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The Effect of Fly Ash and GGBFS as Cement Replacement on Chloride Binding and Ingress in Mortar Samples

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Abstract:
The effect of chloride binding on chloride ingress was investigated in addition to the binding capacity of fly ash cement and blast furnace slag cement. Chloride binding isotherms and chloride profiles were determined for mortars with w/c= 0.4 and 6% silica fume addition. Ground granulated blast furnace slag (50%) and fly ash (30%) were included as partial replacement for Portland cement. A variant of the equilibrium method was used to determine the chloride binding isotherms. The obtained results agree with much of the present literature. Small standard deviations and clear trends indicate reliable experimental data.

One of the findings of the study is that various cementitious materials exhibit different binding capacities. Of the three tested mortars, the mortar with blast furnace slag cement resulted in the highest binding capacity followed by the fly ash blended cement. Ordinary Portland cement (OPC) had the lowest binding capacity. A non- linear relationship between free and bound chlorides were found, in which the Freundlich isotherm and Langmuir isotherm provided a good fit.

Due to different binding capacities, it follows that binding should be included when comparing chloride ingress in various binders. Chloride profiles were produced in order to evaluate the effect of binding on chloride profiles. The high binding capacity of blast furnace slag cement and fly ash cement resulted in a lower amount of free chlorides in the pore solution. It appears as the binding isotherm determined by $CaCl_2$ gives a better reflection of the binding behavior compared to NaCl.

Generally, the apparent diffusion coefficient is determined by fitting of *total* chloride profiles to the solution of Fick's 2nd law of diffusion. The approach is questionable as it rests on number of simplifying assumptions that rarely are met in a real structure. It seems more appropriate to base the fitting on free chlorides, as only the free chlorides are influenced by diffusion. Therefore, the apparent diffusion coefficient and the surface concentration were determined by fitting of total and free chloride profiles. The results proved that the coefficient is reduced by 28 - 35 % if binding is included.

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Foreword

This study was prepared during spring 2014 at Norwegian University of Technology and Science (NTNU), Department of Civil and Transport Engineering in Trondheim. The thesis constitutes the subject TBA4905 – Building and Material Engineering, Master Thesis. It is limited by available resources and developed as an independent project with technical and professional guidance from Dr. Klaartje De Weerdt and Prof. Dr. Mette R. Geiker. The master thesis is not an extension of the Specialization Project and it was completed within 20 weeks.

I would like to express my gratitude to my supervisor Mette Geiker for guidance and assistance in the choice of subject. Her enthusiasm has inspired me and I have appreciated that she has always been available for discussion during my last year at NTNU. I am especially grateful to Klaartje De Weerdt for superior guidance and support during the writing of this thesis. I would like to thank her for preparing the samples, setting of the initial part of the experiment and helping me during the laboratory work. Thank you for your patient, enthusiasm and humor. I would also like to thank Kristin Mjøen at SINTEF Laboratory for assistance in the lab.

I am also grateful to Tore Kvande for making it possible to write this thesis. A final thank to my fellow students in room 2-239 for the great work environment.

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Summary

Reinforcement corrosion has been identified as the predominant deterioration mechanism for reinforced concrete structures (*fib*, 2006), and is usually caused by carbonation or chloride attack. Chloride- induced corrosion is triggered by an increasing concentration of chloride ions in the pore solution. Corrosion seriously affects the serviceability and safety of concrete structures, and can cause major maintenance costs. Therefore, precise information and understanding of chloride ingress and chloride binding may enable better prediction of service life of concrete structures. The aim of this study is to gather information on chloride binding capacity of supplementary cementitious materials and its effect on chloride profiles. The use of fly ash and ground granulated blast furnace slag are known to increase the binding capacity thus lowering the free chloride content available for corrosion initiation. This can most likely be linked to a high alumina content in which chemical binding capacity increases. Additionally, blast furnace slag and fly ash can increase the formation of C-S-H which enhance the physical binding capacity.

The effect of chloride binding on chloride ingress was investigated in addition to the binding capacity of fly ash cement and blast furnace slag cement. Chloride binding isotherms and chloride profiles were determined for mortars with w/c= 0.4 and 6% silica fume addition. Ground granulated blast furnace slag (50%) and fly ash (30%) were included as partial replacement for Portland cement. A variant of the equilibrium method was used to determine the chloride binding isotherms. Hydrated samples were grounded and exposed to solutions of $CaCl_2$ and NaCl of varying concentrations at 20°C. The determined binding isotherms were used to calculate bound and free chloride profiles for mortars exposed to NaCl for 6 months. The obtained results agree with much of the present literature. Small standard deviations and clear trends indicate reliable experimental data.

One of the findings of the study is that various cementitious materials exhibit different binding capacities. Of the three tested mortars, the mortar with blast furnace slag resulted in the highest binding capacity followed by the fly ash blended cement. Ordinary Portland cement (OPC) had the lowest binding capacity. A non- linear relationship between free and bound chlorides were found, in which the Freundlich and Langmuir isotherm provided a good fit.

Due to varying binding capacities, it follows that binding should be included when comparing chloride ingress in various binders. Chloride profiles were produced in order to evaluate the effect of binding on chloride profiles. The high binding capacity of the ground granulated blast furnace slag cement resulted in a lower amount of free chlorides

in the pore solution. It appears as the binding isotherm determined by $CaCl_2$ gives a better reflection of the binding behavior compared to the NaCl binding isotherm.

Generally, the apparent diffusion coefficient is determined by fitting of *total* chloride profiles to the solution of Fick's 2nd law of diffusion. The approach is questionable as it rests on number of simplifying assumptions that rarely are met in a real structure. It seems more appropriate to base the fitting on free chlorides, as only the free chlorides are influenced by diffusion. Therefore, the apparent diffusion coefficient and the surface concentration were determined by fitting of both total and free chloride profiles. The results proved that the coefficient is reduced by 28 - 35 % if binding is included.

Sammendrag

Armeringskorrosjon har blitt identifisert som den dominerende nedbrytningsmekanismen av armerte betongkonstruksjoner (*fib*, 2006). Korrosjon kan påvirke sikkerheten av betongkonstruksjoner og kan forårsake store vedlikeholdskostnader. Derfor vil ytterligere informasjon og forståelse av kloridinntrengning og kloridbinding muliggjøre bedre estimering av betongkonstruksjoners levetid. Målet med denne studien er å samle informasjon om bindingskapasiteten til tilsetningsmaterialer og effekten av binding på kloridprofiler. Den høye bindingsevnen til flyveaske og slagg reduserer andel frie klorider som er tilgjengelig for initiering av korrosjon i porene. Den høye bindingsevnen kan mest sannsynlig knyttes til et høyt alumina innhold som øker den kjemisk bindingskapasiteten. I tillegg kan slagg og flyve aske øke dannelsen av CSH som også øker den fysiske bindingskapasitet.

Bindingsisotermer og kloridprofiler ble bestemt for mørtelprøver med w / c = 0,4 og 6 % silikastøv. Slagg (50%) og flyveaske (30%) ble inkludert som delvis erstatning for Portlandsement. En variant av «the equilibrium method» ble brukt for å bestemme bindingsisotermene.

Ett av funnene i denne studien er at ulike tilsetningsmaterialer har ulik evne til å binde klorider. Av de tre testede mørtlene, hadde mørtelen med slagg den høyeste bindingskapasiteten. Flyveaskesementen hadde høyere bindingsevne sammenlignet med vanlig Portlandsement. Forholdet mellom frie og bundne klorider kunne best beskrives av de ikke- lineære bindingsisotermene, Freundlich- isotermen og Langmuir- isotermen.

Ettersom de ulike bindemidlene har ulik evne til å binde klorider, bør også binding inkluderes når man sammenligner kloridprofiler. Kloridprofiler ble derfor produsert for å vurdere effekten av binding. Resultatene viser at $CaCl_2$ bindingsisotermen gir en bedre beskrivelse av kloridinntrengning sammenlignet med NaCl bindingsisotermen. Både slaggsementen og flyvaskesementen har et lavt kloridinnhold ca 10 mm fra den eksponerte overflaten sammenlignet med den rene Portlandsement mørtelen.

Som regel bestemmes diffusjonskoeffisienten ved å tilpasse totale kloridprofiler til løsning av Fick 2.lov om diffusjon. Denne metoden er tvilsom ettersom den baseres på en rekke antagelser som sjeldent er oppfylt. Det virker mer hensiktsmessig å basere tilpasningen på de frie kloridene ettersom det bare er de frie kloridene som påvirkes av diffusjon. Diffusjonskoeffisienten og overflatekonsentrasjonen ble derfor bestemt ved tilpasning av både totale og frie kloridprofiler. Resultatene viser at koeffisienten reduseres med 28 - 35 % hvis binding inkluderes.

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Glossary of notations and terms

Cement chemistry short hand notation;

C	CaO
S	SiO_2
A	Al_2O_3
F	Fe_2O_3
H	H_2O
$\underline{S}$	SO_3

The notation of the anhydrous phases and hydrates;

C_3S	$3CaO \cdot SiO_2$	Tricalcium silicate
C_2S	$2CaO \cdot SiO_2$	Dicalcium silicate
C_3A	$3CaO \cdot Al_2O_3$	Tricalcium aluminate
C_4AF	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	Tetracalcium aluminoferrite, ferrite
CH	$Ca(OH)_2$	Calcium hydroxide
C-S-H	$3CaO \cdot 2SiO_2 \cdot 3H_2O$	Amourphous calcium silicate hydrate
	The main hydration product of Portland cement. Can also be formed by the pozzolanic reaction with CH.	
C-A-S-H	C-S-H with higher aluminate content	

Additional abbreviations;

AFt- phases	The phase formed by hydration of Portland cement derived from pure ettringite with partial substitution of A by F, and SO_4^{2-} by other ions (De Weerdt, 2011)
AFm- phases	The phase formed by hydration of Portland cement derived from pure monosulphoaluminate with partial substitution of A by F, and SO_4^{2-} by other ions (De Weerdt, 2011)

HNO_3	Nitric acid
$AgNO_3$	Silver nitrate

OPC	Ordinary Portland Cement
FA	Fly ash
GGBFS	Ground granulated blast furnace slag
XRD	X- ray diffraction

1

INTRODUCTION

1.1 Background

Reinforcement corrosion has been identified as the predominant deterioration mechanism for reinforced concrete structures (*fib*, 2006). Chloride attack of reinforcement in concrete structures exposed to marine environment or de- icing salts are one of the main causes of corrosion. The corrosion process is triggered by an increasing concentration of chloride ions in the pore solution. The chlorides penetrates through the concrete cover and may cause pitting corrosion when a critical level is reached in the area of the steel rebars. A reduction of the reinforcement cross section area due to corrosion causes a loss of the load carrying capacity, thus limit the service life of the structure.

Chloride ions can either be physically or chemically bound, or exist as free ions in the pore solution. The use of supplementary cementitious materials, such as fly ash and blast furnace slag, affects the concretes ability to resist penetration of chloride ions and other aggressive substances. Research shows that supplementary cementitious materials exhibited a greater ability to bind chlorides (Zibara, 2001, Dhir et al., 1996, Arya et al., 1990, Xu, 1997, Thomas et al., 2012, Arya&Xu, 1995), thus reducing the amount of free chlorides available for corrosion initiation.

Chloride profiles are usually determined when evaluating chloride ingress in concrete. Generally, the profile shows the total chloride content, including both free and bound chlorides, as a function of depth into the concrete. Hence, there is no differentiation between free and bound chlorides. Only the free chlorides present in the pore solution are able to break down the protective layer of the steel surface. As cement and supplementary cementitious materials are capable of physical and chemical binding of chlorides, certain quantities of chlorides are removed from the pore solution. These chlorides are unable to affect corrosion directly, though the bound chlorides may be released due to changes in the environment.

The apparent diffusion coefficient and the surface concentration of a given system are determined by fitting of total chloride profiles to the solution of Fick's 2nd law of diffusion. The calculated fitting parameters are then often used to evaluate long- term performance of a cementitious system. However, the approach rest on a series of simplifying assumptions, such as linear relationship between free and bound chlorides

and no leaching or chemical activity. It is a questionable approach as only free chlorides move by diffusion and they are only a small share of the total chloride content.

1.2 Objective

Corrosion seriously affects the serviceability and safety of concrete structures and may cause major maintenance costs. Therefore, precise information and understanding of chloride ingress and chloride binding as well as factors influencing the binding process is important in order to better predict long- term performance of concrete structures. The aim of this study is to evaluate the impact of various binders and the cation of the chloride salt on the binding capacity of mortars. The study focuses on a better understanding of chloride ingress in concrete prepared with Ordinary Portland cement, fly ash and blast furnace slag.

Better understanding of binding properties of a given cementitious system and appropriate binding relationship enables consultants and contractors to better estimate chloride penetration depths, thus time to depassivation. The obtained results can also be used as a basis for selection of binders for structures subjected to chlorides.

1.3 Summary of used methods

Chloride binding experiments were conducted using a technique based on the method developed by Tang and Nilsson (Tang&Nilsson, 1993). The method involves exposing mortar samples to chloride solutions of known concentration. After achieving equilibrium, automatic potentiometric titration was used to determine the chloride content of the pore solution. Mortar samples with w/c= 0.4 and 6% silica fume addition were used throughout the study. Two supplementary cementitious materials were added; fly ash (30%) and ground granulated blast furnace slag (50%). Typical Norwegian concretes used in marine environments inspired the mix design.

For binding isotherms, grounded samples were exposed to solutions of NaCl and $CaCl_2$ for about 3 months. For determination of chloride profiles, mortar samples were exposed to NaCl solutions after 1 week of curing for 6 months. Before analysis, the samples were profile ground into 6 -7 sections. The total chloride content of the resulting mortar powder was then determined.

1.4 Structure

This thesis was carried out as a partial literature study and laboratory work. The experimental work can be divided into two main phases; 1) determination of chloride binding isotherms and 2) determination of total, free and bound chloride profiles. A literature review is first presented in order show the main features of the present research, which provides the basis for the discussion. The methods used are described in detail, before the results are presented. A discussion of the results and a conclusion are given at the end. Relevant abbreviation and terms used in the study are presented before the introduction.

2

CORROSION AND CHLORIDE BINDING

2.1 Service life prediction

The deterioration mechanism caused by reinforcement corrosion can be divided into two main time phases, see Figure 2.1;

1. The initiation period: time until depassivation of reinforcement due to the presence of chloride salts or carbonation. Usually considered as service life.

2. The propagation period: reinforcement is corroding, which may lead to cracks and spalling of concrete and finally structural damage.
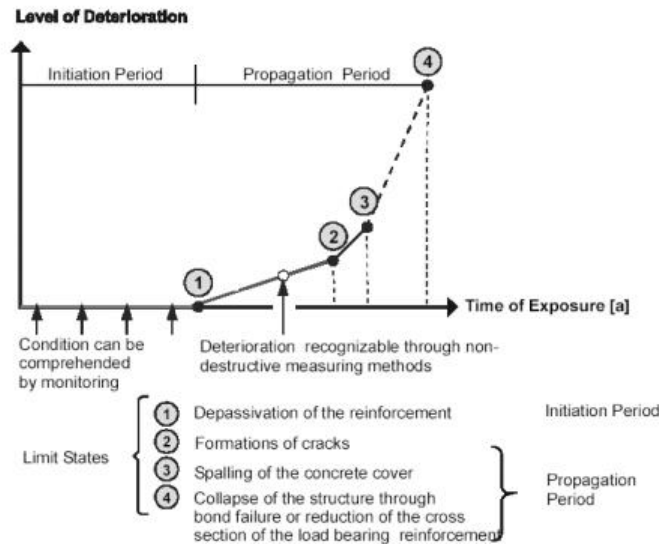
Figure 2.1 - Deterioration of steel reinforcement corrosion (Fib, 2006)

2.2 Corrosion

Corrosion is an electrochemical process depending on, among others, an anode and cathode. An oxidation reaction takes place on the anode. The electrons are released and the iron dissolves;

$$Fe \; \rightarrow \; Fe^{2+} + 2e^{-} \tag{2.1}$$

The reduction reaction takes place on the cathode, where the electrons are consumed;

$$\tfrac{1}{2}O_2 + H_2O + e^{-} \; \rightarrow \; OH^{-} \tag{2.2}$$

Then the total reaction can be expressed by the algebraic sum of the anodic and cathodic reactions. Different types of iron oxides such as $Fe(OH)_2$, Fe_3O_4, Fe_2O_3 may be formed depending on the exposure conditions (Markeset&Myrdal, 2008);

$$Fe_{steel} + \tfrac{1}{2}O_2 + H_2O \; \rightarrow \; Fe^{2+} + 2OH^- \rightarrow \; Fe(OH)_2 \text{ (solid)} \qquad (\,2.3\,)$$

2.3 Chloride- initiated corrosion

The source of chlorides in concrete is usually from the external environment of the structure. Corrosion will only initiate once the chlorides in contact with the reinforcement has reached a certain critical threshold level.

