CHALMERS
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Carbonation of concrete

Effect of mineral additions and influence on transport properties

Master's Thesis in the Master's Programme Structural Engineering and Building Technology

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Department of Civil and Environmental Engineering
Division of Building Technology
Building Materials
CHALMERS UNIVERSITY OF TECHNOLOGY
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Carbonated specimens with three different *w/b* ratios sprayed with phenolphthalein. Photo by Robin Snibb, edited by Emma Kjellstrand, Dinosaur Design

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ABSTRACT

Fly ash and Ground Granulated Blast-furnace Slag (GGBS), two mineral additions used to partly replace ordinary Portland cement, are residues from coal combustion and steel manufacturing, respectively. Desirable properties for concrete containing these two additions are, for example, lower carbon footprint, lower heat development and higher resistance to acid, sulfate and chloride attacks, but they can also cause unwanted properties, such as increased carbonation and reduced strength. Hence, durability is in some aspects improved, while in other reduced. This study investigated how mineral addition influences carbonation, and how carbonation affects chloride migration and transport properties in mortar.

Accelerated carbonation with an elevated CO_2 level of 2% and Rapid Chloride Migration (RCM) were used. These, together with compressive strength tests (SS-EN 196-1) and capillary absorption tests (NT Build 368), were carried out as means of a comparative study of mortar mixtures with different levels of mineral addition and w/b ratios.

Carbonation rate was increased and compressive strength was reduced, by increased amount of mineral addition, as expected. The results also showed an interdependence between different deteriorating processes. Carbonation reduced the porosity, rate of reaching saturation and connectivity of the pore structure, and it also reduced the resistance to chloride migration. Nearly all the effects caused by carbonation were magnified by the amount of mineral addition, except for some reverse effects on high levels of GGBS. The reverse effects can partly be explained by low degree of hydration of GGBS, caused by short curing time in the test method.

Key words: Accelerated carbonation, carbonation, capillary absorption, durability of concrete, fly ash, GGBS, mineral additions, rapid chloride migration

Karbonatisering av betong
Effekter av mineraliska tillsatsmedel och dess inverkan på transportegenskaper

Examensarbete inom Konstruktionsteknik

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SAMMANFATTNING

Flygaska och mald granulerad masugnsslagg (också benämnt GGBS), två mineraliska tillsatsmedel som används för att delvis ersätta Portland cement, är biprodukter från förbränning av kol (flygaska) samt tillverkningsprocessen av stål (GGBS). Betong som innehåller dessa tillsatsmedel har en rad önskade egenskaper, vilka bland andra är mindre koldioxidutsläpp, lägre värmeutveckling och högre motståndskraft mot syra-, sulfat- och kloridattacker. Dock kan dessa tillsatsmedel också föranleda oönskade egenskaper, såsom ökad karbonatiseringshastighet och reducerad hållfasthet. Därmed förbättras betongens egenskaper i vissa avseenden, medan den i andra minskar. Denna studie har undersökt hur dessa mineraliska tillsatsmedel påverkar karbonatisering, samt hur karbonatisering i sin tur påverkar kloridmigration och transportegenskaper i cementbruk.

Accelererad karbonatisering med en förhöjd koldioxidhalt av 2% och påtvingad kloridmigration (RCM-tester) användes vid undersökningarna. Dessa tester, tillsammans med tryckhållfasthetstester (SS-EN 196-1) och kapillära absorptionstester (NT Build 368), genomfördes och låg till grund för en jämförandestudie av cementbruksblandningar med olika halter av mineraliska tillsatsmedel och vattencementtal.

Som förväntat ledde en ökad mängd mineraliskt tillsatsmedel till att karbonatiseringshastigheten ökade, medan tryckhållfastheten reducerades. Resultaten visade också på ett ömsesidigt beroende mellan olika försämringsprocesser. Karbonatisering minskade porositeten och anslutningen mellan porerna, också motståndskraft mot kloridmigration minskade samt att det tog längre tid att nå vattenmättnad hos provkropparna. Nästan alla effekter som orsakas av karbonatisering förstärktes av mängden mineraltillägg, med undantag för vissa omvända effekter på höga nivåer av GGBS. De omvända effekterna kan delvis förklaras av låg hydratiseringsgrad, vilken delvis beror av den korta härdningstiden i försöken.

Nyckelord: Accelererad karbonatisering, beständighet i betong, flygaska, GGBS, kapillärabsorption, karbonatisering, mald granulerad masugnsslagg, mineraliska tillsatsmedel, påtvingad kloridmigration

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Notations

c	*Concentration of CO_2*	[%]
k	*Equivalent performance coefficient*	[-]
f_c	*Compressive strength*	[MPa]
k_{cap}	*Capillary coefficient*	[kg/m$^2\sqrt{s}$]
m_{cap}	*Capillary resistance coefficient*	[s/m^2]
t_{cap}	*Capillary break-point time*	[s]
w/b	*Water/binder*	[-]
w/c	*Water/cement*	[-]
AI	*Activity index*	[%]
C	*Cement content*	[kg]
D	*Mineral addition content*	[kg]
D_{nssm}	*Chloride migration coefficient*	[m^2/s]
K	*Carbonation rate coefficient*	[mm]
Q_{cap}	*Capillary water weight at break point*	[kg]
S_t	*Degree of saturation*	[-]
W	*Water content*	[kg]

List of abbreviations

$CaCO_3$	*Calcium carbonate, limestone*
CaO	*Calcium oxide, quicklime, burnt lime*
$Ca(OH)_2$	*Calcium hydroxide, slaked lime*
CEM I	*Portland cement*
CEM II	*Portland-composite cement*
CEM III	*Blast furnace cement*
CEM IV	*Pozzolanic cement*
CEM V	*Composite cement*
C-S-H	*Calcium silicate hydrate*
EN	*European standard (European norm)*
EPCC	*Equivalent performance of combinations concept*
ECPC	*Equivalent concrete performance concept*
FA	*Fly ash*
GGBS	*Ground granulated blast-furnace slag*
OPC	*Ordinary Portland cement (see also CEM I)*
PC	*Portland cement (see also CEM I)*
RCM	*Rapid chloride migration*
RH	*Relative humidity*
SS	*Swedish standard*
XC	*Exposure class for carbonation*

The materials used to replace Portland cement, such as GGBS and fly ash, are in some literature referred to as secondary cementitious materials, supplementary cementitious materials, cement replacement materials (CRM) or mineral additions. The latter is used in this report.

1 Introduction

In times of environmental awareness as one of the key aspects for a sustainable society, it is important to improve and implement new, more sustainable technologies in the construction industry. Concrete is a widely used building material in nearly all sorts of constructions, such as residential buildings, bridges, roads and airports, to mention a few.

The manufacturing process of cement stands for 70% to 90% of the total environmental impact of concrete, in terms of carbon footprint (Irfan 2011). An investigation carried out by MPA-TCC (2013) shows that the use of ground granulated blast-furnace slag (GGBS) and fly ash, two supplements to ordinary Portland cement (OPC), in terms of CO_2 equivalents is 13.1% and 0.4% respectively, compared to OPC. By partly replacing cement with mineral additions, such as GGBS and fly ash, the environmental impact will decrease. The use of these mineral additions does not only have positive environmental effects, but may also lead to better material properties, e.g. sulfate and acid resistance (Matthews 2014). However, these materials also have drawbacks, such as increased carbonation and decreased early age strength.

1.1 Background

Mineral addition in concrete, such as GGBS and fly ash, has been used for a long time because of their desirable properties, lower carbon footprint and lower cost per unit weight compared to OPC. The first production of Portland-slag-concrete was introduced in 1892 by Godhard Prüssig in Germany (Esping et al. 2011). The application of concretes containing mineral additions is, however, not used in Sweden to the same extent as in the rest of Europe. For example, over 80% of the total cement consumption in Switzerland is represented by other cements than CEM I-cements (Hunkeler 2012). Sweden has a total cement production of almost 2.5 million tons and a GGBS production of approximately 50.000 tons, in other words, GGBS stands for only about 2% of the total volume of produced cement (Stripple et al. 2005).

Several attempts have been made in Sweden to introduce concrete containing GGBS, e.g. from 1950 to 1974 a cement "*vulkancement*" with 30% to 50% GGBS and during the 70s and 80s a cement "*massivcement*" with 65% GGBS were introduced for water dams for hydroelectric plants, (Stripple et al. 2005). Later on, cracks were found in some of the constructions with *massivcement*, probably due to high temperatures and moisture gradients. Because of this setback, among others, the market never grew and GGBS did not become common practice in the Swedish concrete production (Stripple et al. 2005). Fly ash, on the other hand, has historically not been used to a large extent as a binder in Swedish concrete, partly due to negative experiences, such as low early-age strength and therefore delayed construction time, especially in cold-weather concreting (Thomas 2007). Fly ash produced today is however of a higher and more consistent quality than those investigated during the 80s and 90s (Esping et al. 2011) and fly ash cements (CEM II/A-V) have recently been introduced on the Swedish market (Cementa 2016).

To enable more extensive use of mineral additions, and still assure sufficient durability, there is a need for studies regarding durability, especially on the main

deteriorating processes, carbonation induced and chloride induced corrosion, for concretes containing blended cements allowed and available in Sweden.

The newly revised standard SS 137003, *the application of SS-EN-206 in Sweden*, enables the use of equal performance based design, and opens up for a more extensive use of mineral additions.

1.2 Aim

The aim of this study is to investigate carbonation resistance of concrete mixtures with different levels of GGBS or fly ash with varying *w/b* ratios, and to examine how carbonation affects porosity and chloride migration. The main purpose is to provide recommendations on the suitability of mineral additions and equal performance design concepts in newly revised Swedish and European standards, regarding carbonation of blended concretes. The results of these tests are to be used as input to further national standardization work.

1.3 Method

The relative carbonation resistance of concretes containing blended cements is based on equal performance design described in SS-EN 206. However, this is a pilot study that does not follow these standards strictly, but gives an indication of interesting mixtures for further analysis. The focus lies on a comparison between carbonation rate of mortars with mixtures allowed and not allowed in exposure class XC3 in accordance to standard SS 137003. To verify the carbonation resistance, tests are carried out regarding the carbonation effects on capillary absorption, giving an indication on the porosity change. Furthermore, relative tests regarding chloride migration in carbonated specimens are carried out to give an indication how carbonation affect chloride ingress.

A variety of mortar mixtures, with different *w/b* ratios and levels of mineral additions, are compared with a reference mortar, containing solely CEM I, after being exposed to an elevated CO_2 concentration using accelerated carbonation tests according to prTS 12390-12. Tests regarding effects of GGBS fineness and different CEM I is also carried out as side projects.

1.4 Limitations

This study focuses on the most commonly used mineral additions, GGBS and fly ash, even though there exist other types, such as silica fume and other pozzolanic materials. The OPC, GGBS and fly ash that are used consist of one type of mineral composition each, thus there is no account taken for variety in material properties, e.g. from different producers. The tests carried out are performed solely on mortar mixtures, cast in either cylinder or prism moulds, depending on test standard, even though the tests are supposed to be used and interpreted as concrete. Thereby, effect of e.g. coarse aggregates is disregarded in this study.

The access to materials, space in carbonation chamber and preparation time set limitations on the number of specimens. This determined the number of different mixtures and thereby the variety of different proportions of mineral additions that

have been tested. Three different proportions of GGBS and two different proportions of fly ash and two reference mixtures with CEM I were mixed at three different *w/b* ratios, respectively. The restricted number of specimens limits the variation of curing time to only one period, thus there is no investigation regarding effects of different curing periods.

The main focus of this study is the investigation of carbonation and its effects on capillary absorption and chloride migration. Other processes affected by carbonation, such as carbonation induced corrosion of the embedded reinforcement will therefore not be investigated here. The deadline of the project limits the duration of carbonation, which rules out the possibility of natural carbonation, hence accelerated carbonation has been used. This study is also limited to Rapid chloride migration tests, which does not entirely describe chloride penetration in a natural process. Compressive strength was tested only to validate the mortar mixtures and to verify requirements, the effects carbonation have on the strength was however not tested since such an investigation demands fully carbonated specimens, or at least equally carbonated. This was not possible to achieve within the actual time frame.

2 Literature study

The composition of concrete consists of aggregates and cement paste, where the cement paste is the product of cement and the mixing water, which hardens during the hydration process. Traditional Portland cement can to some extent be substituted with other cementitious materials, such as fly ash or GGBS, or with "nearly inert" material like limestone filler. These substitutes are either interground or blended with Portland cement. GGBS shows significant hydraulic behavior, meaning that it by itself reacts and contributes to the hydration process (Bertolini et al. 2004). Fly ash can show both hydraulic and pozzolanic behavior, depending on whether it has high or low calcium content. However, the European standard EN 206 does only allow fly ash with low calcium content. Such pozzolanic fly ash reacts only in the presence of calcium hydroxide, thus it needs the calcium hydroxide in Portland cement to obtain cementitious properties. These mineral additions affect the durability of the concrete. In particular, this applies to the deterioration process caused by carbonation, where CO_2 in the atmosphere reacts with the concrete. Carbonation degrades the passive layer around the reinforcement, which normally would protect it from corrosion.

2.1 Blended cements

The production of traditional Portland cement is an energy consuming process which also requires decarbonation of the raw material which generates CO_2. GGBS, on the other hand, is a residue from the steel manufacturing industry and fly ash from coal combustion, and will therefore contribute to a lower carbon footprint of the concrete production, when replacing Portland cement. Portland cement and mineral additions contain a wide range of different constituents that give them their properties. Some typical compositions of the main constituents are presented in Table 2-1 below.

Table 2-1 Typical compositions of main constituents in cement, expressed in % by mass (Taylor 1997)

Constituent	Portland cement	GGBS	Fly ash (low CaO)
Na_2O	-	*0.39%*	*1.5%*
MgO	-	*5.99%*	*1.6%*
Al_2O_3	*5%*	*13.29%*	*27.9%*
SiO_2	*22%*	*33.48%*	*48.7%*
P_2O_2	-	*0.13%*	*0.2%*
SO_3	-	*0.04%*	*1.2%*
K_2O	-	*0.70%*	*4.2%*
CaO	*67%*	*42.24%*	*2.4%*
TiO_2	-	*0.55%*	*0.9%*
MnO	-	*0.64%*	-
FeO	-	*1.24%*	-
Fe_2O_3	*3%*	-	*9.5%*
C	-	-	*1.5%*
Other components	*3%*	*1.31%*	*0.4%*
Total	*100%*	*100%*	*100%*

The most common fly ash is a pozzolanic material with low content of CaO (Bertolini et al. 2004), usually replacing Portland cement by 20% to 40% of total binder weight. As described above, a pozzolanic material have no binding properties itself, but together with Portland cement it will have sufficient amount of $Ca(OH)_2$ to react, and therefore have similar hydration products as pure Portland cement (see simplified reactions 1.1 and 1.2 below). The amount of fly ash replacing Portland cement is therefore limited by the amount of available $Ca(OH)_2$ produced in the hydration of Portland cement. GGBS, unlike fly ash, can be used as a hydraulic binder, without access of $Ca(OH)_2$, but still requires some Portland cement (or another alkali activator) to create an alkaline environment that activates and speed up the otherwise slow hydration process (Bertolini et al. 2004). GGBS replacement of the cement usually ranges from 40% to 70% by weight of total binder and is often classified by its activity index (Thomas 2012). The hydration of both pozzolanic materials and GGBS consumes $Ca(OH)_2$, which decreases the alkalinity in the hardened concrete compared to a PC concrete.

$$Portland\ cement + water \rightarrow C\text{-}S\text{-}H + Ca(OH)_2 \quad (1.1)$$

$$Pozzolanic\ material + water + Ca(OH)_2 \rightarrow C\text{-}S\text{-}H \quad (1.2)$$

Mineral additions have been used in concrete for a long time in high performance concrete. It changes many of the concrete properties, even small replacement levels affect both fresh and hardened states. Some examples are less heat development and better resistance to chemical attack in GGBS concretes and better freeze-thaw resistance and workability in fly ash concretes (Matthews 2014; Neville 1995), compared to PC concrete. Another effect of using fly ash and GGBS is that it saves energy and natural resources (Neville 1995). However, the downside is that it generally increases the rate of carbonation (Sulapha et al. 2003; Lye et al. 2015).

One can also expect a lower 28-day strength for concretes containing GGBS or fly ash, compared to a concrete containing 100% Portland cement, due to the slower hydration process (Matthews 2014). The decrease in hydration rate may lead to a slower progress of the construction works and therefore higher costs; it may however be desirable in some cases, such as mass concrete pours, e.g. water-dam construction. The slow hydration process does not necessarily imply a decrease in final strength. Research by Islam & Islam (2010) shows that strength increases with an increasing amount of fly ash up to an ideal percentage, given that the concrete is water cured for 90 days. According to this study, a concrete containing 40% fly ash had a 28-day strength of 99% of the corresponding strength of 100% PC, but 114% when cured for 90 days. Similar behavior has been found in concretes containing GGBS (Siddique 2014).

Mineral additions can be part of cement marketed as a product, manufactured by a cement producer. These cements are controlled by the standard EN 197-1. However, it can also be blended in mixing of concrete, by a concrete manufacturer, governed by concepts in SS-EN 206. Hereafter, to distinguish these two ways of using mineral addition the terms cement and blended cement are used, respectively.

2.2 Durability of concrete

Concrete is, if properly designed and produced, a highly durable material, but the steel reinforcement is a weak point that demands special requirements to provide sufficient strength over time (Bertolini et al. 2004; Taylor 1997). Concrete is generally a good environment for steel, due to its alkalinity creating passivation against corrosion. However, the passivation layer may decrease during degrading processes such as carbonation and chloride ingress. A thin concrete cover thickness might therefore lead to a premature depassivation of the steel.

Structures with insufficient durability have an increased risk of premature failure, which often causes costs associated with either repairing damages or early reconstruction (Matthews 2014). Matthews refers to studies carried out by BCA, showing that 50% of all cases with deteriorated concrete structures are caused by corrosion of the reinforcement due to either carbonation or chloride ingress. Insufficient durability also has environmental impacts, such as shorter service life and the use of more material in repairs, which results in higher CO_2 emissions.

When testing durability with respect to carbonation, there are two different approaches, namely natural carbonation and accelerated carbonation. Natural carbonation testing, described in prEN 12390-10, is carried out in a laboratory with an

environment similar to atmospheric conditions. The accelerated procedure of carbonation involves an elevated level of CO_2, described in prTS 12390-12.

Sufficient durability for concrete compositions are assured by a number of prescriptive limiting values; maximum *w/c* ratio, minimum cement content, cement class and amount of mineral addition, governed by requirements in SS 137003, presented in Table 2-2. The high-lighted exposure class, XC3, is the one investigated in this study. These requirements concern the quality of the concrete, thus targeted to the concrete manufacturer.

Table 2-2 Requirements on exposure classes X0 and XC1 - XC4, extracted from SS 137003

Requirement	No risk of corrosion	Corrosion induced by carbonation			
Exposure class	*X0*	*XC1*	*XC2*	*XC3*	*XC4*
Maximum w/c	-	*0.90*	*0.60*	*0.55*	*0.55*
Minimum cement content	-	-	*200*	*200*	*200*
Strength class for cement [MPa]	*≥ 32.5*	*≥ 32.5*	*≥ 32.5*	*≥ 42.5*	*≥ 42.5*
Amount of PC clinker of total binder [%]	*≥ 30*	*≥ 35*	*≥ 35*	*≥ 65*	*≥ 65*
Amount of fly ash of total binder [%]	*≤ 35*	*≤ 35*	*≤ 35*	*≤ 35*	*≤ 35*
Amount of GGBS of total binder [%]	*≤ 70*	*≤ 65*	*≤ 65*	*≤ 35*	*≤ 35*

There are also requirements regarding construction detailing, such as minimum cover thickness, governed by requirements in EKS10, which depends on *w/c* ratio and service length of the structure (Boverket 2016). These requirements, unlike those in SS 137003, are design parameters of the minimum allowed cover thicknesses, presented in Table 2-3.

Table 2-3 Minimum allowed cover thickness, requirements extracted from EKS10 (Boverket 2016)

Exposure class	Maximum *w/c*	L 100	L 50	L 20
X0	-	-	-	-
XC1	*0.90*	*15*	*10*	*10*
	0.60	*10*	*10*	*10*
XC2	*0.60*	*25*	*20*	*15*
	0.55	*20*	*15*	*10*
	0.50	*15*	*10*	*10*
XC3, XC4	*0.55*	*25*	*20*	*15*
	0.50	*20*	*15*	*10*

All the above mentioned requirements are governed by the operative exposure class of the concrete. These exposure classes are divided in five different categories, depending on which environment the structure is exposed to, see Table 2-4. The limiting values vary a lot in Europe, even between countries relying on the same standard, EN-206 (CEN/TR 15868). Sweden, for example, does not have requirements on compressive strength of the concrete in terms of exposure class which some countries have, e.g. UK.

Table 2-4 Description of exposure classes X0 and XC1-XC4, extracted from SS-EN 206

Class designation	Description of the environment	Informative examples where exposure classes may occur
No risk of corrosion		
X0	*For concrete without reinforcement or embedded metal: All exposures except where there is freeze/thaw, abrasion or chemical attack.* *For concrete with reinforcement embedded metal: Very dry*	*Concrete inside buildings with very low air humidity*
Corrosion induced by carbonation		
XC1	*Dry or permanently wet*	*Concrete inside buildings with low air humidity; Concrete permanently submerged in water*
XC2	*Wet, rarely dry*	*Concrete surfaces subject to long-term water contact; Many foundations*
XC3	*Moderate humidity*	*Concrete inside buildings with moderate or high air humidity; External concrete sheltered from rain*
XC4	*Cyclic wet and dry*	*Concrete surfaces subject to water contact, not within exposure class XC2*

2.3 Deterioration of concrete caused by corrosion of reinforcement

Deterioration of concrete is caused by various processes, chemical or physical. Many of these processes occur simultaneously and may affect each other, but will primarily be treated and described separately in this study. The rate of deterioration depends highly on the ability of water, oxygen, CO_2 and compounds that can penetrate into the concrete. Thus, permeability and pore structure are key factors in determining the durability of concrete (Thomas 2012).

The basic problem is that steel corrodes in the presence of oxygen and high humidity, which reduces the cross sectional area of the reinforcement bars and consequently

decreased strength of the concrete. Furthermore, the corrosion products also accelerate the deterioration of the concrete by causing cracking and spalling.

There are two simplified models of durability that can be used to describe the life cycle of concrete structures, in terms of carbonation and chloride ingress, see Figure 2-1 (Matthews 2014). The traditional model of corrosion (Tuutti 1982), is divided into two phases. In the first phase, called initiation, carbonation or ingress of chlorides starts to penetrate the concrete from the surface. The second phase, called propagation, starts when the carbonation or chloride front has reached the reinforcement and the steel becomes depassivated, enabling the steel to corrode. Looking at Tuutti's traditional model, there is a distinct line between the initiating phase and the propagation phase. However, corrosion does actually occur even in the initiation phase. Therefore, the progressive model of corrosion was introduced by Bamforth, a model with a smooth transition between what in Tuutti's model is described as initiation and propagation (Matthews 2014).

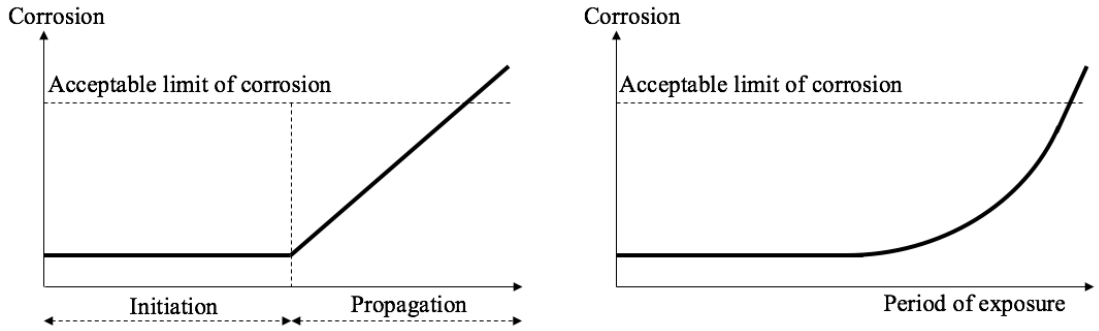


Figure 2-1 Tuutti's and Bamforth's models of corrosion

2.4 Permeability and porosity

Porosity affects the rate of deterioration, by influencing the diffusion of CO_2 during carbonation and the ingress of chlorides. Generally, reduced total porosity leads to less connectivity between the capillary pores, which decrease permeability and penetration of chlorides and the rate of CO_2-diffusion. From a durability point of view, there is a critical value of capillary porosity around 25%, above which the permeability increases significantly. The increase in permeability consequently increases capillary absorption, through which water containing chlorides and CO_2 can penetrate (Bertolini et al. 2004).

Both the capillary porosity and the pore size decrease by decreased *w/c* ratio and increased degree of hydration. The degree of hydration depends on factors like curing time and amount of GGBS or fly ash. Therefore, an increase in GGBS and fly ash generally increase the total porosity, especially in early ages, due to its slower reactions compared to OPC (Taylor 1997). However, after longer curing (>91 days), total porosity decreases with increasing amount of GGBS and fly ash (Bertolini et al. 2004).

According to Nagala & Page (1997) carbonation reduces the total porosity, in both blended concretes and PC concretes, but with a redistribution of the pore size, showing a slight increase of the proportion of large capillary pores (diameters above

30nm) in PC concretes and a significant increase in blended concretes. This effect is caused by the reduction of hydration products, e.g. calcium hydroxide, as a result of the larger volume in the formation of $CaCO_3$ (Dyer 2014). An increase in capillary porosity results in an increase of, for example, the diffusion of oxygen (Nagala & Page 1997).

A study carried out by Wu & Ye (2015) does however show that cement pastes containing high levels of mineral additions increases porosity. This is explained by an increase in porosity when C-S-H is carbonated, while carbonation of $Ca(OH)_2$ decreases porosity. As earlier described, mineral additions contain less $Ca(OH)_2$ compared to Portland cement, which explains differences in porosity-change after carbonation between concretes with high and low amount of mineral addition.

2.5 Carbonation and carbonation induced corrosion

There are two main reactions in the carbonation process: Firstly, CO_2 dissolves in the pore solution of the cement paste, creating carbonic acid, see equation 2.1. Secondly, carbonic acid reacts with the hydration products, e.g. $Ca(OH)_2$, see equation 2.2. The reaction consumes OH^-, thus lowering the pH-level in the concrete (Taylor 1997).

$$CO_2 + H_2O \rightleftarrows CO_3^{-2} + 2H^+ \tag{2.1}$$

$$CO_3^{-2} + 2H^+ + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O \tag{2.2}$$

The reaction is described, for simplicity, with $Ca(OH)_2$, which constitutes the main part of the carbonation, but carbonation can occur in other carbonatable constituents, e.g. parts of the C-S-H gel and various aluminoferrite phases (Thomas 2012).

