Master Thesis
Chloride ingress of carbonated blast furnace slag cement mortars

P.E. Holthuizen

Materials and Environment
Master Thesis

Chloride ingress of carbonated blast furnace slag cement mortars

by

P.E. Holthuizen

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H. De Vries, Rijkswaterstaat

An electronic version of this thesis is available at http://repository.tudelft.nl/.
Preface

I would like to start by saying what an great time it has been. From the moment of receiving my Bachelor degree at The Hague University, I started this new exciting journey at the TU Delft. I would like to share some words with you that pushed me through my study and my struggle through my MSc-thesis ending in this report you see before you:

*Ones more into the fray...*

*Into the last good fight I'll ever know.*

*Life and die on this day...*

*Life and die on this day...*

This master thesis is the result of the work performed during the past year, in order to obtain the Master of Science degree in Civil Engineering at the Technical University of Delft. The work contained herein was carried out in cooperation with the Microlab at the section of Materials and Environment, Faculty of Civil Engineering and Geosciences at Delft University of Technology.

Many people assisted in establishing the thesis, therefore I would like to express my gratitude.

First I would like to express my gratitude to my committee, consisting of Prof. dr. Rob Polder, Dr. Oğuzhan Çopuroğlu, MSc., Dr. ir. C. Van der Veen and H. De Vries.

I would like to thank the head of my graduation committee, Professor Rob Polder for his interest in the topic, his criticism and guidance throughout the project.

Furthermore also thanks to the other committee members, for their view on the topic. In order to increase relevance, I am grateful to Hans de Vries from Rijkswaterstaat together with Rob Polder for providing me with the Hattemerbroek case study.

Especially my daily supervisor must be greatly acknowledged, Oğuzhan Çopuroğlu. His enthusiasm, support, expertise and advice on the research have been of great help, both for the project aspects as for researching in general. He gave me an insight in what it takes to become a researcher for which I am very grateful.

For execution of the experiments the people of the Microlab and Stevin laboratory have been of great assistance, therefore thanks to: Arjan Thijssen, John van den Berg, Ger Nagtegaal and Paul Verhoeven. Last but definitely not least I would like to thank Maiko van Leeuwen who certainly was a great help during casting and performing multiple tests.

Other thanks goes to Martin Hunger from ENCI Heidelberg cement group for providing me with cement and multiple advises on my research.

As well I would like to thank all colleagues of the Materials and Environment section for the pleasant time and advises when I was stuck during my research.

And not forgetting I really would like to thank my amazing office mates who gave me a place to work and helped me continuously. Wenhao Guo thanks for the great laughs, although it was only for a short while. Stefan Chaves Figueiredo thanks for the amazing time and advises you gave me during my research and helping me to form my report. Marija Nedeljkovic thank you for your eternal patience with me, for helping me and not to forget our countless laughing moments.

Last but not least I would like to thank my friends, classmates and colleagues for their support, advice and good company which have been very motivating.

Finally I would like to express my gratitude to my parents and brother for supporting me during my education and their infinite believe in me.

PE. Holthuizen
Delft, June 2016
Abstract

In the Netherlands infrastructural works, such as bridges and overpasses, are generally constructed using blast furnace slag cement (BFSC) concretes, because of the relative high resistance against chloride penetration from de-icing salts. However, sheltered elements constructed in BFSC concrete are prone to carbonation, for example abutments and support beams. From the field investigation at the Hattemerbroek overpass, concrete damages were found at the abutments and attributed to chloride induced corrosion enhanced by carbonation.

This research focusses on the influence of carbonation on the chloride penetration resistance of BFSC mortars and the effect of slag content. For the influence of carbonation on chloride penetration resistance it is assumed that there is a sheltered carbonation period before exposure to chlorides, like an abutment exposed to chlorides after a joint starts to leak.

This research was needed since there are up to 2000 concrete structures like Hattemerbroek, executed in BFSC and prone to carbonation enhanced chloride induced corrosion.

In order to identify the influence of different slag contents (0-70%) on carbonation, chloride penetration resistance and their coupled effect, 12 slag cement blends were tested. For this research purpose the samples were subjected to accelerated carbonation at 3% CO₂ and 60-75% RH conditions.

For all cement blends the influence of carbonation on the pore structure and mineral composition was studied on cement pastes. Additionally, influence of carbonation on the chloride transport properties was investigated on mortars. Chloride penetration resistance was expressed by means of electrical resistivity and chloride diffusion coefficient determined from the RCM-test in accordance with NT Built 492.

Research shows that carbonation of slag cement mortars increases the porosity, consequently decreasing the chloride penetration resistance. A 70% slag sample with a relative high chloride penetration resistance before carbonation was found to have a significantly lower resistance after carbonation. The chloride penetration resistance is strongly dependent on the carbonation duration and its corresponding carbonation depth. Mortar specimens with a slag content between 35-55% carbonated before chloride exposure showed less influence of carbonation on the chloride penetration resistance.
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<th>Description</th>
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<tbody>
<tr>
<td>ASR</td>
<td>Alkali Silica Reaction</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BFSC</td>
<td>Blast Furnace Slag Cement</td>
</tr>
<tr>
<td>BFS</td>
<td>Blast Furnace Slag</td>
</tr>
<tr>
<td>CEM</td>
<td>Calcium Enriched Mixture</td>
</tr>
<tr>
<td>CEM-I</td>
<td>Portland cement</td>
</tr>
<tr>
<td>CEM III</td>
<td>Blast Furnace Slag Cement</td>
</tr>
<tr>
<td>CEM-III/B</td>
<td>Blast Furnace Slag Cement, slag content =±70%</td>
</tr>
<tr>
<td>CEN</td>
<td>European Committee for Standardization</td>
</tr>
<tr>
<td>DCMF</td>
<td>Design, Construct, Maintain and Finance</td>
</tr>
<tr>
<td>EC</td>
<td>EuroCode</td>
</tr>
<tr>
<td>EN</td>
<td>European Norm</td>
</tr>
<tr>
<td>MIP</td>
<td>Mercury Intrusion Porosimetry</td>
</tr>
<tr>
<td>NA</td>
<td>National Annex</td>
</tr>
<tr>
<td>NT</td>
<td>NordTest</td>
</tr>
<tr>
<td>OPC</td>
<td>Ordinary Portland Cement</td>
</tr>
<tr>
<td>PPL</td>
<td>Plain Polarized Light</td>
</tr>
<tr>
<td>RCM</td>
<td>Rapid Chloride Migration</td>
</tr>
<tr>
<td>RH</td>
<td>Relative Humidity</td>
</tr>
<tr>
<td>ROK</td>
<td>Richtlijn Onwerp Kunstwerken, Recommendation Design Structures</td>
</tr>
<tr>
<td>RWS</td>
<td>Rijkswaterstaat, Department of Waterways and Public Works</td>
</tr>
<tr>
<td>SL</td>
<td>Service Life</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>XC</td>
<td>Corrosion induced by carbonation, cyclic wet and dry</td>
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<tr>
<td>XD</td>
<td>Corrosion induced by chlorides other than from sea water, cyclic wet and dry</td>
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<td>w/c-ratio</td>
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<table>
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<td>CaCO₃, C.C</td>
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<td>Ca(OH)₂, C.H</td>
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<td>Calcium Oxide</td>
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<td>Carbon dioxide</td>
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<td>CO₃</td>
<td>Carbonate, Carbon trioxide</td>
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<td>CSH</td>
<td>Calcium Silica Hydrate</td>
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<tr>
<td>pH</td>
<td>numeric scale for alkalinity, power of hydrogen</td>
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<tr>
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<td>Carbonation diffusion coefficient</td>
</tr>
<tr>
<td>D&lt;sub&gt;cl&lt;/sub&gt;</td>
<td>Chloride diffusion coefficient</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
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<tr>
<td>kN</td>
<td>kilo Newtons</td>
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<td>Mega Pascal</td>
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<td>N</td>
<td>newton</td>
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General Introduction

For concrete structures exposed to aggressive environments durability is a major concern. There are numerous examples of infrastructural works, for instance the overpass at Hattemerbroek[47], which suffers from several damages within there structural life.

Approximately 50 % of the turnover of major construction companies is destined for repair and maintenance of existing structures, carrying a lot of economical risks. Securing a continuous infrastructure by maintaining functionality and safety makes Service Life predictions a national economical concern[41].

Due to the shift in contract-forms the building contractors become more and more responsible for designing and constructing durable civil engineering structures. For example DCMF-contract cause the contractor to be financial responsible for repairs and maintenance over a certain contractual period of time. Repairs are seen as a expensive necessity in order to satisfy the Service Life, therefore lifetime prediction are momentarily in demand.

Damage occurring after a period of time, aside from collision damage, are generally caused by concrete degradation mechanisms or other durability issues. In current design practise, Eurocode, concrete structures are designed by focussing on the governing durability issue, e.g. chloride induced reinforcement corrosion is predominant over carbonation induced corrosion.

However in practice not only the dominant degradation mechanism will occur, but there is a combined degradation with multiple mechanisms. Atmospheric carbon dioxide will always affect the structure and most likely influences the chloride penetration properties of concrete structures.

Since no combined degradation mechanisms are consider in the Eurocode design philosophy, this research focusses on a combined mechanism where carbonation occurs before chloride ingress exposure of blast furnace slag cement mortars.

1.1. Research background

One of the most occurring durability issues of a infrastructural reinforced concrete structure is reinforcement corrosion, since abutments, girders, support beams and columns all are possibly susceptible to reinforcement corrosion. Spalling of concrete cover or cracks in concrete due to reinforcement corrosion might be initiated by chloride ingress or carbonation. In the Eurocode different environmental classes are given so the designer can indicate the expected climate at a concrete structure as a standard class. The governing class will give the corresponding minimum concrete cover depth to the reinforcement that needs to be applied. In reinforcement corrosion inducing environment conditions this means that chloride induced corrosion, environmental class XD, is governing over carbonation induced corrosion(XC).

Degradation mechanisms can act simultaneously which is not taken into account in the current design philosophy, therefore additional research is required to investigate the influence of carbonation on chloride ingress. The frequent use of blast furnace slag cement in Dutch civil engineering structure is the main reason for focussing this research on blast furnace slag cement. It is still not clear what the influence of slag content is on chloride ingress of (un)carbonated blast furnace slag mortar, therefore this additional research is required.
1.2. Problem definition

Eurocode NEN-EN1992-1-1 deals with durability by selecting the governing Environmental Class with the corresponding minimal cover depth. CUR-guideline 1 is published as an addition to the Eurocode based on the DuraCrete program and gives insight in "Durability of concrete structure with regard to chloride induced corrosion". This guideline only considers chloride induced corrosion, because this is the main driving force for corrosion damage to concrete structures. The additional ROK-guideline imposed by the Dutch government requires the use of BFSC concretes with 50 to 70% slag, as this guideline refers amongst others to chloride induced corrosion environmental conditions. Although it is fair to say that reinforcement corrosion due to chloride ingress is more important than carbonation, a combination of these two corrosion initiation processes have not been taken into account in design procedures.

From field measurements it can be seen that chloride penetration and carbonation can occur simultaneously, which was the case for the concrete structure in Hattemerbroek. Apparently there are concrete elements which are susceptible to concrete degradation caused by multiple sources, which is not taken into account using the traditional design procedure. An example of combined degradation mechanisms is carbonation and chloride ingress, XD and XC environmental classes respectively. Bridge support beams are normally in sheltered conditions, ideally for carbonation. But during periods of frost a lot of de-icing salts are used on infrastructural structures. These salts will dissolve in water and will flow towards the joints. When these joints start to leak, due to creep or any other deformation de-icing salts can come in contact with carbonated concrete such as a support beam, see Figure 1.1.

1.3. Significance of the study

There already have been multiple studies published on the effect of carbonation on durability of OPC concrete, including chloride penetration resistance properties[12, 13, 15, 19, 28, 45]. Carbonation of OPC concretes decreases the porosity and therefore increase the chloride penetration resistance.

However in the Netherlands concrete structures are mainly constructed using slag cements, e.g. bridges and overpasses. The use of slag cements decreases the porosity of concrete, consequently increases the chloride penetration resistance. However it is expected that carbonation changes the transport properties of a BFSC concrete and therefore will influence the chloride diffusion into the concrete.

From field measurements, e.g. the Hattemerbroek overpass, it was observed that chloride penetration and carbonation can occur simultaneously on structures constructed with BFSC concrete. In the Netherlands there are more than 2000 structures similar to the Hattemerbroek overpass, hence BFSC concrete structure exposure to carbonation and chloride ingress. It can be seen that over time these structure might generate similar damage, due to reinforcement corrosion.

Using knowledge of combined carbonation and chloride ingress corrosion initiation for designing new structures damages due to this combined degradation mechanism might be prevented. The same mechanism can be applied on existing structures to predict potential damage.
1.4. Aim and objectives of this research

In this research the main priority is to get a better understanding of degradation due to a combination of carbonation and chloride ingress in slag cement pastes and mortars as a function of slag content.

If there is a mutual influence of both degradation mechanisms a range of slag content is investigate to obtain the longest remaining Service Life after a period of carbonation.

1.5. Primary research questions

What is the influence of carbonation on the chloride ingress of BFSC-mortars and the effect of slag content?

To answer this broad research question it can be divided in several sub questions.

1. What will happen to the strength development of blended cement mortars with changing blast furnace slag content?
2. Will the resistivity in mortar specimen change with a changing slag content?
3. Is there a difference in resistivity before and after carbonation of the blended cement mortars?
4. What is the influence of the slag content on the carbonation rate and carbonation depth?
5. Is there a difference in porosity of blended cement paste specimens after carbonation and what is the influence of slag contents?
6. If 100% of carbonation depth in a CEM III cement paste is reached when tested with phenolphthalein, is all calcium hydroxide then consumed too?
7. Are the chloride ingress properties of the blended blast furnace slag cement mortar different after carbonation and what is the influence of slag content?
8. Can the influence of the changing chloride diffusion coefficient be illustrated by means of the Service Life of a concrete structure?
9. Is there an optimum slag content for BFSC concrete structures prone to carbonation and chloride induced corrosion?

1.6. Hypothesis

In environmental conditions(XD, XS) where chloride ingress is governing for reinforcement corrosion BFSC concretes are generally advised. BFSC concretes have a denser cement matrix than OPC concretes, so chlorides will penetrate slower.

Structures in marine conditions, XS environmental classes, carbonation is very slow since the structure is most of the time wet and therefore neglected.

But for sheltered structural elements, e.g. abutments, in XD environmental conditions carbonation can occur prior to any chloride exposure. Therefore this research focusses on XD environmental conditions, with chloride from de-icing salts.

These sheltered elements are generally constructed with BFSC concrete too. However the carbonation rate of BFSC concretes is faster than of OPC concretes.

It is expected that carbonated mortar using a BFSC lead to an increase in porosity and permeability of the material. With a higher permeability and a more open pore structure chlorides will penetrate faster, which will lead to a shorter Service Life.

So, if less slag is used this is good against carbonation but bad against chloride ingress and vice versa. By considering these properties it is expected that there should be an optimal slag content with the highest...
chloride penetration resistance in carbonated and uncarbonated state. This hypothesis is illustrated in Figure 1.2 by means of the chloride diffusion coefficient ($D_{cl}$) of the material. Using more slag in uncarbonated material will result in a lower chloride diffusion coefficient, since the resistance against chloride penetration increases. However when slag containing cementitious material carbonate the porosity increases and the chloride diffusion coefficient will increase too, on the contrary carbonated OPC will decrease the chloride diffusion coefficient.

1.7. Assumptions, Limitations, Scope and Delimitations

- **One of the most important delimitations is that this research only focusses on blast furnace slag cement types.**
  This specific focus can be explained because it can be seen that in the Netherlands a lot of infrastructural structures are built by using slag cements in the concrete composition which is as well recommended in the ROK.

- **The research is limited to a range of 20-70% slag content and CEM I is used as an reference.**
  These blended cements will be self-mixed using CEM I and CEM III/B standard mixture.

- **Testing chloride ingress of carbonated specimens will only be done on mortar specimens.**
  Mortars are used to assure a more homogeneous mixture and to have one less uncertainty in the matrix.

- **Only a w/c-ratio of 0,5 is considered in order to reduce the scope of this research.**

- **Research is focussed on the influence of carbonation prior to chloride expore.**
  Wet-dry cycles (carbonation and chloride ingress cycles) are left out of the scope.

- **Carbonation of specimens will be done in controlled conditions in 3% CO$_2$-content.**
  Using the set-up available at the TU-Delft's Stevin laboratory.

- **Ø100x50 specimen will carbonate in order to be used in RCM-test set-up.**
  According to the NT Built 492.

- **Cement paste Ø50-30 samples will be carbonated in order to measure the influence of carbonation on a cement paste matrix for all cement blends.**

- **Curing of specimens will be done in a curing room in TU-Delft's Stevin laboratory.**
  With a temperature of 20°C and a RH of approximately 95%.

1.8. Outline of this thesis

Chapter 2 presents a literature study on concrete degradation mechanisms, namely carbonation and chloride ingress. In order to get a better understanding of the current gap in knowledge with regard to combined degradation the current design procedures are studied. Tests, such as X-ray diffraction analysis (XRD), thermogravimetric analysis (TGA), mercury intrusion porosimetry (MIP), rapid chloride migration (RCM)-test, are reviewed in order to obtain a better understanding of these tests before using them.

Chapters 3 and 4 focus is on execution and analysis of the tests. Chapter 3, the procedure of cement preparation with different slag content will be clarified. Tests and measuring methods discussed in chapter 2 will be elaborated further in chapter 3 and an explanation is given on the applied tests set-ups and materials. With the use of graphical and tabular impressions the test results will be presented in chapter 4.

A model incorporating partial carbonation in a chloride ingress model for blast furnace slag cement mortars is also discussed in chapter 4. This "two-layer" model of a carbonated and uncarbonated layer is only based on the remaining chloride penetration time after a period of carbonation.

Furthermore chapter 4 will be used to discuss the results and executed test procedures. Relation between the test results are sought and the proposed model will be elaborated on further.

Chapter 5 will present sound conclusions from observations during the research and an answer to the main research will be given.

Recommendations on future research or adjustment in the research are proposed in chapter 6.
Figure 1.3: Thesis outline
2 Literature Study

2.1. Carbonation induced corrosion

One of the many environmental phenomena that is known to significantly influence the durability of reinforced concrete structures is carbonation. Carbonation causes structural deterioration and therefore has a major influence on increasing the crack development and decreasing the durability. Carbonation is the reaction of hydration products dissolved in pore water with the carbon dioxide in the atmosphere, approximately 0.04% by volume of air [19].

The high pH of cementitious material will create a passive oxide film around the reinforcement. During carbonation the calcium baring phases are converted to calcium carbonate, leading to a reduction in pH of concrete pore solution from at least 12.5 to less then 9. The passive oxide film around steel reinforcement may be destroyed and develop uniform corrosion.

