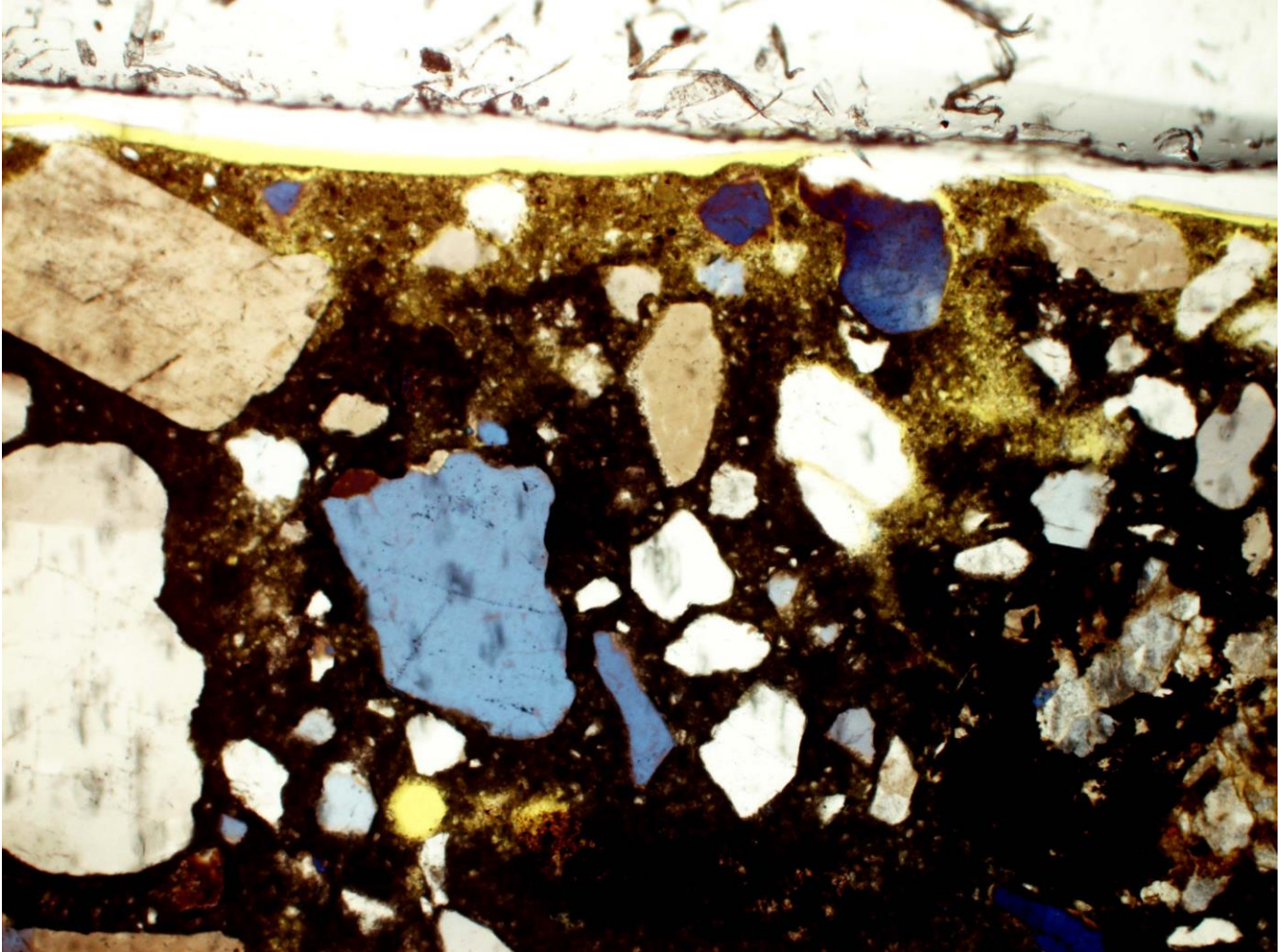




**CHALMERS**  
UNIVERSITY OF TECHNOLOGY

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# **Effect of Leaching on Compressive Strength of Cement Mortar**

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

FREDRIK BENGTTSSON

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Department of Civil and Environmental Engineering  
*Division of Structural Engineering*  
*Concrete Structures*  
CHALMERS UNIVERSITY OF TECHNOLOGY  
Master's Thesis BOMX02-17-54  
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Cover:  
Thin section with a leached zone at the top surface.

Department of Civil and Environmental Engineering, Göteborg, Sweden, 2017



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### ABSTRACT

Cementitious materials that are in contact with soft water will eventually be leached with a following degradation. It is mainly lime compounds formed during the hydration that is dissolved and transported away leading to increased porosity and reduced strength. This effect on the material properties appear in a leached zone and depends primarily on the loss of portlandite from the cement paste. Various types of concrete structures can be exposed to an attack, but leaching can also result in an impact when cement strength is determined in laboratories.

The present work consists of experimental investigations on the influence of the curing water when the compressive strength of cement prisms is determined according to the standard EN 196-1. The lack of specific demands on the storage condition can result in variations of pH and ion concentration which can influence the result. Different mixes of Portland cements and mineral additions were tested and evaluated with regard to the compressive strength at 28 days. Further analyses were conducted with SEM and thin sections to estimate the extent of the leaching and examine the alteration of the properties within this zone.

The result of the study showed a general loss of strength for prisms stored in water with low pH and ion concentration. The effect was seen to be larger for the mixes with a slow hydration process, which is expected as leaching is more detrimental before a dense structure is achieved. The leached zone was estimated to be around 0.5 mm for specimens stored in low pH water, while a minor leached zone was also detected from storage in other waters.

Comparison of storage waters from several laboratories normally used when assessing the compressive strength showed large variations, both regarding pH and ion concentration.

Key words: Cement, Compressive strength, Leaching, Scanning electron microscopy, Thin section

Effekt av Lakning på Tryckhållfasthet för Cementbruk

Examensarbete inom masterprogrammet *Structural Engineering and Building Technology*

FREDRIK BENGTTSSON

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Avdelningen för konstruktionsteknik

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## SAMMANFATTNING

Cementbaserade material som är i kontakt med mjukt vatten kommer med tiden att lakas ur och därmed försvagas. Det är främst kalkhaltiga hydratiseringsprodukter som löses upp och transporteras bort vilket leder till ökad porositet och reducerad hållfasthet. Denna försämring av materialegenskaper som uppkommer i den lakade zonen beror till största del på förlusten av portlandit från cementpastan. Olika typer av betongkonstruktioner kan utsättas för angrepp, men lakning kan även orsaka problem vid bestämning av normhållfasthet för cement i laboratorier.

Arbetet som presenteras i denna rapport består av experimentella undersökningar angående olika härdningsvattens påverkan på tryckhållfastheten av cementprismor som testas enligt standarden EN 196-1. Detta med anledning av att specifika krav gällande lagringsvattnet saknas och variationer av pH-värde och jonkoncentration kan påverka resultatet. Ett antal olika blandningar av några vanliga Portland cement och tillsatsmaterial testades och utvärderades med hänsyn till hållfastheten vid 28 dygn. Ytterligare analyser genomfördes med SEM och tunnslip för att bedöma lakningens omfattning samt undersöka förändringen av egenskaper i denna zon.

Utfallet av studien påvisade en generell hållfasthetssänkning för de prismor som lagrades i vatten med lågt pH och låg jonkoncentration. Effekten var större för blandningar med en långsam hydratisering vilket förklaras av att lakningen enklare kan orsaka skada innan en tät struktur erhålls. Den lakade zonen uppskattades till omkring 0,5 mm för de prismor som lagrades i vatten med lågt pH, medan en mindre zon också upptäcktes efter lagring i andra vatten.

Lagringsvattnet från olika laboratorier som normalt används vid bestämning av tryckhållfasthet visade på stora variationer gällande både pH och jonkoncentration.

Nyckelord: Cement, Lakning, Svepelektronmikroskop, Tryckhållfasthet, Tunnslip

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## **Preface**

This project was initiated at Thomas Concrete Group and was carried out in cooperation with Cements Research and Chalmers University of Technology with the aim to investigate the influence of the storage water during compressive strength tests of cement prisms. The main part of the work was performed at Thomas Concrete Group's C-lab in Gothenburg between January and June 2017.

Special gratitude is directed to Ingemar Löfgren who provided broad and deep knowledge and put a lot of effort into making the present study achievable.

The work was further supervised by Helén Jansson and Filip Nilenius who was helpful in guiding the project in the right direction. The laboratory work was performed with the instructions and assistance from Stina Åkerström which is appreciated. Some test specimens were analysed in SEM and with thin sections by Bo Nitz and Martin Eriksson at Cements's laboratory in Slite which is gratefully acknowledged. Particular gratitude goes to Niklas Johansson for the Gotland visit. The gratitude is further extended to all colleagues at Thomas Concrete Group for their help and support.

Gothenburg, June 2017  
Fredrik Bengtsson

# Notations

## Symbols

$A$	<i>Pressure area</i>	[m <sup>2</sup> ]
$A_d$	<i>Area of degraded zone</i>	[m <sup>2</sup> ]
$A_t$	<i>Total area</i>	[m <sup>2</sup> ]
$\alpha$	<i>ANOVA confidence level</i>	
$D_{app}$	<i>Apparent diffusion coefficient</i>	[m <sup>2</sup> /s]
$E$	<i>Young's modulus</i>	[Pa]
$e$	<i>Leached depth</i>	[m]
$F$	<i>Failure load</i>	[N]
$f_c$	<i>Compressive strength</i>	[Pa]
$\phi_t$	<i>Total porosity</i>	[%]
$n$	<i>Number of results</i>	
$t$	<i>Time</i>	[s]
$\nu$	<i>Poisson's ratio</i>	
$w/c$	<i>Water-to-cement ratio</i>	[kg/kg]

## Abbreviations

A	<i>Aluminium oxide</i>	[Al <sub>2</sub> O <sub>3</sub> ]
ANOVA	<i>Analyse of variance</i>	
BSE	<i>Back scattered electrons</i>	
C	<i>Calcium oxide</i>	[CaO]
C <sub>3</sub> A	<i>Tricalcium aluminate</i> (Aluminate)	
C <sub>4</sub> AF	<i>Tetracalcium aluminoferrite</i> (Ferrite)	
C <sub>2</sub> S	<i>Dicalcium silicate</i> (Belite)	
C <sub>3</sub> S	<i>Tricalcium silicate</i> (Alite)	
CH	<i>Calcium hydroxide</i> (Portlandite)	[Ca(OH) <sub>2</sub> ]
CEM I	<i>Portland cement</i>	
CEM II	<i>Portland-composite cement</i>	
CEM III	<i>Blast furnace cement</i>	
CEM IV	<i>Pozzolanic cement</i>	
CEM V	<i>Composite cement</i>	
C-S-H	<i>Calcium silicate hydrate</i>	
EDS	<i>Energy-dispersive spectrometry</i>	

F	<i>Iron oxide</i>	[Fe <sub>2</sub> O <sub>3</sub> ]
FA	<i>Fly ash</i>	
FE	<i>Finite element</i>	
GGBS	<i>Ground granulated blast furnace slag</i>	
HCP	<i>Hardened cement paste</i>	
NMR	<i>Nuclear magnetic resonance</i>	
OPC	<i>Ordinary Portland cement (also CEM I)</i>	
S	<i>Silicon dioxide</i>	[SiO <sub>2</sub> ]
SE	<i>Secondary electrons</i>	
SEM	<i>Scanning electron microscopy</i>	
TGA	<i>Thermogravimetric analysis</i>	
XRD	<i>X-ray diffraction</i>	



# 1 Introduction

Concrete is the most widely used building material in the world and appears in a large variety of different types of structures, including some that are in long term contact with water. Different compounds in concrete are soluble in water to a certain degree and may be leached from the solid phase. Leaching of calcium compounds is a possible deterioration mechanism of cementitious materials that are exposed to an aggressive solution, usually soft water, for a long period of time. Large concentration gradients between the interstitial pore solution and the surrounding water causes an attack that could weaken the mechanical properties and reduce durability. As different hydrate phases are lost from the material the microstructure is changed leading to increased porosity and reduced strength. In most structures leaching will probably not cause major degradation but problems has been reported for different types of hydraulic structures including dams (Rosenqvist et al, 2017) and could be important for the long term durability of nuclear waste repositories (Babaahmadi, 2015). When concrete structures are exposed to soft water leaching could also interact with other degradation mechanisms such as freeze/thaw attack to enlarge the effect.