The main factors influencing the rate of carbonation are the diffusion of CO_2 through the pore network of the concrete, governed by the porosity and pore structure, and its reactions with the $Ca(OH)_2$, governed by the alkalinity. In turn, these factors are influenced by the ambient environment. For example, higher CO_2 concentration in the atmosphere increases the diffusion of CO_2 and thereby the rate of carbonation. The concentration of CO_2 in the atmosphere varies from 0.03% to 0.1%, depending on whether it is a rural or urban area (Bertolini et al. 2004), both these concentrations will probably increase in the future, due to greenhouse gas emissions (Yoon et al. 2007). Emissions will also cause an increase in temperature, which also has been shown to slightly increase the rate of carbonation (Dyer 2014). Furthermore, the carbonation rate will increase by increasing RH up to a certain level, whereafter it will decrease, see Figure 2-2. The decrease of the carbonation rate in the upper span of the RH-scale is explained by the diffusion rate of CO_2, which is 10^4 times higher in air compared to water. Thus, almost no carbonation occurs when the concrete is wet. On the other hand, the carbonation process needs access to water to continue, which is why no carbonation occurs in the lower span of the RH-scale, i.e. in dry concrete. Therefore, RH in the span of 60% to 70% has been shown to cause the highest rate of carbonation (Bertolini et al. 2004).

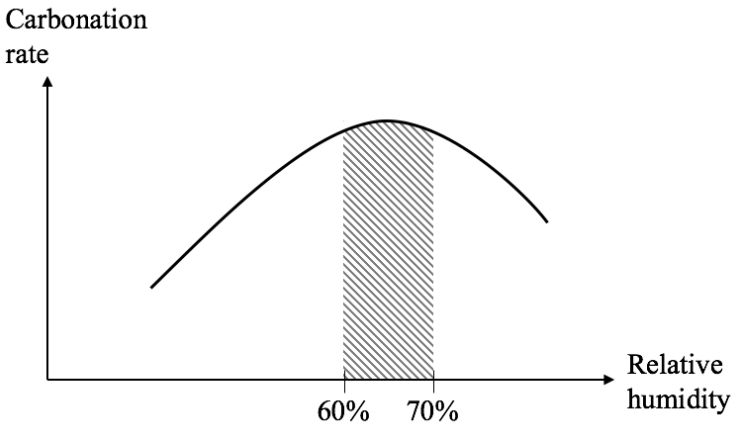


Figure 2-2 Region of RH, where the carbonation is the highest

In a given environment, with constant temperature, CO_2-concentration and RH-level, the mixture and material properties are influencing factors of the rate of carbonation. For example, a decrease in *w/c* ratio leads to a lower rate of carbonation, due to the decrease in capillary porosity of the hydrated cement paste (Tuutti 1983). Type of binder is another influencing factor, because various cementitious materials generate different alkalinity of the cement paste, mainly due to varying amount of CaO, which determines the ability to fix CO_2. Curing is a third important factor, especially for blended cements. For example, Sulapha et al. (2003) and Sisomphon & Franke (2007) show that the rate of carbonation decreases when the time of curing increases. PC concrete benefits from increased curing up to 7 days and GGBS and fly ash concretes from increased curing up to 28 days. Poor curing mainly affects the cover of the concrete, and therefore it has a significant negative effect on the carbonation and chloride penetration.

As mentioned, carbonation is one of the initiating mechanisms for corrosion. It decreases the alkalinity, which causes depassivation of the protective oxide layer of the reinforcement, allowing corrosion to occur. The carbonation and corrosion phases of carbonation induced corrosion have different levels of critical RH. The carbonation phase is the shortest at RH 60% to 70%, as previously described. On the other hand, there is a slow corrosion rate at RH below 80%, because corrosion requires high RH**.** Therefore, the worst case for the structure, from a durability point of view, is when the concrete is subjected to longer alternating wet and dry periods, corresponding to exposure class XC4. Such situations create an environment where both carbonation and corrosion occurs (Tuutti 1982).

The depth of the carbonation front can analytically be described as a parabolic formula, equation 2.3, describing the carbonation depth constant to the square root of time, see Figure 2-3 (Bertolini et al. 2004).

$$d = K\sqrt{t} \tag{2.3}$$

The depth, *d*, described in the formula is interpreted as a distinct line, which is a simplification because the carbonation is in reality a transition zone from high to low pH-value, i.e. partly carbonated to fully carbonated. The carbonation rate, *K*, depends on the factors influencing the rate of carbonation [mm/year$^{0.5}$] and the procedure of

measuring the carbonation front in concrete. The carbonation rate can be used to normalize mortars, which enables a comparison of carbonation between tests measured at different times, showing a fairly accurate prediction (Bertolini et al. 2004).

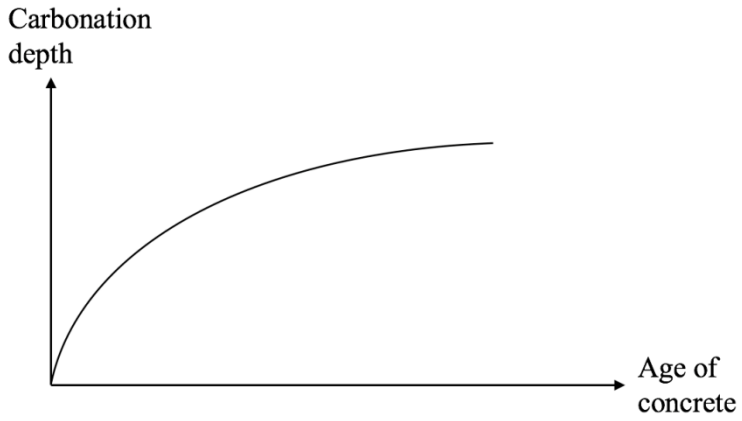


Figure 2-3 Simplified relation between carbonation depth and time

2.5.1 Carbonation of fly ash concretes

As mentioned, in concretes with pozzolanic materials the content of $Ca(OH)_2$ is less, resulting in lower alkalinity in fly ash concretes compared to a PC concrete, which increases the rate of carbonation (Bertolini et al. 2004; Khunthongkeaw et al. 2004). On the other hand, the hydration of blended cement contributes to a denser structure, given that it is properly cured, with a decreased fraction of capillary pores and consequently a decreased diffusion of CO_2, and therefore also a decreased rate of carbonation.

A review made by Lye et al. (2015) shows that there is a higher rate of carbonation for fly ash concretes, compared to PC concretes, both on equal strength basis and equal *w/c* ratio. The reason for this is debated and described in different ways. One argument is that it is due to the decrease in $Ca(OH)_2$ in fly ash concrete, as described above. Another explanation is that the fly ash concrete is generally more porous due to insufficient curing because of the slow pozzolanic reactions and slower hydration of the cement paste, thus easier for CO_2 to penetrate its surface (Lye et al. 2015).

Carbonation affects concretes with varying amount of fly ash differently. When comparing a PC concrete to a fly ash concrete, one can see that the fly ash concrete is of a denser and less permeable character than PC concrete after 28 days of curing, but less dense and more permeable after carbonation (Sulapha et al. 2003).

2.5.2 Carbonation of GGBS concretes

The review *Carbonation resistance of GGBS* made by Lye et al. (2016) supports the claim that carbonation resistance of GGBS concrete decreases with increasing content of GGBS. The reason for this relation is, similarly to fly ash, due to lower alkalinity in GGBS concrete caused by less $Ca(OH)_2$, compared to PC concrete. Similar to fly ash concretes, the other reasoning suggests that the increase in carbonation is causing an

increased porosity and coarser pore structure in GGBS concrete, due to insufficient curing. To prevent a porous structure, longer curing is needed for a GGBS concrete compared to a PC concrete. This is also supported by Tuutti (1983), stating that GGBS concretes are extra sensitive to carbonation in an early age due to its slower reaction of the cement paste, compared to a PC concrete, especially for high replacement levels.

In sheltered exposure the GGBS concrete tends to carbonate faster than PC concrete, whereas in wet and marine environment it is the other way around (Lye et al. 2016). Lye et al. also show that the difference in carbonation rate is higher on an equal *w/c* basis than on equal strength basis, given the same time of curing. It is even shown that concretes with low GGBS content (<30%) on an equal strength basis, at full hydration, have the same carbonation resistance as PC concrete.

According to the reviews *Carbonation resistance of GGBS concrete* (Lye et al. 2016) and *Carbonation resistance of FA concrete* (Lye et al. 2015), fly ash concrete shows higher carbonation rate than GGBS concrete, at an equal level of addition. On the other hand, GGBS is permitted in higher replacement levels (<50%), due to higher reactivity, which leads to more carbonation. Another effect shown by Sulapha et al. (2003) is that an increase in GGBS fineness decreases the rate of carbonation.

2.6 Chloride ingress and chloride induced corrosion

The chloride induced corrosion starts when chlorides penetrate to the depth of the steel, and the concentration of chloride ions reaches a critical threshold value for corrosion. The threshold depends mainly on the electrochemical potential of the reinforcement, but also on type of cement, *w/c* ratio, moisture content, chloride concentration and temperature. Together, these factors determine the initiation time of chloride induced corrosion (Bertolini et al. 2004).

The passive oxide layer on the steel is attacked by chloride ions (Cl^-), working as a catalyst in the depassivation process (Broomfield 2007). The depassivation is therefore not caused by an overall drop of pH, as in the case with corrosion caused by carbonation. In the chloride induced corrosion process, the chloride ions are competing with hydroxyl ions (OH^-) to fill gaps in the passive layer. Hence, the threshold for corrosion is dependent on the chloride/hydroxyl ratio. Therefore, chlorides reduce the passivation around the reinforcement, without influencing the pH-level, creating a cathodic area (Bertolini et al. 2004). Such reduction can lead to pitting corrosion, where the negatively charged chloride ions at the cathodic areas flow to the anodic area, increasing the chloride content locally and creating weak spots in the reinforcement. The steady chloride flow increases the chloride concentration and decreases the passivation layer faster (Tuutti 1982).

Chlorides penetrated from the outside can originate from salt water in marine environment, splash water from de-icing salts in road environments or airborne chlorides (Bertolini et al. 2004). There are different driving mechanisms for penetration of chloride ions. Dry concretes subjected to chloride containing liquids absorb ions through capillary action, which causes high rate of chloride penetration (Tuutti 1982). Another mechanism is that, when concrete is fully saturated in water, the chloride ions penetrate due to the difference in concentration, but in this case with

a lower rate compared to capillary absorption. Chlorides in concrete can also originate from the concrete mixing, when using aggregates containing chlorides (e.g. sea-dredged sand), mixing sea water or admixtures containing chlorides (e.g. calcium chloride as accelerator) (Bertolini et al. 2004).

2.7 Relation between chloride ingress and carbonation

Carbonated concrete does not have the same ability to bind chlorides as a non-carbonated concrete (Tuutti 1982). Therefore, the carbonated front in concretes containing chlorides in the mixture causes a front of free chlorides that gets pushed into the concrete as the carbonated front progresses (Hailong et al. 2016). Tuutti (1982) describes the phenomenon as a carbonated front that ploughs the chlorides into the concrete.

A blended concrete is expected to show higher resistance against chloride ingress, given that it is well cured and that it is subjected to an environment with low risk of carbonation, e.g. in permanently wet environment such as splash or submerged zones. The rate of chloride penetration can however be increased in blended cements after being carbonated, due to an increase of the large pores and the reduced capacity to bind chlorides (Nagala & Page 1997).

2.8 Accelerated carbonation

Testing carbonation resistance by using the standard for natural concentration of CO_2 (TS 12390-10) is time-consuming, therefore accelerated carbonation using an elevated concentrations of CO_2, is sometimes preferable. A standard for using *Accelerated carbonation method*, prTS 12390-12, is proposed but has not been approved (Harrison et al. 2012), thus it is currently not available for use. The accuracy of this method is debated. Some argue that the increased concentration of CO_2 can change the process and generate more/other carbonated products, which can form a denser and less porous concrete than in natural carbonation (Bernal et al. 2012). Visser (2014) on the other hand argues that the carbonation process is the same, but other factors can affect the rate of carbonation, e.g. increased rate of evaporation of water created under carbonation being a decisive mechanism over the diffusion of CO_2. Younsi et al. (2011) also question the use of accelerated testing, especially in using mineral additions with low amount of carbonatable constituents, e.g. $Ca(OH)_2$, because accelerated carbonation is shown to be highly dependent on the carbonation resistance, i.e. the reaction with carbonatable constituents, while natural carbonation is more dependent on the diffusion of CO_2.

A study by Cui et al. (2015), covering carbonation with different CO_2 concentrations, shows that diffusion mechanisms of CO_2 differs between high (20% to 100%) and low (2% to 20%) concentrations, and that concentrations above 20% should not be used to predict natural carbonation. Furthermore, research by Lye et al. (2015) shows that the increase in carbonation of fly ash concrete, compared to PC concrete, is of the same magnitude for tests subjected to accelerated (2% to 10%) and natural exposure conditions. Also Khunthongkeaw et al. (2004) show a strong relation between the carbonation rate in accelerated (4%) and natural environment. These two latter findings give some validation to the relative comparing when using an accelerated carbonation chamber at concentrations around 2% to 10%. Rozière et al. (2009) also

support the use of accelerated carbonation in equivalent performance design to compare carbonation resistance, due to their consistent results between natural and accelerated tests.

The main problem with using accelerated carbonation is the difficulty to transfer the data from accelerated testing to natural carbonation, i.e. to predict the real carbonation depth over time. However, this is less of a problem in a comparative method like equivalent performance design, since the real carbonation depth in natural environment is not of interest.

2.9 Concrete standards in Sweden and Europe

Concretes used in structures designed in accordance with EN 1992-1-1 are covered in the European standard of concrete production, EN-206. This standard covers concrete specification, performance, production and conformity. In addition to SS-EN 206, Sweden has a national application standard, SS 137003 - *Application of SS-EN 206 in Sweden*.

In the previous version of EN-206, concrete mixture regarding carbonation resistance was based solely on prescriptive requirements on maximum *w/c* ratio, minimum cement content and maximum amount of mineral additions (ERMCO 2013). However, the newly revised European standard, EN 206:2013, also allow classification of concrete based on an equivalent performance concept for concrete mixtures that does not conform with these prescriptive requirements, instead ensuring sufficient durability by comparing an unknown test mixture to a reference mixture with known durability (Rozière et al. 2009). The compared mixture needs to be at least equally durable as a mixture complying with the prescriptive mixtures in the standard. If this is fulfilled and the test mixture is shown to be equally durable, it is assumed to fulfill the same prescriptive requirements as the reference mixture.

Table 2-5 Accepted combinations of cements conforming to SS-EN 197-1, extracted from SS 137003

Exposure class	XC1	XC2	XC3	XC4
Cements conforming to SS-EN 197	*CEM I* *CEM II/A-S* *CEM II/B-S* *CEM II/A-D* *CEM II/A-V* *CEM II/B-V* *CEM II/A-LL* *CEM II/A-M** *CEM II/B-M*** *CEM III/A*	*CEM I* *CEM II/A-S* *CEM II/B-S* *CEM II/A-D* *CEM II/A-V* *CEM II/B-V* *CEM II/A-LL* *CEM II/A-M** *CEM II/B-M*** *CEM III/A*	*CEM I* *CEM II/A-S* *CEM II/B-S* *CEM II/A-D* *CEM II/A-V* *CEM II/B-V* *CEM II/A-LL* *CEM II/A-M** *CEM II/B-M***	*CEM I* *CEM II/A-S* *CEM II/B-S* *CEM II/A-D* *CEM II/A-V* *CEM II/B-V* *CEM II/A-LL* *CEM II/A-M** *CEM II/B-M***

** Only cements with S, V, D or LL*
*** Only cements with S, V or D*

The new equivalent performance concepts in EN-206 enable more extensive use of mineral additions and it introduces three concepts for using mineral additions: the *k-value concept*, the *Equivalent Performance of Combinations Concept* (EPCC) and *the Equivalent Concrete Performance Concept* (ECPC) (ERMCO 2013). However, these equivalent performance concepts are not of interest for cements combinations marketed as a product, since they already conform to requirements on cements in accordance with SS-EN 197, shown in table 2-5. In SS 137003 these different prescribed cements are assumed to be equally durable, even though that is not the case. Norwegian standards, unlike Swedish, also requires decreasing *w/b* ratio by increased amount of mineral addition for the prescribed cement (Maage 2015).

These concepts mentioned above are to be used by concrete manufacturer in mixing design, when combining cement conforming to SS-EN 197 with a mineral addition, such as GGBS (EN 15167-1) or fly ash (EN 450-1). These three specific equivalent performance concepts are described more in detail below.

2.9.1 The *k*-value concept for fly ash and GGBS

The concept is based on a prescriptive *k*-value, see Table 2-6, used as multiplier to calculate an equivalent *w/c* ratio (w/c_{eq}), see equation 2.4, and an equivalent cement content (c_{eq}) of the mixture containing mineral addition. The calculated values need to fulfill requirements regarding w/c_{eq} and C_{eq}, for the chosen exposure class, presented in Table 2-2, extract from SS 137003.

Table 2-6 Prescriptive k-values in SS-EN 206 and the elevated k-value (described below) in SS 137003

Mineral addition	*k*-value (elevated *k*-value)
Fly ash	*0.4 (0.5)*
GGBS	*0.6 (0.8)*

$$\frac{w}{C_{eq}} = \frac{water}{cement + k \cdot mineral\ addition} \tag{2.4}$$

This method is imprecise, since the addition of GGBS and fly ash enhances the durability in some aspects and reduces it in others, as described in previous sections. The prescribed *k*-value concept is therefore a lower bound approach stating the durability on the safe side, and does not account for the efficiency of a specific fly ash or GGBS. The suitability of the prescriptive *k*-value is evaluated later in the report, comparing the prescriptive *k*-values to calculated *k*-values based on data from strength tests and carbonation tests, respectively.

The cement used in mixtures with fly ash or GGBS, based on the *k*-value concept, needs to be CEM I or CEM II/A conforming to SS 197-1 (SS-EN 206). The type of cement determines maximum content of mineral addition in the mixture, according to Table 2-7.

Table 2-7 Maximum mineral addition, expressed in percentage of total binder, allowed in mixing with CEM I and CEM II

	CEM I	CEM II
Fly ash	*25%*	*20%*
GGBS	*50%*	*50%*

If greater amount of mineral addition is used in mixing, the excess amount is not countable in w/c_{eq}.

In Sweden there are two different ways of using the *k*-value: either use the prescriptive value in accordance to SS-EN 206 or use elevated *k*-value[1] in accordance to SS 137003.

2.9.2 Elevated *k*-value according to SS 137003

k-values, other than the recommended values for general use in SS-EN 206, are allowed where the suitability of another *k*-value has been established. However, this sets stricter requirements on the mixtures. In SS 137003 elevated *k*-value of 0.5 for fly ash is permitted if the activity index is shown to be at least 75% , the fly ash is mixed with a CEM I with strength class 42.5 or higher and that the amount of fly ash is no more than 20%. Same analogy is used for GGBS, but with a $k = 0.8$, if activity index is at least 80% and the total amount of GGBS does not exceed 50%. If these requirements are not fulfilled the general *k*-value in accordance to standard SS-EN 206 shall be used.

Table 2-8 Requirements regarding elevated k-value for fly ash and GGBS

	Fly ash	GGBS
Elevated k-value	*0.5*	*0.8*
Amount of mineral addition	*≤20%*	*≤50%*
Activity index	*≥75%*	*≥80%*

2.9.3 Equivalent Performance of Combination Concept (EPCC)

Similar to the *k*-value concept, *The Equivalent Performance of Combination Concept* is a way of allowing other combinations of cement and mineral additions to be used. The method compares a combination of cement and mineral addition (test cement) with the performance of standardized cement (reference cement) (CEN/TC 104 2011). This method is based on strength as proxy criterion for durability. The basic idea is

[1] Swedish: förhöjt k-värde

that the compressive strength of the blended concrete, containing the test cement, needs to exceed the minimum required compressive strength with a statistical margin (SS 137003). If this criterion is satisfied it is assumed to fulfill the same requirement as for the *w/c* ratio and minimum cement content of the reference cement. This concept allows a more extensive use of mineral additions, compared to the *k*-value concept, since it is not a lower bound approach with standard value covering a wide range of combinations.

For EPCC the reference cements in the equivalent durability concepts ought to conform to table 1 in CEN/TR 16639, stating that the following cements can be used as a reference for exposure class XC: CEM I, CEM II/A-S, CEM II/B-S, CEM II/A-V, CEM II/B-V, CEM III/A and CEM III/B. This is however not in consensus with what is stated in SS 137003, see Table 2-5 above, where CEM III/B for example is not allowed in neither of the XC classes.

2.9.4 Equivalent Concrete Performance Concept (ECPC)

The ECPC has been used in the Netherlands for about 15 years (CEN/TC 104 2011). This concept sets requirements on the conformity between the test concrete and reference concrete. In contrast to EPCC, the limiting proportion might vary, if equal resistance is proven by testing (ERMCO 2013). Thus, a concrete with another *w/c* ratio and/or cement content than allowed in accordance to the limiting values in SS 137003 may be used when applying this method. This method requires both testing that proves equal compressive strength and equal durability. However, this concept is not yet assessed in the *Swedish Application of SS-EN 206*, SS 137003, since there are requirements regarding national reference concretes that are not yet fulfilled.

The requirements of this method is not clear. Recommendations according to the technical report CEN/TR 16639 (2014) state that the reference and the test concrete shall have cement content equal to binder content, *w/c* ratio equal to *w/b* ratio and the same type of aggregate and grading. This contradicts what is mentioned in the section above, and inhibits the ability to vary the *w/c* ratio of the test concrete. SS-EN 206 on the other hand permits amendments from the maximum *w/c* ratio and minimum cement content. The same amendments apply in the technical report CEN/TC 104 (2011) that states: "*the proportions of the test concrete may vary from those of the reference concrete"*.

3 Experimental program

The test program is based on the test matrix presented in Table 3-1 showing the *w/b* ratios, type of cement and amount of mineral addition.

Table 3-1 The test matrix, of which all performed tests are based on

Cement type	PC	Mineral addition	Amount of addition	w/b ratio	Performed tests
CEM I	*42.5N SR3*	-	-	*0.4*	*a,b*
CEM I	*42.5N SR3*	-	-	*0.5*	*a,b*[1]*,c,d*
CEM I	*42.5N SR3*	-	-	*0.6*	*a,b*
CEM I	*52.5N STD*	-	-	*0.4*	*a,b*
CEM I	*52.5N STD*	-	-	*0.5*	*a,b*[1]*,c,d*
CEM I	*52.5N STD*	-	-	*0.6*	*a,b*
CEM II/A-V	*52.5N STD*	*Fly ash*	*20%*	*0.4*	*a,b*
CEM II/A-V	*52.5N STD*	*Fly ash*	*20%*	*0.5*	*a,b*[1]*,c,d*
CEM II/A-V	*52.5N STD*	*Fly ash*	*20%*	*0.6*	*a,b*
CEM II/B-V	*52.5N STD*	*Fly ash*	*35%*	*0.4*	*a,b*
CEM II/B-V	*52.5N STD*	*Fly ash*	*35%*	*0.5*	*a,b*[1]*,c,d*
CEM II/B-V	*52.5N STD*	*Fly ash*	*35%*	*0.6*	*a,b*
CEM II/B-S	*52.5N STD*	*GGBS*	*35%*	*0.4*	*a,b*
CEM II/B-S	*52.5N STD*	*GGBS*	*35%*	*0.5*	*a, b*[1]*,c,d*
CEM II/B-S	*52.5N STD*	*GGBS*	*35%*	*0.6*	*a,b*
CEM III/A	*52.5N STD*	*GGBS*	*50%*	*0.4*	*a,b*
CEM III/A	*52.5N STD*	*GGBS*	*50%*	*0.5*	*a,b*[1]*,c,d*
CEM III/A	*52.5N STD*	*GGBS*	*50%*	*0.6*	*a,b*
CEM III/B	*52.5N STD*	*GGBS*	*65%*	*0.4*	*a,b*
CEM III/B	*52.5N STD*	*GGBS*	*65%*	*0.5*	*a,b*[1]*,c,d*
CEM III/B	*52.5N STD*	*GGBS*[2]	*65%*	*0.5*	*a,b*[1]*,c,d*
CEM III/B	*52.5N STD*	*GGBS*	*65%*	*0.6*	*a,b*

a Carbonation resistance
b Compressive strength
c Chloride migration
d Capillary absorption

[1] *Compressive strength also performed with CEN Normensand*
[2] *GGBS with increased fineness*

As shown in the test matrix, the emphasis was put on mixtures with *w/b* 0.5 for which all tests were carried out, including capillary absorption, chloride ingress and 28-day compressive strength. Mixtures with *w/b* 0.4 and 0.6 were only tested for carbonation resistance and 28-day strength. In other words, the comparison of carbonation resistance and 28-day strength are made both between different *w/b* ratios and levels of additives, while the capillary absorption and chloride ingress are solely made between different levels of additives. The tests were carried out on mortar prisms with either sea sand from Denmark, sieved to sieve-size <2 mm, or CEN Normensand. The matrix generated a total of 239 test specimens consisting of 29 unique mixtures.

3.1 Materials

This section presents the materials used in this study. There are two different cements used, whereas one is the reference cement used to obtain other cement types containing mineral addition, also presented in this section.

3.1.1 Cement

According to SS 137003, it shall be presumed that the cement contains the lowest amount of Portland cement clinker allowed in SS-EN 197-1, i.e. maximum amount of other additions. However, in the mixing design in this study it is the other way around, where Portland cement is assumed to consist of 100% clinker, while in reality it can be down to 95%. This assumption is on the safe side since the tests analyze the negative effect of blended cements, i.e. less Portland cement is assumed to give less of the desirable properties. There are two different CEM I used in this study, one with cement class 42.5 and the other with cement class 52.5, properties of both are presented in Table 3-2. The latter was also used in mixing with the mineral additions to produce other cement types.

Table 3-2 Properties and compositions of the two CEM I's used in this study

	CEM I 52.5[1] (Cemex 2014)	CEM I 42.5[2] (Cementa 2015)	Unit
Physical properties			
Fineness	*420*	*330*	*[m^2/kg]*
Particle density	*3150*	*3200*	*[kg/m^3]*
Setting time	*160*	*170*	*[min]*
Loss on ignition	*1.0*	*2.25*	*[% by mass]*
1-day strength	*20*	*10*	*[MPa]*
7-day strength	*33*	*35*	*[MPa]*
28-day strength	*59*	*54*	*[MPa]*
Chemical composition			
CaO	*63*	*64*	*[% by mass]*
SiO_2	*19*	*22*	*[% by mass]*
Al_2O_3	*4.3*	*3.7*	*[% by mass]*
Fe_2O_3	*3.1*	*4.5*	*[% by mass]*
MgO	*3.4*	*0.9*	*[% by mass]*
SO_3	*3.4*	*2.6*	*[% by mass]*
Alkali, equiv. Na_2O	*0.9*	*0.49*	*[% by mass]*
Water-soluble chloride, Cl^-	*0.07*	*0.02*	*[% by mass]*
Water-soluble chromium, Cr^{6+}	*<2*	*<2*	*[mg/kg]*
Mineral composition			
C_3S	*58*	*58*	*[% by mass]*
C_2S	*14*	*18*	*[% by mass]*
C_3A	*6*	*2*	*[% by mass]*
C_4AF	*9*	*14*	*[% by mass]*

[1]*CEM I - CEMEX standard 52.5N*
Cemex standard is produced in the Cemex factory Broceni, in Lithuania, in accordance with standard SS-EN 197-1.