Carbonation can either have a positive or a negative effect on concrete durability, depending on the cement type. Portland cement, given the larger molar volume of carbonates compared to portlandite, seems to densify concrete surfaces and reduce porosity and permeability during carbonation. The amount of calcium hydroxide available in OPC is generally large enough to prevent the CSH itself being affected. On the other hand blast furnace slag cement seems to decrease in strength and increase the porosity, resulting in a more open microstructure. During the hydration process slag cements will already consume calcium hydroxide and produce secondary CSH. When all Ca(OH)$_2$ is consumed from the hydrated paste during carbonation CSH will liberate CaO which will also carbonate, depending on the porosity and moisture content[43]. The chemical reaction for carbonation of calcium baring bodies is as follows:

OPC:

$$H_2O + CO_2 \rightarrow H_2CO_3 \rightarrow Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + H_2O \tag{2.1}$$

BFSC:

$$H_2O + CO_2 \rightarrow H_2CO_3 \rightarrow CSH + H_2CO_3 \rightarrow CaCO_3 + H_2O + SiO_2.H_2O \tag{2.2}$$

2.1.1. Carbonation conditions

The rate of carbonation depends mainly on the relative humidity, the concentration of CO$_2$ and the temperature of the environment where concrete is placed[6]. RH has a major influence on the carbonation rate since carbonation only proceeds when the concrete is dry enough to allow carbon dioxide to ingress, however sufficient moisture should be present to allow the chemical reactions necessary for carbonation.

At a RH above 70% carbonation slows down due to the slower rate of diffusion of CO$_2$ through water filled pores. Carbonation only proceeds when the concrete is dry enough to allow the ingress of CO$_2$, but should not be too dry. In a relative humidity below 50% there is insufficient amount of moisture available to allow carbonation reactions to take place. The maximum level of carbonation if reached when the RH is between 50 and 70%[11].

The CO$_2$-level in the atmosphere is approximately 0.04% by volume. Carbonation is known to be a long-term reaction, therefore accelerated carbonation is desired for short term research purposes. The easiest way to accelerate the carbonation process is by increasing the CO$_2$ concentration, as according to Henry’s law the
concentration in pore water is directly related to the concentration in the pore air. The resistance against carbonation is a material property, therefore the resistance against accelerated carbonation is supposed to be similar to carbonation at ambient conditions[46].

2.1.2. Carbonation test set-up

An easily constructed accelerated test chamber which is suitable for evaluating the carbonation rate of mortar specimens, might offer a solution to reduce the carbonation time. There is little description in literature as to how to set-up a accelerated carbonation test, as there is no universal set-up considered as ideal. As indicated before there are several parameters that are adjustable in order to accelerate the carbonation process. To determine the best exposure condition for this accelerated carbonation process, other research test set-ups and parameters are reviewed.

For instance one of the set-ups for carbonation makes use of a so called Leeds apparatus. This apparatus can control 4 parameters: temperature, pressure, relative humidity and CO$_2$-concentration. During testing the RH and the temperature are kept constant are 65±5% and 20°C, respectively. The CO$_2$ concentration was slowly increased to 5% following a prescribed procedure. Concrete specimens at different curing ages and curing conditions were exposed for 2 weeks and afterwards the carbonation depth was measured using a pH indicator[6].

Another accelerated carbonation testing unit was built in house at University College Dublin (UCD) to determine the resistance to the diffusion of CO$_2$ into concrete specimens. The user is capable to set the desired temperature and CO$_2$ content, but the relative humidity is not controlled. Although experience with this set-up has shown that the RH will stay constant during testing. Sensors in the carbonation chamber will measure the CO$_2$ content, temperature and the relative humidity. The desirable conditions are CO$_2$ content of 5% and a temperature of 20°C, controlled via a control program connected to a CO$_2$ supply and an internal heater[9].

One practical chamber was described by Dhir and other with a sample capacity of 1.5 m$^3$. Two separate chambers constructed using 200 litre barrels are considered, for which one of them is the environment supply chamber. In this chamber the air is conditioned to a CO$_2$-concentration of 4%, relative humidity at 60±2% and temperature around 25°C. The relative humidity will be controlled with multiple pans of saturated salt solution (NaNO$_2$ and water). Temperature regulation will take place via a 250W heat lamp connected to a control loop. The chambers need to be isolated in order to limit the heat losses and stabilizing the temperature. The CO$_2$ content in the test atmosphere was created using compressed CO$_2$ gas supply, a CO$_2$-sensor and a control loop. The EN-13295 standard suggest to use a supply of 1% CO$_2$ in air as a premixed bottled form, but to shorten the test period a 4% CO$_2$-concentration was chosen[24].

The EN-13295 is a European Standard proposing an accelerated laboratory method for determining the resistance against carbon dioxide penetration through repair products and systems. The method is suitable for determining the carbonation in repair grouts, mortars and concretes without a protective coating. Samples are exposed to an atmosphere containing 1% CO$_2$ at a temperature of 21±2 °C and relative humidity of 60±10%. The concentration of 1% CO$_2$ in air develops the same reaction products with hydrated cement as a normal atmosphere at 0,04% CO$_2$. The relative humidity of 60 ±10% results in the fastest rate of carbonation

Figure 2.1: Accelerated carbonation test set-ups
(a) Proposed set-up by C.D. Atis
(b) Proposed set-up by Dhir et al and cited by P.E. McGrath
The TU Delft dispose of a box intended to obtain accelerated carbonation conditions and is similar to the carbonation chamber proposed by C.D. Atis[6]. A CO$_2$ cylinder is connected to the box and using a sensor the CO$_2$-level is maintained at approximately 3%. The RH in the carbonation is adjustable and obtained by adding water to a salt (NaCl) pan, maintaining a desired RH of 60±10%.

2.1.3. Carbonation indication
Carbon dioxide ingress in cementitious material takes place by means of diffusion according to Fick's Law and will generally be modelled as a jump change of CO$_2$-concentration in this zone[46]. This carbonation front may be recognized in the field by presence of a discoloured zone in the surface, but this light gray discoloration might be difficult to recognize. The traditional method of determining the carbonation depth by visual inspection is spraying a phenolphthalein indicator, a known pH indicator, onto the surface of freshly broken concrete which has been cleaned of dust and loose particles. Phenolphthalein is prepared as a 1% solution in 70% ethyl alcohol and 30% distilled of deionised water[34]. Normal concrete pore solution is alkali containing K$^+$ and Na$^{2+}$-ions giving concrete the typical pH of 13 to 14. The colourless base indicator will turn magenta if the pH is above 9 (alkaline). The colourless region will indicate carbonated concrete, because the process of carbonation will decrease the pH of the pore solution below 9. The average depth is measured over multiple points perpendicular to the edges of the split face[8, 33].

In confirmation of this visual inspection, optical microscopy using thin sections or scanning electron microscopy using polished sections show carbonation effects at greater depths than indicated by phenolphthalein indicator. Nevertheless, this test is quick, easy, widely used and very useful as a means of making an initial assessment[48].

Other methods for studying carbonation but less widely used are TGA and XRD, as carbonation of cementitious material can be generalized as the consumption of calcium hydroxide and the formation of calcium carbonate.

Thermogravimetric analysis (TGA) is a method for determining the chemical composition of cementitious materials by measuring the change in mass by thermal decomposition. The thermal decomposition is analysed by plotting the temperature as a function of mass loss, obtaining thermogravimetric curves (TG-curves). The mass losses can provide information regarding the dehydration of Ca(OH)$_2$ and thermal decomposition of CaCO$_3$ of calcium bearing phases. For TGA a powder sample is required and 30-50 mg is placed in a small holder, otherwise known as a crucible, and the temperature will increase from room temperature to 1000°C at a rate of 10 or 20°C/min.

![Figure 2.2: Example of TG and DTG-curves][16]

To analyse the thermal effects in the cement paste, one have to study the TG-curve and the DTG-curve (first derivative of the TG-curve). The DTG curves have marked inflexion points and plateaus, features that are not present in the TGA curves. Therefore, DTG curve better marks all different processes than its primitive, the TG-curve. A change in TG slope is reflected as a peak in DTG, as can be seen in Figure 2.2.

Figure 2.2 shows an example of the TG and DTG curve as could be found for a cementitious material. These curves show some characteristics at specific temperatures[23].
1. 180–300 °C: weight loss due to loss of bound water by dehydration of several hydrates (CSH, carboaluminate, ettringite, etc.)

2. 450–530 °C: dehydration of the portlandite (calcium hydroxide)

3. 700–900 °C: decarbonation of calcium carbonate

Decarbonation of calcium carbonate can be divided into two categories that can be distinguished using TGA and XRD.

Carbonation of calcium hydroxide will form a well-crystallized form of CaCO$_3$ and decomposes in a temperature range of 760-900 °C, known as calcite.

On the other hand, carbonation of CSH-gel will lead to the formation of vaterite, a meta-stable type of calcium carbonate with imperfect crystallinity. From TGA this calcium carbonate form can be indicated from a mass loss at a temperature range of 530-760 °C [16].

Another analytical technique in material characterisation is X-ray diffraction (XRD). XRD is commonly used in characterisation of crystalline and fine grained materials, such as cements. Appropriate executed XRD-analysis of cement paste will give reliable qualitative and quantitative data of crystal structural phases. XRD technique is mostly used in qualitative, phase identification and quantitative phase analysis. The XRD-analysis for this research purpose can therefore being used to verify the presence of multiple calcium carbonate phases. To verify the identification of calcium carbonate phases in TGA a qualitative XRD-analysis is sufficient.

X-rays are generated when electrons produced by heating up a copper filament are accelerated by applying a voltage are bombarding a target material, such as copper. When the electrons have sufficient energy when hitting the electrons of the target materials a characteristic X-ray spectra is produced [7]. Diffraction of X-rays by crystalline material will produce an XRD pattern. The pattern consist of peaks of varying intensities at characteristic diffraction angles. XRD-analysis produces patterns that characterise different crystal structures and enable identifying their presence in the material by peak position and relative intensities. Qualitative analysis is based on comparison of peaks in measured XRD pattern to a database, containing peak patterns of known phases. The XRD software will indicate candidate patterns of which the user needs to interpret whether these phases might be present [21].

For solely indicating the carbonated zone in cementitious materials, visual inspection by phenolphthalein indicator would suffice. However if more information regarding the change in chemical composition or “degree of carbonation” is required, additional TGA and XRD-analysis are recommended.

2.1.4. Property consequences

Cement-based materials, such as concretes and mortars, are known to be heterogeneous materials, composed of aggregates and a binding hardened cement paste that holds all the aggregates in place. The properties of the binder is important for the performance of the mortar or concrete as a whole. Carbonation is the chemical reaction that takes place between carbon dioxide and portlandite or CSH, which both is present in hydrated cement. The basic factor influencing carbonation is the diffusivity of the hardened cement paste. The type and amount of cement, porosity of the material and time of curing are on their turn influencing the diffusion rate. Hydrated cement is known to be a porous material with a large range of pore sizes, e.a. gel pores and capillary pores. Especially the amount of pores and connectivity is important, because it strongly affects the material resistance to harmful penetrants [19].

During this research 12 cements are studied, with a slag content varying from 0% until 70%. From each cement a carbonated and uncarbonated specimen will be tested, in order to indicate the influence of slag
2.2. Chloride induced corrosion

An important basis for durability design of concrete structures is chloride ingress, which is a common cause for concrete deterioration. Chloride ions from de-icing salts are the primary cause of reinforcement corrosion in infrastructural structures. Chloride ions are transported through the concrete pore network and microcracks via a variety of mechanisms causing depassivation of the oxide film covering the reinforcement steel. Mechanisms for chloride penetration in crack-free concrete are for instant capillary absorption, hydrostatic pressure and the predominant diffusion. Chloride-induced depassivation of steel reinforcement leads to accelerated corrosion and through expansion disrupts the concrete. The ingress of chloride ions into concrete strongly depends on the internal pore structure which in turn is dependent on mix design, degree of hydration, curing conditions and use of supplementary cementitious materials[40].

Incorporating supplementary cementitious materials (SCM), such as fly ash and blast furnace slag, into the cement in order to increase the durability of concrete structures is already an established method. Blast furnace slag cement has a slower hydration time and will, by forming secondary CSH, be more dense than CEM I. Chloride ingress in CEM III cement is more difficult now and therefore generally prescribed in chloride induced corrosive environments because of this property.

However as mentioned in section 2.1 it can be seen that the resistance against carbonation are the other way around. As carbonation and chloride ingress can occur simultaneously it is important to investigate the chloride ingress properties of carbonated and uncarbonated specimens.

2.2.1. Chloride immersion test

An chloride immersion experiment described in Nordtest Method NT Built 443 and intended for long-term ponding. Test specimens with a diameter of 75mm and a minimum height of 100mm should be older than 28 days maturity, free of cavities and visible cracks. The sample with a freshly cut surface end is immersed (one plane only) in a 165 g NaCl/L chloride solution for 100 days at a constant temperature of 20°C. All other...
non exposed, surfaces are then dried at room temperature. At the end of the period the exposed surface to the chloride solution is then ground and powders is collected. The chloride content of the powders will be determined by the Volhard titration according to NT Built 208[25, 38].

Similar to the NT Built 443, the European Standards specifies in the EN-13396 a method for determining the resistance to chloride ion penetration of hardened cement or mortar samples. To minimise the chloride uptake by absorption the samples will be saturated under vacuum. The chloride ingress will be accelerated by immersing the cylindrical specimen in a 3% NaCl chloride solution. After the testing period the chloride content is determined at three depths from the exposure surface in compliance with the EN-14629 [29].

2.2.2. Chloride migration test

Immersion tests are seen to be a realistic representation of natural diffusion, however the disadvantage is that testing requires a lot of time. Instead of accelerating the chloride penetration by increasing the chloride concentration under natural diffusion one can use migration of ions driven by a electric field. The CHLORTEST research program has shown a good correlation between results from chloride diffusion experiments and chloride migration experiments[17].

The Nordtest method NT Built 492 prescribes another procedure for determining the chloride migration coefficient in concrete, mortar or cement paste. This method will require a cylindrical specimen with a diameter of 100 mm and a thickness of 50 mm. Before subjecting the test specimens to the RCM-test they will be saturated under vacuum in a Ca(OH)\(_2\) solution, to minimise the chloride uptake by absorption during testing. A reservoir needs to be filled with approximately 12 litre of 10% NaCl solution, which becomes a catholyte reservoir after applying a current. The specimens provided with a rubber sleeve secured with clamps will be placed on an inclined plastic supports in this catholyte reservoir under an angle of 32 degrees. The sleeve above the specimen is filled with 300 millilitre 0.3 molar NaOH solution, the anolyte solution. Immerse the anode in the anolyte solution and connect both the anode and cathode to the power source. An electrical potential, with the voltage preset of 30 V, is applied axially across the specimen forcing the chloride ions outside to migrate into the specimen. The voltage might need to be adjusted dependent on the initial current through the specimens at the preset voltage of 30 V. After a certain test duration, also dependent on the initial current through the specimen, the specimen is terminated and taken out of the test set-up. All samples are then rinsed with water, to remove all residual chloride solution. Then the specimens are split axially and inspected visually[26].

One of the easiest ways to identify the chloride penetration depth is by visual inspection as indicated in the NT Built 492. After the specimen is split axially it will be sprayed with a 0.1M silver nitrate solution. By spraying silver nitrate on the freshly broken surface a white silver chloride precipitation will be visible after about 15 minutes. The chloride penetration depth can be measured from the precipitation depth using a ruler. Seven measurements needs to be taken from the centre to both edges at intervals of 10 mm. Using this depth a chloride migration coefficient can be calculate afterwards[26].

![Figure 2.5: Rapid Chloride Migration test setup](From Nordtest method NT Built 492)
2.2.3. Electrical resistivity
One of the ways of indirectly measuring the corrosion rate of steel is by measuring the electrical resistivity of concrete. Electrical resistivity of concrete can be related to corrosion initiation and propagation. It has been proven that there is an inverse correlation between concrete electrical resistivity and chloride diffusion rate.

Concrete is conductive due to the presence of water in the capillary pores, which contains dissolved ions and will act as an electrolyte. More pore water or a higher amount and wider pores, due to a higher w/c-ratio, cause a lower resistivity. Resistivity of concrete is related to the susceptibility of chloride penetration, namely low concrete resistivity is related to rapid chloride penetration and a high corrosion rate. As mentioned before blast furnace slag brings about the pozzolanic reaction and will increase the cohesiveness of paste at early age, therefore increase the resistivity of concrete and is more beneficial than OPC in the presence of chloride ions. Beside the pozzolanic reaction the resistivity can be increased by a lower w/c-ratio and longer curing hydration too.

Concrete resistivity that describes the electrical resistance can be non-destructively measured as the ratio between applied voltage and resulting current through at least two electrodes. Measuring the resistivity can be done by using two electrodes placed on the two opposing concrete surfaces. A normal resistance meter should apply a sinusoidal current of frequencies between 50 Hz and 1kHz. Each electrode should make contact with the concrete surface via a conducting electrolyte, usually a wetted sponge. Specimens that are taken directly from a fog room should be exposed to dry air for 10 minutes to an hour, in order to evaporate the water film on the surface. Resistivity is obtained by multiplying the ratio between voltage and current, otherwise known as resistance, with a conversion factor. Since the resistance measurement is executed with two plates a geometrically calculated constant (area/length) is used as the conversion factor for calculating the resistivity[19, 39].

2.3. Design procedures
In current practice a concrete structure is designed by using the so called design codes. Currently it is mandatory to use the Eurocode (EC) if designing a European public work, additionally each country may use there own national annex[2]. Besides these design codes there are also client specific recommendations and guidelines which may be of use during designing a concrete structure. As an example Netherlands largest client for infrastructural works, RWS, has decide to write the ROK recommendation containing some additional requirements on top of the Eurocode to realize a structure more suitable to their specific demands.

In this part of the literature survey the current design procedures are studied, involving the Eurocode and client specific recommendations such as the ROK and CUR-guidelines. It will be investigated how each code or recommendation deals with durability of concrete structures. How will they deal with carbonation and chloride ingress separately and if there is a way to deal with a combined degradation of carbonation and chloride ingress. And what are the most important requirements that should be taken into account during this research and during the case study.

2.3.1. Eurocode
NEN-EN1992-1-1 is concerned with the requirements for resistance, serviceability, durability and fire resistance, therefore a complete section is dedicated to durability.[30]

In section 4 "Durability and Cover to reinforcement" of NEN-EN1992-1-1 several requirements are stated in order to design a durable structure which shall meet the required strength throughout its design working life. The required protection of the structure depends on use, design working life, maintenance programs and actions. Both degradation mechanisms, carbonation and chloride ingress, are causes for reinforcement corrosion. Corrosion protection of reinforcement depends on cracking, concrete cover density, quality and thickness.

Concrete density and quality will control the maximum w/c-ratio and minimum cement content, according to NEN-EN206-1. In addition to the mechanical actions the structure can be exposed to chemical and physical actions. In design phase the environmental conditions will be classified based on the NEN-EN
206-1. The NEN-EN206-1 introduces 6 different exposure classes:

- **XO** - No risk of corrosion or attack
- **XC** - Corrosion induced by carbonation
- **XD** - Corrosion induced by chlorides other than from sea water
- **XS** - Corrosion induced by chlorides from sea water
- **XF** - Freeze/thaw attack with or without de-icing agents
- **XA** - Chemical attack

From this classification it can be seen that the exposure classes of corrosion induced by carbonation or chlorides from de-icing salts are XC and XD, respectively.

If we consider the reference project, Hattemerbroek, the structure is in an environment in which both carbonation and chloride ingress exist. Parts of reinforced concrete that are exposed to spray containing chlorides (including de-icing salts) and are cyclic wet and dry are classified as XD3. When a reinforced concrete surface is exposed to air and subject to water contact it is classified as XC4. Table F.1 of NEN-EN206-1 prescribes the maximum w/c-ratio and minimum cement content, for the Hattemerbroek case this is summarised in Table 2.1.

