	×	×	×	×	×	
$OPC(\mathbf{II})$		×	×	×	×	×	×	×	
FA23 (\mathbf{I})	×		×	×	×	×	×	×	
FA23 (II)		×	×	×	×	×	×	×	
FA35 (I)	×			×	×		×		
FA35 (II)		×		×	×		×		
Mortar samples	3								
M OPC (\mathbf{I})	×								×
M OPC (II)		×							×
M_{FA23} (I)	×								×
M_FA23 (II)		×							×

From Table 4 it can be seen that a specimen of OPC and FA23 with and without chloride exposure are investigated for each test. All paste specimens except the ones used for sorption isotherms were processed in order to stop hydration prior to XRD, TGA, MIP, and XRF. The procedure of stopping the hydration is explained in *Section* 5.3

Furthermore, additional paste samples with increased FA content (FA35) were examined by TGA, XRD, and DVS. Due to the time limitation of this project is was only possible to execute the full experimental program on FA23 specimens, even though the effects of higher fly ash substitution are of great interest. Sorption isotherms on OPC and FA23 specimens were done both by the desiccator method and with a dynamic sorption balance (DVS).

The mortar specimens were solely cast to investigate moisture transport properties more extensively. Since the main experimental program was done on paste specimens, the forthcoming sections will contain information about paste specimens. The mixing, casting, and pretreatment of the mortar samples will be introduced in *Section* 5.8.

In the forthcoming sections, readers should be familiar with the indexation. Specimens not exposed to chloride will be referred to as " \mathbf{I} ", and specimens exposed to chloride during the migration test will be referred to as " \mathbf{II} ".

5.1 Composition, Mixing and Casting

In the current study, the main objective was to investigate the difference between concrete with and without fly ash. Therefore the constituents were kept to a minimum to avoid disturbance from other admixtures or aggregates. It has previously been demonstrated that aggregates have little effect on the pore structure [39], hence the pore structure of concrete could be investigated on paste samples. The constituents used for the paste are listed in Table [5].

Material	Brand Name	Description	Density $[kg/m^3]$
Cement	Aalborg Portland	RAPID CEM I 52.5 N (Certified i.a.w. [66])	3140
Fly Ash	Emineral	EmiFlyveAske B4 (Certified i.a.w. [23])	2300
Water	-	Demineralized water	1000

Table 5: Information about used materials.

The chemical composition of the used materials provided by the manufactures has previously been presented by Hasholt et al. 8 and is shown in Table 6.

Compound	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O	SO_3	Na ₂ O eq	Cl^{-}	LOI
Cement Fly Ash	$64.5 \\ 3.9$	19.7 56.4	5.2 21.6	$3.8 \\ 5.4$	$3.3 \\ 0.6$	0.6 2.9	$\begin{array}{c} \leq 0.05 \\ \leq 0.05 \end{array}$	$ \begin{array}{c c} 1.7 \\ 2.1 \end{array} $

Table 6: Chemical composition of powders [% of powder mass].

Two different paste mixtures were designed with and without fly ash (FA). The amount of fly ash substitution was chosen based on other studies [25], [8], [39], [6], whereby it was concluded that substitution of FA by 23 % of the binder would be sufficient to see a considerable difference between OPC paste and paste with FA. However, since OPC and FA23 showed many similarities, a paste consisting of 35 % FA of the binder content, was also designed to investigate the critical limit of fly ash substitution.

The water-to-binder (w/b) was fixed at 0.45 for all specimens, where the binder consist of both cement and fly ash (OPC+FA). Fixed w/b was chosen prior to water-to-cement (w/c) to avoid the complication of using the right efficiency factor k, when using a supplementary cementitious material (SCM). Since the paste samples are to be evaluated on a microscopic level, the strength reduction is of minor concern in this study. The mixture proportions for the pastes are shown in Table [7] for a paste volume of 0.4 liter.

The paste was mixed using high shear mixing in accordance with ASTM C1738 [67]. The constituents were weighed on a scale with 0.01 g accuracy. Before mixing, the dry binder materials were homogeneously stirred together. The paste was mixed on a Waring Commercial; 8011S -Lab Blender, with "no load" rotation speeds of resp. 15 800 rpm and 22 000 rpm (cf. *Appendix A*). According to ASTM C1738/1738M [67] speeds of resp. 4000 rpm and 10 000 rpm should be used, but since the actual speed ratings with paste in the blender could not be tracked, "no load" speeds of 15 800 rpm and 22 000 rpm were chosen for low and high speed mixing, respectively.

ID	w/b [-]	Water [kg]	Cement [kg]	Fly ash [kg]
OPC FA23 FA35	$0.45 \\ 0.45 \\ 0.45$	$\begin{array}{c} 0.2348 \\ 0.2268 \\ 0.2225 \end{array}$	$\begin{array}{c} 0.5219 \\ 0.3876 \\ 0.3214 \end{array}$	0.1163 0.1731

 Table 7: Mixture proportions for 0.4 liter paste.

The temperature of the room and mixing water were measured prior to mixing (cf. Appendix A). Mixing water was poured into the blender and low speed was turned on. Dry materials were added within 30 s and paste was mixed on low speed for an additional 30 s. Mixing was stopped and set to rest for 150 s before mixing at high speed for 30 s.

The paste was cast in lightly oiled $\emptyset 22 \text{ mm} \times 120 \text{ mm}$ tube moulds with a bung used in each end to seal the sample. The mould was gradually filled while gently tapping with the ball of a hand to avoid large air voids in the paste sample. When the specimen has been properly sealed, it was placed in a rotation machine situated in a climate chamber (23 °C) for the first 24 hrs of curing to avoid separation of the sample. The specimen was stored in the climate chamber for a total of 28 days. The specimen was demoulded and sealed in airtight bags on the 17th day of curing due to a limited number of moulds (cf. *Appendix A*).

5.2 Chloride Migration Test

The Chloride migration test was carried out according to NT BUILD 492 [48] after 28 days of curing. NT BUILD 492 prescribes cylindrical specimens with a diameter of 100 mm and a length of 50 mm. The paste specimens in the present study had a diameter of 22 mm and cutting was done to obtain the prescribed length of 50 mm in accordance with NT BUILD 492 [48]. The cuttings of the specimen are shown in Figure 10]



Figure 10: Cutting of paste specimen prior to migration test.

The cutting of the specimens was done with a water cooled Struers Discotom-65 saw. The accurate length of piece **II** was measured in three different places, and the averaged is noted and can be seen in *Appendix B*. After sawing, excess water was wiped off, and the three pieces; **I**, **II**, and **I** were put into a vacuum container. The pressure was kept at approx. 25 mbar for

3 hrs before saturated $Ca(OH)_2$ solution was sucked into the container to fully immerse the pieces. The solution was made of demineralized water and $Ca(OH)_2$. The vacuum was kept for an additional hour before allowing air to enter the container by opening the valve. The pieces were kept in the solution for 18 hours. Piece II was removed from the solution and excess $Ca(OH)_2$ solution was wiped off. I-pieces remained in the reservoir with $Ca(OH)_2$ while chloride migration test on piece II was done.

Piece II was placed in the sleeve shown in Figure 11. The sleeve was specially designed and cast in silicone elastomer 68. The sleeve was designed with a diameter of 22 mm in the bottom part to perfectly match the diameter of the piece to avoid leakage along the perimeter.



Figure 11: Specially designed silicon elastomer sleeve for migration test. Cross section of the sleeve in 3D (left) and with measures (right).

A container with an inclined bed of 32° was filled with approx. 121 of 10% NaCl as a catholyte solution. The specimen enclosed by the sleeve was placed on the inclined bed in the container and the anolyte solution was poured on top. The anolyte and catholyte solutions were kept at the same water level to avoid any moisture transport induced by hydrostatic pressure. The anolyte solution was made by 12 g NaOH in 11 demineralized water resulting in a 0.3 N NaOH solution. An anode was immersed in the anolyte solution and connected to the positive pole of the power supply. The cathode, placed underneath the specimens on the inclined bed, was connected to the negative pole of the power supply. The test setup is illustrated in Figure 12. The temperatures of the room, anode solution, and cathode solution were measured and noted.



Figure 12: Test setup for chloride migration in accordance with NT Build 492 [48] with the exception of specimen size (cf. Figure 11).

The current was recorded by reading the display of the power supply and from a more precise electronic data collector designed for this purpose. The date collector made it possibly to track the current during the experiment in order to examine the change in conductivity throughout the experiment.

The power supply was preset to 30 V and turned on to record the initial current through the specimen. From the initial current the voltage to apply was read of Table 8 Due to the changed geometry of the specimens the test voltage stated in NT BUILD 492 [48] had to be converted into suitable measures for the smaller specimens used in this study. This conversion was done from the chloride exposed surface area of the intended specimens and the actual specimens used. The ratio between the two different surface areas was calculated and used to reduce the initial current (cf. Appendix B). The converted test entities can be seen in Table 8.

An initial experiment showed that the initial current at 30 V was above 17.42 mA. According to NT BUILD 492 [48] this would result in a test duration of 6 hrs. However, the test duration was changed and fixed to 24 hrs to ensure a proper chloride penetration depth. This was done to ensure enough chloride penetrated material to perform the later experiments.

Initial current l_{30V} [mA]	Applied voltage U [V]	Possible new initial current $l_0 [\text{mA}]$	Test duration t [hrs]
$l_0 < 0.24$	60	$l_0 < 0.48$	96
$0.24 \le l_0 \le 0.48$	60	$0.48 \le l_0 \le 0.97$	96
$0.48 \le l_0 \le 0.73$	60	$0.97 \le l_0 \le 1.45$	48
$0.73 \le l_0 \le 0.97$	50	$1.21 \le l_0 \le 1.69$	24
$0.97 \le l_0 \le 1.45$	40	$1.21 \le l_0 \le 1.94$	24
$1.45 \le l_0 \le 1.94$	35	$1.69 \le l_0 \le 2.42$	24
$1.94 \le l_0 \le 2.90$	30	$1.94 \le l_0 \le 2.90$	24
$2.90 \le l_0 \le 4.36$	25	$2.42 \le l_0 \le 3.63$	24
$4.36 \le l_0 \le 5.81$	20	$2.90 \le l_0 \le 3.87$	24
$5.81 \le l_0 \le 8.71$	15	$2.90 \le l_0 \le 4.36$	24
$8.71 \le l_0 \le 17.42$	10	$2.90 \le l_0 \le 5.81$	24
$l_0 \ge 17.42$	10	$l_0 \ge 5.81$	6

Table 8: Converted test voltage and duration time for paste specimens used in present test i. a. w.NT BUILD 49248

The specimen was removed from the reservoir and dismantled from the sleeve. Following, the specimen was rinsed with demineralized water and excess water removed. Two specimens were tested in parallel, one was used to documented ingress depth, the other for further testing. Ingress depth was documented by initially making a longitudinal cut with a saw to encourage a clean perpendicular splitting. The specimens were then split axially with a hammer and chisel into two pieces.

Penetration depth was measured by spraying a 0.1 M AgNO₃ solution on the freshly split surface from a distance of approx. 30 cm. After 10 min a white surface consisting of AgCl precipitations was visible on the surface, the depth of the white surface is measured roughly as shown in *Appendix B*. After measuring penetration depth, the samples were tossed and not used for further examinations.

5.3 Arresting Hydration

The hydration was stopped by removing the pore solution in the paste. The followed procedure was suggested by Lothenbach et al. (Chapter 5, **53**). This procedure is the recommended pretreatment for Thermogravimetric Analysis (TGA), and this procedure was used prior to XRF, XRD, TGA, and MIP. The hydration of each specimen was stopped after ended migration test, so all specimens had the same curing age.

The specimen was crushed quickly with a hammer and put into a glove box with a flow of CO_2 -free air to avoid carbonation. This box is shown in Figure 13a. The specimen was ground using mortar and pestle. The ground sample was then sieved to ensure particle size < 0.150 mm.



Figure 13: Equipment used for arresting hydration. (1) Rubber gloves, (2) Flow of CO₂-free air to avoid carbonation, (3) Morter and pestle, (4) 0.150 mm sieve, (5) Vacuum pump, (6) Büchner funnel, (7) Excess solution, (8) Isopropanol, (9) Dietehylether.

The powder sample was mixed with 10 ml of isopropanol per gram and set to rest for 15 min to remove the pore solution. The isopropanol was removed from the suspension by filtrating in a Büchner funnel connected to a vacuum pump (cf. Figure 13b). Furthermore, the solid is clensed for excess isopropanol by adding 1 ml diethyl ether per 10 ml isopropanol. The vacuum pump was applied until the color of the sample was lighter, which took approx. 15 min. The powder sample was then placed in a petri dish, spreaded out, and dried in a 40 °C oven for 10 minutes. The equipment used and actual measures for each specimen where hydration has been arrested, is provided in Appendix C.

5.4 X-Ray Fluorescence

X-Ray Fluorescence analysis (XRF) was performed to identify the chemical composition prior to analyzing XRD data. The analysis was performed by a technician at the laboratories of the Department of Civil Engineering at the Technical University of Denmark. Paste powder (cf. Table 4) and anhydrous composites (i.e. cement and fly ash) was analyzed.

XRF analysis was conducted on an Epsilon4 model from PANalytical. The powders were loaded into circular polyester holders coated in the bottom with plastic wrap. The holders have a height and diameter of 28 mm. The height of each sample was measured with a caliper, and the mass of each sample was measured on a scale and put into the program of the XRF analysis.

The samples were analyses as powder samples on the program setting "Omnia", which looks after all elements in the periodic system except for the first 8 elements. The first 8 elements are undetectable by XRF analysis, and the instruments have limited ability to precisely and accurately measure the abundances of elements with Z < 11 [69].
5.5 X-Ray Diffraction

X-ray diffraction (XRD) was conducted to determine the proportion by mass of different crystalline phases. Powder samples of paste (cf. Table 4) as well as anhydrous composites (i.e. cement and fly ash) was examined. Sample preparation was done in accordance with *Section* 5.3 for the paste samples and composite materials were correspondingly grinded and sieved to ensure the same particle size as the pulverized paste samples.

Powder was back loaded into circular sample holders with a diameter of 26 mm used in the XRD equipment (cf. *Appendix E*). In order to reduce preferred orientation of the powder and to ensure a uniform surface of the sample 57.

The measurements were carried out using a X'Pert PRO diffractometer from the manufacturer PANalytical. The model uses Bragg-Brentano θ -2 θ geometry with a fixed goniometer radius of 240 mm. The source is CuK α_1 x-rays generated using 40 mA and 45 kV tube operating conditions. The configurations of the diffractometer can be seen in Figure 14.



Figure 14: Configuration of Diffractometer [70].

The soller slit of the incident beam has a radius of $0.04 \,\mathrm{rad}$ and the incident anti-scatter slit were fixed at 1°. The incident divergence slit was programmed to a distance of 140 mm from the sample with a irradiated length of 10 mm. A fixed incident beam mask with the length of 10 mm was used and air scattering was reduced by a beam knife for MPD systems [57].

The diffracted x-ray goes through an anti-scatter slit fixed at 1° and was limited in axial divergence by a soller slit with a radius of 0.04 rad. Before entering the receiver the beam goes through a 0.02 mm thick $k\beta$ -filter made of nickel. The data was received continuously by a linear position-sensitive X'Celerator detector with a active length of 2.122° 2 θ .

During measurements the sample was spinning around the vertical axis of the goniometer in a rate of 8 sec/spin (approx. 7 rpm), to improve particle statistics. Data collection were executed over an angular range of 5 ° to 70 ° 2 θ in steps of 0.0167 ° 2 θ . The time at each step was 1 min resulting in a total measurement time of approximately 30 min. A report from actual XRD analysis confirming the above mentioned settings is provided in *Appendix E*

5.6 Thermogravimetric Analysis

Thermogravimetric analysis TGA was performed to identify bound water, portlandite, calcite and Friedel's salt [53]. The powdered samples (cf. Table 4) together with the anhydrous composites; cement and fly ash have been analyzed thermogravimetrically. Paste samples were prepared in accordance with Section [5.3] and the anhydrous composites were not processed.

The analysis was performed on a NETZSCH STA 449 F3 Jupiter Simultaneous Thermal Analysis instrument (cf. *Appendix F* and technical specification [71]). The schematic principles of the equipment is shown in Figure 15. Initial calibration of the equipment was done with empty crucibles and set to "correction" to correct for heat expansion and the buoyancy caused by the protective gas flow. For the actual measurements on powder specimens, the equipment was set to "correction+sample" to subtract the calibration curve measurements.



Figure 15: NETZSCH STA 449 F3 Jupiter Simultaneous. (1) Heating element, (2) Sample crucible, (3) Reference crucible, (4) Protective tube, (5) Insulation tube, (6) Exhaust gas outlet, (7) Balance system, (8) Hosting device, (9) Gas inlet.

The analysis was run by placing the preferable powder mass (cf. Section 4.5) in an aluminiumoxide (Al₂O₃) crucible with a weight of 141.2 ± 6.7 mg (cf. Appendix F). Measurements were done under constant flow of N₂ as the protective gas with a flow rate of 30 ml/min [53]. Temperature inside the furnace was controlled by signals from thermocouples placed underneath the crucibles. The equipment measures temperatures underneath the sample and reference crucible to account for the delay caused by sample heating. Both crucibles were positioned with forceps and the mass of the crucible and sample was tared and stored before starting the analysis. Temperature was increased from 30 to 1050°C with intervals of 10 °C/min. Hence, the test took approximately 1 hr and 45 min followed by an cooling period of equal length.

The obtained TG data and the derivative of the curve (DTG) was extracted for further analysis. The DTG data was smoothed using Savitzky–Golay filter to lower data scatter and to make important peaks more visible. Savitzky–Golay filter uses the principle of least-squares smoothing to reduce scatter. In presented case the method was applied in MatLab by using the build-in "sgolayfilt" function with a third degree polynomial and with a frame length of 521. Smoothing was based on a subjective best fit with focus on reproducible data (cf. Appendix F).

5.7 Sorption Isotherm

Sorption isotherms were obtained by the desiccator method and from Dynamic Vapor Sorption (DVS). Due to the time of one DVS measurement addressed in Section 4.6 the analysis was performed on samples cast at different time but performed such that the hydration time of each sample was coincident with one another (cf. Table 4). The time horizon of the desiccator method is dependent on the time required for specimens to be in equilibrium, and therefore the 1^{st} cast was chosen for this test.

Prior to sorption analysis, the saturated samples were grounded using mortar and pestle to pass a 0.150 mm sieve inside a fume cabinet under a flow of CO_2 -free air to prevent carbonation. A saturated solution of potassium sulfate (K₂SO₄) was placed inside the fume cabinet 7 days before grinding to ensure RH of approx. 98% to prevent the samples from drying during grinding.

5.7.1 Desiccator method

The desiccator method was performed in accordance with DS/EN ISO 12571 [62] to determine desorption isotherms. The experimental setup can be observed in Figure [16] Prior to the test, saturated salt solutions were mixed with distilled water and placed in each of their respective desiccators. Due to limited sample material, the five different salt solutions shown in Table [9] was chosen. Desiccators with salt solutions and empty cups were placed in a climate chamber at 20 °C for 7 days before the experiment was initiated to ensure stable conditions.

Desiccator	Saturated Salt Solution	Relative Humidity [%]
1	Lithium Chloride (LiCl)	11.31 ± 0.31
2	Potassium Acetate $(KC_2H_3O_2)$	22.51 ± 0.32
3	Magnesium Chloride $(MgCl_2)$	33.07 ± 0.18
4	Sodium Chloride (NaCl)	75.57 ± 0.40
5	Potassium Nitrate (KNO_3)	94.62 ± 0.66

Table 9: The relative humidities obtained from saturated salt solutions at 20 °C 62.

The sample was weighted to an accuracy of 0.01% and approx. 1-2 g was placed in a cup for each of the five different RHs (cf. *Appendix G*). The cup and lid were weighed before placing the sample. The open cups were placed in their corresponding desiccator so that each specimen was stored at five different RHs. Desiccators were sealed with vacuum of approx. 100 mbar to minimize carbonation and placed in a climate chamber at 20 °C to ensure stable conditions.



Figure 16: Experimental setup for the desiccator method 62.

The cups were weighed every 2 weeks. According to DS/EN ISO 12571 **[62]** the cups should be weighted until the last 3 consecutive measurements changed less than 0.1% of the total mass per day. When measuring the samples, the lid for each cup was put on the cup immediately after opening the desiccator.

5.7.2 Dynamic Vapor Sorption Method

Dynamic Vapor Sorption was conducted on a DVS Advantage from Surface Measurement systems (cf. Appendix G). The instrument continuously measures the mass with an analytical balance during exposure to predefined relative humidities. The predefines RH levels were obtained by demineralized water and a vapour humidifier. The schematics of the equipment is shown in Figure 17. Before using the instrument, the balance was calibrated with a 100 mg ultra class stainless steel weight made by Troemner.



Figure 17: Dynamic Vapor Sorption. (1) Gas inlet, (2) Solvent and vapour humidifier, (3) Gas transfer, (4) Temperature and RH probes, (5) Sample holder, (6) Analytical balance, (7) Opening mechanism, (8) Reference sample.

Approx. 10 mg of the crushed specimen was placed in the sorption balance holder and measurements were started. The designed program has a predefined RH-sequence at 20 °C. The program starts at 94 % RH and performs desorption of the specimen by slowly lowering the RH in the predefined RH steps. The upper RH limit of the experiment is a constrain enforced from the instrument since higher relative humidities could result in condensation inside the sorption balance. When the program reaches 11 % RH, the desorption of the specimen stops. Then an adsorption isotherm of the specimen is conducted back to 94 % RH. The program is defined with the relative humidities corresponding to the salts used in the desiccator method with the exception of one extra step at RH = 53 %.

The DVS program was designed to have a maximum duration of 7 days. Each RH-step was limited to take 15 hrs, so the program continues to the next RH after 15 hrs or if the mass change per minute is less than 0.0001 (dm/dt [%/min]). The RH-sequence and the maximum time steps of the measurement are shown in Table 10.

Table 10: Relative humidities and maximum time duration at each step for the DVS measurement.

RH [%]	94	75 53 33	22 11	22 33	53 75 94
Time [hrs]	15	$15 \mid 15 \mid 15 \mid$	15 15	15 15	15 15 15

5.8 Cup Test

The cup test was performed to determine the water vapor transmission properties of mortar specimens. Henceforth, a new specimen type and casting technique are introduced in this section (i.e. mortar specimen instead of paste). The casting of mortar specimens was done in accordance with DS/EN 196-1 [72]. The same materials as listed in Table 5 was used together with CEN-Normsand EN 196-1 (Density; 2640 kg/m³). The DS/EN 196-1 reference mix was adjusted using Lyse's rule to obtain a w/b ratio, corresponding to the paste specimens. The mortar mixture can be seen in Table 11

Table 11: Mortar mixture modified from DS/EN 196-1 $\boxed{72}$. Constituents is given in kg/m³mortar.

ID	w/b [-]	Water	Cement	Fly ash	Sand
M_OPC M_FA23	$0.45 \\ 0.45$	251 247	$558 \\ 423$	- 127	$1507 \\ 1485$

The mixing procedure proposed in DS/EN 196-1 was changed to account for available equipment. Mixing was done on a TEDDY BEAR Varimixer conforming to the standard and thus having two speed settings (i.e. low speed: $140 \pm 5 \text{ rpm}$ and high speed: $285 \pm 10 \text{ rpm}$). The mixing procedure is explained in the list beneath:

0s - 15s	Water added to the anhydrous materials while mixing on low speed.
15s - 30s	Hand mixing with a spoon to release trapped material from the bottom of the bowl
$30\mathrm{s}$ - $45\mathrm{s}$	Mixing on low speed.
$45\mathrm{s}$ - $75\mathrm{s}$	Adding sand while mixing on low speed.
$75\mathrm{s}$ - $105\mathrm{s}$	Mixing on high speed.
$105\mathrm{s}$ - $195\mathrm{s}$	Mixture resting
$195\mathrm{s}$ - $225\mathrm{s}$	Finale mixing on high speed

The mortar was cast in Ø100 moulds. Moulds were filled and vibrated one third at a time to remove larger air voids. Samples were demoulded after 24 hr and placed in air tight bags before being cured for additionally 27 days in a climate chamber at 23°C.



Figure 18: Cutting of mortar specimens. (1) Part of cylinder not used for further testing. (2) Chloride exposed sample used to check penetration depth. (3) Chloride exposed specimen and penetration depth marked with darker color. (4) Unexposed specimen.

The mortar cylinder was sawed as shown in Figure [18] This was done to obtain a non-chloride exposed disc sample (I) and two discs that could be chloride penetrated from migration test (II), where one on them solely was used to check the penetration depth. Chloride migration test was performed on the specimens in accordance with NT BUILD 492 [48] with the only exception that the test duration was fixed at 48 hr. The changed test duration was based on an initial experiment showing chloride penetration depth of approx. 1 cm for 24 hr exposed specimens.

The experimental setup was designed with in-house equipment and based on standardized principles described in DS/EN ISO 12572 [63] and ASTM E96-90 [64]. The setup can be observed in Figure [19]. The saturated disc samples were measured in four places to control the height and the mass of each disc was noted down. Rubber gaskets were placed between the cup and the disc to ensure unidirectional vapour transport through the sample. A saturated KNO₃-solution with 94% RH was placed inside the cup. The initial mass of the cup setup was measured to the accuracy of \pm 0.001 g before placing the cup in a desiccator. Relative humidity of 75% was maintained inside the desiccator with a saturated NaCl-solution. Furthermore, the desiccator was equipped with 10 g Soda lime Carbosorb to prevent carbonation, a fan to ensure air circulation, and a relative humidity sensor. The fan runs 5 min every hour to distribute the relative humidity uniformly. The desiccator was placed in a 19 °C climate chamber to control the environment.