[2]*CEM I - Cementa Anläggningscement 42.5N SR3 MH/LA*
Anläggningscement is a commonly used sulfate resistant cement in Swedish construction industry. This cement is produced by Cementa in Degerhamn, Sweden in accordance with standard SS-EN 197-1.

3.1.2 Mineral additions

The used GGBS goes by the name Slag Bremen, produced in Germany. It fulfills the requirements according to GGBS-standard SS-EN 15167, and is produced to be used in accordance with SS 137003 (Thomas Concrete Group 2014). The fly ash is produced in the power plant of Kraftwerks- und Netzgesellschaft mbH in Rostock, and satisfies the requirements according to standard SS-EN 450. Material properties for both GGBS and fly ash are stated in Table 3-3.

Table 3-3 Properties and activity index for the GGBS and fly ash used in this study

	GGBS, Werk Bremen[1]	Fly ash, Rostock block 1[2,3]	Unit
Loss on ignition	*-*	*2.60*	*[% by mass]*
Fineness	*420*	*340*	*[m^2/kg]*
CaO	*40*	*0.40*	*[% by mass]*
SO_3	*0.29*	*0.80*	*[% by mass]*
Cl	*0.004*	*<0.01*	*[% by mass]*
Alkali, equiv. Na_2O	*0.78*	*2.4*	*[% by mass]*
Particle density	*2900*	*2100*	*[kg/m^3]*
Activity index 7d	*>55**	*>70%***	*[%]*
Activity index 28d	*>75**	*>80%***	*[%]*
Activity index 91/90d	*>100**	*>90%***	*[%]*

[1] Thomas Cement AB (2014)
[2] Thomas Cement AB (2009)
[3] Warnow-Füller (2009)

**100% OPC (CEM I) relative to a mixture 50% Slagg Bremen and 50% OPC*
*** 100% OPC (CEM I) relative to a mixture of 25% Fly ash and 75% OPC*

3.2 Experimental methods

After casting, all specimens were immediately put in a sealed plastic box with a few centimeters of water in the bottom, creating an environment with RH of 100%. Thereafter, the box was placed in a climate room with a constant temperature of 20 °C and 65% RH. The RH in the room is not supposed to influence the humidity in the sealed box. 24 h after casting, the specimens were demoulded and placed in $Ca(OH)_2$ saturated water at a temperature of 20 ± 2 °C until preparation or testing, as described in the following sections.

3.2.1 28-day strength

The tests on compressive strength were based on the SS-EN 196-1, where all tests were performed on specimens casted in prisms with dimensions 160×40×40 mm, using the arithmetic mean of six results. With respect to the standard strength of cement, compressive strength must conform to the requirements stated in SS-EN 197-1, see Table 3-4. No tests regarding early strength were carried out in this study.

Table 3-4 Standard classes and the limits of the standard strength

Strength class	Standard strength, lower limit	Standard strength, upper limit
32.5 (L,N and R)	*32.5 [MPa]*	*52.5 [MPa]*
42.5 (L,N and R)	*42.5 [MPa]*	*62.5 [MPa]*
52.5 (L,N and R)	*52.5 [MPa]*	-

Loading of the specimens during the compressive strength test was made in accordance with SS-EN 196-1, the velocity of the loading cylinder was set to 2.40 kN/s. To assess the compressive strength of the specimens, the load at failure was divided with the cross-sectional area of the specimen on which the compressive force acted, see equation 3.1:

$$f_c = \frac{F}{A_c} \tag{3.1}$$

Standard cement strength tests (SS-EN 196-1)
To assess the compressive strength of the investigated cement and binder combinations a standardized test method, SS-EN 196-1, was used. The standard tests were performed on mortar mixtures with a *w/b* 0.5 using standardized CEN Normensand. The method was used to assure that the strength of the tested cement fulfills the requirements on cement class prescribed in each exposure class in SS 137003. As described in SS-EN 196-1, these mixtures were blended in a 5 liter Hobart (Figure 3-1a), filled in prisms in two steps and vibrated using a jolting apparatus (Figure 3-1b).

a) *b)*

Figure 3-1 a) Hobart mix b) Jolting apparatus

The results from compressive strength of mortars containing additions (x_1) together with the ones from the reference mortars (x_2) were used to calculate the activity index (*AI*), using equation 3.2:

$$AI = 100 * \frac{x_1}{x_2} \tag{3.2}$$

The activity index was used to interpret and compare the strength development and the activity of a cement with mineral addition compared to an ordinary Portland cement at 28 days.

Mortar strength tests (SS-EN 196-1)

The mortars were blended by using a hand-held concrete mixer, the moulds were filled twice and vibrated for 10-30 seconds each time. The vibration was dependent on the consistency of the concrete mixture, which varied depending on the *w/b* ratio and type of mineral addition, due to varying viscosity and thereby risk for bleeding.

3.2.2 Accelerated carbonation testing

The mortars used for accelerated carbonation testing are from the same batch as the ones from the mortar strength tests, and the procedure of casting was the same. However, the curing time differs. After being demoulded, the specimens were cured in water for additional 6 days, followed by 21 days of preconditioning in a climate room with a constant temperature of 20.0 ± 1.0 °C and relative humidity of 65 ± 5%. The specimens were placed in such a way that air could circulate freely around the exposed surfaces. The reason for the preconditioning period was to equilibrate the pore saturation, i.e. dry the concrete (Harrison et al. 2012) to the climate in the chamber, because the CO_2 can only penetrate the surface through pore air, since the

CO_2 resistance in water is significantly higher than in air, as described in section 2.5. Before carbonation, the top and bottom faces were sealed with a two-component paint to prevent diffusion of CO_2, to obtain carbonation only from the non-painted sides and prevent side effects in the measurements.

Standard levels of RH, temperature and CO_2 concentration for accelerated testing are not available, since a standard method is not approved. In the tests carried out in this study the accelerated carbonation chamber was held at moisture and temperature conditions equal to those in the climate room (20.0 ± 1.0 °C and 65 ± 1%). and an elevated CO_2 concentration of 2 ± 0.1%. There is a difference of opinion regarding the level of CO_2 concentration as previously discussed, and there is no common practice or standards stating limitations of CO_2 concentration. It is within the scope of 1% to 10% in most research, and in this study 2% are chosen, based on the time perspective and type of specimen. The climate in the chamber corresponds to the exposure class XC3, with constant climate conditions with moderate humidity. Varying climate would cause the highest risk with regard to carbonation induced corrosion, as previously discussed. However, it does not cause the highest carbonation depth, therefore constant climate is more suitable in this study.

Figure 3-2 Accelerated carbonation chamber

A phenolphthalein solution was sprayed on a freshly broken concrete surface to indicate the line where pH-level is 9, with an accuracy of a few millimeters (Tuutti 1982). This is interpreted as the carbonation front. However, a limitation with this method is that it does not show regions that might be partly carbonated.

3.2.3 Rapid chloride migration (RCM) tests

Chloride migration was tested on cylinders, cut to the desired thickness. The cylinder had the dimensions 200×100 mm (height × diameter). The moulds were filled and vibrated in three steps. Thereafter, the cylinder was covered with a steel lid before put into a sealed plastic box. The specimens were demoulded after 24h and water-cured for additional 6 days, thereafter the circumference surface was painted with two-component paint to prevent carbonation and chloride migration from the sides.

The test procedure for RCM was carried out in accordance with NT Build 492, to determine the chloride migration coefficient. The purpose of these tests was to investigate what effects carbonation and level of mineral addition have on the migration of chlorides; a comparison was therefore made between carbonated and non-carbonated concrete with different amount of mineral addition. The test method suggested cylindrical specimens of dimension 50×100 mm (height × diameter) and that three specimens should be used. In this study, the test was limited to two specimens with the dimension 40×100 mm due to the limited space in the carbonation chamber.

The first step in the test was preconditioning of the specimens with the purpose of filling the pores with $Ca(OH)_2$, thus obtaining an equal resistivity in the pore solution. The surface-dry specimens were placed in a desiccator and the absolute pressure was reduced to the range of 1-5 kPa by connecting a venturi nozzle to the container and letting the water flow. After maintaining the vacuum for three hours the container was filled with saturated $Ca(OH)_2$ solution. The vacuum was kept one hour after the solution was added to the container before released to atmospheric pressure. The specimens were then kept in the solution for 18 ± 2 hours.

After a total of 22 ± 2 hours of preconditioning, the specimens were attached inside a rubber sleeve and tightened with clamps. The rubber sleeve was filled with approximately 300 ml anolyte solution (0.3 M NaOH) and placed in the catholyte solution (10% NaCl), see Figure 3-3. The anode and cathode were placed in the anolyte and catholyte, respectively and the power was turned on with a preset voltage of 30 V, which then was adjusted in accordance with NT Build 492, depending on the initial current. When the final voltage was set, the initial temperature, current and time was recorded. After 24 hours, when the migration test was over, the final temperature, current and time were recorded. Some adjustments of the final voltages were made for carbonated specimens, due to large penetration depths.

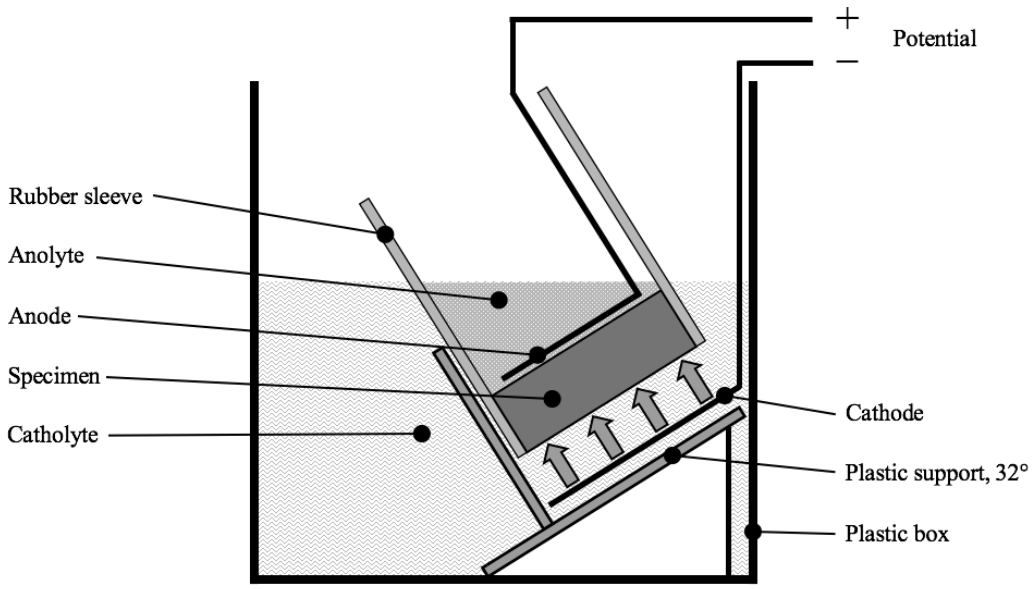


Figure 3-3 Arrangement of the chloride migration set-up

For the measurement of the chloride penetration depth, the specimens were disassembled from the rubber sleeve, rinsed in tap water and axially cut in half by a saw. Directly after the cut, the specimens were sprayed with 0.1 M silver nitrate solution on the cross section. After approximately 45 minutes the penetration depth was clearly visible and measured from the center of both edges at intervals of 10 mm, as shown in Figure 3-4. Measurements were taken from both halves, thus a total of 14 measuring points.

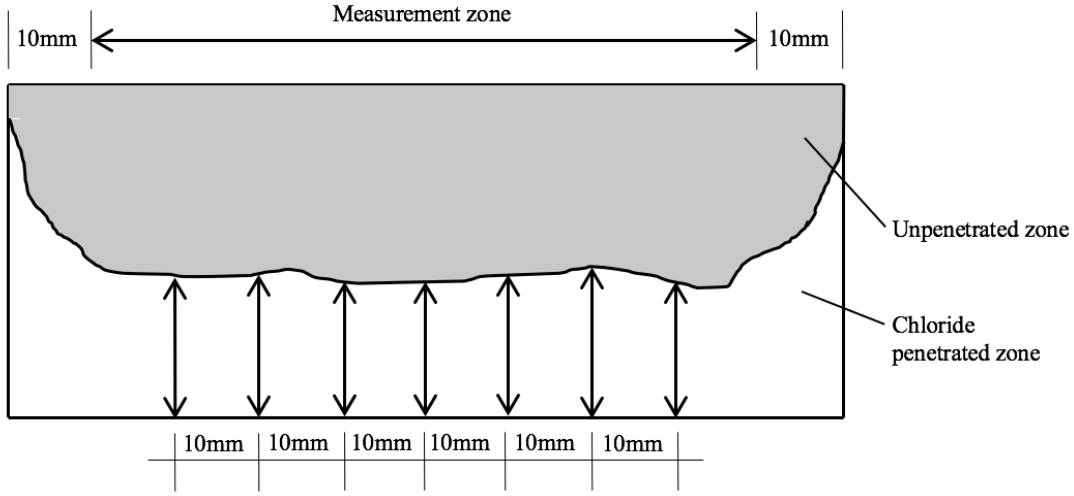


Figure 3-4 Measurement intervals of chloride migration specimens

3.2.4 Capillary absorption

The procedure of casting and curing the specimens tested for capillary absorption were the same as for the casting procedure of chloride migration specimens. The cylinders were sawn to a thickness of 20mm with a diameter of 100mm. The method is based on the principles of NT Build 368, but with a different preconditioning. All

the specimens where preconditioned in a drying kiln at 40 °C (>7 days) to equilibrate the specimens to approximately the same level of saturation.

The weight was measured during the testing at 10 min, 30 min, 1h, 2h, 4h, 6h and 1d, 2d, 3d and 4d in order to obtain the completion of capillary absorption. The completion is interpreted from the break point where the rate of the weight-gain decreases, see t_{cap} and Q_{cap} in Figure 3-5. The break-point refers to the intersection of the two trend lines obtained from regression analysis of the weight-data. The reason for the decreased weight-gain after the break-point is the difference in water absorption due to capillary absorption and diffusion, i.e. after completion of capillary absorption, only diffusion occurs which is a slow process compared to capillary absorption.

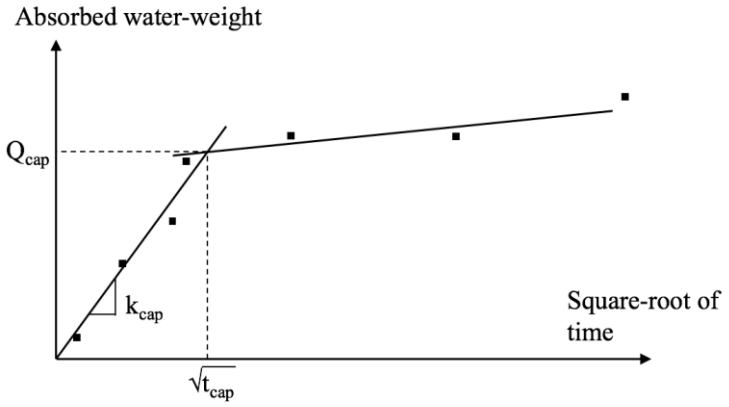


Figure 3-5 Schematic curve of capillary absorption

The capillary absorption tests obtain two main coefficients. Firstly, the resistance coefficient, m_{cap}, based on the time at which the break-point occurs, and the specimen thickness, h, see equation 3.3. Secondly, the capillary coefficient, k_{cap}, reflecting the rate of which the water is absorbed in the concrete, based on the water weight and the time at which the break-point occurs, see equation 3.4.

$$m_{cap} = \frac{t_{cap}}{h^2} \tag{3.3}$$

$$k_{cap} = \frac{Q_{cap}}{\sqrt{t_{cap}}} \tag{3.4}$$

m_{cap} is mainly influenced by the pore structure and not as much by the total porosity, in contrast to the k_{cap}. k_{cap} is describing the rate of capillary absorption, effected by the fineness and the connectivity of the capillary pores. High value of k_{cap} indicates a faster rate of capillary absorption, caused by a finer pore size distribution and/or increased connectivity of the capillary pores. However, both k_{cap} and m_{cap} are also affected by changes in total porosity.

Submerged weights were measured on vacuum saturation and saturation at 1 atm. The weight after saturation at 1 atm pressure gives results of capillary porosity. The

specimens were thereafter dried at 105 °C until no further weight change was observed, and weighed in order to obtain the total open porosity.

The weight loss when drying the specimens in 105 °C, from being saturated, relates to the evaporable water content, equation 3.5. By using the density of water, the volume of the evaporated water was calculated and this is interpreted as the total open porosity, equation 3.6.

$$m_{saturated} - m_{dry} = m_{evaporable} \tag{3.5}$$

$$\frac{m_{evaporable}}{\rho_{water}} = V_{total\ open\ porosity} \tag{3.6}$$

3.3 Effects of GGBS fineness

A small investigation on GGBS fineness was carried out as a side project in this study. The GGBS used in the mixtures were compared to another GGBS with increased fineness, both conforming to EN 15167-1. The two different GGBS do not have the same origin, but have similar composition, see Table 3-5. The tests were carried out on chloride migration, carbonation and capillary absorption, on the cements with the highest amount of GGBS, i.e. those containing 65%.

Table 3-5 Mineral composition of the two investigated GGBS

	GGBS, Werk Bremen	GGBS, inc. fineness
Density	*2900 kg/m^3*	*2900 kg/m^3*
Fineness	*420 m^2/kg*	*520 m^2/kg*
Na_2O	*0.42%*	*0.43%*
MgO	*7.0%*	*9.8%*
Al_2O_3	*13.6%*	*10.4%*
SiO_2	*36.3%*	*35.1%*
S^{2-}	*0.89%*	*1.79%*
Cl	*0.004%*	*0.003%*
K_2O	*0.54%*	*0.69%*
CaO	*40.0%*	*39.8%*
TiO_2	*0.85%*	*1.12%*
MnO	*0.45%*	*0.19%*
Fe_2O_3	*0.7%*	*0.5%*

3.4 Effects of different CEM I

Influence of different cement (CEM I) in the mortars was investigated as a side project in this study. The CEM I 52.5N was used as a reference cement and mixed with the mineral additions to obtain different blended cements. In addition, a CEM I 42.5N SR3 was mixed as a PC mortar. Both PC mortars were tested in the same manner, including compressive strength, accelerated carbonation, chloride migration and capillary absorption, as described earlier. The result from the two different PC mortars are compared and discussed in section 5.7, to identify the effects that can be associated with the choice of cement. This was of interest since both of these cements are allowed as reference cement in the equivalent performance concept, described in section 2.9.

4 Results from testing

This chapter presents the result from the tests, including compressive strength, accelerated carbonation, RCM and capillary absorption, described in previous chapter. The mortars containing mineral additions are referred to as the replacement level + type of mineral addition, e.g. 50% GGBS, while the reference cement is referred to as CEM I 52.5N.

4.1 Compressive strength

The strength tests include standard compressive strength of cements (in accordance with SS-EN 196-1) and compressive strength tests of all the mortar mixtures. The standardized strength of the cements was used in the calculations of activity index and to control whether the blended cements fulfil minimum requirements in SS 137003. The compressive strength tests on all the mortars are used to evaluate how the strength development varies with *w/b* ratio and amount of mineral addition.

4.1.1 Standard compressive strength (CEN Normensand)

The standard compressive strength tests (SS-EN 196-1) using CEN Normensand were carried out by the method described in section 3.2.1. A statistical margin of 5 MPa is required on the cements compressive strength when used in the equal performance, in accordance to SS 137003. The general strength requirement on the cements in exposure class XC3 (Table 2-2) is 42.5 MPa, visualized as a dotted line in Figure 4-1. Figure 4-1 show the result from the compressive strength test, together with the requirement of 42.5 + 5 MPa.

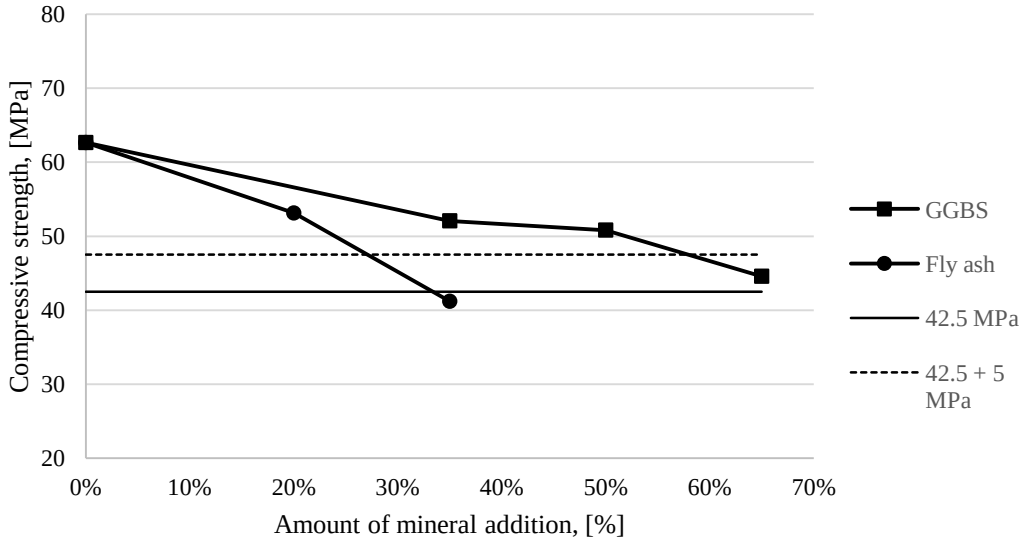


Figure 4-1 Compressive strength of mortars with CEN Normensand

4.1.2 Activity index (28-day)

Based on the previous result the activity index of the blended cements is calculated using equation 3.2. It is observed from Table 4-1 that the activity index decreases with increasing amount of mineral additions.

Table 4-1 Activity index for the investigated cement mixtures

Cement mixture	Activity index
Fly ash 20%	*85%*
Fly ash 35%	*66%*
GGBS 35%	*83%*
GGBS 50%	*81%*
GGBS 65%	*71%*

4.1.3 Compressive strength of mortars

The compressive strength test of all the mortars is based on the method described in section 3.2.1. The results from the strength tests are presented in Figure 4-2 and Figure 4-3 below. As expected, the strength decreases with increasing amount of mineral addition and *w/b* ratio.

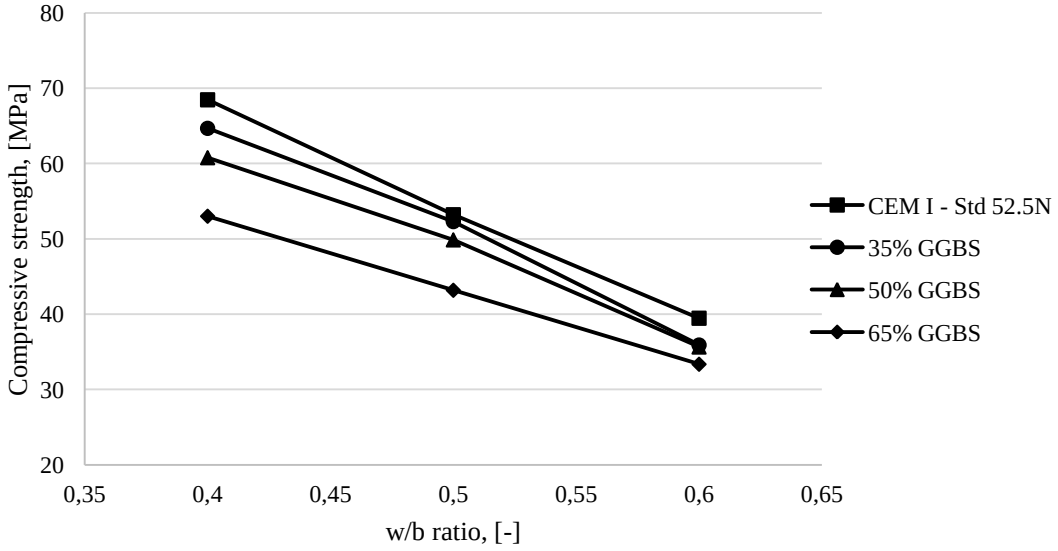


Figure 4-2 Compressive strength for mixtures with different proportions of GGBS

The differences in strength for GGBS concrete are more dependent on amount of mineral addition for low *w/b* ratios than for high *w/b* ratios (Figure 4-2). In other words, there is less variability in strength, caused by amount of mineral addition, for high *w/b* ratios. Fly ash, on the other hand, shows the same strength difference, independent of *w/b* ratio (Figure 4-3).

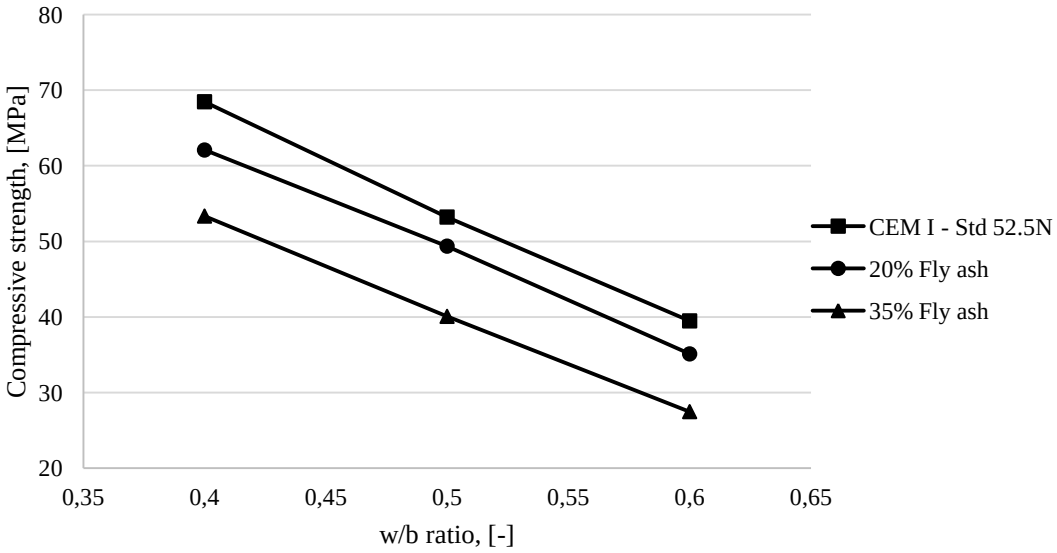


Figure 4-3 Compressive strength for mixtures with different proportions of fly ash

4.2 Accelerated carbonation tests

The accelerated carbonation tests were carried out using the method described in section 3.2.2. It was based on phenolphthalein measurement after 5 and 7 weeks. The carbonation rate, K_{acc}, based on these two measuring times, is also presented in this section. Furthermore, the obtained carbonation rate, K_{acc}, was used to calculate a natural carbonation rate, K_{nat}, based on the carbon dioxide concentration difference between a natural (0.04%) and accelerated exposure (2%).