Table 2.1: Recommended value for concrete compositions

<table>
<thead>
<tr>
<th>Exposure class</th>
<th>maximum w/c-ratio</th>
<th>minimum cement content [kg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>XD3</td>
<td>0.45</td>
<td>320</td>
</tr>
<tr>
<td>XC4</td>
<td>0.50</td>
<td>300</td>
</tr>
</tbody>
</table>

Besides the recommendation regarding the concrete composition, NEN-EN1992-1-1 prescribes using Table 4.3N and 4.4N a minimal required cover depth. The minimal concrete cover depends on the exposure classes, structural classes and the design criterion, such as design working life of 100 years. Reflecting on the Hattemerbroek case, XD exposure class gives the largest minimum cover depth. If multiple exposure classes occur the EC prescribes to use the exposure class which provides the largest cover depth in order to make sure that both degradation mechanisms do not lead to reinforcement corrosion. In case of Hattemerbroek, as for most other cases, chloride induced corrosion requires a larger cover depth than carbonation induced corrosion and is therefore seen as the governing exposure class.

The degradation due to corrosion induced by carbonation and chloride ingress can occur simultaneously but their influence on each other is not regarded or taken into account in the NEN-206-1 or NEN-EN1992-1-1.

### 2.3.2. CUR-1 guideline

The "CUR-1-Durability of concrete structures concerning chloride induced reinforcement corrosion" aims to bring clear structure in the durability approach for reinforced concrete structures subjected to chloride induced reinforcement corrosion. Due to the new contract forms, such as DCMF-contracts, designers step aside from the "deemed to satisfy-method" which creates more freedom to innovate for contractors. But if contractors would like to use alternative concrete compositions this cannot be checked using the EC requirements, therefore the CUR-1 recommendation was necessary as an new method of Service Life design. This recommendation is applicable for the design of reinforced concrete structures which are exposed to XD or XS exposure classes for a desired Service Life of 80 years or more. In order to apply this recommendation the design should satisfy several design codes too, such as the EC-2 and EN-206-1. It makes it possible to formulate, in deliberation with the client, custom made requirements regarding the durability of concrete structures subjected to chloride induced reinforcement corrosion. The EN-206-1 is still applicable in full, although Service Life has not been clearly explained. The Eurocode 2 contains a requirement regarding 100 years Service Life of concrete structures in XD and XS exposure classes, without distinguishing the performances of different binders. The CUR-1 anticipated in context of the EN-206’s alternative performance design method to identify cement type performances with respect to chloride ingress.
One of the starting points of the recommendation is the DuraCrete method for durability. Boundary conditions in form of requirements of existing guidelines exclude the lack of durability as a result of carbonation. General idea is that if reinforced concrete complies to the relevant concrete regulations carbonation induced corrosion generally will not occur. Other degradation mechanisms are outside the scope of this CUR-1 recommendation.

Designing concrete cover and concrete composition the required Service Life and exposure class(es) need to be known beforehand. Based on these data the minimum concrete cover and maximum chloride diffusion resistance ($D_{RCM}$ based on NT Built 492 test), where different types of binders are distinguished, can be determined. DuraCrete developed an chloride diffusion equation depending on time. Using the diffusion coefficient, required Service Life and the applied cover depth it is possible to calculate whether the critical chloride content at the level of reinforcement is exceeded over the life time of a concrete structure or not.

A concrete structure, such as Hattermernbroek, hypothetically designed using the CUR-1 guideline only takes the XD exposure class into account. As mentioned before the CUR-1 assumes that if the concrete mixture complies with the requirements of the Eurocode that carbonation will not influences the durability.

### 2.3.3. ROK recommendation

The ROK is a collection of special requirements which the design of a new concrete structure for RWS should satisfy. As an addition to the EC’s and its national annexes (NA’s) RWS has some more specific requirements, because the government found some of the requirements in the EC’s not strict enough or they do not even exist. With this ROK recommendation RWS hopes to give one clear guideline for designing new structures. [44]

The ROK also refers to other recommendations and guidelines as an addition to the EC’s, e.g. CUR-guidelines, CROW-guidelines and RWS-guidelines. If contradictory in the collection of binding codes, guidelines and recommendation should occur, they should be reckoned with using the following order:

1. Contractual requirements
2. ROK recommendations
3. RWS guidelines
4. EC’s + NA’s + CUR-recommendations + CROW-documents

One can see that the ROK-recommendations are governing over the EC requirements, if contradictory. The ROK does not have another way of dealing with durability issues than the EC. For exposure classes of concrete structures the ROK refers to the EN-206-1, just as the EC. However an additional requirement is that it is no longer permitted to use an alternative design rule deviating from the prescribed minimum cover depth. Herewith, among other things, the use of the CUR-1 is not permitted. For some locations it is prescribed to increase the cover depth, such as locations difficult to inspect. On the other hand it is allowed to decrease the cover depth for concrete structures in an exposure class XD and XC if following requirements are satisfied:

- w/c-ratio less or equal to 0.45
- 2/3 times the largest grain size is not larger than the cover depth.

The ROK specifies requirements concerning the cement type in order to deal with durability issues for concrete strength classes up to C55/67. RWS demands the use of blast furnace slag cement (CEM III) with a slag content $>50\%$ or portland flyash cement (CEM II-B-V) with a fly ash content $>25\%$

At the root of these requirement concerning the cement composition are the following arguments:

- The given cement choice concerns the option from the CUR-recommendation 89 to prevent the damaging effects of ASR and gives with most certainty that the damaging effects of ASR will not occur during the expected service lifetime of the structure.
- With a good execution the given cement choice will result in a dense concrete which will limit chloride, alkaline and other aggressive substances ingress to a small depth, therefore will not cause reinforcement corrosion.
- For a dense concrete as considered above assuming a good execution carbonation will be limited as well.
• The prescribed cement choice will limit the use of Portland clinker and therefore decrease the CO$_2$ emission during the cement production.

From these arguments it may be concluded that deleterious ASR will not occur when a BFSC with a slag content $>$50% is used. Besides it is also the best cement choice for environments in which chloride induced or carbonation induced corrosion are potential degradation mechanisms.

If we reflect this on the Hattemerbroek case in which exposure classes XD3 and XC4 both occur, nothing is changed in the maximum w/c-ratio and minimum cement content if we compare it with the EC. The ROK only gives additional requirements, if necessary. In these situations the EC is still binding, therefore Table 2.1 is still normative. However the ROK does demand the use of at least 50% amount of blast furnace slag cement or 25% fly ash cement.

This research on combined degradation mechanisms of carbonation and chloride ingress might indicate a lower "optimal" range of slag content than by the ROK minimal prescribed slag content of 50%.

2.4. Reflecting on Hattemerbroek damage investigation

In order to gain a better insight in the consequences of combined degradation damages a reference project is reviewed. RWS provides a case study regarding a concrete overpass in Hattemerbroek. It has been built in 1976 and is 40 years old, see Figure 2.7. With visual inspection of the structure a clear blue coloured concrete was found, it is therefore concluded that blast furnace slag cement (CEM III) was used. During inspection a lot of damage has been found in girders, columns, support beams and abutments as indicated in Figure 2.7. To investigate whether these damages are caused by chloride induced corrosion, a advanced technical inspection has been conducted. This inspection focussed on corrosion damages and gaining information about the remaining durability of the structure subjected to carbonation and chloride induced corrosion\[47\].

To assess whether damages occur due to carbonation, cover depth and carbonation depth measurement have been conducted on abutments, girders, columns and support beams. Cover depth measurement show that most of the location do not satisfy the requirement of the present design codes. The carbonation depth is approximately equal to the cover depth, therefore there is a real chance of local damages due to carbonation induced corrosion.

Chloride induced corrosion can be indicated by measuring the chloride concentration and check whether this exceed a certain threshold, for example 0.4% chloride concentration related to cement mass.

Most abutments, girders, support beams and columns contain a high amount of chloride, therefore more damages is expected in the future due to these elevated chloride concentrations.

It has been found that the occurring damages in abutments, support beams and columns are the result of chloride induced corrosion enhanced by carbonation and damages to the main girders are due to chloride ingress only. Despite uncertainties in measurements for the main girders, the conclusion is found to be a reasonable explanation for the occurring damage especially since the carbonation depth is very low.

After reading the technical report it is still unclear what the enhancing factor of carbonation on chloride ingress is, which is introduced in the conclusion. From measurements it could be concluded that both degradation mechanisms are present in excessive form. Research into this combined behaviour should give more insight in the mechanisms of the found damages.
2.4. Reflecting on Hattemerbroek damage investigation

Figure 2.7: Hattemerbroek overpass including observed damage
(a) Hattemerbroek overpass
(b) Damaged abutment by reinforcement corrosion[47]
Experimental program

In this research the influence of slag content on carbonation and chloride ingress is investigated on blended cements with slag contents in the range of 20-70% and a CEM I (0% slag) cement is used as a reference sample. The material choice and mixing procedure for these blended cements is explained in section 3.1.

For each cement blend the mechanical properties are tested using compressive and flexural tensile strength test, as will be clarified in section 3.2. Beside the cured specimens and stored in the curing room before testing, carbonated specimens are required as well. The carbonation set-up and testing conditions are explained in section 3.3.

After carbonation, multiple tests are performed at different specimens. To characterise the mineral composition of all blended cements, carbonated or uncarbonated, TGA and XRD-analysis is used. Specimen preparation, test equipment and the test procedure is evaluated in sections 3.4 and 3.5.

MIP is used to identify changes in the porosity before and after carbonation for all cement paste samples with different slag contents. The preparation of the samples and used test set-up is explained in section 3.6.

The resistivity measurement is a non destructive quick test and will give an indication for susceptibility of the specimen to chloride penetration. Section 3.7 will clarify the use of this resistivity measurements by means of the two-electrode method.

The RCM-test is described in section 3.8 for a fast chloride diffusion test, as diffusion is the governing transport phenomenon for chloride penetration into cementitious materials.

3.1. Material and sample preparation

In cooperation with ENCI cements with different slag content are prepared. The choice for cement types to prepare the blended cements, was either to match the finenesses or the 28 day strengths of the cements. As fineness is an indication for the hydration rate of the cement it can influence the strength development. It is suggested that the 28-days compressive strength is a better criterion for comparing the performance of cements instead of fineness. The use of CEM I 42,5N and CEM III/B 42,5N, delivered by ENCI, provides almost the same 28-days compressive strength for both mixtures. Product information and chemical analysis of CEM I 42,5N and CEM III/B 42,5N cements can be found in Appendix A.

In order to obtain a blended cement with for instance 30% slag content the CEM I (0% slag) and CEM III/B (70% slag) need to mixed in the right proportions, for which an example calculation can be found below.

Example calculation blended cement mix design; 30% slag:

\[
\begin{align*}
\text{30/70} & \times 100 = 42.9\% \text{CEM III/B} \\
100 - 42.9 & = 57.1\% \text{CEM I} \\
\rho_{\text{mean}} & = 3130 \times 0.571 + 2940 \times 0.429 = 3048.6\text{[kg/m}^3]\end{align*}
\]

A standard mortar consists of 1350 gr aggregates, 450 gr cement and 225 gr water. (w/c-ratio = 0.5)

Expressing them in volume:
Ag g r e g a t e: \( \text{mass/density} > 1.35 \text{[kg]/2600[kg/m}^3 \] = 0.000519[m}^3 \]
C e m e n t: \( \text{mass/density} > 0.45 \text{[kg]/3048.6[kg/m}^3 \] = 0.0001476[m}^3 \]
W a t e r: \( \text{mass/density} > 0.225 \text{[kg]/1000[kg/m}^3 \] = 0.000225[m}^3 \]

Expressing in percentage of total volume:
Ag g r e g a t e: 58.22%
C e m e n t: 16.55%
W a t e r: 25.23%

Total required cement volume can be calculated from the total volume of moulds and multiplied with the percentage. The required weight CEM I and CEM III/B cement can now be back calculated:

\[
\begin{align*}
\text{CEM I: Total volume} \times \%_{\text{CEMI}} \times \rho_{\text{CEMI}} &= 1.622 \text{kg} \\
\text{CEM III – B: Total volume} \times \%_{\text{CEMIII}} \times \rho_{\text{CEMIII}} &= 1.143 \text{kg}
\end{align*}
\]

The in calculated cement weights for CEM I and CEM III/B cements for each blended cement is distributed by weight in a 10 litre bucket, which will not fill the complete bucket. The remaining space in the bucket is necessary in the mixing process of both powders. The bucket is placed in a paint mixing machine as shown in Figure 3.1, tightened and shaken for at least three minutes. Afterwards the blended cement powder is transferred in another bucket and stored until casting.

The mixing procedure of cement powder to make blended cement mixture in this research is not a widely used approach. Therefore it is necessary to check whether the mixing has been performed sufficiently, by checking the homogeneity of the mixture. The downside of mixing with a paint mixer is cluster formation of slag particles, since this was not observed it is assumed that the cement powder has a good homogeneity. In Figure 3.2 a microscopy image is made of the blended cement using different lighting techniques.

On the left plain polarized lighting is used and on the right side the same image is observed in cross polarized light. As no accumulation of slag particles in both pictures were observed, it is concluded that the mixture is mixed sufficient.
3.2. Strength development tests

Standard mortar should consist, as shown in the example calculation, of 1350 gr sand, 450 gr cement and 225 gr water which corresponds to a w/c-ratio of 0.5.

If design code are considered and relate mix design to durability classes, then the w/c-ratio is 0.5 and 0.45 for XC and XD respectively. However a w/c-ratio of 0.45 is ideal for XD, but against formwork or on top of fresh concrete surfaces the w/c-ratio if always a bit higher. From product information of CEM I and CEM III/B cements it was found that the 28-days compressive strength is almost equal at a w/c-ratio of 0.5 [4]. To limit the research scope only cement pastes and mortar samples with a w/c-ratio of 0.5 are tested.

Preparation of cement paste and mortar specimens is in accordance with the NEN-EN-196-1. All required moulds were prepared with a oil layer in order to avoid adhesion of the hardened mixture to the mould. For each cement blend three 160x40x40mm prisms were cast using cast iron moulds, which will be tested at 7, 28 and 90 days curing. Each mould is filled in 2 layer and in between vibrated on a vibrating table. The filled mould is stroke off in a sawing motion using a straightedge and specimen is covered using impermeable plastic foil.

The RCM-test requires a cylinder with a diameter of 100 mm and a height of 50 mm according to NT Built 492, as mentioned in section 2.2.2. There is no standard mould as there is for the prisms, therefore the mould cylinder need to be fabricated beforehand. The mould is fabricated from a PVC-tube with a height of 300 mm, diameter of 100 mm and a wooden bottom plate. As mentioned before all mould needed to be pretreated with a thin oil layer, this mould not excluded. To make sure the bottom plate is water tight, moulding clay is applied around the gap between the tube and the bottom plate. Just like casting the prisms these cylinders are also cast in two layers and vibrated between filling the 2 layers.

After one day curing in ambient conditions the mortar prisms and cylinder are demoulded and placed in the fog room at TU Delft's Stevin laboratory to cure for 7,28 or 90 days.

In order to obtain the 25 mm and 50 mm thick cylindrical specimens required for the RCM-test, the ø100-300 cylinders were cut. The cylinders were cut after two and three weeks of curing using a water cooled sawing blade, see Figure 3.3. In the curing phase it is still allowed to saw with water cooling, in contrast to after carbonation.

After cutting all cylinders the disk will be stored back in the curingroom, avoiding stacking as can be seen in Figure 3.4. Besides mortar samples, cement pastes were prepared too and cast in ø50-100 mm lab beakers. Three days after casting these specimens are demoulded by destroying the plastic beaker. After demoulding these specimens are stored in the similar way as the mortar cylinders in the fogroom. These cement paste specimens are only required to prepare powder samples for MIP and TGA after a certain required curing time. After approximately two weeks curing these samples are sawn into three smaller disks of ø50-30 mm, to gain sufficient samples in order to monitor the carbonation progress on top of the required tests.

When all specimens have been demoulded, cut and prepared they are stored back into the fogroom for further curing. In Table 3.1 further use of these test specimens is summarized.

3.2. Strength development tests

As described all blended cements were mixed using CEM I 42,5N and CEM III/B 42,5N cements. These cement mixtures both have approximately the same 28 days compressive strength but have a different strength development, as OPC has generally a higher early age strength in comparison with BFSC.

The strength development and 28d strength of cements CEM I and CEM III/B delivered by ENCI are well
known. However the strength development for the blended cements were unknown. They should have the same 28d compressive strength, as this was the criterium for mixing the CEM I 42,5N and CEM III/B 42,5N. In order to identify the material characteristics of all blended cements, the compressive and flexural tensile strength are tested at 7, 28 and 90 days curing.

In accordance with the NEN-EN-196-1 40x40x160 mm mortar prisms are used for flexural tensile and compressive strength tests. After the required curing time the test specimens are taken out of the fogroom and dried for 30 minutes in ambient conditions. The testing apparatus should be capable to apply loads up to 10kN at a rate of 50N/sec. At TU-Delft's Stevin laboratory the Matest Servo Plus Evolution is used for strength tests and can load up to 50kN.

The 40x40x160 mortar prisms was placed in the 3-point apparatus, such that the cast surface faces the user. The specimen were kept perpendicular to the, two supporting and one loading, roller direction. The mortar prisms were placed all the way back in the holder with the cast surface facing forwards, assuring loading on a smooth surface.

Flexural tensile test was started at a start load of 0.5 kN and slowly increased at a rate of 50 N/sec until fracture, as shown in Figure 3.5.

The two broken halves of the prism were then tested for compressive strength. The specimens were placed on their sides, with the finished surface to the front. The half prisms were centred laterally to the platens (40x40 mm) of the machine, the end face of the prisms overhang the platens. Due to the platens a cube of 40x40x40 mm is loaded in compression. The compressive test started at a load of 2 kN with an increasing load of 1.0 kN/sec and loaded until fracture.

---

<table>
<thead>
<tr>
<th>Type of test</th>
<th>Specimen size</th>
<th>Specimen type</th>
<th>Nr. of test specimen Carb.</th>
<th>Uncarb.</th>
<th>Curing age</th>
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<tr>
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<td>7 days</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>2</td>
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<td></td>
<td>90 days</td>
</tr>
<tr>
<td>Flex. tensile strength</td>
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<td></td>
<td>7 days</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>1</td>
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<td>28 days</td>
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<td></td>
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<td></td>
<td>90 days</td>
</tr>
<tr>
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<td>Mortar</td>
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<td></td>
<td></td>
<td>1</td>
<td></td>
<td>90 days</td>
</tr>
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<td>Cement paste</td>
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<td>-</td>
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<tr>
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<td>Cement paste</td>
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<tr>
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<td>1</td>
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</tr>
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<td>1</td>
<td>23 weeks</td>
</tr>
<tr>
<td></td>
<td>ø100x50 mm</td>
<td></td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
3.3. Carbonation

Samples that needed to be carbonated for further testing were ø100x50 mm mortars, ø100x25 mm mortars and ø50x30 mm cement paste. After 28 days curing the mortar samples together with the first batch of cement paste samples were placed in the carbonation box. The second batch of cement paste samples stayed in the curing room to cure for 90 days and were placed in the carbonation box afterwards.

The specimens cannot be placed directly from the curing room into the carbonation box, because of the big difference between RH of both rooms. An increase in RH will only slow down the carbonation and therefore undesired. To avoid elevation of RH in the carbonation box by placing the specimens from a high RH (curing room) into a lower RH (carbonation box), the specimens were first dried in ambient conditions for 4 days.