During hydration of cement a highly alkaline pore solution with an pH of about 13- 14 is obtained. Initially, the steel corrodes and a very thin and dense oxide layer of Fe(OH) is created on the steel surface. The impermeable layer act as a physical barrier against aggressive substances from environment, but dissolves when pH drops to a level of about 9 (Markeset&Myrdal, 2008). Depassivation of the protective film is mainly caused by carbonation or penetration of chlorides. In the presence of chlorides, there is an adsorption of chlorides on the steel surface, which causes the breakdown of the oxide film. Unless the steel is repassivated, active corrosion is initiated and the corrosion rate may increase considerably. Once the passive film is broken, there will be a competition between the hydroxide ions (film repair) and the chloride ions (active corrosion). Therefore, the risk of corrosion is often expressed as C_{Cl}/C_{OH}. Figure 2.2 gives a schematic presentation of pitting corrosion.
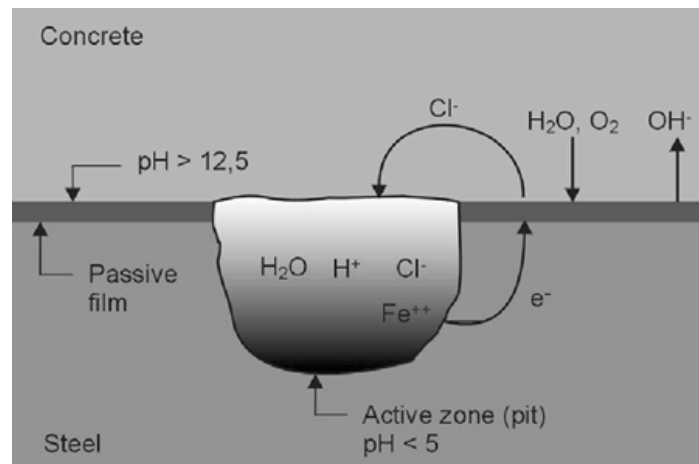
Figure 2.2 - Pitting corrosion of steel in concrete (Bertolini et al., 2004)

2.4 Chloride ingress

Penetration of chloride ions in concrete often occurs by diffusion, which is caused by a concentration gradient. Diffusion is assumed to be the dominating transport mechanisms of chloride ions in concrete, though other transport mechanism such as capillary suction may also play a role in the outer millimeters. Chloride ions diffuse only when dissolved in pore water and it follows that the diffusion is more effective in saturated compared to partially saturated pores. Chloride ingress in concrete obeys Fick's second law of diffusion assuming non- steady state process (Glasser et al., 2008);

$$\frac{\partial C}{\partial t} = D_{app} \frac{\partial^2}{\partial x^2}$$

(2.4)

where   C – chloride concentration in solution
      D_{app} – apparent diffusion coefficient
      x – depth from concrete surface
      t – time

The equation assumes that the surface concentration ($C = C_s$) is constant in time and that the coefficient of diffusion (D_{app}) does not vary in time. Traditionally, chloride ingress by diffusion is modelled with an analytical solution to Equation (2.4) given by;

$$C(x,t) = C_s - (C_s - C_i) \cdot erf \left(\frac{x}{2\sqrt{D_{app} \cdot t}} \right)$$

(2.5)

where   C(x,t) – total chloride content at depth x and time t [%mortar]
      D_{app} – apparent diffusion coefficient for chloride [m^2/s]
      C_S – surface chloride concentration
      C_i – initial chloride concentration
      t – concrete age

The model is often used to mathematically describe the experimentally obtained profiles of chloride content found in non- steady state laboratory experiment or from structures exposed in the field. The apparent diffusion coefficient, D_{app}, describes the materials ability to resist penetration of chloride ions. Depending on concrete properties and exposure conditions, the diffusion coefficient may vary from 10^{-13} m^2/s to 10^{-10} m^2/s (Bertolini et al., 2004). Low D_{app} means a high resistance to chloride penetration. The apparent diffusion coefficient is reduced with increasing addition of pozzolana or slag. The coefficient depends on factors such as exposure conditions and time of exposure. Hence, results obtained from laboratory testing may not be applicable

to other exposure conditions (Bertolini et al., 2004). The diffusion coefficient changes amongst others due to binding, continued hydration, the slow hydration reaction of supplementary materials and moisture. It will usually decrease with time as the capillary pore system will be altered as hydration products continue to form (Nokken et al., 2006). Laboratory testing has confirmed that the diffusion coefficient is improved over time and can be expressed mathematically by (Fluge, 2001);

$$\frac{D(t)}{D_0} = \left(\frac{t_0}{t}\right)^\alpha \qquad (\text{ 2.6 })$$

where   D(t) – time dependent chloride diffusion coefficient

t – age of concrete

D_0 – measured reference diffusion coefficient at t_0

$\propto$ – parameter determined by regression of test results

Equation (2.5) can be used to mathematically predict future chloride profiles. A chloride profile describes the varying chloride content as a function of depth into the concrete, characterized by a high chloride content near the surface and gradual decrease at greater depths, as seen in Figure 2.3.
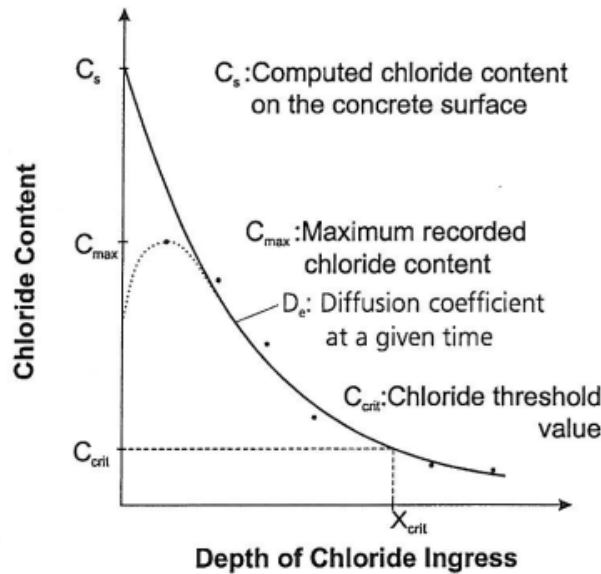
Figure 2.3 - Typical chloride profile in concrete exposed to seawater determined by regression analyses of data measured in the structure (Fluge, 2001)

2.5   Chloride binding

Generally, the chloride content is defined as the total chlorides, which includes both free chlorides and bound chloride in accordance to Equation (2.7). Despite the fact that only the free chloride, i.e. the dissolved chlorides in the pore solution, directly

affect the corrosion process. The bound chlorides are regarded fixed to the solid hydrates and are unable to move freely in the pore solution. Hence, the bound chlorides will not directly be available for the initiation of reinforcement corrosion. However, the bound chlorides may be released when the temperature or pH changes (Markeset&Myrdal, 2008).

$$C_{total} = C_{Cl} + C_{bound} \qquad (\,2.7\,)$$

Generally, the chloride binding process can be classified into two main categories based on the mechanism involved in the binding (Larsen, 1998, Zibara, 2001);
- Chemical binding
- Physical binding

2.5.1 Chemical binding

The chemical reaction between chloride ions and cement phases can be regarded as chemical binding in which the chloride ions are bound to the solids. Although there are disagreements on the complex process, it is well- accepted that the chlorides can react with certain cement phases to form new compounds. The C_3A phase in Portland cement plays a major role in binding of chlorides, particularly for mixed- in chlorides. Higher content of C_3A contributes to a larger amount of bound chlorides through the formation of calcium- chloro- aluminates such as Friedel's salt. This also explains why sulphate resisting Portland cement, with a low C_3A content, binds considerably less chlorides than ordinary Portland cement (Arya et al., 1990, Larsen, 1998). The phase reacts with chlorides to form calcium chloro- aluminates, such as Friedel's salt and Kruzel's salts in accordance to Equation (2.8) and (2.9) (Zibara, 2001, De Weerdt et al., 2014b). However, it should be noticed that this is a simplification and that normally Friedel's salt and Kruzel's salt are formed from other AFm phases which have been formed before chloride penetration.

$$C_3A + Ca(OH)_2 + 2Cl^- + 10H_2O \rightarrow$$
$$C_3A \cdot CaCl_2 \cdot 10H_2O \text{ (Friedel's salt)} + 2OH^- \qquad (\,2.8\,)$$

$$C_3A + 0.5Ca(OH)_2 + 0.5CaSO_4 + 2Cl^- + 10H_2O \rightarrow$$
$$C_3A \cdot (CaCl_2)_{0.5} \cdot (CaSO_4)_{0.5} \cdot 10H_2O \text{ (Kruzel's salt)} \qquad (\,2.9\,)$$
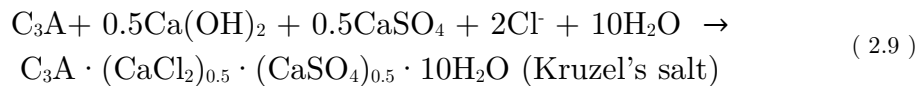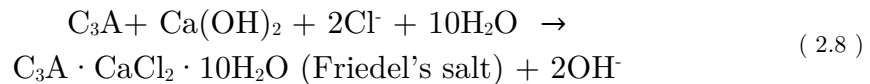
A similar reaction takes place with C_4AF. Other phases such as C_3S and C_2S contribute to binding process through physical binding.

2.5.2 Physical binding

Physical binding is the process in which chloride ions are physically absorbed on the surface of the C-S-H hydrates. The physical absorption is the result of electrostatic or Van der Waals forces between charged particles (Zibara, 2001). According to Claus Larsen (Larsen, 1998) the mechanism can be explained with the electrical double layer theory. An electrical diffuse double- layer is formed due to the absorption of cations in the alkaline solutions. The cations are absorbed on the negatively charged surface of the hydrated cement, which makes the surface appear to be positive. The chlorides are then absorbed in the interface between the pore solution and the solids, driven by electroneutrality. Figure 2.4 illustrates the electrical double layer theory. However, it is important to bear in mind that the extent and mechanism behind the process is not yet fully understood.
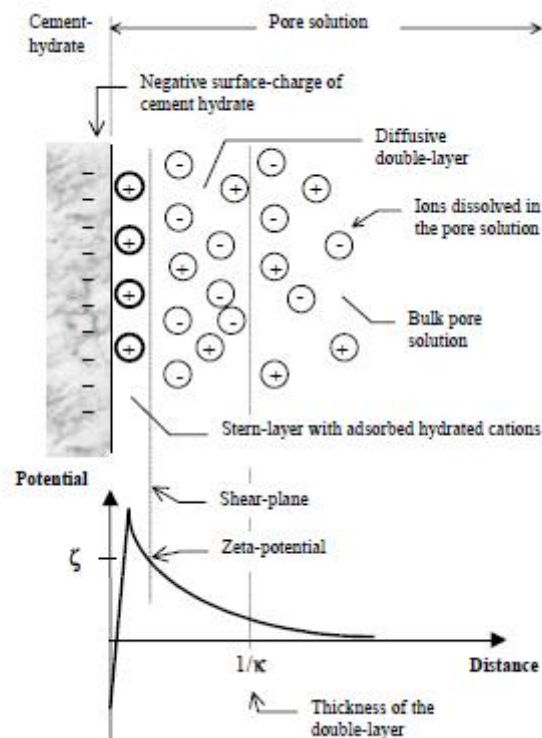
Figure 2.4 - Illustration of the electrical double layer (Larsen, 1998, Mørk, 2004)

2.6 Factors influencing chloride binding

Most studies on chloride- induced corrosion emphasize on the complexity of the binding process. Several parameters are known to influence the capacity, including chloride concentration, pH, temperature, carbonation, the coexisting cations, sulphates and the use of supplementary cementitious materials.

2.6.1 Cement composition

Chlorides can be bound to the alumina phases or to the C-S-H. As the composition of the binder heavily influences the properties of the hydrates, in terms of type and amount, it follows that the cement composition strongly affects the binding capacity.

C_3A

Most studies emphasizes on the importance of the alumina content (Suryavanshi et al., 1995, Glass&Buenfeld, 2000, Zibara, 2001, Thomas et al., 2012). Higher content of C_3A contributes to a larger amount of bound chlorides. Zibara (2001) investigated the influence of external chlorides introduced after hydration. The results showed highest amount of bound chlorides for pure C_3A pastes. Generally, the C_3A content of cement plays a major role in the binding capacity at high chloride concentrations (1 - 3M). The effect was however not as decisive at low chloride concentrations (0.1M). Thus, the C_3A content may be a good indicator of the binding capacity of the cement at high concentrations. Zibara suggests that the effect can be related to the sulphate content, as a high sulphate content reduces the effect of C_3A. This corresponds to the findings of Delagrave et al. (1997) and Arya et al. (1990). Arya et al. (1990) suggest that the C_3A content only to a small extent influences the binding capacity of cement for externally derived chlorides and that other factors also are important in the binding of chlorides in cement. Delagrave et al. (1997) conclude that it is more reasonable to attribute the binding capacity and the formation of chloroaluminates to the total aluminate content (C_3A and C_3AF) rather than the content of C_3A alone.

C_4AF

The importance of C_4AF is gradually more recognized. In cements rich in C_3AF, such as sulphate resisting Portland cement, ferrite based chloro- complex ($3CaO.Fe_2O_3.CaCl_2.10H_2O$) analogous to Friedel's salt is formed (Suryavanshi et al., 1996). The research of Zibara (2001) show that the C_4AF phase binds considerably amounts of chlorides. The author suggests that the binding capacity of C_4AF is about one third of the binding capacity of C_3A.

C_3S and C_2S

C_3S and C_2S are generally considered to be less important in the binding process (Glass et al., 1997). The phases are known to contribute to physical binding, as there is little evidence to suggest that they affect chemical binding. The binding in C-S-H is purely physical as the chloride ions are either absorbed in the interface between the pore solution and the C-S-H, or concentrated in the diffuse part of the electrical double-layer (Larsen, 1998). Hence, a higher content of C_3S and C_2S increase physical binding, as the amount of C-S-H increases. The contribution of C_3S to the binding capacity could range from 25% to over 50% (Yuan et al., 2009). Tang&Nilsson (1993) concluded

that the content of C-S-H strongly influences the binding capacity of ordinary Portland cement, regardless of w/c ratio and the addition of aggregates. The same trend was found by Larsen (1998). He found 95% bound chloride in C-S-H for OPC with w/c 0.60 and mixed- in chloride.

2.6.2 Supplementary cementitious materials

The use of supplementary cementitious materials (SCMs) increase both the chemical and the physical binding capacity of cement pastes. The SCMs influence the pore system of the cement paste as well as the composition, hence affecting chloride ingress.

2.6.2.1 Blast furnace slag

Most studies indicate that the use of ground granulated blast furnace slag (GGBFS) as partial replacement of OPC increases the chloride binding capacity (Zibara, 2001, Dhir et al., 1996, Arya et al., 1990, Xu, 1997, Thomas et al., 2012, Arya&Xu, 1995). The effect is greater for increasing GGBFS replacement levels of the OPC. It is suggested that the improved binding capacity can be linked to high alumina content present in the GGBFS leading to formation of Friedel's salt. An observed increase in the amount of absorbed chlorides may also contribute to higher binding capacity. Additionally, GGBFS cement is known to provide high resistance to chloride ingress due the low permeability of the resulting hydrated cement paste.

Dhir et al. (1996) investigated the binding capacity of GGBFS pastes with the use of the equilibrium method. The binding capacity increased for increasing GGBFS replacement levels (33.3%, 50% and 66.7%) and chloride exposure concentration (0 – 5M). At high chloride concentration the binding capacity increased by a factor of 5. The authors attribute the improved binding to an increase in production of Friedel's salt due to the high aluminate level of GGBFS. Arya et al. (1990) measured a 40% increase in the binding capacity for GGBFS blended cement (70% replacement) compared to the corresponding OPC for internal chloride. They suggest that there is a substantial increase in the amount of absorbed chlorides leading to the improved binding capacity. For external chlorides the effect was less apparent, though the GGBFS blend did bind more chlorides than the pure OPC. Xu (1997) found that OPC with 65% GGBFS replacement binds more chlorides, but that the capacity is depending on the sulphate content. A high sulphate content leads to a lower binding capacity. Hence, Xu concludes that GGBFS modified cement blends bind more chlorides due to the low sulphate content.

Zibara (2001) found that the effect of GGBFS (25 – 40% replacement) is highly depending on the w/c ratio (0.3 and 0.5). The GGBFS ternary blends (and fly ash blends) performed better than the control OPC mixture only at w/c = 0.5. Zibara

suggests that the higher hydration rates in mixtures with w/c= 0.5 leads to higher pozzolanic activity, which results in formation of more C-A-H, C-A-S-H and C-S-H phases. As a consequent, chemical and physical binding increase.

On the other hand, Potgieter et al. (2011) found that OPC performed better than GGBFS blended pastes up to 30% addition of GGBFS. Mixed- in chlorides of 0.25, 0.5, 1.0 and 2.0% of total mass of cement paste was added, and the pore expression method was used to analyze the chloride content. They suggest that OPC and GGBFS have a limited binding capacity. Once this limit is exceeded, the chloride ions will be freely available in the pore water and can then pose a corrosion threat to the reinforcement.

2.6.2.2 Silica fume

It is generally accepted that the use of silica fume as partial replacement of ordinary Portland cement causes a decrease of the binding capacity (Larsen, 1998, Arya et al., 1990, Thomas et al., 2012). Page&Vennesland (1983) concluded that the use of silica fume leads to a substantial change in the chemical composition of the pore solution phase of the hydrated products leading to a decrease of the alkalinity of the pore solution. As a result the solubility of calcium- chloro- aluminate increases and the chloride binding capacity of the cement declines (Page&Vennesland, 1983, Arya et al., 1990). The same trend was found by Arya et al. (1990) for cement pastes with 15% silica fume replacement for both external and internal chlorides. The research of Thomas et al. (2012) showed that an partial substitution of 8% silica fume results in a significant reduction of chloride binding at w/c= 0.4. The trend was less obvious at w/c= 0.5.

However, Byfors (1990) found an increased binding capacity for cement pastes with 10% silica fume addition compared to pure Portland cement pastes. The results were however uncertain as only one sample per mixture was investigated.

It is generally considered that an increase in C-S-H increase the binding capacity. Nevertheless, the addition of silica fume normally reduces the binding capacity, despite an increase in C-S-H. It is suggested that silica fume influences binding in three ways (Thomas et al., 2012); 1) dilution of the C_3A which may reduce binding, 2) reduction of the pH of the pore solution which should increase binding, 3) increase in the amount of C-S-H which should increase physical binding of chlorides. The incorporation of silica fume is known to reduce the CaO/SiO_2 ratio (C/S) of the C-S-H. Lower C/S ratio results in less bound chlorides. Glass et al. (1997) suggest that this will lead to a reduction in the amount of chlorides that can physically be absorbed onto the C-S-H surface and that this effect dominates the binding process. Thus, there is an overall effect of reduced binding capacity associated with silica fume addition. Slag and fly

ash, which also is known to reduce the C/S ratio, have a high alumina content and subsequently formation of C-A-S-H may result in higher binding capacity.

2.6.2.3 Fly ash

There are less studies on the effect of fly ash. However, most of them conclude that partial replacement of fly ash results in higher binding capacity than pure OPC mixtures (Zibara, 2001, Thomas et al., 2012, Arya et al., 1990, Arya&Xu, 1995). However, the binding capacity can vary significantly for different types of fly ash Thomas et al. (2012) generally found higher binding capacities for cement pastes with 25% fly ash replacement and varying calcium content at w/c = 0.5 than OPC. Yet no clear relationship existed between the binding capacity and the alumina content of the fly ash (or total calcium content). Thus, a high alumina content in fly ash is not directly an indication of high binding capacity in fly ash cement pastes.

Arya et al. (1990) studied the effect of fly ash for both internal and external chlorides. They found that the binding improved for increasing replacement levels of fly ash (15 – 35%). The authors suggest that the C_3A content is the main reason for the improved capacity for internal chlorides, but that it plays a less important role for externally-derived chlorides.

Zibara (2001) reported that three different fly ash blends (25 – 40% replacement) exhibited higher binding capacity compared to the OPC control paste. There was no obvious criteria for the ranking, indicating the possibility of more than one factor influencing the performance of fly ash. Nevertheless, the fly ash paste with the highest binding capacity contained a high amount of alumina and a relatively high calcium content. Zibara suggests that the binding do not depend on the total content of alumina and silica, but on the quantity of reactive alumina and silica, since only the reactive part of the alumina and silica participates in the pozzolanic activity of the fly ash, and consequently the binding reaction.

2.6.3 Chloride concentration

Most studies report increasing binding capacity for increasing chloride content of the pore solution (Thomas et al., 2012, Arya et al., 1990, Dhir et al., 1996, Tang&Nilsson, 1993, Larsen, 1998).

Dhir et al. (1996) investigated GGBFS cements exposed to external chlorides. The results showed an increasing binding capacity for increasing chloride concentration in the pore solution for all replacement levels of GGBFS. It appeared that the binding capacity is directly proportional to the exposure solution concentration and that the relationship is linear. The same trend was found by Tang&Nilsson (1993). However,

the relationship between free and bound chlorides was non- linear and was best described by Langmuir and Freundlich isotherms for low and high chloride concentrations respectively.

Likewise, Thomas et al. (2012) found a non- linear relationship between free and bound chlorides. The amount of bound chlorides increased as the chloride concentration of the exposure solution increased. The Freundlich isotherm provided the best fit to all the experimental data. Byfors (1990) also obtained a non- linear relationship between bound and free chlorides. The relationship seemed to follow the shape of the Langmuir isotherm at low chloride concentrations until a certain concentration. Then at higher concentrations, the chloride binding increases sharply. Byfors suggests that the chloride adsorption on the pore walls increases at higher concentration after exhaustion of the chemical binding capacity.

2.6.4 Cations associated with chloride

Most studies on chloride- induced corrosion include cations such as sodium chloride (NaCl), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), potassium chloride (KCl) or hydrogen chloride (HCl) (Zhu et al., 2012, Arya et al., 1990, Page&Vennesland, 1983, Tritthart, 1989b). Different associated cations of the chloride salt influence the corrosion behavior of reinforcement in concrete. NaCl is the main de-icing agent used on roads and bridges (Norwegian Public Roads Administration, 2008), though $CaCl_2$ and $MgCl_2$ can be used. In addition, they are a major components of seawater and are therefore relevant when dealing with chloride binding and chloride ingress in concrete.