4.2.1 Carbonation depth 5 and 7 weeks

The carbonation of the mortars subjected to accelerated carbonation showed even and easily measured fronts, see Figure 4-4.

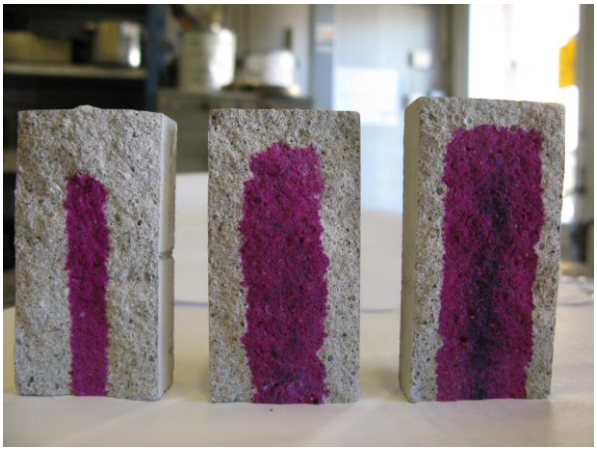


Figure 4-4 Carbonation front of specimens sprayed with phenolphthalein

The results from the accelerated carbonation tests show an increasing carbonation depth with increasing amount of *w/b* ratio, for both GGBS (Figure 4-5 and Figure 4-6)

and fly ash (Figure 4-7 and Figure 4-8), and the same trend was observed after both 5 and 7 weeks. The results also show increasing carbonation depth with increasing amount of mineral addition for a given *w/b* ratio, interpreted from the elevation of each line. This effect is clearer in the plot of carbonation rate, K_{acc}, and amount of mineral addition in section 5.2 (Figure 5-1 and Figure 5-2).

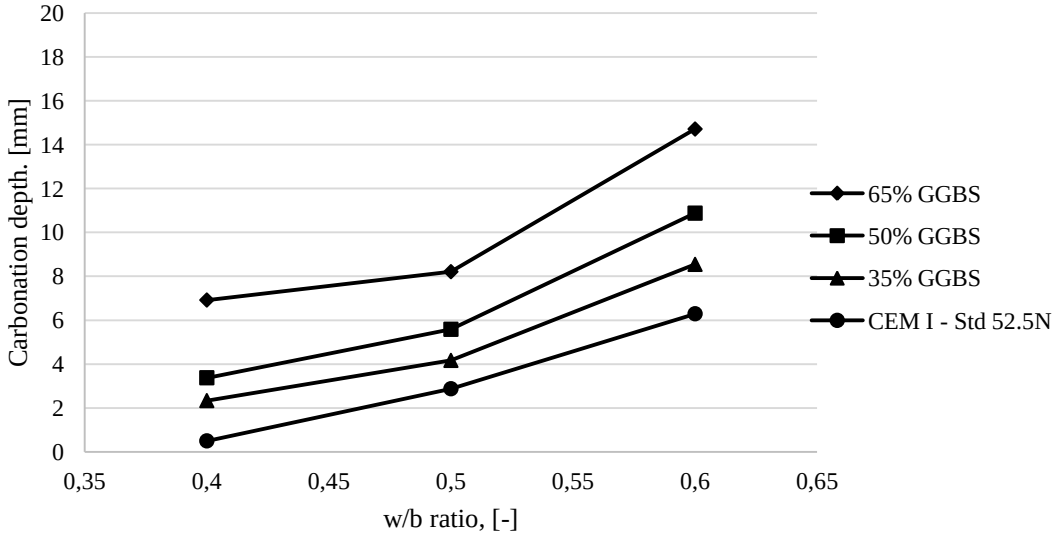


Figure 4-5 Carbonation depth after 5 weeks for different proportions of GGBS

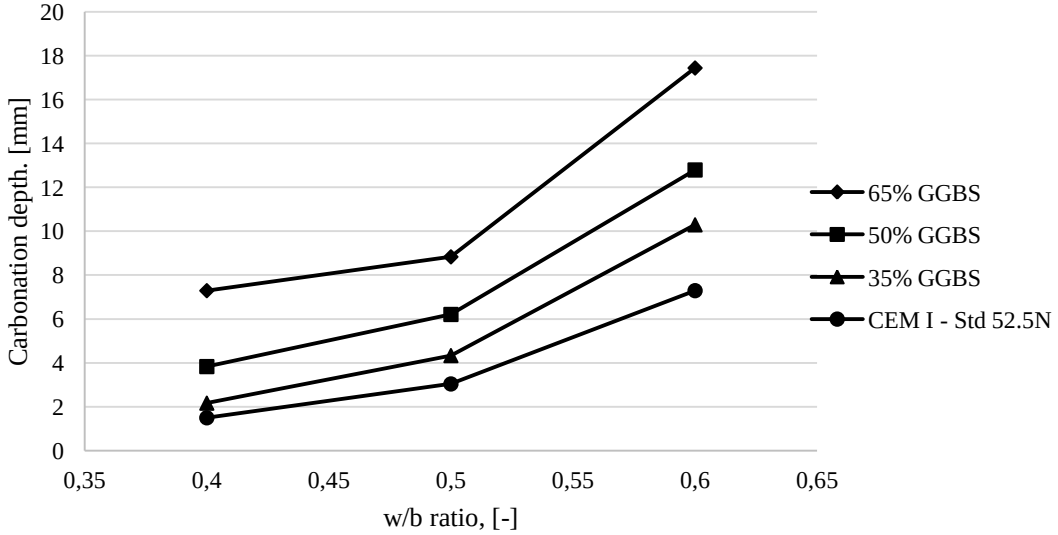


Figure 4-6 Carbonation depth after 7 weeks for different proportions of GGBS

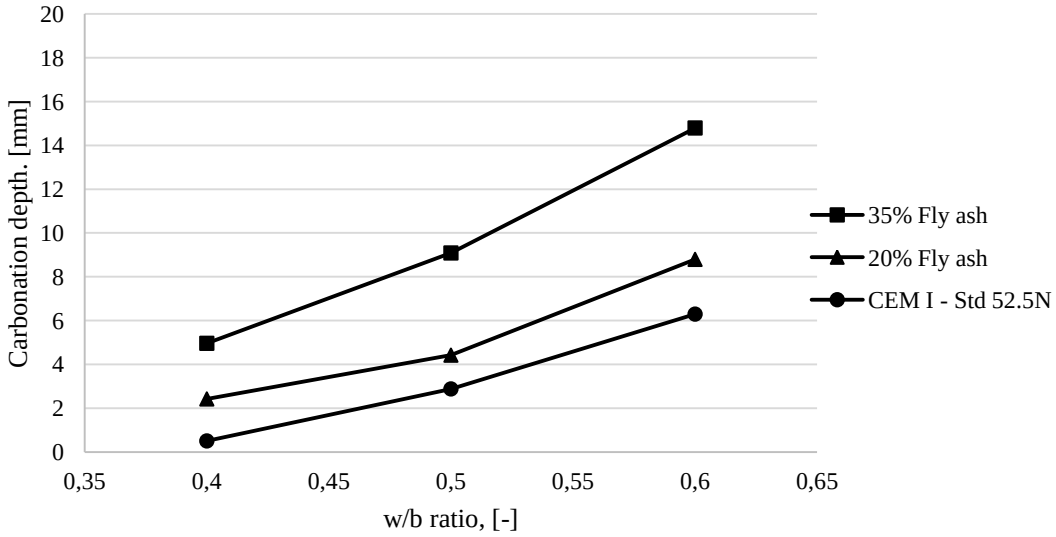


Figure 4-7 Carbonation depth after 5 weeks for different proportions of fly ash

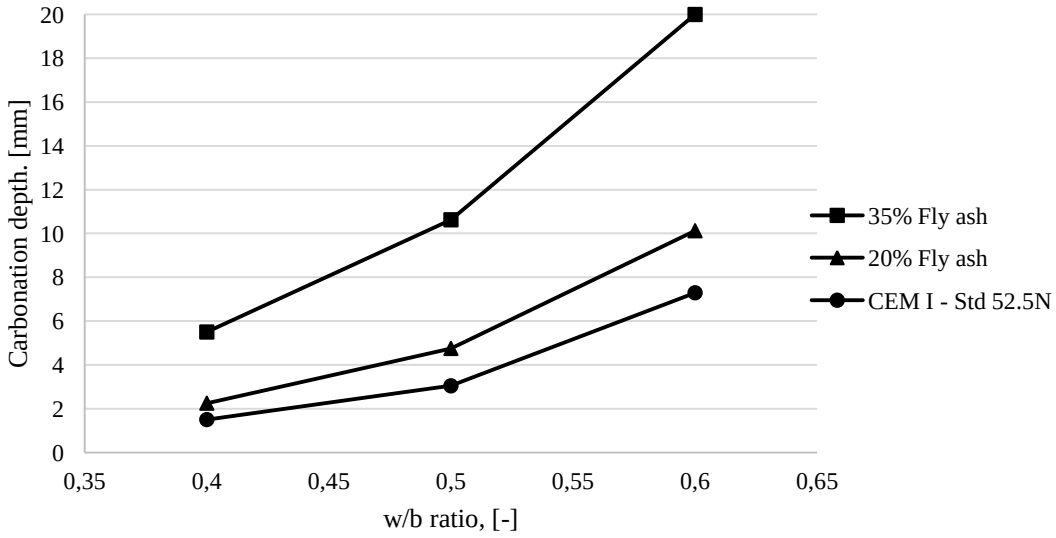


Figure 4-8 Carbonation depth after 7 weeks for different proportions of fly ash

4.2.2 Carbonation rate, *K*

Another way of expressing the carbonation depth data is by calculating the carbonation rate, *K* [mm/year$^{0.5}$], based on the square root of time relationship to carbonation depth, see equation 2.3, described in section 2.5. It normalizes the measurements and gives an average value of the measured exposure times, which makes it easier to compare to other research and data with another exposure time.

The validity of the square root of time relationship is discussed later, in section 5.2. The carbonation rate, Figure 4-9 and Figure 4-10, was calculated as the average from the rate at 5 and 7 weeks. Ideally, there should not a big difference between the shorter and longer exposure time when evaluating *K*. However, this is not entirely the case, as can be observed in Appendix A1.

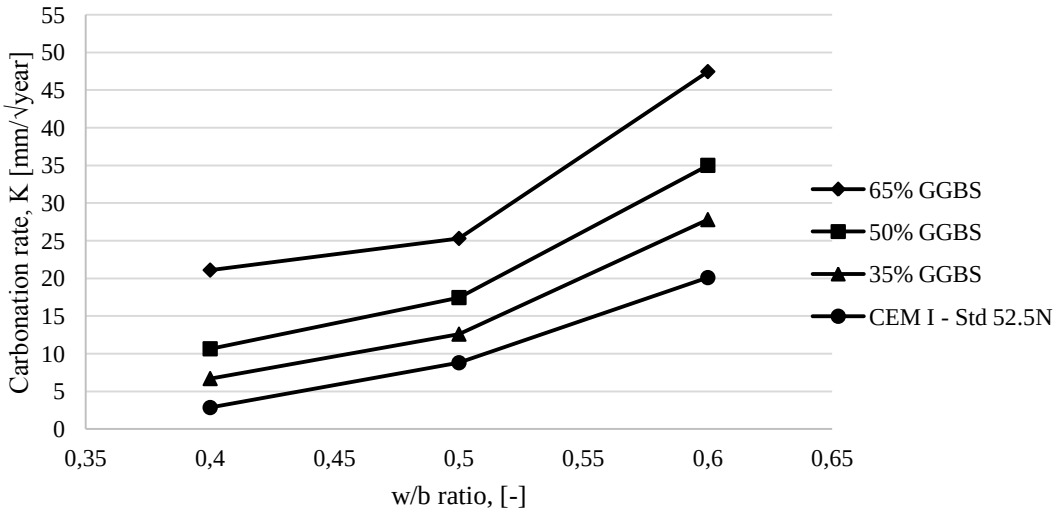


Figure 4-9 Accelerated carbonation rate for different proportions of GGBS

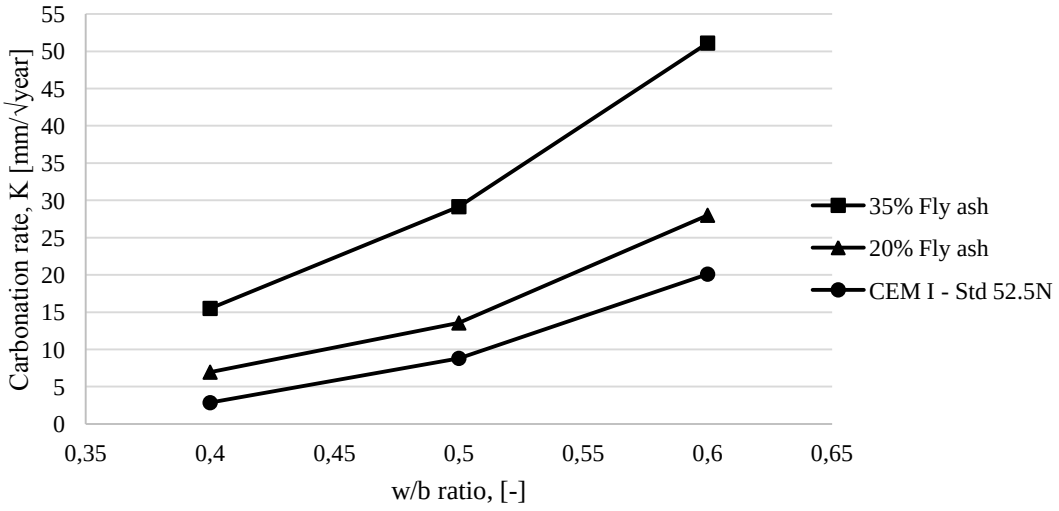


Figure 4-10 Accelerated carbonation rate for different proportions of fly ash

Table 4-2 shows both K_{acc} and K_{nat}. The calculation of "natural" carbonation rates is based on Fick's law of diffusion and the assumption that the carbonation rate is proportional to the square root of the concentration of CO_2. Thus, to obtain the natural carbonation rate from the accelerated test, the accelerated carbonation rate was

divided by the square root of the quote between the elevated concentration and the natural concentration of CO_2, see equation 4.1. The validity of this assumption is discussed in section 5.2.2.

$$K_{nat} = \frac{K_{acc}}{\sqrt{\frac{c_{elevated}}{c_{natural}}}} \quad (4.1)$$

Table 4-2 Accelerated and natural carbonation rates

Cement mixture	*w/b* ratio	Carbonation rate, *K* [mm/year$^{0.5}$]	
		K_{acc}* *[2% CO_2]*	K_{nat}** *[0.04% CO_2]*
CEM I 42.5N SR3	*0.4*	*3*	*0.4*
CEM I 42.5N SR3	*0.5*	*14*	*2.0*
CEM I 42.5N SR3	*0.6*	*30*	*4.3*
CEM I 52.5N	*0.4*	*3*	*0.4*
CEM I 52.5N	*0.5*	*9*	*1.2*
CEM I 52.5N	*0.6*	*20*	*2.8*
Fly ash 20%	*0.4*	*7*	*1.0*
Fly ash 20%	*0.5*	*14*	*1.9*
Fly ash 20%	*0.6*	*28*	*4.0*
Fly ash 35%	*0.4*	*16*	*2.2*
Fly ash 35%	*0.5*	*29*	*4.1*
Fly ash 35%	*0.6*	*51*	*7.2*
GGBS 35%	*0.4*	*7*	*0.9*
GGBS 35%	*0.5*	*13*	*1.8*
GGBS 35%	*0.6*	*28*	*3.9*
GGBS 50%	*0.4*	*11*	*1.5*
GGBS 50%	*0.5*	*17*	*2.5*
GGBS 50%	*0.6*	*35*	*4.9*
GGBS 65%	*0.4*	*21*	*3.0*
GGBS 65%	*0.5*	*25*	*3.6*
GGBS 65%	*0.6*	*47*	*6.7*

**Average carbonation rate, measured after 5 and 7 weeks.*
***Based on the assumption that the K-value is proportional to the square root of the CO_2 concentration.*

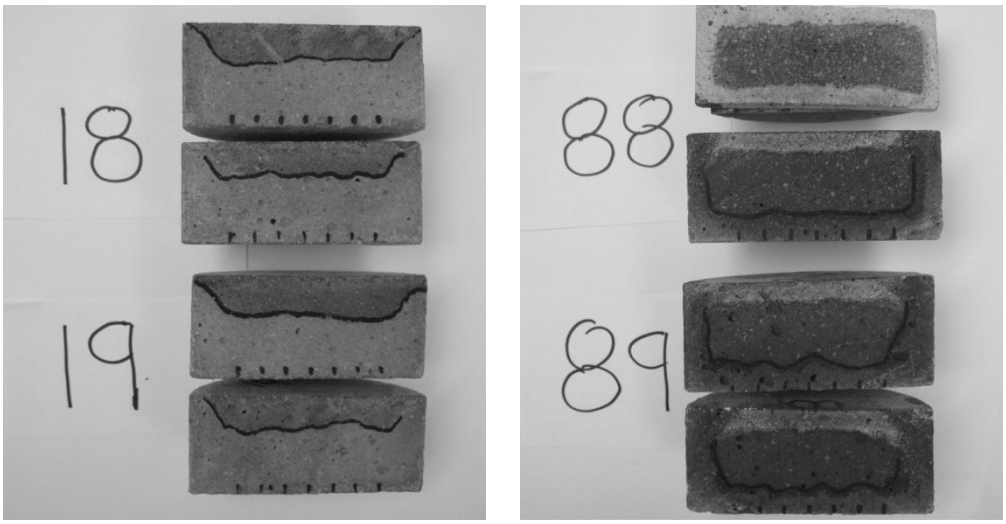
4.3 Rapid chloride migration (RCM) tests

The RCM tests were carried out based on the method described in section 3.2.3. The carbonated specimens subjected to chloride migration had varying carbonation depths, depending on the mixture. Some were fully carbonated, and some only partially carbonated. The carbonation depth for the chloride migration specimens was not measured, since the carbonation depth and chloride migration cannot be measured on the same samples. However, the carbonation can be assumed to be equal to the prisms of the same mixture, subjected to 7 weeks of 2% CO_2 concentration, see Table 4-3.

Table 4-3 Chloride migration coefficient and standard deviation for both non-carbonated and carbonated specimens

Cement mixture	Average carbonation depth [mm]	Chloride migration coefficient, D_{nssm} $\times 10^{-12}$ [m^2/s]			
		Non-carb.	*Std.*	*Carb.*	*Std.*
CEM I 52.5N	*3.1*	*11.0*	*0.1*	*9.5*	*0.2*
Fly ash 20%	*4.8*	*4.2*	*0.4*	*9.6*	*1.3*
Fly ash 35%	*10.6*	*3.5*	*0.1*	*8.0*	*1.1*
GGBS 35%	*4.3*	*4.2*	*0.1*	*6.7*	*0.5*
GGBS 50%	*6.2*	*2.6*	*0.3*	*7.4*	*0*
GGBS 65%	*8.8*	*2.3*	*0.2*	*8.0*	*0.5*

The first tests of the carbonated specimens showed an unexpected low level of resistance to migration, thus some of the specimens had an almost fully penetrated chloride front when following the guidelines of the method (NT Build 492), see Figure 4-11a. This is further discussed in section 5.5. The voltages were adjusted to approximately one third of the tabulated value. The adjusted voltages gave sounder results regarding the depth of the chloride front, see Figure 4-11b.



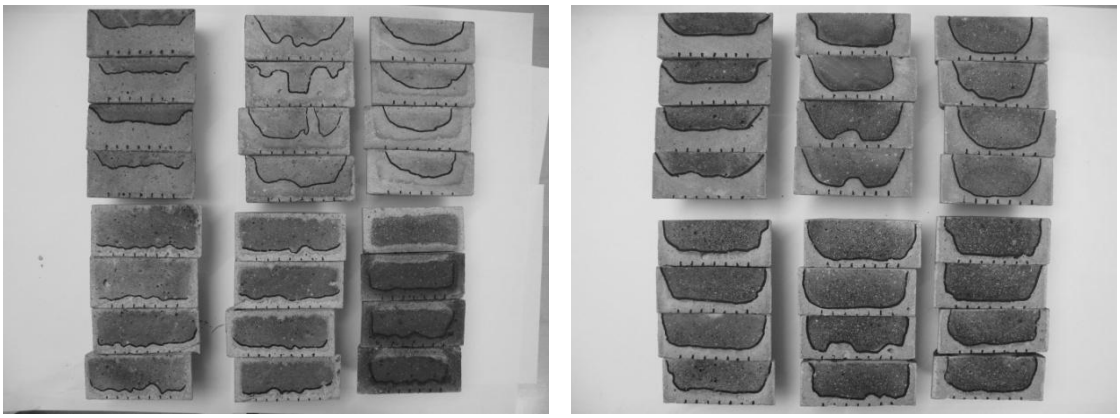
a) *b)*

Figure 4-11 a) almost fully penetrated specimens (35V on carbonated mortar)
b) sounder results (15V on carbonated mortar)

There were also effects of disturbed migration front, due to pores from insufficient compaction of some mortars, see Figure 4-12. This caused large standard deviations of the chloride migration coefficient for some mortars presented in Table 4-3.

Figure 4-12 Large pores in the specimens influencing the RCM-front

All mortars were more or less fully penetrated through the sides, see Figure 4-13. This is believed to be caused by the coating used to prevent carbonation from the sides, and not due to carbonation, since both carbonated and non-carbonated specimens are showing this effect. This is further discussed in section 5.5.



a) *b)*

Figure 4-13 Chloride migration front on, a) carbonated specimens and b) non-carbonated specimens

This caused difficulties when measuring, due to an uneven migration front in some mortars. This can also be observed in the standard deviations of some chloride migration coefficient, see Table 4-3.

4.4 Capillary absorption

The results from capillary absorption were based on the method described in section 3.2.4, including total open porosity, rate of capillary absorption and resistance to water penetration. The degree of saturation, S_t, against time is also computed (result presented in Appendix B2), based on the full saturation of the total open porosity. For the capillary absorption of the carbonated specimens it should be noted that the carbonation depth was not equal for the different mortars, same as for the chloride migration shown in Table 4-3.

4.4.1 Total open porosity

All the carbonated mortars showed a reduction in total open porosity, see Table 4-4. Fly ash mortars showed the greatest decrease in total open porosity, with increasing porosity-reduction by increasing amount of mineral addition. GGBS mortars, on the other hand, shows a peak in porosity-reduction at 50% GGBS. However, the differences are quite small and the test was based on limited number of specimens. Therefore, the individual values are quite uncertain.

Table 4-4 Total open porosity before and after carbonation

Cement mixture		*w/b* ratio	Total open porosity	
			Non-carb.	*Carb.*
CEM I 52.5N		*0.5*	*20.0%*	*18.7%*
Fly ash	*20%*	*0.5*	*20.1%*	*17.7%*
Fly ash	*35%*	*0.5*	*20.6%*	*17.0%*
GGBS	*35%*	*0.5*	*19.5%*	*17.8%*
GGBS	*50%*	*0.5*	*20.1%*	*18.2%*
GGBS	*65%*	*0.5*	*20.1%*	*18.7%*

4.4.2 Capillary absorption curves

As interpreted from the graphs showing the capillary absorption over time (Figure 4-14 to Figure 4-19) there is a significant difference in water absorption between carbonated and non-carbonated specimens. The horizontal lines in Figure 4-14 to Figure 4-19 indicate total amount of absorbed water when vacuum saturated, i.e. absorbed water in all the open pores. The origin in the graphs represents the 105 °C-weight, i.e. when all free water has evaporated, and the initial value of absorption represents the initial absorbed water, i.e. the difference between initial weight after drying in 40 °C and the weight after drying at 105 °C. The steep slope is the water absorbed by capillary action, and the flat line is the continuing diffusion.