Figure 19: Test setup for cup test: (1) Cup lid, (2) Saturated KNO₃-solution, (3) Disc sample, (4) Grid to prevent overtopping during weighting, (5) Rubber gasket, (6) Ventilation fan, (7) Carbon absorption agent, (8) Relative humidity sensor, (9) Saturated NaCl-solution.

The cups were removed from the desiccator every 14 days to measure the mass. The time duration of these measurements was minimized to prevent carbonation due to contact with atmospheric air. The specimens were considered to be in equilibrium when the mean of five successive determinations of the mass change per time did not change more than $\pm 5\%$ of the average mass change rate (cf. Section [4.7]). The experimental setup is elaborated in Appendix H.

6 Results and Discussion

"Tell me and I forget. Teach me and I remember. Involve me and I learn."

– Benjamin Franklin

R esults shown in this section will be discussed and argued continuously for the different experiments. An interdisciplinary discussion of the different obtained results, in regard to the hypothesis, will be provided in *Section* 6.8 and 6.7.

6.1 Chloride Migration Test of Paste

Current data for all paste specimens was logged during the chloride migration experiment (cf. Section 5.2, *i.e.* NT BUILD 492 [48]). This was done to observe possible transport differences between specimens with- and without fly ash. Current data can be observed on Figure 20] It should be noted that the applied voltage was fixed at 10 V for all experiments and that the current was measured on two specimens at a time.



Figure 20: Current data from NT BUILD 492 [48]. The initial drop of the currents are shown on a refined scale.

On Figure 20a the five black curves show the logged current data for the OPC reference specimens. In Figure 20b the four red curves represent the FA23 specimens and the three green curves are FA35 specimens. The different number of red and black curves is caused by a measurement error for the fourth chloride migration experiment with a FA23 specimen. The error occurred due to a big air void that caused current readings to max out when chloride ions penetrated all the way through the specimen. The discarded data and picture documentation can be observed in *Appendix B*. Air voids of this magnitude were not observed elsewhere.

It can be seen from the zooms provided in Figure 20, that the logged current experience an initial drop within the first 10 min. This drop is attributed to delays in the measuring equipment. Furthermore, it was noticed that the curves are systematically displaced in chronological order

with the date they were obtained. In other words, the top graph in both Figure 20a and 20b are from the first experiment executed, the second highest graphs are from the second experiment and so on. This could indicate that the measurement device was gradually fatigued, that the casting process of the specimens was improved, or it could simply just be a coincidence. However, it should still be noted that the curve shape seems similar for the same specimens.

Two curves on Figure 20b have more noise, which is attributed to an unsteady power supply. Between the experiments, the power supplies were both replaced and changed, but the reason for the noise was not found. Nevertheless, the difference in regards to the current between FA and OPC is still significant. Since R is inversely proportional to I through Eq. (13). This means that when the current decreases, the resistance of the specimens increases correspondingly since the voltage was kept constant throughout the experiment.

The current data for the OPC specimens have a more or less steady progress the first 5-10 hours. Then it decreases gradually for a period and this tendency flattens out towards the end of the test. The high current at the beginning of the test means that chloride ions penetrate easily through the specimen, which indicates a more porous microstructure at this stage. The current decrease occurs because some of the products, that are formed from the chloride ions, interact with the paste. These products could likely fill up the pores and thus causing a lowered current. It is also likely that the chemical composition of the pore liquid is changed, which also influences the conductivity of the sample. This topic will be dealt with in the last paragraph of this section.

For FA specimens the progress of the current data does not follow the same pattern as the reference OPC. The first thing to notice is that the current is generally lower than for the OPC samples. This means that the resistance of the FA specimens is generally higher. It is therefore expected that it should be harder for the chlorides to penetrate through the specimens. This could have something to do with the reduction of the pore size or more tortuous pores in FA specimens 25, 18. The current slightly increase after the initial drop, which means that the resistance decreases. Thus, indicating that the specimen becomes more permeable. This is an interesting observation that is not seen for the OPC specimens. A possible explanation could lie in the hydration process of fly ash blended systems which is a two step reaction process. The hydration of OPC proceeds faster than the pozzolan reaction, hence the first step is hydration of cement, and the second step is the fly ash hydration (cf. *Chapter*). The decrease of the resistance in the FA blended specimens thus indicates that the solids from the reaction products of fly ash are more soluble.

The non-steady-state migration coefficient, D_{nssm} was calculated from the measured ingress zone and Eq. (12). The measured penetration depth is shown in *Appendix B* together with the calculations of D_{nssm} . It should be mentioned, that the measuring method of the ingress zone is not in accordance with NT BUILD 492 [48]. The smaller samples made it difficult to take the average of 7 different ingress depths, and the accuracy is not within 0.1 mm. Instead, only one ingress depth was estimated with a caliper and the accuracy is approx. 0.5 mm.

Table	12:	Chloride	ingress	depth,	non-steady-state	migration	coefficien	ts and	averaged	l electrical	re-
sistance	e bas	ed on the	e current	t meası	rements and calc	ulated fron	n Eq. (12)	and E	Eq. (13).		

	$OPC(\mathbf{II}))$	FA23(II)	FA35(II)
$\begin{array}{cc} x_d & [\mathrm{mm}]\\ \overline{D}_{nssm} & [\cdot10^{-12}\mathrm{m}^2/\mathrm{s}] \end{array}$	10.4 ± 0.6 12.9 ± 0.8	$\begin{array}{c} 11.8 \ \pm \ 0.4 \\ 15.2 \ \pm \ 0.8 \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
$\begin{array}{ll} \overline{R}_i & \left[\Omega/\mathrm{mm} \right] \\ \overline{R}_f & \left[\Omega/\mathrm{mm} \right] \\ \Delta R & \left[\% \right] \end{array}$	$\begin{array}{r} 34.0 \pm 1.7 \\ 37.9 \pm 1.8 \\ 11.4 \end{array}$	$\begin{array}{c} 41.6 \pm 1.7 \\ 43.0 \pm 1.6 \\ 3.3 \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

The initial current was measured for each specimen before initiating the experiment. The initial drop in current was eliminated by not taking the first 20 current measurements into account in the following way. The percentage drop of the first 20 measurements was used to correct the initial current measured on each specimen. The electrical resistance was calculated by Eq. (13) based on the current. The average of the initial resistance is assigned \overline{R}_i in Table 12. Likewise, a final reading of the current was done after the experiment, and from this, an average final resistance, R_f was calculated for each of the different specimen types.

The calculated initial and final resistances shown in Table 12 is calculated as resistance per mm specimen. The changed resistance ΔR is shown as the percentage increase of the initial resistance. From the results shown in Table 12 it can be seen that the resistance becomes higher with more fly ash replacement. The increased resistance of fly ash blended cement is also expected from the theory (cf. Section 2.7.1). As suggested earlier this is likely because of the filler effect of fly ash and the reduction of the pore size and/or more tortuous pores.

The migration coefficients in Table 12 are increasing with increased FA content, which is caused by the higher ingress zones of the FA specimens. This finding is rather contradictory to the observed higher resistance of the FA specimens. If the FA specimens have higher resistance, why would the migration coefficient then be higher? The lowered pH of FA specimens would cause the chlorides to be more easily bound, but the higher resistance of the FA specimens implies that the free chloride ions would find it more difficult to penetrate through the specimen.

The current on Figure 20 is a measure for the total conductivity of the specimens and is thus influenced by the ion mobility in the pore solution. However, different ions have different transport properties. In chemistry, this phenomenon is known as electrophoresis [73]. The ionic mobility in a solution is influenced by the viscosity of the solution, characteristics of the ions themselves, and the applied electrical field [74]. For the present study this means that if the reaction seen in Eq. (11) happens, CO_3^{2-} does not necessarily have the same drift velocity through the specimen as CI^- . This will affect the current and the chloride penetration depth differently. Therefore, electrical resistance and penetration depth are not necessarily proportional.

6.2 X-Ray Fluorescence

The data obtained from the XRF analysis of all the elements that were detected are shown in *Appendix F*. Since the first 8 elements in the periodic table are non-detectable, the total sum of the analyzed powder samples does not add up to 100%. The total percentage of species detected by XRF for the different powder samples is shown in Table 14 as "Raw data". Since the elements in cementitious material (both anhydrous and hydrated powder) are bound in oxides, the amount of oxide can be calculated for each detected compound from stoichiometric calculations. The relevant compounds where the oxides are assumed to be present are the following; Na₂O, MgO, Al₂O₃, SiO₂, SO₃, K₂O, CaO, TiO₂, MnO₂, and Fe₂O₃.

An example of the stoichiometric calculation is shown in Table 13 where it is assumed that a detectable mass of 10 g silicon (Si) is found with XRF. Natural silicon exists as silicon dioxide (SiO₂) at ambient conditions, and then the total mass of SiO₂ can be determined.

	Si	+	2 O	\rightarrow	SiO_2
Mass, m [g]	10.0		11.4		21.4
Molar mass, $M [g/mol]$	28.1		15.0		60.1
Amount of pure substance, $n \text{ [mol]}$	0.36		0.71		0.36

Table 13: Example of stoichiometric calculation of SiO_2 .

In other words, if 10 g silicon is detected it corresponds to $\approx 21.4 \text{ g SiO}_2$ in the analyzed sample. The actual calculations for the data obtained by XRF are shown in *Appendix F*. The total percentage of detected compounds with the calculated oxides taken into account are shown in Table 14 as "Calculated with oxides".

	Cement	Fly ash	$\big \mathrm{OPC}(\mathbf{I})$	$OPC(\mathbf{II})$	$FA23(\mathbf{I})$	FA23(II)
Raw data	67.0	39.8	60.4	68.3	55.7	55.6
Calculated with oxides	98.8	71.4	88.9	95.5	83.8	82.8

Table 14: Detected compound percentage [Detectable mass-% of sample].

The "Raw data" from XRF shows, that for both cement and fly ash, less than 70 % of the mass is recognized as elements in the periodic system with Z > 8. Both the "Raw data" and the calculated "Relevant with oxides" also shows that the XRF has a lower detection rate for both anhydrous fly ash and fly ash blended pastes. Contradictory, the detection rates for chloride exposed specimens are higher for OPC specimens, and somewhat the same or slightly lower for FA specimens. If the relevant oxides are taken into account, the total mass of pure anhydrous cement is close to 100 %, thus indicating that the oxide assumption is a reliable way to determine the total content in pure cement. The detectable mass-% is lower for the paste samples, which is also expected since non-detectable bound water is present in the paste samples.

The chemical composition from the manufacturers of the used cement and fly ash was presented in Table 6 (cf. Section 5.1). In Table 15 the chemical composition obtained from XRF and with the oxides added to the relevant compounds is shown. The chemical composition from the manufacturer is shown again and a weighted averaged for a blend of fly ash and cement (23/77)was calculated. This weighted average was also calculated for the anhydrous compounds with the intention to make comparisons to the paste sample with 23% fly ash substitution. Besides the results from XRF, the LOI found from TGA is also shown in Table 15 to compare with the data from the manufacturer.

Table 15: Chemical composition obtained from XRF [% of powder mass]. *Calculated weighted average from 77 % cement and 23 % fly ash.

	CaO	SiO ₂	Al ₂ O ₃	$\rm Fe_2O$	SO_3	MgO	TiO	MnO ₂	Na ₂ O eq.	Cl-	LOI
From manufacturer											
Cement Fly Ash Blend [*]	$64.5 \\ 3.9 \\ 50.5$	$ \begin{array}{c}19.7\\56.4\\28.2\end{array}$	$ \begin{array}{c c} 5.2 \\ 21.6 \\ 9.0 \end{array} $	$3.8 \\ 5.4 \\ 4.2$	$ \begin{array}{c} 3.3 \\ 0.6 \\ 2.7 \end{array} $				$0.6 \\ 2.9 \\ 1.1$	$ \begin{vmatrix} \le 0.05 \\ \le 0.05 \\ \le 0.05 \end{vmatrix} $	$ \begin{array}{c c} 1.7 \\ 2.1 \\ 1.8 \end{array} $
Anhydrous compounds											
Cement Fly Ash Blend [*]	76.7 3.6 59.8	$ \begin{array}{c c} 9.7 \\ 36.6 \\ 15.9 \end{array} $	$ \begin{array}{c c} 2.2 \\ 12.1 \\ 4.5 \end{array} $	$5.8 \\ 12.3 \\ 7.3$	$3.0 \\ 0.7 \\ 2.5$	$ \begin{array}{c c} 0.3 \\ 0.4 \\ 0.3 \end{array} $	$0.2 \\ 1.0 \\ 0.3$	0.1 0.1 0.1	$0.3 \\ 1.7 \\ 0.6$	$\begin{array}{c} 0.03 \\ 0.04 \\ 0.3 \end{array}$	$1.8 \\ 0.9 \\ 1.6$

The presented numbers in Table 15 show that the obtained chemical composition for the anhydrous components does not conform with that of the manufacturer. For cement, the calcium and iron contents are considerably larger than expected. The silicon and aluminum content detected from XRF is less than half of the expected value. This could indicate that XRF has difficulties detecting compounds with low atomic numbers. The same tendency is observed for fly ash, where the detected mass of silicon and aluminum is much lower and the detected mass of iron is higher than expected. The LOI for anhydrous cement corresponds with the declared LOI from the manufacture, but for fly ash, it is considerably lower.

It was expected that the XRF results of the anhydrous components would not deviate more than approx. 10 % from that of the manufacturers. Hence, it is questionable whether the results obtained are reliable. Nevertheless, the different results obtained for the paste samples shown in Figure 21 still gives an indication of what happens with the composition of elements in the paste if fly ash is added and if the specimens are chloride exposed.



Figure 21: Oxides composition of paste samples from XRF

As expected, it can be seen from Figure 21 that the fly ash containing specimens have a higher content of silicon, aluminum, and iron. The content of calcium is decreased considerably and the content of gypsum is also smaller for FA specimens. An interesting observation is the content of chloride. From the theory, it was expected that more chloride would be bound in FA specimens, but the results from XRF show that the chloride content is almost the same with a small lead in the OPC specimens.

6.3 X-Ray Diffraction

HighScore Plus[©] software from Panalytical was used to analyze the observed XRD diffractograms. The software can assist in determining crystalline phases in each sample and with estimating weight distributions. The wt-% can be found by whole pattern Rietveld refinement as described in Section \overline{A} . Initial phase search was limited by the chemical compounds found by the XRF analysis. The complete refinement strategy can be seen in Appendix E.

Crystallographic information files (.CIF) was provided by the Inorganic Crystal Structure Database (ISCD) under the Leibniz Institute for Information Infrastructure (web version 4.5.0) and used to carry out the Rietveld refinement. Every crystalline structure has a designated ISCDnumber. Numbers used in the present report was found in the literature and the selection was based on data quality and publication year [57], 58 (cf. Appendix E). The files for hemicarbonate and aluminate was provided by the Crystallography Open Database, which is an open source database under the University of Cambridge [75]. The Leibniz Institute does not recognize these files and consider them incomplete. This might be a source of error in the Rietveld refinement. However, the overall trend should not be affected and it was concluded that leaving out these structures would cause significant uncertainties.

Figure 22a and 22b present the crystalline phase distribution and the amorphous content of anhydrous RAPID AALBORG CEMENT[©](CEM I 52.5N) and fly ash from Emineral. The found composition of clinker minerals can be compared to Table 2. Here, it can be seen that the composition is as expected, with the exception of aluminate (C₃A). 8 wt-% C₃A was expected, but only 4.6 wt-% is estimated from XRD. Saoüt et al. (2010) **58** studied the application of Rietveld refinement on anhydrous cement and discovered that C₃A is often underestimated with up to 0.6 wt-%. Also, the anhydrous material was not taken from a new bag so the possibility of contamination can not be rejected.



Figure 22: Composition of the anhydrous compounds based on XRD Rietveld analysis. The distribution is made with a calculated G-factor of $G=1.69 \cdot 10^{-53}$.

Other major clinker mineral phases like alite, belite and ferrite is often overestimated due to preferred orientation 58. This is probably the case of alite in Figure 22a. The detected calcite most likely originates from the up to 5% limestone filler and the bassanite comes from the added gypsum. The total clinker mineral content of the 4 main clinker minerals only add up to 90 wt-% on Figure 22a. This is slightly lower than the proclaimed 93 wt-% (cf. Table 2). However, the Rietveld analysis has uncertainties and the goodness of fit for the anhydrous cement is 2.7. The number of overlapping phases in cement furthermore adds to the complexity of the refinement which promotes uncertainties in the estimation 57. The data obtained in this project has furthermore not been good enough to quantify different polymorphs of the same phases like alite M1 and M2 as proposed by Saoüt et al. (2010) 58.

Figure 23 shows the Rietveld refinement results for all paste samples. It can be seen that the amorphous content increases with increasing fly ash replacement. This was expected because fly ash is highly amorphous as seen on Figure 22b. It is evident that chloride exposure by NT

BUILD 492 increases the amorphicity. This can be attributed to the formation of amorphous binding products and will be discussed later. The increased amorphicity also influence the total wt-%. The two main crystal phases in harden paste, i.e., ettringite and portlandite, gradually make up less of the total mass with increasing FA content and with chloride exposure. The AFm phases are harder to detect accurately in XRD due to their lower crystallinity and variation in composition. Quantification of cementitious paste by Rietveld analysis is consequently not as reliable as for strong crystalline phases. Nuclear magnetic resonance (NMR) is better to detect these phases, but due to the almost equal chemical shifts of the different AFm phases, the distinction between them is still not possible [38]. This redistribution, due to increased amorphicity, is also likely to be the reason for the decreasing quartz content in FA specimens. However, the tendency looks opposite for the mullite phase. The reason for this is not known.



Figure 23: Composition of the paste samples based on XRD Rietveld analysis. The distribution is made with a calculated G-factor of $G=1.72 \cdot 10^{-53}$.

Another interesting observation from XRD is that monocarbonate decreases when chlorides are present. This indicates that the reaction in Eq. [1] does indeed proceed and monocarbonate reacts with Cl^- to form Friedel's salt. This conforms with the finding by [45] and rejects the idea that this reaction does not occur as proposed by [44]. It can also be seen that the mentioned reaction seems to be inhibited in FA blends. The exact reason for this remains unknown, but it is likely that the chloride ion finds it more favorable to react with amorphous compounds. It is also possible that the increased tortuosity of FA blends makes the distribution of chlorides more uneven and thus the reaction proceeds slower. The transformation of monocarbonate to Friedel's salt will release a carbonate ion $(CO_3^{2^-})$ that is likely to form calcite or a calcite like phase. This is not confirmed by the XRD. However, some of the carbonates might react to form amorphous calcium carbonate that would not be detected by the XRD.

From Figure 23 it can also be seen that Friedel's salt is decreasing with increasing FA content. Decreasing amounts of Friedel's salt do not necessarily indicate less chloride binding. It simply indicates that the binding does not happen as Friedel's salt. Based on increasing amorphicity and the presented theory it is evident to assume that some of the chloride ions are absorbed by the C-S-H gel as previously proposed **6**. Nevertheless, it is not unlikely that other amorphous binding products may form.

The quantification through the external standard method uses the MAC coefficient for calculation. The most correct approach for the calculations would be to calculate the MAC based on the XRF as the sum of the oxides weight percentage multiplied with the density. However, due to doubt about the correctness of the XRF results the XRD calculated MAC was used. Attention should be paid to the sample preparation process, where carbonation and heat development are to be avoided. The comminution process used in this thesis is developed based on a literature study. Previously, wet grinding has been used to prevent heat development. This might be damaging because the process is likely to cause decomposition of the hydrated phases [57]. It is generally suggested that the powder should be of a particle size $< 5 \,\mu$ m. However, during the present experiment, the samples were not sieved to this size because sieving is likely to withhold harder particles, thus creating a systematic error.



Figure 24: Observed diffractograms for paste samples. Significant peaks and peaks of interest is pointed out. E=Ettringite, H=Hemicarbonate, M=Monocarbonate, F=Ferrite, CH=Portlandite, A=Alite, B=Belite, Q=Quartz and FS=Friedel's salt.

The actual diffractograms for paste samples can be observed in Figure 24. The diagrams give a good impression about the crystalline phase layout but also visualize some of the major drawbacks with the refinement of complex multi-phase systems. The peak overlap problem is to some extent accounted for by the Rietveld refinement, but it still has limitations in severe overlap cases. One of these cases is shown with and without chloride exposure in Figure 25.



Figure 25: Zoom of the problematic area 10.5-12 2θ degrees from FA35.

During chloride exposure, Friedel's salt (FS) is formed. FS's main peak is located very close to hemicarbonate leading to significant overlap. However, visual examination of the peaks confirms that hemicarbonate seems to decrease. This is not seen on the Rietveld refinement results and thus hemicarbonate is possibly overestimated for FA35(II). The wide shape of the FS peak does furthermore indicate that hemicarbonate is still present in the sample.

From Figure 25 it is also evident that monocarbonate actually decrease in chloride exposed samples. In the Figure, it can be seen that the main peak of monocarbonate around 11.75° 2θ decreases when FA35 is exposed to chlorides. From its secondary peak shown in Figure 24 around 24° 2θ it can also be seen that this is the same trend for all chloride exposed specimens. Hence, this tendency is confirmed both by visual examination and by whole pattern Rietveld analysis. This means that the reaction, shown in Eq. (11), actually occurs which causes CO_3^{2-1} ions to leak into the pore solution. CO_3^{2-1} ions might react with calcium to form calcite or amorphous calcium carbonate. The formation of calcite is not directly confirmed by the XRD.

6.4 Thermogravimetric Analysis

The TG and DTG curve for the anhydrous compounds RAPID AALBORG CEMENT[©] (CEM I 52.5N) and fly ash from Emineral is presented in Figure 26. The peaks of gypsum, portlandite, and carbonated phases are shown on the DTG graph for rapid cement in Figure 26a. As it can be seen in the Figure, only small amounts of water are released from the anhydrous compounds in the temperature range from 0-600 °C. This confirms that it is indeed anhydrous compounds, and no significant hydration has occurred.



Figure 26: TG and DTG for the anhydrous compounds.

The preliminary study of the anhydrous compounds was executed to lay the foundation for the later paste analysis by verifying that the compounds have the expected phases. From Figure 26a it can be seen that the expected phases of gypsum, portlandite, and carbonated phases are present in the cement. If assuming that all the carbonated phases shown in Figure 26a are calcite this corresponds to a calcite content of 3.1%, which is acceptable according to the requirement of maximum 5% limestone filler. An example of how phases are quantified from the DTG graph is shown later. The high content of carbonated phases could influence the results of the paste specimens. Additionally, an indication of hydration is shown by the presence of portlandite. This is likely due to moisture exposure from the atmospheric environment during storage or handling of the sample.

The anhydrous fly ash shows little mass reduction undergoing TGA measurement (cf. Figure 26b). This was not expected either, since FA is formed through the intense heat of a coal furnace, where the temperature reaches $1200 \,^{\circ}\text{C}$ [17]. It is therefore not prone to further mass reduction from heat exposure by TGA, which is only up to $1050 \,^{\circ}\text{C}$. The moisture released from 0-600 $\,^{\circ}\text{C}$ is below 0.5% and can be attributed to the atmospheric conditions, that the FA has been stored in. The mass reduction from 600-1050 $\,^{\circ}\text{C}$ is difficult to quantify but is most likely attributed to the presence of unburned coal. The fly ash from Emineral is a Category A fly ash, which means that the LOI should be lower than 5% by mass according to DS/EN 450-1 [23]. It is therefore not unlikely that the mass reduction from 600-1050 $\,^{\circ}\text{C}$ is caused by the residue of unburnet coal.

The average TGA and DTG curves for all paste samples are shown in Figure 27. The average consists of three measurements for each sample type. The graphs for each sample can be observed in *Appendix F* where it can be seen the triple measurement are almost identical. From Figure 27 it can generally be seen that the content of portlandite and ettringite is decreasing with in-

creasing FA content. This was also expected since these phases are formed from cement hydration and with increasing fly ash content, the cement content is correspondingly lowered. Furthermore, the pozzolan reaction uses portlandite which would further reduce the amount of portlandite in the FA containing specimens.



Figure 27: Average TG and DTG results form all tests. Marked areas can be observed on Figure 28

According to Figure 27 it also looks like the chloride exposure alters the content of ettringite. For OPC and FA23 the shift of the curves between chloride and non-chloride exposed specimens are in the same range (cf. marked area 1) on Figure 27). A zoom of this shift will be provided in Figure 28a. What can be seen in Figure 27 is, that the decreased ettringite content from chloride exposure is more pronounced for FA35 specimens. The peaks around 150 °C marked as area (2) are slightly ambiguous in the view provided in Figure 27. In Figure 28b a closer view on this peak will be shown and the phases causing the peak will be examined.

The peak in the temperature range of 600-750 $^{\circ}$ C is caused by decarbonation of calcite. The connection between fly ash, chloride exposure and amount of calcite is rather inconclusive from Figure 27, but this will be examined later. Furthermore, a peak in the temperature range of 800-1000 $^{\circ}$ C is observed. The reason for this mass loss is unknown and could not be explained from any available literature known to the authors. However, the peak likely comes from a compound that decomposes into carbon dioxide because of the high temperature. Unburned coal could likewise be a possibility but both FA blends and OPC samples show some extent of reduction. The peak does however look more pronounced for the chloride exposed specimens with fly ash.