## 1.1 Background

Another situation where leaching could result in an impact is when cement strength is assessed in laboratories. The strength of cement is determined on specimens that are mixed, cured and tested according to a standard. Cement strength determined in accordance with the European standard EN 196-1 is performed by testing of prisms of the dimension 40x40x160 mm. It is stated that the prisms are to be demoulded 20-24 hours after casting followed by storage in water until testing, which is performed at an age of 28 days. The procedure of the testing should be such that factors influencing the result are eliminated in order to obtain uniform results when the same cement is tested. The curing environment is one factor that could have an impact on the result. Concerning the storage water it is only specified that tap water should be used to fill up the storage container when starting a new curing bath, and that no more than half of the water is allowed to be substituted at one and the same time. However, there exists no regulations when it comes to the properties of the storage water meaning that important factors such as pH and ion concentration are not fixed following the standard. A variation of these properties of the water could potentially influence the result of the testing and therefore lead to different results between laboratories when the same cement is tested. It can also be so that the routines of changing water is not the same in all laboratories and the tap water might be of different quality, especially between different countries.

ATILH (Association Technique de l'Industrie des Liants Hydrauliques) is a French association that organises a campaign of inter laboratory testing every year. The campaign provides data for comparison between laboratories, and the reproducibility of the methods can be verified. The testing programme involves compressive strength and it has been found that there can be a significant difference between laboratories, see Figure 1. Some of this difference could

possibly be explained by leaching that occurs during the storage of the prisms in water.

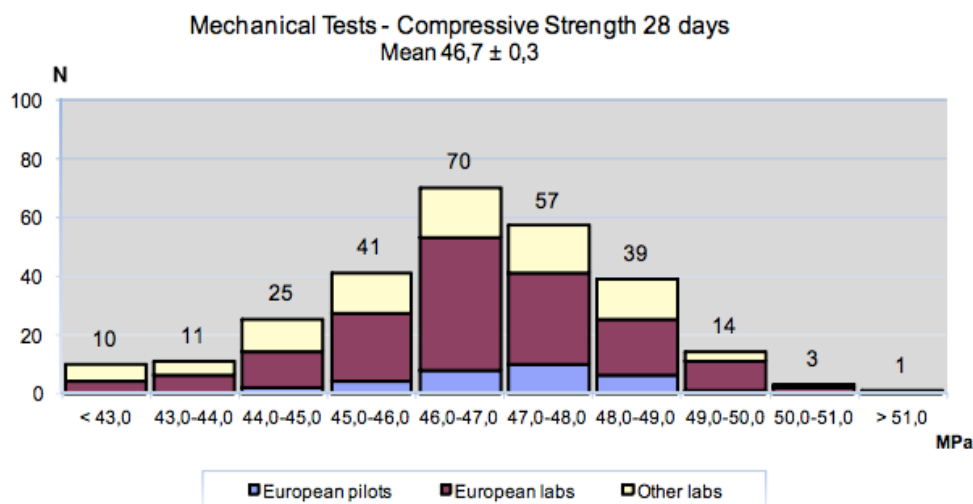


Figure 1: Comparison of compressive strength tests between laboratories according to EN 196-1 using the cement CEM II/B-M 32.5 R (ATILH, 2015).

## 1.2 Aim and objectives

The main objective of this project is to investigate how the compressive strength of cement prisms are affected by different storage conditions during curing and to examine the alteration of the leached zone. The result of the study aims to give an indication on how much of the spread between laboratories during compressive strength tests that can be explained by leaching due to variations of the storage water. If found necessary, recommendations for change of the standard should be provided. A minor objective is to investigate how a leached zone with increased porosity can be modelled in order to estimate the degradation of material properties, depending on the extent of the leached zone and the impact on the compressive strength.

## 1.3 Method

A literature review was first conducted to obtain the needed information about both cement and leaching to investigate and analyse the problem at hand. Previous research on the subject was examined in order to improve the understanding on the effects of leaching.

The main part of the work consisted of laboratory experiments. Different mixes of cement and mineral additions were compared and evaluated with regard to the compressive 28 days strength tested according to the standard EN 196-1. The cement prisms were stored in water with different properties in order to be able to evaluate the significance of variations in pH and ion concentration. Analyses with scanning electron microscopy (SEM) and thin sections were also performed to study the microstructure of the cement prisms and obtain relevant information including the depth of the leached zone and its change of properties.

Modelling of the effects of leaching was carried out in the FE software ABAQUS. The results of the modelling was compared with the experiments.

## 1.4 Scope and limitations

Regarding the scope of the project, the investigations should consider the effect on several types of binders as various properties could influence the result differently. Included in the project was to investigate and assess: (1) how the storage conditions for cement prisms impact the compressive strength; (2) how deep the leached zone was and how this influence the porosity; and (3) how the leaching affected the storage water.

The experiments was limited by the availability of different types of cement and also by the amount of specimens that could be tested during the time frame of the project. The cement specimens were for that reason focused on a few different Portland cements and some of the most common mineral additions, ground granulated blast furnace slag and fly ash. Also, the number of storage waters concerning variations of pH and ion concentration was limited. The specimens analysed with SEM and thin sections were chosen from the most interesting ones considering the result of the compressive strength test as it was not possible to analyse all of them. The effects on the early strength was not investigated.

## 1.5 Outline

In *Chapter 2* a review of the literature is presented which works as an introduction to the subject. First some basics of cement is described and then the most important information about leaching is given.

*Chapter 3* describes the experimental procedure and the methods that was used. The investigated curing conditions as well as the mixes of cement and mineral additions are presented.

In *Chapter 4* the outcome of the experiments are presented, analysed and discussed. The results include observations on the storage water, the compressive strength, the leached depth, the porosity and the chemical composition of the leached zone.

In *Chapter 5* the modelling of the effect of a leached zone is described and compared to the results from the experiments.

In *Chapter 6* some key points from the project is discussed and recommendations for the standard is provided.

The most important conclusions that can be drawn from the project together with some suggestions for further studies are presented in *Chapter 7*.

## 2 Literature Study

Leaching is for most structures not considered to be the dominant deterioration mechanism as it requires relatively long periods of time with exposure in an aggressive environment. The attack can however be expected to be more detrimental at an early age of the cement as the microstructure is not yet completely developed, which is the case when testing the strength of cement prisms. In order to investigate and understand the influence of leaching during compressive strength tests in laboratories some information on both cement and leaching is presented in this Chapter.

### 2.1 Cement

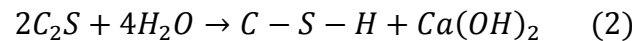
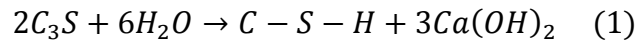
The binding material in concrete consists of cement that is mixed with water and which together with aggregate and possibly also admixtures forms the concrete. Portland cement is the most common cement in the world contributing to more than 95% of cement used in concrete (Domone & Illston, 2010). The main raw materials needed during manufacturing are limestone, clay and sand or materials of similar composition which are mixed in certain proportions. The mixed materials are heated to around 1450°C in a rotary kiln leading to the formation of cement clinker. Cement is produced when the clinker together with gypsum and possibly some other minor additions are grinded. Based on the raw materials used in the manufacturing process the main components of Portland cement are lime and silica. Some normal compositions of oxides in different cements are given in Table 1. These oxides are normally abbreviated as: CaO = C; SiO<sub>2</sub> = S; Al<sub>2</sub>O<sub>3</sub> = A; Fe<sub>2</sub>O<sub>3</sub> = F. Together they form the main compounds of Portland cement. The compound content can be estimated based on the oxide content by the use of Bogue's equations (Bogue, 1955). As seen in Table 1, a minor change of oxides will have a large influence on the composition of compounds and therefore also on the properties of the produced cement. Some minor compounds that may occur in smaller amounts are SO<sub>3</sub>, MgO and the alkalis K<sub>2</sub>O and Na<sub>2</sub>O. The two calcium silicates, C<sub>3</sub>S (Alite) and C<sub>2</sub>S (Belite), are the main constituents that together form most of the cement.

Table 1: *Three different cements and their oxide and compound composition [% by mass] (Neville, 1995).*

Oxide	(1)	(2)	(3)
CaO	66	63	66
SiO <sub>2</sub>	20	22	20
Al <sub>2</sub> O <sub>3</sub>	7	7.7	5.5
Fe <sub>2</sub> O <sub>3</sub>	3	3.3	4.5
Others	4	4	4
<b>Compound</b>			
C <sub>3</sub> S	65	33	73
C <sub>2</sub> S	8	38	2
C <sub>3</sub> A	14	15	7
C <sub>4</sub> AF	9	10	14

### 2.1.1 Cement hydration

Cement is a hydraulic binder and after being mixed with water chemical reactions occur and the hydration starts which forms the cement hydrate phases. It is during this process that the cement will harden and obtain its strength and stiffness. The hydration reactions will proceed for a long time and the degree of hydration is normally used as a measure of how much of the cement that has reacted with water. The two calcium silicates are the most important reactants during the hydration by contributing to most of the strength and stiffness (Domone & Illstone, 2010). The C<sub>3</sub>S is faster and provides significant amounts of early strength with about 70% reacting in 28 days and almost all in 1 year, while C<sub>2</sub>S makes an important contribution to the long term strength with 30% reacting during the first 28 days and 90% in 1 year (Taylor, 1997). The reactions of the calcium silicates with water could schematically be written as:



In which Ca(OH)<sub>2</sub> can be written CH in short and is also known as portlandite. The produced CH appear in the shape of crystals, which are large in relation to the other hydration products. The hardened cement paste (HCP) has alkaline properties which is due to the CH and some of the minor oxides (Domone & Illston, 2010). Normally the pore solution of cement has a pH value ranging between 12.5 and 13. In a cement with high alkali content the pH can however be well above 13 (Hobbs, 1988).

The calcium silicate hydrate is usually mentioned as the C-S-H phase or gel of the HCP and is the main contributor to the strength. There are some uncertainties concerning the C-S-H as the mineralogical structure is rather complex. It is composed of CaO, SiO<sub>2</sub> and H<sub>2</sub>O giving a certain ratio between lime and silica. It is reported that no exact value of the Ca/Si ratio is determined as the result is affected by the test method, however the ratio is normally given as 1.5-2 (Neville, 1995). The structure of the C-S-H phase is reported to be of amorphous character to poorly crystalline (Hewlett, 1998).

The other main compounds of cement, C<sub>3</sub>A and C<sub>4</sub>AF, will also participate in the hydration and will after reactions form products including ettringite (AFt phase) and other aluminate phases, such as monosulfates (AFm phases). The presence of gypsum in the cement helps controlling the setting and stiffening of the paste which is otherwise fast due to the reaction of C<sub>3</sub>A and water (Hewlett, 1998).

### **2.1.2 Strength of cement**

One of the most important properties of cement is the strength; normally it is the compressive strength that is used to characterise the cement in strength classes according to EN 197-1. The strength will continue to increase for a long time as not yet hydrated cement grains react with water which can then contribute. The completeness of the hydration, which will increase with time, is therefore significant.

The development of the stiffness of cement is rapidly increased after the dormant period, usually about 2-4 hours after mixing with water. A couple of hours later the mix will start to obtain strength and during the following days it will increase at a fast rate. Then a period of at least a couple of months will follow where the strength will be obtained at a decreasing rate. For a normal Portland cement with access to sufficient amounts of water the hydration is about 90% complete at 28 days (Domone & Illston, 2010).

The early strength is mainly dependent on the rate of hydration and a cement with increased fineness and specific surface will obtain strength faster as there will be a larger contact area with the mixing water. The surface area of a normal Portland cement is about 300-350 m<sup>2</sup>/kg while it is a bit higher for a rapid hardening cement, 400-550 m<sup>2</sup>/kg (Hewlett, 1998).

As the hydration proceed the porosity will decrease leading to a more dense material. The porosity is essential for the strength as less material and an increased fraction of pores will reduce the load bearing capacity. Figure 2 shows the relation between strength and porosity for porous materials. The main factor governing the porosity of HCP is the water-to-cement ratio in which a larger ratio means that more water is used in a mix leading to increased porosity. The size of the pores are also important as those of greater size such as capillary pores have a larger impact on the strength than the fine gel pores (Hewlett, 1998).