The temperature in the carbonation box was set in accordance to the EN-13295 at 20,0±1,0°C. But due to the presence of specimens from other researchers in the carbonation box the relative humidity was elevated to 75-80% from the start of the carbonation process.

After ten weeks of carbonating the first batch, 28 days curing, of cement paste samples is carbonated enough to use in TGA, XRD and MIP-tests. At the same time, the second batch of cement paste samples after 90 days curing and four days drying in ambient conditions was ready to be placed in the carbonation chamber. With the change of cement paste samples, the carbonation conditions were changed. The RH was stabilized at the required RH of 65±2% and the temperature was kept at 20,0±1,0°C.

Carbonation is a process of CO₂ diffusion into the specimen. In order to obtain the largest carbonated area all specimens were expose from all sides. Since there is only limited space in the carbonation box and stacking should be avoided, stacking brackets were used. The air circulation will go around whole sample now, thereby ensuring even carbonation from all sides. The cement paste samples are to small to place on these brackets, in order to stack the cement paste samples, small reinforcement bars were used. The bars create enough space between samples and assured air flow.

The uncarbonated specimens for comparison are kept in the fogroom, in a high RH, to avoid any carbonation in ambient climate conditions.

Carbonation will continue until fully carbonated specimens are acquired. The carbonation process is monitored by measuring the carbonation depth by colorimetric method.

The samples will be split by means of a hammer and chisel and sprayed with phenolphthalein indicator. The average carbonation depth is then measured using multiple measuring point with an intermediate distance of 10 mm. The cement paste and mortar samples are kept in the carbonation box for a total of 10 and 23 weeks respectively.

3.4. Thermogravimetric Analysis

In order to indicate mineralogical changes in the cement paste due to carbonation a thermogravimetric analysis is performed on cement paste of 28 and 90 days curing. After 10 weeks carbonation the cement paste sample of all cement blends were taken out of the carbonation box and from these ø50x30 mm cylinders powders samples were prepared. The cylinder was broken into 2 halves of which one half will be sprayed with phenolphthalein indicator. Using this indicator a clear indication of the carbonated area can be made for the other half which is required for making the sample powder. The set-up as shown in Figure 3.7 was then used to grind off approximately 1.0 grams of carbonated cement paste powders. These powders are stored in a lab beaker and put in a 96% ethanol solution to prevent further carbonation.
Besides carbonated specimens the uncarbonated specimens, taken from the curing room, were prepared in the same way without the use of the phenolphthalein indicator.

To start the TGA analysis on the cement powder, the powder first need to be removed from the ethanol and the residue was then dried for five minutes in ambient condition. After it solidifies it is milled back to a powder and dried for 10 to 15 additional minutes in an oven at 105°C.

The crucible, measuring cup intended for TGA, is then filled with 40,0 ± 10,0 mg of the cement paste powder.

Residual cement powder of carbonated specimens will be stored in a 96% ethanol solution again and can later be used for the XRD-analysis.

The crucible is then closed with a lid and placed in the NETZSCH STA 449 F3 Jupiter, using a TG-DSC measuring head. Before any analysis is conducted a so called zero measurement is made with an empty crucible. The data from this measurement will be used for all analysis. The weight profile of an empty crucible will be subtracted automatically, so the measurement will only be for the material in the crucible.

The sample is heated up from 40°C until 1000°C at a rate of 10K/min. Both for the protective and purge gas argon has been used with a gas flow of 20 and 50 mL/min, respectively. The sensitivity and temperature calibration was used for 10K/min under argon gas. After approximately 2.5 hours the NETZSCH will cool down and the crucible is taken out, after the temperature drops below 100°C. The just tested crucible content is thrown away and the crucible is cleaned using the procedure as explained earlier. The whole procedure can now be repeated is necessary.

3.5. X-Ray Diffraction analysis

The powder sample prepared from cement paste specimens after 90 days curing and 10 weeks carbonation are subjected to this XRD-analysis, after a TGA is performed first. After this TGA the powder sample was submerged in an 96% ethanol solution, to prevent any carbonation. In order to dry the cement powder the same procedure as for the TGA preparation, as described in section 3.4, was followed.

The dry cement paste powder is compressed in a circular holder for the XRD. This compressing has to be repeated several times to ensure tight compaction, necessary for the turning movement during testing. To gain tight compaction sand was added on top of the holder and pressed into the holder, since there was
not enough cement paste powder available. The material that needed to be measured needs to be spread along the whole circle and have sufficient thickness. Sand consist mainly of quartz crystals, so if there is not enough cement powder sand is used to fill up the holder. The results of such measurement might indicate a high amount of quartz but this can be assigned to sand, because there is generally no sand or quartz present in cement paste.

The sample holder is then placed in the Philips PW 3020 XRD-apparatus. The sample is subjected to X-rays generated from a copper tube at a power of 40kV and a current of 40mA. These x-rays target the specimen over an angle from 5 to 120 degrees, equal to 2 Theta. Using Bragg’s law a XRD pattern will be produced which will be qualitatively analysed in chapter 4.

![Figure 3.9: XRD apparatus and sample holder](image)
(a) X-ray diffraction apparatus, Philips PW 3020
(b) XRD sample holder

### 3.6. Mercury Intrusion Porosimetry

The half cylinder of hardened cement paste which was previously used in preparation of cement powder sample for TGA and XRD is afterwards used in the sample preparation for the MIP-test. The carbonated front up to a thickness of $5.0 \pm 2.0$ mm is sawn off using a ethanol cooled cutting blade. Ethanol will not react with the products formed in carbonation on contrary to water. The sawn slices of (un)carbonated specimens that are required for testing are broken into small pieces and stored in plastic lab beakers with holes in them, to ensure the same climate inside the beaker as outside.

These samples are then placed under vacuum in a freeze dryer, with a temperature of around $+16^\circ$C. Every week the weight loss was measured and the samples were kept in the freeze dryer until the weight loss between measurements was less then 1%.

The sample is removed from the freeze dryer and $6.0 \pm 2.0$ gr is placed in a penetro as shown in Figure 3.10. The penetro is closed off with a cap and sealed. The weight of the penetro and sample is measured to determine the exact penetro mass. The penetro is then first placed in the low pressure valve. Mercury will intrude into the pores until a pressure of approximately 100 kPa. After the low pressure test is finished the penetro is measured again with the combined mass of penetro, sample and mercury to determine the intruded mercury mass. The penetro is afterwards placed in the high pressure valve, taking care that the air in the oil underneath the penetro can escape. The high pressure MIP-test intrudes the pores until a pressure of approximately 250 MPa. Autopore IV9500, the associated software, will record the data and produce a data file containing intruded mercury volume, corresponding pressures and pore size distribution.

### 3.7. Electrical resistivity measurement

The resistivity was measured using the two-electrode method for several samples of different sizes and age, for which saturated conditions were consider to be ideal. This two-electrode method is in accordance with the RILEM TC-154 technical recommendation[19, 39]. Electrical resistivity measurements is used as an indication for susceptibility of the specimens to chloride penetration.

After 28 days hydration the mortar cylinders were taken from the curing room and the resistivity was measured directly, before placing them in the carbonation box. After 90 days curing mortar prisms were taken from the fog room to perform the strength measurements.
Before these flexural and compressive strength tests, the resistivity was measured on these specimens. Besides measuring the influence of curing time on resistivity, the influence of carbonation was investigated too. For specimens which later will be subjected to the RCM-test, resistivity measurements were performed in advance.

Carbonated specimens, taken from the carbonation chamber, were stored in an average RH of 65% and therefore regarded as dry before they are saturated in a calcium hydroxide solution. These "dry" specimens are expected to have a very high electrical resistivity and therefore were therefore not measured. Specimens were measured at 3 different moments: before Ca(OH)$_2$ saturation, after saturation and after the RCM-test.

To measure the electrical resistivity the saturated/wet specimen is first dried in ambient conditions for 10 minutes, in order to evaporate all excessive water. Then the specimen is placed between two metal plates with a sponge cloth on the inside. These sponge cloths are moistened with a soap solution to enhance the conduction. The two plates are then connected to a multimeter and it is chosen to apply an alternating current with a frequency of 1000 Hz. To ensure good contact of the plates during measurement a heavy object was placed on top. A concrete block was chosen which was used for every measurement and can be seen as constant. Resistivity can be calculated by multiplying the measured resistance $R$ [Ohm] with a geometrical constant, the contact area divided by the thickness of the specimen.

$$\rho = \frac{R \times A}{L} \quad [\Omega m]$$

where $\rho$ is electrical resistivity, $R$ is resistance, $A$ is contact area and $L$ is specimen thickness.

### 3.8. Rapid Chloride Migration test

Carbonated and uncarbonated specimens are taken from the carbonation or curing room respectively and subjected to vacuum saturation in saturated Ca(OH)$_2$-solution. NT-Built 492 prescribes to put the specimens in a vacuum for 3 hours after which the Ca(OH)$_2$-solution is added under vacuum. This vacuum saturation is kept for one hour. The vacuum is shut off, subsequently air is allowed back in and the specimen will stay submerged in the solution for 18±2 hours. Afterwards the specimens are taken out and the surface is dried with a cloth. The electrical resistivity of these specimens were measured using the procedure as prescribed in section 3.7, before putting them in the RCM set-up.

The test specimens are fit in a rubber sleeve and secured with 2 clamps, to prevent any leakage these clamps are firmly fixed. The specimens are then placed in the catholyte reservoir. The catholyte reservoir
3.8. Rapid Chloride Migration test

contains a 18 litre solution of a 10% NaCl by mass in tap water. The NT-Built 492 prescribes just to use a NaCl solution. However the pure chemical NaCl was out of stock. Table salt is also known as NaCl, but the question is to which extend.

Iodide is commonly used in salt, but for this research a type of table salt without the addition of iodide was purchased. The producer of the salt, AkzoNobel, has published a data sheet for the retail which gives insight in the composition and grain sizes. 99.9% of the salt is NaCl, as shown in Appendix A. Therefore it was concluded that the use of this type of kitchen salt is appropriate.

The sleeve is filled with 300 mL anolyte solution (0.3M NaOH) and the anode is immersed in this solution. The cathodic and anodic sides are connected to the power supply with a multimeter connected in series. The power supply is set at initial voltage of 30V, using the multimeter the current is measured for each specimen. Using NT-Built 492’s Table 1 the power will be adjusted and the initial current is measured. After the pre-set test duration, generally 24 hours for a voltage between 10 and 60V, the final current is measured again. The test is terminated and the specimens are rinsed with tap water and the surface is dried with a cloth.

The specimens subjected to the RCM-test are split into two halves. One half is sprayed with a 0,1M silver-nitrate solution, the other half is sprayed with phenolphthalein solution if a carbonated specimen is tested. The chloride ingress depth is measured, without using 10 mm of both sides because of the chance of leakage along the sides. From this chloride penetration depth the chloride diffusion coefficient is calculated using equation 3.2, as indication for the chloride penetration resistance on the material[26].

\[
D_{cl} = D_{nsm} = \frac{0.0239(273 + T)L}{(U-2)t(x_d - 0.0238)}(\frac{(273 + T)x_d}{U-2})
\]

(3.2)

where \(D_{cl}\) is chloride diffusion coefficient [x10^{-12}m^2/s], T is temperature [°C], L is thickness of specimen [mm], U is absolute value of the applied voltage [V], t is test duration [hr] and \(x_d\) is the average value of the penetration depths [mm].
In this chapter results of the tests described in chapter 3 are presented. The test specimens are characterised under three properties, namely mechanical, physical and chemical. This will include the change in material properties under the influence of carbonation, as will be presented in section 4.1.

Furthermore, material transport property results are reported and discussed in section 4.2.

4.1. Material characterisation
For all 12 cements selected material properties are characterised. The material characteristics are split into three parts, mechanical properties, physical changes expressed as pore structural changes and mineralogical composition.

4.1.1. Mechanical properties
The mechanical properties that were tested are compressive and flexural tensile strength. For each mixture mortar prisms were tested at an age of 7, 28 and 90 days and reported. For each binder a mortar prism is subjected to one flexural strength test and two compressive strength tests, as described in chapter 3.

All measured data from the flexural and compressive strength test are gathered in a table and presented in Appendix B.

From this data the compressive strength can be presented including, a measuring scatter, as for flexural strength only a single value can be presented. Any abnormal observation during testing or from the results was written down in a logbook. It should be noted that for compressive strength testing there is a standard measuring error of 5-10%, as for flexural strength testing this measuring error was 20%.

Figure 4.1 shows the compressive strength development for all cement blends. The presented value for, measurements with a low scatter, each value is the average of the two compressive strength
measurement. For measurements with a large scatter the highest value is taken into account. Nonetheless all values, including all measuring errors, are represented in Figure 4.2.

![Figure 4.2: Compressive strength development of mortar specimens; w/c-ratio=0.5; n=2.](image)

From Figure 4.1 and 4.2 it can be seen that the compressive strength development is different for CEM I (0% slag) and CEM III/B (70% slag). The mortars with higher slag content have a lower early age strength than with a low amount of slag. For the 7 days results, a decreasing slope can be distinguish with increasing slag content.

The 90 days age result shows that by applying more than 25% slag the long term strength will increase noticeably. From product information it is known that CEM III/B (70%) has a higher 90 days strength than CEM I (0%), which is also observed from the test results.

The 28 days curing compressive strength for 0% and 70% slag content, CEM I and CEM III/B cements respectively, can be related to ENCI data. According to the ENCI specification the 28 day compressive strength of CEM I and CEM III/B should be around 47.4 and 46.5[N/mm²] respectively[4]. One can see in Figure 4.2 that these values have been exceeded, also by all the blended cement types. Nonetheless the results are still in the same strength range and do not differ more than ±10% from the standardized values provided by ENCI.

From Figure 4.2 one can observe that for slag contents between 25% and 50% the compressive strength at an age of 28 days and 90 days is higher than all other cements.

There is no microstructural data on these specimens, therefore it is hard to say using only these measurements why there is a higher strength in the middle slag content range. Although it might be caused by the fact that self mixed blended cements are used in this research.

Flexural tensile strength of all mixtures vary around values of about 10 to 12 [N/mm²]. Cement, mortar or concrete is always weak in tension, therefore compressive strength is more representable as indication for the mechanical properties of the mixtures and flexural tensile strength will not be governing.

The 90 days flexural tensile strength of some slag contents, such as 40, 50, 55 and 60%, are not shown in Figure 4.3. The measured flexural tensile strength after 90 days curing was lower than the strength measured at 28 days curing. The specimens were not subjected to any loading and were stored in the curing room, for which hydration continues. In continued hydration the strength development should continue, resulting in a higher 90 days strength. From the typical inaccuracy of the test method, the lower 90d strength results is assigned to a measuring error.

For all blended cements the observed strength values are in the same range, therefore the results are all cement blends considered to be acceptable in terms of strength.
4.1. Material characterisation

4.1.2. Pore structure

In section 2.1.4 it is explained that carbonation can cause a change in physical properties of cementitious materials, such as porosity. As theory suggests, the change in physical properties is different for cements containing slag than for OPC. The effects of slag content on carbonation on porosity were tested using the MIP-test and presented in this section.

As explained in section 3.6 the cement paste samples were cured for a duration of 28 and 90 days. For both curing ages the specimen is either subjected to carbonation for 10 weeks or stored in a freeze dryer. Each cement blend is tested four times for different curing age and exposure, as shown in Table 4.1. These preconditions result in a total of 48 tests and are presented as a single value.

Table 4.1: Test specimen precondition depending on curing age and exposure condition

<table>
<thead>
<tr>
<th>Test specimen precondition</th>
<th>Exposure</th>
<th>28 days</th>
<th>90 days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Uncarbonated</td>
<td>Carbonated</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>4</td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>

From the MIP-results a characteristic pore size distribution differential curve is made for each sample. The pore size distribution, dV(d), is defined as the pore volume per unit interval of pore diameter. The pore size distribution differential curve for two characteristic cement mixtures, 0% and 70% slag, are presented in Figure 4.4. The pore size distribution for all cement mixtures are reported in Appendix C.

The critical pore diameter, \( d_{crit} \), is the most encountered pore size and illustrated in Figure 4.4 as the pore size for which the curves show the largest pore volume, indicated by the largest peak.

The most encountered pore size, \( d_{crit} \), has a large contribution on the total porosity and subsequently on the durability of the cement paste. Therefore the \( d_{crit} \) is taken as an indication for the porosity of each test specimen and is presented in Table 4.2 and illustrated by Figure 4.5.

From Figure 4.5 it can be seen that for uncarbonated specimens the critical pore diameter decreases, when the slag content in the cement paste samples increases. For both curing ages this was observed, indicating that curing age longer than 28 days will not affect the critical pore size of uncarbonated specimens.

The critical pore size for OPC paste is around 45 [nm], on the other hand the average critical pore diameter is approximately 25 [nm] for a slag content >55% as presented in Table 4.2. The decreasing critical pore size can be related to the decreasing porosity, which is in line with the presented background information in
section 2.1. For uncarbonated specimens it is concluded that with an increasing slag content the critical pore diameter decreases.

In cement pastes with a low slag content, carbonation is expected to cause a densification of the material, due to the conversion of Ca(OH)$_2$ into CaCO$_3$. However one can see that for the cement mixtures 0% and 20% slag there is a small increase in critical pore diameter. This may be noted as an increase that is not substantial. Carbonation has a small influence on the porosity of cement paste samples with a low slag content.

Carbonation has an increasing influence on the $d_{crit}$ when the slag content increases. A linear relation can be seen in the increasing critical pore diameter as the slag content increases. The critical pore size is significantly increased for the samples with a higher slag content compared to uncarbonated samples. For CEM III/B cement, with 70% slag, there is an increase of around 12 times the critical pore diameter. In Figure 4.4b it can also be observed that the peak in the pore diameter shifts to the right (larger pores) when the specimen is carbonated. On the contrary the $d_{crit}$ peak in Figure 4.4a for OPC-sample stayed approximately at the same pore diameter. It can be concluded that carbonation has an increasing influence on the porosity with an increasing slag content in the cement mixtures. There is a significant increase in porosity for cement mixtures with a slag content >40%.

For the cement mixtures with a slag content between 25 and 50% it appears that curing age has an influence on the critical pore diameter after carbonation. Looking at the 28 days cured carbonated samples up to a slag content of 40% an average critical pore diameter of 0.08 [um] can be found. 45 and 50% slag content both have a critical pore size of 0.25[um] after 28 days curing. However the critical pore diameter increases significant when the curing time increases from 28 days to 90 days.

On the other hand it seems that for slag content >50% there is no influence of curing age any more. OPC (0% slag) and 20% slag cement pastes do not show an increase in critical pore diameters with increasing curing time either.
An explanation for the increasing critical pore diameter when the curing age increases was found in the hydration process of slag cements. The results from mechanical strength tests presented in section 4.1.1 indicate hydration, due to the increase in strength with an increase curing age from 28 days to 90 days.

Equation 2.2 shows that slag consumes calcium hydroxide during hydration. The longer the cement is kept under hydration conditions the more calcium hydroxide is converted into secondary CSH. Carbonation of calcium hydroxide will form calcium carbonates and is generally known to decrease the porosity. But because of ongoing hydration there will be less calcium hydroxide present in slag cements prior to carbonation. The lack of calcium hydroxide will therefore cause carbonation of the CSH-gel. Carbonation of CSH will cause carbonation shrinkage and increase the porosity.