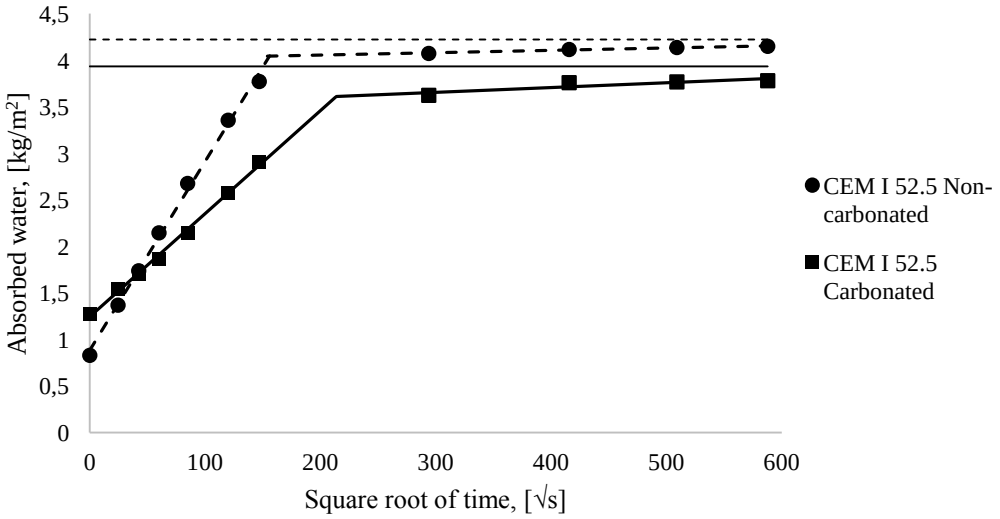


Figure 4-14 Capillary absorption curve for non-carbonated and carbonated CEM I specimens

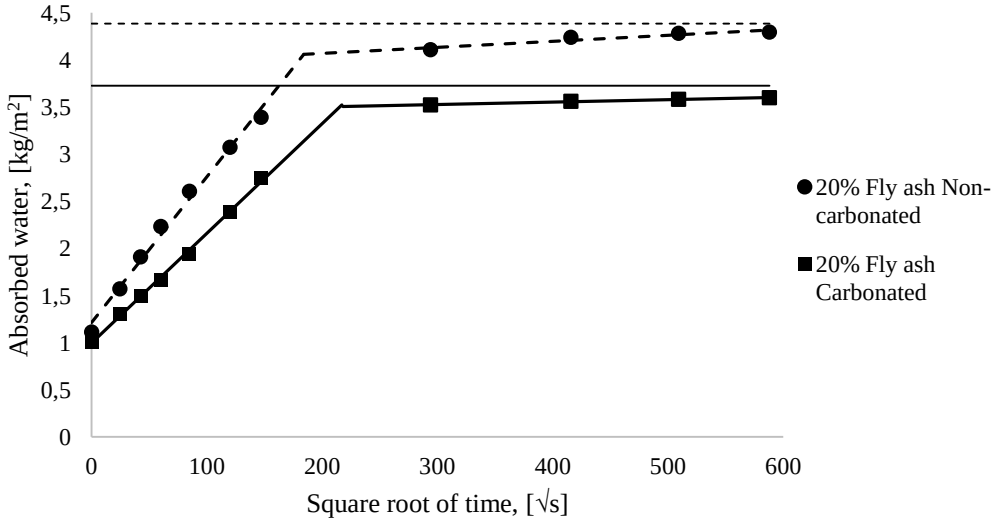


Figure 4-15 Capillary absorption curve for non-carbonated and carbonated specimens with 20% fly ash

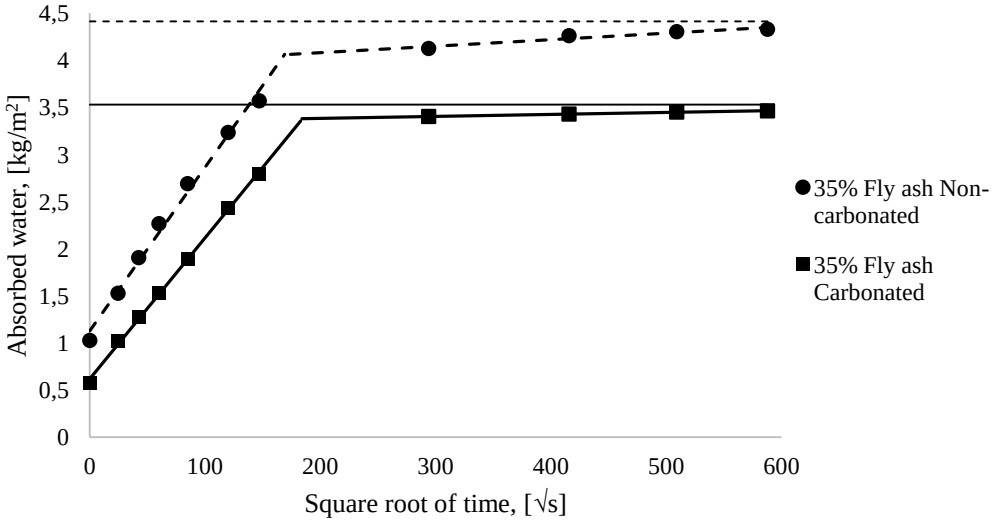


Figure 4-16 Capillary absorption curve for non-carbonated and carbonated specimens with 35% fly ash

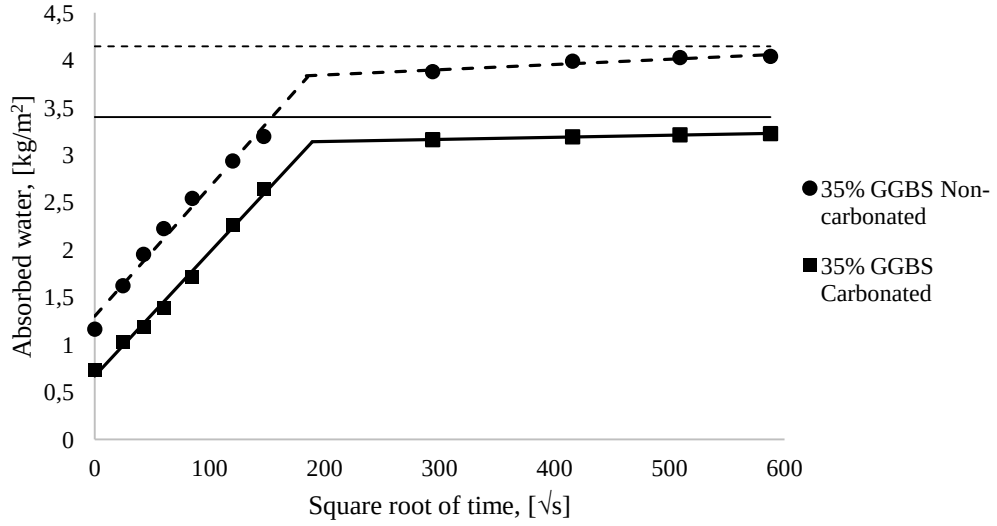


Figure 4-17 Capillary absorption curve for non-carbonated and carbonated specimens with 35% GGBS

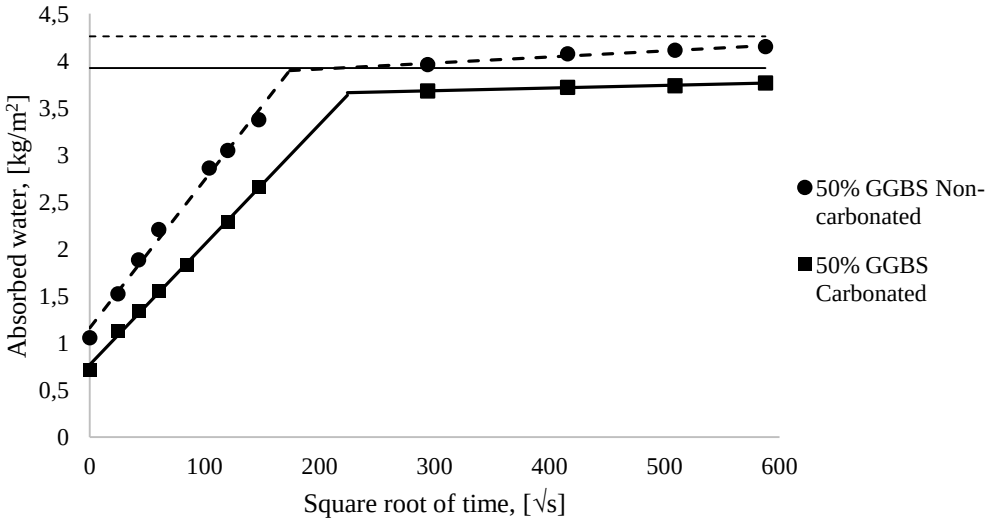


Figure 4-18 Capillary absorption curve for non-carbonated and carbonated specimens with 50% GGBS

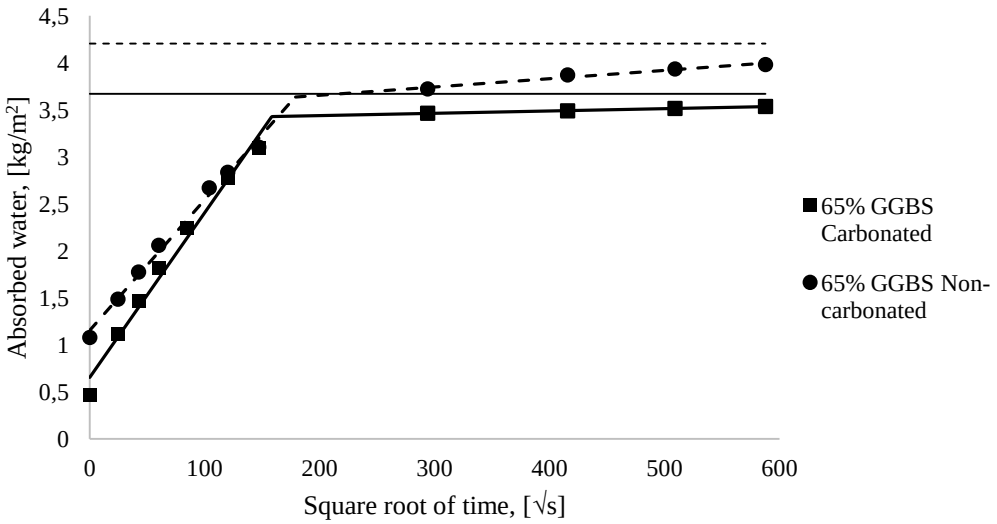


Figure 4-19 Capillary absorption curve for non-carbonated and carbonated specimens with 65% GGBS

Figure 4-14 to Figure 4-19 show capillary absorption, diffused water and total absorbed water of each individual mixture, which gives an indication on the degree of saturation of the open pores. Another way of expressing this result is the degree of saturation against time. These results are presented in Appendix B2, where $S_t = 1$ is a fully saturated specimen, in terms of open pores. This result is further discussed in section 5.8.

4.4.3 Capillary coefficient, k_{cap}, and the resistance coefficient, m_{cap}

Since there is a slight variety in thickness of the tested cylinders, m_{cap} and k_{cap} are more useful parameters than Figure 4-14 to Figure 4-19, when comparing the effects caused by carbonation. These coefficients were calculated using equation 3.3 and 3.4 (section 3.2.4), respectively. The result is presented in Table 4-5, where k_{cap} describes the rate at which the capillary water front penetrates the mortar and m_{cap} is an indication of the resistance to water absorption.

m_{cap} increases with carbonation of the mortars, for all mixtures except for the mixture with 65% GGBS, see Table 4-5. This phenomenon can also be seen in Figure 4-19 above, where the break-point of absorption curve is slightly moved to the left, unlike the curves for other amount of mineral addition. The k_{cap} decreases with carbonation, i.e. a slower absorption of water for carbonated specimens, except for blended cement with high amount of GGBS (65%), where it is the other way around.

Table 4-5 Capillary coefficient and resistance coefficient for non-carbonated and carbonated cement mixtures

Cement mixture		k [10^{-3} kg/m$^2\sqrt{s}$]	m [10^6 s/m^2]	k [10^{-3} kg/m$^2\sqrt{s}$]	m [10^6 s/m^2]
		Non-carbonated		*Carbonated*	
CEM I 42.5N SR3		*25*	*34*	*8*	*190*
CEM I 52.5N		*21*	*53*	*11*	*102*
Fly ash	*20%*	*16*	*66*	*12*	*103*
Fly ash	*35%*	*18*	*60*	*15*	*77*
GGBS	*35%*	*15*	*70*	*13*	*99*
GGBS	*50%*	*17*	*58*	*13*	*105*
GGBS	*65%*	*15*	*69*	*19*	*58*
*GGBS**	*65%*	*11*	*81*	*14*	*93*

**Increased fineness*

5 Analysis and discussion

In this chapter, the results from previous chapters are analyzed and combined to describe and discuss the observed mechanisms and effects. Based on the results on mortars, conclusions regarding concrete are presented. Therefore, PC concrete and blended concretes are used as terms when describing general effects and conclusions.

The mortar containing CEM I 42.5 is disregarded in the chloride migration and capillary absorption, because the blended concretes do not contain this cement, which makes a comparative study misleading.

The relationship between strength and *w/b* ratio is approximately linear, except for some anomalies in 35% GGBS (Figure 4-2). Linear interpolation and extrapolation are therefore a good approximation to predict the compressive strength of a concrete with a *w/b* ratio other than the ones tested.

5.1 Requirements of cement class and activity index

Figure 4-1 indicates that the blended cements with high levels of mineral addition do not fulfill the requirements on cement class in SS 137003. The calculated activity indices presented in Table 4-1 show similar values as the activity indices (28d) in accordance to the material data presented in section 3.1. Furthermore, the activity index decreases with increased amount of mineral addition, which is expected, since the hydration process is slower when adding fly ash and GGBS.

5.2 Accelerated carbonation

Regarding the mixtures with low *w/b* ratio, and with low amount of mineral addition, the carbonation front was too shallow to be measured, which causes inconsistent result of the carbonation rate for these mixtures. For example, Appendix A2 show results of higher carbonation depth after 5 weeks compared to after 7 weeks. Therefore, the carbonation results of mortars with low *w/b* ratios and low levels of mineral addition are uncertain. Hence, the calculated carbonation rate of 5 weeks and 7 weeks show good results, see Appendix A1, except for PC mortars with low *w/b* 0.4.

The results showing the carbonation rates related to *w/b* ratio, in section 4.2, are linearly interpolated between the measuring points. There is an uncertainty associated with this estimation, since the results does not show a linear dependence. Especially, extrapolation to estimate carbonation rates for *w/b* ratios outside the tested *w/b* ratios causes uncertain result.

When interpreting the slopes between different levels of mineral additions, it is clear that the depth is increasing more with increasing amount of mineral addition, for the high *w/b* ratios, especially for fly ash, see Figure 5-1 and Figure 5-2. However, the exact amount of mineral addition where the break-point actually occurs is hard to tell based on the data in this study, since the lines are simply interpolated. To evaluate at which exact amount of fly ash or GGBS this significant increase in carbonation rate occurs, additional mixtures are required.

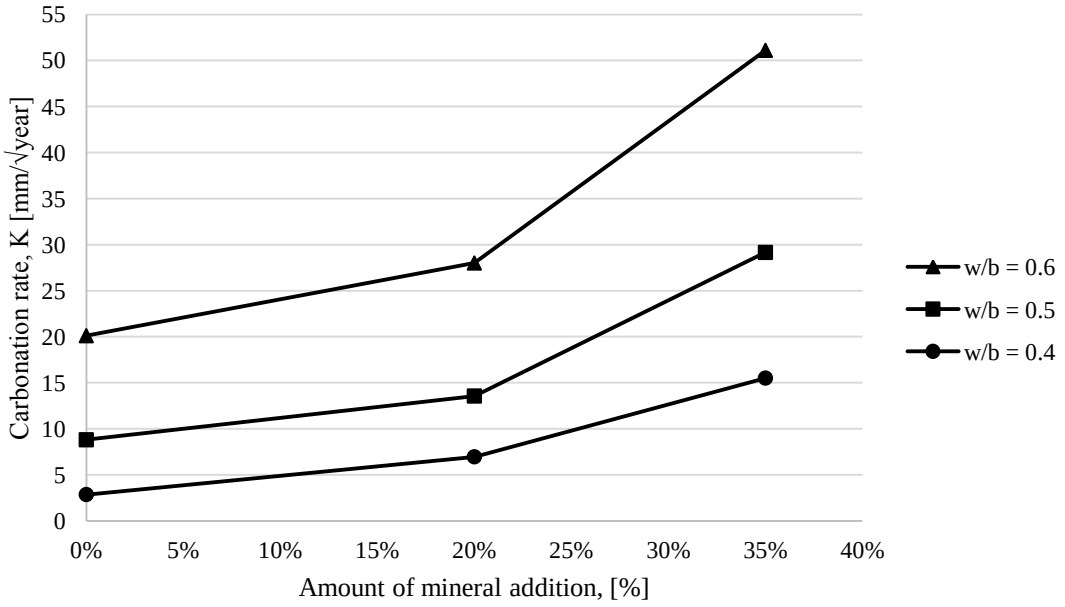


Figure 5-1 Carbonation rate for fly ash mixtures

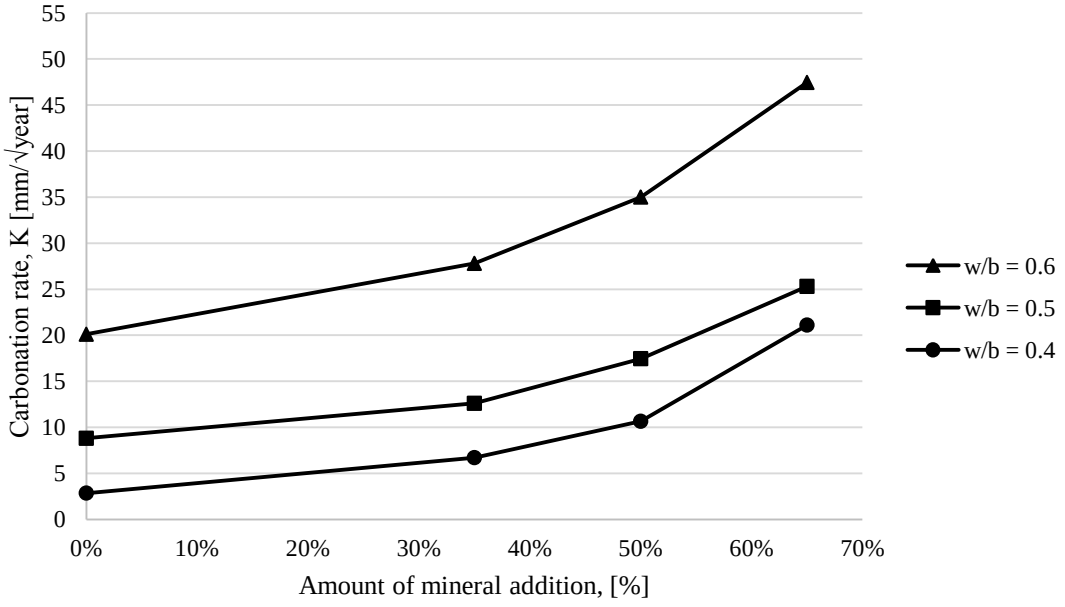


Figure 5-2 Carbonation rate for GGBS mixtures

5.2.1 Accelerated carbonation and effects of curing and age

As discussed previously, insufficient curing affects the rate of carbonation, especially for accelerated carbonation test. Seven days of water curing, as in this study, is considered as adequate for PC concretes based on studies by Balayssac et al. (1995). However, it is not considered as adequately cured for blended concretes (Sulapha et al. 2003). An optimum would be to cure the mortars even more than 28 days, since

carbonation in concretes with high levels of GGBS and fly ash has shown to continue decreasing even after 28 days (Sulapha et al. 2003). In other words, blended concretes are more sensitive to inadequate curing when using accelerated carbonation, since the concrete does not have time to reach equal maturity compared to PC concrete, at the time carbonation has started. Therefore, enlarging negative effects in blended concretes have been shown by Jia et al. (2003) amongst others, when using accelerated carbonation, especially for concretes with high amount of mineral addition.

Sufficient curing period was not possible due to the time frame of this project. Therefore, the magnitude of carbonation might be overestimated, compared to a concrete in a natural environment, since the specimens are not fully hydrated at the age of exposure in this study. When comparing the result to each other it is expected to yield more accurate result, due to same exposure condition for all the specimens. However, there is still a difference in rate of hydration between mineral addition and Portland cement, which will cause varying degree of hydration after 7 days depending on the amount of mineral addition in the mortar. It probably causes an overestimation of the carbonation rate of mortars with high levels of mineral addition. This overestimation of carbonation is on the safe side, since the suitability of mineral additions are investigated.

5.2.2 Validity of the calculated natural carbonation rate, K_{nat}

The calculated natural carbonation rate is only an estimation of the natural carbonation depth, since the relation between natural and accelerated carbonation do not only depend on the concentration difference and diffusion of CO_2. In reality, the carbonation depends on differences of natural and accelerated factors, such as curing, CO_2 diffusion capacity and amount of carbonatable materials in the different cementitious materials (section 2.5). Generally, the carbonation rate for structure exposed to atmospheric concentration of CO_2 concentration and protected from rain varies from 2 to 15 mm/year$^{0.5}$ (Bertolini et al. 2004), which is somewhat higher than the obtained values in Table 4-2. However, the result has shown to be quite consistent when comparing it to minimum requirement and data collected by Lagerblad (2003), described further below.

One way of verifying the calculated K_{nat} is by comparing the values to the requirements in Swedish national standard. Table 5-1 show the results from a backward calculation of the carbonation rate, based on the cover thickness, required for a certain design life (L100, L50 and L20) and its required *w/c* ratio (Boverket 2016). Note, if the requirements in Sweden, regarding cover thickness and service life, would rely entirely on the square root of time relation (equation 2.3), the K_{req} (Table 5-1) for a certain *w/c* ratio would have been the same.

Table 5-1 Required K-values for XC3, based on cover thickness prescribed in EKS10 (Boverket 2016)

	w/c ratio	$K_{req.100}$ [mm/year$^{0.5}$]	$K_{req.50}$ [mm/year$^{0.5}$]	$K_{req.20}$ [mm/year$^{0.5}$]
XC3	*0.55*	*2.5*	*2.8*	*3.4*
	0.50	*2.0*	*2.1*	*2.2*

When comparing K_{req} (Table 5-1) and K_{nat} (Table 5-2), it can be observed that, for *w/c* 0.5, the carbonation rate:

- for the PC mortar, K_{nat}, is below K_{req}
- for the moderate amount of mineral addition (20% FA and 35% GGBS) K_{nat} is equal to K_{req}
- for high amount of mineral addition (35% FA and 65% GGBS) K_{nat} is above K_{req}.

Table 5-2 Natural carbonation rates converted from accelerated carbonation rates, extracted from Table 4-2

Cement mixture	*w/b* ratio	K_{nat} [mm/year$^{0.5}$]
CEM I 42.5N SR3	*0.5*	*2.0*
CEM I 52.5N	*0.5*	*1.2*
Fly ash 20%	*0.5*	*1.9*
Fly ash 35%	*0.5*	*4.1*
GGBS 35%	*0.5*	*1.8*
GGBS 50%	*0.5*	*2.5*
GGBS 65%	*0.5*	*3.6*

Since the requirements should be lower bound, the tested values should all be below the requirements in Table 5-1. However, that is not the case for high levels of mineral additions. As mentioned before, there are magnifying carbonation effects of mixtures with high amount of mineral additions when using accelerated carbonation (section 5.2.1). Furthermore, this comparison is on a *w/b* basis and not on an equivalent *w/c* basis as in the concepts in EN 206, and the result would probably be more consistent on an equivalent *w/c* or compressive strength basis.

The obtained carbonation rates, K_{nat}, can also be compared to in-situ testing. Fridh & Lagerblad (2013) have calculated a carbonation rate of 2.6 mm/year$^{0.5}$, based on carbonation front measured with phenolphthalein on a cellar wall with *w/c* 0.6 (CEM

I). The temperature and humidity in the cellar is assumed to be similar to the climate in the accelerated carbonation chamber. The in-situ tested carbonation rate is close to the obtained K_{nat} of 2.8 mm/year$^{0.5}$, calculated from accelerated testing of the PC mortar with *w/c* 0.6, in this study.

The natural carbonation rates, K_{nat}, can also be compared to estimated carbonation rates based on former research carried out by Lagerblad (2003). According to Lagerblad, a concrete containing CEM I 52.5 has an estimated the carbonation rate of 2.5 mm/year$^{0.5}$, in a sheltered outdoor environment, which is a similar climate as the accelerated chamber. This value is similar to the K_{nat} of 2.8 mm/year$^{0.5}$ obtained in this study.

To conclude, the comparisons to requirements in standard and former research show similar carbonation rate for PC mortar, but for high levels of mineral additions the standards may be on the un-safe side.

5.3 Evaluation of the *k*-value concept

The calculated *k*-value, using strength and carbonation, is based on the same theory as the prescriptive *k*-value (section 2.9.1) concept in SS-EN 206 and SS 137003. However, it is important not to equalize the prescriptive *k*-value and the calculated *k*-value, since the prescriptive *k*-value assures durability, taking all different deteriorating processes into account. The *k*-values calculated in this section regard 28-day strength and carbonation individually, showing the full potential compared to the reference mortar. In other words, the two calculated *k*-values show how the blended mortars perform, relative to the reference mortar, regarding either 28-day strength or carbonation.

Therefore, the calculated *k*-value based on the carbonation rates are suitable regarding carbonation resistance, but it says nothing about resistance against for example chloride ingress, which the prescriptive *k*-value in the standard does. The calculated *k*-values in this study can be used to evaluate the suitability of the prescriptive *k*-values in Swedish standards, from a carbonation and strength perspective.

All the calculated *k*-values are stated in Table 5-3 below. They were calculated by equation 5.1, based on the $(w/c)_{ref}$ obtained from the test results. $(w/c)_{test}$ and $(w/c)_{ref}$ is the *w/c* ratio for the PC mortar (reference) and blended mortar (test), respectively, with the same compressive strength (or carbonation), as illustrated in Figure 5-3.

$$k = \frac{\left(\frac{(w/c)_{test}}{(w/c)_{ref}} - 1\right)}{\left(\frac{D}{C}\right)} \tag{5.1}$$

D/C = mass fraction of mineral addition and cement [kg/kg]

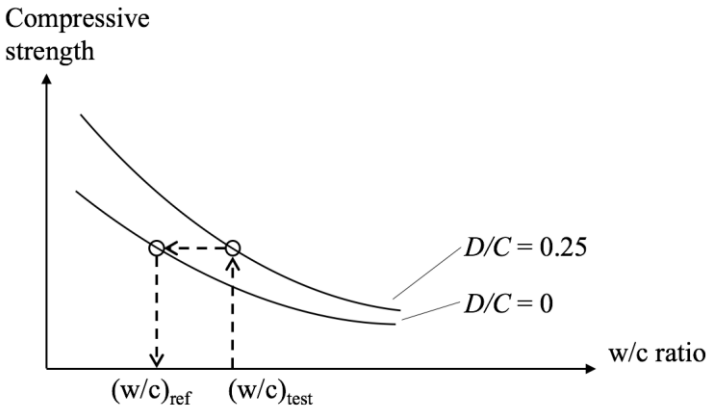


Figure 5-3 Schematic graph, showing how $(w/c)_{ref}$ is obtained. Note: to obtain k-value for carbonation, carbonation rate represents the y-axis

Note that the result from strength and carbonation of the reference concrete is linearly extrapolated when obtaining the high *w/c* ratio (0.6) of the reference concrete for a given compressive strength and carbonation rate of the test concrete. This is probably a good estimation regarding the compressive strength, since it is almost linearly dependent of the *w/b* ratio, see section 4.1. The carbonation rate, on the other hand, does not vary linearly to the *w/b* ratio. Therefore, this extrapolation gives an uncertainty in the *k*-values corresponding to high *w/c* ratios, especially for those *k*-values based on carbonation rate. Furthermore, there are uncertainties regarding the measurement of the low *w/b* ratio, since the reference mortar was difficult to measure, due to low penetration depth, as described in section 5.2. Since both w/c 0.4 and 0.6 are uncertain, the analysis of the k-values focuses on w/c 0.5 in the analysis bellow.

Higher *k*-value corresponds to better utility of the blended cement, i.e. higher efficiency of the mineral addition. The grey high-lighted *k*-values in Table 5-3 do not conform to the requirements in SS 137003, presented in section 2.9.2, i.e. not allowed when using the *k*-value concept.