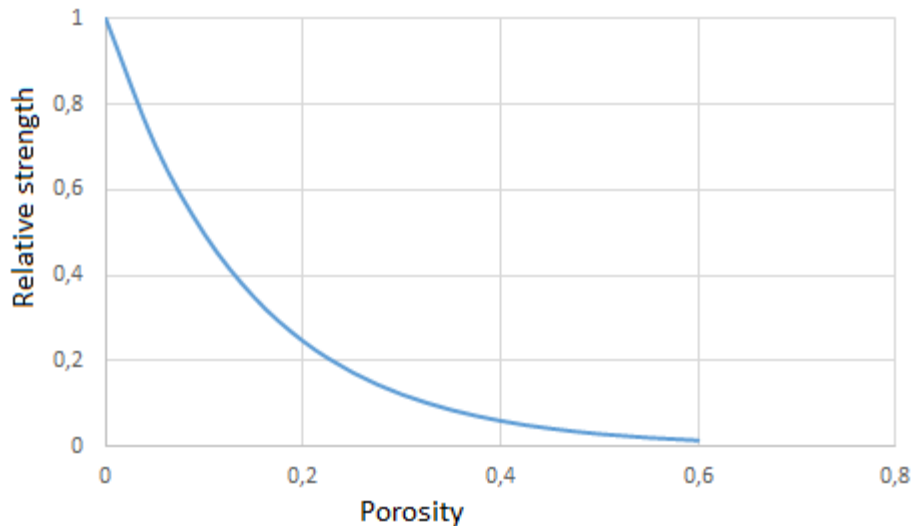


Figure 2: Relation between porosity and relative strength based on various porous materials and several tests. The curve gives the equation:  $Relative\ strength = e^{-7*Porosity}$  (Beton-Bogen, 1985).

Another factor influencing the strength is the temperature during hydration. The rate of the hydration reactions will be increased with higher temperatures leading to increased early strength. However, with higher curing temperatures follows a different formation of the microstructure which includes an additional porosity and the strength at 28 days can therefore be lower (Neville, 1995). The strength properties are also affected by the type of binder that is used including mineral additions.

The standard EN 197-1 classifies the cement according to its composition and by the compressive strength measured in MPa. There are three classes of standard strength: 32.5, 42.5 and 52.5. Included is also three classes for early strength, N meaning ordinary early strength, R meaning high early strength and L meaning low early strength. Presented in Table 2 is an extraction of the requirements of compressive strength for some different classes.

Table 2: Strength classes according to EN 197-1

Strength class	Compressive strength [MPa]			
	Early strength		Standard strength	
	2 days	7 days	28 days	
32.5 N	-	$\geq 16$	$\geq 32.5$	$\leq 52.5$
32.5 R	$\geq 10$	-		
42.5 N	$\geq 10$	-	$\geq 42.5$	$\leq 62.5$
42.5 R	$\geq 20$	-		
52.5 N	$\geq 20$	-	$\geq 52.5$	-
52.5 R	$\geq 30$	-		

### 2.1.3 Mineral additions

Cement can be partly replaced by cement replacement materials, also called mineral additions, which can be either blended in the cement by the producer or added separately at the time of mixing the concrete. Some of the most common ones are ground granulated blast furnace slag (GGBS) and fly ash. Blast furnace slag is a by-product of steel manufacturing while fly ash is a combustion product of pulverized coal. Some normal limits of the main components in fly ash and GGBS are given in Table 3.

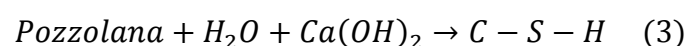
Table 3: *Example on composition of fly ash (Germany) and GGBS (Sweden & Finland) [% by mass] (Löfgren, 2017).*

Component	Fly ash	GGBS
SiO <sub>2</sub>	34-50	30.7-37.0
Al <sub>2</sub> O <sub>3</sub>	21-30	8.3-13.1
Fe <sub>2</sub> O <sub>3</sub>	8-29	-
CaO	2-12	30.7-39.8
MgO	1-5	9.8-17.3
SO <sub>3</sub>	0.1-2.1	-
K <sub>2</sub> O + Na <sub>2</sub> O	1.4-7	0.8-1.9
TiO <sub>2</sub>	-	1.71-3.21
S	-	1.20-1.39
MnO	-	0.06-0.62

A benefit of using mineral additions instead of only Portland cement is that it consumes less natural resources and energy (Neville, 1995) and the environmental impact regarding CO<sub>2</sub> can be reduced (Kurdowski, 2014), but the properties of the concrete will also be altered.

GGBS has a hydraulic behaviour and will react with water to participate in the hydration, but will however require some Portland cement or alkali content to be activated. The hydration of cements with GGBS will result in similar products as those of only Portland cement but the amounts of CH is reduced. The use of GGBS in concrete will result in less heat development (Taylor, 1997) and improved durability (Neville, 1995).

Fly ash on the other hand can show either hydraulic or pozzolanic behaviour depending on the calcium content, where a low amount of calcium will give a pozzolanic behaviour. In order to participate in the hydration reactions a pozzolanic material consumes CH when reacting with water, forming products similar to those of Portland cement. The silica is the most important reactant of fly ash and the reaction of a pozzolanic material could be written in a simplified way:



As fly ash consumes CH the amount that can be used to replace cement in a mix is limited, normally to a maximum of around 35% by mass (in EN 197-1). The particles of fly ash are spherical with a high fineness and when used in concrete it reduces the need of water and improves the workability (Neville, 1995).

The strength development and the ultimate strength are both influenced as mineral additions are used. The addition of GGBS to the concrete mix can considerably affect the short term strength as the hydration reactions are slowed down. The long term strength can however even be increased (Taylor, 1997). Mixes including fly ash will also obtain strength at a slower rate due to the pozzolanic reactions, which are secondary to the reaction of Portland cement (Domone & Illston, 2010). As both GGBS and fly ash has a slower hydration process than Portland cement the porosity is increased at early age (Taylor, 1997).

## 2.2 Leaching

Cementitious materials are to some extent soluble in water, especially important is the dissolution of portlandite. Pure water dissolves CH to an amount of 1.85 g/l at 0°C and 1.65 g/l at 20°C (Boynton, 1980) and may be detrimental to concrete structures. Examples of such water that are aggressive can in the nature be found in e.g. lakes, rivers, glaciers and in the groundwater (Duchesne & Bertron, 2013).

In concrete with high porosity and permeability large amounts of water can be transported, increasing the risk of problems with leaching. It has also been seen that local maximums of leaching appear around cracks that creates weaker zones as water have good access there (Rombén, 1997). If concrete with low porosity and permeability is exposed to leaching the attack is likely to not be as severe as less water is transported through the material. The mechanism of leaching is normally a slow process that needs long periods of time before any problems can occur.

The type of structures where leaching is of concern are therefore most often in long term contact with soft water. Major degradation has been detected for water pipes and conduits (Taylor, 1997). Hydro power structures has sometimes been observed to be exposed to soft water with low pH and can consequently suffer from leaching damages (Ekström, 2003). Another example is the storage of nuclear waste, which includes concrete barriers with extensive service life periods. SKB (Swedish Nuclear Fuel and Waste Management Company) manages the disposal of nuclear waste in Sweden and are responsible for the long term durability of the repositories. Leaching is in this case considered to be one of the important degradation mechanisms, see (Lagerblad, 2001). In Figure 3 a typical leaching damage is seen. Some of the material has been lost due to leaching and the aggregate is exposed.



Figure 3: *Damage due to leaching (photo: Anders Lindvall).*

### 2.2.1 Mechanism of leaching

Leaching of cement based materials mainly refers to lime compounds formed during the hydration being leached. The mechanism of leaching includes the transportation of ions from the solid phase into the surrounding environment. The pore solution of a cementitious material is as previously mentioned a very basic solution with high pH. This means that when water is surrounding a cementitious material a concentration gradient will be present due to a lower ion concentration in the external water than in the pore solution. This concentration gradient will act as the driving force as compounds are transported by diffusion through the material. As diffusion occurs compounds must be dissolved to maintain equilibrium between the pore solution and the solid material. Water with low pH and ion concentration will therefore be aggressive to cementitious materials. Leaching is mainly described as a coupled diffusion/dissolution process and can be summarised with the two following mechanisms:

- Diffusion: The concentration gradient between the interstitial pore solution and the surrounding water causes compounds to diffuse out of the material.
- Dissolution: The equilibrium between the pore solution and the solid material is disturbed leading to dissolution of compounds.

The order in which compounds will be dissolved depends mainly on its solubility in water. NaOH (sodium hydroxide) and KOH (potassium hydroxide) has a high solubility and are the first compounds to be leached. In solutions with increasing concentration of NaOH or KOH the solubility of Calcium compounds will be continuously reduced (Ekström, 2003). Most lime that is leached comes from CH (calcium hydroxide) because of its high solubility and large quantity but lime will

also leach from AF-phases and C-S-H, although in much smaller amounts and mainly after CH has been leached.

The Calcium ion concentration in the pore solution and in the solid material can be related with a solid-liquid equilibrium curve describing dissolution of CH and C-S-H, see Figure 4. According to Duchesne & Bertron (2013) dissolution of CH takes place when the Calcium ion concentration in the pore solution drops below 22 mmole/l (= 880 mg/l). The C-S-H is progressively decalcified between 2 and 22 mmole/l leading to the Ca/Si ratio decreasing to about 1. At concentrations of less than 2 mmole/l (= 80 mg/l) total decalcification of C-S-H occurs and the solid phase turns into a silica gel. For equilibrium reasons CH would therefore be the first lime compound to be attacked but according to Taylor (1997) due to the greater specific surface of C-S-H and aluminate phases the attack is in practice probable to happen at the same time. In Duchesne & Bertron (2013) it is however stated that CH is the first compound to dissolve at a pH of 12.5 which is followed by ettringite at 10.7 while C-S-H starts to dissolve in the range of 10.5-8.8.

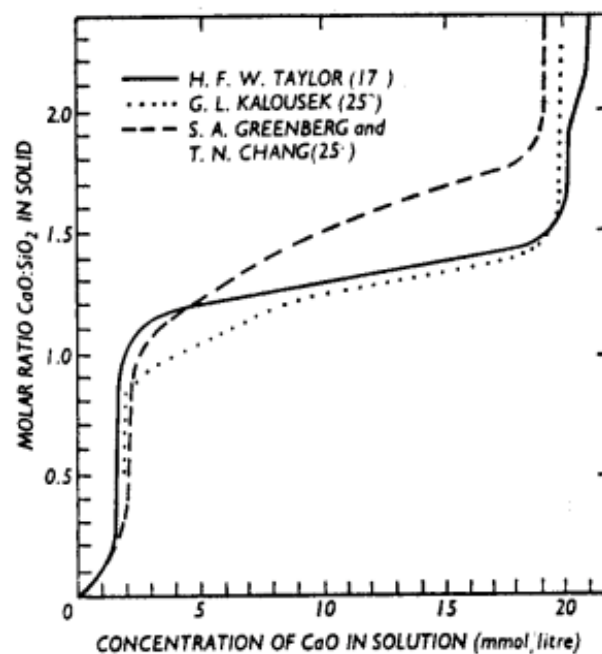


Figure 4: Equilibrium curve describing the Ca/Si ratio of C-S-H and the CaO concentration in the solution (Lea, 1983).

The leaching process is characterised by a degraded zone where complete dissolution of CH and a decalcification of the C-S-H and other compounds has occurred. The C-S-H will progressively lose calcium resulting in a gradient of Ca/Si in the leached zone. The leached zone is commonly referred to as the degraded area ( $A_d$ ) and with the total area ( $A_t$ ) of the specimen the degradation ratio can be calculated as:

$$\text{Degradation Ratio} = \frac{A_d}{A_t} \quad (4)$$

The leached zone can be further divided into several zones where leaching of different compounds has occurred. One model showing different zones are

presented in Figure 5. In the inner sounds zone no leaching has occurred. The border between the leached and unleached zone are defined by the dissolution of CH. The outermost zone is composed only of a C-S-H that has been highly decalcified.