However verifying this assumption with the results from the thermogravimetric analysis, this mechanism was not confirmed. In Figure 4.6 it can be seen that the initial calcium hydroxide presence before carbonation does decrease when the slag content is increased. However there is no decrease in calcium hydroxide content with increasing curing age, on the contrary there was an increase in Ca(OH)$_2$-content observed for slag content between 30 and 70%.

Because this increase is so small and does not make sense from point of hydration, it is regarded as it is an measuring scatter. Further explanation on obtaining the values presented in Figure 4.6 is found in section 4.1.3.

There are more uncertainties that has to be considered in interpreting the results and more extended research is advised.

4.1.3. Mineralogical composition

Longer exposure in the curing room can lead to ongoing hydration and changes in the mineral composition, therefore 2 different curing ages were tested. Besides curing time, carbonation can also lead to a change in mineralogy, as discussed in section 2.1. Similar to the MIP-test, the test specimens were prepared as indicated in Table 4.1 resulting in 48 tests without considering test scatters.

The mineralogical changes in the specimens due to hydration and/or carbonation is evaluated by means of TGA and XRD analysis on a total of 48 samples. XRD is only used as a verification method for the presence of multiple calcium carbonate forms formed during carbonation.

From these TG-analysis thermograms were made for all samples. A thermogram show TG-curves which represent the mass loss of the sample and DTG-curves as the first derivative of the TG-curve which gives an indication for the starting point of a significant change in mass.
Thermogravimetric analysis

TGA was used to investigate the influence of carbonation on cement paste with different amounts of slag. As carbonation influences the calcium bearing phases it is assumed that the thermographs show mass losses for 4 major phases. The important characteristic peaks for calcium bearing phases are Ca(OH)$_2$ dehydration and 2 types of CaCO$_3$ decarbonation at respective temperatures of approximately 430, 680 and 760°C.

Additionally a loss of mass observed at 140°C can be assigned to dehydration of various sources such as ettringite, monosulphate and/or CSH. However exactly determining the mineral at this temperature was left out of the scope of this research. As it is known that carbonation consumes calcium hydroxide and potentially CSH and produces calcium carbonate, therefore it was found important to focus on the changes in Ca(OH)$_2$ and CaCO$_3$ forms only.

The fourth major calcium bearing phase is the CSH-gel created during hydration. Determining the content of this fourth major calcium phase is done via a calcium balance, which will be explained later.

In Appendix F the thermograms are shown separately for all uncarbonated specimens for 28 and 90 days hydration in humid curing conditions.

The same thermograms for all slag contents at 2 different curing ages were made for carbonated specimens as well and collected in Appendix E.

At the end of appendixes E and F a comparison between the curing times is made for 4 carbonated or uncarbonated mixtures, namely with a 0%, 30%, 50% and 70% slag content.

From a thermogram, such as presented in Figures 4.8, 4.9 or 4.10, the Ca(OH)$_2$ or CaCO$_3$ content can be expressed as percentage of dry weight at a "stable" temperature using the formulas as expressed below.

The stable temperature, $T_{stable}$ was chosen at a point behind $T_{after}$ where the mass loss was found to be stable again[14]. The temperature directly before the mass loss, $T_{before}$, and the temperature directly after the mass loss, $T_{after}$, were determined using the DTG-curve.

$$\text{Ca(OH)}_2[\%] = \frac{w_{T_{before}} - w_{T_{after}}}{w_{T_{stable}}} \times \frac{M(\text{Ca(OH)}_2)}{M(H_2O)}$$

$$\text{CaCO}_3[\%] = \frac{w_{T_{before}} - w_{T_{after}}}{w_{T_{stable}}} \times \frac{M(\text{CaCO}_3)}{M(H_2O)}$$

where $w_{T_{before}}$ is the sample mass before the temperature drop, $w_{T_{after}}$ is the sample mass after the temperature drop, $w_{T_{stable}}$ is the sample mass after the temperature drop where the mass loss was stable again and M is molar mass [g/mol].
The calcium carbonate content in carbonated specimens is expressed using formula 4.2 as illustrated in Figure 4.7. From Figure 4.7 it is concluded that curing age does not influence the amount of calcium carbonate formed due to carbonation. This was also concluded for the formation of calcium hydroxide due to hydration, presented in Figure 4.6 as mentioned in section 4.1.2.

On top of this, the comparison between different curing ages was also done visually using the TG and DTG-curves for the carbonated and uncarbonated mixtures with a 0%, 30%, 50% and 70% slag content. As can be found in appendixes E and F the TG and DTG-curves overlap or are parallel to each other, which enhances the conclusion that curing age does not influence the mineral composition in the cement paste mixtures significantly.

The mass loss at 680°C, assigned to a calcium carbonate form, does show a small scatter with increasing curing age. Each specimen with its corresponding preconditioning and exposure is tested only once. The measured scatter in calcium carbonate formation can also be attributed to measuring uncertainties, although this can only be confirmed by means of extended research.

Despite this small difference in calcium carbonate formation the other minerals do coincide and show similar mass losses. Further comparisons or analysis will only focus on 90 days cured specimens.

A comparison between uncarbonated and carbonated cement paste blends was only done for specimens with a 90 days curing age and can be found in Appendix D. However in this comparison the uncarbonated OPC sample of 28 days curing age was used. It was found that the measurement for 90 days curing age was unreliable, because of the presence of a high calcium carbonate content. From hydration point of view this was not expected and therefore considered as an unreliable test result. From the uncarbonated cement paste of 28 days curing age far less calcium carbonated was present before carbonation. The high amount of CaCO$_3$, detected at 680°C from TGA, might be due to a preparation error. If the prepared powder specimen was not covered with ethanol solution appropriately it may have carbonated to some extend.

Here 3 cement mixtures, namely with a 0%, 45% and 70% slag content, are reflected to explain what the characteristics of these thermograms are and comparing the mineral composition before and after carbonation.
Figure 4.8 shows the TG and DTG curves for carbonated and uncarbonated cement paste specimens using an OPC-mixture, 0% slag.

In Figure 4.8 it can be seen from the DTG-curve that there are 4 characteristic peaks indicating a mass loss. These peaks at 160, 480, 680 and 760°C can be identified as minerals as explained before.

In uncarbonated state it was found that the material loses mass at 160, 480 and 680°C, where the mass loss at 160°C is left out of the scope. At 480°C a large peak from the DTG-curve was observed, indicating a change in mass loss due to dehydration of calcium hydroxide. From the TG-curve a mass loss of ±5% was measured. Between 680 and 750 a much smaller mass loss was measured, appointed to calcium carbonate.

The thermogram after carbonation is clearly different from the thermogram before carbonation. The change in TG-curve indicates a change in mineral composition of carbonated material.

At a temperature between 140 and 160°C a similar mass loss was observed as in uncarbonated material. However it should be noted that the mass loss was less for this carbonated material. It seems that carbonation had effect on the minerals decomposing at this temperature, however mineral indication for this temperature range was left out of the scope. A small amount of calcium hydroxide was still present in the carbonated material since a mass loss can be measured at 480°C. The DTG-curve for carbonated material shows 2 larger peaks at 680 and 760°C, which can be assigned to calcium carbonate as explained in 2.1.3. The mass loss at 680°C is assigned to a meta-stable form of calcium carbonate, vaterite, that might be formed from carbonation of the CSH-gel[16]. The peak in the DTG-curve and large mass loss in the TG-curve between 760 and 850°C is assigned to calcite. Calcite is a well-crystallized form of CaCO₃ formed from carbonation of Ca(OH)₂.

This can also be observed from Figure 4.8, since the mass loss of Ca(OH)₂ in uncarbonated state changes to a mass loss of CaCO₃ at 760°C for carbonated material.

The thermograms for carbonated and uncarbonated cement paste with 40% slag are compared in Figure 4.9. For carbonated and uncarbonated materials both TG-curves roughly overlap until 460°C. The uncarbonated cement paste contains calcium hydroxide which dehydrates at 460°C. The mass loss is less than for an OPC sample, indicating a lower presence of Ca(OH)₂ in this sample with 40% slag as is presented in Figure 4.6.

It was noted that the mass loss at 760°C for uncarbonated cement paste samples, indicating calcium carbonate, is lower than for OPC.

In carbonated specimen calcium carbonate is decarbonated at 760°C, but the amount of calcite is lower than for OPC. Because of the lower amount of Ca(OH)₂ in uncarbonated paste there is less material to be converted to CaCO₃ during carbonation.
From Figure 4.10 the mass loss for carbonated cement paste at a temperature of 160°C is less than for uncarbonated paste, which was also observed for OPC and other slag contents from Appendix D. From approximately 200°C the TG-curves deviate from each other.

Compared with all cement blends, cement paste with 70% slag contains the lowest amount of Ca(OH)$_2$ after hydration, since the mass loss at 480°C from the TG-curves is the lowest.

A carbonated sample no longer contains calcium hydroxide, indicating Ca(OH)$_2$ was fully consumed during carbonation. Carbonation of this 70% slag cement paste convert the Ca(OH)$_2$ into calcite, represented by a peak in the DTG-curve or as a mass loss in the TG-curve at 760°C. Because of the limited presence of Ca(OH)$_2$ before carbonation there also less CaCO$_3$ produced during carbonation.

From all thermograms it was found that initially before carbonation there was a calcium carbonate form present, as presented in Figures 4.8, 4.9 and 4.10. If we regard the standard hydration processes for either OPC or BFSC it cannot be explained why or how this calcium carbonate was formed.

One of the causes might be that natural carbonation of powders happens faster than in solid state. Specimens were not exposed very long to natural conditions and were stored inside an ethanol solution directly after grinding.

Another explanation might be the presence of calcium bearing fillers in the cements delivered by ENCI. ENCI is allowed to use up to 5% fillers as a cement replacement, as can be found in Appendix A. In consultation with ENCI, it was found that the 5% fillers they use may contain calcium carbonates as the fillers are produced from the dust of raw materials collected from the pre-heater [18].

**X-Ray diffraction analysis**

In order to confirm the presence of 2 types of calcium carbonate in cement paste after carbonation XRD-analysis has been performed on these samples. In Figure 4.11 XRD-patterns for OPC and CEM III/B are shown, obtained after the XRD-analysis. The patterns for all cement blends can be found in Appendix G.

From qualitative analysis of the XRD-patterns as shown in Figure 4.11 it can be found that 4 crystalline minerals are observed in the carbonated material. Quartz, Calcite, Vaterite and Aragonite are the minerals detected for all cement blends.

The presence of quartz is only observed in OPC, but can be assigned to a preparation error. As explained in 3.5 the cement paste powder samples initially used for TGA were later on used in the XRD-analysis. Because the TGA was done before the XRD, the amount of test material was limited. In order to compress the test powder in the XRD-holder, fine milled sand is added on top of the test material. In cement paste there is no addition of sand an no reason for quartz to be present. The measured quartz is therefore related to this sand using in compaction of the powder sample.

Calcite, vaterite and aragonite found in the XRD-patterns are all calcium carbonate forms. If the XRD-pattern and the decomposing temperatures from the TGA match then it can be concluded that the two CaCO$_3$ forms are calcite and vaterite. Since aragonite has also another decomposition temperature than found in this TG-analysis at was concluded that the 2 peaks at 680 and 760°C are vaterite and calcite respectively.

Additionally it can be concluded from the XRD-patterns that there is no longer Ca(OH)$_2$ present in carbonated cement paste samples.

For the carbonated OPC sample, for which the TG-curve indicated the presence of Ca(OH)$_2$, this was not found in the XRD-pattern. Therefore it is concluded that for OPC-samples after carbonation no Ca(OH)$_2$ was present.
Calcium balance

Since it is proven that there are 2 CaCO$_3$ forms present in carbonated cement paste, it is possible to calculate the amount of CSH-gel for carbonated and uncarbonated cement paste samples using a calcium balance.

The calcium content from Ca(OH)$_2$ and CaCO$_3$ forms are subtracted from the total available calcium in the cement paste and is appointed to the CSH as the fourth major calcium bearing phase.

In email conversation with ENCI it was given that the raw CEM I cement powder contains 63.8% of CaO and CEM III/B 45.2%[18].

From this it is possible to calculate the weight of the calcium present in the sample.

Calcium is used in the hydration process to form multiple phases. Since it is assumed that cement paste only consist of 4 major calcium bearing phase, calcium is distributed over the CSH, Ca(OH)$_2$ and CaCO$_3$ forms. The mass losses for the calcium hydroxide and calcium carbonate, as also presented in Figures 4.6 and 4.7, are expressed in fractions of total samples weight. Using the mass composition by element [gr/mol] of each phase it is possible to calculate the amount of calcium present in all phases.

Using the knowledge of atomic weight the calcium content of CaO, Ca(OH)$_2$ and CaCO$_3$ is 71.5%, 54.1% and 40.0% respectively expressed as mass percent.

A calcium balance is made for both uncarbonated and carbonated cement paste samples. Comparing both balances for all cement blends it can indicate what happens to the mineral composition of cement paste after carbonation.

In Figure 4.12 vaterite is illustrated by the gray coloured bars as purple is presenting calcite.

The calcium balance for carbonated cement paste samples show a division in vaterite forms. Because of the two gray scales it is possible to distinguish whether the material was formed during carbonation or already present in the uncarbonated sample.

The presented calcium content in Figure 4.12 is normalized for all slag contents. Note that the total amount of calcium in OPC is higher than in 70% since CEM I cement contain 63.8% CaO compared to 45.2 for CEM III/B cement.

From 4.12, as previously explained, it was noted that the calcium hydroxide content decreases with increasing slag content for uncarbonated samples.

From the calcium balance for all cement blends is was found that all Ca(OH)$_2$ was converted into calcite during carbonation. Although OPC show a presence of Ca(OH)$_2$ after carbonation it was concluded from XRD-analysis that this can be assigned to a measuring error.

The amount of calcium that was present in the calcium hydroxide before carbonation can partly be found back in the calcium carbonate after carbonation. The total amount of calcite formation cannot be only formed from calcium hydroxide since there is less calcium available in Ca(OH)$_2$ than is found in calcite after
carbonation.

This points to the fact that carbonation of CSH-gel will form vaterite and calcite. The formation of vaterite can be found since the amount of calcium present in vaterite increases after carbonation, hence formation of vaterite.

It should be noted that there is a chance that in uncarbonated samples the mineral decomposing at a temperature of 680°C is not vaterite. It might be also calcite that is burned at a lower temperature before carbonation reactions. Or it is a completely other mineral and no calcium carbonate form at all. However because of the lack of XRD-analysis on uncarbonated samples it is impossible to give a solid conclusion on this. More samples should be tested and additional XRD-analysis on uncarbonated specimens should be conducted in later research.

4.2. Transport properties

In this research both carbonation and chloride ingress properties of blended cement are tested. For both carbonation and chloride penetration the predominant transport property is diffusion. Diffusion can be explained by the so called Brownian motion for random particle movements in liquids and gases. This transport phenomenon is later expressed by Einstein as the mean squared displacement in terms of the time elapsed and the diffusivity. From this expression Einstein argued that the displacement of a Brownian particle is related to the square root of time, instead of time\(^{1}\).

\[
x = \sqrt{q_i D t}
\]

(4.3)

This can be related to an expression for time

\[
t = \frac{x^2}{2D}
\]

(4.4)

where \(x\) is penetration depth, \(t\) is time, \(D\) is diffusion coefficient and \(q_i\) is a constant expression for dimensional diffusion, in the case for a 1D analysis this value is 2.

These expressions are later used to rewrite the obtained diffusion coefficient from the RCM-test into an expected penetration time.

The carbonation process has been monitored over the whole test period, which can later be expressed as a carbonation rate for all mixtures.
4. Test results and discussion

Using a non-destructive testing method the resistivity measurements would give an indication for the chloride transport properties of the mortar specimens. Later, these mortar specimens were subjected to the RCM-test in order to measure the chloride penetration under a imposed electrical field. From these measurements a chloride diffusion coefficient was calculated, from which chloride penetration is related to time for carbonated mortars prior to chloride exposed.

It should be noted that the uncarbonated specimens were stored in the curing room while the carbonated specimens were exposed to the elevated CO$_2$ content. The carbonated specimens were taken from the curing room after 28 days and left for 5 months in the carbonation room. Comparing carbonated and uncarbonated series of results it should be noted that the degree of hydration might be different. This holds for mortars, but also for cement pastes as they were stored for 10 weeks in the carbonation while the uncarbonated specimens were left in the curing room.

4.2.1. Carbonation rate

For a period of 23 weeks the carbonation depth was monitored for all test mixtures while exposing to an elevated CO$_2$-content of 3%. For tests such as MIP, TGA and XRD only a small amount of carbonated cement paste was needed to be sampled. After 10 weeks of exposure it was found that enough carbonated paste was available for further testing.

Since the chloride resistance properties were tested only on mortar specimens it was decided to determine the carbonation rate for mortar specimens only.

The aim was to obtain fully carbonated mortar cylindrical specimens prior to the RCM-test. Since measurements of the carbonation depth were used indicatively for mortar specimens it was found that visual inspection using a colorimetric method with phenolphthalein indicator was sufficient.

In the carbonation chamber the specimens were exposed from all sides, because of placement on brackets. After splitting the specimen the ingress depth was measured from all sides. The average carbonation depth is determined by taking 8 measuring points on both of the long edges, see Figure 4.13.

The carbonation progress was monitored during the accelerated carbonation exposure. Over a time span of 23 weeks 6 measurements were taken for each cement blend. For each cement blend there were two carbonation depth measurements for mortar specimens, because both the 25 mm and 50 mm cylindrical specimens were monitored. The average carbonation depth is related to time, expressed as the carbonation progress in mortar specimens, for which 5 blends are presented in Figure 4.14a. The carbonation progress for all 12 mixtures can be found in Appendix H.

After 161 days of exposure in a 3% CO$_2$-content it was found that only the 25 mm mortar cylinders with a slag content higher than 60% were carbonated over the full specimen depth. Because of the limited research time it was decided to proceed while not all specimens were fully carbonated. As seen in Figure 4.13 if a specimen is not carbonated over its full depth, there is an uncarbonated zone in the middle, surrounded by an evenly carbonated zone.

From the carbonation progress, as illustrated in Figure 4.14a, it is concluded that increasing slag content causes increasing carbonation depth. Mortar with a slag contents of 55 and 70% show that the carbonation depth is in relation with the square root of t, as equation 4.3 suggests.

For lower slag contents carbonation depth and time seems to have a linear relation in Figure 4.14a, however the $\sqrt{t}$-relation to carbonation holds for all specimens since diffusion dominates the carbonation progress. The square root time relation will be visual when the specimens will be longer exposed in the accelerated carbonation conditions.

Figure 4.13: Measuring carbonation depth mortar specimen after 23 weeks; 40% slag content; thickness=50mm; w/c-ratio=0,5
The carbonation rate can be expressed by means of the carbonation diffusion coefficient, $D_{\text{carb}}$. The $D_{\text{carb}}$ presented in Figure 4.14 is determined using the carbonation depth after 23 weeks exposure to an increase CO$_2$-content of 3%.

A high diffusion coefficient indicates that CO$_2$ ingresses the sample easier than materials with a low $D_{\text{carb}}$. The high $D_{\text{carb}}$ for high slag contents is related to the large ingress depth as was observed in the carbonation progress in Figure 4.14b.