Figure 28: DTG curves from marked areas on Figure 27 Legends is consistent with Figure 27

In Figure 28a, a zoom of the ettringite peak is shown. The peak area does include multiple phases like C-S-H and monocarbonate, but it is widely recognized that the presence of ettringite controls the magnitude of the peak 53. As mentioned earlier, FA blends show decreasing amounts of ettringite compared to OPC because FA substitution decrease the amount of ettringite formed from C_3A and C_4AF . Observing the effect of chloride exposure shows that chloride ingress causes the ettringite peak to increase. This could be explained by the transformation of monosulfate into Friedel's salt (FS). This reaction would free a sulfate ion as seen in Eq. (10). The free sulfate ion can react with more monosulfate and calcium hydroxide (Ca(OH)₂) to form more ettringite. This was proposed by Wolter (2020) [10] and can be seen in Eq. (32).

$$\underbrace{\overbrace{\text{Ca}_4\text{Al}_2\text{SO}_4(\text{OH})_{12} \cdot 6\text{H}_2\text{O}}^{\text{Monosulfate}} + 2\text{Ca}(\text{OH})_2 + 2\text{SO}_4^{2-} + 18\text{H}_2\text{O} \rightarrow \underbrace{\overbrace{\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}}^{\text{Ettringite}}}_{\text{(32)}} (32)$$

However, it is unlikely that this reaction should be more pronounced for FA35 specimens since less monosulfate is present from the beginning. Unless there is some other compound in FA that reacts with free chloride or sulphate ions to form ettringite, the observation from Figure 27 with higher ettringite content in FA35(II) compared to FA35(I) cannot be explained.

The ambiguous peak on Figure 27 and 28b in the temperature range from 130-190 °C is clearly different for chloride exposed samples. The peak that is visible around 170 °C is likely to be monocarbonate. After chloride exposure this peak becomes smaller, which might confirm that monocarbonate reacts with chloride to form Friedel's salt (cf. the reaction shown in Eq. (11)). Around 150 °C the curve is shifted downwards after chloride exposure. This is ascribed to the first layer of water that evaporates from Friedel's salt. The difference in Friedel's salt content between OPC and FA is not clear from the first layer of water that evaporates from FS (peak around 150 °C). However, the peak of FS is slightly larger for OPC samples. This is later confirmed by calculating the mass loss from the main peak of FS (cf. Figure 29 and Table 16).

The amount of non-overlapping phases can be calculated based on the amount of H_2O or CO_2 that is released during heating. The baseline for this type of calculation is established based on visual fit and is vulnerable to the operators' experience. Henceforth, some uncertainties exist regarding the repeatability of this type of calculation 53.

Figure 29 shows how different phases are quantified from their mass loss. For estimations of Friedel's salt the baseline is established as the DTG of the non-chloride exposed counterpart. Quantification of FS relies on the assumption that the observed difference, between (I) and (II) is only due to the formation of FS. This assumption is confirmed by observing the temperature zone on Figure 8 and 9. Only monosulfate has a coinciding peak that could influence the result. The calculation methodology for FS is likewise common in literature 6 45.



Figure 29: Areas used for phase calculations based on DTG data. Example from FA23(II).

The content of the three quantifiable phases shown on Figure 29 can be calculated from Eq. (18), (19), (20) and (21) shown in *Section* (4.5). An example of the calculation of the portlandite content is shown beneath.

$$m_{CH} = ML_{\text{TGA}:400-500} \cdot \frac{M_{\text{Ca(OH)}_2}}{M_{\text{H}_2\text{O}}} = \underbrace{\overbrace{1.98\,\text{g}/100\text{g}}^{\text{CH-area: Fig.29}}}_{1.98\,\text{g}/100\text{g}} \cdot \frac{74\,\text{g/mol}}{18\,\text{g/mol}} = 8.09\,\text{wt\%}$$
(33)

The result from Eq. (33) is rescaled to account for the degree of hydration with Eq. (34). Hence, the weight percentage is in unit g per 100 g paste.

$$m_{\rm CH,norm} = \frac{m_{CH}}{ML_{\rm TGA:>600} \cdot (1 + \rm w/b)} = \frac{8.09 \,\rm wt\%}{77.72 \,\rm wt\% \cdot (1 + 0.45)} = 7.2 \,\rm wt\%$$
(34)

The weight percentage of each phase is calculated for each DTG graph and the averaged results are shown in Table 16. For FA35 only one measurement was done. Hence, the results are not mean values, and no standard deviation is shown in Table 16 for FA35. Furthermore, the percentage difference between (I) and (II) is calculated to shown what happens with each phase, when the specimen is chloride exposed.

In Table 16 it can be observed that the chemically bound water (CBW) is decreasing with increasing FA content. This was expected and is likely due to the nature of the pozzolan reaction which does not consume water (cf. Section 2.5). No clear relationship can be established between CBW and chloride exposure. However, for OPC and FA35 samples it seems to increase.

The CH content decreases with increasing FA content. This can be attributed to the smaller amounts of alite and belie and the consumption of CH by the pozzolan reaction, as stated by Eq. (1), (2) and (9). The portlandite content decreases after chloride exposure for both OPC and FA23. This tendency is not observed for FA35, where the portlandite content is the same

before and after chloride exposure. The calcite content is highest for chloride exposed OPC specimens, but also without chloride exposure OPC has a slightly higher calcite content than FA23 and the calcite content of FA35 is very low. After chloride exposure, the calcite content increases significantly for all specimens. This finding supports the reaction shown in Eq. (11), where monosulfate reacts with the chlorides and releases a CO_3^{2-} ion. The finding implies that the CO_3^{2-} ion further react with calcium to form calcite.

	CBW	СН	$ $ $C\overline{C}$	FS
$\begin{array}{c c} \operatorname{OPC}(\mathbf{I}) & [\operatorname{wt-\%}] \\ \operatorname{OPC}(\mathbf{II}) & [\operatorname{wt-\%}] \\ \varDelta \operatorname{OPC} & [\%] \end{array}$	$23.8 \pm 0.6 \\ 24.1 \pm 0.6 \\ + 1.3$	$\begin{array}{c} 10.9 \pm 0.3 \\ 9.6 \pm 0.3 \\ - 12.5 \end{array}$	$\begin{array}{c} 1.4 \pm 0.1 \\ 2.7 \pm 0.3 \\ + 98.3 \end{array}$	2.6 ± 0.4
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$21.4 \pm 0.2 \\ 21.2 \pm 0.8 \\ - 0.9$	$\begin{array}{c} 8.3 \pm 0.2 \\ 6.8 \pm 0.3 \\ -17.4 \end{array}$	$\begin{array}{c} 1.2 \pm 0.3 \\ 1.8 \pm 0.4 \\ + 51.1 \end{array}$	- 2.0 ± 0.1 -
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$ \begin{array}{r} 10.6 \\ 12.5 \\ + 17.9 \end{array} $	$ \begin{array}{c c} 3.3 \\ 3.3 \\ + 0.3 \end{array} $	$egin{array}{c} 0.5 \\ 1.3 \\ + 160.0 \end{array}$	1.8

Table 16: Average values of Chemically Bound Water (CBW), portlandite (CH), calcite (\overline{CC}) and Friedel's Salt (FS). *Only one experiment. The value is not an average and has no standard deviation.

FS is only observed in specimens exposed to chlorides, which was expected because it is a binding product of chloride ions. As it was also expected from Figure 27 the amount of FS seems to become lower with increasing FA content. This might confirm the theory presented by Thomas et al. (2011) [46] on the idea that aluminate-silicate crystals like mullite is not able to react with Cl⁻ ions to form FS. In regards to this, it should be noted that it is still possible that more chloride binding occurs because chloride can be bound in C-S-H.

6.5 Sorptions Isotherms

Sorption isotherms were obtained from the desiccator method and the sorption balance. Desorption isotherms can be utilized to estimate the pore size distribution of the paste samples. The present thesis focuses on desorption curves instead of adsorption curves because the specimens are in saturated conditions before the start of the experiments. The lowest RH in the experiment is 11% because lower RH could influence and destroy the pore system [18]. This weight is considered the dry weight of the samples in these experiments. Hence, the obtained results are shown as moisture content normalized with the obtained moisture content at RH=11%.

6.5.1 Desiccator Method

Figure 30 shows the desorption curves from the desiccator method. It can be observed that the pore system changes due to chloride exposure. In the RH range of 11-22% chloride exposure increase the volume of the smaller pores. This could be explained by a pore refining chemical reaction in the paste due to the chloride ions. For larger pores, the trend is different, which will be discussed further in combination with results from the sorption balance. The chloride exposed samples indicate that the FA blends have a higher volume of pores than OPC samples.

Based on the desorption isotherms from the desiccator method it can be seen that non-chloride exposed samples with and without fly ash follow a similar pattern. The samples are only 28 days, so it could be expected that the refinement of the pores from the pozzolan reaction is not yet fully developed [39]. However, the trend is not very pronounced in the obtained results.



Figure 30: Sorption isotherms determined from desiccator method.

The sample size in the desiccator method should be of 10 g acc. to DS/EN ISO 1257 [62]. In this study the sample at each RH varies between 0.88 g and 1.81 g. The mass could not be larger due to the limited chloride penetrated sample from the migration test.

6.5.2 Dynamic Vapor Sorption

Results from the sorption balance can be observed in Figure 31. Primary results are shown as desorption isotherms (i.e. bright colors on Figure 31) because the samples started in near saturated conditions. The adsorption isotherms (i.e. dotted lines on Figure 31) are likely to include uncertainties as the pore system could be damaged at this stage.



Figure 31: Sorptions isotherms determined from sorption balance. The dashed curves mark the adsorption and the bright colors are the desorption.

The data shown in Figure 31 is given as the average of the final 10 data points for each relative humidity. The mass equilibrium curves for samples in relation to each RH can be observed in *Appendix C*. Among others, Linderoth et al. (2020) 39 used an exponential function to estimate the final equilibrium at each RH. However, in this article they point to the fact, that sorption curves do not follow this function in certain RH ranges. Furthermore, the method is highly dependent on the visual fit of the parameters, and therefore the sorption isotherms in the present thesis were not corrected by this fitting method. The obtained accumulated moisture volume can be seen in Figure 32 where the moisture content at each of the different RH ranges is also shown.



Figure 32: Accumulated pore volume for the different RH intervals.

When observing FA blends and OPC regarding chloride ingress, the distribution of pore volume above RH 45% change in opposite directions. It is evident that chloride ingress increase the volume of pores in the lower RH range of 11-33%. This can be observed on Figure 31 and 32.

Figure 32 illustrate that the volume of the pores in the RH range of 33-53% decreases. This implies that the microstructure of the system is restructured by the refinement of the pores in the RH range of 33-53%. That chloride ingress increase the volume of small pores could be explained by binding products refining the pore system. The tendency is most pronounced for chloride exposed FA blends. The sorption balance hence confirms that different microstructural altering processes are taking place in FA blends compared to reference OPC. In the RH range above 53% the samples follow a similar slope, which indicates that the chloride exposure does not influence the volume of pores in this RH range.

The adsorption isotherms on Figure 31 shows that all samples follow a similar pattern during the adsorption. This tendency indicates that considerable damage has been inflicted to the pore system during the desorption. The damage likely happened at low RH because the diffusion force is biggest in this range. However, if damage happens during higher relative humidities it will cause an error in the results at lower RH. The extent of this error is not known, but desorption isotherms are commonly accepted as a strong tool with little error.

6.5.3 Comparison

On Figure 30 and 31, it can be seen that at approximately RH 33% the same tendency can be observed for both experiments. As explained in *Section* 4.6 it was expected that results from the two methods would variate with up to 10%, mainly in the RH range of 30-50% [61]. Observing Figure 30 and 31 confirms the difference. The sorption balance shows a greater volume of smaller pores compared to the desiccator method, which estimates more pore volume at higher

RH. The desiccator method generally estimates more pore volume as it can be seen on the diagrams in Figure 33. The volume of pores at the RH range from 22-33% and 33-53% from the sorption balance has been combined, to compare with the results from the desiccator method.



Figure 33: Accumulated pore volume based on water vapor from the desorption isotherms.

The difference between the two methods have been studied by Linderoth (2020) **[13]** but no exact correlation or reason was established. The study points to the considerable difference in sample mass as a possible explanation. Another reason could be the much shorter time steps of the sorption balance that do not allow the sample to reach equilibrium. However, more research is needed to establish the exact reason for the difference and this is not the objective of this thesis. The difference in results between the desiccator method and the sorption balance is generally attributed to the known difference between the two methods.

The mixing procedure plays an important role in the formation of the pore structure. The effect of high shear mixing on the reaction time is not well understood. A study by Han et al. (2015) [76], did however find evidence that high shear mixing might increase the hydration rate. Hence, it is likely that the pore structure of the 28 day old specimens in the current study is more developed compared to other studies. In the further discussion of the results in this project, the results from the sorption balance will primarily be used. This choice was made because both methods show the same tendencies, but the sorption balance seems to have a more refined estimation of the small pore volume. Both the desiccator method and the sorption balance show that this area is of interest regarding chloride ingress (cf. Figure 30 and 31).

6.6 Cup Test

Cup test was performed on mortar specimens as explained in Section 5.8 and the measurements and calculations is provided in Appendix H. Two tests were performed for each specimen type. The first is called cast 7 and the second is referred to as cast 8. As the naming implies, the two tests are from two different casts, but the respective OPC and FA23 specimens from each cast are the same and have the same curing age.

6.6.1 Chloride Migration Test on Mortar Samples

Chloride migration test was performed on some specimens prior to the actual cup test. Due to voltage limitation of the data logger equipment, the current could not be logged continuously throughout the experiment. Initial and final currents were noted for all specimens. The non-steady-state migration coefficient, D_{nssm} were calculated from the measured ingress zone and

Eq. (12). The measured penetration depth is shown in *Appendix H*. The ingress zone is not measured in accordance with NT BUILD 492 [48], but estimated with a caliper and picture examination. For FA specimens from cast 7, the ingress zone was very U-shaped (cf. *Appendix H*), which implies that the clamps to secure the sleeve around the specimen was not tightened sufficiently. The estimated penetration depth and migration coefficients are shown in Table [17].

From Table 17 it can be seen that the chloride penetration depth of FA23 from cast 8 is higher than for the OPC specimens. The voltage was higher for the FA23 specimens and therefore the penetration depths of OPC and FA23 cannot be compared directly. Disregarding FA23 from cast 7 due to the described errors, it can be seen that the migration coefficients of OPC and FA23 lie within the same range. There is a big measurement error attached to the penetration depth since the chloride profile varied a lot throughout the specimens (cf. Appendix H).

		M_OH	PC(II)	$M_{FA23}(II)$		
$\frac{x_d}{\overline{D}_{nssm}}$	[mm] $[\cdot 10^{-12} m^2/s]$	Cast 7 29 10.1	Cast 8 30 10.7	Cast 7 (33) (9.2)	Cast 8 37 10.4	
$U \\ \overline{R}_i \\ \overline{R}_f \\ \Delta \overline{R}$	$\begin{bmatrix} V \end{bmatrix}$ $\begin{bmatrix} \Omega/mm \end{bmatrix}$ $\begin{bmatrix} \Omega/mm \end{bmatrix}$	$\begin{array}{c} 20 \\ 6.3 \pm 0.5 \\ 6.9 \pm 0.5 \\ 0.6 \pm 0.3 \end{array}$		$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	5 = 1.7 = 0.9 = 0.3	

 Table 17:
 Chloride ingress depth, non-steady-state migration coefficients and averaged electrical resistance of mortar samples.

The voltage and the calculated average resistance is also shown in Table 17 It is interesting to see that the change in resistance is not the same for OPC and FA23 specimens. The resistance increases for the OPC specimens and for FA23 it decreases.

6.6.2 Moisture Transport

The cup test was performed on disc specimens. In Figure 34 the measurements are shown and the last five mass decreases used to calculate the water vapor flow rate are highlighted.



Figure 34: Mass loss during the cup test.

Figure 34 is shown, to display that the mass loss measured every week is close to linear at the end of the experiment. This implies that the moisture transport through the specimens is close to equilibrium as prescribed by DS/EN ISO 12572 [63]. However, if studying the last five measurements more carefully, the difference in mass loss between the first and the last is approx. 0.11 g, whereas the average difference between each of the five measurements is only 0.03 g (cf. Appendix H). Furthermore, if looking at the single mass loss at each weighing, the mass loss decreases from measurement to measurement. This shows, that the moisture transport was not completely constant, but due to the time limitations, the experiment had to be stopped. A more steady moisture transport could have been obtained if the experiment had been continued.

Figure 34 shows the initial mass of the assembled cup. Since both the mass of the cups and the amount of salt solution variate from specimen to specimen (cf. Appendix H), this figure is not a measure of the difference in densities of the specimens. The density of each specimen was calculated based on an initial measurement of dimension and mass. The approximated densities of the mortar specimens are provided in Appendix H. The densities of the discs vary from 2190-2290 kg/m³, but no pattern between chloride or non-chloride exposed specimens nor OPC and FA23 specimens were found.

The water vapor flow rate is calculated from the average mass loss of the five last measurements as explained in *Section* 5.8, with the reduction from masked edges. The calculated water vapor flow rates are shown in *Appendix H* where it can be seen that the and the two different experiments show the same tendency. The average of the two tests is therefore shown in Figure 35. The chloride exposed specimens have a higher flow rate and fly ash containing specimens have a lower flow rate than OPC specimens.



Figure 35: Water vapor flow rate $[\cdot 10^{-7} \text{kg/m}^2 \text{s}]$.

The reduced water flow rate of FA23 specimens implies that the pore structure is different from that of the OPC specimens. The reduced moisture transport means that the permeability of the FA23 specimens is less pronounced than for OPC specimens. As outlined in *Section* 2.6 FA blends are known to increase the tortuosity and decrease the connectivity of the pores, which will inhibit the moisture transport through the pores. This theory is supported by the findings of this experiment. Since smaller and more tortuous pores will impede the moisture content, the results shown in Figure 35 implies that the FA23 specimen has more tortuous or fewer pores.

As also shown in Figure 35, the moisture transport is enlarged by chloride exposure. However, the enlargement does not seem to be more pronounced for FA23, so according to this study, the chloride exposure is not more detrimental for the moisture transport for FA blended specimens than for regular OPC specimens. The findings show evidence of a more permeable structure due to chloride ingress which could be due to reduced solid material and bigger pores.

6.7 Chemical Changes during Chloride Ingress

The difference between chloride exposed FA blends and OPC specimens are investigated chemically through XRF, XRD, and TGA. The findings from the XRF implies that slightly less chloride is bound in FA blends. This finding is supported by XRD and TGA, which estimate more Friedel's salt in OPC samples. It is important to notice that decreasing amounts of Friedel's salt does not necessarily means less chloride binding since part of the Cl⁻ binding happens in the C-S-H gel **[6]**. The results from XRF is rather questionable and XRD and TGA do not show all Cl⁻ binding products. Hence, the total difference in chloride binding in FA and OPC specimens is not found in this study.

Results from XRD and TGA both show that portlandite and ettringite decrease with increasing FA content. This is expected because both phases are formed from the clinker minerals. With decreasing cement content due to the substitution of fly ash, these reaction products will correspondingly decrease. Estimation of portlandite from XRD and TGA show similar trends as shown in Figure <u>36b</u>. XRD estimates slightly more portlandite than TGA but it is likely that TGA underestimates due to the decomposition of C-S-H. Concerning chloride ingress, both XRD and TGA show that portlandite decrease even more for both OPC and FA specimens. The ettringite peak increases after chloride exposure for all specimens. Results from TGA furthermore show that the amount of ettringite in FA35 increases more after chloride exposure than for OPC and FA23 (cf. Figure <u>27</u>). The peak of ettringite in the thermogravimetric analysis is however not only a measure of ettringite and the observation was not supported by results from x-ray diffraction. This indicates that the larger release of water around 100 °C for FA35(II) is more likely attributed to changed amounts of C-S-H and monocarbonate.



Figure 36: Comparison of TGA and XRD results for selected compounds.

The results from the thermogravimetric analysis in Table 16 shows that calcite levels after chloride exposure increase significantly with 98.3, 51.1, and 160% for OPC, FA23 and FA35, respectively. However, the calcite levels from TGA are not in agreement with the XRD findings as shown in Figure 36a. The difference from the 1:1 trend is illustrated in Figure 36a. The figure shows that the TGA-detected calcite content is generally higher than the content estimated from XRD. In the XRD analysis, only FA23 samples have increasing calcite content due to chloride exposure. The reason why TGA shows higher levels of calcite could be explained by the presence of amorphous calcite. Amorphous compounds are non-crystalline and would not be detected by

XRD but TGA can detect them. If more amorphous calcite is generally present after chloride exposure, this could likewise explain why all samples have an increasing amorphicity after chloride exposure (cf. Figure 23). The carbonate ion could also react to form hemicarbonate. This would explain why the content of hemicarbonate increases after chloride exposure as shown in Figure 23, but this reaction is not supported by the literature.

Figure 27 shows a peak in the range of 800-1000 °C. This peak is related to the release of carbon and not water because of the high temperature. The exact reason for this peak is not known, but it is possible that it belongs to binding products that come from carbonate ions. Another suggestion for this peak is a simple combustion process, even though the protective nitrogen flow should reduce the risk by removing the oxygen. Studies have shown that unburnt coal from fly ash burns at these temperatures and release CO_2 . Even with the lack of oxygen, it is still possible because the high temperature might cause other compounds to release oxygen [53]. However, the exact reason for the release of carbon in this peak is not established during the experiments and should be investigated further. The XRD did not confirm the presence of graphite (i.e. main crystalline compound of coal) but it could be present in smaller amounts.

The quantity of AFm phases like monosulfate and monocarbonate are challenging to measure due to their amorphous nature but play an important role regarding chloride ingress as described in the theory (cf. Section 2). The first hypothesis of present study especially concerns the capability of monocarbonate to form Friedel's salt as it can be observed in Eq. (11). Results from the XRD on Figure 23 reveals that the amount of monocarbonate decreases due to chloride exposure. This trend is more noticeable for the OPC references compared to FA blended samples. Nevertheless, quantifying how much of the produced Friedel's salt that comes from monocarbonate is difficult because XRD only detects the crystalline part of monocarbonate. Figure 36c compare Friedel's salt quantification's from thermogravimetric analysis and XRD. The results of the amount of Fridel's salt determined from the two methods show a good correlation, although TGA estimates slightly less FS than XRD. The difference could be attributed to uncertainties in the assumption that FS can be quantified from TGA solely on the dehydration of the main water layer. Both methods confirm that less Friedel's salt is formed in FA blends.

The results from TGA (cf. Figure 27 and 28a) shows that the amount of monocarbonate decreases due to chloride exposure. However, it should be noted that the monocarbonate peak is situated in a temperature range, where other compounds decompose too. Henceforth, the quantification by TGA can only be accomplished based on visual examination and no direct comparison to the results obtained from XRD can be made (like the ones shown in Figure 36). Based on presented observations for monocarbonate from TGA and XRD, there is evidence that the reaction in Eq. (11) occur since the amount of monocarbonate decreased after chloride exposure. This does conform to the finding by Shi et al. (2017) [45]. The reaction will release a carbonate ion that might react with compounds like calcium to form calcite (cf. Eq. (35)).

$$\mathrm{CO_3}^{2-} + \mathrm{Ca}^{2+} \to \mathrm{Ca}\mathrm{CO_3} \tag{35}$$

Ions that are released from Eq. (35), impose a change to the paste pore solution that is of interest regarding the accelerated chloride migration test, NT BUILD 492 [48]. Ion compounds move because of the electric field and it is unlikely that they will migrate with the same velocity. In chemistry, this phenomenon is called electrophoresis. However, the phenomenon of electrophoresis has not been studied in this thesis but should be studied further. If the reaction shown in Eq. (11) does occur and the carbonate is more easily transported, they might migrate through the specimen into the anolyte solution and will therefore not be detectable in the paste sample. In that case, the migration test will not imitate natural conditions and the finding might not embody naturally occurring events. This migration is furthermore likely to be different in

OPC and FA blends because of the microstructure. The sorption isotherms in Figure 32 and the cup test results on Figure 35 explain this subject and it can be seen that the transport properties are somehow different. This means that released ions are transported in different ways and shows the importance of the pore systems tortuosity and connectivity.

The above mentioned findings are less clear when observing the tendencies regarding the amount of fly ash substitution. It can be concluded that if monocarbonate reacts to form Friedel's salt, this reaction appears to be less pronounced for FA blends. Since less monocarbonate is present in FA blends initially, the reaction would be more limited. However, observing XRD results on Figure 23 shows that FA23 have higher levels of monocarbonate compared to the reference OPC. The results can however be disputed because of XRDs difficulties to quantify AFm phases.

This dissertation aims to answer two central questions regarding different alterations from chloride ingress in OPC and FA blends. The first hypothesis relates to the chemical processes, which have been discussed in this section. The following hypothesis was proposed.

• When cement paste is exposed to chlorides, free chlorides reacts with monocarbonate and form Friedel's salt, whereby carbonate ions are released. The carbonate ions take part in new reactions. It is the reaction of the carbonate ions that are different, depending on if fly ash is present in substantial amounts.

Concerning the first hypothesis, there is evidence of the reaction seen in Eq. (11), but the reaction appears less pronounced for FA blends. Henceforth, limestone filler added to cement does influence the properties regarding chloride ingress in cement paste and FA blends. The finding emphasizes the importance of considering fly ash pastes as a ternary compound system that consists of cement, limestone filler, and fly ash. The reaction releases a carbonate but the whereabouts of this ion is not clear based on the experimental program. Some evidence can be found for different amounts of products being formed in OPC compared to FA blends. However, the extent to which the reaction (cf. Eq. (11)) occur remains to be shown.

6.8 How does Chloride Ingress alter the Microstructure?

The chloride exposed specimens in this study were mainly paste specimens. For the cup test, also mortar specimens were chloride exposed, but the current during the migration test could not be logged continuously. The current of FA blends and OPC did not undergo the same change during chloride exposure. For the paste specimens the resistance increased noticeably more for OPC than for FA23 and FA35 (cf. Figure 20). It was also seen that the resistance of FA blends decreased a bit at the beginning of the chloride migration test. For mortar specimens, the resistance of OPC increased whereas the resistance of FA23 decreased (cf. Table 17).

Olsen (2020) D made a similar study on concrete specimens. In his mix design, he took the correction factor for fly ash substitution into account, which means that results from these FA specimens are not directly comparable with the results for FA specimens in the current study. However, if calculating w/b without any correction factors for his FA20 specimens, they have the same w/b as the FA23 specimens in the present study. Olsen found increasing initial resistance with increasing fly ash content. For both paste and mortar specimens in this study, the initial resistance of FA blends was also higher than that of OPC. This shows that there already before chloride exposure is a difference between whether the specimens contain fly ash or not.