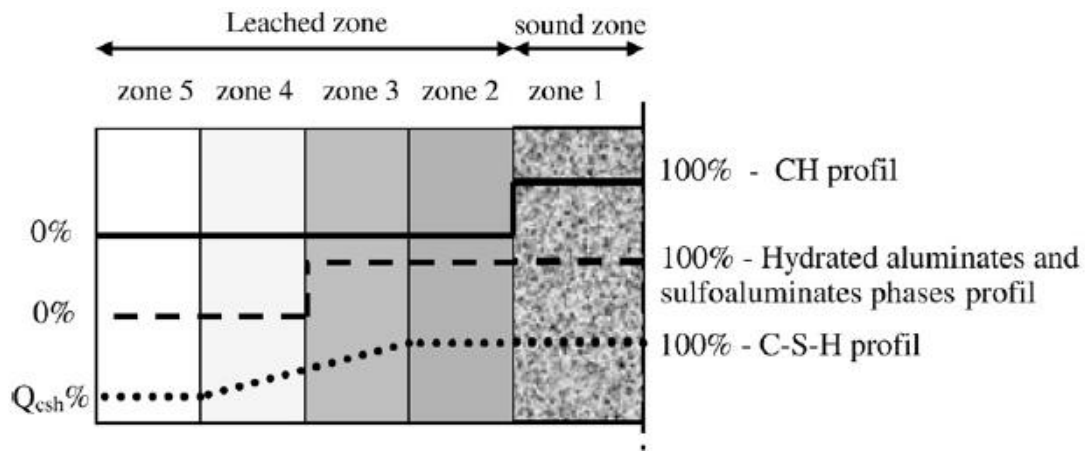


Figure 5: A model for different zones due to leaching (Bernard et al, 2008).

Leaching is mainly dependent on the diffusion mechanism and the leached depth is therefore approximately proportional to the square root of time, see e.g. Haga et al (2005) and Mainguy et al (2000). This results in a faster leaching in the beginning which slows down over time, see Figure 6. In Dyer (2014) the leached depth is described as:

$$e = \sqrt{D_{app} * t} \quad (5)$$

In which  $e$  is the depth of the leached zone,  $t$  is time and  $D_{app}$  is the apparent diffusion coefficient of the degraded zone. It should however be noted that even though diffusion is the governing transportation mechanism of leaching some dissolved compounds can be transported by convection when water flows through the material (Ekström, 2003).

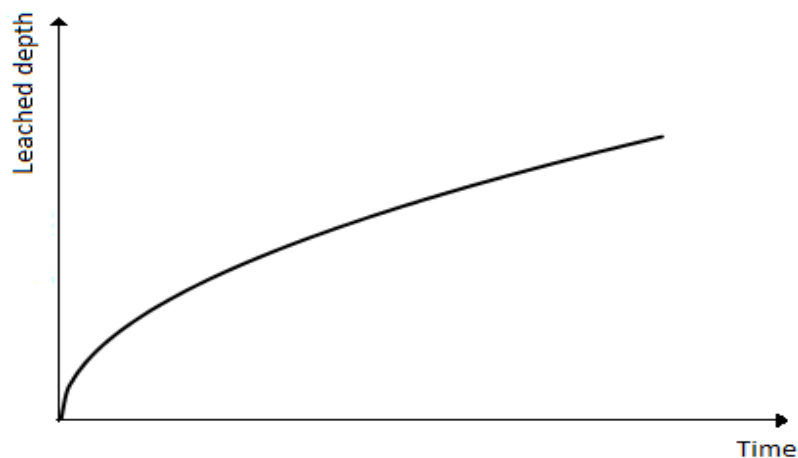


Figure 6: Simplified relation between leached depth and time of exposure.

### 2.2.2 Effects of leaching

The hydration products being leached is of great importance for properties such as strength and durability. The main effect of leaching is an increase of the porosity in the degraded zone due to the dissolution of compounds leading to a decrease of the compressive strength.

It is the leaching of calcium hydroxide that has most impact on the change of compressive strength, while decalcification of C-S-H and leaching of other compounds will only have a minor influence. Carde & Francois (1999) attributed this to the calcium hydroxide affecting the macroporosity while C-S-H influences the microporosity. As the calcium hydroxide appear in relatively large crystals they will leave larger voids after being leached resulting in a greater impact on the compressive strength. Carde & Francois (1999) concluded after experiments and modelling that the decalcification of C-S-H lead to 1/3 of the increase in porosity but only 1/12 of the loss of strength. This result clearly highlights the importance of CH crystals leaching in relation to decalcification of the C-S-H gel.

Jain & Neithalath (2009) investigated the influence of leaching on the porosity, see Figure 7. The change of porosity was measured for specimens that had been leached for 28, 56 and 90 days in deionized water after first curing for 90 days. It can be seen that all tested pastes experience an increase of the total porosity as the leaching goes on. The plain paste had the largest CH content from the start and it was also this paste that got the largest increase of porosity. In Carde & Francois (1997) it is reported that complete leaching resulted in an average increase of porosity by 19.3%.

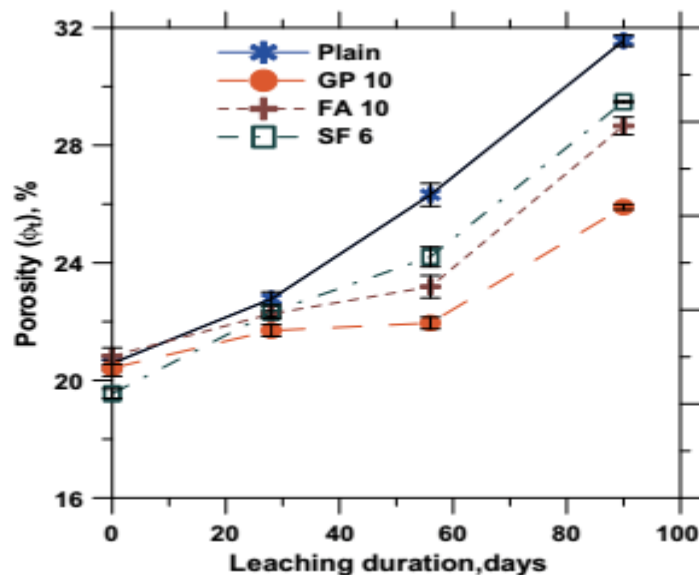


Figure 7: Change of total porosity at different leaching durations for cement pastes. GP 10 is a glass powder replacing 10% by mass of the cement, FA 10 is fly ash also replacing 10% of the cement and SF 6 is a 6% silica fume replacement (Jain & Neithalath, 2009).

At complete degradation the loss of compressive strength can be very extensive. In experiments by Carde & Francois (1997) the average residual strength after complete leaching was determined to be 24% of the initial strength.

Nguyen et al (2007) observed that concrete cylinders with diameter 110 mm and height 220 mm had a residual Young's modulus of about 36% and underwent a loss of compressive strength from around 53 MPa to about 15 MPa after complete leaching.

Bediako et al (2015) investigated how the compressive strength of 50 mm cubes of Portland cement and of a mortar with 30% replacement by powdered waste clay brick was affected by curing in tap water and lime saturated water. It was found that the increase of compressive strength when curing occurred in lime saturated water for 28 days compared to tap water was 19% for the Portland cement and 27% for the brick replacement mortar.

### **2.2.3 Factors influencing the leaching process**

A number of different factors will influence the rate of leaching and the depth of the leached zone. These factors are related both to the environment in which the leaching occurs and to the composition of the exposed material.

The rate of CH dissolution for a Portland cement was determined by Haga et al (2005) to be more rapid for larger pore volumes leading to increased leaching. In a more porous material the permeability is higher resulting in increased water accessibility and transportation properties. The leaching solution can then infiltrate further into the material causing dissolution. Higher porosity is therefore expected to result in a higher rate of leaching.

In Kamali et al (2008) the influence of temperature, water-to-cement ratio, type of binder and the solution used for leaching was investigated. The specimens were cured for three months before leaching. It was observed that the leached depth was at least five times smaller when mineralised water was used instead of pure water.

It has also been concluded that mineral additions (both fly ash and GGBS) may decrease the leaching kinetics. Kamali et al (2008) explained it to be the result of a decrease of both ionic diffusivity (for well cured specimens) and CH content as more mineral additions were used.

The leached depth increase when the water-to-cement ratio or the temperature increase. A larger water-to-cement ratio leads to an increase of porosity and ionic diffusivity which explain the faster rate of leaching. The effect of temperature was attributed by Kamali et al (2008) to be an increase of ionic diffusivity, a more rapid dissolution process (for most compounds) and the evolution of a larger porosity. This is also supported by results from Nakari et al (2006) who concluded through both modelling of calcium leaching and experiments that an increase in temperature or water-to-cement ratio leads to an accelerated leaching process.

#### 2.2.4 Leaching of cement prisms

When the strength of cement is determined according to the standard EN 196-1 prisms should be demoulded at an age of 20-24 hours and then stored in water until testing of strength is performed at an age of 28 days. The storage water should be of temperature  $20\pm 1^{\circ}\text{C}$  and it is stated that tap water is used to fill up the storage container when starting a new curing bath. If the water in the storage container is replaced no more than 50% should be substituted at the same time. It is however not stated in what case the water actually should be replaced. Concerning properties of the water such as pH and ion concentration no information is given.

As the prisms will only be submerged in the storage water for 27 days any deterioration due to leaching can only occur for a short period of time, thus complete leaching is not expected. The leaching is however going to take place during a young age of the cement meaning that the hydration is not as far developed. The prisms will therefore not be very compact as the porosity is high at early age and the surrounding water will have good access and possibility to dissolve and leach ions from the cement paste. As hydration takes place the porosity will decrease meaning that the prisms are likely to be most vulnerable to deterioration early on. The rate of obtaining strength is of importance as a rapid cement will achieve a dense structure faster which is expected to result in reduced leaching.

It has been mentioned that the use of mineral additions in some other experiments resulted in less leaching. It is however important to note that in those cases the specimens were cured before leaching. When taking the slower hydration process and the increased early porosity of mineral additions into account the results can possibly change.

The size of the prisms are rather small, being 40x40x160 mm, which will magnify the effect as the ratio of the specimens surface area to volume is large. The leached depth may be similar compared to a larger specimen but the degradation ratio would be increased for smaller specimens leading to a larger effect.

When the specimens are stored in water any leaching is expected to lead to an increasing pH and ion concentration as ions diffuses. The concentration gradient will therefore be reduced over time and the leaching is then expected to slow down. The amount of storage water compared to the volume of the prisms in the storage container is therefore of interest as more water in relation to prisms means that the gradient will decrease at a slower rate. If water is substituted the concentration gradient will be at least partly restored.

### 3 Experiments

A number of different experiments and analyses has been carried out in order to investigate the impact of the storage condition for cement prisms and to examine the effects of leaching. The main focus has been on the assessment of compressive strength according to the standard EN 196-1. Some specimens were further investigated by SEM and thin sections to examine the alteration of the leached zone. Below follow the specification of the materials that was used and information about the test-set up, the preparations and the implementation of the experiments.

#### 3.1 Materials

In Table 4 the tested mixes of cement and mineral additions used for the cement prisms are listed. As can be seen three different cements were combined with two mineral additions giving a total of seven mixes.

Table 4: *Mixes of cement and mineral additions for the cement prisms used in the experiments [% by mass].*

Classification according to EN 197-1	Cement brand	Cement amount	Fly ash	GGBS
CEM I 52.5 N	CEMEX Standard	100 %	-	-
CEM I 52.5 R	SH Skövde	100 %	-	-
CEM I 42.5 N	Anläggningscement Degerhamn	100 %	-	-
CEM II/A-V	SH Skövde	85 %	15 %	-
CEM II/B-V	SH Skövde	70 %	30 %	-
CEM II/A-S	SH Skövde	80 %	-	20 %
CEM III/A	SH Skövde	50 %	-	50 %

##### 3.1.1 Cement

*CEMEX standard* is a normal Portland cement. *SH Skövde* is a rapid hardening cement with a faster hydration. *Anläggningscement Degerhamn* (CEM I 42.5 N – SR 3 MH/LA) is a sulphate resistant cement with moderate heat development and low alkali content that has a slower hydration. In Table 5 the specification of the cements used is presented.