The cations can change the properties of the cement paste when blended in the paste. $CaCl_2$ creates a more open pore structure which allows easier diffusion and higher electrical conductivity, and it reduces the pH of the pore solution (Hansson et al., 1985). The addition of NaCl increases the porosity to a smaller extent.

Literature shows that the behavior of $MgCl_2$ is similar to the behavior of $CaCl_2$ (Arya et al., 1990, Zhu et al., 2012, De Weerdt et al., 2013). Research show that Mg^{2+} and Ca^{2+} increase the chloride binding capacity significantly compared to Na^+ (Arya et al., 1990, De Weerdt et al., 2013). Arya et al. (1990) attributes the improved binding capacity to a more rapid formation of chloroaluminates in the case of $CaCl_2$ exposure. In addition, there is a pH reduction associated with $CaCl_2$. This causes a higher C/S ratio and a higher binding capacity of C-S-H, subsequently resulting in more bound chlorides (De Weerdt et al., 2013). The use of NaCl results in less change in the hydroxide concentration and the C-S-H composition. The difference between NaCl and

CaCl$_2$ increase with increasing chloride concentration (Tritthart, 1989b). The same trend was reported by Arya et al. (1990) and De Weerdt et al. (2013).

2.6.5 Influence of sulphate

The presence of sulphate, present either in the cement composition or as part of the chloride host solution (external), has a negative effect on the binding capacity. External sulphates are known to influence both the chemical and physical binding capacities, while sulphates from the cement mainly influence chemical binding capacity. The sulphate content in cement influences the type and the quantity of calcium aluminate hydrates that are produced, which in turn influences the binding capacity of cement especially at low chloride concentrations (Zibara, 2001). Zibara (2001) found that the binding capacity of C$_3$S and C$_2$S are reduced in the presence of sulphates in the exposure solution. XRD results showed less Friedel's salt indicating the negative effect of sulphates on chemical binding. Zibara suggests that the presence of sulphates in the pore solution leads to a competition between SO$_4^{2-}$ and chloride ions for adsorption sites on the C-S-H surface, thus reducing the physical binding capacity. The same trend was reported by Xu (1997) and De Weerdt et al. (2014a).

2.6.6 Temperature

Larsen (1998) investigated the effect of temperature (5, 21 and 40°C) on chloride binding. For samples immersed in NaCl solutions, the highest binding capacity was observed at 5°C and the lowest at 21°C, with 40°C a bit higher than at 21°C. For mixed- in chlorides, the binding capacity gradually decreased from 5 to 21 to 40°C. This trend was most likely caused by the difference in chloride concentration of the two exposures. The effect of temperature also became weaker for decreasing pH and C$_3$A content (Larsen, 1998). One problem arise in warm weather as a rise in temperature will lead to dissolution of some of the bound chloride. Hence, the chloride content in the pore solution will increase, the chloride diffusion will accelerate and the chloride will penetrate deeper into the concrete surface (Larsen, 1998). At the end, the chloride threshold value may be reached and corrosion is initiated. The increased temperature also reduce the concrete resistivity, potentially leading to increased corrosion rate.

Zibara (2001) found that the effect of temperature was influenced by chloride concentration of the exposure solution. The capacity was slightly reduced as the temperature rose from 0°C to 23°C to 28°C at 0.1 M and 1.0 M chloride concentrations. At higher chloride concentrations (3M) an increase of temperature resulted in slightly more bound chlorides. Zibara suggest the trend can be explained by the transformation of the ettringite phase into Friedel's salt at a much faster rate for 3 M.

Yuan et al. (2009) pointed out the fact that thermal vibrations increase due to higher temperature, resulting in less bound chloride. It is well known that the reaction rate of a chemical reaction increases as the temperature rise. Thus, elevated temperatures accelerate hydration. The degree of hydration will affect binding by altering the pore structure and pore solution composition (Glass et al., 1997). However, high temperatures may also increase the solubility of Friedel's salt.

2.6.7 Carbonation

There are not many studies of the influence of carbonation of chloride binding. Generally, literature shows that carbonation reduces the binding capacity. Carbonation is the process in which CO_2 from the air penetrates into the concrete and reacts with calcium hydroxyl as follows;

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (2.10)$$

Zibara (2001) exposed carbonated cementitious pastes to chloride solutions. In most of the cases, the carbonated samples experienced a reduced binding capacity of more than 90% compared to non- carbonated samples. Zibara explains the severe negative effect of carbonation as a result of the transformation of C-S-H and C-A-H into $CaCO_3$ in the presence of CO_2.

According to Larsen (1998), both samples carbonated before and after chloride exposure will contain less bound chlorides. The results showed that samples carbonated before exposure had no bound chlorides, while samples carbonated after exposure had more bound chlorides.

2.6.8 Moisture state

The moisture state influences the chloride concentration in the pore solution, and consequently also the chloride binding (Byfors, 1990). Drying of the concrete leads to a more concentrated pore solution containing more chlorides, while wetting results in a dilution of the pore solution and lower chloride concentration. At a certain moisture state, an equilibrium between bound and free chlorides is achieved. Byfors (1990) used the pore solution expression method to investigate the magnitude of these changes in chloride concentration of the pore solution of four different binder mixtures with mixed-in chlorides. The results showed an increase of the chloride concentration in the pore solution of 30- 50% when the samples were dried from 100% RH to 80% RH. Byfors reported the same trend regardless of binder mix, w/c- ratio and quantity of chloride cast in.

2.6.9 Water-to-cement ratio

Generally, high w/c- ratios results in more bound chlorides. Thomas et al. (2012) found that the impact of w/c ratio was particularly pronounced for binders containing SCMs, especially SCMs with a high alumina content. The authors suggest that this may indicate that the hydration and pozzolanic reaction is restricted at low w/c ratios and that much of the alumina present is not available in the formation to Friedel's salt. Zibara (2001) found reduced amount of bound chlorides for fly ash pastes as w/c was reduced from 0.5 to 0.3. He suggests that the behavior might be related to the degree of hydration and/ or changes in the microstructure of the pastes.

Arya et al. (1990) suggest an increase in porosity and permeability at higher w/c ratios allowing more chlorides to access the cement particles. The influence of w/c was almost insignificant in the research of Tritthart (1989b). An increase of w/c from 0.5 to 0.7 only resulted in a slightly higher uptake of chlorides.

2.6.10 Hydroxyl ion concentration

The study of Tritthart (1989b) confirmed that identical concretes exhibit different chloride concentrations for different hydroxide concentration. High pH values lead to a reduced amount of bound chlorides. The use of $CaCl_2$ and $MgCl_2$ resulted in a reduction of pH, while the use of NaCl resulted in a much lower reduction, thus a lower amount of bound chloride. Tritthart explains that the change in pH is caused by the insolubility of calcium and magnesium ions in alkaline solutions such as the pore solution of hardened concrete. The ions precipitate as solid $Ca(OH)_2$ and $Mg(OH)_2$ leading to a lower hydroxide concentration of the pore solution. Tritthart points out that there is a competition between the hydroxyl ions and the chloride ions in the absorption on the surface of the hydration products. At high total chloride concentrations, a greater difference between the pH- values between samples of $CaCl_2$ and NaCl was observed.

Zibara (2001) found the same decrease in the chloride binding capacity for higher hydroxyl ion concentrations of the host solution. The effect was greater at low chloride concentration (0.1 M) than at high concentrations (1.0 M, 3.0 M). As well, the effect was insignificant for small variations in pH and more severe for lager variations. Zibara suggests that an increase in the hydroxyl ion concentration of host solution negatively affect the chemical and physical binding capacities.

This contradicts to the conclusions of Arya et al. (1990) who reported an increase in binding capacity with an increase in the alkali content for OPC pastes exposed to external chlorides. Arya attributes this trend to the decrease in solubility of Friedel's salt associated with an increase in the pore solution alkalinity.

2.7 Techniques of introducing chlorides

There are mainly two techniques used to introduce chlorides to concrete;

1. Internal chloride: a certain amount of chlorides are added to the mixing water
2. External chloride: chloride ions intrude into already hardened cement paste or concrete

For existing concrete structures, internal sources of chlorides usually include admixtures such as calcium chloride accelerators or chloride contaminated mixing materials. External sources of chlorides are usually connected to de- icing salts or seawater in marine environment.

2.7.1 Internal chloride

In this method, a fixed amount of chloride is added to the mixing water. The chloride concentration in the pore solution is a function of the added chloride content. The concentration of chlorides in the pore solution must be measured in order to determine the amount of bound chloride. Pore expression methods are usually used in combination with mixed- in chloride. The method is described in Section 2.8.2. A disadvantage with the method is that the chlorides influence the microstructure of the cement paste and the hydration products, thus influencing the binding capacity. Therefore, two mixtures of otherwise identical composition may not be directly comparable. Internal chloride is mostly relevant in cases where chloride- admixtures or chloride-contaminated aggregates are used. Mixed- in chlorides are not considered a realistic way of expressing chloride binding based on chloride ingress, as externally derived chloride resembles more to the real process.

2.7.2 External chloride

Chloride ions are introduced after hydration and are allowed to penetrate into the concrete through diffusion. The hardened cement paste or concrete takes up more chlorides as a consequence to increasing the concentration of the exposure solution. External chlorides are usually used in combination with the equilibrium method.

2.8 Analysis techniques

Several of experimental methods can be used to determine the binding isotherms. Some of the most common techniques include (Larsen, 1998, Yuan et al., 2009, Zibara, 2001);

1. Equilibrium method: powdered concrete, mortar or cement paste samples is stored in a solution of a known chloride content
2. Pore solution expression technique: uses high pressure to squeeze out the pore water
3. Leaching methods; is based on mixing powdered samples with a solvent and measuring the amount of chlorides passing into the solution

2.8.1 Equilibrium method

In the equilibrium method, samples are stored in solutions of known chloride concentration until equilibrium is reached. The equilibrium method is one of the most widely applied test methods for determination of binding isotherms and is considered to be quite accurate (Yuan et al., 2009). According to Tang&Nilsson (1993), adsorption equilibrium could be reached within the first seven days, depending on the size of the samples. The cement paste or mortar should be at least three months old in order to ensure a certain degree of hydration (Byfors, 1990). After centrifuging the samples, the liquid supernatant is pipetted and analyzed by potentiometric titration using 0.01 M $AgNo_3$ and a silver selective electrode. The content of bound chlorides are obtained by calculating the difference between the initial chloride content and the concentration after equilibrium is reached (Yuan et al., 2009, Larsen, 1998). The consumed chlorides are considered as bound, either chemically or physically (Byfors, 1990).

Yuan et al. (2009) pointed out some concerns regarding the method and it's accuracy; 1) the method does not consider the effect of leaching of other species such as hydroxyl ions, 2) in order to reach equilibrium faster, the samples are crushed which might result in carbonation and allow further hydration.

2.8.2 Pore solution expression technique

The method uses very high pressure to squeeze out the pore solution of hardened cement or concrete. An advantage of the method is that comprehensive information is obtained not only on chloride content but also the type and concentration of all substances dissolved in the pore water (Tritthart, 1989a). Breaking up of samples before pressing should be avoided. It might be challenging to obtain enough pore solution, especially at low w/c ratios. Therefore, samples should not be too dry and low w/c should be avoided. Additionally, some loosely bound chloride ions may be released under pressure leading to an overestimation of free chloride concentration (Yuan et al., 2009).

According to Larsen (1998), the chloride concentration is not significantly influenced by pressure. However, he experienced that homogeneous samples are important in order to achieve low errors in the determination of pore solution composition. The standard error of the results for chloride and hydroxyl concentration were 10% and 15%.

2.8.3 Leaching methods

The leaching methods are similar to the pore expression method, except that the free chloride content is determined using leaching instead of pore squeezing (Zibara, 2001). Leaching is based on mixing powdered samples with a solvent and measuring the amount of chlorides passing into the solution (Arya et al., 1987). There are several different leaching techniques, which differ in both type of solvents (water or alcohol) and mixing regimes. Tritthart (1989a) and Arya et al. (1987) showed that ethyl alcohol was ineffective as a solvent in leaching of chlorides and thereby underestimating the free chloride content. Arya et al. (1987) compared the pore expression method with various leaching techniques using water as a solvent. The results showed that the total chloride content of the sample will decide the most appropriate technique to adopt.

3

EXPERIMENTAL PROGRAM

3.1 Introduction

Three different mortars were prepared;

1. Ordinary Portland cement, CEM I (OPC)
2. Ordinary Portland cement with 30% replacement of fly ash, CEM I+FA (OPC-FA)
3. Ordinary Portland cement with 50% replacement of blast furnace slag, CEM I+ slag (OPC- slag).

Mortar samples were chosen because it is more manageable than concrete samples and it gives a better reflection of the binding process compared to cement pastes. One avoids the risk of shrinkage and cracks due to high curing temperatures typically associated with cement pastes. Additionally, the ITZ zone is not neglected. The equilibrium method was used to analyze the chloride binding capacity.

3.2 Materials

The cement used in the experiment was a CEM I 42.5 R Portland cement in accordance to NS- EN 197-1:2011. The mineral composition of Portland cement is given in Table 3.1. Table 3.2 shows the chemical composition of the Portland cement and the supplementary cementitious materials used in the study. X-ray fluorescence analysis (XRF) was used to determine the composition of the materials. More details on the materials can be found in Appendix A.

Table 3.1 - Mineral composition of cement determined by XRD Rietveld

	Chemical notation	OPC [%]
C_3S	$3CaO \cdot SiO_2$	55.7
C_2S	$2CaO \cdot SiO_2$	15.4
C_3A	$3CaO \cdot Al_2O_3$	5.7
C_4AF	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	10.9

Table 3.2 - Oxide composition of cement and supplementary cementitious materials determined by XRF

Amount [%] by weight	OPC	Slag	Fly Ash	Silica Fume
LOI 950°C	2.41	-	3.76	1.96
SiO_2	19.62	35.36	54.67	95.05
Al_2O_3	4.51	12.76	22.05	0.95
Fe_2O_3	3.45	0.77	5.54	0.14
CaO	61.6	40.1	5.36	0.13
MgO	2.43	7.03	2.14	0.42
K_2O	1.0	0.51	2.39	1.03
Na_2O	0.45	0.18	0.93	0.08
SO_3	3.36	1.67	0.16	0
Total	99.38	99.38	98.65	99.82
Blaine [cm²/g]	3900	4540	3640	-
Density [g/cm³]	3.12	2.92	2.21	2.3
Mullite	-	-	12.0	-

3.3 Mix design

Typical Norwegian concretes used in marine environment inspired the mix design. Mortars with w/c ratio of 0.4 and sand to cement ratio of 2.5:1 were prepared. Silica fume was added in all the mortars by 6% replacement of Portland cement. The ratio of the volume of water to the volume of powder, and the ratio of the volume of the binder (water + cementitious materials) to the volume of the sand were kept constant. This will provide more equal diffusion properties. Superplastiziser (SP) was added in order to obtain good compaction, while air demper was added to reduce the amount of entrained air. Only distilled water was used. The samples were cured sealed and saturated in 125 ml polypropylene bottles. The sealed bottles were stored in an acclimatized room of 20°C and 100% RH. Both top side and bottom side of the samples were in contact with a small amount of water in order to prevent self- desiccation and carbonation. The mix design is presented in Appendix A.

3.4 Adoption of method

A variant of the equilibrium method was used to analyze the chloride concentration of the pore solution. It is reasonable to believe that equilibrium was reached prior to the analysis. Usually equilibrium is found to be reached within a couple of weeks (Tang&Nilsson, 1993, Delagrave et al., 1997, Zibara, 2001), depending on w/c ratio, particle size and the use of SCMs. The equilibrium method assumes that after equilibrium is reached between the exposure solution and the pore solution, the

reduction in chloride concentration of the external solution is attributed to chlorides bound by the cement.

The equilibrium method was used to determine the binding isotherms, despite the fact that it causes a high solid to solution ratio. A high water content is accepted, as it allows comparison of binding in a controlled and reliable manner. The method is fast and easy to apply, and makes it possible to analyze samples from existing concrete structures. Compared to the pore solution expression method, the equilibrium method is faster and does not require any special equipment.

Internally introduced chlorides is known to affect the microstructure of hardened cement paste. The pore structure becomes coarser and a greater total porosity is observed (Hansson et al., 1985). There are little difference between the effect of $CaCl_2$ and NaCl in the fine pore structure. The effect is not desirable when studying chloride ingress and binding. Therefore, externally- derived chlorides were used throughout the study as it gives a more realistic approach to the actual process.

3.5 Chloride binding isotherm

3.5.1 Sample preparation

After about one year of curing, the hydrated samples were crushed with a jaw crusher to a size < 2 mm. Subsequently, the samples were subdivided using a splitter in order to ensure homogenous samples of approximately 35 grams. The exact weight of the samples were determined prior to the analysis.

Chloride exposure solutions of $CaCl_2$ and NaCl were prepared. The following mother solutions were made; 1 M NaCl and 1 M $CaCl_2$. Furthermore, the solutions were diluted in order to achieve different concentrations of chlorides as follow;
- $CaCl_2$; 2, 1, 0.5, 0.25, 0.125, 0.063 and 0.031 M
- NaCl; 1, 0.5, 0.125 and 0.031 M

The concentrations were chosen to reflect real exposures. Low chloride concentrations (less than 1M) represent structures submerged in seawater, whereas higher chloride concentrations (1M - 2M) represent areas such as the splash zone or bridge decks exposed to de- icing salt (Zibara, 2001). The exact chloride concentrations of the exposure solutions was verified by titration and used for further calculations of bound chloride concentration. More details on the exposure solutions can be found in Table A.6 in Appendix A.

Three identical series were made for exposure to $CaCl_2$, while two series were made for exposure to NaCl, see Table 3.3.

Table 3.3 - Samples prepared for experiment

No.	Exposure solution	Cement	Number of parallel series
1		OPC	3
2	CaCl$_2$	OPC- FA	3
3		OPC- slag	3
4		OPC	2
5	NaCl	OPC- FA	2
6		OPC- slag	2

Furthermore, the crushed samples were mixed with 15 ml exposure solutions of CaCl$_2$ and NaCl, and stored in polypropylene bottles with airtight screw caps, see Figure 3.2. The hydrated mortar samples were exposed to the chloride solutions in an acclimatized room of 20°C. It is assumed that the samples were not carbonated during this time. The mixed samples were shaken regularly and stored in a climate room of 20°C for about three months until analysis.

Figure 3.1 - Centrifuge
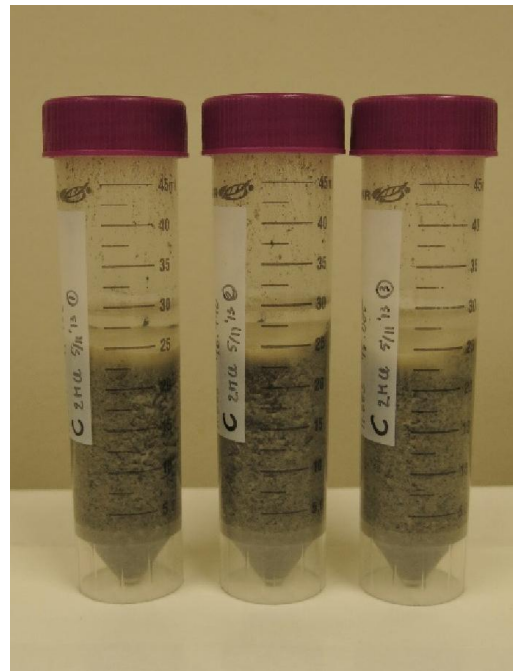
Figure 3.2 - Centrifuged samples

The content of free water in the hydrated mortar samples was determined in order to correct for the effect of the dilution of the exposure solution. The mortar samples were dried at 105°C over night. The measured weight loss, i.e. the free water content, is presented in Table 3.4.