The calculated $D_{\text{carb}}$ for a exposure in a 3% CO$_2$-content is assumed to be equal to the diffusion coefficient for carbonation in ambient conditions. By taking the CO$_2$ exposure conditions into account, the carbonation depth in ambient conditions can be determined, using equation 4.5. For CO$_2$ exposure in ambient conditions, $c = 0.04\%$. The carbonation depth for ambient CO$_2$ exposure is determined and presented in Figure 4.15.

$$t = \frac{x^2}{2 \times c \times D_{\text{carb}}}$$  \hspace{1cm} (4.5)

where $x$ is penetration depth, $t$ is time, $D$ is diffusion coefficient and $c$ is CO$_2$-content [%].

From Figures 4.14 and 4.15 it is concluded that more slag replacement will lead to a higher carbonation rate. From the total carbonation depth it can be seen that mortar samples with a high slag content carbonate more than twice as fast as for OPC-mortars.
4.2.2. Resistivity

Resistivity of concrete is related to the susceptibility of chloride penetration, measured by means of a non destructive two electrode test method. The influence of slag content on resistivity was measured for several hydration periods and exposures.

Curing time is related to the hydration process, which on its own turn influences the microstructure, e.g. longer hydration can lead to a denser microstructure. To investigate the influence of curing time on the resistivity of mortar with different slag contents, 3 curing ages were tested. After 28 days, 90 days and approximately 6 months (just before the RCM-test) curing in the fog room the resistivity was measured. The influence of curing time was only tested for uncarbonated specimens. These specimens stored in the fog room were assumed to be saturated and can therefore be tested after 10 minutes of drying in ambient conditions to evaporate excessive surface moisture.

The use of slag in cement causes a densification of the cement matrix, due to the conversion of Ca(OH)$_2$ into secondary CSH. The use of slag will lead to a smaller porosity, subsequently causing a higher resistance to chloride penetration due to a denser structure.

A linear relation between increasing slag content and resistivity can be found for all 3 curing ages, as presented in Figure 4.16.

Resistivity measurements after 28 days curing were performed on 3 ø100x50 mm cylindrical mortar specimens per cement blend, resulting in a measuring scatter as indicated in Figure 4.16. For both 90 days and 6 months cured specimens no scatter is presented, since only one specimen was tested for each mixture.

From the increase between 90 days and 6 months cured mortar specimens it can be seen that hydration is an ongoing slow process. The ongoing hydration will cause an increase in density and therefore increase the resistivity of the specimens. One should note that the represented values in Figure 4.16 for 6 month cured specimens with a slag content higher than 40% were only measured on 25 mm thick specimens instead of the average value. All values for 28, 90 days and 6 months curing time up to and including 40% slag content is the average of measurements on 25 and 50 mm thick cylindrical mortar specimens.

The resistivity measurements of mortar specimens with a thickness of 50 mm at 6 months curing time, measured directly after taking from the curing room and before exposure to a Ca(OH)$_2$ saturation, was unfortunately omitted.

According to the RCM-test procedure the specimens need to be vacuum saturated in a saturated calcium hydroxide solution prior to performing the RCM-test. In order to investigate whether this saturation process of specimens influences the resistivity, the resistivity was measured before and after saturation. As explained in section 3.7 solely uncarbonated specimens are compared, since uncarbonated specimens were already
To complete the comparison of resistivity over several stages during the RCM-test, the resistivity was measured after RCM-test too.

Only 4 mixtures are presented in Figure 4.17, which was found enough to investigate the influence of the testing stage on the resistivity.

The presented values in Figure 4.17 deviate from all other graphs, since the results for 65% slag are given instead of the results for a 70% slag content.

The resistivity for a slag content of 70% increases after saturation compared with the measurement before saturation. However the resistivity should always be lower after saturation than before, because saturation will fill the empty pore (before saturation) with a conductive Ca(OH)$_2$ solution.

Therefore the single resistivity measurement for a mortar specimen with a 70% slag content was regarded as a measuring error and it was found not to be representative in the comparison.

The increasing resistivity with increasing slag content that was observed in each testing phase is equal to the observation from Figure 4.16 and can be explained by means of the change in porosity. A higher slag content causes a decrease in porosity by means of producing secondary CSH in the hydration process. Porosity is a measure of voids in the total volume, hence decreasing porosity means less voids. If there are less pores there is less conductive pore solution available to conduct the current, hence a higher resistivity.

For each cement blend a decrease in resistivity is perceived over the testing phases. The highest resistivity was measured before saturation in the Ca(OH)$_2$ solution and the lowest resistivity after the RCM-test.

Vacuum saturation in a Ca(OH)$_2$ solution will fill pores with this solution which were filled with air prior to saturation. The resistivity after saturation is enhanced by the extra filled pores with the conductive Ca(OH)$_2$ solution. There is more conductive pore water available in the pore system and therefore will decrease the resistivity.

The influence saturation has on the resistivity decreases when the slag content increases. For OPC the resistivity decreases with 30-35% after saturation, compared to only a 5% decrease for a slag content of 60 or 65%. The decreasing influence of the saturation on the resistivity can be assigned to the decreasing porosity. OPC-mortar have a larger porosity than mortar with 70%, as shown in Figure 4.5. A bigger porosity will lead to more pores that can be saturated with the Ca(OH)$_2$ solution. For 70% slag content the pores are much smaller than for OPC, lower porosity, it is harder to saturated these samples. Therefore less change in resistivity after saturation.

Figure 4.17 shows the decrease in resistivity after the RCM-test for uncarbonated specimen, however this was also observed for carbonated specimens for all slag contents and thickness's.

With the RCM-test, chloride ions from the, catholyte, NaCl-solution will penetrate into the sample from the bottom under the influence of an applied current.

The chloride ions will penetrate the sample via pore water and increase its ionic concentration of the with
Table 4.3: Carbonation depth and chloride penetration depth from RCM-test; w/c-ratio=0.5; n=1; 6mo. 3% CO$_2$ exposure

<table>
<thead>
<tr>
<th>Specimen size</th>
<th>ø100x50 mm</th>
<th>ø100x50 mm</th>
<th>ø100x25 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCM-test time</td>
<td>24 hours</td>
<td>6 hours</td>
<td>6 hours</td>
</tr>
<tr>
<td>Slag content</td>
<td>A B C D</td>
<td>A B C D</td>
<td>A B C D</td>
</tr>
<tr>
<td>0%</td>
<td>4.0 42.0 4.0 50.0</td>
<td>1.0 45.2 3.8 13.7</td>
<td>4.0 17.0 4.0 15.0</td>
</tr>
<tr>
<td>20%</td>
<td>5.0 40.0 5.0 25.5</td>
<td>2.3 44.4 3.2 10.3</td>
<td>2.8 19.4 2.8 14.4</td>
</tr>
<tr>
<td>25%</td>
<td>2.6 44.8 2.6 21.3</td>
<td>4.8 40.9 4.3 9.7</td>
<td>3.6 17.9 3.6 13.3</td>
</tr>
<tr>
<td>30%</td>
<td>3.8 42.4 3.8 21.0</td>
<td>3.6 41.3 5.1 11.7</td>
<td>4.1 16.8 4.1 11.2</td>
</tr>
<tr>
<td>35%</td>
<td>5.0 40.0 5.0 22.1</td>
<td>5.1 39.1 5.8 10.9</td>
<td>6.0 13.0 6.0 10.7</td>
</tr>
<tr>
<td>40%</td>
<td>5.6 38.8 5.6 21.1</td>
<td>6.2 37.2 6.6 11.8</td>
<td>7.3 10.3 7.3 12.6</td>
</tr>
<tr>
<td>45%</td>
<td>5.3 36.3 8.5 20.9</td>
<td>8.4 34.7 6.9 10.8</td>
<td>7.4 10.2 7.4 12.0</td>
</tr>
<tr>
<td>50%</td>
<td>5.5 34.3 10.2 22.0</td>
<td>10.0 29.8 10.2 8.0</td>
<td>10.0 5.0 10.5 13.9</td>
</tr>
<tr>
<td>55%</td>
<td>7.9 33.3 8.8 19.0</td>
<td>9.4 30.8 9.8 7.9</td>
<td>10.8 3.4 10.8 22.7</td>
</tr>
<tr>
<td>60%</td>
<td>10.1 28.1 11.8 20.4</td>
<td>11.0 25.6 13.4 10.6</td>
<td>12.5 0.0 12.5 25.0</td>
</tr>
<tr>
<td>65%</td>
<td>11.3 24.6 14.2 24.9</td>
<td>13.5 22.1 14.4 13.7</td>
<td>12.5 0.0 12.5 25.0</td>
</tr>
<tr>
<td>70%</td>
<td>10.4 24.5 15.1 23.4</td>
<td>16.0 18.3 15.7 13.1</td>
<td>12.5 0.0 12.5 25.0</td>
</tr>
</tbody>
</table>

NOTE: Bolt values indicate fully carbonated specimens.
NOTE: A = Carbonation depth measured from the top [mm], B = Uncarbonated zone [mm], C = Carbonated depth measured from the bottom [mm], D = Chloride ingress depth measured from the bottom [mm]

The influence of carbonation on the resistivity was measured on mortar specimens with a thickness of 25 and 50 mm. The 50 mm thick carbonated specimens were tested for 24 hours complying with the NT-Built 492 and for 6 hours to compare them with the measurements on 25 mm thick specimens.

The 25 mm thick specimens, carbonated or uncarbonated, were tested for 6 hours avoiding power breakdown, because of the limited thickness. The presented resistivity values are an average of the measured values for 25 and 50 mm thick mortar specimens. The resistivity of carbonated specimens is compared with the resistivity of uncarbonated specimens after saturation in Figure 4.19.

Figure 4.18 indicates a carbonated test specimens that were subjected to the RCM-test and resistivity measurements. It can be seen that these test specimens were not carbonated over the complete depth, but contain an uncarbonated core.

This uncarbonated core will subsequently also influence the resistivity measurements. In Table 4.3 the penetration depths are noted for all carbonated test specimens subjected to the RCM-test and resistivity measurements.

The resistivity results for these partly carbonated specimens can be found in Appendix I.

It should be noted that only 3 test specimens were carbonated over the full depth, as shown in Table 4.3. The 25 mm specimens with a slag content of 60, 65 and 70% are fully carbonated and will therefore indicated the true resistivity of a carbonated mortar.

All other test specimens, that were partly carbonated, will give a good indication for the influence of carbonation on the resistivity. However these values are not the true resistivity of carbonated mortar, as for 60, 65 and 70% slag ø100x25 mm samples.

As explained in section 2.1 the chemical reaction for carbonation of OPC-mortar is different than BFSC-mortars indicated by equations 2.1 and 2.2. Carbonation of OPC-mortars produce CaCO$_3$ from Ca(OH)$_2$, resulting in a denser microstructure and pH reduction. Both a decrease in pH and an decrease in porosity
4.2. Transport properties

Figure 4.19: Resistivity change after 6mo. carbonation of mortar specimens, w/c-ratio 0.5; n=2; 28 days curing; 3% CO$_2$ exposure
NOTE: Carbonated sample with thickness of 25mm and a >60% slag content were fully carbonated.

have a positive influence on the resistivity of mortars with 0% slag. A drop in pH means less ions present in
the pore solution eventually leading to a decrease in ionic value, e.g. conductive ions. In carbonated state it is
relatively more difficult for the imposed current to be conducted through the pore solution of OPC-mortars,
since there are less conductive ions present in the denser pore structure after carbonation.

Carbonation of BFSC-mortars decomposes the CSH in order to form CaCO$_3$, subsequently increasing the
porosity as already was concluded from the MIP-results. The high porosity after carbonation decreases the
resistivity significantly.

From Figure 4.19 it can be seen that the resistivity increases for carbonated mortars with a slag content up
to and including 45%. When the slag replacement is higher than 50% the resistivity decreases significantly,
which can mainly be attributed to the increasing porosity properties of carbonated area.

4.2.3. Diffusion of chloride ions

By means of the RCM-test, the chloride penetration properties for the mortar specimens are expressed as a
chloride diffusion coefficient.

Uncarbonated

The uncarbonated material were tested for two different thicknesses, 50 mm is the standard prescribed
specimen thickness according to the NT Built 492. Obtaining specimen that are carbonated over a full depth
of 50 mm in the limited research time turned out to be impossible, even with exposure from all sides as can
be seen in Figure 4.13.

A specimen with a smaller thickness will reach a full carbonated state much quicker, therefore the 25 mm
thick cylindrical specimens were tested too.

The calculated diffusion coefficient is dependent on the test duration, specimen thickness, applied volt-
age, temperature and the observed chloride penetration depth.

In order to exclude the change in size parameters in the comparison between carbonated and uncarbon-
ated specimens, the uncarbonated specimens with a thickness of 25 mm were tested too. The thickness is
much thinner than the standard suggests and therefore it was decided to shorten the testing time from 24 to
6 hours in order to prevent chlorides penetrating through the entire depth.

The uncarbonated specimens were tested for two different thicknesses and 2 corresponding testing times.
The chloride diffusion coefficient is calculated for both test specimens and presented in Figure 4.20.

From this figure it can be concluded that the calculated diffusion coefficient is almost similar for both
thicknesses.

For both thicknesses a similar decaying trend line can be observed. For specimens with no or very low slag
replacement, the diffusion coefficient is relatively high. The measured resistivity for uncarbonated specimens from Figure 4.19 can be related to this, a high diffusion coefficient is related to a low resistivity.

The opposite should be noted for mortars with a high slag content. A very low diffusion coefficient was obtained from the RCM-test, corresponding to a very high resistivity.

**Carbonated**

The calculated D is very dependent on the time and amount of uncarbonated depth. From Table 4.3 and/or Appendix J it can be seen that the carbonated area for 50 mm thick specimens subjected to 6 hour and 24 hour testing are almost similar. This was expected since the specimens have almost the same curing age and same exposure time, as the exposure time only deviate 1 week.

The tests result for 0% slag content for 24 hour RCM-testing was considered unreliable and is not presented in Figure 4.20.

From the silver nitrate indication it was observed that the complete specimen was penetrated with chloride, therefore it was impossible to measure the penetration depth. After the RCM-test on uncarbonated specimens for 6 hours a penetration depth was obtained for a 0% slag content. The chloride penetration over the full depth of the specimen tested for 24 hours was therefore attributed to a too high applied voltage and/or inadequate sealing of the specimen with the rubber sleeve, causing leakage along the sides of the specimen.

It can be seen that the diffusion coefficient calculated for 50 mm thick mortar specimens after 6 hours testing is higher than the one calculated for 24 hours testing. Especially for specimens with a high slag content the difference is substantial. This difference in diffusion coefficient is related to the exposure time and carbonation depth of partly carbonated specimens.

The carbonated zone of mortars with high slag replacement is assumed to have very low resistance against chloride, while the uncarbonated zone has a very high resistance. Because of the low resistance of the carbonated zone it will not take very long to be penetrated. Then the uncarbonated material is reached, which has very high resistance against chloride penetration and the migration slows down. After 6 hours the uncarbonated zone will be reached and a small depth will be penetrated, but after 24 hours the penetration depth is only twice as deep after a 4x enlarged exposure time. From this it is concluded that test duration has a large influence on the penetration depth and diffusion coefficient of partly carbonated specimens. The longer the specimen will be exposed to the RCM-test the lower the coefficient will be, because the influence of the uncarbonated middle section will become larger.

The behaviour for OPC-mortars is presumably opposite, since carbonation increases the resistivity. But this cannot be checked since the result of 24 hours testing is considered unreliable, due to an execution mis-
If the diffusion coefficient for ø100x50 mm and ø100x25 mm for 6 hours testing are compared a decrease is observed in the diffusion coefficient for slag contents up to 50%.

From Table 4.3 it is observed that for ø100x25 mm sample the carbonated area for slag contents >45% almost covers the whole specimen thickness. This subsequently means that the 25 mm specimen has less uncarbonated zone in comparison to the 50 mm specimen. As long as there is a sufficient uncarbonated zone, this will be a dominant factor for the chloride diffusion coefficient, as the decrease in $D_{cl}$ until 45% slag suggests. For slag contents >45% the carbonated zone in 25 mm specimens is significant and therefore influences the diffusion coefficient a lot. When for the 25 mm thick specimen the carbonation depth is bigger and the uncarbonated area is less this will result in a increase in diffusion coefficient, hence a worse resistance against chloride migration.

From Table 4.3 it be observed that there are 3 different chloride penetration profiles.

For partly carbonated specimen either the chlorides penetrate the carbonated and uncarbonated area or the chloride penetrate only in the carbonated area and to not reach the uncarbonated core.

For fully carbonated samples, consequently the chloride only penetrate the carbonated area.

However for the 3 ø100x25 mm specimens with a slag content ≥ 60% it was found that the chlorides penetrate through the entire specimen.

Because of the very low resistance of carbonated material the specimen was fully penetrated with chlorides. Therefore it is not possible to measure the chloride penetration depth, consequently it is not possible to calculate the $D_{cl}$ for these samples.

The maximum chloride diffusion coefficient for a 25 mm thick mortar in a 6 hours RCM-test is 28.9 $\times\ 10^{-12}$ m$^2$/s as indicated in Figure 4.21. If the values from a slag content of 45-55% is linearly extrapolated a diffusion coefficient of 45 $\times\ 10^{-12}$ m$^2$/s could be found for a slag content of 70%. It is concluded that carbonation of a 70% slag mortar will increase the chloride diffusion coefficient by 20 fold, hence strongly influencing the resistivity of the material. In Appendix J all the test data and results from the RCM-test can be found, including all calculated chloride diffusion coefficients.

![Figure 4.21: Chloride diffusion coefficient after 6mo. carbonation of mortar specimens, w/c-ratio 0.5; 28d curing; n=1
NOTE: 25mm specimens >60% slag = fully carbonated
NOTE: 50mm specimen for 6hr test >50% slag = chloride ingress only in carbonated zone
NOTE: For all other specimens the chloride penetrates in carbonated and uncarbonated zones](image URL)
4.2.4. Chloride penetration time

From inspection of the concrete overpass at Hattemerbroek it was concluded that multiple structural elements suffer from concrete damages due to chloride induced corrosion enhanced by carbonation, e.g. abutments and support beams.

This research describes this combined degradation of carbonation and chloride ingress as two separate phases. First there is an initial period of a sheltered concrete element prone to carbonation and after a certain time the carbonated surface is exposed to chlorides, for instance due to a leaking joint.

Carbonation and chloride ingress are, as described before, dominated by diffusion. Using equation 4.3, the $D_{\text{carb}}$ as determined in section 4.2.1, the carbonation depth after a carbonation exposure time can be determined.

\[ x_{\text{carb}} = \sqrt{2D \times t} \quad (4.6) \]

where $x$ is carbonation penetration depth, $t$ is time, $D$ is diffusion coefficient.

To evaluate different carbonation period, there are time steps of 5 years starting from 0 up to a carbonation period of 50 years. In figures below the carbonation depth is illustrated for periods of 0, 20 and 50 years ambient carbonation exposure.

After this period of carbonation, the concrete surface is exposed to chlorides. The chloride penetration time is dependent on the resistance of two parts of the concrete cover, a carbonated and an uncarbonated part. For both parts the $D_{cl}$ is calculated in section 4.2.3. The chloride penetration time is determined for a cover depth of 50 mm, using equation 4.4.

\[ t_{cl} = \frac{x^2}{2D} \quad (4.7) \]

where $x$ is cover depth, $t$ is chloride penetration time, $D$ is diffusion coefficient.

This cover depth is generally prescribed by the NEN-EN-1992-1 as minimum cover for concrete elements in exposure class XD3 and structural class SS, [30].