Table 5-3 k-values for the tested mixtures, CEM I 52.5 concrete as reference

Cement mixture		*w/b* ratio	Calculated *k*-value		Prescriptive *k*-value[1]	
			Based on compressive strength	*Based on carbonation rate*	*Normal*	*Elevated*
Fly ash	*20%*	*0.4*	*0.55*	*0.29*	*0.4*	*0.5*
Fly ash	*20%*	*0.5*	*0.73*	*0.58*	*0.4*	*0.5*
Fly ash	*20%*	*0.6*	*0.77*	*0.46*	*0.4*	*0.5*
Fly ash	*35%*	*0.4*	*0.43*	*0.17*	*0.4*[2]	*0.5*[2]
Fly ash	*35%*	*0.5*	*0.55*	*0.24*	*0.4*[2]	*0.5*[2]
Fly ash	*35%*	*0.6*	*0.64*	*0.09*	*0.4*[2]	*0.5*[2]
GGBS	*35%*	*0.4*	*0.82*	*0.59*	*0.6*	*0.8*
GGBS	*35%*	*0.5*	*0.96*	*0.81*	*0.6*	*0.8*
GGBS	*35%*	*0.6*	*0.90*	*0.69*	*0.6*	*0.8*
GGBS	*50%*	*0.4*	*0.79*	*0.54*	*0.6*	*0.8*
GGBS	*50%*	*0.5*	*0.92*	*0.75*	*0.6*	*0.8*
GGBS	*50%*	*0.6*	*0.93*	*0.63*	*0.6*	*0.8*
GGBS	*65%*	*0.4*	*0.69*	*0.47*	*0.6*[2]	*0.8*[2]
GGBS	*65%*	*0.5*	*0.81*	*0.65*	*0.6*[2]	*0.8*[2]
GGBS	*65%*	*0.6*	*0.90*	*0.55*	*0.6*[2]	*0.8*[2]

[1] *Prescriptive k-value based on the requirements stated in section 2.9*
[2] *Does not fulfill the requirements regarding maximum amount of mineral addition*

Table 5-3 indicates that the elevated prescriptive *k*-values (Table 2-6) are on the unsafe side on all the concretes regarding carbonation, except for 20% fly ash and 35% GGBS, while it is generally on the safe side for the normal prescriptive *k*-value (Table 2-6). Regarding *k*-values based on compressive strength, the prescriptive *k*-values, both normal and elevated, are generally on the safe side. Furthermore, this difference between k-value based on compressive strength and carbonation causes uncertainties using strength as a proxy criterion for durability, since the relative increase in carbonation caused by mineral addition, is larger than the relative strength reduction. However, the accelerated carbonation measurements, as described in section 5.2.1, can magnify the difference between strength and carbonation in this study.

5.4 Pore structure changes after carbonation

The analyses in the capillary absorption are focused on the comparison between non-carbonated and carbonated mortars. In addition, some conclusions are also made on

effects of amount and type of mineral addition. Important to bear in mind, in the analysis of the capillary absorption tests, is that the PC mortar has a high degree of hydration compared to the blended mortars. Low degree of hydration generally implies a higher total open porosity (Taylor 1997). However, the blended mortars in this study shows slightly lower total open porosity before carbonation than the PC mortar (Table 4-4). This observation would probably be even clearer on an equal degree of hydration basis, since further hydration of the blended mortars would decrease the initial total open porosity even more.

Another factor influencing the results is that all mortars tested for capillary absorption are carbonated for 7 weeks. Thus, the PC mortars were less carbonated than the blended mortars, as described in section 4.2. This might affect the magnitude of the change between the different mixtures, when comparing carbonated and non-carbonated mortars. Therefore, the described effect on k_{cap} and m_{cap} of PC mortars might be underestimated in this study, since the PC mortars show significantly lower degree of carbonation, see Table 4-2. In other words, this effect on PC mortar is probably larger on an equal carbonation basis.

Despite different degree of hydration between PC mortar and blended mortars, the capillary absorption tests show quite consistent results in the majority of the mixtures, regarding k_{cap}, m_{cap} and total open porosity, both before and after carbonation. Generally, the carbonated mortars show significant increase in the resistance to water absorption, as shown by the difference in m_{cap} between carbonated and non-carbonated mortars, see Figure 5-5, indicating less connectivity in the pore structure on all the mortars after carbonation, except for 65% GGBS. This is probably caused by the formation of $CaCO_3$ during carbonation, since $CaCO_3$ occupies larger space than $Ca(OH)_2$ (Dyer 2014). The same formation is probably the reason for the observed decrease in total open porosity after carbonation, see Figure 5-4. This supports Nagala & Page (1997) showing that carbonation is reducing the total porosity, as described in section 2.5.

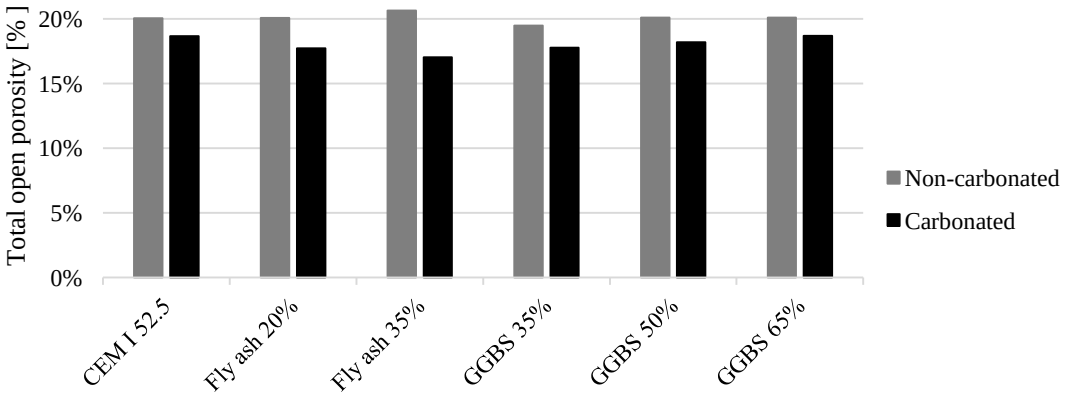


Figure 5-4 Total open porosity before and after carbonation

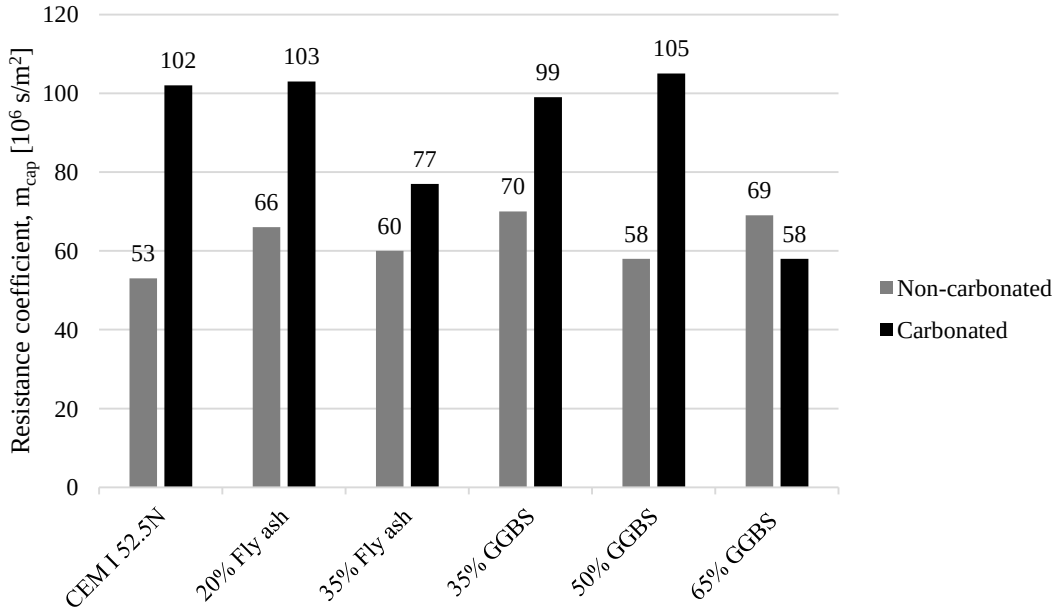


Figure 5-5 Resistance coefficient, m_{cap}, for non-carbonated and carbonated mortars

However, these observations do not comply entirely to the mixture with 65% GGBS, where k_{cap} is decreased after carbonation. This effect can be caused by carbonation of the C-S-H, due to less $Ca(OH)_2$ in GGBS to be carbonated, since the carbonation of the C-S-H increases the porosity (Wu & Ye 2015). However, the 65% GGBS still show a decrease in total open porosity, which would not be expected if only the C-S-H was carbonated. This indicates a possible combined effect between the formation of $CaCO_3$ and carbonation of the C-S-H. Despite the reduction of total open porosity, the results indicate on an increased connectivity of the pore structure. It might also be related to the low degree of hydration, since the increased fineness has shown to affected the result of capillary absorption tests.

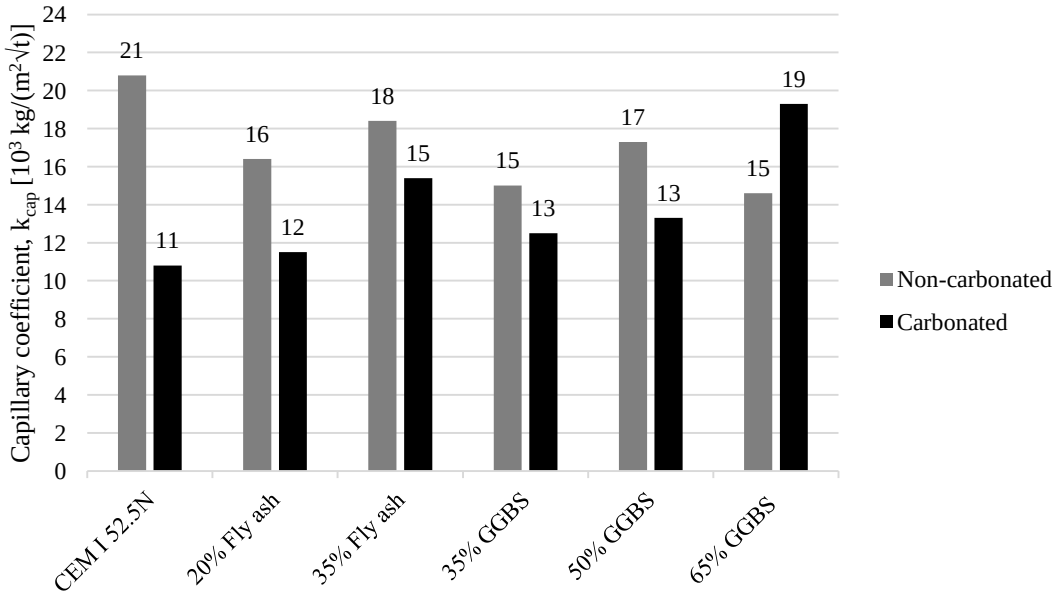


Figure 5-6 Capillary coefficient, k_{cap}, for non-carbonated and carbonated mortars

Similar effects on decreased k_{cap}-value and decreased total porosity in mortars with high amounts of GGBS, after being carbonated, are also shown by Utgenannt (2004). However, insufficient curing (14 days) were used in the test carried out by Utgenannt. Therefore, the question whether this effect is caused by the slow hydration or by carbonation of the C-S-H still remains.

The PC mortar show the largest increase in m_{cap} and largest decreases in k_{cap} after carbonation. Thus, carbonation results in m_{cap} and k_{cap} equal to the blended mortars, showing similar, or even higher, resistance to water absorption. Therefore, the common perception that blended concretes has more resistant pore structure than PC concretes (Bertolini 2004) might be misleading, since it requires that no carbonation has occurred. The reason for the high increased resistance after carbonation of the PC concrete can be that it has more carbonatable material ($Ca(OH)_2$), enabling the formation of more $CaCO_3$ during carbonation, which fills up the pores.

5.5 Chloride migration

This section analyses the trends and phenomena observed in the RCM tests. The effects of blended cement regarding carbonation, described in section 5.2.1, influences the chloride migration results of carbonated mortars. The tests were carried out with *w/b* 0.5, while there are usually requirements on lower *w/b* ratios in exposure classes related to chloride attacks in SS 137003. Furthermore, the most severe exposures to chloride attacks have cyclical wetting and drying, or permanently wet, which causes lower carbonation. Similarly, the XC3 condition, with moderate humidity, causing highest rate of carbonation, does not cause severe chloride attacks. Therefore, severe combined effect of carbonation and chloride attack, as investigated in this study, is less likely in a natural exposure.

The result of chloride migration coefficient in Figure 5-7 shows a decrease in chloride migration resistance after carbonation for all the blended mortars, despite the reduced

connectivity of the pore structure, described in section 5.4. This phenomenon is probably related to a reduced chloride binding capacity after carbonation, described in section 5.5.3. However, for the PC mortar, the chloride migration resistance increases. This effect might be related to the large decrease in connectivity observed from the capillary absorption test. It is also significant difference in degree of hydration between the PC mortar and blended mortars that can favor the PC mortar in this comparison.

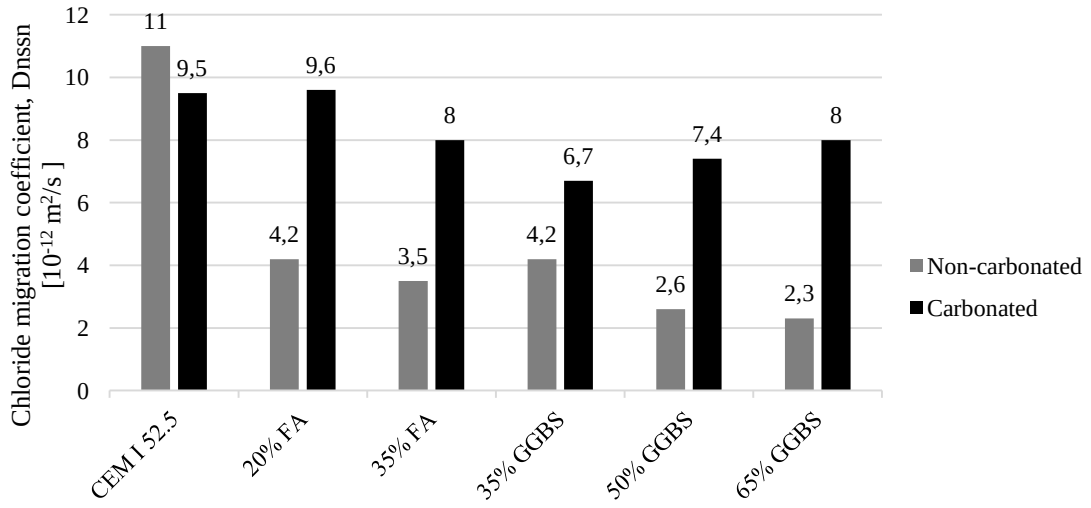


Figure 5-7 Chloride migration coefficient for non-carbonated and carbonated mortars

Chloride migration coefficients for the blended mortars, see Figure 5-7, are lower than for the PC mortar, before carbonation, indicating a higher resistance against chlorides, despite lower degree of hydration of the blended mortars. However, the chloride resistance is almost equal after carbonation. Therefore, the reasoning that blended concretes are more resistance to chloride attack, might be misleading, since it is greatly affected by carbonation. However, this exposure with such high rate of carbonation and chloride attack simultaneously, might not correspond to a natural scenario, as described above. Furthermore, the decrease of chloride resistance is also affected by the insufficient curing of the blended cements, described in section 5.2 and 0, which influences the pore structure and the carbonation of the blended mortars negatively. Therefore, this equalizing effect on the chloride resistance of PC mortar and blended mortars is probably lower in a natural case.

5.5.1 Relation between carbonation and chloride migration

As can be observed from Figure 5-7, there is a clear trend that the chloride migration coefficient is higher for the carbonated than for non-carbonated mortars. The only exception is the PC mortar, where it is slightly lower. This means that carbonated concrete has less resistance to chloride migration, since an increased chloride migration coefficient correlates to a decrease in chloride migration resistance.

Porosity and connectivity in the pore network are influencing factors regarding chloride penetration that changes after carbonation, as shown from the capillary absorption tests, discussed in section 5.4. Since total open porosity and the connectivity in the pore structure decrease with carbonation we would expect a decreased chloride migration. However, there was an increased chloride migration, despite these observations. This phenomenon can be explained by the reduced chloride binding capacity in concrete after carbonation.

Chlorides can exist both in bound and free form in the concrete. However, only the free chloride ions in the pore solution are moveable due to chemical potential (Tang 1999). Therefore, chloride binding capacity is an important factor regarding chloride penetration, since the chemical binding is likely to slow down the penetration of chlorides (McGrath & Hooton 1996). As discussed in section 2.7, carbonation inhibits the ability to bind chlorides in the concrete. Therefore, carbonation enables more migration of chlorides through the concrete, since there is less restriction by chemical binding of the chloride ions as the front progresses. Therefore, it is concluded that the effects from decrease of chloride binding capacity in carbonated concretes exceed the effects from reduced connectivity in the pore structure.

How diffusion is influenced by carbonation is not investigated in this study, which is needed to explain a natural process of chloride penetration. However, this observed effect from chloride migration, that the carbonation accelerates the chloride penetration, has also been seen in testing of combined accelerated carbonation with chloride diffusion (Yoon 2007b). Yoon´s investigation shows that carbonation has a significant effect on chloride diffusion. Furthermore, Yoon also show that there are less effect for the opposite scenario, i.e. carbonation is not severely affected by the chloride ingress.

5.5.2 Relation between chloride migration and mineral addition

As described above, there is an overall increase in chloride resistance for the blended cement after carbonation. This section analyses chloride migration coefficient and amount of mineral addition, for non-carbonated mortars (Figure 5-8) and carbonated mortars (Figure 5-9), individually. Since some of these tests were disturbed and there were difficulties adjusting the correct voltage, as described in section 4.3, a detailed analysis like this is associated with uncertainties.

The non-carbonated mortars containing fly ash and GGBS show a decreased chloride migration coefficient with increased levels of mineral addition. Thus, indicating an increased resistance to chlorides when adding fly ash or GGBS. Furthermore, there are a small difference between 50% GGBS and 65% GGBS, which might be related to low degree of hydration and a more porous C-S-H.

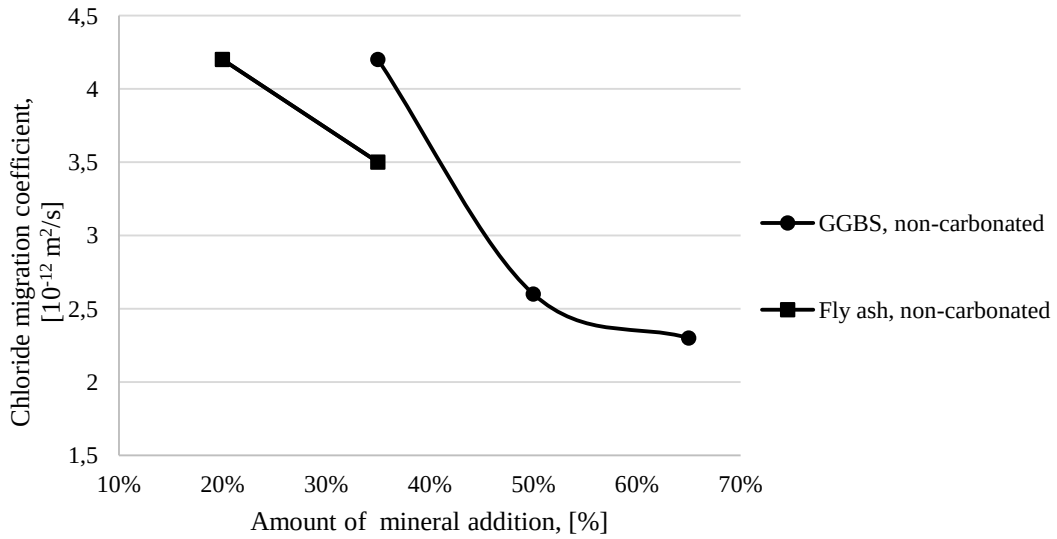


Figure 5-8 Relation between chloride migration coefficient and amount of mineral addition for non-carbonated specimens

Fly ash show similar trend for both non-carbonated and carbonated mortars, but for GGBS the trend is reversed. After carbonation the chloride migration coefficient increases with increased amount of GGBS, see Figure 5-9, opposite to the trend for non-carbonated GGBS. The reason for this observation is difficult to explain based on the data collected in this study, and it might be caused by disturbances in the tests or something else, and further studies are needed. One might reason that is has to do with the carbonation of the C-S-H, causing an increased connectivity of the pore structure, as discussed in section 5.4. If that is the case, there is a significant carbonation of the C-S-H of the 50% GGBS as well.

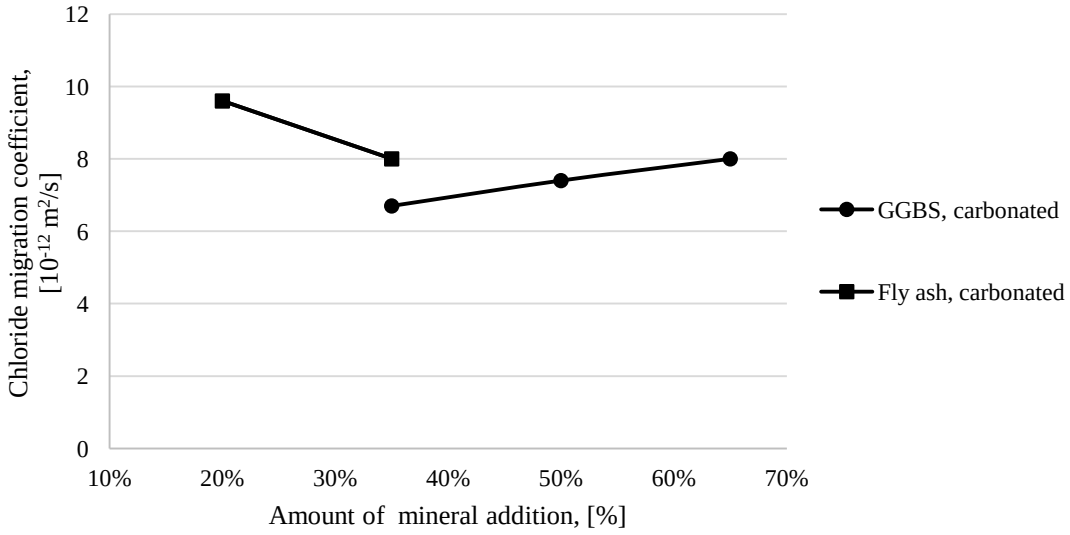


Figure 5-9 Relation between chloride migration coefficient and amount of mineral addition for carbonated specimens

5.5.3 Relation between resistivity, carbonation and mineral addition

As described earlier, the tabulated voltages in NT Build 492 for the RCM test are a guideline that determines what voltage to set for each individual specimen, based on a non-carbonated CEM I concrete. For each individual test, these tabulated voltages are based on the obtained initial current from 30 V over the tested mortar, and which is reflecting the resistivity of the specimen. The purpose of the adjusted voltage is to obtain a chloride migration front that is visible and measurable but not fully penetrated.

Test showed a decreased conductivity in the carbonated mortars, i.e. increased resistivity, see Table 5-4. However, the increased resistivity did not reflect a decreased chloride migration depth, which one might think, making the tabulated voltages based on non-carbonated PC mortars not conform to the carbonated mortars in this study. The resistivity is reflecting the mobility of ions in the pore solution, governed by the amount of ions and the connectivity of the pore structure. Therefore, the initial resistivity is reflecting the mobility of OH^-, related to either the amount of OH^- or the connectivity of the pore structure.

Table 5-4 Initial resistance of RCM-tests, all corresponding to 30 V

Cement mixture		Resistance[1] corresponding to 30 V [Ω]	
		Non-carbonated	**Carbonated**
CEM I 42.5N SR3		*222*	*1000*
CEM I 52.5N		*286*	*759*
Fly ash	*20%*	*462*	*667*
Fly ash	*35%*	*500*	*750*
GGBS	*35%*	*600*	*857*
GGBS	*50%*	*667*	*857*
GGBS	*65%*	*857*	*751*

[1] *All specimen have the same thickness*

There are two observed trends regarding the resistivity. Firstly the resistivity increases with the amount of mineral addition for non-carbonated mortars, and secondly it increases by carbonation (Table 5-4). These observations have mainly one thing in common, both carbonation and pozzolanic reactions decreases the amount of OH^-, i.e. the alkalinity, in the pore solution, through reactions of $Ca(OH)_2$. Such a decrease of OH^- increases resistivity of the electrochemical system (Dong et al. 2016). However, it can also be related to the connectivity of the pore structure, as mentioned above.

Observations from the non-carbonated capillary absorption tests (section 5.4) did not indicate on clear reduced connectivity of the pore structure with increased amount of mineral addition, as one might expect, compared to the significant increased resistance of the non-carbonated mortars with increased amount of mineral addition observed from Table 5-2. The connectivity of the pore structure of the blended mortars was probably influenced by the insufficient curing, described in section 5.2.1. Therefore, it is assumed that the resistance was mainly affected by a reduced amount of OH^-.

Due to these observations of the non-carbonated mortars, it was assumed that the mortar was not saturated with $Ca(OH)_2$ solution, which was the intention with the preconditioning described in the method, see section 3.2.3, since a saturation of $Ca(OH)_2$ would equalize the resistivity of the different mortars, before carbonation.

However, regarding the carbonated mortars the pore structure change is believed to have a significant influence on the resistance. The inconsistent resistivity for the carbonated blended mortars (Table 5-4) indicates that the decrease in OH^- was not the only reactions affecting the result, i.e. after carbonation there is no clear relationship between resistance and amount of mineral addition any more. Thus, the change in connectivity of the pore structure due to carbonation is probably affecting the resistivity as well.

The reduced resistivity, opposite effect than expected by the reduction of OH^-, can be observed from the capillary absorption tests. From discussions in section 5.4, it is shown that there is a decrease in connectivity of the pores after carbonation, for all mortars except 65% GGBS. In particular, this reduction is obvious in the CEM I 42.5, showing the largest reduction in connectivity of the pore structure from the capillary absorption tests, see section 5.7, and the largest increase of resistivity, Table 5-2. This shows that the reduced connectivity after carbonation has a significant effect on the resistivity.

Another indication on the interdependence between resistivity from the chloride migration test and the connectivity of the pore structure from capillary absorption tests, is the observed results from 65% GGBS. This was the only mortar that showed a decreased resistivity after carbonation (Table 5-4), and it was also the only mortar that showed increased connectivity of the pore structure in the capillary absorption test after carbonation (Figure 5-5 and Figure 5-6). This also shows how the connectivity of pore structure, caused by carbonation, affects the resistivity.

5.5.4 Voltage difference over the specimen

It is obvious that the side-effects have affected the chloride migration, as seen in Figure 5-10. This is not a significant problem itself, because the sides are disregarded in the measurements of the chloride migration front. However, it is not sure whether it only affects the chloride migration front, or if the resistivity is changed on the sides as well. If the resistivity is changed, it contributes to a parallel connection in the circuit, giving rise to one voltage over the core and another voltage over the side. Therefore, the over-all voltage used in the equation of the chloride migration coefficient might not reflect the voltage that affects the core, on which the chloride migration front is measured. However, this do not affect the relative comparison of the chloride

migration coefficient if the side effects are in the same magnitude in all the specimens, which seem to be the case, see Figure 5-10. Still, it causes uncertainties in the obtained migration coefficients. Furthermore, the resistance changes after carbonation, which also causes a series connection of the circuit due to one carbonated part and one non-carbonated part of the specimen.