Table 3.4 - Free water content measured for all three mortar samples

	Free water content [% mortar]
OPC	2.73
OPC- FA	3.04
OPC- slag	3.15

3.5.2 Analysis of free chloride content

The free chloride concentration was measured with the use of automatic potentiometric titration. Titration is a laboratory method used to determine an unknown concentration of a titrate with a known volume. The titrate is dissolved in a solution (the titrant) of known concentration and volume. The samples were shaken and thereafter centrifuged for 5 minutes before analysis, see Figure 3.1. The chloride concentration of the liquid supernatant was analyzed with a Titrando 905 from Metrohm, see Figure 3.3. pH measurement was done using a Metrohm 6.0225.100 Profitrode, see Figure 3.4.

Figure 3.3 - Automatic potentiometric titration from Metrohm

Figure 3.4 - Metrohm Profitrode used for pH measurements

1 ml of the supernatant was mixed with 1 ml of 1:10 HNO_3 and 1 ml of 0.2% polyvinyl alcohol before the samples were titrated with 0.01 M $AgNO_3$. For low chloride concentrations (0.031 M) the samples were titrated with 0.001 M $AgNO_3$ to ensure any results. The titrator added approximately 50 ml water.

The total chloride content ($C_{Cl,\,total}$) added to the sample expressed as concentration in the pore solution assuming no chloride binding, can be calculated as follows;

$$C_{Cl,total} = \frac{C_{Cl,added} \cdot V_{Cl,added}}{V_{H_2O} + V_{Cl,added}}$$

(3.1)

where $V_{Cl,added}$ – volume of exposure solution (15 ml)

V_{H_2O} – volume of free water available in the hydrated samples

$C_{Cl,added}$ – chloride concentration of the added solution

Subsequently, the bound chloride content ($C_{Cl,\,bound}$) can be calculated as follows;

$$C_{Cl,bound} = \frac{(C_{Cl,tot} - C_{free}) \cdot (V_{H_2O} + V_{Cl,added}) \cdot M_{Cl}}{(m_{sample} - m_{H_2O}) \cdot 1000}$$

(3.2)

where C_{free} – measured equilibrium chloride concentration in the liquid phase

m_{Cl} – molar mass of chloride; 35.4527 g/mol

m_{sample} – measured weight of the sample, approximately 30 g

m_{H2O} – mass of free water available

3.5.3 Chloride binding isotherms

An equilibrium tends to establish between free and bound chlorides, depending on the composition of the cement and its binding capacity. Chloride binding isotherms express the relationship between the concentration of free chlorides present in the pore solution and the bound chlorides. The unique isotherms are influenced by the cementitious system's composition in terms of C_3A content, supplementary cementitious materials, SO_3 content and pH (Zibara, 2001). Each measured chloride concentration represents a point in the binding isotherm. For each concentration, the free chloride concentration at equilibrium is plotted against the bound chloride concentration. There are mainly two non- linear mathematical models for presenting the chloride binding isotherms. According to Tang&Nilsson (1993) the *Langmuir isotherm* is best suited for free chloride concentrations of less than 0.05 M;

$$C_b = \frac{\propto \cdot C_f}{(1 + \beta \cdot C_f)}$$

(3.3)

where C_b – bound chlorides

C_f – free chlorides

α – constant depending on binder composition

β – constant depending on binder composition

Tang&Nilsson (1993) concluded that the chloride binding isotherm obeys *Freundlich isotherm* at concentrations greater than 0.01 M;

$$C_b = \propto \cdot C_f^\beta \qquad (\,3.4\,)$$

3.6 Chloride ingress

3.6.1 Sample preparation

Mortar samples were produced as described in Section 3.3. The plastic bottles was removed by sawing and cutting, and the top of the sample was sawed off. The samples were dried over silica gel in a desiccator for 2 hours before they were covered with epoxy on all sides except the top side. Furthermore, the samples were dried for one day and covered with epoxy again, see Figure 3.5. Epoxy was used to ensure transport of ions in only one direction. The samples were left to dry for another day and stored in distilled water for 2 days in order to make sure that the samples were saturated before exposure to solutions of NaCl. The samples were weighted twice a day in order to ensure that the weight did not increase by more than 0.1%/ 24 hours.
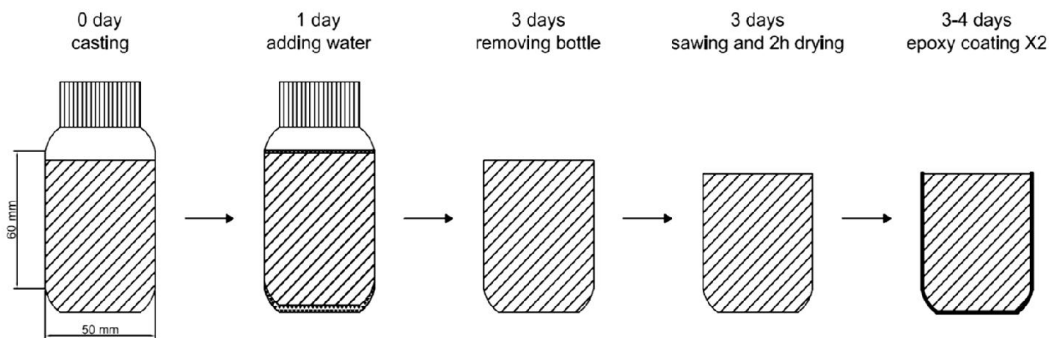
Figure 3.5 - Sample preparation before exposure

The cured samples were exposed to NaCl solutions after 7 days of curing. The NaCl exposure solution had a chloride content of 0.545 mol/l, which reflects the chloride content of the fjord of Trondheim, see Table A.7. The samples were weighted prior to contact with the exposure solution and placed in a sealed box. Exposure solutions were added into the boxes so that $3 - 5$ mm of the sample was submerged in the solution. A fine plastic grid was placed under the samples to assure the entire surface was exposed to the solution, see Figure 3.6. The solution was changed every $3 - 4$ days during the first three weeks and once a week after that. The samples were exposed to the NaCl solution for 6 months.

At the end of the exposure period, the samples were ground into intervals of; 0-1, 1-3, 3-5, 5-7, 7-9, 9-13, 13-17 mm. The depth of grinding is based on the visual inspection of 0.01 M $AgNO_3$ sprayed sample. Most of the experimental description presented is based on the descriptions in De Weerdt et al. (2012).
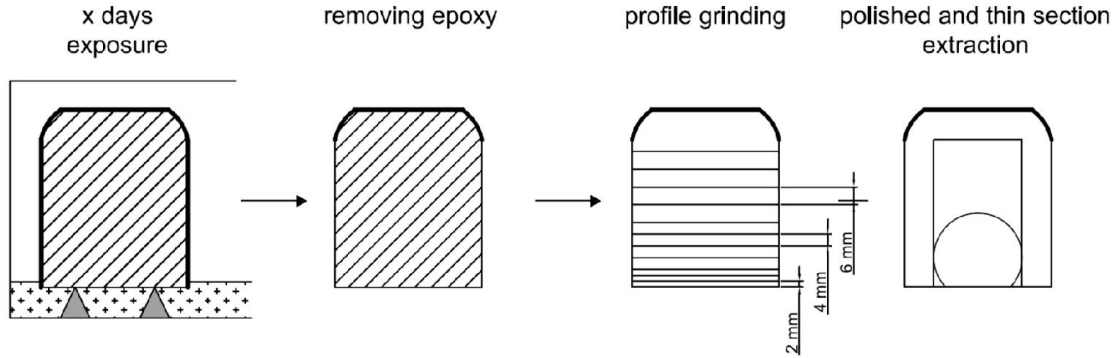
Figure 3.6 - Exposure condition and sample extraction

3.6.2 Analysis of total chloride content

The total chloride content of the ground samples were measured using potentiometric titration with Metrohm Titrando 905. Before the analysis, 2- 4 g of the powdered samples were weighted into 75 ml glass beaker. The powder and the beaker were weighted. The samples were dried at 105°C for one night and cooled in a desiccator over silica gel. The dried samples were weighted again and dissolved in 40 ml HNO_3 of 80°C. The suspension was stirred and left to stand for about one hour. The solution was filtrated with a syringe and a microfilter. Subsequently, 1 ml of the samples were analyzed with titration using 0.01 M $AgNO_3$. Lower chloride concentrations are difficult to measure, therefore the sample volume was increased to 10 ml. In addition, 10 ml of 100% glacial acetic acid was added.

The chloride analysis with the titrator is described more in details in Section 3.5.2. However, calculation of chloride concentration for chloride profiles are based on the following equation;

$$Cl \ = \frac{V_{titrant}EQ \cdot C_{titrant} \cdot 35.45 \cdot V_{HNO_3} \cdot 0.001}{V_{sample} \cdot \ m_{sample} \ \cdot (1 - \frac{moist\ cont}{100})} \qquad (\ 3.5\ )$$

where   Cl – measured chloride concentration [% mass of mortar]

     $V_{titrant}$EQ – volume of titrant and equivalent point [ml]

     $C_{titrant}$ – concentration of the titrant [mol/l]

     V_{sample} – volume of sample [ml]

     m_{sample} – weight of sample [g]

     V_{HNO_3} – volume of acid [ml]

     moist cont – measured content of free water from hydrated samples

3.6.3 Determination of chloride profiles

When studying chloride ingress, chloride profiles of total chloride content are plotted against concrete depth. Profiles for samples exposed to NaCl for 6 months were determined. The calculations of free and bound chloride concentration are based on the measured total chloride content and the determined binding isotherms given in Table 4.1. The Langmuir binding isotherm was adopted for further calculations and in combination with Equation (2.7) it follows that;

$$Cl_{total} = \ Cl_{free} \cdot \ V_{sol} \cdot m_{Cl} + \ \frac{\alpha \cdot Cl_{free}}{1 + \ \beta \cdot C_{lfree}} \qquad \text{(3.6)}$$

where m_{Cl} – molar mass of chloride, 35.45 g/mol

V_{sol} – free water content, see Table 3.4

Cl_{total} – measured Cl concentration from chloride profile

α and β – constants from Langmuir fitting, see Table 4.1

Solving Equation (3.6) for Cl_{free} and setting Cl_{free} equal to x, gives the second order equation;

$$(\beta \cdot V_{sol} \cdot 35.45)x^2 + (V_{sol} \cdot 35.45 + \alpha - \beta \cdot Cl_{total})x - Cl_{total} \ = 0 \qquad \text{(3.7)}$$

Equation (3.7) can be used to calculate the free chloride content (Cl_{free}) expressed in mol/l. Then the solution to Equation (3.7) can be used calculated the free chloride content (Cl_{free}) and the bound chloride content (Cl_{bound}) as a percentage of mortar;

$$Cl_{free} = x \cdot \ 35.45 \ \cdot \ V_{sol} \qquad \text{(3.8)}$$

$$Cl_{bound} = \ \frac{\alpha \cdot x}{1 + \ \beta \cdot x} \qquad \text{(3.9)}$$

3.6.4 Calculation of chloride diffusion coefficient

The diffusion coefficient for total and free chloride profiles were calculated based on a simplification of Equation (2.5). The coefficient was determined by fitting the experimental data of both total and free chloride content against depth with Equation (3.10). The surface concentration (C_s) and the apparent diffusion coefficient (D_{app}) were found by iteration giving the best fit by least mean squares. The initial chloride concentration (C_i) is accounted for in the fitting (only for total). It is assumed that all the pores are water saturated. Together with the determined diffusion coefficient and surface concentration, the chloride penetration depth can be extrapolated to longer times. Details of the chloride diffusion calculations can be found in Appendix C.

$$C(x,t) = C_s \left(1 - erf \frac{x}{2\sqrt{D_{app} \cdot t}} \right)$$

(3.10)

4

RESULTS AND ANALYSIS

4.1 Binding isotherm for exposure to CaCl₂ and NaCl

Chloride binding isotherms for hydrated mortar samples of OPC, OPC- FA and OPC-slag cement exposed to solutions of NaCl and $CaCl_2$ containing varying chloride concentrations are presented. Both the Langmuir isotherm and the Freundlich isotherm were applied for all three mortars. The calculations of the binding coefficients in Equation (3.3) and (3.4) for the Langmuir and Freundlich isotherm were done in SigmaPlot. A coefficient of determination (R^2) closest to 1 gives the best fit and is chosen for further calculation and analysis. The results in Table 4.1 indicate that the Freundlich isotherm provides the best fit, mainly for samples exposed to $CaCl_2$. The Langmuir isotherm provides the best fit for samples exposed to NaCl except for the OPC- FA sample.

Table 4.1 - Coefficients of Langmuir and Freundlich isotherm with corresponding coefficient of determination

		Freundlich			Langmuir		
		α	β	R^2	α	β	R^2
CaCl₂	OPC	0.55	0.5598	0.9989	1.4	1.4512	0.9811
	OPC-FA	0.73	0.536	0.9992	2.08	1.7785	0.9848
	OPC-slag	0.95	0.459	0.9902	4.76	4.0727	0.9862
NaCl	OPC	0.24	0.3934	0.9815	2.26	9.6253	0.9938
	OPC-FA	0.32	0.4256	0.9903	2.80	8.9246	0.9845
	OPC-slag	0.5	0.4315	0.9861	4.14	9.0438	0.994

The calculated coefficients are based on the average of the three series for each mixture and concentration. Figure 4.1 shows the relationship between free chlorides (C_f) and bound chlorides (C_b) at equilibrium of the OPC sample. The corresponding Langmuir or Freundlich isotherm are also plotted. It is clear that the chloride binding is non-linear.
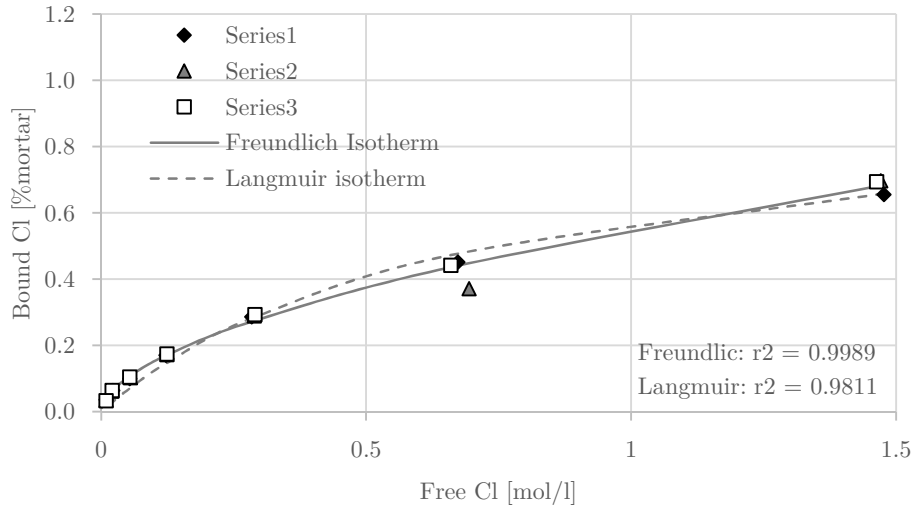
Figure 4.1 - Freundlich and Langmuir isotherm for OPC exposed to CaCl$_2$

The relationship between free and bound chlorides at equilibrium for the experimental data and the "best-fit" binding isotherm are presented Figure 4.2 and Figure 4.3. The corresponding isotherm is plotted based on the coefficients, α and β, from Table 4.1. In all cases, the figures show that OPC has the lowest binding capacity, while OPC-slag binds more chlorides compared to OPC- FA and OPC. The capacity seems to depend on both the chloride concentration of the exposure solution and the pH. For both CaCl$_2$ and NaCl, the binding capacity increases continuously with increasing chloride concentration of the exposure solution, see Figure B.3 in Appendix B. The trend continues for all chloride concentrations. The quite low spread between the three parallel series indicate reliable results. The binding isotherm is also plotted on a logarithmic scale in order to better observe the fit of the isotherm at low chloride concentrations, see Figure B.1 and Figure B.2 in Appendix B.

For CaCl$_2$, OPC- slag binds 47% more chlorides, while OPC- FA binds 32% more than OPC at high chloride concentrations (2M). The Langmuir isotherm provides a reasonable fit to the experimental data, but the Freundlich isotherm provides a better fit. Figure B.1 shows that the Freundlich isotherm also gives a good fit at low chloride concentrations.

NaCl binds considerably less chlorides and reaches levels of 0.41 g Cl/ g hydrated mortar for OPC- slag and 0.21 g Cl/ g hydrated mortar for OPC, see Table 4.2. The results indicate that the Langmuir isotherm is the best fit. Figure B.2 shows a good correlation of the binding isotherm also at low chloride concentrations. The slope of the Langmuir isotherm tends to approach zero as the free chloride content increases, suggesting that there is an upper bound in the amount of chlorides being bound (Martin-Pérez et al., 2000). Hence, the rate of binding is gradually reduced as the chloride concentration increases.
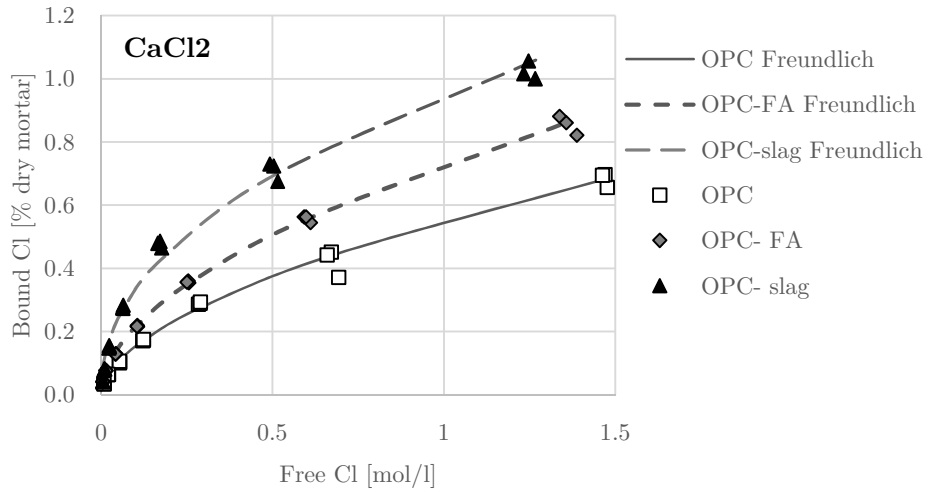
Figure 4.2 - Best fit chloride binding isotherm for OPC, OPC- FA and OPC- slag mortars exposed to CaCl$_2$
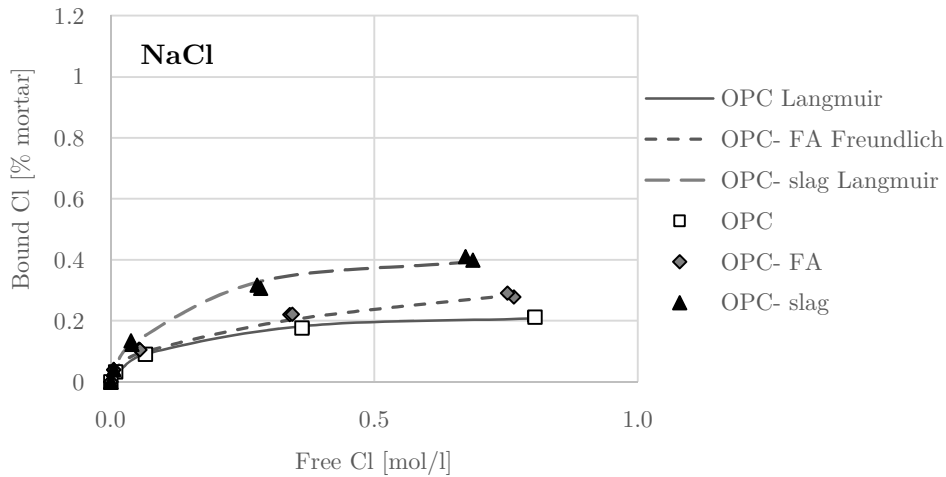
Figure 4.3 - Best fit chloride binding isotherm for OPC, OPC- FA and OPC- slag mortars exposed to NaCl