Table 5: *Properties and composition of the cements used in the experiments.*

<b>Physical properties</b>	CEMEX Standard	SH Skövde	Anläggningscement Degerhamn
1 day strength [MPa]	20	31.8	11.8
2 days strength [MPa]	33	43.9	22.7
28 days strength [MPa]	59	63.7	53.1
Specific surface [m <sup>2</sup> /kg]	420	531	338
Density [kg/m <sup>3</sup> ]	3 150	3 125	3 189
Setting time [minutes]	150	124	166
<b>Chemical composition</b>			
CaO [% by mass]	63	62.9	63.8
SiO <sub>2</sub> [% by mass]	19	19.1	21.4
Al <sub>2</sub> O <sub>3</sub> [% by mass]	4.3	5.2	3.6
Fe <sub>2</sub> O <sub>3</sub> [% by mass]	3.1	3.0	4.4
MgO [% by mass]	3.4	1.3	0.95
Na <sub>2</sub> O [% by mass]	0.1	0.17	0.10
K <sub>2</sub> O [% by mass]	1.2	1.3	0.62
SO <sub>3</sub> [% by mass]	3.4	4.0	2.8
Na <sub>2</sub> O ekv. [% by mass]	0.9	1.03	0.51
Cl [% by mass]	0.07	0.03	0.01
Loss on ignition [% by mass]	1.0	2.6	2.0
Water soluble chrome [mg/kg]	< 2	< 2	< 2
<b>Compound composition</b>			
C <sub>2</sub> S [% by mass]	14	8.3	16.3
C <sub>3</sub> S [% by mass]	58	61.6	59.8
C <sub>3</sub> A [% by mass]	6	8.5	2.1
C <sub>4</sub> AF [% by mass]	9	9.3	13.5

### 3.1.2 Mineral additions

The GGBS that was used in the experiments are named *Slagg Bremen* and originates from iron manufacturing in Germany. The used fly ash is called *Swecem PFA* and is produced in Denmark. Some properties of the used mineral additions are presented in Table 6.

Table 6: *Properties and composition of the mineral additions used in the experiments.*

<b>Physical properties</b>	GGBS	Fly ash
Specific surface [m <sup>2</sup> /kg]	420	-
Density [kg/m <sup>3</sup> ]	2 900	2 300
Activity index 7/28/91 d [%]	≥ 55/75/100 <sup>a</sup>	≥ -/75/85
Setting time	≤ 1.3 <sup>a</sup>	-
<b>Chemical composition</b>		
SiO <sub>2</sub> [% by mass]	35.23	≥ 25
Al <sub>2</sub> O <sub>3</sub> [% by mass]	13.29	-
Fe <sub>2</sub> O <sub>3</sub> [% by mass]	0.56	-
Sum SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /Fe <sub>2</sub> O <sub>3</sub> [% by mass]	-	≥ 70
CaO [% by mass]	39.80	< 1.5 free, < 10.0 reactive
MgO [% by mass]	7.58	≤ 4.0
MnO [% by mass]	0.27	-
K <sub>2</sub> O [% by mass]	0.55	-
Na <sub>2</sub> O [% by mass]	0.45	-
Na <sub>2</sub> O ekv. [% by mass]	0.81	< 5.0
SO <sub>3</sub> [% by mass]	0.28	≤ 3.0
Cl [% by mass]	0.006	< 0.02
TiO <sub>2</sub> [% by mass]	0.82	-
S [% by mass]	0.67	-
Loss on ignition [% by mass]	≤ 2.0	-
Residues of coal [% by mass]	-	< 5.0

<sup>a</sup> 50% OPC (CEM I 42.5) and 50% GGBS relative to 100% OPC.

### 3.1.3 Storage water

The storage water used in the experiments had different properties concerning pH and ion concentration. Initially a total of three variations of water properties was used having low, middle and high pH. A fourth storage water was later added in the project and this was lime saturated. Some deviations from the standard were made in order to obtain water with different properties.

All storage containers were sealed and placed in a climate room (20±1°C), except for the middle pH container which was temperature controlled. The pH was continuously measured throughout the experiment and samples of water were taken for ion analysis.

For the cement prisms the following curing conditions were examined:

- Middle pH:
  - This is a storage water normally used when assessing the strength of cement prisms at Thomas Concrete C-lab.
  - All prisms in this study were therefore stored in one large container together with other prisms not included in the experiment.
- High pH:
  - The idea of this storage water was to create an environment where no leaching would occur.
  - A container was prepared by allowing some cement to leach in advance and further boosted by adding NaOH and Ca(OH)<sub>2</sub>.
  - All prisms were stored in the same container.
- Low pH:
  - With this water the idea was to favour an aggressive environment where as much leaching as possible would occur.
  - Deionized water was used for the first day and thereafter tap water (pH about 8.1) was used to renew all of the water after 1, 2, 7, 14 and 22 days of storage. At the time of renewal the prisms were taken out of the water for approximately five minutes as the substitution took place.
  - Each type of cement was stored in separate containers.
  - The size of the storage containers were not the same for all types of cements leading to different ratios of volume of storage water to volume of prisms. CEM II/A-V and CEM II/A-S were placed in containers with the ratio being approximately 27 while the rest of the mixes had a ratio of approximately 21.
- Lime saturated water:
  - This storage water was added at a later stage in the project after assessing the results from the other waters. The idea was similarly to the high pH container to create an environment where no leaching would occur.
  - The water was boosted by adding Ca(OH)<sub>2</sub> to a storage container until saturated, which was seen as the dissolution of the calcium hydroxide stopped.

- All prisms were stored in the same container.

In Figure 8 two examples of storage containers used in the experiments can be seen.



Figure 8: Left: One of the low pH storage containers. Right: The high pH storage container.

### 3.2 Experimental procedure and methods

The prisms were cast according to EN 196-1 using mortar including a CEN Standard sand (three parts), cement (one part) and water (half part) giving a water-to-cement ratio of 0.50. In the cases of using mineral additions, cement was replaced so that the amount of cement and mineral addition together was constant, see Table 7 for mix proportions. Tap water was used in the mix.

Table 7: Mix proportions giving one mould of cement prisms.

Material	CEN Standard sand	Cement + Mineral additions	Water
Amount [g]	1350	450	225

The prisms were cast in moulds that gives three prisms each. All three prisms from one mould was of the same mix and stored in the same storage water. The specimens were mixed for four minutes using a Hobart mixer and then filled and compacted in two layers using a Jolting table, see Figure 9. The moulds were stored in a curing chamber during the first day (20-24 hours), keeping constant temperature (20°C) in a moist environment (about 90% RH). After demoulding the prisms were immediately submerged in the storage water.



Figure 9: *Left: Hobart mixer. Right: A mould filled with cement placed on the jolting table.*

For most of the tested mixes double sets of prisms were cast for each storage water. This was done in order to further verify the testing as the measured cement strength will have a certain variation, and fluctuations of the results will appear naturally due to e.g. small unintended variations in the procedure when filling the moulds. Double testing will decrease the risk of errors and deviations and be helpful in determining whether any influence on the results can be attributed to the water or if it appeared by chance.

### **3.2.1 Compressive strength**

At an age of 28 days the compressive strength of the cement prisms was determined. When assessing the strength each prism are divided in two parts which are both tested. This mean that one mould will result in six individual values of which the arithmetic mean is reported as the compressive strength. In case one value deviates more than 10% from the mean this value is excluded according to the standard (EN 196-1). The prisms were divided by cutting out the middle part (approximately 2 cm) which for some of the specimens were sent for further analyses. Figure 10 shows the compression of a specimen.



Figure 10: Testing of the compressive strength for one half of a prism.

The testing was performed by applying a load that is increased by 2.4 kN/s until failure occurs. The ultimate load is recorded and the strength of each tested part is calculated as:

$$f_{ci} = \frac{F_i}{A_i} \quad (5)$$

Where  $F_i$  is the recorded load and  $A_i$  is the pressure area (normally 1600 mm<sup>2</sup>). The compressive strength was then calculated as the mean of all prisms from the same mould:

$$Mean = \frac{\sum_{i=1}^n f_{ci}}{n} \quad (6)$$

Where  $n$  is the number of results (normally 6). The standard deviation was also calculated to see the variation of the results within the testing:

$$Standard\ deviation = \sqrt{\frac{\sum_{i=1}^n (Mean - f_{ci})^2}{n - 1}} \quad (7)$$

### 3.2.2 SEM analysis and thin sections

The microstructure of some of the specimens were analysed with scanning electron microscopy (SEM) and thin sections at CEMENTA Research. After the middle parts were cut out from the prisms they were wrapped up in plastic foil and aluminium foil to protect them from any deterioration during the time until analyses were performed. Of the mixes that was decided to be further studied prism number 1 (the one to the left in Figure 9) from respective mould was chosen.

To be able to study the microstructure and obtain information with SEM the samples needs to be properly prepared. First they were vacuum dried for about two hours in approximately 45°C and then they were impregnated with epoxy resin, which is a low viscous polymer.

The impregnation was performed by placing the sample in a plastic can in a vacuum chamber. The epoxy (NM Injektering INP 003) was mixed with a hardener which was then applied to the sample. This was done under vacuum to ensure that all of the porosity created from leaching gets occupied. The epoxy was left to harden which took about one day. A thin slice of the edge from the sample (which gets covered with epoxy) was then sawn of and the surface of the remaining part was polished in order to get an undisturbed section. The polishing was performed using a Struers DP-U2 having cloths with diamonds of size 6  $\mu\text{m}$  impregnated rotating at around 100 rpm, see Figure 11.



Figure 11: *Left: Impregnation of epoxy resin. Right: Polishing device.*

After the polishing was complete the samples were ready to be analysed in the SEM. The electron microscopy sends an electron beam hitting the sample after which several signals can be detected including secondary electrons (SE), back scattered electrons (BSE) and characteristic X-rays. These signals have different resolutions and energy levels (Scrivener et al, 2016). The weight of the epoxy is lower than that of the cement paste which gives a contrast in the SEM as molecules of lower weight will appear darker on the image. In this way determination of the leached depth is made possible. A HITACHI S-3200N was used for the analyses, see Figure 12. The analyses were performed in vacuum mode with an accelerating voltage of 25-30 kV.



Figure 12: *The scanning electron microscopy used for analyses.*

Some of the specimens were also analysed with thin sections. After impregnating the samples with epoxy a thin part were cut out from the sample and ground to a thickness of about 70  $\mu\text{m}$ . It was then glued to a cover slip and further ground until it was around 20  $\mu\text{m}$  thick using a suspension oil including diamonds of 1-3  $\mu\text{m}$  in size. The thin section was then ready to be examined and the results can be compared to the SEM images.

### **3.2.2.1 Elemental analysis**

The SEM used was equipped with an X-ray detector (Bruker XFlash detector 5030) which makes it possible to perform a chemical analysis and to quantify the amount of different elements using energy-dispersive spectrometry (EDS). This was used to examine the decrease of calcium content in the leached zone.

### **3.2.2.2 Depth of leached zone and porosity**

With images from SEM the depth of the leached zone and its porosity can be estimated. The method for porosity estimation was performed by finding the inflection point of the cumulative brightness histogram of a BSE image. This was performed on an 8-bit image using a greyscale 0-255 in the image analysis program ImageJ, see Wong et al (2006). From the thin sections the leached depth can also be assessed and compared to the SEM images.

### **3.2.3 Water chemistry**

Samples of water were taken from the different curing baths in order to quantify the amount of different ions. For the low pH containers samples were taken after the first day of storage (in deionized water). For the high pH water samples were taken before submerging any prism and after one day of storage. For the middle pH water a single sample was taken at a random time while no sample was taken from the lime water as it was used at a later stage of the experiments.

Moreover, water samples from containers normally used for storage of prisms at several laboratories in Sweden were collected and analysed to be able to compare existing variations that appear under normal circumstances.

The concentration of Na and K are of interest as they are the first to be dissolved. Also, as the concentration of those are increased the solubility of calcium compounds will be decreased. The calcium content is of interest as it can provide indications on the amount of lime that has leached. The water samples were analysed by Eurofins Environment Testing Sweden AB.