Olsen (2020) [9] also found that the final resistance of FA specimens is lower than the initial. This complies with the findings of our study done for mortar specimens. The reason for the different trends of $\Delta \overline{R}$ for FA paste and mortar specimens is attributed to the difference between paste and mortar/concrete specimens and the mixing procedure. The paste specimens in the

present study are prepared with high shear mixing and the mortar specimens are prepared with a mixing procedure similar to DS/EN 196-1 [72]. When Tang et al. [77] suggested the chloride migration test in 1995, they found that the pore structure of paste specimens is finer than for concrete, especially for specimens with high w/c. The high shear mixing and finer pore structure of paste specimens in combination with the different densities in the ITZ are likely to cause the different change in resistance between FA paste and mortar specimens.

Regarding the change of D_{nssm} for FA blended paste, the chloride migrations test showed that increasing FA content increased the non-steady-state migration coefficient. From the observed higher resistance of FA blends, it was expected that this would have been the other way around. The literature also generally observe the opposite tendency than what is observed for the paste specimens [9, 25]. Jain et al. (2009) [25] used respectively 10 and 20% class F fly ash replacement, and found that for 28 days concrete specimens the D_{nssm} decreased from approx. $10 \text{ m}^2/\text{s}$ for OPC specimens to approx. $7 \text{ m}^2/\text{s}$ with 20% fly ash replacement [25]. The calculated D_{nssm} on mortar specimens did not show any clear tendency between FA and OPC after chloride exposure. The results of the chloride migrations test on paste specimens was a rather contradictory observation which imposes the question of, whether the different ion velocity of Cl⁻ and CO₃²⁻ would influence the measured current. If this is the case, this could shed light on why the D_{nssm} and the measured resistance show conflicting results.

Baert et al. (2008) [47] did however also find increasing D_{nssm} with increasing fly ash substitution for 1 month old specimens. In their study, concrete specimens of OPC and specimens with substitution of low calcium fly ash were compared in the NT BUILD 492 migration test. The study expected that the FA blends would have a reduction of pore sizes, which would lead to less permeable paste. The study also points out that concrete with fly ash would be more vulnerable to carbonation, which was also confirmed by the RILEM TC report by Greve-Dierfeld et al. (2020) [78]. This will increase the porosity of the specimens and thus influencing the structures resistance on chloride ingress [47]. In their study, the one month old FA35 has a D_{nssm} of approx. $9.5 \cdot 10^{-12} \text{m}^2/\text{s}$ and OPC has D_{nssm} of approx. $8 \cdot 10^{-12} \text{m}^2/\text{s}$. However, this trend is reversed for specimens cured for 12 month. Here, D_{nssm} for FA35 and OPC are approx. $2 \cdot 10^{-12} \text{m}^2/\text{s}$ and $6 \cdot 10^{-12} \text{m}^2/\text{s}$ respectively. This finding shows that the pore refinement from FA substitution might not be as pronounced for 1 month old specimens, which could explain why the migration coefficients for FA blends in the present study are higher than OPC.

Another explanation to the conflicting increased resistance but higher D_{nssm} value of FA blends could be found from the findings in the study by Yuan et al. (2008) [79]. In this study, it is shown that even a small alteration of the pH will lower the concentration of chlorides in the color changed ingress zone. Due to the lowered pH in FA blends, it is possible that the measured ingress zones in FA blends cannot be compared directly with the ingress depths of OPC, since the chloride concentration where the color change occurs is not the same for the different specimens. In other words, if measuring the penetration depth of FA blends and OPC at the same chloride concentration, the chloride penetration depth of FA blends actually might be lower. This would cause the actual D_{nssm} to be lower as well. The chloride migration test performed in this study did however overall show evidence that the microstructure of both hardened paste and mortar was altered differently depending on if the specimens contain fly ash or not.

The pore structure and the transport properties were examined through sorption isotherms and a cup test. The results from the sorption isotherms show that the total porosity of FA blends was slightly higher than of OPC. Linderoth (2020) [18] did a similar study of the effect of fly ash replacement on the pore structure with desorption isotherms. His study shows that for 28 days old specimens, the fly ash blends had more pore volume in the range of RH=70-95 % and less in the range of RH=11-70 %. The same tendency is somewhat seen on Figure 31 and 32 FA35(I) and FA23(I) show less pore volume in the range of RH=11-33 % and more volume in

the range of RH=33-94 %, compared to OPC(I). Linderoth points to the pozzolan reaction as pore refining and ascribes it to the fact that larger $Ca(OH)_2$ crystals are replaced with fine C-S-H gel. Based on Figure 31 it would be expected that the more porous microstructure of FA samples would lead to higher moisture transport which was further studied by a cup test.

The results from the cup test did however show that the water vapor flow rate was lower for FA blends (cf. Figure 35). An interesting result which might also support the increased electrical resistance of FA blends found for both paste and mortar samples by NT BUILD 492. Linderoth (2020) [18] did a similar study of FA containing specimens, and observed that his FA blends also have a reduced water vapor flow. In his study, the reduction was however much more pronounced than in this study. The moisture transport of his FA15 and FA35 at 20 °C was reduced from $4 \text{ m}^2/\text{s}$ for OPC to 1.5 and $0.8 \text{ m}^2/\text{s}$, respectively. Linderoth also attributed the decreased moisture transport to the changed tortuosity in FA blends. FA reacts slower than OPC, and FA thus forms its products in the available spaces after the OPC reaction, causing a more refined structure by filling up the largest pores [18]. The overall trend for the FA blend could thus be that the microstructure is less permeable before chloride exposure.

The water vapor flow rate increases 31.0% for OPC specimens and 26.5% for FA23 specimens due to chloride exposure. This shows that the moisture transport in FA blends will be less affected by chloride ingress than OPC. From the sorption isotherms presented in Figure 31 the reason for this is however not completely clear. If looking at the total porosity after chloride exposure the volume of pores in the OPC specimen is decreased and increased for FA blends. From this finding, one would expect that the moisture transport was reduced for chloride exposed OPC specimens and increased for chloride exposed FA specimens, which is not the case. If looking at the refinement of pores both OPC and FA blends get a larger amount of pores in the changed impact on chloride ingress for OPC and FA blends is not due to the pore refinement, but rather because of more torturous pores in FA blends. This can be related to the second hypothesis that is formulated this way.

• Chloride ingress will alter the microstructure of hardened paste differently, depending on whether the specimens contain fly ash or not.

Overall, the sorption isotherms indicate that FA blends would have a more permeable structure, but the cup test did not support this finding. This shows that some other difference between chloride exposed FA blends and OPC specimens is likely the reason. This difference could be found in the tortuosity and connectivity in the pores of FA blends.

7 Conclusion

"I alone cannot change the world, but I can cast a stone across the water to create many ripples."

Mother Teresa

T he experimental work comprehend thermogravimetric analysis, X-ray diffraction, X-ray fluorescence, sorption isotherms and a cup test to examine specimens exposure to chlorides by NT Build 492 [48]. Specimens included a reference OPC and specimens with 23% and 35% of the binder substituted with fly ash. The test methods are found to provide useful insights on the microstructure and pore structure and can be recommended for future research within this field. A future in which supplementary cementitious materials (SCM) appears increasingly attractive to reduce the anthropogenic CO_2 -emission. Even though, the consumption of fly ash as SCM is decreasing, understanding its properties is crucial in order to come up with better alternatives for SCMs in the future. However, the project also points to difficulties in quantifying phases with overlapping peaks in thermogravimetric analysis and to X-ray diffraction's limitations regarding correct estimation of amorphous AFm phases. Based on the test methods it can be concluded that the used methods give an overall picture of the processes in the specimens but more refined analyses are needed.

Thermogravimetric analysis and X-ray diffraction show evidence of monocarbonate reacting with chloride ions to form Friedel's salt. This reaction will release a carbonate ion into the pore solution. From the results of the TGA measurements, the amount of calcite increased with respectively 98, 50, and 160% for OPC, FA23, and FA35 samples after chloride exposure. Thus, indicating that the released carbonate ion reacts to form calcite. This finding was not supported by the XRD results, but this increased phase in the TGA measurement is a carbonate phase, and the authors attribute the difference between XRD and TGA to XRDs inability to detect amorphous phases and to the uncertainties about the Rietveld refinement methodology. However, more research is needed to estimate to which extend monocarbonate reacts and if the released ion reacts differently in fly ash blends. TGA and XRD furthermore show that the main crystalline chloride binding product is Friedel's salt. OPC specimens form more Friedel's salt than FA specimens, and the level of Friedel's salt decreases with increasing fly ash substitution. However, it can not be concluded based on this study that fly ash bind fewer chloride ions. It can only be concluded that it does not happen as Friedel's salt.

Based on the sorption isotherms and the results from the cup test, it can be concluded that chloride ingress refines the pore structure and enhance transport capabilities. With chloride exposure the water vapor flow rate increases 31.0% for OPC specimens and 26.5% for FA23 specimens. This show that the moisture transport in FA blends will be less affected by chloride ingress than OPC for specimens cured for 28 days. Sorption isotherms showed that the pore structure detected in the range of 33-53% is refined since the volume of pores in the RH range decreased and more volume at RH 11-33% was detected after chloride exposure. This refinement process was slightly more pronounced for FA samples, but no clear relationship between increasing fly ash content and the pore refinement was established. The total volume of pores detected from the dynamic vapor sorption was lower for OPC samples than for samples with fly ash substitution, but the moisture transport of OPC specimens was higher than of specimens with fly ash substitution. The authors therefore point to the connectivity and tortuosity of the pores as being more important for the transport properties.

8 Further Research

"Many of life's failures are people who did not realize how close they were to success when they gave up." – Thomas A. Edison

The topic of fly ash substitution and the microstructural changes in the concrete when added is not fully understood. The slow nature of the pozzolan reaction is something that is not investigated by this study since all specimens were tested after 28 days. It would be interesting to do the experimental work of this thesis on the same OPC and FA specimens cured for 6 month and 1 year. This might show more interesting findings in the change of the solid products and microstructure depending on the fly ash content.

As outlined in the discussion of the migration experiment, the non-steady-state migration coefficient and the electrical resistance did not match very well in this study. The cause of this would be relevant to investigate further. Whether it is the lowered pH in the FA specimens causing a larger measured penetration depth, the release of carbonate ions causing the resistance to be higher for FA blends, or a third explanation should be investigated further. This could be investigated by determining the amount of carbonate in the anolyte solution of NT Build 492 or by measuring the actual chloride content at different penetration depths after exposure. For an investigation of the phenomenon of electrophoresis, the authors suggest that this could be done as a mixed study between civil engineering and chemical engineering. A study on the difference between paste and mortar/concrete specimens could also be of interest.

Based on the XRF results shown in *Section* <u>6.2</u> it is suggested that XRF of pastes with fly ash is prone to further research. The authors did not find the expected amount of compounds in the anhydrous cement and fly ash and thus do not trust the results obtained. A study on how to determine the composition of paste samples by use of the XRF available at the Technical University of Denmark is hence needed.

The volume of different pore sizes is investigated through sorption isotherms. Initially, it was anticipated that the pore structure should be examined from Mercury Intrusion Porosimetry (MIP), but due to technical issues and the Corona situation, this part of the study was not performed. An investigation of the pore structure by a MIP test would be a great supplement to the sorption isotherms.

As suggested by Wolter (2020) [10] it would also be of great interest to investigate the binding of chlorides more carefully in OPC and FA blends. As previously mentioned only binding of chlorides as Friedel's salt is investigated in this study. However, the binding of chlorides in the amorphous C-S-H and/or other binding products would be a relevant topic of further research.

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Appendices

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APPENDIX A

Documentation of Mixing and Casting of paste samples

This appendix contains additional information on the used equipment for the mixing and casting. A non-traditional European casting procedure was chosen for the casting of the paste samples to get a more liquid homogeneous paste. The mixing procedure follows ASTM C1738/C1738M-19 for high shear mixing of hydraulic cement paste. However, this procedure requires a blender with a rotation speed of respectively 4000 rpm and 10 000 rpm. The blender used in this study has a "no-load" rotation speed of respectively 15 800 rpm and 22 000 rpm. These values were obtained through mail correspondence with Waring Commercial Lab Products.

This appendix also contains pictures taken at the actual mixing and casting of the paste samples showing the mixing procedure illustrative. The temperatures of the room and mixing water when casting paste samples are also provided in this appendix.

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Overview of casting	A3
Demoulding and sealing in bags	A3



Waring Commercial, 8011S - Lab blender

Figure 37: Waring Commercial, 8011S - Lab blender; Used for mixing paste samples

Table 18: Segment of the LAB CATALOG PRODUCT INFORMATION obtained from mail correspondence with Operations Director Tom Tremblay for Waring Commercial Lab Products.

Model Number	Voltage [V]	Speed (low) [rpm]	Speed (High) [rpm]	Approvals
8011S	220-240	15800	22000	RoHS

Mixing and casting procedure



(a) Equipment



(b) Mixing



(c) Casting

Overview of casting

The identification of the sample is shown in Table 19 together with the dates of casting. Two of each mixtures (OPC and FA23) were cast five times with one or two weeks in between. The casting dates was chosen to analyze the samples in different ways at the same curing age. One of samples for each mixture were exclusively used to examine the chloride penetration depth and the other one was used for further testing. Later on FA35 samples were cast with 6 days in between. Table 19 additionally contains the temperatures of the room at casting and of the mixing water.

Table 19:	Overview	of dates	and	temperatures
-----------	----------	----------	-----	--------------

	$\begin{array}{c} OPC_I\\ FA23_I \end{array}$	$0PC_2$ $FA23_2$	OPC_{-3} $FA23_{-3}$	OPC_{-5} $FA23_{-5}$	OPC_{-6} $FA23_{-6}$	$FA35_9$	$FA35_10$
Date of Casting Time of Casting Date of de-moulding	24-08-20 7:50 8:15 10-09-20	31-08-20 7:55 8:25 17-09-20	07-09-20 7:50 8:10 24-09-20	21-09-20 7:50 8:10 08-10-20	28-09-20 8:00 8:20 15-09-20	20-10-20 10:15 06-11-20	26-10-20 8:15 12-11-20
Temperature Room [°C] Mixing water [°C]	$\begin{array}{c c} 22\\ 22 & 22 \end{array}$	$\begin{array}{c c} 23\\ 22 & 22 \end{array}$	$\begin{array}{c} 22\\ 22 & 22 \end{array}$	23 23 22	$\begin{array}{c}23\\22&22\end{array}$	21 20	22 21

De-moulding and sealing in bags



(a) De-moulding







(c) Sealed specimen

Figure 39: De-moulding and sealing of specimen

APPENDIX B

Chloride Migration test and penetration depth

This appendix contains additional information of the used equipment for the chloride migration test. The saw used to cut the sample prior to migration test is shown together with pictures at the actual cut specimen. Besides the used equipment for the migration test this appendix also contains the calculated ratio between the surface area of the specimens required in NT Build 492, and the specific surface area used in present test. This ratio is used to convert the initial current from NT Build 492 into suitable measures for the present test performed in this study. Furthermore, the procedure for splitting of the sample after end migration test is also shown with pictures.

Additionally, the measurements of sample size, current and voltage measurements before and after the migration test is also attached in this appendix.

CONCON

Pictures
Initial current NT Build conversion; Paste sample
Pictures; Splitting the sample
Chloride Penetration Depth
Current for FA23_5B(II) specimen
Calculation of migration coefficients
1^{st} cast specimens
2^{nd} cast specimens
$3^{\rm rd}$ cast specimens
5^{th} cast specimens
6^{th} cast specimens
9^{th} cast specimens
10^{th} cast specimens

Sawing of the specimen



(a) Saw; Struers Discotom-65



(b) Sample sawed into items

Figure 40: Saw used for cutting and sample cut into items.

Figure 41: Vacuum desiccator and pump

Vacuum pump and desiccator



(a) Vacuum pump



(b) Vacuum desiccator



(c) Valve

Chloride migration test set-up



(a) Piece II in sleeve with anolyte solution



(b) Pipette to apply anolyte solution $(Ca(OH)_2)$ on top



(c) Reservoirs with specimens attached to current logging device and computer

Figure 42: Chloride Migration test

Converting initial current from NT Build 492 into suitable measures

The values for the initial current stated in the standard NT 492 is converted into suitable measures by calculation of the ratio between the surface area of the specimens required in the standard, and the specific surface area used in present test. The Initial current provided in the standard is the converted into the current used in present test by dividing the standard value with the ratio calculated.

Table 20:	Dimensions	of test	specimens	from	NT	Build	and	present	study
-----------	------------	---------	-----------	------	----	-------	-----	---------	-------

Diameter of specimens acc. NT BUILD 492 Diameter of specimens in present study	$\begin{array}{c} 100\mathrm{mm} \\ 22\mathrm{mm} \end{array}$
Surface area of specimens acc. NT BUILD 492 Surface area of specimens in present study	$\frac{7854\mathrm{mm}^2}{380\mathrm{mm}^2}$
Ratio	20.66

Splitting the sample



(a) Initial longitudinal cut done with a saw



(b) The approx. 1 mm deep cut after sawing

Figure 43: Splitting of the sample



(c) Splitting sample with hammer and chisel

Chloride Penetration Depth

Specimens with the index B was used to check the chloride penetration depth by spraying with silver nitrate. The actual experiments was done on the specimens with index A. The penetration depths of the B specimens is show and this is used as reasoning for how much of specimen A could be used for experiments. After chopping of the estimated chunk of specimen that should be penetrated with chlorides, the remaining piece of specimens A was then split to verify that only chloride penetrated specimen was used.

OPC 1A(II) 1B(II OPC 1B(II FA_1A(II)

Specimens; OPC 1A(II), OPC 1B(II), FA23 1A(II) and FA23 1B(II)

Specimens; OPC 2A(II), OPC 2B(II), FA23 2A(II) and FA23 2B(II)

Figure 44: Chloride penetration depth of B-specimens and check on used A-specimens for experiments

OPC 2A(II) FA_2B(II) OPC 2B(II FA_2A(II)

(a) Penetration depth of OPC 2B(II) and FA23 2B(II)

Figure 45: Chloride penetration depth of B-specimens and check on used A-specimens for experiments







Specimens; OPC_3A(II), OPC_3B(II), FA23_3A(II) and FA23_3B(II)

(a) Penetration depth of $OPC_3B(II)$ and $FA23_3B(II)$

(b) Check

Figure 46: Chloride penetration depth of B-specimens and check on used A-specimens for experiments

Specimens; OPC_5A(II), OPC_5B(II), FA23_5A(II) and FA23_5B(II)



(a) Penetration depth of OPC_5B(II) and FA23_5B(II)



(b) Check

Figure 47: Chloride penetration depth of B-specimens and check on used A-specimens for experiments



Specimens; OPC 6A(II), OPC 6B(II), FA23 6A(II) and FA23 6B(II)

(a) Penetration depth of OPC_6B(II) and FA23_6B(II)





Specimens; $FA35_9A(II)$ and $FA35_9B(II)$

(a) Penetration depth of FA35_9B(II) and FA35_9D(II)

(b) Check

Figure 49: Chloride penetration depth of B- and D-specimens and check on used A- and C-specimens for experiments

Specimens; $FA35_{10A(II)}$, $FA35_{10B(II)}$, $FA35_{10C(II)}$ and $FA35_{10D(II)}$



Figure 50: Chloride penetration depth of of $FA35_10A(II)$ and $FA35_10B(II)$



Current for FA23 5B(II) specimen and reason.

Figure 51: Reason to take this current measurement out of data

In Figure 51 the current measurement from the migration test on FA23 specimens is shown. As it can be seen the current is stable on almost 16 mA through out the experiment. The current read of from the display on the power supply also showed a constant current through out the experiment, this was however on 17 mA. It seems that the logger has reached its maximum, which we had been told from the technician should be around 15 mA. The specimen had a larger hollow void and had not been cast correctly. Therefor this current measurement has been taken out of the results. In Figure 47a the penetration depth on the hollow specimen FA23_5B(II) is shown. When during the actual further testing, specimen FA23_5A(II) was used instead, and as it can be seen on Figure 47b only chloride penetrated material has been used.

	Cast 1		Ca	st 2	Cast 3		Ca	st 5	Cast 6		Ca	st 9	Cas	t 10
	OPC	FA23	OPC	FA23	OPC	FA23	OPC	FA23	OPC	FA23	FA35	FA35	FA35	FA35
x _d [mm]	10	12	10	12	11,5	12	10,5		10	11	13	14,5	14	13
U [V]	10,00	10,00	10,00	10,00	10,00	10,00	10,00		10,00	10,00	10,00	10,00	10,00	10,00
T [K]	19,50	19,50	20,00	20,00	19,50	19,50	19,50		19,00	19,00	19,00	19,00	19,00	19,00
L [mm]	49,44	51,08	50,05	51,11	49,19	49,82	50,54		49,95	50,04	48,95	50,09	48,96	51,45
t [hr]	24,00	24,00	24,00	24,00	24,00	24,00	24,00		24,00	24,00	24,00	24,00	24,00	24,00
$D_{nssm} [\cdot 10^{-12} m^2/s]$	12,24	15,69	12,37	15,72	14,47	15,38	13,22		12,32	13,87	16,68	19,34	18,22	17,36
OPC FA23 FA35														
Manual In	1		1/	14										

Calculation of migration coefficients

 OPC
 FA23
 FA35

 Mean x_d [mm]
 10,4
 11,8
 13,63

 Standard deviation
 0,6
 0,4
 0,6

 Mean D_{nasm}
 12,9
 15,2
 18,01

 Standard deviation
 0,8
 0,8
 1,0

Current, end (Each) [mA]

Clock; When ending test

Penetration Depth

Software; Current, end (Each) [mA]

Paste samples

1 st cast specimens	21/09 - 23/09 2020										
	OPC 1A	OPC 1B	FA23 1A	FA23 1B							
	(II)	(IĪ)	(II)	(II)							
Clock; De-moulded	09:01	09:08	09:13	09:22							
Length ₁ [mm]	47.13	49.43	50.35	51.16							
Length ₂ [mm]	47.11	49.53	50.59	51							
Length ₃ [mm]	47.18	49.35	50.39	51.09							
Av. Length [mm]	47.14	49.44	50.44	51.08							
Vacuum											
Date		21-09-2020									
Room Temperature [°C]		2	20								
Clock; Pressure applied		09):36								
Clock; Pressure constant at 25mbar		09):41								
Clock; Essicator shut off		12	2:41								
Clock; Start to fill with Ca(OH)2		12	2:42								
Clock; Filled with Ca(OH) ₂		12	2:43								
Clock; Pressure applied	12:44										
Clock; Pressure achieved 25mbar		12	2:49								
Clock; Air allowed in		13	:50								
Migration											
Date		22-09	9-2020								
Room Temperature [°C]		2	21								
Cahode solution Temperature [°C]	20 20										
Anode solution Temperature [°C]	20	20	20	20							
Voltage pre-set											
Initial current [mA]	21	21	15	16							
Corrected applied voltage [V]	1	10	1	0							
New current, start (Each) [mA]	6	6	4	5							
Software; New current, start (Each) [mA]	6.50	6.63	5.03	5.25							
New current, start (Both) [mA]	1	12		9							
Software; New current, start (Both) [mA]	12	2.37	9.	89							
Clock; When starting test		80	3:38								
Date		23-09	9-2020								
Room Temperature [°C]		2	20								
Clock; When reading of Temperature		07	7:58								
Cahode solution Temperature [°C]	1	19									
Anode solution Temperature [°C]	19	19	19 19								
Clock; When reading of current	08:28										
Current, end (Both) [mA]	1	11		9							
Software; Current, end (Both) [mA]	11	.18	9.	9.41							

5

5.73

-

5

5.65

4

4.81

-

08:38 10 4

4.82

12

2nd cast specimens

Paste samples

28/09 - 30/09 2020

	OPC 24	OPC 2P	EA22 2A	EA22 2B						
			$\begin{bmatrix} 17A23 \\ (II) \end{bmatrix}$	(II)						
Clock: De-moulded	08:50	08:53	08:59	09:08						
Length [mm]	50.19	50.05	50.55	51.13						
Length ₂ [mm]	50.28	50.11	50.49	51.08						
Length ₂ [mm]	50.15	50	50.59	51.11						
Av. Length [mm]	50.21	50.05	50.54	51.11						
Vacuum	<u> </u>									
Date	28-09-2020									
Room Temperature [°C]		2	1							
Clock; Pressure applied		09	:26							
Clock; Pressure constant at <u>24</u> mbar		09	:34							
Clock; Essicator shut off		12	:34							
Clock; Start to fill with Ca(OH) ₂		12	:35							
Clock; Filled with Ca(OH) ₂		12	:36							
Clock; Pressure applied		12	:37							
Clock; Pressure achieved <u>26</u> mbar		12	:40							
Clock; Air allowed in		13	:40							
Migration										
Date		29-09	-2020							
Room Temperature [°C]		2	1							
Cahode solution Temperature [°C]	2	0	2	0						
Anode solution Temperature [°C]	21	21	21	21						
Voltage pre-set		30	V							
Initial current [mA]	19 20 15 1									
Corrected applied voltage [V]	1	1	0							
New current, start (Each) [mA]	5	6	4	4						
Software; New current, start (Each) [mA]	6.01	6.29	4.89	4.63						
New current, start (Both) [mA]	12 9									
Software; New current, start (Both) [mA]	11	.87	9.	02						
Clock; When starting test		08	:36							
Date	30-09-2020									
Room Temperature [°C]		1	9							
Clock; When reading of Temperature		08	:01							
Cahode solution Temperature [°C]	2	0	2	0						
Anode solution Temperature [°C]	19	19	19	19						
Clock; When reading of current		08	:35							
Current, end (Both) [mA]	1	0		8						
Software; Current, end (Both) [mA]	10	.66	8.	48						
Current, end (Each) [mA]	5	5	4	4						
Software; Current, end (Each) [mA]	5.42	5.52	4.45	4.36						
Clock; When ending test		08	:36							
Approx Penetration Depth [mm]	-	10	-	12						