Table 4.2 - Maximum bound chlorides for the mortars exposed to CaCl$_2$ and NaCl containing 1 M chlorides

	Max bound chlorides [% mortar] CaCl$_2$	Max bound chlorides [% mortar] NaCl
OPC	0.42	0.21
OPC- FA	0.56	0.28
OPC- slag	0.72	0.41

Figure 4.4 express the effect of SCMs and cation type at low (0.031M) and high (1M) chloride concentrations. In addition, the standard deviation, being a measure of how widely the values in each series are dispersed compared to the average, are included. The figures show a noticeable difference in binding capacity of OPC and OPC- slag at

high chloride concentrations, but a less pronounced effect at low concentrations. Additionally, the results clarify the difference between the binding characteristics of NaCl and CaCl$_2$. It can be seen that the two chloride compounds produce different residual chloride content in the samples of otherwise identical composition. The results confirm that the binding capacity of the mortars for NaCl exposure is lower than the binding capacity for CaCl$_2$ exposure; NaCl results in 50.0 % lower chloride binding for OPC and OPC- FA compared to CaCl$_2$, and 43.1 % less for OPC- slag.
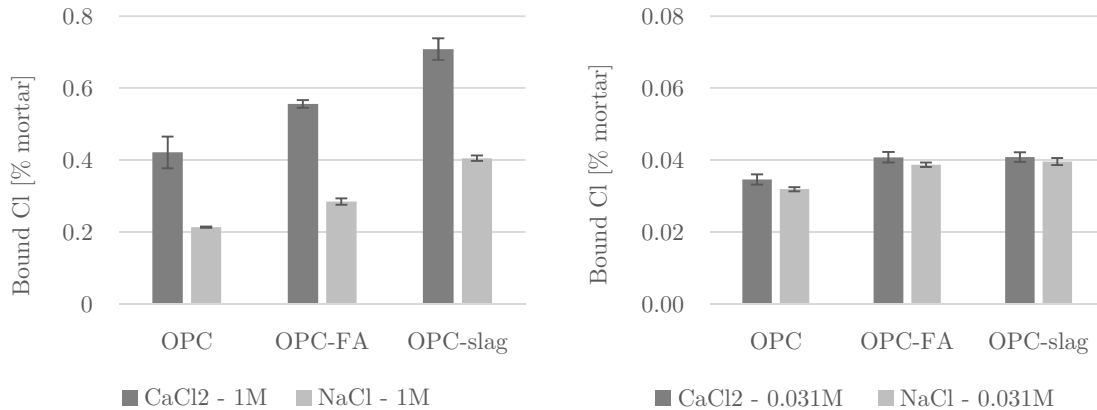
Figure 4.4 - Bound chloride for high and low chloride concentrations for the mortars with corresponding standard deviation

4.2 The effect of pH

The results of this study show that a higher chloride binding capacity for all three mortars is associated with a reduction of pH (from 13.0 to 11.7). Figure 4.5 shows the amount of bound chlorides as a function of the pH of the pore solution. A clear relationship exists between the pH for CaCl$_2$ exposure solutions. Figure 4.6 show that the pH is depending on the chloride content of the pore solution. For CaCl$_2$ exposure solutions, the pH reduces as the chloride content of the exposure solution increases, while the pH remains relatively constant for NaCl. Generally, it can be observed that the fly ash blend exhibit a slightly lower pH.
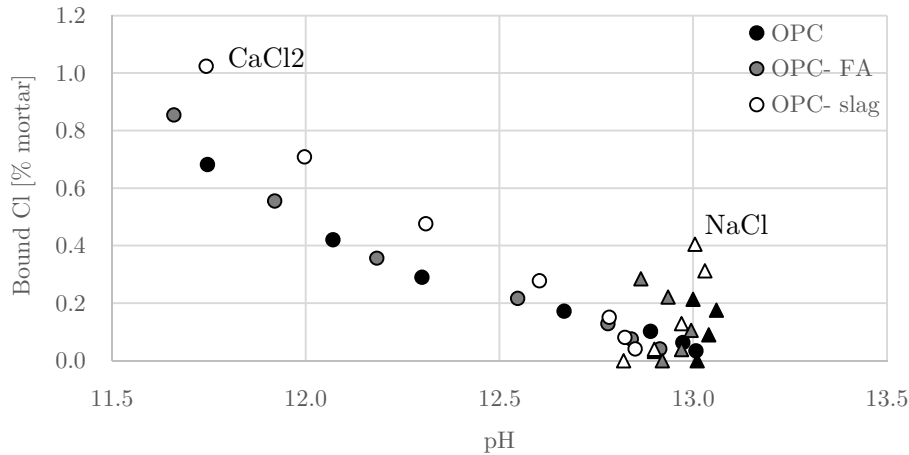
Figure 4.5 - The effect of pH on the amount of bound chloride
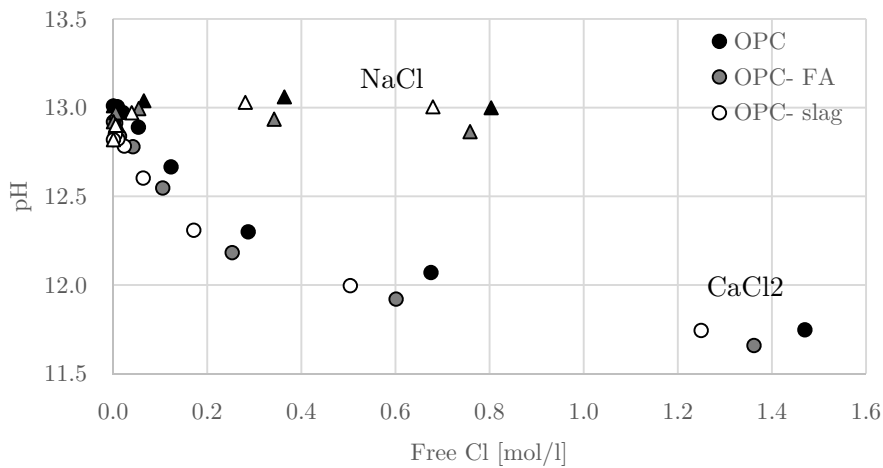
Figure 4.6 - The effect of pH on free chloride concentration

4.3 Chloride ingress profiles

Figure 4.7 shows the total chloride profile for the mortars, where there is no differentiation between free and bound chlorides. The average of the three parallels and the standard deviation are also plotted. The trend is similar for all binder types; lower chloride concentrations with increasing depths. OPC reaches a maximum total chloride concentration of 0.6 Cl/% mortar, OPC- FA reaches 0.65 Cl/% mortar and OPC- slag reaches 0.7 Cl/% mortar for NaCl exposure.

The chloride profile shows the effect of binder type. It can be observed that the GGBFS blended cement has the highest total chloride content near the surface, but the lowest at 12 mm. OPC exhibit different diffusion properties compared to the GGBFS and fly ash cements. The GGBFS blend and the fly ash blend have a steeper profile, which indicates the rate of change in chloride content is changing more rapidly with increasing depth. The chloride ions appear not to be able to penetrate as deep into the concrete

as for OPC. It is worth noticing that the maximum chloride content is reached a few millimeters from the surface for the fly ash cement.
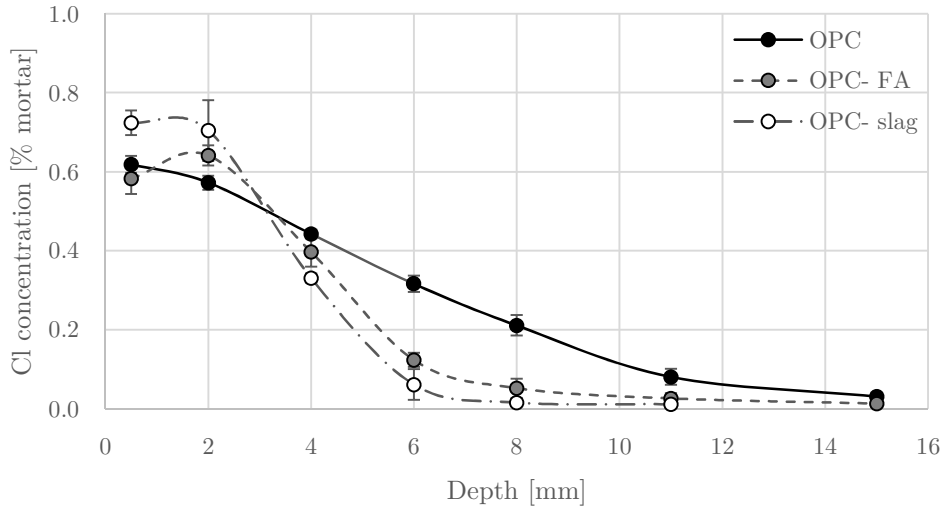
Figure 4.7 – Total chloride profile for the mortars exposed to NaCl

4.4 Chloride profiles of total, free and bound chlorides

In order to better understand and describe the effect of binding on chloride ingress, profiles of bound and free chloride were determined. The determined binding isotherms for both $CaCl_2$ and NaCl from Section 4.1 were tested. From Figure 4.8 - Figure 4.10, it appears that the binding isotherm determined by $CaCl_2$ gives a better reflection of the binding behavior compared to NaCl. It seems like the bound chloride content is underestimated by NaCl binding isotherm determined by the equilibrium method. The comparison of free and bound chlorides using NaCl and $CaCl_2$ binding isotherms will be discussed in Section 5.2. Further calculations are based on only the $CaCl_2$ binding isotherm.
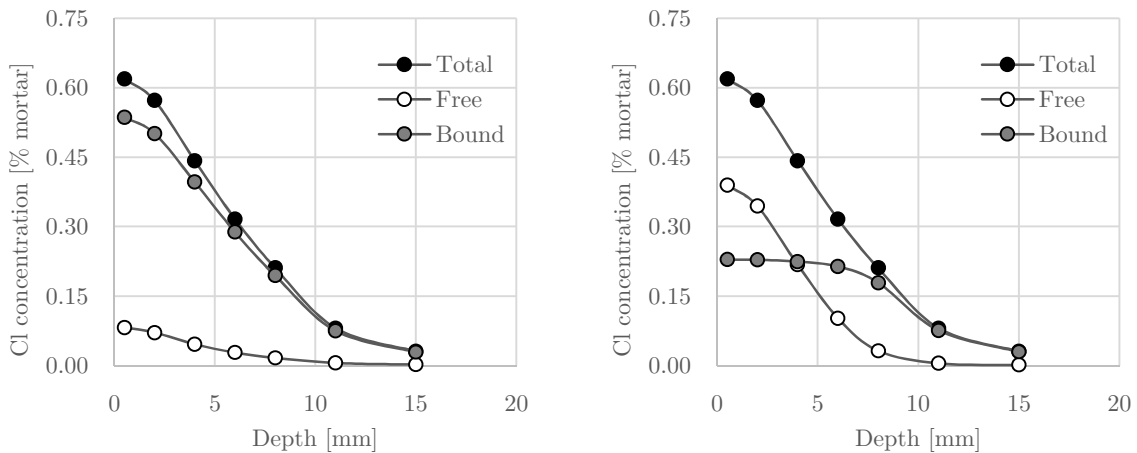
Figure 4.8 -The measured total chloride profile and calculated bound and free chloride profile based on $CaCl_2$ binding isotherm (Left) and NaCl binding isotherm (Right) for OPC
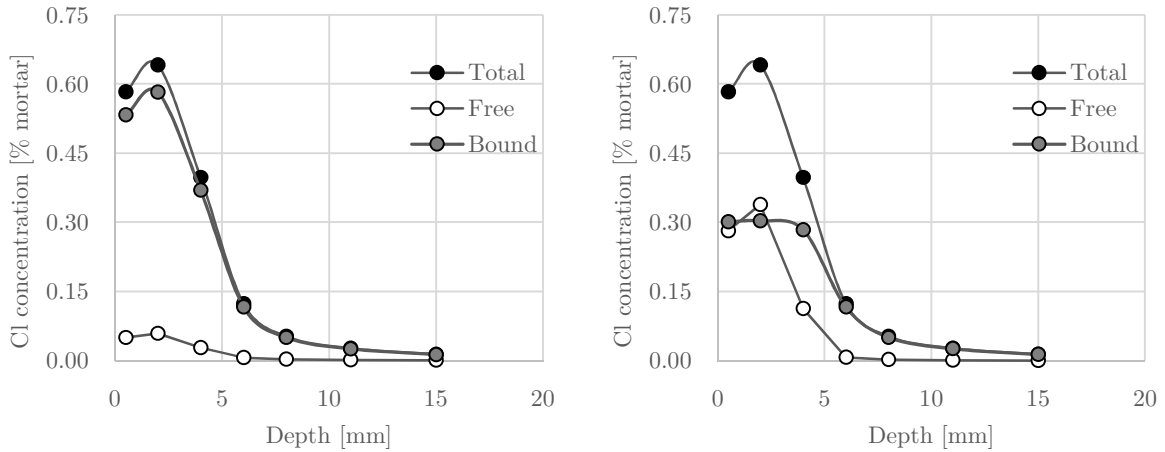
Figure 4.9 – The measured total chloride profile and the calculated bound and free chloride profiles based on the fitted Langmuir isotherm for CaCl₂ (Left) and NaCl (Right) for the fly ash blended cement
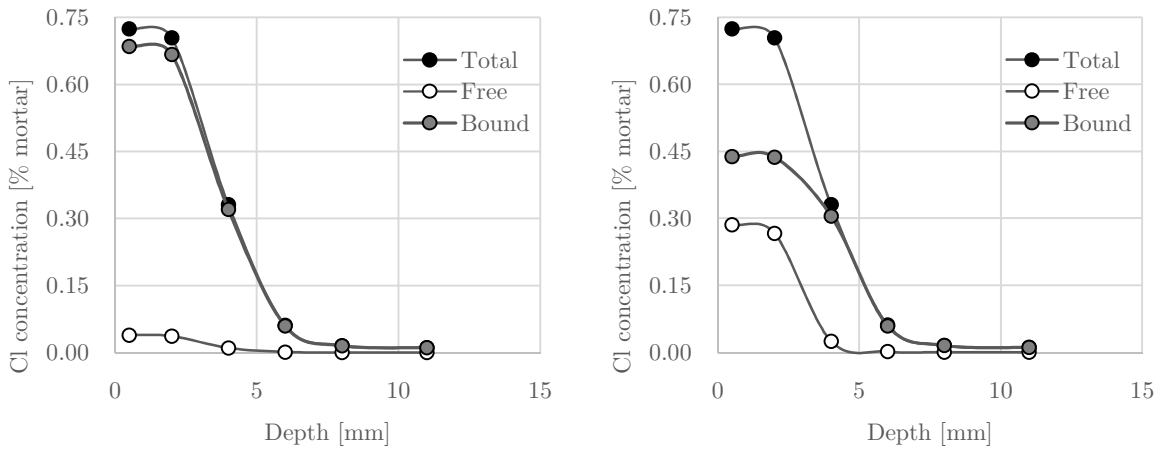
Figure 4.10 - The measured total chloride profile and the calculated bound and free chloride profiles based on the fitted Langmuir isotherm for CaCl2 (Left) and NaCl (Right) for the GGBFS blended cement

Figure 4.8 - Figure 4.10 show the effect of chloride binding and SCMs on chloride ingress. As discovered previously, the GGBFS blended cement exhibit higher binding capacity. The result is removal of chloride ions from the pore solution, which reduces the amount of free chlorides and thereby changes the concentration gradient driving diffusion. Consequently, increased binding results in a higher total chloride content near the concrete surface and a decrease of free chloride content at all depths, see Figure 4.9. The same trend is found for the fly ash blend, however with slightly lower total chloride content and higher free chloride content. In addition, the figures show a lower chloride content at 10 mm for the GGBFS and the fly ash cements compared to OPC. The total chloride content at depth of 8 mm has decreased by 92 % (from 0.21% by mortar to 0.016% by mortar) if GGBFS cement is used rather than pure OPC. As well, it can be observed that the free chloride concentration gradient for the GGBFS and the fly ash blends is small suggesting a lower rate of diffusion compared to OPC.

4.5 Chloride diffusion coefficient

The calculated apparent chloride diffusion coefficients (D_{app}) and the surface concentration (C_s) for OPC, OPC- FA and OPC- slag cements are presented in Table 4.3. Both total and free chloride profiles were used to determine the coefficients. Two different initial chloride concentrations (C_i) of 0.01 % and 0.005% were considered, assuming a lower initial chloride content in the cement than the upper limit required by NS- EN: 197-1:2011 (0.1%). The potentiometric titration method, as applied in the study, is able to measure chloride concentrations greater than approximately 0.01% Cl/ g concrete. However, experience from other methods and the results in Table B.1, indicate lowest chloride concentration of 0.005%. In this case, the effect of C_i is very small and has an almost insignificant influence on the fitting. An initial chloride concentration of 0.005% was used for further calculations, see Table C.2.

The obtained results represent the average diffusivity of the mortars during the period from beginning of exposure until sampling, see Table 4.3. The approach does not take into account the time dependent changes of the diffusion coefficient and the surface concentration. Therefore, the results only apply for samples of a certain age and for certain exposure conditions. There is an observed reduction in the calculated diffusion coefficient when binding is considered and only the free chloride content is used. This corresponds to the results in Figure 4.8 - Figure 4.10. The OPC- slag possesses the lowest coefficient, while OPC possesses the greatest change due to binding. This also agrees to calculated chloride profiles. Other studies show that the diffusion coefficient is similar at early ages but are much lower for slag and fly ash mixtures at later ages (Thomas&Bamforth, 1999).