Due to the parallel connection from the side effects and the parallel connection from the carbonation, the voltage used in the calculation of the chloride migration coefficient (NT Build 492) does not fully correspond to the measurements of the chloride migration front. The chloride migration coefficient obtained in this study can therefore be used only in the relative comparison as in this study, but not in a comparison to tests from other research. In further studies, the series connection from carbonation could be compensated for, since the carbonation depth is known.

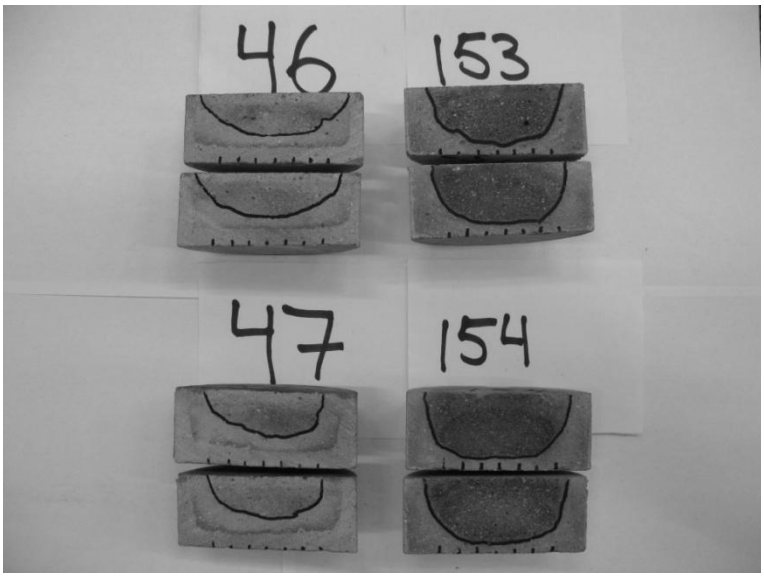


Figure 5-10 Side effects of carbonated (46 and 47) and non-carbonated (153 and 154) specimens, all from the same batch

5.6 Effects of GGBS fineness

To consider the effects of GGBS fineness and reactivity, the Slag Bremen GGBS was compared to Ruukki GGBS with a similar composition, but with increased fineness. In this section, Slag Bremen GGBS (fineness 420 m^2/kg) is referred to as *65% GGBS* and Ruukki GGBS (fineness 520 m^2/kg) is referred to as *65% GGBS**. The tests only covered the mixtures containing 65% GGBS and *w/b* 0.5.

As discussed in previous sections, there are uncertainties regarding the cause of the effects observed for high levels of GGBS, compared to lower levels. Plausible reasons are either less amount of $Ca(OH)_2$ or lower degree hydration caused by inadequate curing. However, the amount of $Ca(OH)_2$ is assumed to be equal in 65% GGBS and 65% GGBS*, since the levels are the same. Therefore, the following observed differences in compressive strength, carbonation rate, chloride migration and capillary absorption are assumed to be caused by the difference in degree of hydration of the cement.

As interpreted from Table 5-5, 65% GGBS* show a higher compressive strength, compared to 65% GGBS. This relationship indicates a higher degree of hydration for the 65% GGBS*, since the hydration of the cement is contributing to the strength in the mortar.

Table 5-5 28-day strength of the two GGBS mortars, standardized cement strength and mortar strength test (SS-EN 196-1)

Cement mixture	Fineness	Standardized cement strength	Mortar strength
65% GGBS	*420 m^2/kg*	*45 MPa*	*43 MPa*
*65% GGBS**	*520 m^2/kg*	*61 MPa*	*54 MPa*

The difference in strength indicates that the 65% GGBS used in the RCM tests and the capillary absorption tests were probably inadequately cured, since these mortars were only water cured in 7 days.

Assuming that the compositions of the GGBS are similar, there are several observations that can be associated to a higher degree of hydration of the 65% GGBS*, interpreted from the four figures below:

- Lower accelerated carbonation rate, K_{acc} (Figure 5-11), thus lower natural carbonation rate (Appendix A3)
- Decreased influence of carbonation on the chloride migration (Figure 5-12)
- Hydration changes the carbonation effect on the resistance coefficient, m_{cap} (Figure 5-13)
- Low dependence between the hydration and the rate of capillary absorption, k_{cap} (Figure 5-14)

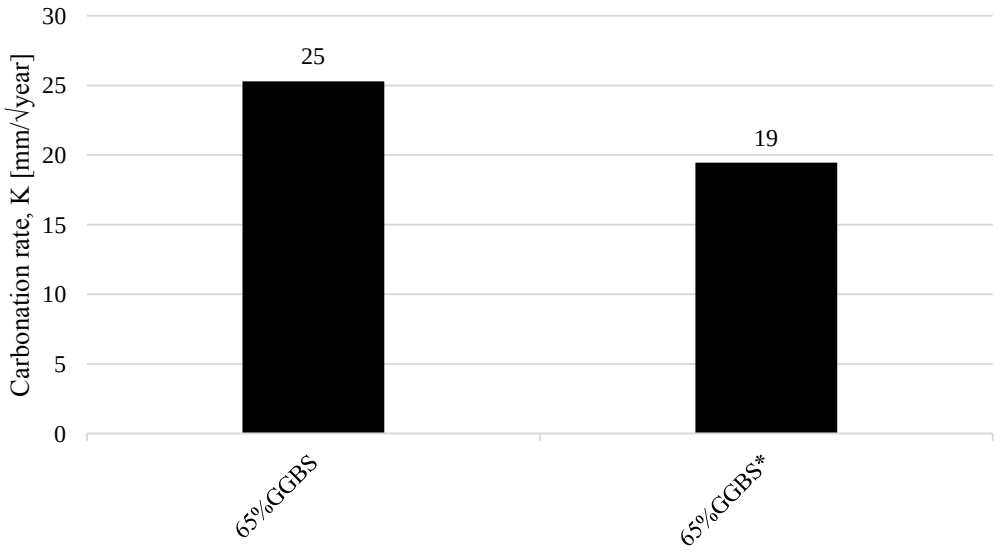


*Figure 5-11 Carbonation rate (K_{acc}) of 65% GGBS and 65% GGBS**

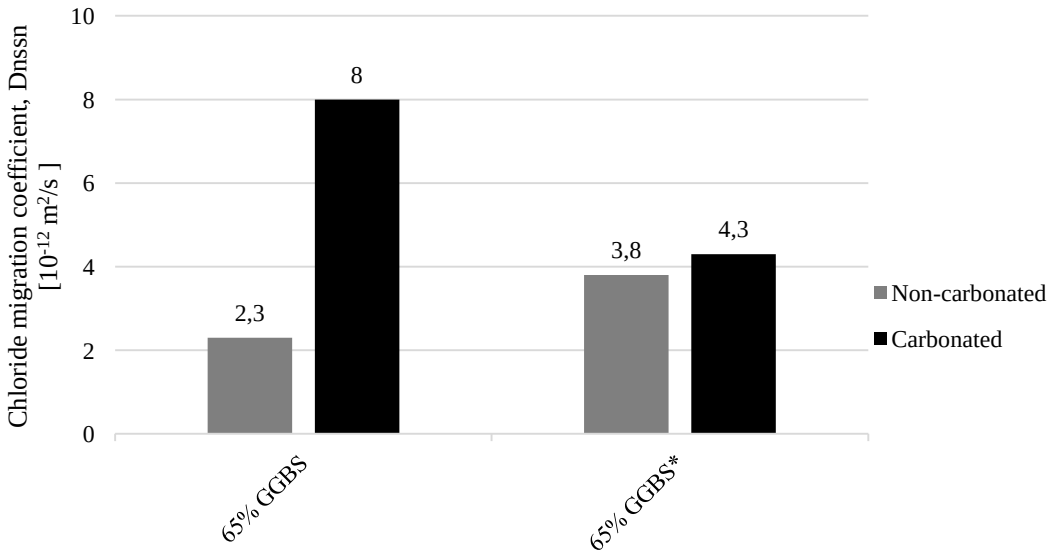


*Figure 5-12 Carbonation effects on chloride migration coefficient, D_{nssn}, of 65% GGBS and 65% GGBS**

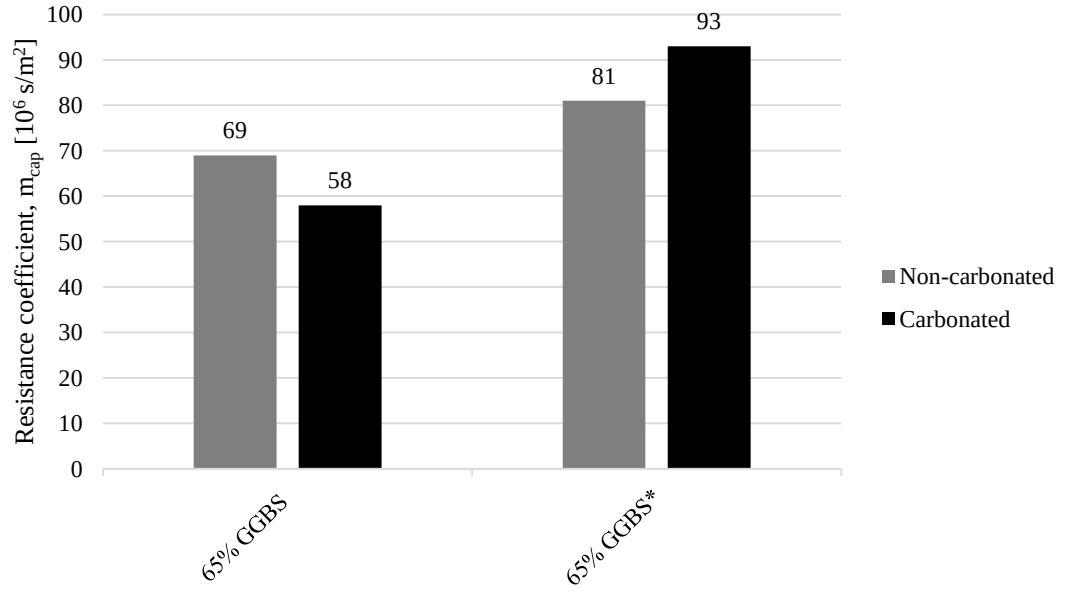


*Figure 5-13 Carbonation effects on the resistance coefficient, m_{cap}, of 65% GGBS and 65% GGBS**

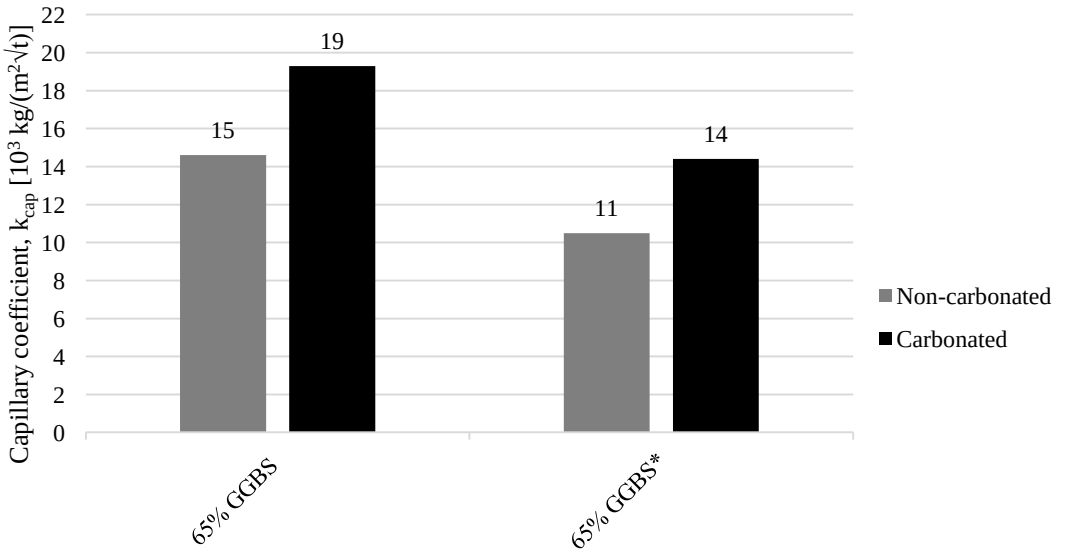


*Figure 5-14 Carbonation effects on the capillary coefficient, k_{cap}, of 65% GGBS and 65% GGBS**

The decreased carbonation rate is also observed by Sulpha (2003), described in section 2.5. The decreased carbonation with increased fineness (Figure 5-11) can explain some of the reducing effect of carbonation on chloride migration (Figure 5-12), but probably not all. Another observation in Figure 5-12 is that the non-carbonated 65% GGBS* has lower resistance to chloride migration than the non-carbonated 65% GGBS, a finding which is unexpected since the increased fineness ought to cause higher resistance to chloride migration. However, this could also be related to the different chemical compositions of 65% GGBS and 65% GGBS*.

*Table 5-6 Carbonation effects on total open porosity of 65% GGBS and 65% GGBS**

Cement mixture		*w/b* ratio	Total open porosity	
			Non-carbonated	*Carbonated*
GGBS	*65%*	*0,5*	*19%*	*18%*
*GGBS**	*65%*	*0,5*	*19%*	*17%*

As described above, the magnitude of the difference chloride migration, due to fineness can be related to the degree of carbonation. It can also be related to the change in pore structure, observed from the capillary absorption tests.

It is difficult to explain the exact reason for these observations, but one conclusion is that the degree of hydration has a significant effect on the test results. Since the degree of hydration is related to the curing time, the curing time also has a significant effect on the result, and therefore cannot be disregarded as an influencing factor. In other words, curing time must be taken into account in analyzing the accelerated test results when using high levels of mineral additions. However, one must bear in mind that the compositions of the GGBS are not equal since they have different origin.

5.7 Effects of different CEM I

In this section, the results from compressive strength tests, accelerated carbonation tests and capillary absorption tests of the two PC mortars (CEM I) are presented, compared and discussed. The PC mortars are based on the CEM I 52.5N and another PC mortar containing CEM I 42.5N SR3, they are hereafter referred to as CEM I 52.5 and CEM I 42.5, respectively. The results from RCM test were disregarded in this comparison, since the CEM I 42.5 was disturbed during testing, due to inaccurate voltage settings, described in section 5.5.

The PC mortars are, unlike the blended mortars, assumed to have reached high degree of hydration, since seven days are considered as an adequate curing time for ordinary Portland cement (Balayssac et al. 1995). Therefore, the effects observed from the accelerated carbonation test and capillary absorption test are assumed to be directly related to the type of cement, and not to the degree of hydration.

The CEM I 42.5 shows lower 28-day strength than CEM I 52.5 (Figure 5-15), which is expected since it had a lower cement class. A similar trend, but reversed, can be observed for the carbonation rate (Figure 5-16), where CEM I 42.5 tends to carbonate faster and similar to the mixes with 20% FA or 35% GGBS. Since the CEM I 42.5 had higher degree of carbonation, the magnified results from the capillary absorption tests after carbonation were expected. These magnified effects can be observed in Figure 5-17 and Figure 5-18, showing the results of k_{cap} and m_{cap} from the capillary absorption tests.

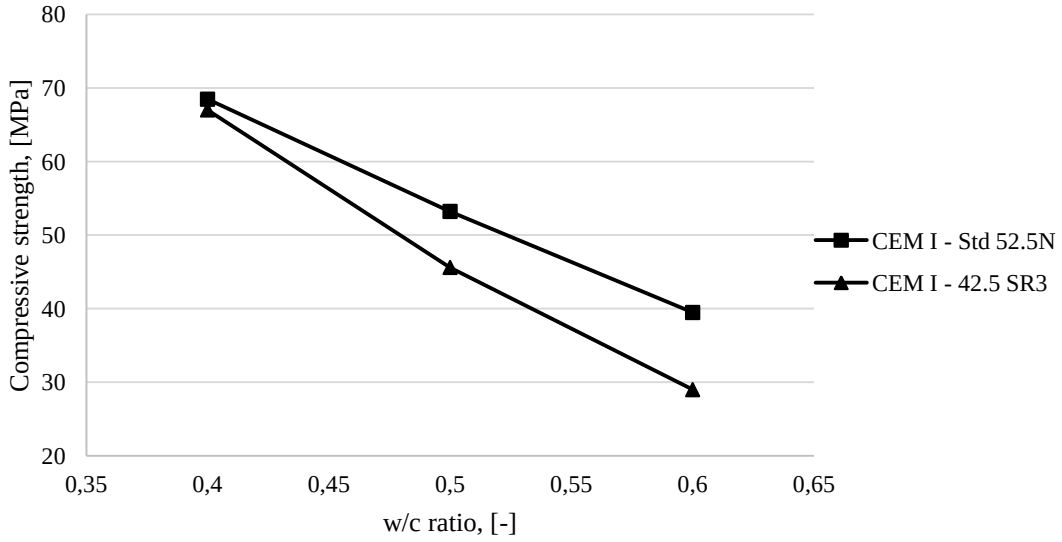


Figure 5-15 Relation between compressive strength and w/c ratio for the two investigated PC mortars

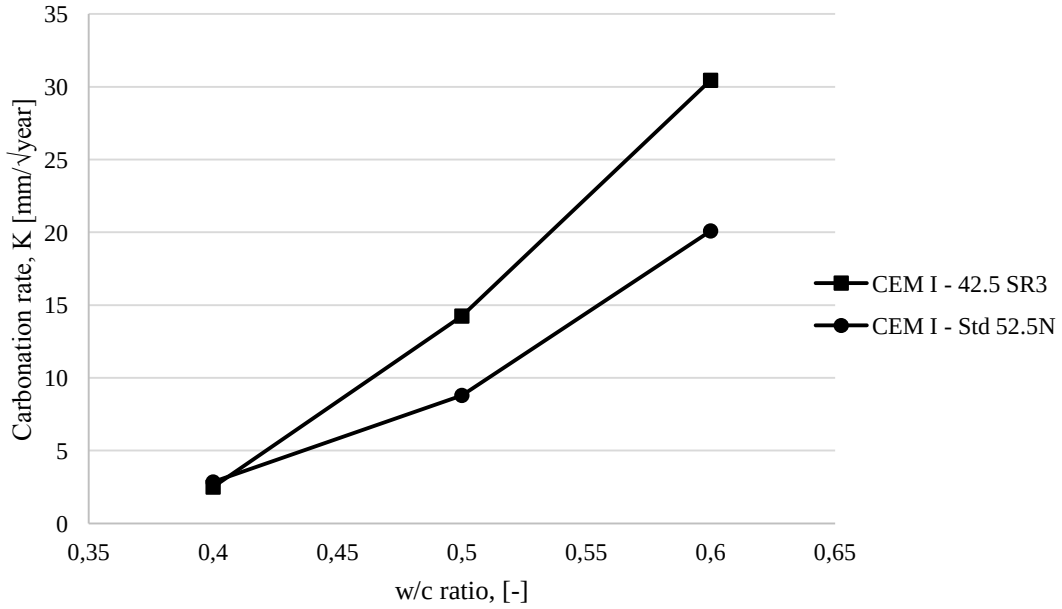


Figure 5-16 Relation between carbonation rate and w/c ratio for the two investigated PC mortars

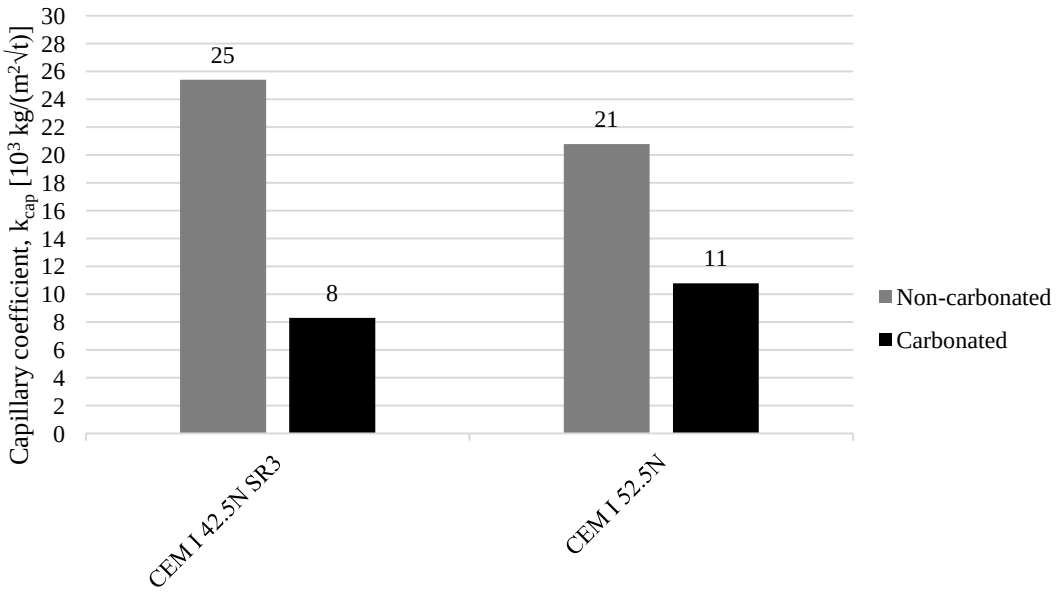


Figure 5-17 Diagram showing the capillary coefficient k_{cap} before and after carbonation for the two investigated PC mortars (w/c 0.5)

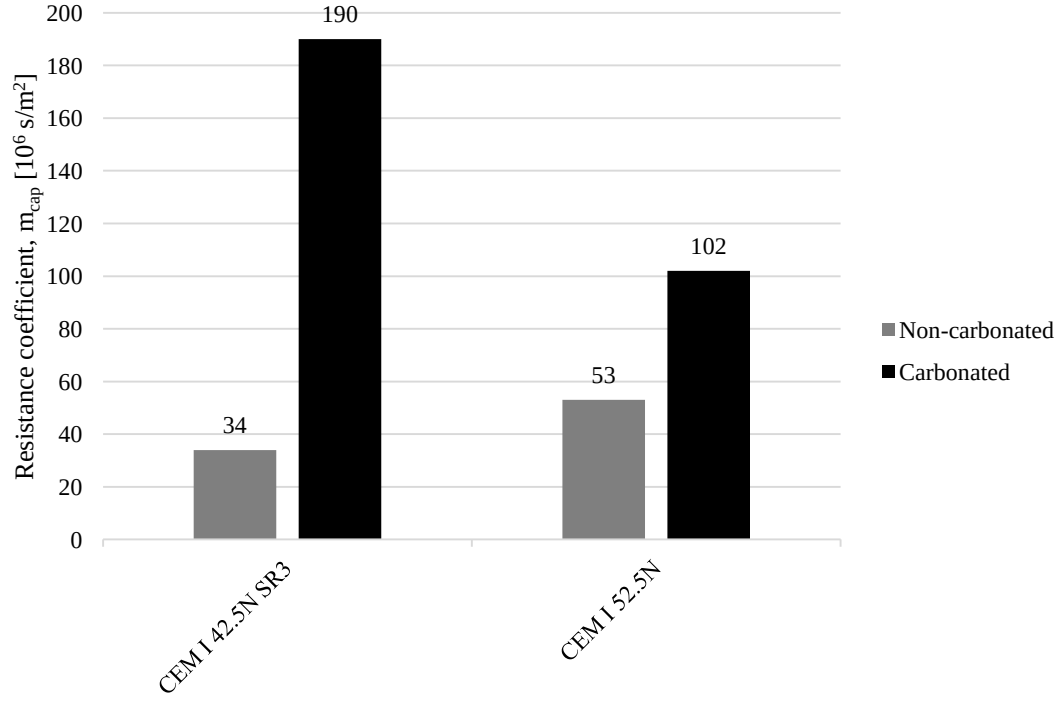


Figure 5-18 Diagram showing the resistance coefficient m_{cap} before and after carbonation for the two investigated PC mortars (w/c 0.5)

The comparison between the two PC mortars shows that they respond differently to carbonation, probably related to their strength classes. Furthermore, the carbonation influences the transport properties, in terms of reduced capillary absorption rate, k_{cap}, reduced total open porosity and increased capillary resistance, m_{cap}, indicating on a

decreased connectivity of the pore structure, especially for the CEM I 42.5, since it is more carbonated.

How the CEM I 42.5 will respond as reference cement with mineral addition, is hard to tell, since the blended cements in this study respond differently to carbonation. Carbonation of the blended cements tends to reduce the effects from the capillary absorption tests, compared to its reference cement (Figure 5-5 and Figure 5-6). Therefore, further studies are needed to find what influence the type of reference cement has on blended mortars, i.e. tests on the same amount and type of mineral addition, but with different reference cements.

5.8 Degree of saturation

The results showing the degree of saturation as a function of time (Appendix B2) is a another side project, based on the capillary absorption tests. It does not say much about chloride resistance or carbonation, studied in this research. However, the degree of saturation influences freeze-thaw resistance, since the water has to fill the pores for the expansion to damage the concrete. Therefore, there is a critical degree of saturation, typically ranging from 80% to 90% (Dyer 2014). The rate at which concrete reaches the critical degree of saturation, when being subjected to water, therefore influences the resistance to freeze-thaw. This can be interpreted from the result in Appendix B2.

Since the initial degree of saturation is similar for carbonated and non-carbonated specimens (Appendix B2), trends regarding the rate of reaching high degree of saturation can be observed. There is no significant difference in the degree of saturation for blended mortars with moderate amount of mineral addition. However, for the PC mortar, carbonation reduces the rate of reaching saturation, while for 65% GGBS a reverse process is observed, similar to observations by Utgenannt (2004). This is probably due to the increase in resistance, m_{cap}, of the PC mortar and the reduced resistance for 65% GGBS, as described earlier. Based on these observations, PC concrete should improve and 65% GGBS weaken its resistance to freeze-thaw, whilst the other mixtures could be more or less unaffected, as shown by Löfgren et al. (2016). It is however important to note that it might be other factors affecting the freeze-thaw resistance that is not considered in this study.

5.9 Side-effects from using coating paint

A two-component paint was used on almost all the specimens. The aim was to have carbonation and chloride migration in one dimension, making it easier to measure and to eliminate side effects from carbonation. The paint was supposed to seal the surface from diffusion, this was however not working properly.

The first observation was oxidation of the GGBS concrete. When splitting a GGBS mortar, the core showed a blue/green colour, from the iron sulphide and manganese sulphide present in GGBS. When exposed to oxygen this colour fades to a regular grey mortar colour. If the covering paint would protect against diffusion, no oxygen would have penetrated the surface, and the mortar would be green/blue all the way to the surface. However, this was not the case when looking at the freshly split GGBS mortars.

There was also carbonation at the painted sides, which requires diffusion of CO_2 through the paint. However, the clearest effect from the covering paint was the negative side effects in the RCM tests. The chloride migration front was fully penetrated on the sides on almost every tested mortar, see Figure 4-13. The initial suggestion was that this was caused by the carbonation that occurred from the side despite the covering paint, since the carbonation had an accelerated effect on the chloride migration, shown in section 4.3. However, this was contradicted since the side-effect was observed on the non-carbonated specimens as well, see Figure 5-10. Therefore, it is suggested that the coating itself is the cause of these side-effects. However, this is not entirely proven, since no tests have been carried out on unpainted specimens. One test where the paint was grinded off was carried out, but the result showed that the side penetration persisted. Due to the persistent effects after grinding of the coating, might have reacted with the surface layer of the concrete.