3rd cast specimens

Paste samples

05/10 - 07/10 2020

	OPC_3A	OPC_3B	FA23_3A	FA23_3B		
Clock: De-moulded	07.47	07:43	07:52	07:55		
Length, [mm]	50.03	49.11	49.3	49.81		
Length [mm]	50.08	49.17	49.25	40.70		
Longth [mm]	50.07	40.20	40.27	40.07		
Ary Longth [mm]	50.07	49.20	49.27	49.07		
	50.00	49.19	49.27	49.82		
Vacuum	T	05.14	2020	_		
Date		05-10	0-2020	_		
Room Temperature [*C]		-	20	_		
Clock; Pressure applied		30	5:12			
Clock; Pressure constant at <u>26</u> mbar		08	5:17			
Clock; Essicator shut off			:17			
Clock; Start to fill with $Ca(OH)_2$		11	.:17			
Clock; Filled with Ca(OH) ₂		11	:18			
Clock; Pressure applied		11	:18			
Clock; Pressure achieved 27 mbar	-	11	:23			
Clock; Air allowed in		06-10	0-2020	_		
Migration	-			_		
Date		06-10	0-2020			
Room Temperature [°C]			20			
Cahode solution Temperature [°C]	2	20	2	!0		
Anode solution Temperature [°C]	20	20	20	20		
Voltage pre-set		30	0 V			
Initial current [mA]	19	20	15	16		
Corrected applied voltage [V]	1	0	1	0		
New current, start (Each) [mA]	6	6	4	5		
Software; New current, start (Each) [mA]	6.00	6.35	5.05	5.33		
New current, start (Both) [mA]	1	2	9	9		
Software; New current, start (Both) [mA]	11	.96	9.	87		
Clock; When starting test		08	3:38			
Date		07-10	0-2020			
Room Temperature [°C]		3	20			
Clock; When reading of Temperature		08	3:07			
Cahode solution Temperature [°C]	1	9	1	9		
Anode solution Temperature [°C]	19	19	19	19		
Clock; When reading of current		08	3:38			
Current, end (Both) [mA]	10 9					
Software; Current, end (Both) [mA]	10	.43	9.	31		
Current, end (Each) [mA]	5	5	4 4			
Software; Current, end (Each) [mA]	5.16	5.46	4.77	4.82		
Clock; When ending test		08	3:38			
Approx Penetration Depth [mm]	-	11	1.525.7	12		

Chloride Migration Test: 5th cast specimens

Paste samples

5 th cast specimens	19/10 - 21/10 2020								
	OPC 5A	OPC_5B	FA23 5A	FA23_5B					
	(II)	(II)	(II)	(II)					
Clock; De-moulded	08:24	08:28	08:35	08:38					
Length ₁ [mm]	49.38	50.45	50.66	51.65					
Length ₂ [mm]	49.50	50.54	50.62	51.62					
Length ₂ [mm]	49.44	50.63	50.68	51.72					
Av. Length [mm]	49.44	50.54	50.65	51.66					
Vacuum									
Date		19-10	-2020						
Room Temperature [°C]		2	20						
Clock; Pressure applied		09	:53						
Clock; Pressure constant at 26 mbar		09	:55						
Clock; Essicator shut off		12	:54						
Clock; Start to fill with Ca(OH)2		12	:55						
Clock; Filled with Ca(OH) ₂		12	:55						
Clock: Pressure applied		12	:56						
Clock; Pressure achieved 26 mbar		13	:01	-					
Clock; Air allowed in		14	:02						
Migration									
Date		20-10)-2020						
Room Temperature [°C]		2	21						
Cahode solution Temperature [°C]	1	9	1	9					
Anode solution Temperature [°C]	20	20	20	20					
Voltage pre-set	1	3() V						
Initial current [mA]	18	19	46	15					
Corrected applied voltage [V]	1	0	1	0					
New current, start (Each) [mA]	5	6	13	4					
Software; New current, start (Each) [mA]	5.92	6.29	13.49	4.63					
New current, start (Both) [mA]	1	1	1	7					
Software; New current, start (Both) [mA]	11	.67	15,94	(max)					
Clock; When starting test		08	:15						
Date		21-10)-2020						
Room Temperature [°C]		2	20	_					
Clock; When reading of Temperature		.08	:14						
Cahode solution Temperature [°C]	1	9	1	9					
Anode solution Temperature [°C]	19	19	19	19					
Clock; When reading of current		08	:15						
Current, end (Both) [mA]	1	0	1	7					
Software; Current, end (Both) [mA]	10	.32	15,94	(max)					
Current, end (Each) [mA]	5	5	13	4					
Software; Current, end (Each) [mA]	5.16	5.43	13.17	4.30					
Clock; When ending test		08	:15						
Approx Penetration Depth [mm]	1 - 6 -	10.7		22					

6th cast specimens

Paste samples 26/10 - 28/10 2020

	OPC_6A	OPC_6B	FA23_6	FA23_6		
	(II)	(II)	A (II)	B (II)		
Clock; De-moulded	09:56	09:58	10:04	10:06		
Length ₁ [mm]	49.73	49.98	49.73	50.02		
Length ₂ [mm]	49.84	49.96	49.86	50.06		
Length ₃ [mm]	49.8	49.95	49.79	50.05		
Av. Length [mm]	49.79	49.96	49.79	50.04		
Vacuum						
Date		26-10-2	2020			
Room Temperature [°C]		20	(
Clock; Pressure applied		10:5	55			
Clock; Pressure constant at 24,5 mbar		11:0	00			
Clock; Essicator shut off		14;(00			
Clock; Start to fill with Ca(OH)2		14:()9			
Clock; Filled with Ca(OH) ₂		14:1	0			
Clock; Pressure applied		14:1	1			
Clock; Pressure achieved 27 mbar		14:1	9			
Clock; Air allowed in		15:1	9			
Migration						
Date		27-10-2	2020			
Room Temperature [°C]		20	(
Cahode solution Temperature [°C]	1	9	19			
Anode solution Temperature [°C]	19	19	19	19		
Voltage pre-set		30	V			
Initial current [mA]	18	19	15	15		
Corrected applied voltage [V]	1	0	1	0		
New current, start (Each) [mA]	5	6	5	4		
Software; New current, start (Each) [mA]	5.63	5.82	5.11	4.84		
New current, start (Both) [mA]	1	1	0	9		
Software; New current, start (Both) [mA]	11	.10	9.	.67		
Clock; When starting test		08:5	55			
Date		28-10-2	2020			
Room Temperature [°C]		20	1			
Clock; When reading of Temperature		08:5	54			
Cahode solution Temperature [°C]	1	9	1	9		
Anode solution Temperature [°C]	19	19	19	19		
Clock; When reading of current		08:5	5			
Current, end (Both) [mA]	1	9	3	8		
Software; Current, end (Both) [mA]	9.	66	9.	.02		
Current, end (Each) [mA]	4	5	4	4		
Software; Current, end (Each) [mA]	4.79	5.03	4.78	4.52		
Clock; When ending test		08:5	55			
Approx Penetration Depth [mm]		10.2	1 4 1	11.2		

Paste samples

9th cast specimens

17/11 - 19/11 2020

	FA35_9A	FA35_9B	FA35_9C	FA35_9D				
Clock: De-moulded	08:11	08.13	08.30	08.20				
Length. [mm]	51.04	49.00	50.92	50.12				
Length [mm]	51,04	49,00	51.15	50,00				
	51,05	40,95	51,15	50,09				
Length ₃ [mm]	51,05	48,93	51,05	50,07				
Av. Length [mm]	51,04	48,95	51,04	50,09				
Vacuum	1							
Date	17-11-2020							
Room Temperature [°C]		2	20	_				
Clock; Pressure applied		08	:46					
Clock; Pressure constant atmbar		08	:54					
Clock; Essicator shut off		11	:52					
Clock; Start to fill with Ca(OH) ₂		11	:53					
Clock; Filled with Ca(OH) ₂		11	:54					
Clock; Pressure applied		11	:55					
Clock; Pressure achievedmbar		12	:00					
Clock; Air allowed in		13	:20					
Migration								
Date		18-11	-2020					
Room Temperature [°C]		1	9	_				
Cahode solution Temperature [°C]	1	9	l l	19				
Anode solution Temperature [°C]	19	19	19	19				
Voltage pre-set		30) V					
Initial current [mA]	13	15	14	16				
Corrected applied voltage [V]	1	0	3	10				
New current, start (Each) [mA]	4	4	4	5				
Software; New current, start (Each) [mA]	4,25	4,77	4,51	4,91				
New current, start (Both) [mA]		8	1	9				
Software; New current, start (Both) [mA]	8,	40	9.	19				
Clock; When starting test		07	:53					
Date		19-11	-2020					
Room Temperature [°C]		2	20					
Clock; When reading of Temperature	-	07	:50					
Cahode solution Temperature [°C]	1	9	1	19				
Anode solution Temperature [°C]	19	19	19	19				
Clock; When reading of current	07:52							
Current, end (Both) [mA]		7	1	8				
Software; Current, end (Both) [mA]	7.	97	8.	.62				
Current, end (Each) [mA]	3	4	4	4				
Software; Current, end (Each) [mA]	4,03	4,36	4,23	4,53				
Clock; When ending test		07	:53					
Approx Penetration Depth [mm]	÷	13	-	14,6				

10th cast specimens

Paste samples

23/11 - 25/11 2020

	FA35_10A	FA35_10B		
	(II)	(II)		
Clock; De-moulded	10:13	10:15		
Length ₁ [mm]	48,42	51,42		
Length2 [mm]	48,47	51,57		
Length ₃ [mm]	48,48	51,37		
Av. Length [mm]	48,46	51,45		
Vacuum				
Date	23-11	-2020		
Room Temperature [°C]	1	9		
Clock; Pressure applied	10	:34		
Clock; Pressure constant at <u>27</u> mbar	10	:41		
Clock; Essicator shut off	13	:41		
Clock; Start to fill with Ca(OH) ₂	13	:43		
Clock; Filled with Ca(OH) ₂	13	:44		
Clock; Pressure applied	13	:44		
Clock; Pressure achieved <u>28</u> mbar	13	:50		
Clock; Air allowed in	15	:10		
Migration				
Date		24-11-	-2020	
Room Temperature [°C]		20	0	
Cahode solution Temperature [°C]	1	9		
Anode solution Temperature [°C]	19	19		
Voltage pre-set		30	V	•
Initial current [mA]	14	13		
Corrected applied voltage [V]	1	0		
New current, start (Each) [mA]	4	4		
Software; New current, start (Each) [mA]	4,54	4,00		
New current, start (Both) [mA]	5	8		
Software; New current, start (Both) [mA]	8,	35		
Clock; When starting test		09:	00	
Date		25-10-	-2020	
Room Temperature [°C]	1	9		
Clock; When reading of Temperature	09	:05		
Cahode solution Temperature [°C]	1	8		•
Anode solution Temperature [°C]	18	18		
Clock; When reading of current	09	:06		
Current, end (Both) [mA]	8	8		•
Software; Current, end (Both) [mA]	8,	00		
Current, end (Each) [mA]	4	3		
Software; Current, end (Each) [mA]	4,32	3,83		
Clock; When ending test	09	:07		
Approx Penetration Depth [mm]	13	12		

APPENDIX C

Procedure for Arresting Hydration

This appendix contains pictures taken from arresting of the hydration. The used equipment and the procedure are shown. Additionally, this appendix contains the actual date, time, and quantities of powder, isopropanol, and diethyl ether.

Content

Pict	tures		 					•					•					A1	9
2^{nd}	and $3^{\rm rd}$	cast	 				 											A2	0
4^{th}	and $6^{\rm th}$	cast	 		 •				•									A2	$^{!1}$
9^{th}	cast		 				•											A2	2



(a) Equipment for cruching, grinding and sieving



(b) Crushing the sample with a hammer



(c) Fume Cabinet with equipment placed inside





(a) Fume Cabinet



(b) Grinding



(c) Sieving

Figure 53: Grinding and sieving done in glove box $% \mathcal{F}(\mathcal{F})$



(a) Equipment for filtrating suspension in fume hood



(b) Filtrating the suspension in a Büchner funnel



(c) Color of the sample becomes lighter

Figure 54: Filtrating the suspension in a fume hood

Arresting hydration: 2^{na} cast specimens

30-09-2020

Specimens	OPC 2A(II)	OPC 2A(I)	FA23 2A(II)	FA23 2A(I)						
Date	30-09-2020									
Clock; Ended Migration test		0	8:36							
Clock; Removed from reservoir	10:58	09:24	11:39	11:15						
Clock; Crushed with hammer	10:59	09:25	11:40	12:16						
Clock; In Glove Box	11:01	09:26	11:42	12:17						
Grinded sample < 150mm [g]	6,44	11,28	5,87	8,43						
Isopropanol [ml]	≈ 80	≈ 120	≈ 60	≈90						
Clock; Mixed with isopropanol	11:17	09:55	11:57	12:24						
Clock; Start filtrating in büchner funnel	11:32	10:11	12:12	12:49						
Diethyl Ether [ml]	≈10	≈15	≈ 8	≈ 10						
Clock; Adding diethyl ether	11:36	10:13	12:14	12:53						
Clock; End filtrating in büchner funnel	11:50	10:26	12:29	13:08						
Clock; Placed in petri dish	11:51	10:26	12:30	13:08						
Clock; Dried in ovn start	11:52	10:27	12:30	13:09						
Clock; Dried in ovn end	12:02	10:37	12:40	13:19						
Clock; Sealed in bag and tube	12:04	10:40	12:43	13:21						

Arresting hydration:

3rd cast specimens

07-10-2020

Specimens	OPC_3A(II)	OPC_3A(I)	FA23_3A(II)	FA23_3A(I)						
Date	07-10-2020									
Clock; Ended Migration test	08:38									
Clock; Removed from reservoir	10:05	10:38	08:52	09:25						
Clock; Crushed with hammer	10:06	10:39	08:53	09:26						
Clock; In Glove Box	10:08	10:40	08:54	09:27						
Grinded sample < 150mm [g]	6,66	6,57	5,87	5,31						
Isopropanol [ml]	≈ 80	≈ 80	≈ 70	≈ 60						
Clock; Mixed with isopropanol	10:18	10:52	09:06	09:43						
Clock; Start filtrating in büchner funnel	10:33	11:07	09:21	09:58						
Diethyl Ether [ml]	≈8	≈9	≈ 8	≈7						
Clock; Adding diethyl ether	10:36	11:09	09:23	10:01						
Clock; End filtrating in büchner funnel	10:51	11:25	09:38	10:16						
Clock; Placed in petri dish	10:52	11:27	09:39	10:16						
Clock; Dried in ovn start	10:53	11:27	09:40	10:17						
Clock; Dried in ovn end	11:03	11:37	09:50	10:27						
Clock; Sealed in bag and tube	11:05	11:38	09:51	10:28						

Arresting hydration: 5th cast specimens

21-10-2020

Specimens	OPC_5A(II)	OPC_5A(I)	FA23_5A(II)	FA23_5A(I)						
Date	21-10-2020									
Clock; Ended Migration test		0	8:15							
Clock; Removed from reservoir	10:17	10:36	08:49	11:09						
Clock; Crushed with hammer	10:18	10:37	08:52	11:10						
Clock; In Glove Box	10:19	10:38	08:53	11:11						
Grinded sample < 150mm [g]	4,45	7,19	5,62	4,81						
Isopropanol [ml]	≈ 50	≈ 80	≈ 60	≈ 50						
Clock; Mixed with isopropanol	10:28	10:50	09:05	11:20						
Clock; Start filtrating in büchner funnel	10:43	11:05	09:20	11:35						
Diethyl Ether [ml]	≈6	≈9	≈7	≈6						
Clock; Adding diethyl ether	10:45	11:08	09:23	11:37						
Clock; End filtrating in büchner funnel	11:00	11:23	09:37	11:52						
Clock; Placed in petri dish	11:00	11:24	09:37	11:52						
Clock; Dried in ovn start	11:01	11:25	09:38	11:53						
Clock; Dried in ovn end	11:11	11:35	09:48	12:03						
Clock; Sealed in bag and tube	11:12	11:36	09:50	12:05						

Arresting hydration:

6th cast specimens

28-10-2020

Specimens	OPC_6A(II)	OPC_6A(I)	FA_6A(II)	FA_6A(I)						
Date	28-10-2020									
Clock; Ended Migration test	08:55									
Clock; Removed from reservoir	10:04	10:37	09:37	11:04						
Clock; Crushed with hammer	10:05	10:38	09:38	11:05						
Clock; In Glove Box	10:06	10:39	09:39	11:06						
Grinded sample < 150mm [g]	4,17	4,45	3,96	3,92						
Isopropanol [ml]	≈ 50	≈ 50	≈ 50	≈ 50						
Clock; Mixed with isopropanol	10:14	10;48	09:53	11:13						
Clock; Start filtrating in büchner funnel	10:29	11:03	10:08	11:28						
Diethyl Ether [ml]	≈6	≈ 6	≈6	≈6						
Clock; Adding diethyl ether	10:33	11:05	10:12	11:30						
Clock; End filtrating in büchner funnel	10:48	11:20	10:27	11:45						
Clock; Placed in petri dish	10:49	11:21	10:28	11:46						
Clock; Dried in ovn start	10:50	11:22	10:28	11:47						
Clock; Dried in ovn end	11:00	11:32	10:38	11:57						
Clock; Sealed in bag and tube	11:02	11:32	10:40	12:00						

Arresting hydration: 9th cast specimens: FA35

19-11-2020

Specimens	FA35_9A(II)	FA35_9A(I)	FA35_9B(II)	FA35_9B(I)				
Date	19-11-2020							
Clock; Ended Migration test	07:53							
Clock; Removed from reservoir	08:33 09:22 08:58 09							
Clock; Crushed with hammer	08:35	09:23	08:59	09:46				
Clock; In Glove Box	08:36	09:24	09:00	09:47				
Grinded sample < 150mm [g]	5,04	5,87	6,60	5,68				
Isopropanol [ml]	≈ 60	≈ 60	= 70	≈ 60				
Clock; Mixed with isopropanol	08:47	09:33	09:08	09:56				
Clock; Start filtrating in büchner funnel	09:02	09:48	09:23	10:11				
Diethyl Ether [ml]	≈ 8	≈ 8	≈ 7	≈7				
Clock; Adding diethyl ether	09:04	09:50	09:27	10:13				
Clock; End filtrating in büchner funnel	09:19	10:05	09:42	10:28				
Clock; Placed in petri dish	09:20	10:06	09:44	10:28				
Clock; Dried in ovn start	09:20	10:07	09:45	10:29				
Clock; Dried in ovn end	09:30	10:17	09:55	10:39				
Clock; Sealed in bag and tube	09:33	10:21	09:57	10:41				

APPENDIX D

X-ray Fluorescence

This appendix contains the raw data from XRF analysis. The raw data can be seen in the columns under the grey headers. Furthermore, calculations of the oxides mass-% is calculated from stoichiometric calculations for the relevant compounds. This is shown in the columns under the yellow headers.

Content

Rapid Cement	4
[°] ly Ash	5
$\operatorname{OPC}(\mathbf{I}) \dots \dots$	6
$\operatorname{OPC}(\mathbf{II}) \dots \dots$	7
$A23(I) \dots A2$	8
$A23(II) \dots A2$	9

Sample name:			CEM (Anhyd							
Preparation powder		Si	ample amount:	10,3035						
Date:		01-10-2020	Sample height		14,24					
Made by	:	es								
-	Raw dat	a	1			Data proces	ssing			
			Molar mass; O	15,999 g/	mol		Q1	lide		
Com- pound	Conc [%]	Mass [g]	Molar masse [g/mol]	mol	Com- pound	mol ratio	mol	O mass [g]	tot mass	tot [%]
Na	0,0175	0,00181	22,99	0,000079	Na ₂ O	0 (*1/2)	0,00004	0,000628	0,00243	0,02362
Mg	0,1850	0,01906	24,305	0,000784	MgO	0 (*1)	0,00078	0,012547	0,03161	0,30678
AI	1,1450	0,11798	26,982	0,004372	Al ₂ O ₃	O (*3/2)	0,00656	0,104930	0,22291	2,16339
Sī	4,5470	0,46850	28,085	0,016682	SiO ₂	O (*2)	0,03336	0,533775	1,00228	9,72753
s	1,2010	0,12375	32,06	0,003860	SO3	O (*3)	0,01158	0,185259	0,30900	2,99902
CI	0,0329	0,00339	35,45	0,000096						
ĸ	0,4060	0,04183	39,098	0,001070	K ₂ O	O (*1/2)	0,00053	0,008559	0,05039	0,48907
Ca	54,8340	5,64982	40,078	0,140971	CaO	0 (*1)	0,14097	2,255389	7,90521	76,72354
Ti	0,1350	0,01391	204,38	0,000068	TiO ₂	O (*2)	0,00014	0,002178	0,01609	0,15614
v	0,0101	0,00104	50,942	0,000020						
Cr	0,0093	0,00096	51,996	0,000018						
Mn	0,0335	0,00345	54,938	0,000063	MnO ₂	O (*2)	0,00013	0,002008	0,00546	0,05295
Fe	4,0310	0,41533	55,845	0,007437	Fe ₂ O ₃	O (*3/2)	0,01116	0,178483	0,59382	5,76326
Cu	0,0288	0,00296	63,546	0,000047						
Zn	0,0418	0,00431	65,38	0,000066						
As	0,0030	0,00031	26,982	0,000011						
Br	0,0006	0,00006	79,904	0,000001						
Rb	0,0013	0,00013	85,468	0,000002						
Sr	0,1970	0,02030	87,62	0,000232						
Y	0,0016	0,00017	88,906	0,000002						
Zr	0,0085	0,00088	91,224	0,000010						
Sn	0,0160	0,00165	118,71	0,000014						
Sb	0,0068	0,00070	121,76	0,000006						
Te	0,0160	0,00164	127,6	0,000013						
Ba	0,0443	0,00456	137,33	0,000033						
Lu	0,0004	0,00004	174,97	0,000000						
Re	0,0015	0,00016	186,21	0,000001						
Pb	0,0029	0,00030	207,2	0,000001						
SUM	66,958	6,89900			SUM of o	xides	0,20525	3,283756197		31,870298

=

Prepara	tion	powder		Sample amount:	8,3113					
Date:		01-10-2020		Sample height	14,39					
Made b	/:	es								
	Raw da	ta				Data process	ing			
			Molar mass; O	15,999 g/	mol		0	ide		
Com- pound	Conc [%]	Mass [g]	Molar masse [g/mol]	mol	Com- pound	mol ratio	mol	O mass [g]	tot mass	tot [%]
Na	0,0369	0,00307	22,990	0,000133	NazO	0 (*1/2)	0,00007	0,001067	0,00413	0,04973
Mg	0,2280	0,01895	24,305	0,000780	MgO	0 (*1)	0,00078	0,012474	0,03142	0,37808
AI	6,4200	0,53359	26,982	0,019776	Al ₂ O ₃	0 (*3/2)	0,02966	0,474585	1,00817	12,13012
Si	17,0940	1,42073	28,085	0,050587	SiOz	O (*2)	0,10117	1,618680	3,03941	36,56966
P	0,3860	0,03208	30,974	0,001036	P205	0 (*5/2)	0,00259	0,041428	0,07351	0,88445
s	0,2850	0,02369	32,060	0,000739	SO3	O (*3)	0,00222	0,035462	0,05915	0,71167
CI	0,0363	0,00301	35,450	0,000085						
к	2,0880	0,17354	39,098	0,004439	K ₂ O	O (*1/2)	0,00222	0,035506	0,20905	2,5152
Ca	2,5490	0,21186	40,078	0,005286	CaO	0 (*1)	0,00529	0,084572	0,29643	3,56655
Ti	0,8550	0,07106	204,380	0,000348	TiO ₂	O (*2)	0,00070	0,011125	0,08219	0,98886
v	0,0285	0,00237	50,942	0,000046						
Cr	0,0161	0,00134	51,996	0,000026						
Mn	0,0553	0,00460	54,938	0,000084	MnO ₂	O (*2)	0,00017	0,002677	0,00727	0,08752
tol	8,6170	0,71618	55,845	0,012825	Fe ₂ O ₃	O (*3/2)	0,01924	0,307769	1,02395	12,32002
Ni	0,0194	0,00161	58,693	0,000027						
Cu	0,0184	0,00153	63,546	0,000024						
Zn	0,0353	0,00294	65,380	0,000045						
Ga	0,0063	0,00053	69,723	0,000008						
Ge	0.0010	0.00008	72,630	0.000001						
As	0.0116	0.00096	26.982	0.000036						
Se	0,0024	0,00020	78,971	0,000003						
Rb	0.0198	0.00164	85,468	0.000019						
5r	0,4500	0.03740	87,620	0.000427						
Y	0,0107	0,00089	88,906	0.000010						
Zr	0,0899	0,00747	91,224	0,000082						
Nb	0,0059	0,00049	92,906	0,000005						
Sn	0,0175	0,00146	118,710	0,000012						
Sb	0,0072	0,00060	121,760	0,000005						
Te	0,0168	0,00139	127,600	0,000011						
Ba	0,3060	0,02543	137,330	0.000185						
Nd	0,0024	0,00020	144,240	0,000001						
Eu	0.0411	0.00342	151,960	0,000022						
Pb	0.0068	0.00057	207,200	0,000003						
Bi	0,0003	0,00002	208,980	0,000000						
SUM	39 764	3 3048912		04-14-24	SUM of o	xides	0.16409	2 625346007		31 58766985

Sample name Fly Ash (Anhydrous)