Table 4.3- Calculated diffusion coefficients (D) and surface concentration (C_s) for samples exposed to NaCl for 6 months, with initial chloride concentration (C_i) of 0.005 %

OPC			
	Total	**Free**	**Rate of change**
C_s [% mortar]	0.73	0.10	87 %
D [m²/s]	$1.61 \cdot 10^{-12}$	$1.05 \cdot 10^{-12}$	35 %

OPC- FA			
	Total	**Free**	**Rate of change**
C_s [% mortar]	1.04	0.11	90 %
D [m²/s]	$5.27 \cdot 10^{-13}$	$3.78 \cdot 10^{-13}$	28 %

OPC- slag			
	Total	**Free**	**Rate of change**
C_s [% mortar]	1.33	0.08	94 %
D [m²/s]	$3.24 \cdot 10^{-13}$	$2.15 \cdot 10^{-13}$	34 %

Figure 4.11 - Figure 4.13 show the experimental data and the fitted diffusion model based on the calculated diffusion coefficient and surface concentration from Table 4.3. The figures show a good correlation between the model and the data. The first two points of the experimental data are omitted in the fitting. It is important to notice that the calculated surface concentration is much greater than the one measured. The obtained results can be used to calculate future chloride profiles and in service life predictions.
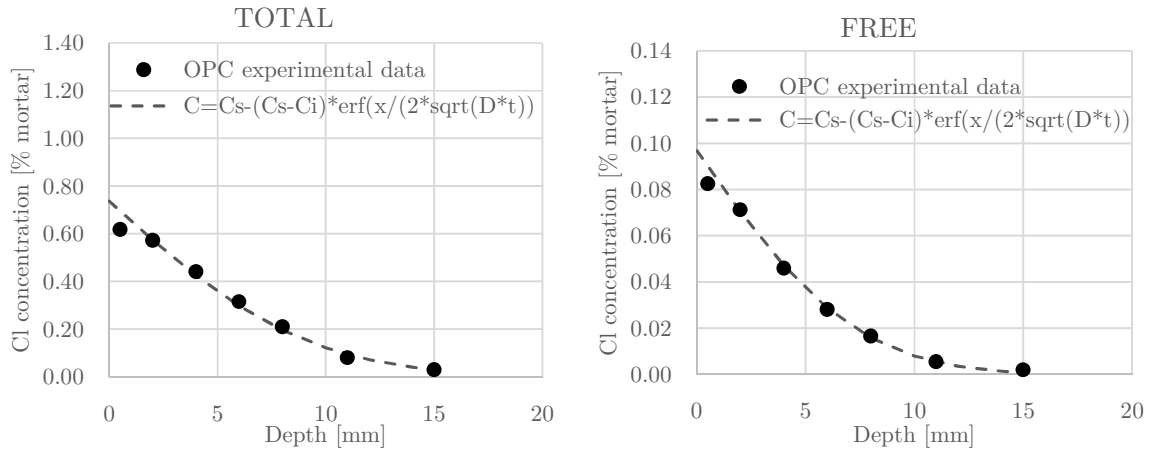
Figure 4.11 - Chloride diffusion for OPC based on total and free chloride concentration
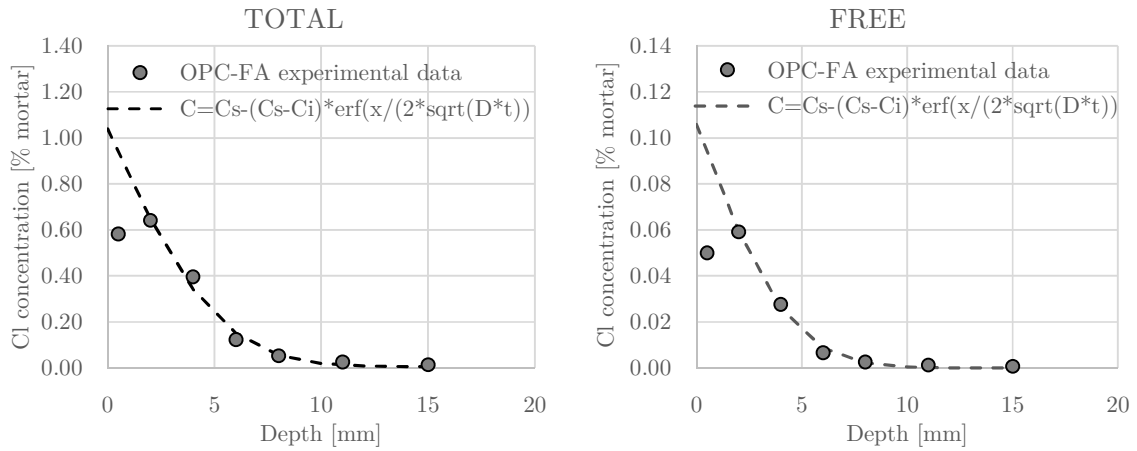
Figure 4.12 - Chloride diffusion for OPC- FA based on total and free chloride concentration
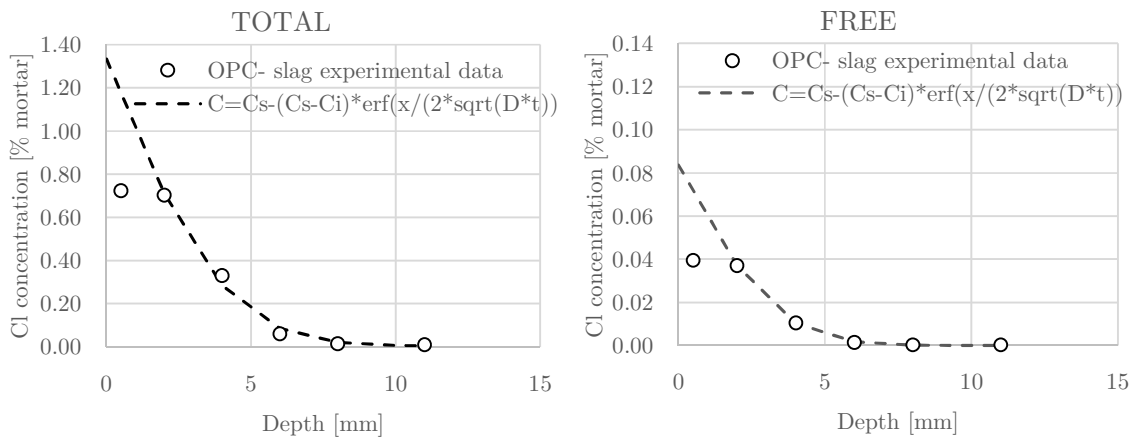
Figure 4.13 - Chloride diffusion for OPC- slag based on total and free chloride concentration

5

DISCUSSION

5.1 Chloride binding isotherms

The chloride binding isotherms obtained from the analysis of the experimental data are similar to the trends reported in the literature (Thomas et al., 2012, Zibara, 2001, Arya et al., 1990, Delagrave et al., 1997). Non- linear binding isotherms were the best fit for both $CaCl_2$ and NaCl exposure, and for both fly ash and BBGFS blended cements. The binding capacity of OPC- slag appears to be greater than the capacity of OPC-FA and OPC, while OPC-FA binds more than OPC, see Figure 4.2 and Figure 4.3. In all cases, the amount of bound chlorides gradually increase as the free chloride concentration rises.

The effect of cation

The presented results show that the cation type changes the pH, subsequently changing the binding capacity. The observed change in pH for $CaCl_2$ exposure may not be attributed to the cation itself, but to the cation's capacity to form insoluble hydroxide, thus lowering the OH^- concentration of the pore solution (Tritthart, 1989b). This should be considered in relation to the observed changes in pH as seen in Figure 4.5 and Figure 4.6. For $CaCl_2$ exposure, there is an observed acidification of the system as the chloride concentration rises. The reduced hydroxide ion concentration can be explained by the fact that calcium becomes practically insoluble and precipitate as solid $Ca(OH)_2$ in highly alkaline solutions such as in the pore solution of concrete (Tritthart, 1989b). Consequently, the hydroxide concentration of the solution is reduced. The mechanism can be explained by the simplified reaction (De Weerdt et al., 2013);

$$CaCl_2 + 2OH^- \rightarrow Ca(OH)_2 \downarrow + 2Cl \qquad (\ 5.1\ )$$
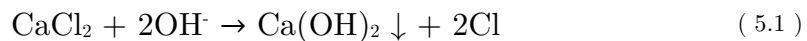
However, it should be noticed that the decrease in pH is not a linear relationship of the $CaCl_2$ concentration added, as observed in Figure 4.6. Lowering of the pH will also lead to higher solubility of Ca^{2+} ions (De Weerdt et al., 2013). The $Ca(OH)_2$ precipitated in the system will therefore dissolves partially.

As expected, the NaCl system exhibits a lower binding capacity compared to $CaCl_2$, which is in accordance to literature (Zhu et al., 2012, Arya et al., 1990, Tritthart, 1989b). The pH is more or less constant, though others have experienced an increase

in pH (Tritthart, 1989b). Ben-Yair (1974) suggests that in exposure solutions of NaCl, NaCl will react with an excess of $Ca(OH)_2$ and form NaOH and $CaCl_2$. The formed $CaCl_2$ would then transform into Friedel's salt or Kuzel's salt as it reacts with e.g. C_3A, according to Equation (5.2). The NaOH would result in higher pH of the exposure solution (Ben-Yair, 1974).

$$C_3A + CaCl_2 + 10H_2O \rightarrow C_3A \cdot CaCl_2 \cdot 10H_2O \qquad (\ 5.2\ )$$
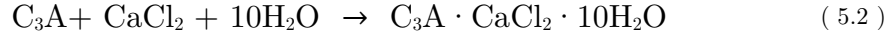
However, there is no increase of the pH associated with the formation of Friedel's salt from monosulphate or monocarbonate alone (De Weerdt et al., 2013). De Weerdt et al. (2013) suggest that the change in pH in the NaCl system is a result of changes in the AFm and AFt phases, i.e. there is a supply of additional hydroxide ions to the system when monosulphate transforms into ettringite or Friedel's salt from hemicarbonate. Hence, if the NaCl system were over- sulphated there would be no increase of pH even though Friedel's salt would form.

The effect of change in pH
There is an observed increase in the binding capacity when the pH reduces (from 13.0 to 11.7), as seen Figure 4.5. The binding capacity is affected by the Ca/Si ratio of the C-S-H (Yuan et al., 2009). A high calcium content leads to a higher Ca/Si ratio and the surface of the C-S-H becomes positively charge. The result is higher chloride adsorption of the C-S-H phase. However, at high pH there will be a competition between the chloride ions and the hydroxide ions. If pH reduces, less hydroxide ions compete on the surface and more chlorides can be bound. This corresponds to the observed high binding capacity of the $CaCl_2$ system compared to the NaCl system. The results are in agreement with the research of Zibara (2001) and Tritthart (1989b). Nevertheless, it is important to bear in mind the also the Ca/Si ratio is influenced by the pH.

Increased binding capacity for GGBFS and fly ash blended cements
Figure 4.2 and Figure 4.3 show that partial substitution of GGBFS (50%) causes higher chloride binding capacity. It is likely that this improvement can be attributed to the high alumina content of GGBFS (12.7 %, see Table 3.2), which leads to increasing chemical binding capacity, subsequently increasing formation of Friedel's salt. Additionally, the GGBFS used in this study is highly reactive, which can be seen by the strength development in Table A.8. The result implicates higher amount of C-S-H, thus a higher physical binding capacity.

The results also show that the OPC- FA cement has a higher binding capacity compared to the pure OPC. Regarding fly ash, there is not such a clear link between

the alumina content and chloride binding. Much of the alumina in fly ash is present in crystalline components such as mullite, which is not available for formation of calcium chloro- aluminates (Thomas et al., 2012). It follows from Table 3.2 that the fly ash used in this study has a high alumina content, and mullite content of 12 %. The amount of unreactive alumina present in the mullite phase can be calculated to 5.6 %. The results is a lower amount of reactive alumina (16.5%) available for formation of Friedel's salt in the fly ash cement. Moreover, the fly ash reacts fairly slow as observed by De Weerdt (2011) who used the same fly ash. Consequently, the fly ash blended cement exhibits a lower binding capacity compared to the GGBFS blended cement.

5.1.1 Comparison with literature

Two articles were chosen for comparison of the obtained results; Thomas et al. (2012) and Zibara (2001). These studies present similar analysis techniques. Only the NaCl binding isotherms have been compared. Details on mix design and methods can be found in Table 5.1 and Table B.3 in Appendix B. Figure 5.1 shows the results presented in mg/ g cement paste for comparison with the results of Zibara and Thomas et al. All the binding isotherms have a similar scale and range, see Table 5.1. Both Zibara and Thomas et al. found that the Freundlich isotherm provides the best fit for exposure to NaCl. This study concluded that the Langmuir isotherm was the best for NaCl exposure.

The results of this study gives a binding capacity between the results of Zibara and Thomas at low chloride concentrations. The studies show that GGBFS binds more than fly ash and OPC at higher chloride concentration (2M - 3M). However, the trend was only found for chloride concentrations higher than approximately 0.7 M in both cases. This trend was not observed in this study. The difference in binding isotherm may be related to difference in methods and mix design;

- Both Zibara and Thomas et al. used a high solution to solid ratio, see Table B.3. Thus, the diluted systems should cause a higher binding capacity due to the reduction of the pH.
- The samples were cement pastes, cured for only 2 – 9 months.
- The difference in amount of bound chlorides may be attributed to the w/c ratio. Generally, Zibara exhibit slightly lower binding capacity, probably caused by restricted hydration and pozzolanic reaction at low w/c (w/c = 0.3). Thomas et al. experienced a slightly higher amount of bound chlorides at w/c = 0.5, which corresponds to presented literature.
- Thomas et al. and Zibara used a lower GGBFS replacement level, which causes a lower binding capacity. Additionally, the GGBFS has a slightly lower alumina content (10%).

- Both Thomas et al. and Zibara used a fly ash with relatively high alumina content (24.7%). This should have resulted in higher binding capacity, especially for Thomas et al. The mullite content and the reactivity of the fly ash is unknown.
- The samples of Zibara and Thomas et al. have been dried at 11% RH, which may change the microstructure of the C-S-H, thus changing the physical binding capacity.
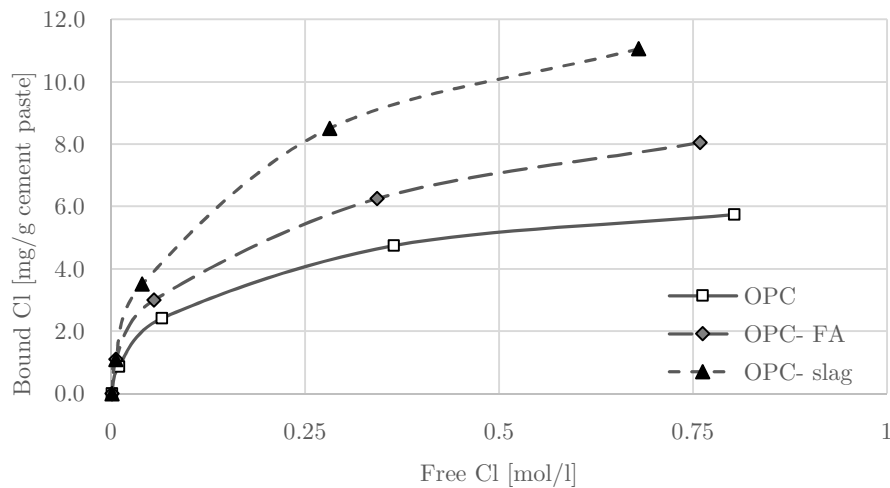
Figure 5.1 - Chloride binding isotherm for mortar samples with w/c=0.4, temperature 20°C, for NaCl exposure solution for comparison with Zibara and Thomas et al.

Table 5.1 - Amount of bound chlorides at free Cl concentration of 0.5 M from the three different studies (NaCl exposure)

	Ytterdal (2014) [mg/g cement paste]	Zibara (2001) [mg/g cement paste]	Thomas et al. (2012) [mg/g cement paste]
OPC	5.3	3.8	6.4
OPC-FA	7.3	3.4	5.9
OPC- slag	10.1	5.7	7.0
w/c	0.4	0.3	0.5
FA	30 %	25 %	25 %
GGBFS	50 %	40 %	25 %
Silica fume	6 %	4.8 - 8 %	0 %
Alumina, GGBFS	12.76 %	10.02 %	10.02 %
Alumina, FA	22.05 %	24.65 %	24.65 %

5.2 Chloride ingress profiles

Few studies include the effect of binding when determining and evaluating chloride profiles. The chloride concentration of the pore solution of different binders may vary, even though the total content is the same. As mainly the free chlorides are influenced by diffusion, one should distinguish between bound and free chlorides when studying chloride ingress by diffusion in different binders.

Precipitation of bound Cl
Some studies suggest that the time for corrosion initiation is also depending on the corrosion risk presented by the bound chlorides. Glass et al. (2000) state that the bound chlorides will precipitate when the pH changes due to local defects and voids close to the steel. Solid phases containing bound chlorides have very similar pH dependent solubility as calcium hydroxide (Glass&Buenfeld, 2000). A small, local drop in pH may therefore cause a dissolution of these phases releasing bound chlorides. There is a disagreement amongst researchers whether bound chlorides should be taken into account when evaluating chloride ingress in concrete.

NaCl vs CaCl$_2$ binding isotherms
The CaCl$_2$ binding isotherm provided a better reflection of binding in concrete. In the case of NaCl binding isotherm, a free chloride content of 4M is obtained near the surface which is in contact with exposure solution of NaCl containing 0.545M chlorides for OPC (see Figure 4.8). It seems like the NaCl binding isotherm achieved with the equilibrium method underestimates the amount of bound chlorides. In contrast, the CaCl$_2$ binding isotherm provides a more realistic free chloride concentration near the mortar surface as the amount of bound chlorides are higher.

Moreover, studies show that neither sodium nor calcium follow the chlorides into the concrete (De Weerdt et al., 2014b). In the case of CaCl$_2$ there is an observed reduction in pH, which is not found for NaCl. This gives a better replication of the actual process, which makes the CaCl$_2$ binding isotherm better suited. Nevertheless, it should be noticed that CaCl$_2$ gives a quite large drop in pH due to the large solution to solid ratio inherent to the equilibrium method. This may indicate that both the CaCl$_2$ and the NaCl binding isotherm determined by the equilibrium method not fully reflect the actual binding behavior, and that the truth lays somewhere in-between.

Therefore, free and bound chlorides are differentiated in Figure 4.8 - Figure 4.10. This simplification of presenting diffusion in concrete, assumes that the bound chlorides are fixed to the solids. Under this assumption, one can compare diffusion in mortars with various SCMs in a more realistic manner. When comparing chloride profiles based on the total chloride content, it appears as the GGBFS blend has a relatively high amount

of chlorides. If including the fact that various binders exhibit different binding capacities, the Portland cement has a higher free chloride content than both the GGBFS blend and the fly ash blend. The results show a significant effect of including binding when representing chloride profiles. Thus, it seems more appropriate to express chloride profiles in terms of free chlorides when comparing chloride ingress in various binders.

5.3 Fick's 2nd law of diffusion

The apparent diffusion coefficient is generally determined by fitting of *total* chloride profiles to the solution of Fick's 2nd law of diffusion. The coefficient integrates both the diffusion characteristics of the material and the effect of chemistry on chloride penetration. Equation (2.5) is often used to estimate service life of partially saturated structures in marine environment. In service life predictions, one assumes that the service life of a reinforced concrete structures subjected to chlorides corresponds to the time until steel depassivation, see Figure 2.1. However, the physical meaning of the apparent diffusion coefficient based on this approach is questionable as it rest on a number of simplifying assumptions which rarely are met in real structures. Pure diffusion can only occur in concrete completely and permanently saturated in water. Capillary suction may often occur close to the surface of dry concrete, and evaporation of water in the outer zones leads to enrichment of chloride ions. Leaching and phase changes may also effect the diffusion process in the first outer millimeters. Furthermore, the free chlorides, which actually move by diffusion, are proved to be a non- linear function of the bound chlorides. Neither electrical coupling nor chemical activity effects are accounted for in the method (Glasser et al., 2008).

Furthermore, both the calculated apparent diffusion coefficient and the surface concentration are only a fitting parameter. In reality, the surface concentration is i*nfluenced by leaching and phase changes in the first outer millimeters of the mortar surface.* As well, the fitted surface concentration is much higher than the actual concentration at the surface, as seen in Figure 4.11 - Figure 4.13.

Porosity

Besides chemical changes, diffusion of chloride ions in concrete is affected by the porosity and the moisture conditions. These factors are neither considered by Fick's 2nd law of diffusion, though it is well established that the use of GGBFS and fly ash as cement replacement reduce permeability. This may be one of the reasons for the observed improved resistant against chloride penetration. Fly ash and slag cement blends appears to be able to resist penetration to a much greater extent than the OPC, as seen in Figure 4.11 - Figure 4.13. The result is a lower chloride concentration close

to reinforcement, which may lead to prolonged time until chloride threshold level is reached, see Figure 2.1.

Using Fick's 2ⁿᵈ law of diffusion
As long as the binding capacity is not exhausted, the flux of material will be affected (Bertolini et al., 2004). The gradual consumption of chlorides due to binding modifies the conditions of diffusion, which no longer can be described by Fick's second law. It follows that it is a questionable approach to use total chloride content in the diffusion model in Equation (2.5), when only the free chlorides move my diffusion and when these only are a small share of the total content. Nevertheless, such a simplification should be used with caution in prediction of long- term performance of reinforced concrete structures exposed to chlorides. The calculated diffusion coefficient and surface concentration is better suited for curve fitting and for description of chloride diffusion of a specific situation under certain conditions.