Effects on the capillary absorption were also observed. The sides absorbed water faster the middle section, indicating on an increased connectivity of the pore structure on the side, which could also explain the increased chloride migration in that part.

6 Conclusions

Different deteriorating processes are often considered separately in standards and test methods. The results in this study show that there is an important interdependence between carbonation and chloride migration of concretes that also need to be considered. It was observed from the results that different processes are linked together. Carbonation affects the chloride migration directly, carbonation affects the pore structure, and the change in pore structure affects the chloride migration. Furthermore, the carbonation also influences the rate of saturation through the change in pore structure, which affects the frost resistance.

The carbonation and compressive strength tests showed expected results, which were in accordance with what has been reported in previous literature. The carbonation rate increased with increased amount of mineral addition, and significantly for mortars with high levels of mineral addition (35% fly ash and 65% GGBS). The carbonation rate also increased with increased *w/b* ratio, and even here increasing significantly for high *w/b* ratios. The effects of high levels of mineral addition at high *w/b* ratio were also observed in the compressive strength, showing a clear reduction in strength when increasing the amount of mineral addition or *w/b* ratio. The carbonation rate increased more, by adding mineral addition, than the compressive strength decreased. This increased spread between compressive strength and carbonation was highest for high levels of fly ash and GGBS. Therefore, the result in this study supports the restrictions of using high levels of mineral additions in equivalent performance concepts, especially when using strength as proxy criterion for durability, as in the ECPC, or when using prescriptive requirements for durability, as in the k-value concept. This reasoning is on the safe side in this analysis, especially for the mortars with high amounts of mineral addition, since the carbonation of the blended mortars has shown to be magnified by the accelerated carbonation, leading to an over-estimated carbonation, while the 28-days strength are not influenced. It should also be pointed out that it was shown that there is a difference between different CEM I allowed in the equal performance concepts, with higher carbonation rates for lower cement strength.

A common perception is that reduced permeability enhances the durability and one can claim that reduced k_{cap}, increased m_{cap} and increased total porosity should enhance the resistant against deteriorating compounds. Since this was observed after carbonation in all mortars in the capillary absorption tests, except for high levels of GGBS, one might argue that carbonation ought to enhance the durability. However, this reasoning is misleading when analyzing the results from the RCM tests, since carbonation lead to increased chloride migration. This effect is probably caused by the reduced ability to bind chlorides in carbonated concretes, which reduces the resistance against chloride ingress.

The results from the RCM tests were a bit uncertain, but some clear trends were observed. The blended cements show higher resistance against chloride migration compared to the reference cement before being carbonated, but this positive effect was reduced after being carbonated. Despite the reduction of chloride migration resistance by carbonation for all the blended mortars, it still maintained higher resistance than the PC mortar, despite the lower degree of hydration and higher carbonation rates of the blended mortars.

The increased resistivity due to carbonation probably reflects a combined effect of reduced connectivity of the pore structure, showed in the capillary tests, and the consumption of OH^-, during carbonation. However, the reduced resistivity caused by the mineral addition is mainly caused by the reduced amount of OH^-, compared to Portland cement.

For low and moderate levels of mineral addition (<20% fly ash and <50% GGBS) the adverse effects on carbonation and capillary saturation were quite limited. Compressive strength and carbonation rates were close to the performance of the reference mortar, on an equal *w/b* basis, despite a low degree of hydration of the blended mortars. There is actually more variability in carbonation rates and changes in pore structure due to carbonation between the two investigated PC mortars, CEM I 42.5N SR3 and CEM I 52.5N, than between the CEM I 52.5N and blended mortars with low and moderate amount of mineral addition. High levels of mineral additions were on the other hand (35% fly ash and 65% GGBS) greatly affected by deteriorating processes, such as chloride migration and carbonation. The magnifying effects of these mortars were shown in all the tests carried out in this study including:

- Lower compressive strength due to insufficient hydration
- Higher carbonation due to less $Ca(OH)_2$

Some specific observations were also made regarding 65% GGBS:

- Increased connectivity in the pore structure after to carbonation, probably related to carbonation of the C-S-H
- Increased reduction of chloride migration resistance after carbonation, probably related to carbonation of the C-S-H
- Decreased resistivity after carbonation, observed from the RCM tests, probably related to the increase in connectivity of the pore structure after carbonation, despite the counter-action by a reduction of OH^- during carbonation
- Increased rate of saturation, influencing deterioration processes such as freeze-thaw attack.

However, the comparison between the two GGBS with fineness 420 and 520 m^2/kg showed that the change of the pore structure and increased carbonation of the 65% GGBS is influenced by the lower degree of hydration, caused by inadequate curing. This comparison also indicates that negative effects at high replacement rates can partly be counteracted by higher reactivity caused by increased fineness of the GGBS.

High amount of GGBS and fly ash might not be suitable for structures exposed to environment with high risk of carbonation, such as climates with moderate humidity. Moderate humidity also prevents further hydration, which is critical if the concrete is not sufficiently cured. Non-carbonated blended cements with higher levels of mineral addition showed high resistance to chloride migration. Therefore, one might reason that such concretes are suitable for submerged constructions or structure exposed to cyclic wetting and drying where chlorides are present. Such environment has low carbonation, due to the high moisture, and the submersion contributes to a prolonged curing, at the same time as the resistance to chlorides of blended cements is fully

utilized. However, high amounts of mineral additions might be susceptible to freeze-thaw damage.

In Sweden, cements conforming to SS-EN 197-1 are considered as equally durable if they are accepted for a certain exposure class, irrespective of the amount of mineral addition in the cement. The results from this study show that such a simplification might cause issues regarding durability, since the different accepted cements in exposure class XC show a significant difference in resistance to carbonation. Based on this, adopting a gradual *w/c* restriction on the cements in SS-EN 197-1, depending on the amount of mineral addition, as is done in Norway (Maage 2015), might be suitable in order to take the difference in resistance against carbonation into account.

The result from laboratory testing, especially accelerated tests, can magnify negative trends with adding mineral addition. Since the hydration, which most likely, would continue and enhance the durability over time in a natural process, unless the conditions are very dry. Particularly, this overestimation includes the mortars with high amount of mineral addition. In other words, the observed adverse effects of blended mortars, especially those with high amounts of mineral additions, are most likely overestimated.

7 Further studies

Since this project is a pilot study, covering a wide range of tests, there are different aspects that need further investigation. This study does only regard a selection of mixtures, with the emphasis on *w/b* 0.5. Therefore, further analysis is needed on a wider range of *w/b* ratios and levels of mineral addition, in order to ensure the accuracy of the results. Furthermore, the mixture is only based on one type of cement, GGBS, fly ash and aggregate. Thus, there is a need for research regarding the influence of other cements and mineral additions, with other origins and compositions.

Using mortar specimen to draw conclusions regarding concrete is a simplification, since there are effects in the transition zone between the aggregate and cement paste that vary with factors like size and shape of the aggregate, and type of cement.

There exists little knowledge about the relationship between carbonation and chlorides. In this study, tests were carried out regarding carbonation and chloride migration, but there are still uncertainties how this is related to chloride diffusion, which is more associated with a natural process. Therefore, there is need for further analysis on chloride diffusion test on carbonated mortar. Furthermore, the obtained chloride migration coefficient is not adjusted for carbonated concrete. Further research and data is needed based on comparisons between natural chloride diffusion and chloride migration of carbonated concrete, in order to adjust the equation for the carbonation effects. In particular, the synergetic carbonation effects on chloride can be of interest when calculating durability, e.g. in the duracrete model, of structures subjected to both chlorides and carbonation, such as marine splash zones.

No effects regarding equal degree of carbonation are regarded in this study, only the equal time of carbonation exposure. Therefore, it might be interesting to investigate the effects on capillary absorption and chloride migration on an equal degree of carbonation basis on mature specimens. Furthermore, the magnifying effects of the accelerated testing was not investigated in this study, since there are no result data from natural carbonation with the same materials and set up as in this study.

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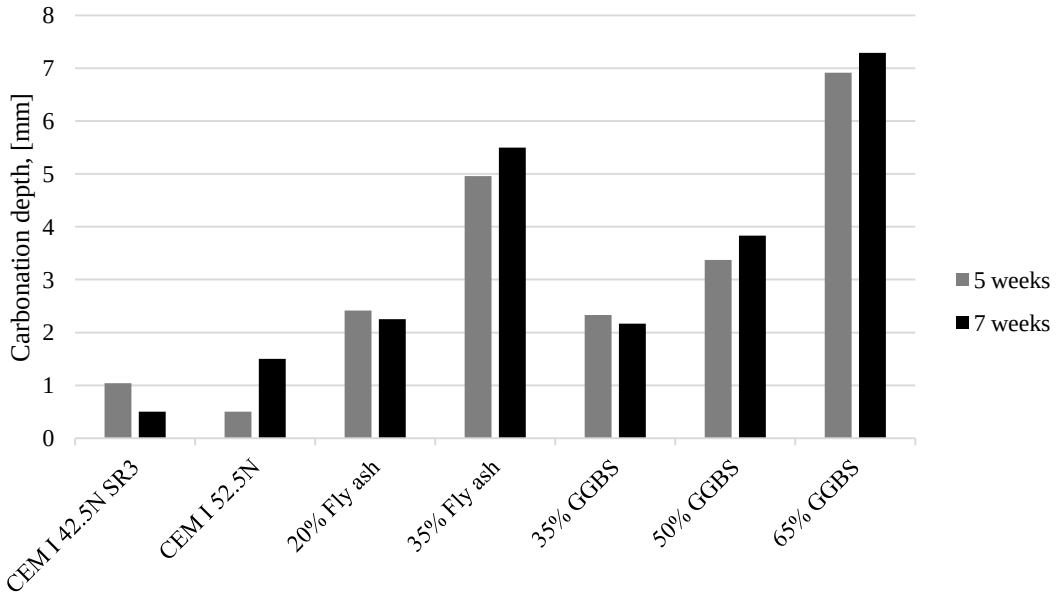
Appendix A Accelerated carbonation

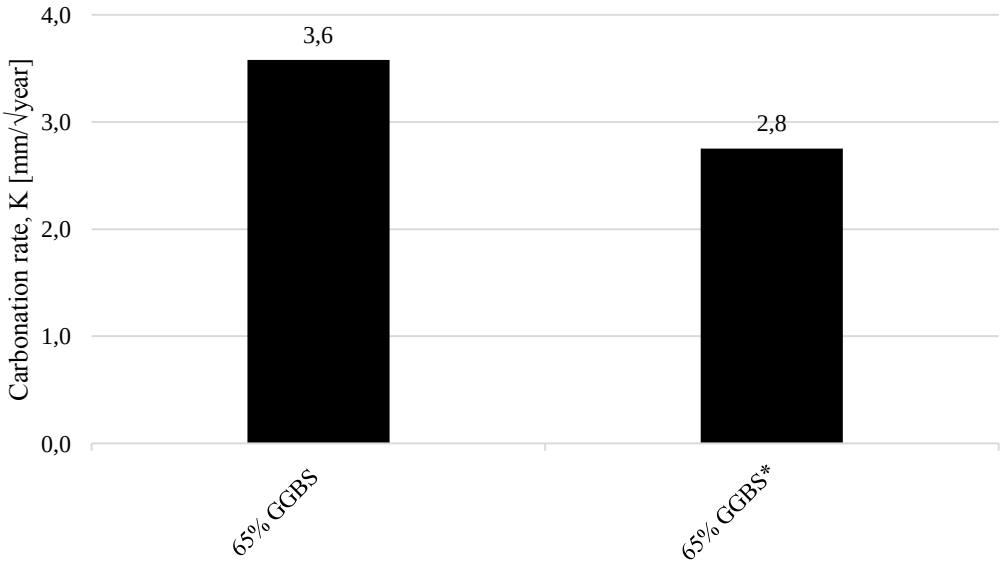
Cement mixture	*w/b* ratio	Carbonation rate after 5 weeks [mm/√year]	Carbonation rate after 7 weeks [mm/√year]
CEM I 42.5N SR3	*0.4*	*4*	*1*
CEM I 42.5N SR3	*0.5*	*14*	*15*
CEM I 42.5N SR3	*0.6*	*31*	*30*
CEM I 52.5N	*0.4*	*2*	*4*
CEM I 52.5N	*0.5*	*9*	*8*
CEM I 52.5N	*0.6*	*20*	*20*
Fly ash 20%	*0.4*	*8*	*6*
Fly ash 20%	*0.5*	*14*	*13*
Fly ash 20%	*0.6*	*28*	*28*
Fly ash 35%	*0.4*	*16*	*15*
Fly ash 35%	*0.5*	*29*	*29*
Fly ash 35%	*0.6*	*48*	*55*
GGBS 35%	*0.4*	*8*	*6*
GGBS 35%	*0.5*	*13*	*12*
GGBS 35%	*0.6*	*28*	*28*
GGBS 50%	*0.4*	*11*	*10*
GGBS 50%	*0.5*	*18*	*17*
GGBS 50%	*0.6*	*35*	*35*
GGBS 65%	*0.4*	*22*	*20*
GGBS 65%	*0.5*	*27*	*24*
GGBS 65%	*0.6*	*47*	*48*
*GGBS 65%**	*0.5*	*20*	*19*

**increased fineness*

Appendix A1 Carbonation rate for accelerated carbonation after 5 weeks and 7 weeks

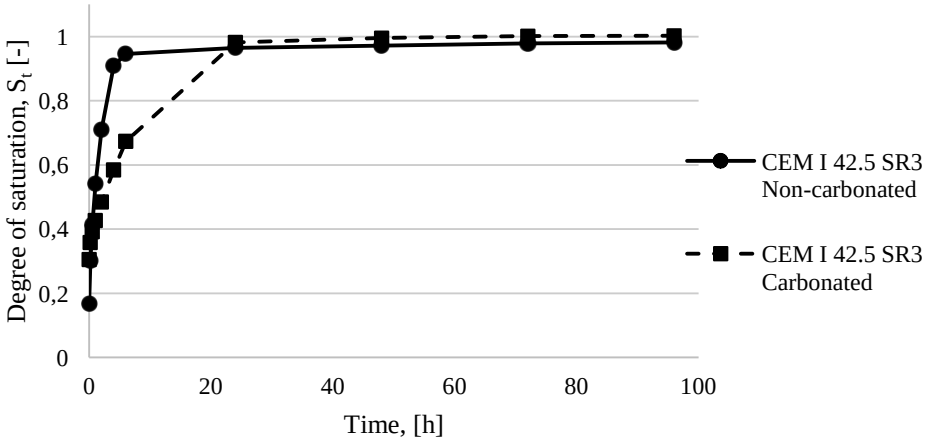


Appendix A2 Carbonation depth for specimens with w/b 0.4

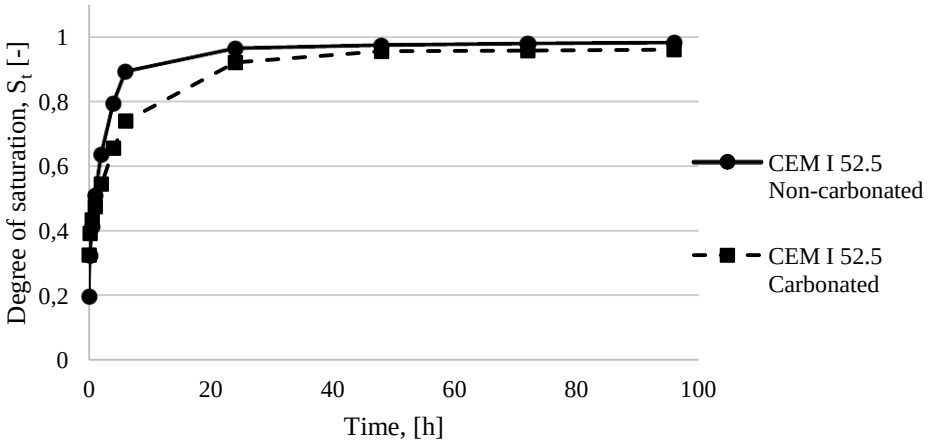


Appendix A3 Natural carbonation rate, K_{nat} of 65% GGBS and 65% GGBS calculated with eq. 4.1*

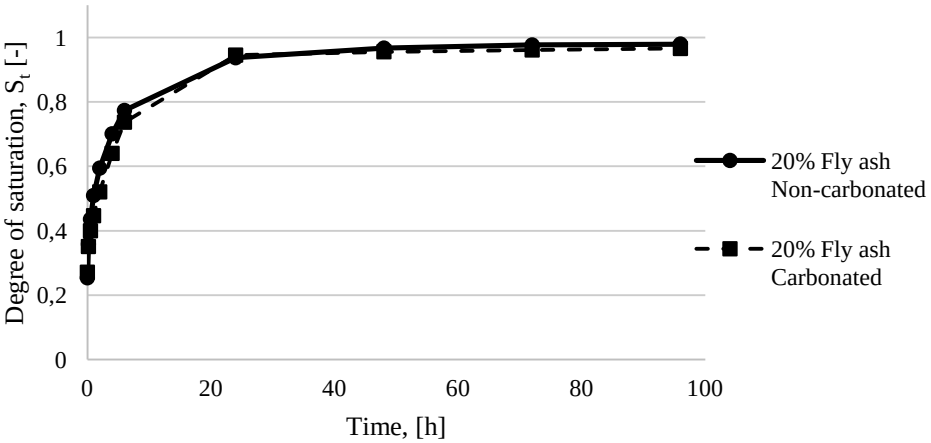
Appendix B Capillary absorption



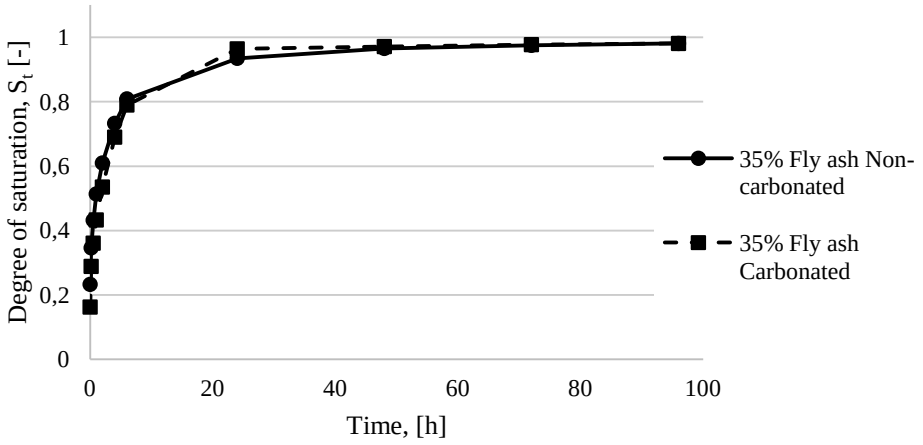
Appendix B1 Degree of saturation for carbonated and non-carbonated specimens containing CEM I 42.5N SR3



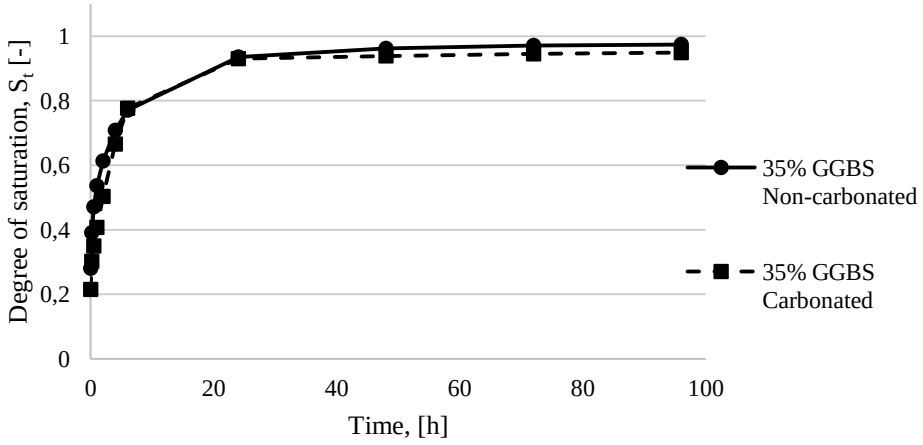
Appendix B2 Degree of saturation for carbonated and non-carbonated specimens containing CEM I 52.5N Std



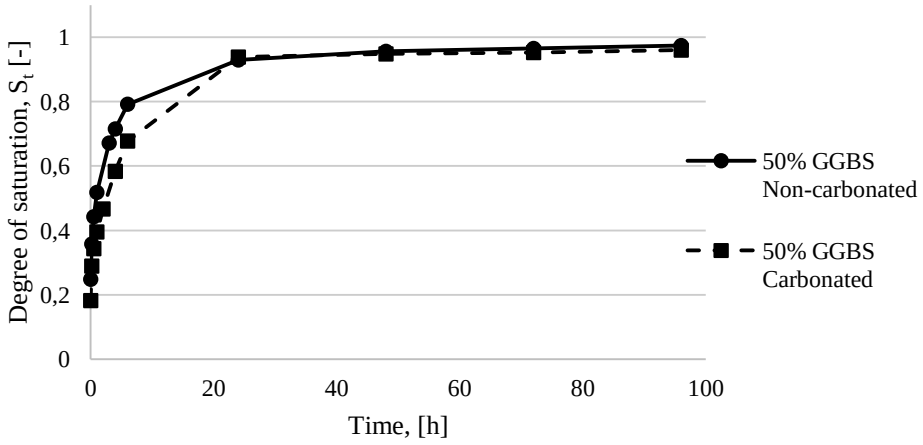
Appendix B3 Degree of saturation for carbonated and non-carbonated specimens containing 20% fly ash



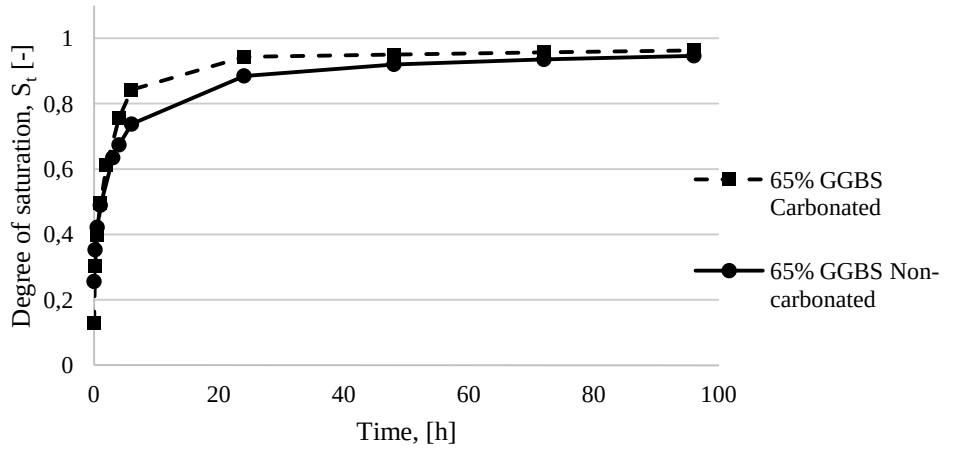
Appendix B4 Degree of saturation for carbonated and non-carbonated specimens containing 35% fly ash



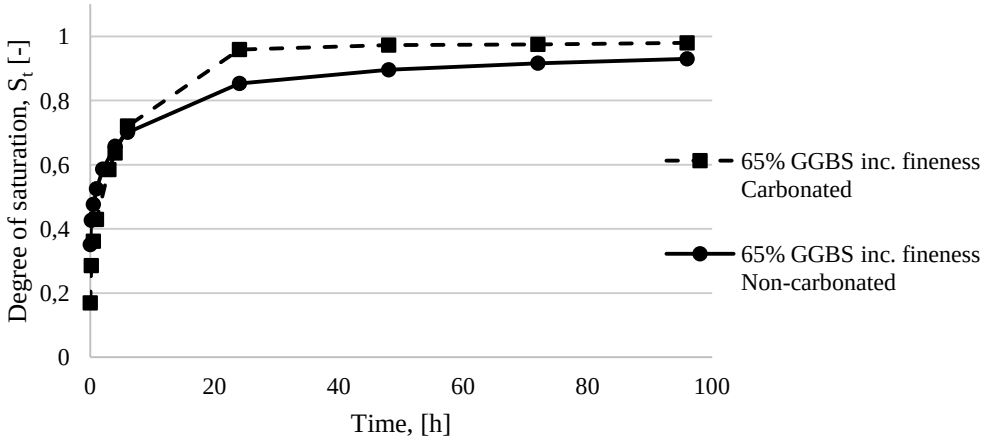
Appendix B5 Degree of saturation for carbonated and non-carbonated specimens containing 35% GGBS



Appendix B6 Degree of saturation for carbonated and non-carbonated specimens containing 50% GGBS



Appendix B7 Degree of saturation for carbonated and non-carbonated specimens containing 65% GGBS



Appendix B8 Degree of saturation for carbonated and non-carbonated specimens containing 65% GGBS with increased fineness

Appendix C Compressive strength

Cement mixture	*w/b* ratio	28-day strength [MPa]	
CEM I 42.5N SR3	*0.4*	*67.0*	
CEM I 42.5N SR3	*0.5*	*45.6*	
CEM I 42.5N SR3	*0.6*	*29.0*	
CEM I 52.5N	*0.4*	*68.5*	
CEM I 52.5N	*0.5*	*53.2*	
CEM I 52.5N	*0.5*	*62.7*	*CEN Normensand*
CEM I 52.5N	*0.6*	*39.5*	
Fly ash 20%	*0.4*	*62.1*	
Fly ash 20%	*0.5*	*49.4*	
Fly ash 20%	*0.5*	*53.1*	*CEN Normensand*
Fly ash 20%	*0.6*	*35.1*	
Fly ash 35%	*0.4*	*53.3*	
Fly ash 35%	*0.5*	*40.1*	
Fly ash 35%	*0.5*	*41.2*	*CEN Normensand*
Fly ash 35%	*0.6*	*27.5*	
GGBS 35%	*0.4*	*64.7*	
GGBS 35%	*0.5*	*52.3*	
GGBS 35%	*0.5*	*52.1*	*CEN Normensand*
GGBS 35%	*0.6*	*35.9*	
GGBS 50%	*0.4*	*60.8*	
GGBS 50%	*0.5*	*49.9*	
GGBS 50%	*0.5*	*50.8*	*CEN Normensand*
GGBS 50%	*0.6*	*35.7*	
GGBS 65%	*0.4*	*53.0*	
GGBS 65%	*0.5*	*43.3*	
GGBS 65%	*0.5*	*44.6*	*CEN Normensand*
GGBS 65%	*0.6*	*33.4*	
*GGBS 65%**	*0.5*	*54.0*	
*GGBS 65%**	*0.5*	*61.0*	*CEN Normensand*

**increased fineness*

Appendix C1 28-day strength for all tested mortar mixtures, including mortars with Normensand