## 4 Results of Experiments

The results from the experiments are presented, analysed and discussed in this Chapter. The specimens stored in lime water were cast at a later stage in the project and could not be further investigated after the compressive strength test. Also, not all mixes were stored in this water.

### 4.1 Water, pH and ion comparison

Figure 13 presents the measured pH values for the rapid hardening cement (CEM I 52.5 R) from the different storage environments. For the middle pH, the high pH and the lime water only small changes of the pH occurred. All prisms were in these cases stored in the same containers and the curves are therefore almost identical between all the mixes (all prisms were not submerged on the same day, hence some minor differences). The sudden drops in the low pH containers corresponds to substitution of the water. The rest of the pH graphs are presented in Appendix A.

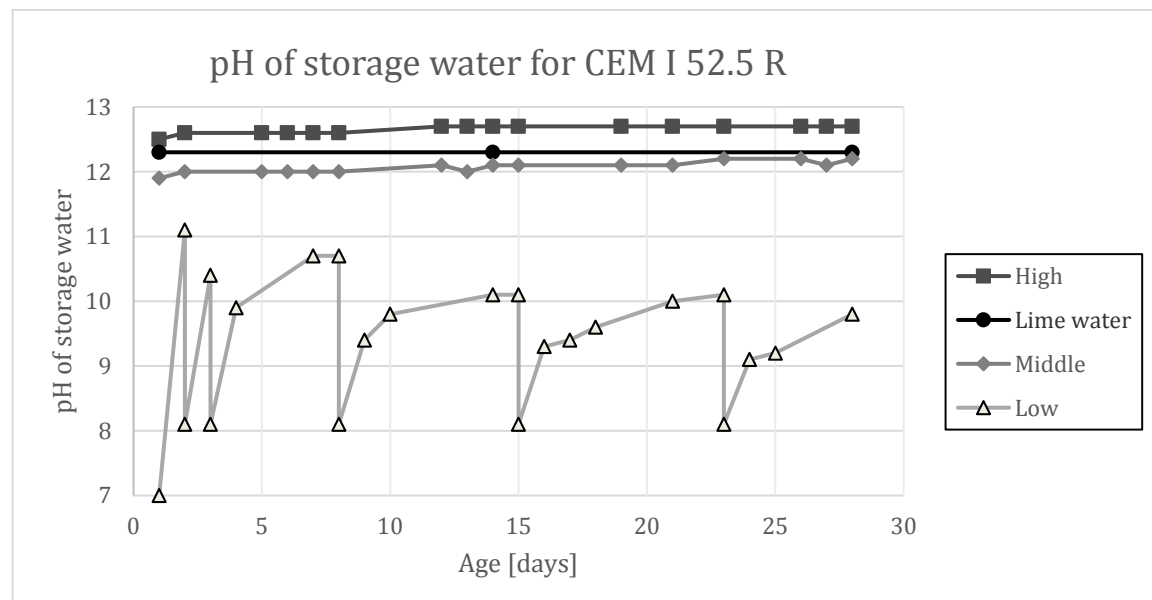


Figure 13: pH values for CEM I 52.5 R in the different storage containers.

From the pH measurements it can be observed that:

- The high pH was 12.5-12.7 throughout the experiments.
- The lime water had a constant pH at 12.3.
- The middle pH was between 11.9 and 12.2.
- The low pH water rapidly increased in pH.

The low pH water was the only case with separate storage containers which allows for comparison between the different mixes. Table 8 lists the pH values measured in the low pH containers the day after substitution of water took place.

Table 8: *pH values in low pH water measured one day after changing the water (at an age of 2, 3, 4, 9, 16 and 24 days).*

	2 days	3 days	4 days	9 days	16 days	24 days
CEM I 52.5 N	10.8	10.2	10.1	9.5	9.2	9.2
CEM I 52.5 R	11.1	10.4	9.9	9.4	9.3	9.1
CEM I 42.5 N	11.0	10.1	10.2	9.5	9.3	9.0
CEM II/A-V	10.9	9.8	-	9.0	8.8	8.6
CEM II/B-V	10.8	9.8	-	9.2	8.7	8.7
CEM II/A-S	10.9	9.5	-	9.2	8.9	8.9
CEM III/A	10.9	10.2	-	9.1	8.6	8.2

The rapid increase of pH for the storage water indicates that leaching occurs. An increasing pH means that OH<sup>-</sup> ions are transported from the prisms to the water. The OH<sup>-</sup> ions are supplied as a result of dissolution and diffusion of compounds.

Following substitution of water the pH is quickly increased for all mixes and each time the water was replaced the pH reached a lower value when measured the day after. This indicates that the leaching slows down over time, which is expected as the leaching time dependency can be described by a square root function (compare to Figure 6 and Equation 5). Furthermore, the prisms gets denser during the hydration by decreasing the porosity which slows down the leaching even more.

The behaviour is similar for all mixes, however the pH seems to not increase as fast when mineral additions were used. This is expected as the cement is diluted by the mineral additions and which in consuming CH decreases the alkalinity compared to the Portland cements. The measured pH for the three CEM I's were relatively similar throughout the whole experiment. It is also of interest to compare the ion content in the waters. The result from the ion analyse on samples taken after one day of storage in the low pH water are presented in Table 9.

Table 9: *Ion comparison of low pH water (after the first day of storage).*

1 day in deionized water	Na (mg/l)	K (mg/l)	Ca (mg/l)
CEM I 52.5 N	1.9	19	3.5
CEM I 52.5 R	1.0	12	3.7
CEM I 42.5 N	< 0.50	9.6	6.8
CEM II/A-V	< 0.50	5.6	7.4
CEM II/B-V	1.6	20	13
CEM II/A-S	< 0.50	4.8	5.2
CEM III/A	1.9	24	14

Sodium and potassium are the first to leach after which calcium compounds are dissolved. From these results it can be calculated how much of the total calcium

content that has been leached from the prisms. The leached zone after the first day can also be estimated based on the results presented in Section 4.3 and Equation 5 giving a depth of 0.1 mm. It can however be argued that the leaching is even faster in the beginning as the hydration is not yet complete. Assuming a leached depth of 0.1-0.2 mm it can be calculated how much of the calcium that has leached from that zone after the first day. Moreover, CH is easily soluble in water compared to C-S-H. Assuming that all leached calcium during the first day originates from CH it can be estimated how large amount of the total CH content that has leached. The results are presented in Table 10, for the calculation see Appendix B.

Table 10: *Calculated amounts of leached Ca and CH (compared to the amount at complete hydration) after the first day. Estimated leached depth after the first day are 0.1-0.2 mm. [% by mass].*

	Loss of total Ca	Loss of Ca in leached zone	Loss of total CH	Loss of CH in leached zone
CEM I 52.5 N	0.028%	1.4-2.8%	-	-
CEM I 52.5 R	0.030%	1.5-3.0%	0.086%	4.3-8.6%
CEM I 42.5 N	0.055%	2.8-5.5%	0.16%	8.0-16%
CEM II/A-V	0.088%	4.4-8.8%	-	-
CEM II/B-V	0.14%	7.0-14%	-	-
CEM II/A-S	0.058%	2.9-5.8%	-	-
CEM III/A	0.14%	7.0-14%	-	-

In general, significant amounts of calcium has been lost from the leached zone after only one day of storage. For the mixes with mineral additions increased amounts of calcium has leached compared to the Portland cements. This may be because the slower hydration and the increased early porosity.

The comparison for loss of CH is based on the amount that is produced after complete hydration. At one day the degree of hydration is about 40% complete (Fagerlund, 2017) which means that 10.8-21.5% for CEM I 52.5 R and 20-40% for CEM I 42.5 N of the so far produced CH in the leached zone has been lost.

In Kurdowski (2014) it is stated that an 18% decrease of lime lead to a 15% reduction of strength while a 27% decrease of lime lead to a strength reduction of 40%. The estimated loss of CH indicate significant leaching which can be expected to have an impact on the compressive strength. CEM I 42.5 N lost considerably more CH than the rapid hardening cement which indicate a larger influence of the leaching in that case. The ion concentrations for the high pH water are presented in Table 11.

Table 11: *Ion comparison for the high pH water.*

	pH	Na (mg/l)	K (mg/l)	Ca (mg/l)
High pH (before)	> 12	12 000	920	13
High pH (after 1 day)	> 12	2 900	1 700	19

After one day of storage in this water large difference in concentration of Na and K were measured. During this first day only prisms of CEM I 52.5 N (six prisms) were stored in the water. Assuming that the concentrations are correct implies that considerable uptake of Na occurred. According to Vollpracht et al (2016) a Portland cement corresponding to the used one (CEM I 52.5 N) has after the first day a pore solution with a K concentration of about 15 600 mg/l and a Na concentration of about 1200 mg/l.

This means that the Na concentration is higher in the storage water than in the pore solution, while it is the opposite for the K concentration. The transportation of Na from the storage water into the prism could therefore possibly happen as the pore solution strive to be in equilibrium with the surrounding water. The concentrations of Ca and K indicate that leaching occurs. Dissolution of CH is possible when the Calcium ion concentration in the pore solution drops below 880 mg/l (compare to Figure 4). For K the increase of concentration is however high compared to the low pH containers and the reason for this is unclear.

Another possible explanation to the large variation of concentrations is that it could depend on how stirred the water was when taking the sample. The water was however taken from the surface while most undissolved compounds gathers at the bottom. The reason for the variations cannot be unequivocally determined, but large amounts of Na was probably present in the water following the addition.

#### 4.1.1 Comparison between laboratories

The variation of storage water taken from curing baths normally used at different laboratories are presented in Table 12.

Table 12: *Comparison of storage water from different laboratories.*

	pH	Na (mg/l)	K (mg/l)	Ca (mg/l)
Laboratory 1	10.3	55	620	1.1
Laboratory 2	11.5	2 200	8 000	3.4
Laboratory 3 <sup>a</sup>	> 12.0	63	260	150
Laboratory 4	9.9	230	1 200	1.6

<sup>a</sup> This is also the storage water named "middle pH" in the experiments.

From these results it is clear that wide variations of storage water currently exists between laboratories both in terms of pH and ion concentration. The reason for the variations are explained by the routines of changing water and if the storage containers are sealed or not.

Some laboratories just refill water as it evaporates. This means that Na and K never will be removed from the water, hence accumulate into high concentrations. Other laboratories substitute water when the pH reaches a certain point meaning that Na and K will be removed with the water.

In a storage container that is not sealed the calcium can react with carbon dioxide in the air leading to a decrease of pH and calcium hydroxide (forms calcium

carbonate) concentration in the water, while in a sealed container calcium hydroxide will be preserved to a greater extent.

## 4.2 Compressive strength

The measured compressive strength are presented in bar charts. Under each bar the exact value is given. The mean of all values from the same mix and storage water is calculated to simplify comparison. Also, the standard deviation within each testing is presented. All values are given in MPa. All results from the compressive strength tests are reported in Appendix C. The results from CEM I 52.5 N is presented in Figure 14.

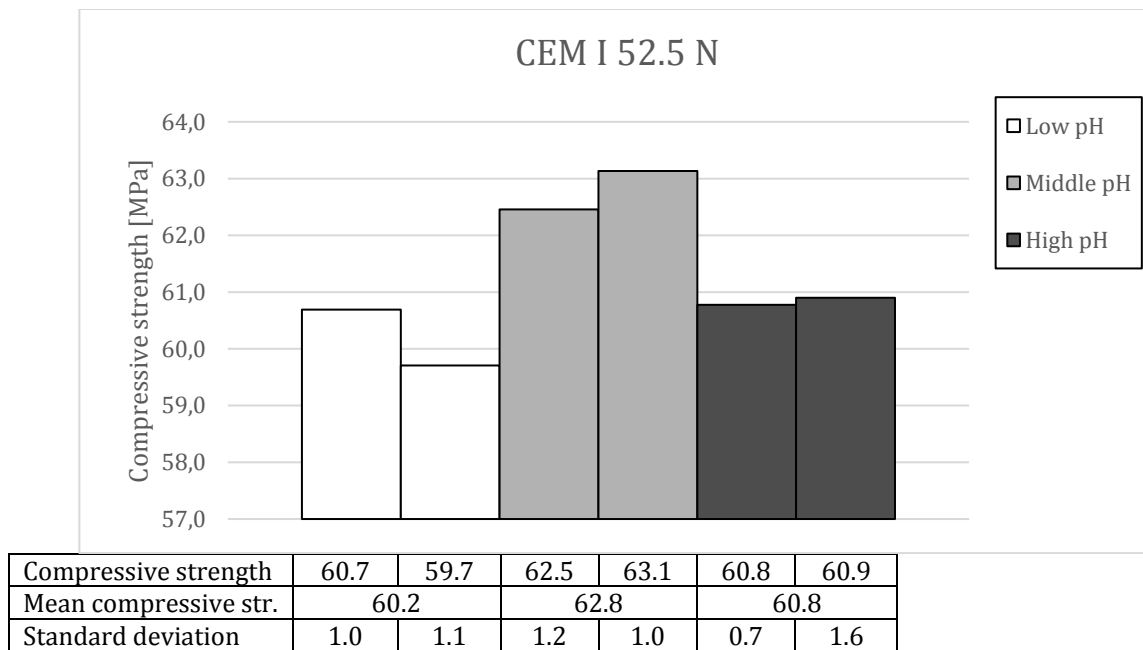


Figure 14: Compressive strength and standard deviation for CEM I 52.5 N.