Fitting of free chloride profiles allows comparing of the diffusion coefficient for total and free chloride content. The results proved that the diffusion coefficient is reduced when fitting is based on only free chlorides.

Service life
Based on the presented data, it may seem as if the GGBFS blend is better suited in chloride aggressive environment compared to both the fly ash blend and the OPC. The use of GGBFS is known to influence the microstructure of concrete, which might improve the ability to resist penetration of chloride ions at a given total chloride content. The GGBFS cement is able to lower the free chloride content of the pore solution due to binding, which may reduce the risk corrosion initiation. However, this should be verified by more research on long- term properties.

Chloride profiles after 30 years were predicted using Equation (2.5) with the time dependent diffusion coefficient as shown in Table 4.3. The aging factors, α, are presented in Table C.3 in Appendix C and is taken from the report of Skjølsvold (2009). The results presented in the left graph of Figure 5.2 are the predicted total chloride profile using the surface concentration and the diffusion coefficient determined by the total chloride profiles as shown in Table 4.3. These were then entered in Equation (2.5) combined with Equation (2.6). The total chloride profiles in the right graph of Figure 5.2, are based on the surface concentration and diffusion coefficient of the free chlorides from Table 4.3. The free chloride profiles after 30 years were first predicted by entering these values into Equation (2.5) combined with Equation (3.6). Then the total chloride profiles after 30 years were calculated by transferring the free chlorides into total chlorides using Equation (3.6). From Figure 5.2 it can be seen

that there is a difference in the surface concentration between the predicted profiles based on the total and the free chloride profiles. However, from approximately 4 mm from the exposed surface and inwards, the predicted chloride profiles are relatively similar and the same ranking between the mortars are obtained, independent on whether the total or free chloride profiles are used. Thus, for the prediction of chloride ingress over time the division between bound and free chlorides does not seem that important.
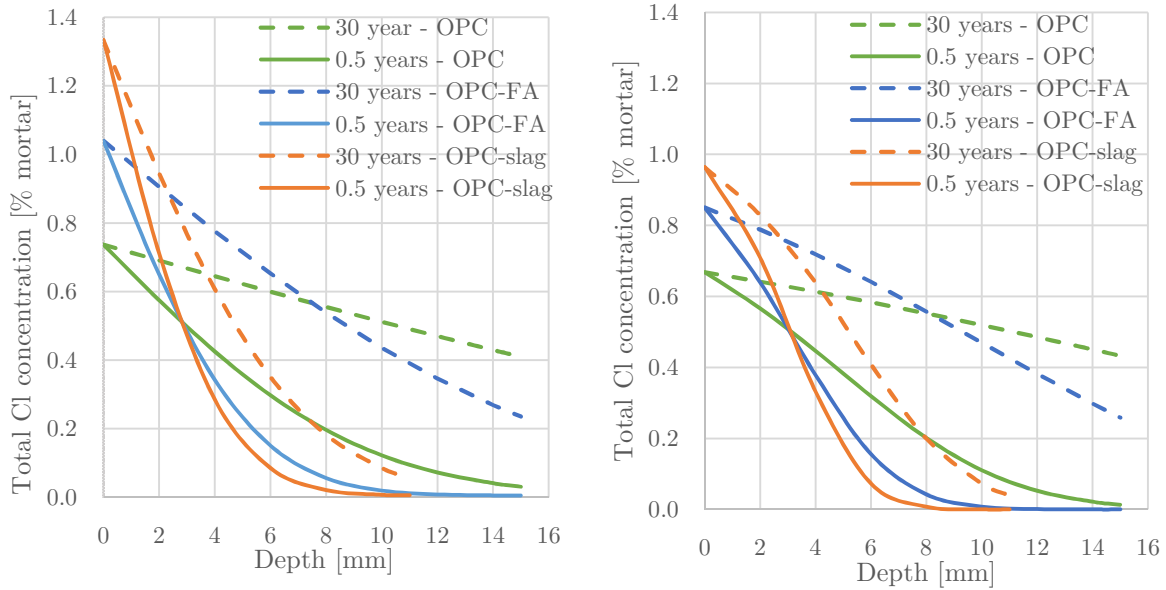
Figure 5.2 - Modelled chloride profiles based on total chloride profiles (Left) and modelled chloride profiles based on free chloride profiles (Right) after 0.5 years and 30 years for exposure to NaCl

6

CONCLUSION

Based on the findings of this study, it is reasonable to conclude that;

- The use of GGBFS as partial replacement of OPC, gives an increase in the binding capacity. The same trend was observed for the fly ash blend. Addition of 50% GGBFS increased the amount of bound chlorides by 50.2 %, while 25% addition of fly ash increased the bound chloride content by 25.2 % compared to OPC. It is likely that this improvement can be attributed to the high alumina content of both GGBFS and fly ash, as it increases the chemical binding capacity. The high binding capacity of the GGBFS blended cement compared to fly ash blend, can most likely be linked to its higher reactivity and thus the increased formation of C-S-H.

- It was proven that the relationship between free and bound chlorides is non-linear. For $CaCl_2$ exposure, the Freundlich isotherm provided the best fit, while the Langmuir isotherm provided the best fit for NaCl exposure.

- The associated cations affect chloride binding, in which $CaCl_2$ exposure results in higher binding capacity compared to NaCl. There is an observed decrease of the pH associated with the high binding capacity for exposure to $CaCl_2$.

- The $CaCl_2$ binding isotherm appears to provide a better reflection of chloride binding in concrete. The NaCl binding isotherm achieved with the equilibrium method seems to underestimates the amount of bound chlorides. However, it should be mentioned that neither the $CaCl_2$ nor the NaCl binding isotherm determined by the equilibrium method fully reflect the actual binding behavior as neither sodium nor calcium follow the chlorides into the concrete.

- Due to a high binding capacity, the use of GGBFS and fly ash reduce the free chloride content of the pore solution. However, a higher total chloride content is obtained near the exposed surface.

- The use of GGBFS and fly ash reduce the coefficient of diffusion. When taking into account the effect of binding on chloride diffusion, a greater reduction of the coefficient of diffusion is observed.

- The physical meaning of the apparent diffusion coefficient based Fick's 2nd law of diffusion is questionable as it rests on a number of simplifying assumptions. As only the free chlorides move by diffusion, it seems more appropriate to express chloride profiles in terms of free chlorides. The results showed a significant effect of including binding when presenting chloride profiles.

- Chloride profiles after 30 years were predicted using Fick's 2nd law of diffusion and the diffusion coefficient and the surface concentration determined by the free and the bound chloride profiles. The predicted total chloride profiles are relatively similar from a few millimeters from the exposure surface and inwards. The same ranking between the mortars are obtained, independent on whether the total or free chloride profiles are used. Thus, for the prediction of chloride ingress over time the division between bound and free chlorides does not seem that important.

7

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Task description

NTNU
Fakultet for ingeniørvitenskap og teknologi
Institutt for bygg, anlegg og transport

MASTEROPPGAVE
(TBA4905 Bygnings og materialteknikk, masteroppgave)

VÅREN 2014
for
Silje Gystad Ytterdal

Effekt av flygeaske og slag som sementerstatning på kloridbinding og
kloridinntrenging i mørtelprøver
eller
The effect of fly ash and ggbfs as cement replacement on the chloride binding
and ingress in mortar samples

BAKGRUNN
Reinforcement corrosion is looked upon as one of the predominant deterioration mechanisms for reinforced concrete structures. The corrosion and the consequent reduction of the cross section of the reinforcement can limit the service life of the structure and might lead to high maintenance and repair costs. Chloride induced corrosion occurs when a critical chloride level is reached at the interface of the steel reinforcement. Nowadays regulations limit the chloride content in the concrete constituents to a minimum, hence chlorides originate from external sources e.g. sea water or deicing salts. Hence, the time to corrosion initiation is determined by the thickness and the material properties of the concrete cover causing resistance to chloride ingress.

OPPGAVE

Beskrivelse av oppgaven
In this study the effect of the cement type on chloride ingress and chloride binding is investigated. The student will be challenged by going into depth in a new field of research by both performing the experiments and interpreting the data.

Målsetting og hensikt
The goal of the study is to improve the understanding of chloride ingress in concrete prepared with different binders i.e. fly ash and slag blended cements.

Deloppgaver og forskningsspørsmål
In the first part, the student will determine the chloride binding capacity on already prepared mortar samples equilibrated with a range of chloride containing solutions. The aim is to evaluate the impact of the binder and the cation of the chloride salt on the binding capacity of the mortar.

As a second part, the student will determined a selection of chloride ingress profiles on already prepared profile ground concrete powder samples.

It is expected that the student can understand and perform the analysis of the samples ($AgNO_3$ titration), and is able to treat the data and make the necessary calculations (complex mol, volume and mass transformations). The student should independently interpret the results and compare it to findings in the literature.

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GENERELT

Oppgaveteksten er ment som en ramme for kandidatens arbeid. Justeringer vil kunne skje underveis, når en ser hvordan arbeidet går. Eventuelle justeringer må skje i samråd med faglærer ved instituttet.

Ved bedømmelsen legges det vekt på grundighet i bearbeidingen og selvstendigheten i vurderinger og konklusjoner, samt at framstillingen er velredigert, klar, entydig og ryddig uten å være unødig voluminøs.

Besvarelsen skal inneholde
➢ standard rapportforside (automatisk fra DAIM, http://daim.idi.ntnu.no/)
➢ tittelside med ekstrakt og stikkord (mal finnes på siden http://www.ntnu.no/bat/skjemabank)
➢ sammendrag på norsk og engelsk (studenter som skriver sin masteroppgave på et ikke-skandinavisk språk og som ikke behersker et skandinavisk språk, trenger ikke å skrive sammendrag av masteroppgaven på norsk)
➢ hovedteksten
➢ oppgaveteksten (denne teksten signert av faglærer) legges ved som Vedlegg 1.

Besvarelsen kan evt. utformes som en vitenskapelig artikkel for internasjonal publisering. Besvarelsen inneholder da de samme punktene som beskrevet over, men der hovedteksten omfatter en vitenskapelig artikkel og en prosessrapport.

Instituttets råd og retningslinjer for rapportskriving ved prosjektarbeid og masteroppgave befinner seg på http://www.ntnu.no/bat/studier/oppgaver.

Hva skal innleveres?
Rutiner knyttet til innlevering av masteroppgaven er nærmere beskrevet på http://daim.idi.ntnu.no/. Trykking av masteroppgaven bestilles via DAIM direkte til Skipnes Trykkeri som leverer den trykte oppgaven til instituttkontoret 2-4 dager senere. Instituttet betaler for 3 eksemplarer, hvorav instituttet beholder 2 eksemplarer. Ekstra eksemplarer må bekostes av kandidaten/ ekstern samarbeidspartner.

Ved innlevering av oppgaven skal kandidaten levere en CD med besvarelsen i digital form i pdf- og word-versjon med underliggende materiale (for eksempel datainnsamling) i digital form (f. eks. excel). Videre skal kandidaten levere innleveringsskjemaet (fra DAIM) hvor både Ark-Bibl i SBI og Fellestjenester (Byggsikring) i SB II har signert på skjemaet. Innleveringsskjema med de aktuelle signaturene underskrives av instituttkontoret før skjemaet leveres Fakultetskontoret.

Dokumentasjon som med instituttets støtte er samlet inn under arbeidet med oppgaven skal leveres inn sammen med besvarelsen.

Besvarelsen er etter gjeldende reglement NTNUs eiendom. Eventuell benyttelse av materialet kan bare skje etter godkjennelse fra NTNU (og ekstern samarbeidspartner der dette er aktuelt). Instituttet har rett til å bruke resultatene av arbeidet til undervisnings- og forskningsformål som om det var utført av en ansatt. Ved bruk ut over dette, som utgivelse og annen økonomisk utnyttelse, må det inngås særskilt avtale mellom NTNU og kandidaten.

(Evt) Avtaler om ekstern veiledning, gjennomføring utenfor NTNU, økonomisk støtte m.v.
Beskrives her når dette er aktuelt. Se http://www.ntnu.no/bat/skjemabank for avtaleskjema.

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Helse, miljø og sikkerhet (HMS):
NTNU legger stor vekt på sikkerheten til den enkelte arbeidstaker og student. Den enkeltes sikkerhet skal komme i første rekke og ingen skal ta unødige sjanser for å få gjennomført arbeidet. Studenten skal derfor ved uttak av masteroppgaven få utdelt brosjyren "Helse, miljø og sikkerhet ved feltarbeid m.m. ved NTNU".

Dersom studenten i arbeidet med masteroppgaven skal delta i feltarbeid, tokt, befaring, feltkurs eller ekskursjoner, skal studenten sette seg inn i "Retningslinje ved feltarbeid m.m.". Dersom studenten i arbeidet med oppgaven skal delta i laboratorie- eller verkstedarbeid skal studenten sette seg inn i og følge reglene i "Laboratorie- og verkstedhåndbok". Disse dokumentene finnes på fakultetets HMS-sider på nettet, se http://www.ntnu.no/ivt/adm/hms/. Alle studenter som skal gjennomføre laboratoriearbeid i forbindelse med prosjekt- og masteroppgave skal gjennomføre et web-basert TRAINOR HMS-kurs. Påmelding på kurset skjer til sonja.hammer@ntnu.no

Studenter har ikke full forsikringsdekning gjennom sitt forhold til NTNU. Dersom en student ønsker samme forsikringsdekning som tilsatte ved universitetet, anbefales det at han/hun tegner reiseforsikring og personskadeforsikring. Mer om forsikringsordninger for studenter finnes under samme lenke som ovenfor.

Oppstart og innleveringsfrist:
Oppstart og innleveringsfrist er i henhold til informasjon i DAIM.

Faglærer ved instituttet: Prof. Mette R Geiker, Dr. Klaartje De Weerdt
Veileder(eller kontaktperson) hos ekstern samarbeidspartner: /

Institutt for bygg, anlegg og transport, NTNU
Dato: 22.05.2014,

Underskrift

Klaartje De Weerdt

Faglærer

APPENDIX A
Experimental program

- Materials
- Mix design
- Composition of chloride exposure solutions
- GGBS strength development

Materials

Table A.1 - Distribution of materials

Mix	w/c	OPC [%]	Silica fume [%]	Fly ash [%]	Blast furnace slag [%]
OPC	0,4	94	6	-	-
OPC-FA	0,4	64	6	30	-
OPC-slag	0,4	44	6	-	50

Table A.2- General composition of mixtures

Material characteristics		
w/p ratio	0.4	for CEM I
Sand/ cement	2.5	
GGBS	50	% of binder
Fly ash	30	% of binder
Silica fume	6	% of cement
SP 130	0.30	% dry content
Demper RM	0.4	% dry content
k_{SF}	2	
k_{FA}	0.4	
k_{GGBS}	0.7	

Table A.3 - Material densities

Material	Density [g/l]
Cement	3120
Slag	2910
Fly Ash	2240
Silica Fume	2310
Sand	2650
Cement + silica fume	3056

Table A.4 - Additional chemical composition determined by XRD

	Chemical notation	OPC	BBGFS	FA
Portlandite	$Ca(OH)_2$	3.3		
Free lime	CaO	0.3		0.3
Periclase	MgO	1.4		0.7
Arcanite	K_2SO_4	0.5		
Aphthitalite	$K_3Na(SO_4)_2$	0.8		
Anhydrite	$CaSO_4$	0.2		0.1
Bassanite	$CaSO_4 * 0,5\ H_2O$	2.9		
Gypsum	$CaSO_4 * 2\ H_2O$	0.2		
Calcite	$CaCO_3$	2.7		
Quartz	SiO_2			10.1
Moissanite	SiC			
Huntite	$CaMg_3(CO_3)_4$			
Albite	$NaAlSi_3O_8$			
Microcline	$KAlSi_3O_8$			
Biotite	$K(Mg,\ Fe^{II})_3[(OH,\ F)_2|(Al,\ Fe)Si_3O_{10}]$			
Chlorite	$(Mg,\ Al,\ Fe)_6[(OH)_8|(Si,\ Al)_4O_{10}]$			
Diopside	$CaMgSi_2O_6$			
Akermanite	$Ca_2MgSi_2O_7$		0.1	
Maghemite	Fe_2O_3			1.2
Mullite	$Al_6Si_2O_{13}$			12.0
Amorphous			99.9	74.4

Mix design

Table A.5 - Mix design for the three mortar mixtures used in the experiment

	OPC [g]	**OPC − FA** [g]	**OPC- slag** [g]
Binder	1620	1460.45	1580.432
Cement	1522.80	960.98	742.80
SF	97.20	61.34	47.41
FA	-	438.14	-
GGBS	-	-	790.22
Water*	638.55	638.55	638.55
Sand	4050.00	4050.00	4050.00
Demper RM	6.08	6.08	6.08
SP130	4.86	4.86	4.86
Volume [L]	2,70	2.70	2.70
V_{water}/V_{dry}	1,22	1.22	1.22
m_w/m_p	0,400	0.440	0.410
Equivalent w/c	0,377	0.511	0.466
SF/binder [%]	6,0	4.2	3.0

* water from SP and demper is subtracted from water

Composition of chloride exposure solutions

Table A.6 – Ideal Cl⁻ concentration and measured Cl⁻ concentration for solution of CaCl₂ and NaCl for binding isotherm

CaCl₂

Ideal concentration of exposure solution	Actual concentration of exposure solution
2	1,978
1	0,989
0,5	0,492
0,25	0,247
0,125	0,123
0,063	0,062
0,031	0,031

NaCl

Ideal concentration of exposure solution	Actual concentration of exposure solution
1	0,987
0,5	0,502
0,125	0,124
0,031	0,031

Table A.7 - Chemical composition of NaCl exposure solution for determination of chloride profiles

	Sea water - ICP-MS		NaCl solution	
	g/l	mol/l	g/l	mol/l
Ca	0.351	0.009	-	-
Cl	19.419	0.548	19.307	0.545
K	0.348	0.009	-	-
Mg	1.134	0.047	-	-
Na	9.455	0.411	12.520	0.545
S	0.861	0.027	-	-
Si	0.006	0.000	-	-

Table A.8 - GGBFS strength development

GGBS Test Results

In accordance with I.S. EN 15167-1:2006 & Annex NE I.S. EN 206-1:2002

Cement Combination :- Reference CEM I 42.5R

Monthly average results for Ringsend Works for: feb-2012

Fineness :   438 m^2/kg   (I.S. EN196-6:2006)

Compressive Strength Test Results (Mpa)

Testing Procedures to I.S. EN 196-1:2005	7 Days	28 Days	56 Days
Cement	47.6	58.0	x
50:50 - GGBS:Cement	36.7	62.2	x
Mininum Required	20.0	42.5	x
Activity Index	77 %	107 %	x
Mininum Required	45 %	70 %	x
70:30 - GGBS:Cement	29.1	x	63.0
Mininum Required	20.0	x	42.5

Initial Setting Time (Mins)

Requirement that GGBS setting time < twice cement setting time	GGBS:	170	Cement: 135

The results above are based on a GGBS composite sample and a cement spot sample taken in accordance with I.S. EN 196-7:2007. They confirm that it is permitted to use up to 70% GGBS in combination with this cement in concrete. The granulated blastfurnace slag used in production was cooled by rapid quenching in water - granulation.