Deserve	lan .	ouder		Formale amounts	10.251					
Preparat	uon p	10 2020		Sample amount:	10,251					
Made h		1-10-2020		Sample neight	15,69					
wade by	n Baurdata	2				Data	recording			
	Kaw data		Melas erats O	15 000 - 4	and i	Data p	rocessing	de la		
Com- pound	Conc [%]	Mass [g]	Molar mass; O [g/mol]	mol	Com- pound	mol ratio	mol	O mass (g)	tot mass	tot [%]
Mg	0,155	0,01589	24,305	0,000654	MgO	O (*1)	0,000654	0,010459	0,026347	0,25703024
AI	0,967	0,09912	26,982	0,003674	Al ₂ O ₃	0 (*3/2)	0,005510	0,088162	0,187284	1,82707521
Si	4,18	0,42847	28,085	0,015256	SiOz	O (*2)	0,030512	0,488168	0,916639	8,942387039
s	0,815	0,08354	32,06	0,002606	SO3	O (*3)	0,007817	0,125070	0,208612	2,035135839
ci	0,03041	0,00312	35,45	0,000088						
к	0,3	0,03075	39,098	0,000787	K _z O	0 (*1/2)	0,000393	0,006292	0,037043	0,361380378
Ca	49,539	5,07800	40,078	0,126703	CaO	0 (*1)	0,126703	2,027118	7,105113	69,31479872
Ti	0,131	0,01343	204,38	0,000066	TiO ₂	Q (*2)	0,000131	0,002102	0,015530	0,15150953
v	0,0092	0,00094	50,942	0,000019						
Cr	0,00864	0,00089	51,996	0,000017						
Mn	0,03248	0,00333	54,938	0,000061	MnO ₂	0 (*2)	0,000121	0,001939	0,005269	0,051397599
Fe	3,852	0,39485	55,845	0,007070	Fe ₂ O ₃	O (*3/2)	0,010606	0,169680	0,564529	5,507335697
Cu	0,02894	0,00297	63,546	0,000047						
Zn	0,04178	0,00428	65,38	0,000066						
As	0,003	0,00031	26,982	0,000011						
Br	0,00054	0,00006	79,904	0,000001						
Rb	0,00106	0,00011	85,468	0,000001						
Sr	0,191	0,01958	87,62	0,000223						
Y	0,00153	0,00016	88,906	0,000002						
Zr	0,00825	0,00085	91,224	0,000009						
Мо	0,00043	0,00004	95,95	0,000000						
Sn	0,01709	0,00175	118,71	0,000015						
Sb	0,0074	0,00076	121,76	0,000006						
Te	0,01664	0,00171	127,6	0,000013						
Ba	0,03817	0,00391	137,33	0,000028						
Lu	0,00053	0,00005	174,967	0,000000						
Re	0,00153	0,00016	186,21	0,000001						
Pb	0,0028	0,00029	173,04	0,000002						
SUM	60,38042				SUM of	oxides	0,1824	2,9190		28,4766
-							Total sum			88,85

Sampl	e name:		OPC(II)							
Preparation powder		Sample amount:								
Date:		01-10-2020		Sample height	9,89					
Made by:		es								
	Raw data	6				Data pro	cessing			
_			Molar mass; O	15,999 g/	mol		Oxi	ide		
Com- pound	Conc [%]	Mass [g]	Molar masse [g/mol]	mol	Com- pound	mol ratio	mol	O mass [g]	tot mass	tot [%]
Mg	0,168	0,00983	24,305	0,000405	MgO	O (*1)	0,000405	0,006473	0,016305	0,27859
AI	0,895	0,05238	26,982	0,001941	Al ₂ O ₃	O (*3/2)	0,002912	0,046591	0,098975	1,69104
Si	3,905	0,22856	28,085	0,008138	SiO2	O (*2)	0,016276	0,260400	0,488955	8,3540
s	0,785	0,04595	32,06	0,001433	SO3	O (*3)	0,004299	0,068785	0,114730	1,96023
ci	1,584	0,09271	35,45	0,002615						
к	0,253	0,01481	39,098	0,000379	K ₂ O	0 (*1/2)	0,000189	0,003030	0,017838	0,30470
Ca	47,506	2,78048	40,078	0,069377	CaO	0 (*1)	0,069377	1,109958	3,890436	66,47023
Tí	0,122	0,00714	204,38	0,000035	TiO2	0 (*2)	0,000070	0,001118	0,008258	0,14110
v	0,01062	0,00062	50,942	0,000012						
Cr	0,00903	0,00053	51,996	0,000010						
Mn	0,03199	0,00187	54,938	0,000034	MnO ₂	O (*2)	0,000068	0,001091	0,002963	0,05062
Fe	3,744	0,21913	55,845	0,003924	Fe ₂ O ₃	O (*3/2)	0,005886	0,094169	0,313301	5,35293
Cu	0,02774	0,00162	63,546	0,000026						
Zn	0,04086	0,00239	65,38	0,000037						
Ga	0,00037	0,00002	69,723	0,000000						
As	0,00037	0,00002	26,982	0,000001						
Br	0,00292	0,00017	79,904	0,000002						
Rb	0,0007	0,00004	85,468	0,000000						
Sr	9,2	0,53847	87,62	0,006145						
Y	0,0000181	0,00000	88,906	0,000000						
Zr	0,00151	0,00009	91,224	0,000001						
Sn	0,0154	0,00090	118,71	0,000008						
Sb	0,03299	0,00193	121,76	0,000016						
Те	0,00047	0,00003	127,6	0,000000						
Ba	0,00259	0,00015	137,33	0,000001						
Lu	0,00034	0,00002	174,967	0,000000						
Re	0,00134	0,00008	186,21	0,000000						
Ir	0,00013	0,00001	192,217	0,000000						
Pb	0,00013	0,00001	173,04	0,000000						
SUM	68,3415181				SUM of	oxides	0,099482	1,5916		27,19
-							Total sum			95,53

Preparation powder Date: 01-10-2020			Sample amount:	7,6078						
		01-10-2020		Sample height	13,42					
Made by	9	es								
	Raw data	t.				Data proce	ssing			
			Molar mass; O	15,999 g	/mol		0)	ide		
Com- pound	Conc [%]	Mass [g]	Molar masse [g/mol]	mol	Com- pound	mol ratio	mol	O mass (g)	tot mass	tot [%]
Mg	0,176	0,01339	24,305	0,0005509	MgO	0(*1)	0,00055	0,00881	0,11585	0,2918
AI	1,71	0,13009	26,982	0,0048215	Al ₂ O ₃	0 (*3/2)	0,00723	0,11571	1,52092	3,23092
Si	5,89	0,44810	28,085	0,0159551	SiOz	O (*2)	0,03191	0,51053	6,71064	12,60064
s	0,729	0,05546	32,06	0,0017299	SO3	O (*3)	0,00519	0,08303	1,09139	1,82039
CI	0,03761	0,00286	35,45	0,0000807						
ĸ	0,512	0,03895	39,098	0,0009963	K ₂ O	O (*1/2)	0,00050	0,00797	0,10476	0,61676
Ca	40,875	3,10969	40,078	0,0775909	CaO	0(*1)	0,07759	1,24138	16,31716	57,19210
Ti	0,302	0,02298	204,38	0,0001124	TIO2	O (*2)	0,00022	0,00360	0,04728	0,34928
v	0,01427	0,00109	50,942	0,0000213						
Cr	0,00969	0,00074	51,996	0,0000142						
Mn	0.04166	0,00317	54,938	0,0000577	MnO ₂	O (*2)	0,00012	0,00185	0,02426	0,06592
Fe	4,96	0,37735	55,845	0,0067570	Fe ₂ O ₃	O (*3/2)	0,01014	0,16216	2,13148	7,09148
Cu	0,02734	0,00208	63,546	0,0000327						
Zn	0,04187	0,00319	65,38	0,0000487						
Ga	0,00133	0,00010	69,723	0,0000015						
As	0,00412	0,00031	26,982	0,0000116						
Se	0,00048	0,00004	78,971	0,0000005						
Br	0,00047	0,00004	79,904	0,0000004						
Rb	0,0039	0,00030	85,468	0,0000035						
Sr	0,234	0,01780	87,62	0,0002032						
Y	0,00304	0,00023	88,906	0,0000026						
Zr	0,02166	0,00165	91,224	0,0000181						
Nb	0,00118	0,00009	92,906	0,0000010						
Sn	0,01704	0,00130	118,71	0,0000109						
Sb	0,00723	0,00055	121,76	0,0000045						
Te	0,01628	0,00124	127,6	0,0000097						
Ba	0,08123	0,00618	137,33	0,0000450						
Re	0,00127	0,00010	186,21	0,0000005						
Pb	0,00359	0,00027	207,2	0,0000013						
Bi	0,00044	0,00003	208,98	0,0000002						

Sample name: Preparation pow Date: 01-1		powder 01-10-2020	FA23(II)	Sample amount: Sample height	5,1453 8,90					
Made by	/i Row do	eş.					arclas			
	Rawoa	ta .	Molar mass: 0	15 999 0/	mol	Data processing		do		
Com- pound	Conc [%]	Mass [g]	Molar masse [g/mol]	mol	Com- pound	mol ratio	mol	O mass [g]	tot mass	tot [%]
Mg	0,185	0,009519	24,305	0,0003916	MgO	0 (*1)	0,000392	0,006266	0,015785	0,30678
AI	1,693	0,087110	26,982	0,0032284	Al ₂ O ₃	0 (*3/2)	0,004843	0,077478	0,164588	3,19880
Si	5,612	0,288754	28,085	0,0102814	SIO2	0 (*2)	0,020563	0,328986	0,617740	12,00590
s	0,715	0,036789	32,06	0,0011475	SO3	O (*3)	0,003443	0,055077	0,091866	1,78543
cl	1,477	0,075996	35,45	0,0021438						
к	0,478	0,024595	39,098	0,0006290	K ₂ O	0 (*1/2)	0,000315	0,005032	0,029627	0,57580
Ca	39,825	2,049116	40,078	0,0511282	CaO	0 (*1)	0,051128	0,818000	2,867116	55,72300
ті	0,293	0,015076	204,38	0,0000738	TIO ₂	0 (*2)	0,000148	0,002360	0,017436	0,33887
v	0,01247	0,000642	50,942	0,0000126						
Cr	0,00941	0,000484	51,996	0,0000093						
Mn	0,04079	0,002099	54,938	0,0000382	MnO ₂	Q (*2)	0,000076	0,001222	0,003321	0,06455
Fe	4,808	0,247386	55,845	0,0044299	Fe ₂ O ₃	O (*3/2)	0,006645	0,106310	0,353696	5,87416
Cu	0,02665	0,001371	63,546	0,0000216						
Zn	0,04116	0,002118	65,38	0,0000324						
Ga	0,00121	0,000062	69,723	0,0000009						
As	0,00428	0,000220	26,982	0,0000082						
Se	0,00046	0,000024	78,971	0,0000003						
Br	0,00056	0,000029	79,904	0,0000004						
Rb	0,0037	0,000190	85,468	0,0000022						
Sr	0,219	0,011268	87,62	0,0001286						
Y	0,00289	0,000149	88,906	0,0000017						
Zr	0,02083	0,001072	91,224	0,0000117						
Nb	0,00121	0,000062	92,906	0,0000007						
Sn	0.01643	0,000845	118,71	0,0000071						
Sb	0,00673	0,000346	121,76	0,0000028						
Те	0,01557	0,000801	127,6	0,0000063						
Ва	0,07617	0,003919	137,33	0,0000285						
Yb	0,00449	0,000231	186,21	0,0000012						
1.1	0.00337	0.000173	173.04	0.0000010						

APPENDIX E

X-Ray Diffraction

This appendix contains information in regard to the XRD analysis and the Rietveld refinement. Included is the experimental setup together with obtained diffractograms and the calculated counterpart. Difference plot and values used for calculations is also shown.

$\mathbf{Content}$

Pictures of equipment and sample preparation	A31
Report from analysis.	A32
Refinement strategy	A33
Diffractograms and difference plots	A35
Rietveld refinement	A38

Sample preparation



(a) Tools for sample preparation



(b) Preparation of sample





(c) Prepared sample

XRD



(a) PANalytical X'Pert Pro diffractometer



(b) Fixed slits

Figure 56: Equipment for XRD $\,$



Figure 57: PANalytical X'pert Pro diffractometer with explanations

Data Viewer

Time stamp

Total time (h:m:s): 00:31:36

Measurement type

Single scan

Used wavelength

Intended Kat wavelength type. Ka1 (A): 1.540598 Kaz (A): 1.544426 Ka2/Ka1 intensity 0.50 ratio: 1.541874 Ka (Å): KB (A): 1.392250

Incident beam path

240.0

Radius (mm): X-ray tube Empyrean Cu LFF HR (9430 033 7310x) DK419845 Name: Anode material: Cu Voltage (kV). 45 Current (mA): 40 Focus Focus type: Line Length (mm): 12.0 width (mm): 0.4 Take-off angle 6.0 (°): Soller slit Name: Soller slits 0.04 rad. 0.04 Opening (rad.) Mask Name: Fixed incident beam mask 10 mm Width (mm): 6.60 Anti-scatter slit Fixed slit 1* Name: Type: Fixed Height (mm): 1.52 **Divergence slit** Programmable divergence slit Name: Distance to 140 sample (mm): Type: Automatic Irradiated length 10.0 (mm); Offset (mm): 0.00

PANalytical

Sample movement

Movement type: Spinning Rotation time (s): 8.0

Diffracted beam path

240.0 Radius (mm): Anti-scatter slit Name: Fixed slit 1° Type: Fixed Height (mm); 1.52 Soller slit Name: Soller slits 0.04 rad. 0.04 Opening (rad.): Filter Name: Beta-filter Nickel Thickness (mm): 0.020 Material: NI Detector Name: X'Celerator detector RTMS detector Type: PHD - Lower 37.0 level (%): PHD - Upper 79.5 level (%): Mode: Scanning Active length (*) 2.122 Source Created by: s153750 Application SW: Data Collector

vs. 4.4a instrument control XPERT-PRO vs. 2.2F 20161117 Instrument ID: 000000011020752

Sample mode

Reflection

SW

Scan

Scan axis: Gonio 5.0000 - 70.0068 Scan range (*): Start position (*): 5.0084 69.9985 End position (*): Step size (*): 0.0167 3890 No. of points. Scan mode: Continuous Counting time (s): 59.690

Beam knife

Name: Beam knife for MPD systems

Figure 58: Report XRD

Rietveld refinement

The following section includes the rietveld refinement strategy used in present thesis. The refinement is done using HighScore Plus software from PANalytica. Henceforth, this section will be presented with the terminology used in the software. The basic concepts however, is likely the same across different softwares.

Refinement of anhydrous cement

- The individual phases is determined with the 'search and match' function. identified peaks is correlated with literature studies to ensure that the findings is reliable.
- The background was refined using a polynomial function with four coefficients and the 1/x term. Furthermore the specimen displacement factor was applied to be refined.
- The zone between 0 and 7 2θ was excluded from the refinement. This was done as no peaks exist in this area and the background is likely to have a poor fit within the small angle zones.
- All phase scale factors was refined together with their unit cells. Variation of the unit cells was constrained at 1%.
- The W-parameter of the cagliotti formula was applied for major phases. However w was not applied for calcite and carbon compounds. The w-parameter is constrained between 0.0001 and 0.2.
- The U- And V-parameter of the cagliotti formula was applied for major phases like alite and belite. The application of these parameters is based on visual examination of the fit together with the difference plot.
- If the peak shape was still not satisfied an 'split shape and width' asymmetry function was applied.
- For major phases like alite and belite preferred orientation was observed. March-Dollase correction was constrained between 0.7 and 1. In the case of large differences spherical harmonics was applied. Coefficients is chosen based on their effect on the difference plot.

Refinement of anhydrous Fly Ash

- The individual phases is determined based on search and match and literature studies.
- The background was refined using the available background due to the large amorphous content.
- The approach was besides the background refinement similar to that of the anhydrous cement.

Refinement of paste samples.

- The individual phases is determined based on search and match together with literature studies.
- The background was refined using the available background due to the large amorphous content.
- The zone between 0 and 7 $~2\theta$ was excluded from the refinement.

- Anhydrous compounds was imported from the refined files. Calcite was left out and imported as new. The phases shown in Table 21 was imported into the respective paste sample file and a refinement was run only for scale factors.
- The Rietveld analysis was run a couple of times.
- If the phase showed zero, the main peak of the phase was investigated from the *Search table* by Lothenbach et al. 57.
- If the main peak was not significant, the phase was deleted from file.
- The Rietveld analysis was run a couple of times until the Rwp did not change.
- Preferred orientations was applied for the portlandite phase. Double March-Dollase was applied with the first factor (1,0,-1) and second (0,0,1).
- The Rietveld analysis was run a couple of times until the Rwp did not change.

Phase name	Chemical formula	ICSD no.	Note
Alite M3	Ca ₃ SiO ₅	94742	
Aluminate cubic	$Ca_3Al_2O_6$		Open source. non-ISCD
Ferrite	$Ca_2Al_{1.35}Fe_{0.651}O_5$	98836	
Brownmillerite	$Ca_2Al_{0.99}Fe_{1.01}O_5$	98839	
Ferrite	$Ca_2Al_{0.55}Fe_{1.45}O_5$	98830	
Calcite	$CaCO_3$	73446	
Bassanite	$Ca(SO_4)(H_2O)_{0.5}$	79529	
Belite β	Ca_2SiO_4	81096	
Mulite	$Al_{2.34}Si_{0.66}O_{4.83}$	158098	
Quartz	SiO_2	200721	
Crystal quartz	SIO_2	10078	
Hematite	Fe_2O_3	201096	
Hemicarbonate	$Ca_4Al_2(OH)_{12}(OH)(CO_3)_{0.5}(H_2O)_5$		Open source. non-ISCD.
Monocarbonate	$Ca_4Al_2(OH)_{12}(CO_3)(H_2O)_5$	59327	
Friedel's salt	$Ca_2Al(OH)_6Cl(H_2O)$	62363	
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}(H_2O)_{26}$	155395	
Portlandite	$Ca(OH)_2$	202220	
Monosulfate	$Ca_2Al(OH)_6((SO_4)_{0.5}(H_2O)_3)$	100138	
Strätlingite	$Ca_2Al((AlSi)_{1.11}O_2(OH)_{12}(H_2O)_{2.25}$	69413	
Aragonite	$CaCO_3$	170225	
Vaterite	$Ca(CO_3)$	15879	
Corundum	Al ₂ O ₃	77810	

Table 21: Crystalline phases and the corresponding crystal file used in the Rietveld refinement.


Figure 59: Observed and calculated diffractrogram for OPC. The difference plot is likewise shown.



Figure 60: Observed and calculated diffractrogram for Fly Ash. The difference plot is likewise shown.



Figure 61: Observed and calculated diffractrogram for OPC(I). The difference plot is likewise shown.



Figure 62: Observed and calculated diffractrogram for OPC(II). The difference plot is likewise shown.



Figure 63: Observed and calculated diffractrogram for FA23(I). The difference plot is likewise shown.



Figure 64: Observed and calculated diffractrogram for FA23(II). The difference plot is likewise shown.



Figure 65: Observed and calculated diffractrogram for FA35(I). The difference plot is likewise shown.



Figure 66: Observed and calculated diffractrogram for FA35(II). The difference plot is likewise shown.

Estimation of Quantities from XRD Rietveld Analysis

Application of External-Standard-Method: G-factor method with Corundum

w/c

0,45

Data from HighScore Plus Software anf the amount of Chemically Bound Water(CBV) is found by TGA analysis

G-factor for	Corundum	16/09-202	0			
	S [-]	rho [g/cm³]	V [ų]	μ(MAC) [cm ² /g]	C [%]	G [-]
Corundum	0,021	3,99	254,76	30,91	1	1,69E-53
Anhydrous c	ement					
_	S [-]	rho [g/cm³]	V [ų]	μ(MAC) [cm²/g]	CBW TGA [%]	w _j [wt-%]
Alite M3	1,6E-05	3,16	4323,02	98,16	0	55,8%
C₃A Cubic	2,1E-06	3,04	3538,21	98,16	0	4,6%
Ferrite 1	2,0E-04	3,75	431,07	98,16	0	7,9%
Brownmillerite	5,2E-05	3,63	426,26	98,16	0	2,0%
Ferrite 2	4,7E-05	3,88	437,99	98,16	0	2,0%
Calcite	2,1E-04	2,72	367,20	98,16	0	4,5%
Bassanite	2,6E-05	2,74	1057,12	98,16	0	4,6%
Belite β	7,7E-04	3,30	346,49	98,16	0	17,7%
Amorphous						0,9%
SUM				1		100,0%
Anhydrous F	ly Ash					
	S [-]	rho [g/cm³]	V [ų]	µ(MAC) [cm²/g]	CBW TGA [%]	w _j [wt-%]
Mulite	4,59E-03	3,14	167,91	35,92	0	8,6%
Quartz	1,26E-02	2,63	113,80	35,92	0	9,1%
Hematite	2,38E-05	5,23	304,06	35,92	0	0,2%
Crystal Quartz	2,01E-03	4,31	46,25	35,92	0	0,4%
Amorphous						81,6%
SUM						100,0%

G -factor for	Corundun	n 21/10-	2020					
	S [-]	rho	[g/cm ³] V[Å ³]		μ(MAC) [cm ² /	/g] C [%]	G [-]	
Corundum		0,022	3,99	254,56	3	0,91	1 1,7	2E-53
OPC_5A(I)_21-	10-2020						-	
	s [-]	rho [g/cm ³]	∨ [Å ³]	µ(MAC) [cm²/g]	CBW TGA [%]	w _i [wt-%]	w _{j pr. 100g paste} [wt-%]	
Alite M3	1,1E-06	3,16	43 23,02	86,71	0,238	3,2%		2,9%
Ferrite	9,4E-05	3,75	431,07	86,71	0,238	3,3%		3,0%
Brown millerite	4,1E-05	3,63	426,26	86,71	0,238	1,4%		1,2%
Belite β	2,4E-04	3,30	346,49	86,71	0,238	4,8%		4,3%
Hemicarbonate	6,3E-06	1,82	1414,19	86,71	0,238	1,2%		1,0%
Monocarbonate	6,0E-05	2,18	4 32,03	86,71	0,238	1,2%		1,1%
Etringitte	1,4E-05	1,79	23 30,78	86,71	0,238	6,7%		6,1%
Portlandite	4,1E-02	2,24	54,88	86,71	0,238	14,1%		12,7%
Calcite	8,0E-05	2,71	3 67,90	86,71	0,238	1,5%		1,3%
Amorphous						62,8%		66,3%
SUM						100,0%		100,0%
OPC_5A(II)_21	-10-2020							
	s [-]	rho [g/cm ³]	∨ [Å ³]	µ(MAC) [cm²/g]	CBW TGA [%]	w _i [wt-%]	w _{j pr. 100g paste} [wt-%]	
Alite M3	8,3E-07	3,16	43 23,02	84,92	0,241	2,4%		2,2%
Ferrite	8,0E-05	3,75	431,07	84,92	0,241	2,7%		2,5%
Brown millerite	3,4E-05	3,63	426,26	84,92	0,241	1,1%		1,0%
Belite β	2,2E-04	3,30	3 46,49	84,92	0,241	4,3%		3,9%
Hemicarbonate	6,3E-06	1,83	1403,63	84,92	0,241	1,1%		1,0%
Monocarbonate	-1,0E-08	2,2	428,29	84,92	0,241	0,0%		0,0%
Fridel's salt	4,0E-05	2,05	909,71	84,92	0,241	3,3%		3,0%
Etringitte	1,3E-05	1,79	23 34,13	84,92	0,241	6,4%		5,8%
Portlandite	3,6E-02	2,24	54,88	84,92	0,241	12,1%		11,0%
Calcite	8,0E-05	2,71	3 67,43	84,92	0,241	1,4%		1,3%
Amorphous						65 ,0%		68,2%
SUM						100,0%		100,0%
FA23_5A(I)_21	-10-2020							
	S [-]	rho [g/cm ³]	∨ [Å ³]	μ(MAC) [cm²/g]	CBW TGA [%]	w _i [wt-%]	w _{j pr. 100g paste} [wt-%]	
Alite M3	2,80E-07	3,16	43 23,02	74,92	0,214	0,7%		0,6%
Ferrite	5,60E-05	3,75	431,07	74,92	0,214	1,7%		1,5%
Bro wn mil lerite	2,57E-05	3,63	426,26	74,92	0,214	0,7%		0,6%
Belite β	1,75E-04	3,3	3 46,49	74,92	0,214	з,0%		2,7%
Hemicarbonate	1,05E-05	1,82	1415,75	74,92	0,214	1,7%		1,5%
Monocarbonate	1,04E-04	2,16	436,44	74,92	0,214	1,9%		1,6%
Etringitte	1,43E-05	1,78	23 37,76	74,92	0,214	6,0%		5,3%
Portlandite	3,69E-02	2,24	54,91	74,92	0,214	10,8%		9,5%
Calcite	5,47E-05	2,69	3 70,80	74,92	0,214	0,9%		0,8%
Mulite	2,18E-04	3,14	167,91	74,92	0,214	0,8%		0,7%
Quartz	2,35E-03	2,63	113,80	74,92	0,214	3,5%		3,1%
Amorphous						68,2%		72,1%
SUM						100,0%		100,0%

FA23_4A(II)_2	1-10-2020				and the second		
	5 [-]	rho [g/cm ⁻¹]	v [Ă ³]	µ(MAC) [cm²/g]	CBW TGA [%]	w; [wt-%]	W WOR prote [Wt-%]
Alite M3	2,50E+07	3,15	43 23,02	73,32	0,212	0,6%	0,6%
Fernite	4,19E-05	3,75	431,07	73,32	0,212	1,2%	1,1%
Brownmillerite	2,18E-05	3,63	426,25	73,32	0,212	0,5%	0,5%
Selite S	1,128-04	3,3	346,49	73,32	0,212	1,9%	1,7%
Hemicarbonate	1,07E-05	1,83	1408,03	73,32	0,212	1,6%	1,4%
Monocarbonate	4,82E-05	2,17	435,22	73,32	0,212	0,8%	0,7%
Friedel's salt	4,01E-05	2,05	906,55	73,32	0,212	2,9%	2,5%
Etringitte	1,235-05	1,79	2330,08	73,32	0,212	5,1%	4,5%
Portlandite	3,20E-02	2,24	54,87	73,32	0,212	9,2%	8,0%
Calcite	8,78E-05	2,7	369,52	73,32	0,212	1,4%	1,2%
Mulite	3,96E-04	3,14	167,91	73,32	0,212	1,5%	1,3%
Quartz	1,765-03	2,53	113,80	73,32	0,212	2,5%	2,2%
Amorphous 5UM	1					70,5%	74,2% 100,0%

1	5 [-]	rho [g/cm3]	V [Ā ³]	µ(MAC) [cm ² /g]	CBW TGA [%]	w [wt-%]	Win. Wie male [wt-%]
Alité M3	1,20E-07	3,15	43 23,02	65,85	0,105	0,3%	0,2%
Ferrite	3,00E-05	3,75	431,07	66,86	5 0,105	0,8%	0,6%
Brownmillerite	1,80E-05	3,63	42 5,28	56,85	5 0,106	0,5%	0,4%
Belite B	8,63E-05	3,3	346,43	55,85	5 0,105	1,3%	1,0%
Hemicarbonate	Z,08E-05	1,82	1416,58	5 55,88	5 0,106	2,9%	2,3%
Monocarbonate	9,31E-05	2,15	436,78	55,86	5 0,105	1,5%	1,1%
Etringitte	1,33E-05	1,79	2334,58	5 56,86	0,105	5,1%	3,9%
Portlandite	3,34E-02	2,24	54,93	65,86	0,105	8,8%	6,8%
Calcite	5,89E-05	2,69	370,93	56,8 f	6 0,106	0,8%	0,7%
Mulite	6,79E-04	3,14	167,93	56,88	5 0,106	2,3%	1,8%
Quartz	3,525-03	2,63	113,80	56,85	5 0,105	4,7%	3,6%
Amorphous SUM						71.0%	77,7% 100,0%

FA35_9A(II)_1	9-11-2020					_	
1 march 1 marc	5[-]	rho[g/cm ³]	V [Å ³]	µ(MAC) [cm ² /g]	CBW TGA [%]	w, [wt-%]	Wiger. 1000 penda [Wt-96]
Alte M3	1,10E-07	3,16	4323,02	55,41	0,125	0,3%	0,2%
Ferrite	2,665-05	3,75	431,07	56,41	0,125	0,7%	0,6%
Brownmillerite	2,185-05	3,63	426,26	56,41	0,125	0,6%	0,4%
Belite ß	5,65E-05	3,3	346,49	56,41	0,125	0,9%	0,7%
Hemicarbonate	1,645-05	1,82	1409,40	56,41	0,125	2,3%	1,8%
Monocarbonate	4,95E-05	2,18	433,06	65,41	0,125	0,8%	0,6%
Friedel's salt	4,21E-05	2,04	911,65	66,43	0,125	2,8%	2,2%
Etringitte	1,24E-05	1,78	233 6,73	55,41	0,125	4,6%	3,7%
Portlandite	2,73E-02	2,24	54,91	66,43	0,125	7,1%	5,6%
Calcite	5,345-05	2,68	371,40	65,41	0,125	0,8%	0,6%
Mulite	7,968-04	3,14	167,91	56,41	0,125	2,7%	2,1%
Quartz	2,735-03	2,63	113,80	56,41	0,125	3,6%	2,8%
Amorphous SUN						73.0% 100.0%	78.7% 200,0%

APPENDIX F

TGA

This appendix contains an overview of all TGA that has been done in this study. The date, time and mass of crucible and powder is provided in Table [22]. The missing crucible masses were due to some recalibration of the TGA equipment, which the undersigned had nothing to do with and did not know how to fix.