The chloride penetration time is illustrated in figures below after a carbonation period of 0, 20 and 50 years. The carbonation depth and chloride penetration time for all other carbonation exposure periods can be found in Appendix K.

Figure 4.22 shows a uncarbonated concrete cover of 50 mm prior to chloride ingress. It can be seen that a mortar sample with 70% slag requires the longest time for chlorides to ingress through the cover. This mixture is also generally recommended by the design recommendations in an environment prone to chloride induced corrosion. It should be noted that the calculated chloride penetration time is not equal to the corrosion initiation time, since the chloride threshold value at the reinforcement is left out of the scope.

When a concrete cover, for instance of 50 mm, is exposed to carbonation it will affect the chloride penetration time significantly. The amount of slag influences the carbonation depth as a slag content of 70% shows the largest carbonation depth after 20 years of carbonation, as indicated in Figure 4.23. Carbonation of slag cement mortars decreases the chloride resistance, hence the chloride penetration time. To total chloride penetration time, $t_{cl}$ for a 70% slag content decreases a lot after a carbonation period of 20 years. The $t_{cl}$ decreases significantly from 21 years prior to carbonation to approximately 8.5 years after 20 years carbonation.

A 45% slag content shows the same $t_{cl}$ as for 70%. The different between the $t_{cl}$ of a uncarbonated cover and a cover that has a carbonation depth of 10 mm after 20 years is not that significant as it is for a 70% slag content. The $t_{cl}$ decreases from approximately 14 years to 8.5 years. From tests it was already concluded that a mixture of 45% gives the highest electrical resistivity and the lowest $D_{cl}$ after carbonation. The carbonated part of a 45% slag content mortar is more resistant to chloride penetration than a carbonated part of a 70% slag mortar.

Finally after a period of 50 years carbonation an OPC mortar is carbonated for 13 mm compared to around 27 mm for a mortar with a 70% slag content. The increase in carbonation depth will decrease the chloride penetration resistance of the concrete cover for a mortar with a 70% slag content. In Figure 4.25 it can be seen that mortars with a high slag replacement have a small chloride penetration time after a carbonation period of 50 years. However the cement blends with a slag content between 35 and 55% show the largest residual...
Looking back at the damage of the concrete element of the Hattemerbroek it can be explained using this "two layer approach". The Hattemerbroek overpass was built in 1976 using a BFSC concrete and is now 40 years old. The sheltered concrete elements, such as abutments and support beams, are prone to carbonation. From the cover depth measurements it was observed that these elements had a concrete cover of approximately 30 mm. The carbonation depths were around 25-30 mm, which from the proposed model coincides with 35 years of carbonation with a 70% content, as shown in Figure 4.24. If this surface is then exposed to chloride, which might be the case for Hattemerbroek due to a leaking joint, the remaining chloride penetration time is maximum 6 years (Note: calculated for 50 mm). From the chloride ingress measurement during inspection it was found that there was a significant amount of chloride present and that corrosion damage might occur in a couple of years. From this two layer approach the concrete damage in Hattemerbroek might be explained.

Figure 4.22: 0 years carbonation exposure prior to chloride exposure, mortar specimen, w/c-ratio=0.5
(a) Carbonation depth
(b) Time needed for chloride ions to penetrate 50 mm cover depth after carbonation.

Figure 4.23: 20 years carbonation exposure prior to chloride exposure, mortar specimen, w/c-ratio=0.5
(a) Carbonation depth
(b) Time needed for chloride ions to penetrate 50 mm cover depth after carbonation.
4. Test results and discussion

4.2.5. Research retrospect

All blended cements with different slag contents used in this research were found to have approximately the same 28-days compressive strength, although they show a different strength development. The difference in strength development is related to the change in hydration process for cements with slag replacement. Mortars made of cement with no or low slag replacement have a relatively high early strength and low strength development, while for mortars with a high slag content the opposite applies.

The change in slag content influences the pore structure and mineral composition of cement paste. During hydration slag will bind the calcium hydroxide and form secondary CSH-gel. The use of more slag replacement result in less Ca(OH)\(_2\) and more CSH-gel after hydration. From TGA it was observed that for a 70% slag content almost no more Ca(OH)\(_2\) was present. On the contrary TGA of a Portland cement, used as a reference sample, does show the presence of a high amount of Ca(OH)\(_2\). With the use of slag the increase in CSH-gel, due to hydration, will densify the cement paste and decrease the porosity. One of the factors for transport processes in cementitious systems is porosity. The critical pore size is used as an indicator for the porosity which could be determined by MIP-analysis. Based on results from the MIP-analysis it can be seen
that the critical pore size in the cement paste decreases with an increase of slag content.

Changes in mineral composition and pore structure of a cement paste influence the transport properties of the material. Mortar samples with a low slag content show a low electrical resistivity, which can be related to the chloride penetration resistance. From the RCM-test it was confirmed that a low resistivity, i.e. poor resistance to chloride penetration, correlate to a high chloride diffusion coefficient. By using more BFS the porosity decreases, densifying the pore structure, furthermore causing an increase in resistivity and decreasing the chloride diffusion coefficient.

The results of MIP and TGA-tests on cement paste show that curing time does not influence the pore structure and mineral composition significantly. However it is found that the increase in strength and resistivity of mortar specimens over time indicates ongoing hydration and changes in microstructure. Cement paste and mortar samples are two different systems, hence the results obtained on cement paste are difficult to relate to results on mortar samples.

Both cement paste and mortar specimens were subjected to accelerated carbonation in a RH of 60-75% and an elevated CO₂-content of 3% CO₂. Carbonation is known to affect only the cement paste, therefore MIP and TG-analysis are used to identify changes in the pore structure and mineral composition after carbonation.

Samples with a high slag content are very susceptible to carbonation, in contrast to the high chloride penetration resistance. As long as there is enough Ca(OH)₂ available in the cementitious material, carbonation will convert the Ca(OH)₂ into CaCO₃, calcite, that densifies the cement paste.

In case of samples with a low slag content, they contain the highest amount of Ca(OH)₂ prior to carbonation. For these samples with a low slag content no significant change in critical pore diameter was found, although a decrease in total porosity was found consequently densifying the material. From TGA it was found that there was no more Ca(OH)₂ present after carbonation, but CaCO₃ was measured in abundance. The lack of Ca(OH)₂ and the occurrence of CaCO₃ indicates a conversion of Ca(OH)₂ into CaCO₃ by means of carbonation. The amount of Ca(OH)₂ prior to carbonation will determine the amount of CaCO₃ after carbonation, as was confirmed from the calcium balance.

Carbonation of samples with a high slag content decomposes the CSH, because in absence of Ca(OH)₂ the CSH liberate CaO to bind with the penetrated CO₂. From the calcium balance, based on the TGA results, it was found that after carbonation there is less calcium originating from CSH, subsequently indicating a loss in CSH. Carbonation of CSH-gel forms unstable calcium carbonates, otherwise known as vaterite and verified by XRD. Formation of CaCO₃ by carbonation of the CSH-gel, otherwise known as carbonation shrinkage, will increase the porosity. The increase in porosity is observed as an increase in critical pore diameter from the MIP-test. Increasing the slag content causes an increase in porosity due to carbonation, e.g. the critical pore size of cement paste with a slag content of 70% is magnified up to 12x after carbonation.

The changes in pore structure and mineral composition caused by carbonation will also change the transport properties of the cementitious material.

Since both carbonation and chloride penetration are transport phenomena dominated by diffusion, the progress can be expressed by means of a diffusion coefficient. From the unit of this diffusion coefficient, mm²/day, it can be seen that the measured carbonation depth relates to the elapsed time.

D_{carb} determined from accelerated carbonation conditions is then used to relate to the amount of years carbonation requires in natural carbonation conditions.

From this it was confirmed that increasing slag content will increase the susceptibility to carbonation of mortar samples, given an increasing D_{carb}. The increasing D_{carb} indicate a faster carbonation penetration than the samples with OPC, which showed a lower D_{carb} consequently the slowest carbonation penetration.

The chloride transport properties of mortar samples is indicated by electrical resistivity and chloride diffusion coefficient. For example carbonation of OPC-mortar specimens will decrease the porosity due to conversion of Ca(OH)₂ into CaCO₃, densifying the material and increasing the chloride resistance. This increasing resistance is related to a decreasing D_{cl}.

On the other hand for mortars with a high slag content the porosity increases during carbonation. Increasing porosity will enhance the transport properties, observed by a decrease in resistivity and increase in the D_{cl}.

Mortars containing a high amount of slag, for instance 70%, will have a significant decrease in resistivity after carbonation. This significant change in resistivity was also observed as a 20x increase of the D_{cl} after carbonation.
The high chloride penetration resistance prior to carbonation of BFSC-mortars is completely lost after carbonation. Therefore it becomes easy for chlorides to penetrate.

From discussing and reflection on the Hatterbroek case study in section 4.2.4 it is concluded that a carbonation period prior to chloride exposure strongly influences the chloride penetration time, confirming the hypothesis.

If there is no carbonation of the mortar/concrete surface prior to chloride exposure a cement mixture with 70% slag content will lead to a dense microstructure and relatively high resistance to chloride penetration. It should be noted that the current design codes already suggest this, by prescribing CEM III/B mixtures.

The case reflected in this research provides that there is a carbonation period prior to chloride exposure, e.g. an abutment that carbonates and is exposed to chloride from de-icing salts when the joint starts to leak. For structural elements that are sheltered and can carbonate before a joint starts to leaks and exposed to chloride. When the carbonation period is longer than 20 years another slag content might be considered, providing a longer chloride penetration time after this carbonation period. It is advised to research slag contents from 35% to 55% in more detail as they give the longer chloride penetration time for carbonated specimens than a CEM III/B cement.
In this chapter, the main thesis conclusions are summarized, based on the results of the scientific research. Subsequently the main research question is answered and the hypothesis is reconsidered. Finally some remarks will be made on this research and corresponding conclusions.

This research on the influence of carbonation on chloride ingress of BFSC mortar only considers cases at which first carbonation occurs before it is exposed to chloride ingress. Any other combination of carbonation and chloride ingress is excluded from this study.

- The slag content in blended cement influences the strength development in mortar prisms, while the 28 days compressive strength is approximately equal for all mixtures.
  
  Mortar specimens show a increase in strength over curing time. Equal 28 days compressive strength on mortar prisms confirms the assumption to use equal 28 days strength for the cement mixing with CEM I 42.5 and CEM III/B 42.5.

- In studied mixtures the use of slag decreases the porosity by densification of the material.

- For slag containing cementitious materials carbonation will increase the porosity of cement paste significantly.
  
  If there is no or low slag replacement the porosity stays approximately equal to uncarbonated material.

- For all cement blends there was no more Ca(OH)$_2$ present after carbonation.
  
  From TGA it was observed that Ca(OH)$_2$ is converted into CaCO$_3$, due to carbonation and that an increasing use of slag will decrease the initial Ca(OH)$_2$ content before carbonation.

- The use of slag will increase the susceptibility of cementitious material to carbonation.
  
  The $D_{\text{carb}}$ will increase for an increase in slag content, hence the carbonation rate will increase.

- The use of slag will increase the electrical resistivity in uncarbonated condition.

- Hydration will increase the electrical resistivity of all cement blends with increasing curing age.

- For mortar specimens with a slag content <50% partial carbonation of the specimen thickness will increase the electrical resistivity. Carbonation will decrease the electrical resistivity of mortars with a slag content $\geq 50%$.

- An increasing slag content in uncarbonated cementitious material will decrease the chloride diffusion coefficient.

- Carbonation of OPC-mortars will decrease the $D_{\text{cl}}$, but for slag containing mortars carbonation will increase the $D_{\text{cl}}$.
  
  The chloride diffusion coefficient for a 70% slag content is determined using extrapolation and is approximately 20x larger after carbonation.
The influence of carbonation on the chloride resistance of mortars is indicated through the chloride penetration time after carbonation, using the $D_{cl}$. In this research Service Life modelling was not included. Neither was the chloride induced corrosion initiation by incorporating a chloride threshold value. The chloride penetration time is used as an indicative method, to show the influence of carbonation on the chloride resistance.

From the "two layer model" of chloride ingress after carbonation a slag content of 35-55% showed promising remaining chloride penetration time after a carbonation period longer than 20 years and should be consider in more detail.

As long as the initial carbonation period is less than 20 years a 70% slag mortar showed the longest chloride penetration time. However, carbonation of a high slag containing mortar influences the chloride resistance significantly.

Research is limited to sheltered concrete structural elements prone to carbonation that is exposed to chlorides after a period of time. Furthermore this research only holds for environmental exposure class XD3 and is not valid for environmental classes XS.

Using these conclusions the research question can be answered as formulated from the start of this research:

What is the influence of carbonation on the chloride ingress of BFSC-mortars and the effect of slag content?

Carbonation of OPC will cause a densification of the material and increases the chloride penetration resistance. On the contrary carbonation of slag cements will decrease the chloride penetration resistance, due to an increase in porosity. Initially a BFSC-mortar has a relatively high resistance to chloride ingress, but if it carbonates these properties will decrease significantly. Therefore chloride penetration resistance is strongly dependent on the carbonation period and the corresponding carbonation depth, confirming the hypothesis from section 1.6.

The chloride penetration resistance of a mixture with 70% slag, generally prescribed in XD environmental classes, decreases significantly after carbonation.

OPC-mortars densifies by means of carbonation, however it still has a relatively low chloride penetration resistance compared to slag cement blends.

By mixing OPC and BFSC these properties seem to mix. Mortars with a slag content between 35% and 55% show less influence by carbonation, consequently less influence on the chloride penetration resistance. This range of slag content should be reviewed in more detail for Service Life of structural elements subjected to carbonation and chloride ingress, e.g. abutments and supporting beams.
Reflection on methods and recommendations for further research

Looking back at the research, some improvements on preparation techniques and procedures are proposed:

• **Results from electrical resistivity and chloride diffusion tests for mortars with <60% slag are based on partly carbonated specimens.**
  
  Since these specimen were not carbonated over the whole thickness of the test specimens, the obtained value is from a composite. The tests should be redone for fully carbonated specimen, to gain more understanding of carbonated properties.

• **Increase the number of test specimens in order to gain more statistical reliable values.**
  
  For mechanical tests, MIP, TGA, XRD, resistivity measurements and RCM-tests.

• **Uncarbonated specimens should not be stored in the fogroom until testing.**
  
  After 28 days curing the specimens should be taken out of fogroom in order to have equal hydration. Storage in the fogroom will give rise to ongoing hydration, hence changing the transport properties. Carbonated and uncarbonated test specimens should have the same curing time, storage of uncarbonated specimens in a desiccator might be the solution.

• **Change storage of carbonated specimens before TGA-test.**
  
  Ethanol can react with cementitious material in high temperatures, changing the mineral composition slightly. Storage in a freeze dryer might be a better solution[20].

• **Improve grinding procedure for obtaining powder-samples for TGA.**
  
  The significant amount of calcium carbonate measured from the TGA of the uncarbonated samples, might be caused by accelerated carbonation of grounded cement paste due to the high surface area.

• **Change from carbonation exposure from all sides to a one dimensional ingress.**
  
  From a one dimensional carbonation front it might be possible to determine the influence of the carbonation depth on transport properties, e.g. electrical resistivity and chloride diffusion.

• **Reduce the exposure time of fully carbonated to the RCM-test in order to obtain the chloride diffusion coefficient.**

• **Prevent chlorides to penetrate through whole thickness of the "fully" carbonated specimens, for this study mortars with a slag content ≥ 60%.**
  
  Using a RCM-test time shorter than 6 hours, it might be possible to determine the $D_{cl}$. 
This research showed promising results for determining the influencing factor of carbonation on the chloride transport properties of BFSC-mortars. Following items are recommendations for further research:

- **Reconsider the influence of this research recommendations on "carbon footprint" of the concrete structure.**
  The use of slag strongly reduces the total CO$_2$ emission of the cement production, therefore the advise of using less slag contradict the current course of reducing CO$_2$-emission in cement production.

- **Expanding the research to a wider spectrum of w/c ratio's and cement contents.**
  Instead of focussing on a w/c-ratio of 0,5, a spectrum of 0,3-0,6 should be considered. The w/c-ratio will influence the hydration process, consequently change the pore structure and the transport properties.

- **Extend research to concrete specimens.**
  It is expected that carbonation influences the chloride resistance of concrete even more than mortar, because concrete is more porous than mortar.

- **Extend research to more cement types.**
  Check the standard CEM cement types prescribed by the EN-197, such as CEM III/A and CEM II/A-S. Incorporate other Supplementary Cementing Materials besides slag, eg. fly ash and silica fume.

- **Obtain cement mixtures with different slag content in cooperation with cement producing factories.**
  Cement blends were checked and is was concluded that the slag particles were adequately dispersed through the cement mixture. However a cement factory might give a more homogeneous cement mixture than mixing by use of a paint mixer.

- **Further investigate the influence of curing time on increased critical pore diameter for carbonated cement paste.**
  For blended cements with a slag content between 25 and 50% there is a significant increase in critical pore diameter for carbonated specimens upon increasing curing age. From TGA measurement there was no mineralogical explanation for this behaviour found. Further microstructural analysis on the cement paste might find the solution or by increasing the number of test specimens can indicate the found values as a measuring error.

- **More research should be done on calcite and vaterite formation during carbonation of cement paste samples.**
  From the calcium balance there is no clear indication that calcium hydroxide and CSH are solely converted into calcite and vaterite respectively.

- **Investigate the influence of carbonation on chloride ingress properties if wet-dry cycles are considered.**
  It strongly depends on the drying rate of the material.

- **Expand XRD-analysis to uncarbonated specimen.**
  Identify the mineral present at 680°C in uncarbonated cement paste.

- **Check influence of natural carbonation on chloride diffusion properties of mortar specimens.**
  Compared to accelerated carbonation in 3% CO$_2$ content and RH of approximately 65%.

- **More research into the influence of specimen thickness and test duration of the RCM-test on the calculated chloride diffusion coefficient.**
  Calculation of the $D_{RCM}$, respectively the $D_{cl}$ is strongly dependent on time, applied Voltage and specimen thickness.

- **More research into the carbonation of CSH and Ca(OH)$_2$.**
  The rate of carbonation of Ca(OH)$_2$ and formation of CaCO$_3$ compared to the carbonation of CSH and its formation of CaCO$_3$ might be different. And is there a difference in this carbonation rate between ambient and accelerated carbonation?
• **Investigate into the changing CSH during carbonation.**
  Is there a change in amount of calcium that the CSH contains before and after carbonation? Perhaps EDS-mapping will give answers, by indicating the calcium content of CSH.

• **Extend research to Service Life modeling.**
  Momentarily determining the chloride penetration time is merely an indicative method. No chloride threshold value for corrosion initiation was considered.
Bibliography


[27] *Porosimetry -brochure*. micromeritics Instrument Corporation, 01/01/01 edition.


Appendixes:
Appendix A:
Product information
Appendix A: Product information

(a) CEM-I 42.5N

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<td>Al2O3</td>
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<td>Fe2O3</td>
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<td>K2O</td>
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</tr>
<tr>
<td>Na2O</td>
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<tr>
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<td>P2O5</td>
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(b) CEM-III/B 42.5N/LH/5R

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Chemical analysis on cement powder by ENCI
## Portlandcement

**CEM I 42,5 N**

### 1. Normen en certificaten

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### 3. Chemische kenmerken

De chemische kenmerken van het cement worden bepaald volgens EN 196-2.