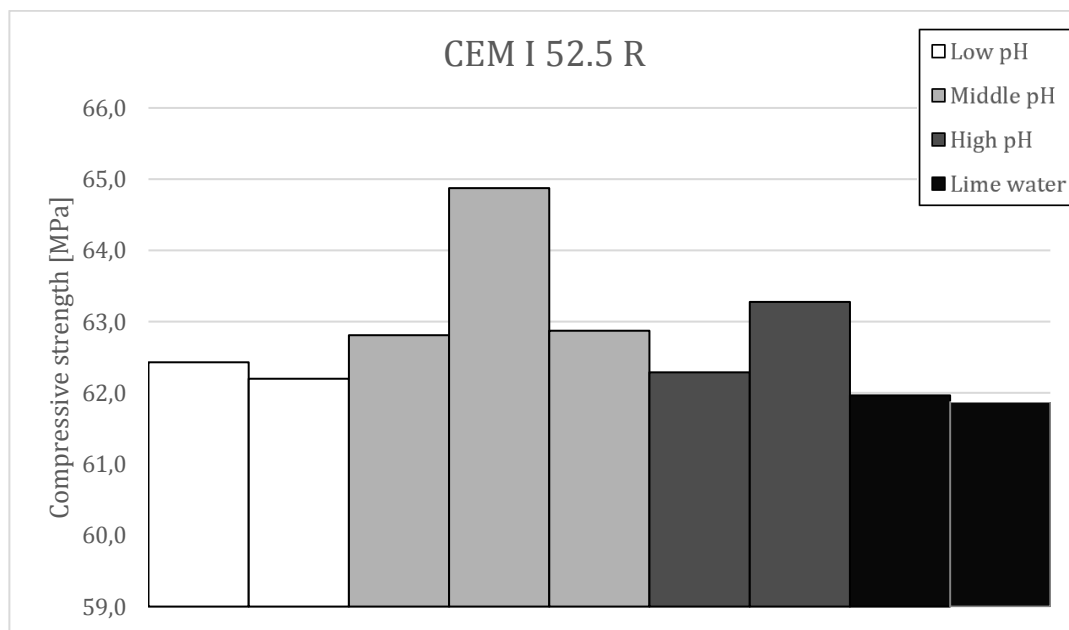
As can be observed, for the CEM I 52.5 N, there are a difference in compressive strength between the storage environments. Also, there are some variations within the same water which could be expected considering natural variations. Comparing the mean strength obtained when storage occurred in low pH water instead of the middle pH water results in a reduction of 2.6 MPa (4.1%). It appears as leaching occurred in the low pH curing environment leading to an impact. However, the specimens from the high pH storage also got lower strength than those from the middle pH water. This is unexpected as there should only be minor leaching in this environment and the specimens should therefore not obtain reduced strength.

It can potentially be so that a mechanism other than leaching influenced the results. The main difference between the high pH water and the middle pH water is the NaOH addition. The idea was that the solubility of calcium compounds would be decreased in a solution of NaOH and therefore further boost the environment to prevent leaching. It has however been found that large amounts of alkalis can have a detrimental impact on the strength when the addition is made to the mixing water.

Smaoui et al (2005) observed that the addition of NaOH to the concrete mixture water significantly reduced the compressive strength (17% decrease at 28 days) and explained it to be due to the evolution of a more porous cement paste in the presence of high alkali content. Mota Gasso (2015) concluded that the addition of NaOH to the mixing water accelerated the very early hydration, but at later ages the degree of hydration were lower. It was seen that the morphology of C-S-H changed in the presence of alkalis, but this was not found to have a considerable influence on the strength development. Instead the decreased strength was attributed to the slower hydration process and an increasing porosity.

Adding large amounts of alkalis to the mixing water can consequently reduce strength, but the effect of alkalis in the storage water remains unclear as it has not been found any investigations regarding that. Even so, there may be similar tendencies as when the addition is made already at the mixing stage reducing the strength also in this case. From the water analysis a large decrease of Na was seen after the first day of storage (with only prisms of CEM I 52.5 N). It is possible that an uptake of Na occurred or that the sodium hydroxide somehow affected the prisms. Thus, the alkali addition may have influenced the results, but probably to a smaller extent as less interaction in the case of alkalis in the storage water than in the mixing water is assumed leading to less impact. This may have had an effect on the results explaining the reduced strength in the high pH storage.

For the results from CEM I 52.5 R, see Figure 15.



Comp. str.	62.4	62.2 <sup>a,b</sup>	62.8	64.9 <sup>a</sup>	62.9	62.3 <sup>a</sup>	63.3	62.0	61.9
Mean comp. str.	62.3		63.5			62.8		61.9	
Std. dev.	2.1	1.1	2.6	1.1	1.9	1.4	1.3	1.1	1.5

Figure 15: *Compressive strength and standard deviation for CEM I 52.5 R.*

<sup>a</sup>Analysed with SEM.

<sup>b</sup>Analysed with thin section.

The results from the rapid hardening cement (CEM I 52.5 R) indicates that the leaching had less effect in this case as the variations between the different storage

conditions are relatively small. One single value from the middle pH water was much larger than the others and is deemed to be an outlier. Disregarding that, uniform results were obtained.

As this cement is more rapid the structure will be dense faster leading to a low porosity at an early stage. Porosity has been identified as an important factor when it comes to the influence of leaching with less water accessibility helping to prevent leaching. The effects of leaching is therefore smaller in this case and it is expected to see less difference between the curing conditions.

For the results from CEM I 42.5 N, see Figure 16.

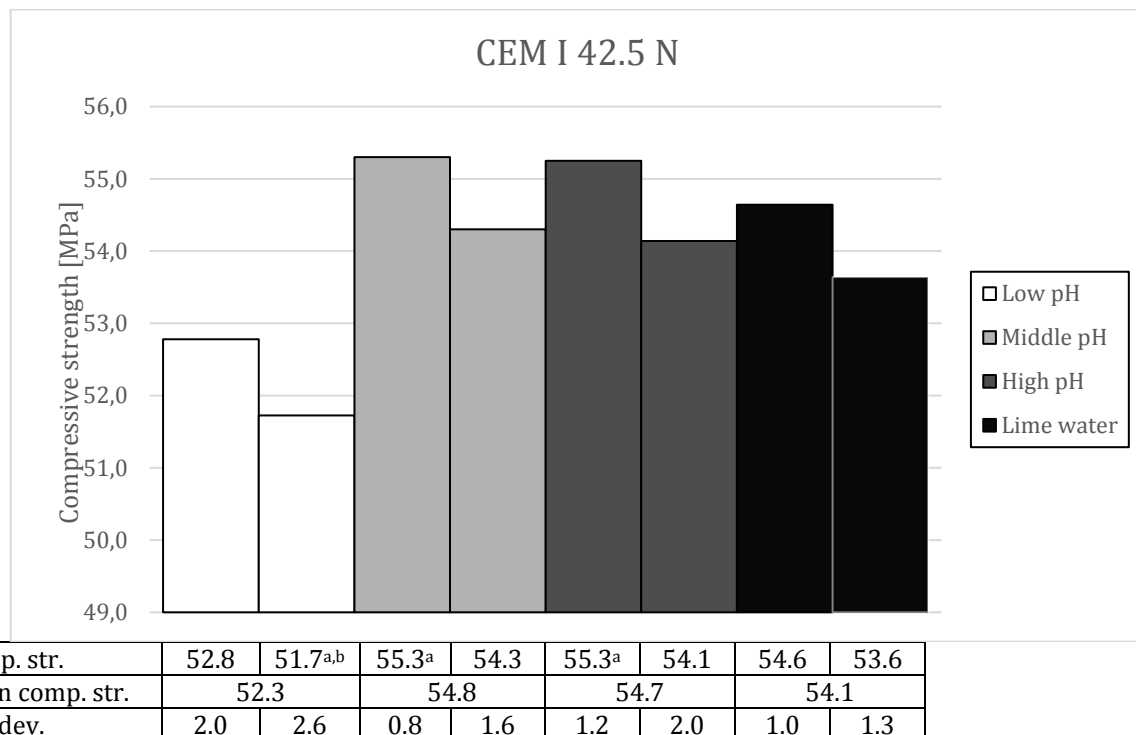


Figure 16: *Compressive strength and standard deviation for CEM I 42.5 N.*

<sup>a</sup>Analysed with SEM.

<sup>b</sup>Analysed with thin section.

For this slower reacting cement (CEM I 42.5 N) there are an apparent influence of the curing environment. The strength was reduced in the low pH water compared to all the other environments, which produced results that agrees well. The average loss of strength when stored in low pH was between 1.8 and 2.5 MPa which corresponds to 3.3-4.6%. Again, the leaching occurring in this water suggests a substantial impact.

Neither this cement nor the rapid hardening was observed to obtain reduced strength in the high pH water, which was the case for CEM I 52.5 N. Assuming that there actually was an uptake of Na by the CEM I 52.5 N prisms would mean that considerably lower Na amounts were present when prisms of other mixes were submerged. In that case the influence of alkali would be lower for these mixes.

Another possible explanation could be that the lower already existing C<sub>3</sub>A and alkali content reduced the effect for CEM I 42.5 N, however the rapid hardening cement which similarly to CEM I 52.5 N have larger amounts of C<sub>3</sub>A and alkali was not seen to be affected. It could be possible that the more rapid hydration reduced the effect also in this case. The influence of alkalis in the storage water is however unclear and needs further investigation to ascertain its impact and how this would differ between various types of binders.

For the results from the mix including 15% fly ash, see Figure 17.