TG and DTG graphs is provided for all samples. In Figure 67, 68 and 69 one of each sample is plotted together for each of the sample sets. In Figure 70 all the OPC samples are plotted together and in Figure 71 all the FA23 are plotted together.

Content

Overview	42
$1^{\rm st}$ set of TGA	42
2^{nd} set of TGA	43
$3^{\rm rd}$ set of TGA	43
All OPC samples shown together	44
All FA23 samples shown together	44

Overview of Thermogravimetric analysis

	ID	Date	Start time	Crucible mass	Sample mass
Anhydrous compounds	Empty crucible CEM Fly Ash Blend	$\begin{array}{c} 15-09-2020\\ 15-09-2020\\ 02-10-2020\\ 02-10-2020\\ \end{array}$	$\begin{array}{c} 09{:}30\\ 15{:}08\\ 08{:}45\\ 14{:}38\end{array}$	$\begin{array}{c c} 139.0430 \\ 134.5610 \\ 144.3791 \\ 144.4595 \end{array}$	-36.8670 42.7648 48.0570
1 st set of paste samples	OPC_2A (I) OPC_2A (II) FA23_2A (I) FA23_2A (I)	30-09-2020 30-09-2020 01-10-2020 01-10-2020	$10:55 \\ 13:55 \\ 09:16 \\ 15:17$	$\begin{array}{c} 135.5095 \\ 140.6075 \\ 147.8700 \\ 138.3375 \end{array}$	55.3160 59.1838 49.8436 52.6220
2 nd set of paste samples	OPC_3A (I) OPC_3A (II) FA23_5A (I) FA23_5A (I)	08-10-2020 08-10-2020 21-10-2020 21-10-2020	14:10 10:42 13:03 10:04	137.4060 138.7560 - -	57.9675 69.3350 62.0745 66.4202
3 rd set of paste samples	OPC_5A (I) OPC_5A (II) FA23_6A (I) FA23_6A (II)	23-10-2020 23-10-2020 29-10-2020 29-10-2020	08:10 11:11 10:59 08:08	- - - -	54.3195 68.3981 52.3070 56.3425
FA35 paste samples	$\begin{array}{c c} FA35_9C (I) \\ FA35_9C (II) \end{array}$	20-11-2020 20-11-2020	14:25 08:00		$55.2230 \\ 64.8938$

Table 22: Overview of samples analyzed thermogravimetric. The date and start time is shown togetherwith the mass of the crucible, and the mass of the sample.

Results from Thermogravimetric analysis



Figure 67: TG and DTG for complete set of paste samples (OPC_2A(I), OPC_2A(II), FA23_2A(I) and FA23_2A(II))



Figure 68: TG and DTG for complete set of paste samples (OPC_3A(I), OPC_3A(II), FA23_5A(I) and FA23_5A(II))



Figure 69: TG and DTG for complete set of paste samples (OPC_5A(I), OPC_5A(II), FA23_6A(I) and FA23_6A(II))



All OPC samples shown together

Figure 70: Graphs of OPC paste samples with and without chloride exposure.



All FA samples shown together

Figure 71: Graphs of paste samples with fly ash with and without chloride exposure.

APPENDIX G

Sorption Isotherm: DVS and Desiccator

This appendix contains information regarding the experimental work with estimating sorption isotherms. Two methods is included in present appendix, the desiccator method and the sorption balance method (DVS).

Results from DVS measurements that describes the degree of equilibrium can be seen on Figure 74 to Figure 81.

Content

Overview
Desiccator test setup
DVS test setup
Degree of equilibrium OPC(I)
Degree of equilibrium $OPC(II)$
Degree of equilibrium $FA23(I)$ A49
Degree of equilibrium $FA23(II) \dots A50$
Degree of equilibrium $FA35(I)$
Degree of equilibrium $FA35(II) \dots A52$
Sorption Isotherm: Desiccator method

Preparation of specimens for Sorption Isotherm

	OPC_1(II)	$OPC_{-}^{I(I)}$	$FA_{-}I(II)$	$FA_{-}^{I(I)}$	$OPC_{-2(I)}$	$FA_{-}3(I)$	$FA_{-}6(II)$	$FA35_{-9(II)}$	$FA35_{-10(II)}$
Date	23-09	23-09	23-09	23-09	30-09	07-10	28-10	19-11	25-11
Out of reservoir	10:20	11:52	11:12	12:22	9:24	9:25	9:37	8:33	9:25
In Glove box	10:23	11:54	11:15	12:25	9:26	9:27	9:39	8:36	9:27
In Desiccators	10:56	12:15	11:36	12:48	-	-	-	-	-
In DVS	10:52	-	-	-	9:36	9:38	9:46	8:42	9:34

 Table 23: Overview of time during preparation of specimens for Sorption Isotherm.

Sorption isotherm; Desiccator test setup



Figure 72: Desiccator test setup

Sorption Isotherm; DVS



(a) DVS Advantage



(b) Filled specimen prior to DVS



(c) Hanging specimen in DVS

Figure 73: Preparation of the sample for DVS.



Degree of equilibrium; DVS: OPC(I)

Figure 74: Desorption equilibrium curves of OPC(I).



Figure 75: Adsorption equilibrium curves of OPC(I).



Degree of equilibrium; DVS: OPC(II)

Figure 76: Desorption equilibrium curves of OPC(II).



Figure 77: Adsorption equilibrium curves of OPC(II).



Degree of equilibrium; DVS: FA23(I)

Figure 78: Desorption equilibrium curves of FA23(I).



Figure 79: Adsorption equilibrium curves of FA23(I).



Degree of equilibrium; DVS: FA23(II)

Figure 81: Adsorption equilibrium curves of FA23(II)..



Degree of equilibrium; DVS: FA35(I)

Figure 82: Desorption equilibrium curves of FA35(I).



Figure 83: Adsorption equilibrium curves of FA35(I).



Degree of equilibrium; DVS: FA35(II)

Figure 84: Desorption equilibrium curves of FA35(II).



Figure 85: Adsorption equilibrium curves of FA35(II).

Sorption Isotherm: Desicator method

1. cast specimens

2019

Empty crucibles were weight	17-sep	and put in there resp. desiccator		
Empty crucibles: weight again	23-sep		Mass of calibration weight of 50g	Correction
0 th measurement was done	23-sep	Weight calibration:	50.00103	0.00103
1 st measurement was done	09-okt	Weight calibration:	50.00103	0.00103
2 nd measurement was done	23-okt	Weight calibration:	50.00103	0.00103
3 rd measurement was done	06-nov	Weight calibration:	50.00088	0.00088
4 th measurement was done	20-nov	Weight cal.; RH, (11,22),(33,75),(94)	50.00075 50.00030 49.9998	0.00075 0.00030 -0.00019
5 th measurement was done	04-dec	Weight calibration:	49.99985	0.00015
6 th measurement was done	16-dec	Weight cal.; RH, (11,22),(33,75,94)	49.99983 49.9997	0.00017 0.00030
7 th measurement was done	17-dec	Weight cal.; RH, (11,22),(33,75,94)	49.99987 49.9999	0.00013 0.00010
8 th measurement was done	18-dec	Weight calibration:	50	0

					N	lass with	out weig	ht calibr	ation					
Salt	RH [%]	Sample ID	Crucible	m _{crucible}	m _{crucible}	minitial [g]	m1 [g]	m ₂ [g]	m3 [g]	m4 [g]	m5 [g]	3 cons	equtive me	asures
-	1100 6		ID	[g]	[g]				2 A.C.			m ₆ [g]	m ₇ [g]	m ₈ [g]
_		Date		75-261	11-sep	- IBniebi	(ifa-60	23-0ht	-da-nov	20-nov	()4-dec	16-dec	17-tiec	18-Uec
		OCP_1(11)	1	22.1742	22.1747	23,4250	23.3819	23.3708	23.3700	23.3697	23.3695	23.3692	23.3707	23.3710
6.	11	OCP_1(I)	2	23.4336	23.4346	25.0552	24,9316	24.9298	24.9291	24,9298	24,9300	24,9291	24.9304	24.9309
10		FA30_1(II)	3	23.2243	24.2256	25.7459	25.6370	25.6338	25.6330	25,6330	25,6320	25.6325	25.6328	25.6349
		FA30_1(I)	4	20.6518	20.6526	22.0946	21.9649	21.9635	21.9633	21.9618	21.9622	21.9623	21.9638	21.9646
	-	OCP_1(II)	5	23.8333	23.8340	24.8356	24.8091	24.8056	24.8042	24.8026	24.8023	24.8019	24.8038	24.8042
01	22	OCP_1(I)	6	25.0923	25.0929	26.5570	26.4506	26.4465	26.4436	26.4420	26.4417	26.4413	26.4433	26.4392
ters	22	FA30_1(II)	7	22.5084	22.5090	23.4716	23.4163	23.4131	23.4144	23.4103	23.4099	23,4100	23.4118	23.4121
	_	FA30_1(I)	8	18.8213	18.8218	20.5901	20.4391	20.4347	20.4329	20.4315	20.4305	-	False	
	_	OCP_1(11)	9	18.6062	18.6068	19.4915	19.4858	19.4777	19.4745	19.4742	19.4757	19.4771	19.4780	19.4797
de	12	OCP_1(I)	10	22.5081	22.5091	24.3145	24.2295	24.2097	24.1983	24.1929	24.1919	24.1933	24.1954	24.1961
18	33	FA30_1(II)	11	22.3069	22.3080	23.2572	23.2314	23.2206	23.2160	23.2133	23.2140	23.2157	23.2172	23.2183
		FA30_1(I)	12	22.3807	22.3814	24.0925	24.0004	23.9827	23.9682	23.9602	23.9594	23.9594	23.9603	23.9614
		OCP_1(II)	13	22.6538	22.6547	23.7073	23.7521	23.7528	23.7534	23.7538	23.7547	23.7551	23.7559	23.7564
ò	70	OCP_1(I)	14	22.4398	22.4405	23.8927	23,9063	23.9052	23.9039	23.9030	23,9033	23,9028	23.9040	23.9039
430	12	FA30_1(II)	15	22.6835	22.6842	23.6378	23.6569	23.6567	23.6570	23.6569	23.6581	23.6583	23.6595	23.6597
		FA30_1(I)	16	23.4206	23.4214	25.0552	25.0568	25.0546	25.0533	25.0512	25.0512	25.0508	25.0517	25.0517
		OCP_1(II)	17	26.0021	26.0036	27.0205	27.1208	27.1243	27.1257	27.1256	27.1269	27.1278	27.1279	27.1273
03	04	OCP_1(I)	18	24.0355	24.0367	25.2967	25.3712	25.3735	25.3747	25.3753	25.3760	25.3772	25.3777	25.3774
42	34	FA30_1(11)	19	21.8411	21.8424	23.2489	23,3505	23.3523	23.3521	23.3521	23.3529	23,3540	23.3536	23.3531
		FA30 1(I)	20	23.3200	23.3211	24.9253	24.9873	24.9879	24.9883	24.9877	24.9886	24.9888	24.9892	24,9889

					4	Mass <u>wi</u>	<u>th</u> weigh	t calibra	tion					
Salt	RH [%]	Sample ID	Crucible	m _{crucible} [g]	m _{crucible} [g]	m _{initial} [g]	m1[g]	m ₂ [g]	m₃ [g]	m4 [g]	m5 [g]	3 conse	qutive me	asures
-			ID	17.000	12.008	22 can.	(W. okt	72 akt	(Dis most)	20-861/	në der	m ₆ [g]	m ₇ [g]	m _s [g]
-	-	OCP 1(III)	1	22 1731	22 1737	23 4 23 9	23 3809	23 3698	23 3691	23 3689	23 3696	23 3694	23 3706	23 3710
		OCP 1(1)	2	23 4326	73 4336	25.0542	24 9306	20.0000	74 9787	24 9291	24.9302	74 9793	24 9303	24 9309
100	11	FA30 1(1)	3	23.4520	74 7745	25.0542	25.6360	25 6327	25 6321	25 6323	25 6372	25,6327	25 6377	25 6349
		FA30 1(1)	4	20.6508	20.6516	22.0935	21.9639	21.9624	21,9674	21.9611	21.9624	21.9625	21.9637	21.9646
-	-	OCP 1(1)	5	23.8323	23,8329	24,8345	24,8081	24.8045	24,8033	24.8018	24,8024	24,8021	24,8036	24.8042
01		OCP 1(i)	6	25.0913	25 0919	26.5559	26.4496	26 4455	26.4427	26.4413	26.4418	26,4415	26.4431	26 4392
Cr's	22	FA30 1(11)	7	22.5073	22.5080	23.4706	23.4153	23,4121	23,4135	23.4096	23.4101	23,4102	23.4116	23,4121
		FA30 1(I)	8	18.8203	18.8208	20.5891	20,4380	20.4336	20.4320	20,4307	20.4307		False	
		OCP 1(II)	9	18.6052	18.6058	19,4904	19,4848	19.4767	19.4736	19.4739	19,4759	19.4768	19,4779	19.4797
20	- CL	OCP 1(1)	10	22.5071	22.5080	24.3135	24,2285	24.2086	24.1974	24.1926	24,1921	24.1930	24.1953	24.1961
NB.	33	FA30_1(II)	11	22.3059	22.3070	23.2562	23.2304	23.2196	23.2152	23.2130	23.2142	23.2154	23.2171	23.2183
		FA30_1(I)	12	22.3796	22.3803	24.0914	23,9994	23.9817	23.9673	23.9599	23.9596	23.9591	23.9602	23.9614
		OCP_1(II)	13	22.6528	22.6537	23.7063	23.7511	23.7518	23.7525	23.7535	23.7548	23.7548	23.7558	23.7564
0		OCP_1(I)	14	22.4387	22.4395	23.8917	23.9052	23.9042	23.9030	23.9027	23.9035	23.9025	23.9039	23.9039
40	15	FA30_1(II)	15	22.6824	22.6831	23.6368	23.6558	23.6557	23.6561	23.6566	23.6582	23.6580	23.6594	23.6597
		FA30_1(I)	16	23.4196	23.4204	25.0542	25,0558	25.0536	25.0524	25,0509	25.0513	25,0505	25.0516	25.0517
		OCP_1(11)	17	26.0011	26.0026	27.0195	27.1198	27.1233	27.1249	27.1258	27.1271	27.1275	27.1278	27.1273
03	04	OCP_1(I)	18	24.0344	24.0356	25.2956	25.3702	25.3725	25.3738	25.3755	25.3762	25.3769	25.3776	25.3774
tw	94	FA30_1(II)	19	21.8400	21.8414	23.2479	23,3495	23.3512	23.3512	23,3522	23.3531	23.3537	23.3535	23.3531
		FA30_1(I)	20	23.3189	23.3201	24.9243	24.9863	24.9869	24.9874	24.9879	24.9887	24,9885	24.9891	24.9889

					N	lass char	nges					
		23-09-2020	09-pki	23-okt	06-1100	20-miv	04-dec	16-dec	17-dec	18-dec	Δm ₆₋₇	∆m ₇₋₈
		m _{initial} - m _{crucible} [g]	m1 [g]	m ₂ [g]	m₃ [g]	m4 [g]	m ₅ [g]	m ₆ [g]	m7 [g]	m ₈ [g]	[%]	[%]
		1.25025	1.20718	1.19613	1.19542	1.19523	1.19595	1.19570	1.19693	1.19733	0.10	0.03
ja		1.62061	1.49699	1.49516	1.49457	1.49546	1.49656	1.49567	1.49667	1.49730	0.07	0.04
		1.52037	1.41143	1.40822	1.40760	1.40773	1.40767	1.40815	1.40815	1.41038	0.00	0.16
		1.44193	1.31228	1.31083	1.31083	1.30946	1.31077	1.31088	1.31206	1.31301	0.09	0.07
402 102		1.00159	0.97511	0.97158	0.97033	0.96890	0.96947	0.96913	0.97068	0.97126	0.16	0.06
	22	1.46401	1.35765	1.35358	1.35081	1.34938	1.34989	1.34956	1.35122	1.34729	0.12	-0.29
	22	0.96262	0.90728	0.90409	0.90555	0.90160	0.90211	0.90220	0.90365	0.90413	0.16	0.05
		1.76829	1.61721	1.61281	1.61119	1.60990	1.60985		False		1 miles	
ch:		0.88466	0.87899	0.87089	0.86784	0.86815	0.87010	0.87104	0.87215	0.87394	0.13	0.21
	22	1.80543	1.72048	1.70059	1.68938	1.68455	1.68406	1.68497	1.68723	1.68807	0.13	0.05
18	22	0.94921	0.92338	0.91262	0.90817	0.90603	0.90719	0.90842	0.91008	0.91132	0.18	0.14
		1.71108	1.61908	1.60134	1.58693	1.57958	1.57921	1.57876	1.57982	1.58106	0.07	0.08
		1.05262	1.09736	1.09809	1.09884	1.09985	1.10111	1.10111	1.10212	1.10271	0.09	0.05
0	75	1.45221	1.46574	1.46470	1.46353	1.46323	1.46396	1,46300	1.46440	1.46440	0.10	0.00
42	13	0.95364	0.97271	0.97258	0.97297	0.97350	0.97511	0.97487	0.97623	0.97657	0.14	0.03
		1.63379	1.63542	1.63325	1.63201	1.63049	1.63098	1.63014	1.63122	1.63134	0.07	0.01
1		1.01685	1.11718	1.12064	1.12225	1.12314	1.12446	1.12489	1.12514	1.12469	0.02	-0.04
.03	04	1.26001	1.33458	1.33682	1.33815	1.33986	1.34054	1.34127	1.34196	1.34177	0.05	-0.01
tu	54	1.40650	1.50814	1.50987	1.50988	1.51088	1.51171	1.51234	1.51217	1.51174	-0.01	-0.03
		1.60417	1.66618	1.66675	1.66728	1.66778	1.66864	1.66840	1.66902	1.66880	0.04	-0.01
r	max	1.80543										
r	nín	0.88466										

		OCP(II)	OCP(I)	FA23(II)	FA23(1)								
	m _{initial} - m _{crucible}					Equi	ilibrium: 11%			OCP(II)	OCP(I)	FA23(II)	FA23(I)
	[%]	100	100	100	100	99		4					
	m ₁ [%]	96.5551	92.3720	92.8346	91.0086	98			m ₂ [%]	0	0	0	0
	m ₂ [%]	95.6713	92.2591	92.6235	90.9080	96		OCP(I)	m ₃ [%]	0	0	0	0
	m ₃ [%]	95.6145	92.2227	92.5827	90.9080	95			m ₄ [%]	0	0	0	0
6	m ₄ [%]	95.5993	92.2776	92.5913	90.8130	93		FA23(ii)	m ₅ [%]	0	0	0	0
v	m ₅ [%]	95.6569	92.3455	92.5873	90.9039	91			m ₆ [%]	0	0	0	0
	m ₆ [%]	95.6369	92.2906	92.6189	90.9115	-90			m7[%]	0	0	0	0
	m ₇ [%]	95.7353	92.3523	92.6189	90.9933				m ₈ [%]	0	0	0	0
-	m ₈ [%]	95.7672	92.3911	92.7656	91.0592				m _{finale}	0	0	0	0
		100	100	100	100		22 % RH						
	m1 [%]	97.3562	92.7350	94.2511	91.4562	100 🥷		OCP(II)	m ₂ [%]	1.3928	0.2145	1.3994	0.3292
	m ₂ [%]	97.0038	92.4570	93.9197	91.2073	98	12 July 1		m3 [%]	1.3225	0.0489	1.6079	0.2285
	m ₃ [%]	96.8790	92.2678	94.0714	91.1157	96	*****		m ₄ [%]	1.1892	-0.1165	1.1554	0.2530
	m ₄ [%]	96.7362	92.1701	93.6611	91.0428	94	-		m ₅ [%]	1.1878	-0.1521	1.2169	0.1497
ter	m ₅ [%]	96.7931	92.2050	93.7140	91.0399	92 000			m ₆ [%]	1.1735	-0.1172	1.1925	false
	m ₆ [%]	96.7592	92.1824	93.7234	false	90	••		m7 [%]	1.2312	-0.0611	1.3551	false
	m7 [%]	96.9139	92.2958	93.8740	false			FA23(I)	m ₈ [%]	1.2578	-0.3937	1.2486	false
	m ₈ [%]	96.9718	92.0274	93.9239	false				m _{finale}	1.2208	-0.1907	1.2654	0.1497
		100	100	100	100		33 % RH						
-	m1 [%]	99.359	95.295	97.279	94.623	100	55 55 111		m ₂ [%]	2.8976	2.0963	3.8022	2.9464
	m ₂ [%]	98.443	94.193	96.145	93.587	98			m3 [%]	2.5982	1.4633	3.3415	2.0200
	m3 [%]	98.099	93.572	95.676	92.744	96	-		m ₄ [%]	2.6511	1.1130	3.0885	1.6537
de	m4 [%]	98.134	93.305	95.451	92.315	94			m ₅ [%]	2.8198	1.0093	3.2249	1.5283
N.B.	m ₅ [%]	98.354	93.278	95.573	92.293	42			m ₆ [%]	2.9524	1.1240	3.3296	1.4909
	m ₆ [%]	98.460	93.328	95.703	92.267	90			m7 [%]	2.9776	1.1920	3.5184	1.4677
	m7 [%]	98.586	93.453	95.878	92.329	36			m ₈ [%]	3.1545	1.1998	3.4956	1.4739
	m ₈ [%]	98.788	93.500	96.008	92.401				m _{finale}	3.0282	1.1719	3.4479	1.4775
		100	100	100	100		"adulati"						1.0
0.57	m1 [%]	104.250	100.932	102.000	100.100	107	75 % RH		m ₂ [%]	9.0397	9.3226	10.1082	9.9649
	m ₂ [%]	104.320	100.860	101.986	99.967				m₃ [%]	9.1790	9.2784	10.2009	9.8815
	m ₃ [%]	104.391	100.780	102.027	99.891	105			m4 [%]	9.2967	9.1910	10.2507	9.8940
à	m4 [%]	104.487	100.759	102.083	99.798	103			m ₅ [%]	9.3561	9.1652	10.4378	9.8171
120	m _s [%]	104.607	100.809	102.251	99.828	101		FA23(II)	m ₆ [%]	9.3789	9.1585	10.3729	9.7514
	me [%]	104.607	100.743	102.226	99.777	6000			m ₇ [%]	9.3668	9,1900	10.5269	9.7253
	m- [%]	104.703	100.839	102.369	99.843	99		FA23(I)	m. [%]	9.3888	9.1440	10.3906	9.6540
	m. [%]	104,759	100.839	102.404	99.850				Mensle	9.3782	9,1642	10.4302	9,7102
		100.000	100.000	100.000	100.000				indic	1111111	4.10.00.00	2. 31 · 9 9 · 4	4.114
	m. [%]	109 867	105 918	107 226	103 866		94 % RH		m. [%]	15 1934	14 99787	15 8987	14,7925
	m. [%]	110.207	106.096	107.349	103.901	114			m. [%]	15.4274	15.15772	15,9505	14.3289
	m. [%]	110 365	106 202	107 350	103 934	109 900		OCPUIN	m. [%]	15 5373	15 23626	16.0166	14 4828
	m, [%]	110.555	106 337	107 421	103.965	122	11111		m- [%]	15 6035	15 21	16.0852	14 4274
4400	m. [%]	110 583	106 391	107 480	104 019	104			m, [%]	15 6719	15 34133	16,0941	14 4013
-	m. [%]	110.505	106.391	107.525	104.019		1	FA23(II)	m, [%]	15 5797	15 37354	16 081	14 3400
	m- [%]	110.650	106 504	107.523	104.004	99			m, [%]	15 /939	15 25877	15 8645	14 2431
	m [0/1	110.030	100.304	107.515	104.045				1118 [20]	15 5015	15 20707	16 0133	14.2431
	118 [70]	110.005	100.489	107.482	104.029				finale	12.2012	12.20181	10.0132	14.3264

APPENDIX H

Cup Test

This appendix contains additional information about how the cup test was executed. The mixer; TEDDY BEAR Varimixer is shown and sawing of the specimens prior to migration test together with the test setup for migration test is also shown. This appendix also showns how the cup test was set up and the penetration depth of the chloride exposed specimens is also documented.