APPENDIX B
Results – chloride binding isotherm

- Results from titration
- Chloride binding isotherm on logarithmic scale
- Details for comparison with literature

Results from titration

Table B.1 – Measured free chloride content and pH determined by titration for exposure to CaCl2 and NaCl

	OPC CaCl2				
Sample Name	Concentration [M]	Empty bottle [g]	Full bottle [g]	Free [mol/l]	pH
A1	2	11.722	45.870	1.477	11.76
A1	1	11.703	45.050	0.673	12.09
A1	0.5	11.763	47.901	0.284	12.31
A1	0.25	11.783	49.255	0.122	12.69
A1	0.125	11.750	47.558	0.054	12.91
A1	0.063	11.723	44.766	0.022	12.96
A1	0.031	11.784	44.305	0.009	13.01
A1	0	11.765	45.952	0.001	13.01
A2	2	11.760	44.652	1.471	11.74
A2	1	11.722	48.380	0.694	12.08
A2	0.5	11.820	46.724	0.289	12.29
A2	0.25	11.723	48.07	0.124	12.66
A2	0.125	11.707	46.222	0.055	12.88
A2	0.063	11.691	47.302	0.020	12.99
A2	0.031	11.765	45.652	0.009	13.00
A2	0	11.765	45.952	0.001	13.01
A3	2	11.767	45.302	1.463	11.74
A3	1	11.687	47.129	0.660	12.04
A3	0.5	11.814	46.082	0.290	12.30
A3	0.25	11.721	47.750	0.124	12.65
A3	0.125	11.765	46.036	0.054	12.88
A3	0.063	11.720	45.716	0.021	12.97
A3	0.031	11.680	46.937	0.009	13.01
A3	0	11.765	45.952	0.001	13.01

OPC-FA CaCl2					
Sample Name	Concentration [M]	Empty bottle [g]	Full bottle [g]	Free [mol/l]	pH
B1	2	11.783	45.878	1.338	11.66
B1	1	11.751	46.348	0.593	11.80
B1	0.5	11.765	45.603	0.256	12.15
B1	0.25	11.785	45.365	0.106	12.55
B1	0.125	11.764	45.354	0.042	12.78
B1	0.063	11.755	46.080	0.014	12.77
B1	0.031	11.733	46.861	0.005	12.92
B1	0	11.684	45.188	0.001	12.92
B2	2	11.815	44.954	1.389	11.68
B2	1	11.765	45.569	0.612	12.00
B2	0.5	11.752	45.394	0.254	12.21
B2	0.25	11.686	45.483	0.107	12.54
B2	0.125	11.731	44.266	0.043	12.78
B2	0.063	11.784	45.470	0.014	12.86
B2	0.031	11.753	44.099	0.0057	12.91
B2	0	11.684	45.188	0.001	12.92
B3	2	11.815	45.421	1.358	11.64
B3	1	11.723	45.772	0.599	11.96
B3	0.5	11.75	46.146	0.251	12.19
B3	0.25	11.75	45.986	0.105	12.55
B3	0.125	11.761	45.173	0.042	12.78
B3	0.063	11.814	46.057	0.014	12.89
B3	0.031	11.723	45.579	0.006	12.91
B3	0	11.684	45.188	0.001	12.92

OPC-slag CaCl2					
Sample Name	Concentration [M]	Empty bottle [g]	Full bottle [g]	Free [mol/l]	pH
C1	2	11.705	45.786	1.267	11.77
C1	1	11.723	47.110	0.516	12.00
C1	0.5	11.764	47.394	0.177	12.31
C1	0.25	11.784	46.141	0.065	12.60
C1	0.125	11.762	46.155	0.024	12.78
C1	0.063	11.686	46.504	0.010	12.82
C1	0.031	11.762	46.289	0.005	12.85
C1	0	11.752	45.446	0.001	12.82
C2	2	11.685	46.94	1.234	11.75
C2	1	11.764	46.465	0.492	12.02
C2	0.5	11.682	46.477	0.172	12.28
C2	0.25	11.761	47.399	0.063	12.60
C2	0.125	11.766	48.560	0.023	12.80
C2	0.063	11.761	45.834	0.011	12.82
C2	0.031	11.784	47.323	0.005	12.86
C2	0	11.752	45.446	0.001	12.82
C3	2	11.683	45.095	1.248	11.71
C3	1	11.723	45.806	0.504	11.97
C3	0.5	11.783	47.728	0.166	12.34
C3	0.25	11.760	47.597	0.064	12.61
C3	0.125	11.686	46.782	0.025	12.77
C3	0.063	11.763	46.393	0.011	12.83
C3	0.031	11.711	45.065	0.005	12.84
C3	0	11.752	45.446	0.001	12.82

OPC NaCl					
Sample Name	Concentration [M]	Empty bottle [g]	Full bottle [g]	Free [mol/l]	pH
A1	1	11.691	46.133	0.802	13.00
A1	0.5	11.813	46.888	0.366	13.06
A1	0.125	11.785	45.751	0.065	13.04
A1	0.031	11.764	47.077	0.010	12.82
A1	0			0.001	13.01
A2	1	11.761	45.888	0.805	13.00
A2	0.5	11.814	47.652	0.363	13.06
A2	0.125	11.710	44.430	0.066	13.04
A2	0.031	11.709	46.136	0.010	12.98
A2	0			0.001	13.01

OPC-FA NaCl					
Sample Name	Concentration [M]	Empty bottle [g]	Full bottle [g]	Free [mol/l]	pH
B1	1	11.764	45.276	0.765	12.86
B1	0.5	11.706	46.183	0.340	12.94
B1	0.125	11.684	45.655	0.054	13.00
B1	0.031	11.764	46.215	0.006	12.97
B1	0	11.684	45.188	0.001	12.92
B2	1	11.750	46.020	0.753	12.87
B3	0.5	11.786	44.878	0.345	12.93
B4	0.125	11.693	45.315	0.056	12.99
B5	0.031	11.722	46.948	0.006	12.97
B6	0	11.684	45.188	0.001	12.92

OPC-slag NaCl					
Sample Name	Concentration [M]	Empty bottle [g]	Full bottle [g]	Free [mol/l]	pH
C1	1	11.689	46.089	0.687	13.00
C1	0.5	11.683	46.829	0.285	13.03
C1	0.125	11.764	47.506	0.041	12.98
C1	0.031	11.707	45.215	0.006	12.90
C1	0			0.001	12.82
C2	1	11.752	47.069	0.673	13.01
C2	0.5	11.762	46.980	0.278	13.03
C2	0.125	11.704	45.269	0.039	12.96
C2	0.031	11.763	46.432	0.006	12.90
C2	0			0.001	12.82

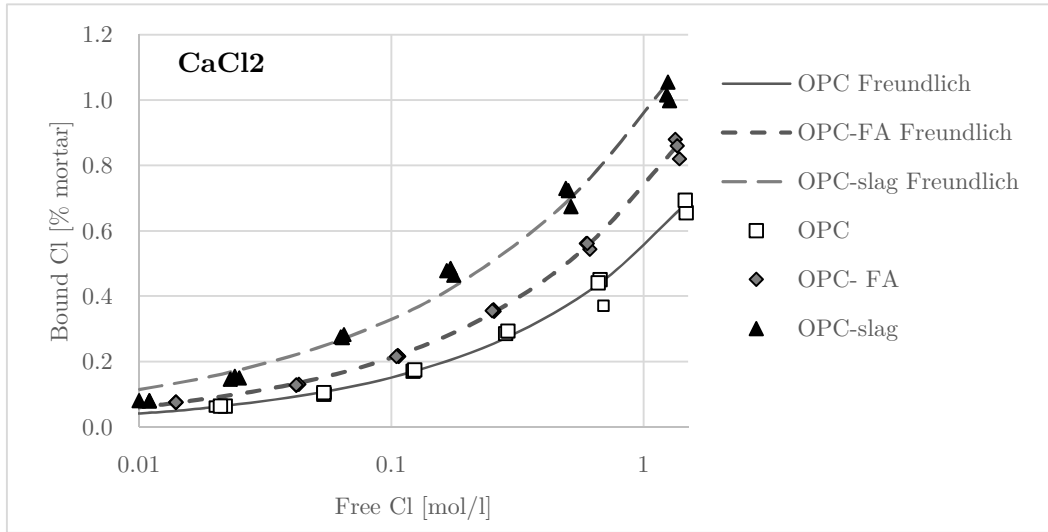# Chloride binding isotherm plotted on logarithmic scale

Figure B.1 - Chloride binding isotherm for OPC, OPC- FA and OPC- slag exposed to CaCl₂ plotted on a logarithmic scale
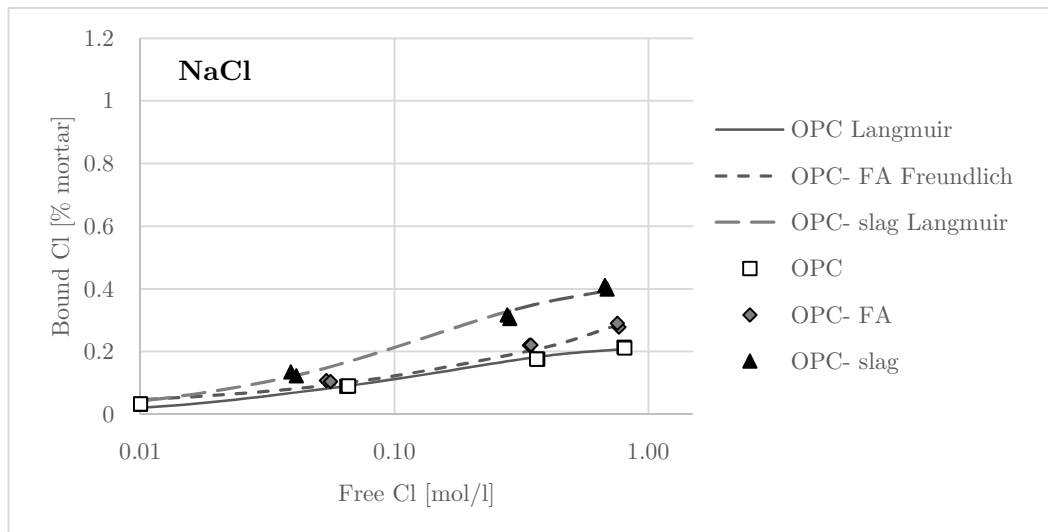
Figure B.2 - Chloride binding isotherm for OPC, OPC- FA and OPC- slag exposed to NaCl plotted on a logarithmic scale
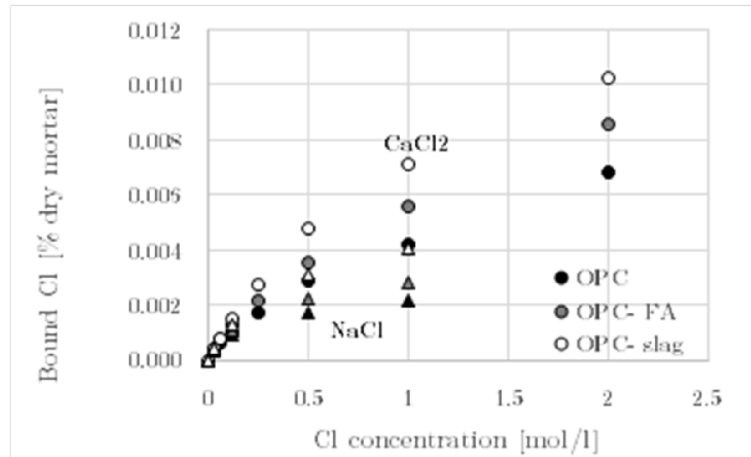
Figure B.3 - Chloride binding as a function of chloride concentration of exposure solution of NaCl and CaCl₂

Details for comparison

Table B.2 - Factors for conversion of units for comparison with literature

Mix	Factor
OPC	2.70 %
OPC- FA	2.83 %
OPC- slag	2.73 %
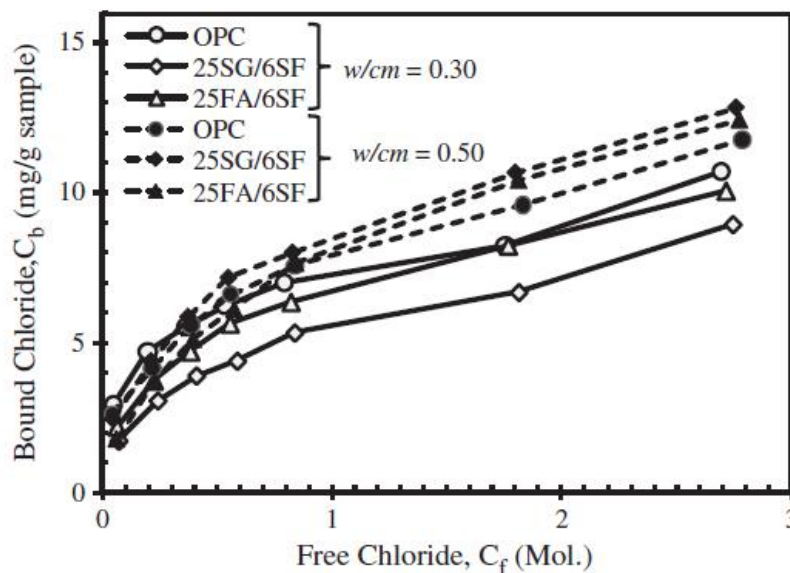
Figure B.4 - Chloride binding isotherms reported by Thomas et al. for ternary blends (w/c= 0.3 and 0.5, T = 23°C)
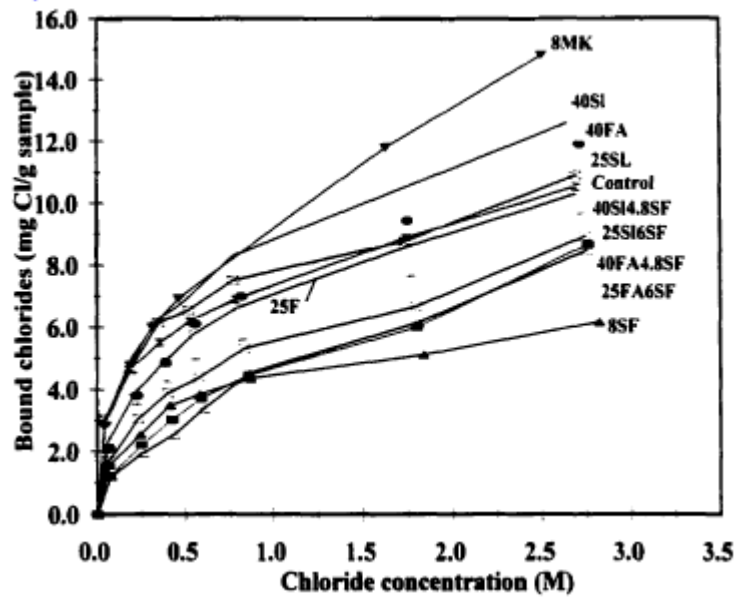
Figure B.5 - Chloride binding isotherms reported by Zibara (2001) with w/c= 0.3, T=23°C

Table B.3 – Summary of methods for the three studies used in the comparison

	Ytterdal (2014) [mg/g cement paste]	**Zibara (2001)** [mg/g cement paste]	**Thomas et al. (2012)** [mg/g cement paste]
Duration of exposure	3 months	6 months	6 weeks
Curing time	1 year	2-9 months	2 months
Powder/ disc	Powder of 35 g, 15 ml NaCl sol	Fragment of 25 g, 100 ml NaCl sol	Fragment of 25 g, 100 ml NaCl sol
Type of samples	Mortar	Cement paste	Cement paste

APPENDIX C
Results – chloride profile

- Results from titration
- Calculations of diffusion coefficient

Results from titration and lab experiment

Table C.1 – Measured total chloride content and weights of samples exposed to NaCl for 6 months

OPC Exposed to NaCl				
Sample Name	Depth [mm]	Weight beaker [g]	Sample [g]	Sample+beaker dry [g]	Cl concentration [% mortar]
AN22	0-1	76.4	1.94	78.31	0.639
	1-3	74.72	2.01	76.7	0.555
	3-5	73.31	2	75.3	0.430
	5-7	75.25	2.04	77.27	0.303
	7-9	82.11	3.02	85.08	0.187
	9-13	75.13	3.98	79.05	0.096
	13-17	76.37	4.03	-	-
AN23	0-1	58.98	1.98	60.92	0.620
	1-3	72.66	2.08	74.68	0.590
	3-5	82.01	2.04	84.01	0.452
	5-7	73.65	3.97	77.54	0.341
	7-9	73.13	3.97	77.03	0.238
	9-13	69.01	4	72.93	0.088
	13-17	75.71	4.01	79.65	0.039
AN24	0-1	68.06	2	70.02	0.597
	1-3	68.08	2.05	70.1	0.573
	3-5	67.71	2	69.67	0.446
	5-7	83.46	4	87.39	0.306
	7-9	68.14	4	72.08	0.208
	9-13	67.4	4.05	71.39	0.058
	13-17	76.01	4.05	79.99	0.023

OPC-FA Exposed to NaCl				
Sample Name	**Depth [mm]**	**Weight beaker [g]**	**Sample [g]**	**Sample+beaker dry [g]**	**Cl concentration [% mortar]**
	0-1	76.42	1.52	77.9	0.624
	1-3	74.72	1.98	76.66	0.613
	3-5	73.32	1.8	75.09	0.356
BN22	5-7	75.26	2.02	77.24	0.110
	7-9	82.12	1.75	83.84	0.048
	9-13	75.12	2	77.09	0.023
	13-17	76.36	2.02	78.35	0.014
	0-1	58.99	2.02	60.96	0.579
	1-3	72.66	2.01	74.62	0.648
	3-5	82.02	1.99	83.97	0.427
BN23	5-7	73.8	2.01	75.62	0.144
	7-9	73.13	4.01	77.06	0.079
	9-13	69.17	3.97	72.9	0.041
	13-17	75.72	4.02	79.65	0.017
	0-1	68.07	2.02	70.04	0.546
	1-3	68.09	2.02	70.05	0.663
	3-5	67.71	2.03	69.7	0.408
BN24	5-7	83.45	2	85.43	0.117
	7-9	68.14	4.01	72.08	0.031
	9-13	67.41	4.04	71.37	0.015
	13-17	76.02	4.08	80.02	0.009

OPC-slag Exposed to NaCl				
Sample Name	Depth [mm]	Weight beaker [g]	Sample [g]	Sample+beaker dry [g]	Cl concentration [% mortar]
CN25	0-1	66.7	1.54	68.2	0.746
	1-3	70.02	2	71.98	0.633
	3-5	67.65	2.02	69.62	0.318
	5-7	67.28	1.99	69.24	0.029
	7-9	68.91	1.99	70.84	0.008
	9-13	67.51	4	71.41	0.016
CN26	0-1	68.5	2	70.45	0.738
	1-3	68.24	2.04	70.22	0.785
	3-5	68.58	2.06	70.59	0.342
	5-7	66.87	3.93	70.72	0.104
	7-9	68.39	3.91	72.24	0.023
	9-13	66.71	4.05	70.67	0.009
CN27	0-1	66.8	1.97	68.73	0.689
	1-3	69.3	2.03	71.29	0.694
	3-5	80.07	2.02	82.04	0.333
	5-7	66.69	3.94	70.54	0.052
	7-9	67.71	4.02	71.64	0.015
	9-13	83.46	4.05	87.4	0.009

Calculation of chloride diffusion coefficient

Table C.2 - Diffusion coefficient calculated for OPC with C_i =0.005 and C_i =0.01

	OPC	
	$C_i = 0.005$	**$C_i = 0.01$**
C_s	0.7387	0.7365
D	$1.66 \cdot 10^{-12}$	$1.61 \cdot 10^{-12}$
r^2	0.9967	0.9962

Table C.3 - The aging factors chosen for calculations of chloride profiles after 30 years

	OPC	**OPC- FA**	**OPC- slag**
$\propto$	0.38	0.46	0.75