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<th>Gemiddelde waarde</th>
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* Overeenkomstig de verordening EG 1907/2006 (Reach) moet het gehalte aan oplosbaar chroom (VI) beperkt zijn tot maximaal 0,0002%. Dit gehalte wordt bepaald volgens EN 196-10.
Hoogovencement  
CEM III/B 42,5 N-LH/SR

1. Normen en certificaten

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<th>Normgrenzen</th>
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3. Chemische kenmerken

De chemische kenmerken van het cement worden bepaald volgens EN 196-2.

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* Overeenkomstig de verordening EG 1907/2006 (Reach) moet het gehalte aan oplosbaar chroom (VI) beperkt zijn tot maximaal 0.0002%. Dit gehalte wordt bepaald volgens EN 196-10.
SALINA KEUKENZOUT

We bieden onze consumenten zoutproducten aan met een rijke traditie. Ons zout wordt gewonnen uit de Europese Zechstein Zee. Deze zee is miljoen jaar geleden opgedroogd. Ons zout, dat uit ondergrondse zeezoutlagen wordt gewonnen, garandeert een hoge zuiverheid en constante kwaliteit. De fijne korrels maken onze zoutproducten gemakkelijk strooibaar.

**PRODUCTBESCHRIJVING**

Voor consumenten zonder medicale beperkingen raden wij Salina Keukenzout aan. Natuur Keukenzout kan worden toegepast voor speciale recepturen waarbij puur zout de voorkeur heeft. Denk bijvoorbeeld aan het conserveren van levensmiddelen, groente in glas of blik, pekelen van groente en vlees, etc. Dit zout is tevens geschikt voor consumenten die overgevoelig zijn voor jodium.

**SAMENSTELLING**

Type zout: fine salt

- Natrium Chloride (NaCl) 99.9 %
- waarvan natrium 39.0 %
- vocht (H2O) < 0.1 %
- anticaking agent (E504) < 0.4 %
- anticaking agent (E535)
- inhoud gemeten als Fe(CN)6
- < 10 mg/kg

* Op basis van gedroogd puur zout

**KORRELGROOTTEVERDELING**

De korrelgrootteverdeling van Salina is gekozen op basis van onderzoek naar toepassingen in de voedselindustrie. Hieronder een opgave van percentages naar korrelgrootteverdeling.

- 3 % < 125 micron
- 94 % van 125 tot 600 micron
- 3 % van 600 tot 1000 micron
- 0,1 % > 1000 micron

De korrelgrootteverdeling kan als gevolg van ontmenging tijdens transport en opslag afwijken.

**STORTEGEWICHT**

1300 kg/m³

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<td>EAN (coll)</td>
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³ Publicatie datum: 25-11-2014
Product Data Sheet, versie datum: 25-11-2014

Product information table salt used for RCM-test by Akzonobel
Appendix B: Strength test results
Compressive and flexural tensile strength results on mortar prisms (40x40x160 mm) according to EN-197; w/c-ratio=0.5

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<th>Slag content</th>
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<td></td>
<td>2</td>
<td>33.5</td>
<td>50.6</td>
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</table>
Appendix C: MIP-results; pore size distribution
Appendix C: MIP-results; pore size distribution

0% slag content; Carbonated and uncarbonated cement paste sample; w/c-ratio=0.5; 28+90 days curing

20% slag content; Carbonated and uncarbonated cement paste sample; w/c-ratio=0.5; 28+90 days curing
Appendix C: MIP-results; pore size distribution

25% slag content; Carbonated and uncarbonated cement paste sample; w/c-ratio=0.5; 28+90 days curing

30% slag content; Carbonated and uncarbonated cement paste sample; w/c-ratio=0.5; 28+90 days curing
Appendix C: MIP-results; pore size distribution

35% slag content; Carbonated and uncarbonated cement paste sample; w/c-ratio=0.5; 28+90 days curing

40% slag content; Carbonated and uncarbonated cement paste sample; w/c-ratio=0.5; 28+90 days curing
Appendix C: MIP-results; pore size distribution

45% slag content; Carbonated and uncarbonated cement paste sample; w/c-ratio=0.5; 28+90 days curing

50% slag content; Carbonated and uncarbonated cement paste sample; w/c-ratio=0.5; 28+90 days curing
55% slag content; Carbonated and uncarbonated cement paste sample; w/c-ratio=0.5; 28+90 days curing

60% slag content; Carbonated and uncarbonated cement paste sample; w/c-ratio=0.5; 28+90 days curing
Appendix C: MIP-results; pore size distribution

65% slag content; Carbonated and uncarbonated cement paste sample; w/c-ratio=0.5; 28+90 days curing

70% slag content; Carbonated and uncarbonated cement paste sample; w/c-ratio=0.5; 28+90 days curing
Appendix D: TG + DTG-curves
Comparison carbonated and uncarbonated specimen
Appendix D: TG + DTG-curves; Comparison carbonated and uncarbonated specimen

0% slag content; cement paste sample; w/c-ratio=0.5; 90d curing; n=1

20% slag content; cement paste sample; w/c-ratio=0.5; 90d curing; n=1
Appendix D: TG +DTG-curves; Comparison carbonated and uncarbonated specimen

25% slag content; cement paste sample; w/c-ratio=0.5; 90d curing; n=1

30% slag content; cement paste sample; w/c-ratio=0.5; 90d curing; n=1
Appendix D: TG + DTG-curves; Comparison carbonated and uncarbonated specimen

35% slag content; cement paste sample; w/c-ratio=0.5; 90d curing; n=1

40% slag content; cement paste sample; w/c-ratio=0.5; 90d curing; n=1
45% slag content; cement paste sample; w/c-ratio=0.5; 90d curing; n=1

50% slag content; cement paste sample; w/c-ratio=0.5; 90d curing; n=1
Appendix D: TG +DTG-curves; Comparison carbonated and uncarbonated specimen

55% slag content; cement paste sample; w/c-ratio=0,5; 90d curing; n=1

60% slag content; cement paste sample; w/c-ratio=0,5; 90d curing; n=1
Appendix D: TG + DTG-curves; Comparison carbonated and uncarbonated specimen

65% slag content; cement paste sample; w/c-ratio=0.5; 90d curing; n=1

70% slag content; cement paste sample; w/c-ratio=0.5; 90d curing; n=1
Appendix E: TG + DTG-curves
Carbonated cement paste specimens
0% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

0% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
Appendix E: TG + DTG-curves; Carbonated cement paste specimens

20% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

20% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
25% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

25% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
Appendix E: TG +DTG-curves; Carbonated cement paste specimens

30% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

30% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
35% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

35% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
Appendix E: TG + DTG-curves; Carbonated cement paste specimens

40% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

40% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
45% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

45% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
50% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

50% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
Appendix E: TG + DTG-curves; Carbonated cement paste specimens

55% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

55% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
60% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

60% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
65% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

65% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
70% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

70% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
Comparison 28d vs 90d curing time; 0% slag content; Carbonated cement paste sample; w/c-ratio=0.5; n=1

Comparison 28d vs 90d curing time; 30% slag content; Carbonated cement paste sample; w/c-ratio=0.5; n=1
Appendix E: TG +DTG-curves; Carbonated cement paste specimens

Comparison 28d vs 90d curing time; 50% slag content; Carbonated cement paste sample; w/c-ratio=0.5; n=1

Comparison 28d vs 90d curing time; 70% slag content; Carbonated cement paste sample; w/c-ratio=0.5; n=1
Appendix F: TG + DTG-curves
Uncarbonated cement paste specimens
0% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

0% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
20% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

20% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
25% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

25% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
30% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

30% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
35% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

35% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
Appendix F: TG + DTG-curves; Uncarbonated cement paste specimens

40% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

40% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
45% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

45% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
50% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

50% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
55% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

55% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
Appendix F: TG + DTG-curves; Uncarbonated cement paste specimens

60% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

60% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
65% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

65% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
Appendix F: TG + DTG-curves; Uncarbonated cement paste specimens

70% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 28 days curing; n=1

70% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; 90 days curing; n=1
Comparison 28d vs 90d curing time; 0% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; n=1

Comparison 28d vs 90d curing time; 30% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; n=1
Comparison 28d vs 90d curing time; 50% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; n=1

Comparison 28d vs 90d curing time; 70% slag content; Uncarbonated cement paste sample; w/c-ratio=0.5; n=1
Appendix G:
XRD-results; diffraction pattern
0% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing
Note: This XRD-pattern is modified by subtracting the amorphous hump as it might be attributed to CSH-gel and unhydrated slag particles.

20% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing
Note: This XRD-pattern is modified by subtracting the amorphous hump as it might be attributed to CSH-gel and unhydrated slag particles.
25% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing
Note: This XRD-pattern is modified by subtracting the amorphous hump as it might be attributed to CSH-gel and unhydrated slag particles.

30% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing
Note: This XRD-pattern is modified by subtracting the amorphous hump as it might be attributed to CSH-gel and unhydrated slag particles.
Appendix G: XRD-results; diffraction pattern

35% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing
Note: This XRD-pattern is modified by subtracting the amorphous hump as it might be attributed to CSH-gel and unhydrated slag particles.

40% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing
Note: This XRD-pattern is modified by subtracting the amorphous hump as it might be attributed to CSH-gel and unhydrated slag particles.
45% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing
Note: This XRD-pattern is modified by subtracting the amorphous hump as it might be attributed to CSH-gel and unhydrated slag particles.

50% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing
Note: This XRD-pattern is modified by subtracting the amorphous hump as it might be attributed to CSH-gel and unhydrated slag particles.
55% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing
Note: This XRD-pattern is modified by subtracting the amorphous hump as it might be attributed to CSH-gel and unhydrated slag particles.

60% slag content; Carbonated cement paste sample; w/c-ratio=0.5; 90 days curing
Note: This XRD-pattern is modified by subtracting the amorphous hump as it might be attributed to CSH-gel and unhydrated slag particles.
Appendix G: XRD-results; diffraction pattern

65% slag content; Carbonated cement paste sample; w/c-ratio=0,5; 90 days curing
Note: This XRD-pattern is modified by subtracting the amorphous hump as it might be attributed to CSH-gel and unhydrated slag particles.

70% slag content; Carbonated cement paste sample; w/c-ratio=0,5; 90 days curing
Note: This XRD-pattern is modified by subtracting the amorphous hump as it might be attributed to CSH-gel and unhydrated slag particles.
Appendix H:
Carbonation ingress
Appendix H: Carbonation ingress

Measured carbonation progress of mortar specimen in a 3% CO$_2$-content; w/c-ratio=0.5; n=2

Calculated carbonation progress of mortar specimens in ambient conditions, w/c-ratio=0.5
Measured carbonation progress of mortar specimen in a 3% CO$_2$-content; w/c-ratio=0.5; n=2

Calculated carbonation progress of mortar specimens in ambient conditions, w/c-ratio=0.5
Measured carbonation progress of mortar specimen in a 3% CO₂-content; w/c-ratio=0,5; n=2

Calculated carbonation progress of mortar specimens in ambient conditions, w/c-ratio=0.5
Appendix I:
Resistivity measurement results.
## Appendix I: Resistivity measurement results.

### Average electrical resistivity measurements on uncarbonated mortar specimens; w/c-ratio=0.5

<table>
<thead>
<tr>
<th>Slag content</th>
<th>( \rho ) at 28 days curing age [( \Omega \text{m} )]</th>
<th>( \rho ) at 90 days curing age [( \Omega \text{m} )]</th>
<th>( \rho ) at 23 weeks curing age [( \Omega \text{m} )] Before sat.</th>
<th>After sat.</th>
<th>After RCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>59.1</td>
<td>83.8</td>
<td>203.6</td>
<td>115.6</td>
<td>66.4</td>
</tr>
<tr>
<td>20%</td>
<td>109.8</td>
<td>130.8</td>
<td>365.0</td>
<td>253.6</td>
<td>171.8</td>
</tr>
<tr>
<td>25%</td>
<td>104.8</td>
<td>137.1</td>
<td>283.0</td>
<td>212.2</td>
<td>114.0</td>
</tr>
<tr>
<td>30%</td>
<td>91.8</td>
<td>146.1</td>
<td>301.5</td>
<td>216.9</td>
<td>133.0</td>
</tr>
<tr>
<td>35%</td>
<td>105.4</td>
<td>161.5</td>
<td>473.8</td>
<td>319.4</td>
<td>168.6</td>
</tr>
<tr>
<td>40%</td>
<td>111.2</td>
<td>254.8</td>
<td>376.9</td>
<td>305.9</td>
<td>191.0</td>
</tr>
<tr>
<td>45%</td>
<td>122.8</td>
<td>253.8</td>
<td>442.0</td>
<td>318.2</td>
<td>190.1</td>
</tr>
<tr>
<td>50%</td>
<td>140.0</td>
<td>256.4</td>
<td>652.2</td>
<td>417.7</td>
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</tr>
<tr>
<td>55%</td>
<td>143.2</td>
<td>328.2</td>
<td>526.8</td>
<td>391.3</td>
<td>203.9</td>
</tr>
<tr>
<td>60%</td>
<td>164.0</td>
<td>350.2</td>
<td>531.5</td>
<td>443.8</td>
<td>204.3</td>
</tr>
<tr>
<td>65%</td>
<td>185.1</td>
<td>347.8</td>
<td>493.4</td>
<td>465.5</td>
<td>206.2</td>
</tr>
<tr>
<td>70%</td>
<td>217.0</td>
<td>359.8</td>
<td>552.9</td>
<td>559.5</td>
<td>228.6</td>
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<table>
<thead>
<tr>
<th>nr. of specimens</th>
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<th>Ø100-25 mm</th>
<th>Ø100-50 mm</th>
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<td>3</td>
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<td>1</td>
<td>1</td>
<td>1</td>
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</table>

### Average electrical resistivity measurements on carbonated mortar specimens; w/c-ratio=0.5; 28 curing age, 6 mo. 3% CO\(_2\) exposure

**NOTE:** bolt values are considered unreliable and not taken into account for the average value, increase resistivity due to finished surface

<table>
<thead>
<tr>
<th>Slag content</th>
<th>( \rho ) After saturation [( \Omega \text{m} )]</th>
<th>( \rho ) After RCM-test [( \Omega \text{m} )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ø100-25</td>
<td>263.4</td>
<td>76.0</td>
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<tr>
<td>Ø100-50</td>
<td><strong>879.6</strong></td>
<td><strong>318.8</strong></td>
</tr>
<tr>
<td>Average</td>
<td>263.4</td>
<td>104.5</td>
</tr>
<tr>
<td>Ø100-25</td>
<td>376.9</td>
<td>105.9</td>
</tr>
<tr>
<td>Ø100-50</td>
<td>317.9</td>
<td>110.9</td>
</tr>
<tr>
<td>0%</td>
<td>312.8</td>
<td>115.3</td>
</tr>
<tr>
<td>20%</td>
<td>347.9</td>
<td>109.8</td>
</tr>
<tr>
<td>25%</td>
<td>331.6</td>
<td>113.0</td>
</tr>
<tr>
<td>30%</td>
<td>347.9</td>
<td>127.5</td>
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<td>35%</td>
<td>336.1</td>
<td>121.8</td>
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<td>40%</td>
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<td>376.9</td>
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<td>347.9</td>
<td>127.5</td>
</tr>
<tr>
<td>70%</td>
<td>357.6</td>
<td>121.8</td>
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- Ø = diameter of specimens
- mm = millimeters
Appendix J:
RCM-Test results
### RCM-test results; Uncarbonated mortar specimens; w/c-ratio=0.5

<table>
<thead>
<tr>
<th>Specimen size</th>
<th>100-50 mm</th>
<th>24 hours</th>
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<td>Slag content</td>
<td>carb. depth [mm]</td>
<td>cl. depth [mm]</td>
</tr>
<tr>
<td>0%</td>
<td>-</td>
<td>29.2</td>
</tr>
<tr>
<td>20%</td>
<td>-</td>
<td>14.9</td>
</tr>
<tr>
<td>25%</td>
<td>-</td>
<td>13.7</td>
</tr>
<tr>
<td>30%</td>
<td>-</td>
<td>14.9</td>
</tr>
<tr>
<td>35%</td>
<td>-</td>
<td>12.6</td>
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<td>40%</td>
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<tr>
<td>45%</td>
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<td>9.6</td>
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<tr>
<td>50%</td>
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<td>9.7</td>
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<tr>
<td>55%</td>
<td>-</td>
<td>10.6</td>
</tr>
<tr>
<td>60%</td>
<td>-</td>
<td>9.1</td>
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<td>65%</td>
<td>-</td>
<td>8.9</td>
</tr>
<tr>
<td>70%</td>
<td>-</td>
<td>7.2</td>
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</table>

Note: \(D_{\text{cl}}\) calculated in accordance with NT Built 492[26].

### RCM-test results; Uncarbonated mortar specimens; w/c-ratio=0.5

<table>
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<th>Specimen size</th>
<th>100-25 mm</th>
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<tr>
<td>Slag content</td>
<td>carb. depth [mm]</td>
<td>cl. depth [mm]</td>
</tr>
<tr>
<td>0%</td>
<td>-</td>
<td>10.6</td>
</tr>
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Note: \(D_{\text{cl}}\) calculated in accordance with NT Built 492[26].
### Carbonated

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Note: D<sub>Cl</sub> calculated in accordance with NT Built 492[26].

Note: Carbonated depth is measured from the chloride ingress surface.

### RCM-test results; Carbonated mortar specimens; w/c-ratio=0.5

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Note: D<sub>Cl</sub> calculated in accordance with NT Built 492[26].

Note: Carbonated depth is measured from the chloride ingress surface.
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Note: D\textsubscript{cl} calculated in accordance with NT Built 492[26].
Note: Carbonated depth is measured from the chloride ingress surface.
Note: Bolt value is maximum measured value.
Appendix K:
Chloride penetration time, dependent on carbonation duration.
Appendix K: Chloride penetration time, dependent on carbonation duration.

0 years carbonation exposure, mortar specimen, w/c-ratio=0.5

5 years carbonation exposure, mortar specimen, w/c-ratio=0.5
Appendix K: Chloride penetration time, dependent on carbonation duration.  

10 years carbonation exposure, mortar specimen, w/c-ratio=0,5

15 years carbonation exposure, mortar specimen, w/c-ratio=0,5
Appendix K: Chloride penetration time, dependent on carbonation duration.

(k) Carbonation depth

(l) Time needed for chloride ions to penetration 50 mm cover depth after carbonation

20 years carbonation exposure, mortar specimen, w/c-ratio=0.5

(m) Carbonation depth

(n) Time needed for chloride ions to penetration 50 mm cover depth after carbonation

25 years carbonation exposure, mortar specimen, w/c-ratio=0.5
Appendix K: Chloride penetration time, dependent on carbonation duration.

**(o)** Carbonation depth

**(p)** Time needed for chloride ions to penetration 50 mm cover depth after carbonation

30 years carbonation exposure, mortar specimen, w/c-ratio=0.5

**(q)** Carbonation depth

**(r)** Time needed for chloride ions to penetration 50 mm cover depth after carbonation

35 years carbonation exposure, mortar specimen, w/c-ratio=0.5
Appendix K: Chloride penetration time, dependent on carbonation duration.

40 years carbonation exposure, mortar specimen, w/c-ratio=0.5

45 years carbonation exposure, mortar specimen, w/c-ratio=0.5
Appendix K: Chloride penetration time, dependent on carbonation duration.

50 years carbonation exposure, mortar specimen, w/c-ratio=0.5