The measurements and calculations of the actual cup test is provided on the pages A62-A67.

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Mixing equipment



Figure 86: TEDDY BEAR Varimixer; Used for mixing mortar samples

Preparation for migration test



(a) Sawing mortar sample into 50 mm discs.



(b) Mortar samples is desiccator

Figure 87: Preparation for migration test on mortar samples

Migration test



(a) Mortar sample in sleeve



(b) Test setup

Figure 88: Migration test on mortar samples

Chloride Migration Test:

7th cast specimens

Mortar samples

02/11 - 05/11 2020

	M_OPC	M_OPC	M_FA23	M FA23		
	7Ā (II)	7B (II)	7Ā (II)	7B (II)		
Clock; De-moulded	10:25	10:25	10:36	10:36		
Length ₁ [mm]	49.09	49.10	48.56	48.56		
Length ₂ [mm]	49.26	48.79	48.90	48.89		
Length ₃ [mm]	49.28	48.97	49.26	48.84		
Av. Length [mm]	49.21	48.95	48.91	48.76		
Vacuum						
Date		02-11	-2020			
Room Temperature [°C]		2	20			
Clock; Pressure applied		11	:15			
Clock; Pressure constant at <u>27</u> mbar		11	:20			
Clock; Essicator shut off		14	:25			
Clock; Start to fill with Ca(OH) ₂		14	:26			
Clock; Filled with Ca(OH) ₂		14	:30			
Clock; Pressure applied		14	:31			
Clock; Pressure achieved <u>27</u> mbar		14	:36			
Clock; Air allowed in		15	:38			
Migration						
Date 03-11-2020						
Room Temperature [°C]	20					
Cahode solution Temperature [°C]	1	9	1	9		
Anode solution Temperature [°C]	19	19	19	19		
Voltage pre-set		30	V			
Initial current [mA]	95	104	85	82		
Corrected applied voltage [V]	2	0	25			
New current, start (Each) [mA]	63	67	71	68		
New current, start (Both) [mA]	12	29	1	39		
Clock; When starting test		10	:49			
Date		05-11	-2020			
Room Temperature [°C]		2	20			
Clock; When reading of Temperature		10	:43			
Cahode solution Temperature [°C]	2	0	2	20		
Anode solution Temperature [°C]	20	20	20	20		
Clock; When reading of current		10	:44			
Current, end (Both) [mA]	12	22	1	70		
		-				
Current, end (Each) [mA]	60	62	87	83		
Clock; When ending test		10	:46			
Approx Penetration Depth [mm]	-	29	-	33		

Chloride Migration Test:

8th cast specimens

Mortar samples

09/11	- 12/11	2020
-------	---------	------

	M_OPC	M_OPC	M_FA23	M_FA23					
	8A (II)	8B (II)	8A (II)	8B (II)					
Clock; De-moulded	10:11	10:11	10:30	10:30					
Length ₁ [mm]	49.87	47.67	49.1	49.89					
Length ₂ [mm]	49.99	47.77	49.24	48.32					
Length ₃ [mm]	50.4	47.98	49.20	46.92					
Av. Length [mm]	50.09	47.81	49.18	48.38					
Vacuum									
Date		09-11-2020							
Room Temperature [°C]		2	0						
Clock; Pressure applied		10:	55						
Clock; Pressure constant at <u>28</u> mbar		11:	00						
Clock; Essicator shut off		14:	04						
Clock; Start to fill with Ca(OH) ₂		14:	05						
Clock: Filled with Ca(OH) ₂		14:	09						
Clock: Pressure applied		14:	10						
Clock; Pressure achieved 28mbar		14:	15						
Clock; Air allowed in		15:	17						
Migration									
Data 10-11-2020									
Boom Temperature [%C]	20								
Cabode solution Temperature [%]	1	0	0 1	0					
Anode solution Temperature [°C]	20	20	20	20					
Voltage pre-set	20	30	V 20	20					
Initial current [mA]	107	93	72	85					
Corrected applied voltage [V]	2	20	72	25					
New current, start (Each) [mA]	69	60	58	70					
				10					
New current, start (Both) [mA]	1	27	1	29					
Clock; When starting test		09:	09						
Data		11_11	_2020						
Boom Temperature [%C]		2	1						
Clock: When reading of Temperature		09.	06						
Cabode solution Temperature [°C]	2	20	2	20					
Anode solution Temperature [°C]	21	21	21	21					
Clock: When reading of current	21	09:	09	21					
Current, end (Both) [mA]	1	13	1	42					
	1		1						
Current, end (Each) [mA]	60	54	64	78					
· · · · · · · · · · · · · · · · · · ·									
Clock; When ending test		09:	10						
Approx Penetration Depth [mm]	-	30	-	37					

Chloride Penetration Depth

Specimens used to check the chloride penetration depth by spraying with silver nitrate. The actual experiments was done on other specimens. the specimens with index A. The penetration depths is shown and this was used to ensure that more than 10 mm of the specimen had been proper penetrated with $\rm Cl^-$ ions.

Specimens; M_OPC_7B(II) and M_FA23_7B(II)





(a) Penetration depth on $M_OPC_7B(II)$

Specimens; M_OPC_8B(II) and M_FA23_8B(II)

(b) Penetration depth on M_FA23_7B(II)

Figure 89







(b) Penetration depth on $M_{FA23}_{8B(II)}$

Figure 90

Sawing discs for cup test



(a) Sawing disc for cup test



(b) Disc for cup test

Figure 91: Discs

Figure 92: Assembling cup. 1) Bowl filled with saturated KNO₃ solution is put in the bottom part of the cup and wire mesh is put on top to avoid splashes on the specimen when weighting samples. 2) Rubber gasket is placed before placing the sample. 3) Specimen and additional rubber gasket. 4) Another rubber gasket to ensure make it easier for the cup to slide when closing tight

Test setup

Assembling cup



(a) Filling salt solution and weighting cups

(b) Test setup

Figure 93: Cup test setup

Cup test:

7 th cast	specimens		05-11-2020	- 01-01-2021	
	Specimens ID	M OPC 7(I)	M OPC 7(II)	M FA23 7(I)	M FA23 7(II)
	Cup ID	41	42	43	44
	Calibration of RH measure device at 75% RH	77	.27	76	0.02
	Clock		1	1:08	
	Initial weight of empty cups	301.480	309.698	311.765	312.028
	Initial weight of cups with salt	445.478	457.667	448.695	458.288
	Samples				
	Thickness ₁ [mm]	10.68	9.48	10.18	10.65
	Thickness ₂ [mm]	10.04	10.10	10.21	11.02
	Thickness ₃ [mm]	10.54	10.75	10.33	11.1
	Av. Thickness [mm]	10.42	10.11	10.24	10.92
	Diameter ₁ [mm]	98.82	100.01	96.70	99.62
	Diameter ₂ [mm]	99.06	98.68	99.93	99.04
	Diameter ₃ [mm]	98.57	99.35	100.01	98.51
	Av. Diameter [mm]	98.82	99.35	98.88	99.06
	Air layer between sample and salt solution [mm]	19.37	18.50	19.21	19.58
	Weight of sample [g]	182.883	177.977	177.214	185.101
	Date and clock		05-11-2	2020 12:04	,1
\mathbf{m}_{i}	Weigh of sample in cup [g]	628 088	635 357	625 658	643 146
	Date deck and DILin decise ster	020.000	09.12	023.030	0/ DU
	Date, clock and RH in desiccator	00-11-2020	08:12	86.41	% RH
	Date, clock and RH in desiccator	10.11.2020	08:37	00./3	70 KH
à	Date, clock and RH in desiccator	10-11-2020	08:23	85.43	% RH
ONTIC	Date, clock and RH in desiceator	12 11 2020	08.00	0J.14 81.59	70 KH 0/ DU
0	Date, clock and RH in desiccator	16-11-2020	08:34	81.38	% PH
	Date, clock and RH in desiccator	17-11-2020	08:53	80.85	% RH
	Date, clock and RH in desiccator	18-11-2020	08:07	80.85	% RH
	Date, elock and for in destection	10 11 2020	20=1	1-2020	/0101
m,	RH in desiccator [% RH]		8	0.80	
m	Weigh of sample in cup [g]	626.734	632.661	623.660	640.30
	Date. clock and RH in desiccator	23-11-2020	08:36	80.23	% RH
atrol	Date, clock and RH in desiccator	24-11-2020	11:40	80.78	% RH
Con	Date, clock and RH in desiccator	25-11-2020	10:21	79.93	% RH
	Date and clock		27-1	1-2020	
m_2	RH in desiccator [% RH]		8	0.43	
	Weigh of sample in cup [g]	626.190	631.965	623.092	639.62
je,	Date, clock and RH in desiccator	30-11-2020	08:07	80.29	% RH
Contra	Date_clock and RH in desiccator	02-12-2020	16:32	80.06	%RH
<u> </u>	Date and clock	02 12 2020	04-1	2-2020	, or tur
m ₂	RH in desiccator [% RH]		8	0.43	
5	Weigh of sample in cup [g]	625.661	631.31	622.586	639.00
~	Date aloak and PH in designator	07-12-2020	08.11	80.35	- 04 DU
mtror		07-12-2020	08.11	80.55	70 KH
<u>C</u>	Date, clock and RH in desiccator	08-12-2020		80.47	% RH
	Date and clock		11-1	2-2020	
m_4	KH in desiccator [% KH] Weigh of sample in cup [g]	625 159	630 716	50.4 622.13	638.44
	weigh of sample in cup [g]	023.139	050.710	022.13	030.44
attol	Date, clock and RH in desiccator	16-12-2020		80.41	% RH
Con	Date, clock and RH in desiccator	17-12-2020		80.67	% RH
	Date and clock		18-1	2-2020	
m_5	RH in desiccator [% RH]		8	0.77	
	Weigh of sample in cup [g]	624.661	630.134	621.696	637.91
	Date and clock		25-1	2-2020	
m ₆	RH in desiccator [% RH]	(21.000	8	0.51	(AB 44
	weign of sample in cup	624.208	629.547	621.310	637.43
	Date and clock		01-0	0.20	
m_7	KH III desiccator [% KH] Weigh of sample in cup [g]	673 770	678.094	0.20 620.040	636.06
		043.740	040.200	040.949	000.90

Cup test:

8 th cast	specimens		12-11-2020	- 08-01-2020	
	Specimens ID	M_OPC _8(I)	M_OPC_8(II)	M_FA23_8(I)	M_FA23_8(II)
	Cup ID	45	46	47	48
	Calibration of RH measure device at 75% RH				
	Clock		10):30	
	Initial weight of empty cups	305.558	302.955	294.786	297.353
	Initial weight of cups with salt	440.594	440.971	442.288	432.705
	Samples		-		
	Thickness ₁ [mm]	10.28	8.32	10.43	10.85
	Thickness ₂ [mm]	10.16	9.21	10.51	10.35
	Thickness ₃ [mm]	10.62	8.65	10.47	10.73
	Av. Thickness [mm]	10.35	8.73	10.47	10.64
	Diameter ₁ [mm]	99.96	99.98	99.93	99.83
	Diameter ₂ [mm]	99.90	99.84	99.73	99.85
	Diameter ₃ [mm]	99.84	99.88	99.75	99.77
	Av. Diameter [mm]	99.90	99.90	99.80	99.82
	Air layer between sample and salt solution [mm]	19.94	20.77	20.56	21.23
	Weight of sample [g]	180.646	155.336	181.65	185.071
m	Date and clock		12-11-2	020 10:50	
m	Weigh of sample in cup	621.099	596.171	623.847	617.678
	Date, clock and RH in desiccator	16-11-2020	08:33	80.94	% RH
	Date, clock and RH in desiccator	17-11-2020	08:57	80.84	% RH
	Date, clock and RH in desiccator	18-11-2020	08:09	80.80	% RH
	Date, clock and RH in desiccator	20-11-2020	08:13	80.17	% RH
	Date, clock and RH in desiccator	23-11-2020	08:42	80.84	% RH
	Date, clock and RH in desiccator	24-11-2020	11:45	80.24	% RH
	Date, clock and RH in desiccator	25-11-2020	10:24	80.72	% RH
	Date and clock		27-1	1-2020	
m_1	RH in desiccator		8	1.19	
	Weigh of sample in cup	619.554	593.554	621.922	615.08
<i>.</i> è	Date, clock and RH in desiccator	30-11-2020	08:13	80.77	% RH
CONT	Date, clock and RH in desiccator	02-12-2020	16:37	80.61	% RH
-	Date and clock		04-1	2-2020	
m ₂	RH in desiccator		80).49	
2	Weigh of sample in cup	619.03	592.803	621.374	614.426
à	Date, clock and RH in desiccator	07-12-2020		81.21	% RH
contro	Date clock and RH in desiccator	08-12-2020		81 39	% RH
-	Date and clock	00 12 2020	11-1	2-2020	Juli
m ₃	RH in desiccator		8	1.44	
-	Weigh of sample in cup	618.536	592.12	620.894	613.837
rof	Date, clock and RH in desiccator	16-12-2020		81.31	% RH
Contr	Date, clock and RH in desiccator	17-12-2020		81.34	% RH
	Date and clock		18-1	2-2020	
m_4	RH in desiccator		8	1.28	
	Weigh of sample in cup	618.04	591.465	620.437	613.270
	Date and clock		25-1	2-2020	
m_5	RH in desiccator		8	1.51	
	Weigh of sample in cup	617.590	590.810	620.044	612.781
	Date and clock		01-0	1-2012	
m ₆	RH in desiccator		8	1.41	
	Weigh of sample in cup	617.155	590.198	619.671	612.282
	Date and clock		08-0	1-2021	
m ₇	RH in desiccator		82	2.20	
	Weigh of sample in cup	616.736	589.335	619.335	611.816

RH in desiccator

Cast	7	8
06-11-2020	88.41	
09-11-2020	86.73	
10-11-2020	85.43	
11-11-2020	85.14	
12-11-2020	81.58	
16-11-2020	81.75	80.94
17-11-2020	80.85	80.84
18-11-2020	80.99	80.80
20-11-2020	80.80	80.17
23-11-2020	80.23	80.84
24-11-2020	80.78	80.24
25-11-2020	79.93	80.72
27-11-2020	80.43	81.19
30-11-2020	80.29	80.77
02-12-2020	80.06	80.61
04-12-2020	80.43	80.49
07-12-2020	80.35	81.21
08-12-2020	80.47	81.39
11-12-2020	80.40	81.44
16-12-2020	80.41	81.31
17-12-2020	80.67	81.34
18-12-2020	80.77	81.28
25-12-2020	80.51	81.51
01-01-2021	80.20	81.41
08-01-2021		82.20

RH in Desiccators (not corrected)



Density calculation:

Specimens ID	M_OPC _7(I)	M_OPC _7(II)	M_FA23 _7(I)	M_FA23 _7(II)	M_OPC _8(I)	M_OPC_ 8(II)	M_FA23 _8(I)	M_FA23 _8(II)		
Cup ID	41	42	43	44	45	46	47	48		
Clock		11	:08			10	:30			
Initial weight of empty cups	301.480	309.698	311.765	312.028	305.558	302.955	294.786	297.353		
Initial weight of cups with salt	445.478	457.667	448.695	458.288	440.594	440.971	442.288	432.705		
Samples										
Thickness ₁ [mm]	10.68	9.48	10.18	10.65	10.28	8.32	10.43	10.85		
Thickness ₂ [mm]	10.04	10.10	10.21	11.02	10.16	9.21	10.51	10.35		
Thickness ₃ [mm]	10.54	10.75	10.33	11.1	10.62	8.65	10.47	10.73		
Av. Thickness [mm]	10.42	10.11	10.24	10.92	10.35	8.73	10.47	10.64		
Diameter ₁ [mm]	98.82	100.01	96.70	99.62	99.96	99.98	99.93	99.83		
Diameter ₂ [mm]	99.06	98.68	99.93	99.04	99.90	99.84	99.73	99.85		
Diameter ₃ [mm]	98.57	99.35	100.01	98.51	99.84	99.88	99.75	99.77		
Av. Diameter [mm]	98.82	99.35	98.88	99.06	99.90	99.90	99.80	99.82		
Weight of sample [g]	182.883	177.977	177.214	185.101	180.646	155.336	181.65	185.071		

Cross-sectional area [mm ²]	7669.2	7751.7	7679.0	7706.5	7838.3	7838.3	7823.1	7825.2
Volumen of specimen [mm ³]	79913.1	78369.6	78633.3	84180.7	81152.3	68402.1	81908.1	83286.3
Density [g/mm ³]	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
Density [g/cm ³]	2.29	2.27	2.25	2.20	2.23	2.27	2.22	2.22
Density [kg/m ³]	2289	2271	2254	2199	2226	2271	2218	2222



Cup test:

Calculations

	Specimens ID	M_OPC	M_OPC	M_FA23	M_FA23	M_OPC	M_OPC	M_FA23	M_FA23
	Cup ID	/(1)	7(II) 12	/(1)	7(11)	8(1)	8(11)	8(1)	8(II) 40
	Calibration of PH mansura davias	41	42	43	44	45	46	47	48
	at 75% RH		77	.27			76	5.02	
	Av. Thickness, d [mm]	10.42	10.11	10.24	10.92	10.35	8.73	10.47	10.64
	Av. Diameter [mm]	98.82	99.35	98.88	99.06	99.90	99.90	99.80	99.82
	Air layer between sample and salt solution,d _s [mm]	19.37	18.50	19.21	19.58	19.94	20.77	20.56	21.23
	Weight of sample	182.883	177.977	177.214	185.101	180.646	155.336	181.65	185.071
	Date and clock		05-11	-2020			12-1	1-2020	
mi	Weigh of sample in cup [g]	628.088	635.357	625.658	643.146	621.099	596.171	623.847	617.678
m.	Date and clock		20-11	-2020			27-1	1-2020	
m	Weigh of sample in cup [g]	626.734	632.661	623.660	640.308	619.554	593.554	621.922	615.08
m2	Date and clock		27-11	-2020			04-12	2-2020	
	Weigh of sample in cup [g]	626.190	631.965	623.092	639.624	619.030	592.803	621.374	614.426
m_3	Date and clock		04-12	2-2020	(20.00-	(10 = 2 (11-12	2-2020	(12.027
	Weigh of sample in cup [g]	625.661	631.310	622.586	639.00 7	618.536	592.12	620.894	613.837
m_4	Date and clock	(25.150	630 716	2-2020	629 445	619.040	18-12 501 465	2-2020	612 270
	Date and deat	025.159	19.12	022.130	030.445	010.040	391.403	020.437	013.270
m ₅	Weigh of sample in cup [g]	624 661	630 134	621 696	637 913	617 590	23-1. 590 810	620 044	612 781
	Date and clock	024.001	25-12	-2020	057.715	017.370	01-0	1-2012	012.701
m ₆	Weigh of sample in cup	624.208	629.547	<u>621.310</u>	637.436	617.155	590.198	619.671	612.282
	Date and clock		01-01	-2021			08-0	1-2021	
m ₇	Weigh of sample in cup [g]	623.728	628.986	620.949	636.961	616.736	589.633	619.335	611.816
Expo	sed surface area, A [mm ²]	6361.725	6361.725	6361.725	6361.725	6361.725	6361.725	6361.725	6361.725
Diam	eter of cup opening, S [mm]	90	90	90	90	90	90	90	90
Temp	erature, T [K]	292.15	292.15	292.15	292.15	292.15	292.15	292.15	292.15
t ₁ [s]		0	0	0	0	0	0	0	0
t ₂ [s]		604800	604800	604800	604800	604800	604800	604800	604800
Avera	age mass change rate, G [kg/s]	-8.142E-10	-9.851E-10	-7.087E-10	-8.806E-10	-7.586E-10	-1.048E-09	-6.743E-10	-8.631E-10
Water	r vapor flow rate, g [kg/m ² s]	-1.280E-07	-1.549E-07	-1.114E-07	-1.384E-07	-1.192E-07	-1.648E-07	-1.060E-07	-1.357E-07
Corr	ection for masked edges								
Width	n of the masked edges, b [m]	0.00441	0.00467	0.00444	0.00453	0.00495	0.00495	0.00490	0.00491
g _{me}		-1.180E-08	-1.417E-08	-1.016E-08	-1.330E-08	-1.126E-08	-1.353E-08	-1.007E-08	-1.306E-08
g _{corr}		-1.162E-07	-1.407E-07	-1.012E-07	-1.251E-07	-1.080E-07	-1.512E-07	-9.591E-08	-1.226E-07
G _{corr} [[kg/s]	-7.391E-10	-8.950E-10	-6.440E-10	-7.960E-10	-6.870E-10	-9.622E-10	-6.102E-10	-7.800E-10
Wate	r vapor pressure	RH ₁₍₄₁₋₄₄₎ =	78.19	RH ₁₍₄₅₋₄₈₎ =	80.55	RH ₂ =	94	δ_a=	1.95E-10
Satur	ation vapor pressure, p _s [Pa]	2199.1143	2199.1143	2199.1143	2199.1143	2199.1143	2199.1143	2199.11433	2199.11433
Vapo	r pressure difference, ∆p [Pa]	-347.6	-347.6	-347.6	-347.6	-347.6	-347.6	-347.6	-347.6
Vapo	r permeance, W _{corr} [kg/m ² s Pa]	3.457E-10	4.208E-10	2.998E-10	3.734E-10	3.208E-10	4.562E-10	2.842E-10	3.668E-10
Wate	r vapor permeability coefficient								
δ [kg/	/m s Pa]	3.602E-12	4.255E-12	3.070E-12	4.079E-12	3.321E-12	3.981E-12	2.975E-12	3.904E-12
Wate	r vapor flow rate								
g _{total}	kg/m ² s]	-1.202E-07	-1.463E-07	-1.042E-07	-1.298E-07	-1.115E-07	-1.586E-07	-9.879E-08	-1.275E-07
g _{totall}	[10 ' kg/m ² s]	1.20	1.46	1.04	1.30	1.12	1.59	0.99	1.28



Deviation of mass losses

	M_OPC 7(I)	M_OPC 7(II)	M_FA23 7(I)	M_FA23 7(II)	M_OPC 8(I)	M_OPC 8(II)	M_FA23 8(I)	M_FA23 8(II)
m ₁ -m _i (14 days)	1.354	2.696	1.998	2.838	1.545	2.617	1.925	2.598
m ₂ -m ₁	0.544	0.696	0.568	0.684	0.524	0.751	0.548	0.654
m ₃ -m ₂	0.529	0.655	0.506	0.617	0.494	0.683	0.480	0.589
m ₄ -m ₃	0.502	0.594	0.456	0.562	0.496	0.655	0.457	0.567
m ₅ -m ₄	0.498	0.582	0.434	0.532	0.450	0.655	0.393	0.489
m ₆ -m ₅	0.453	0.587	0.386	0.477	0.435	0.612	0.373	0.499
m ₇ -m ₆	0.480	0.561	0.361	0.475	0.419	0.565	0.336	0.466

Difference from measurement to measurement

$(m_3-m_2)-(m_4-m_3)$	0.027	0.061	0.050	0.055	-0.002	0.028	0.023	0.022
$(m_4-m_3)-(m_5-m_4)$	0.004	0.012	0.022	0.030	0.046	0.000	0.064	0.078
$(m_5 - m_4) - (m_6 - m_5)$	0.045	-0.005	0.048	0.055	0.015	0.043	0.020	-0.010
$(m_6-m_5)-(m_7-m_6)$	- 0.027	0.026	0.025	0.002	0.016	0.047	0.037	0.033
Average difference	0.012	0.024	0.036	0.036	0.019	0.030	0.036	0.031
Average difference (all)	0.03							

Deviation between m3-m2 and m7-m8

$(m_3-m_2)-(m_7-m_6)$	0.049	0.094	0.145	0.142	0.075	0.118	0.144	0.123
Average of $(m_3-m_2)-(m_7-m_6)$	0.11							