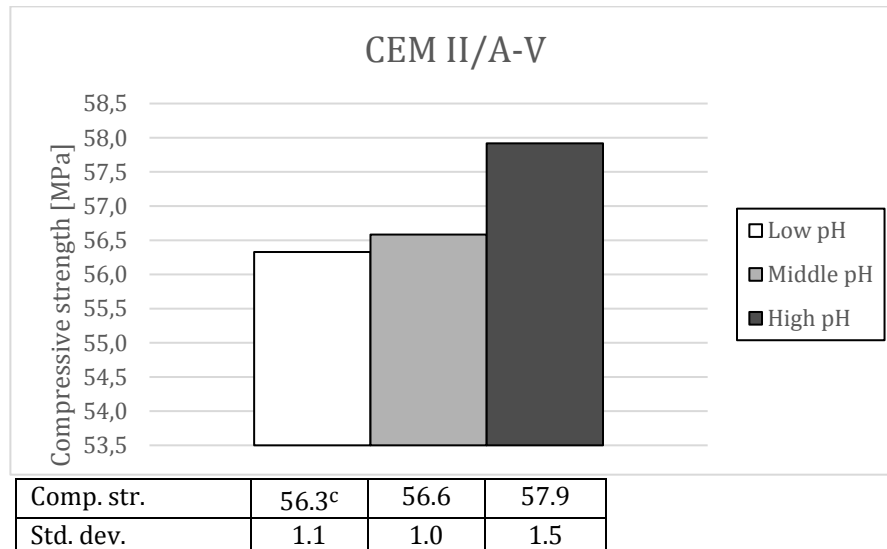
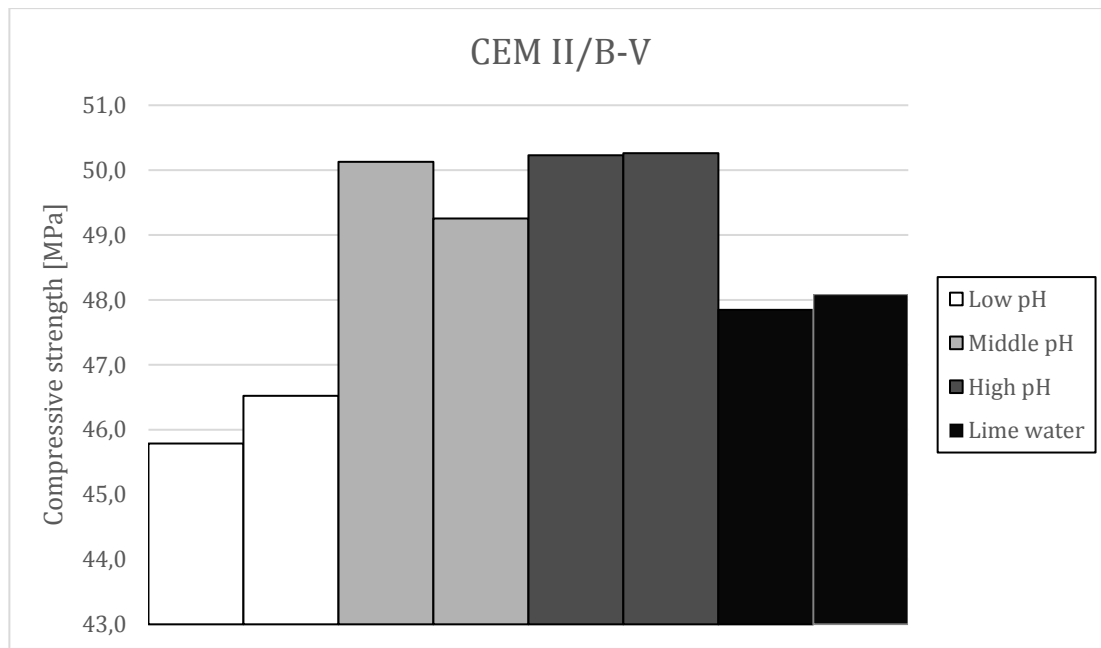


Figure 17: *Compressive strength and standard deviation for CEM II/A-V.*

<sup>c</sup>Based on five results as one deviated more than 10% from the mean.

In the case of 15% fly ash replacement (CEM II/A-V), no major difference between the waters are seen, even though the result from the high pH water was slightly higher than the others. Double testing was not done for this mix making it harder to draw conclusions and it is for that reason difficult to determine the influence of the storage water and any leaching in this case.

For the results from the mix containing 30% fly ash, see Figure 18.



Comp. str.	45.8 <sup>a</sup>	46.5	50.1 <sup>a</sup>	49.3	50.2	50.3	47.8	48.1
Mean comp. str.	46.2		49.7		50.2		48.0	
Std. dev.	1.6	1.4	1.2	0.6	0.8	1.0	2.0	2.0

Figure 18: *Compressive strength and standard deviation for CEM II/B-V.*

<sup>a</sup>Analysed with SEM.

In the case of 30% replacement by fly ash (CEM II/B-V) significant differences were detected. The results from the middle and high pH storage waters were uniform, but in average 3.5-4 MPa larger than those from the low pH water (7.0-8.0% strength reduction in low pH). Cements containing large amounts of fly ash are slow due to the pozzolanic reactions and has increased porosity at early age meaning that the effect of leaching could be expected to be large.

The specimens stored in lime water got lower strength than the middle and high pH storage which is surprising, especially as the difference is rather large at about 2 MPa and double testing was done. Leaching should be well prevented in this environment and the reason for the strength reduction would have to be further investigated to find an explanation.

For the results from the mix containing 20% GGBS, see Figure 19.

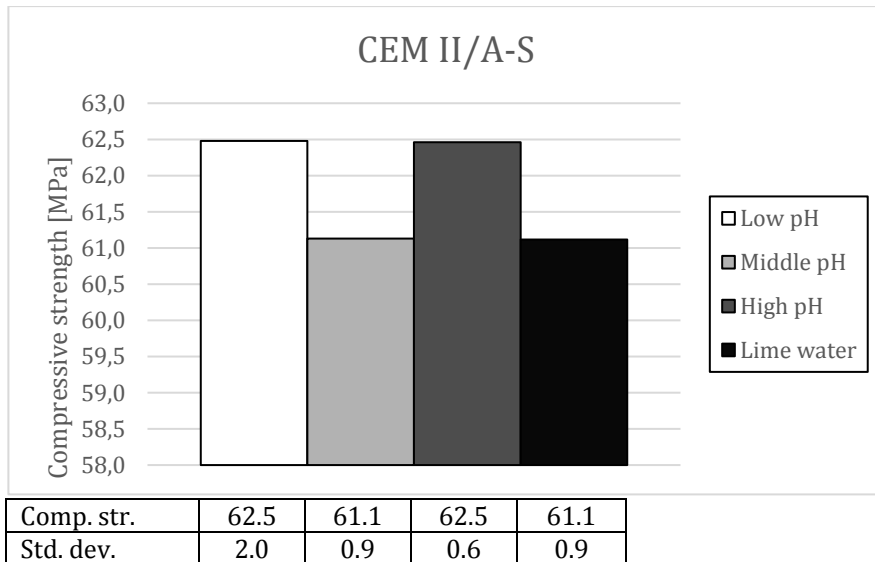


Figure 19: *Compressive strength and standard deviation for CEM II/A-S.*

For this mix with 20% GGBS (CEM II/A-S) no major difference between the curing environments are seen. The specimens cured in low pH water actually got higher strength than the others, which is of course not what could be expected. Again, only single testing were performed and the variation of the results are not unrealistic if the effect of leaching was small in this case.

For the results from the mix containing 50% GGBS, see Figure 20.

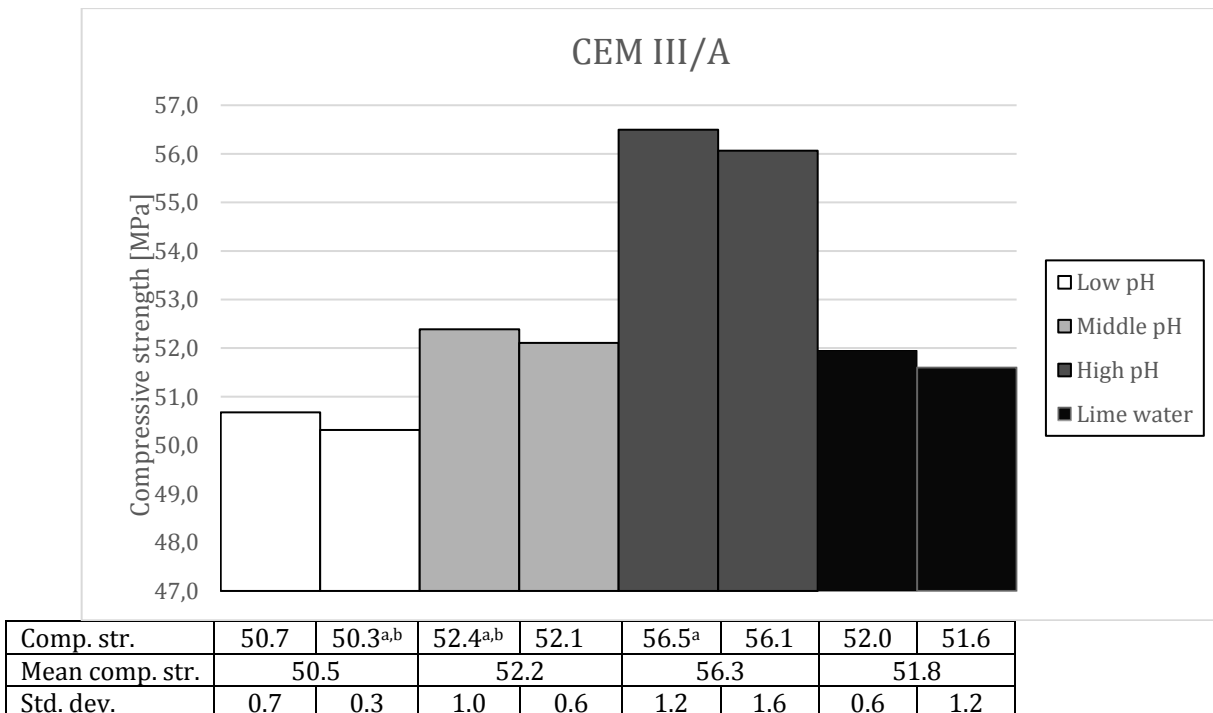


Figure 20: *Compressive strength and standard deviation for CEM III/A.*

<sup>a</sup>Analysed with SEM.

<sup>b</sup>Analysed with thin section.

When 50% slag was used (CEM III/A) the difference between the waters were more prominent. Especially, the high pH water got huge strength compared to the others. This is likely be the result of a more rapid hydration following the alkali addition as it activates the slag, and sodium is a more effective activator than calcium which could explain the results compared to the lime water. This can also be compared to the fly ash mixes, which on the other hand is not activated by sodium, and showed no major difference between the middle and high pH water. Although indications of an impact by alkalis on some of the results are seen, further investigations are needed to sort out its effect.

The results from the middle pH and the lime water corresponded well and was 1.3-1.7 MPa in mean higher than those from the low pH water (strength reduction of 2.5-3.3% in low pH). Again, leaching seems to have a detrimental impact for cement prisms stored in low pH.

Summarising the results it can be concluded that the measured compressive strength is often reduced when stored in the low pH water. This curing environment favours leaching and the following loss of strength is expected. The effect was however not similar for all binders. The influence of leaching on the rapid hardening cement is not obvious as the results was rather uniform. A larger porosity has in the literature been demonstrated to facilitate leaching kinetics, but the quick hydration of this cement leads to low porosity early on and less leaching therefore occurs. There are probably an effect also in this case although it may be so small that the storage water is of less importance in this case. For the other CEM I's the curing environment had an important role which is in line with the slower hydration.

When the lower amounts of mineral additions (15 % fly ash or 20 % GGBS) were used only slight difference between the storage conditions are seen, but when larger amounts (30 % fly ash or 50 % GGBS) were used the results are clearly influenced. As more mineral additions are used the rate of hydration are further slowed down, which explains the more apparent difference for larger amounts of mineral additions. Moreover, the rapid hardening cement was used in the mixes containing mineral additions which could probably decrease the effect of leaching compared to if a slower cement was used.

#### **4.2.1 Statistical assessment**

The storage water appear to influence the compressive strength in some cases, but variations occur naturally and it is therefore of interest to see if the difference is statistically significant. Statistical assessment of the results can be made by analyse of variance (ANOVA), which tests if the means of several groups can be regarded as equal or different. The null hypothesis states that the storage water does not influence the compressive strength, which will be either accepted or rejected in the ANOVA test. If the null hypothesis is rejected the influence of the storage water on the compressive strength is statistically significant meaning that it is unlikely that the results are due to natural variations. The analyses were performed at a confidence level of 95% ( $\alpha = 0.05$ ).

The ANOVA compares the variance of the results within each storage water to the variance between the different storage waters, which gives the F-value. The F-value is then compared to a critical value ( $F_{crit}$ ) which determines if there are any difference between the means. That is, if  $F > F_{crit}$  the null hypothesis is rejected and instead the alternative hypothesis is accepted meaning that the difference is statistically significant. Another equivalent way of rejecting the null hypothesis is when the calculated  $p$ -value is less than  $\alpha$ .

For CEM III/A the results from the high pH water are excluded as they are much higher than the others, most likely as a result of the alkali addition. The ANOVA results are presented in Table 13.

Table 13: Results from ANOVA

Mix	$F$	$p$ -value	$F_{crit}$
CEM I 52.5 N	17.17	$7.7 \cdot 10^{-6}$	3.28
CEM I 52.5 R	2.50	0.070	2.79
CEM I 42.5 N	6.00	0.0016	2.82
CEM II/A-V	2.72	0.098	3.68
CEM II/B-V	21.83	$8.2 \cdot 10^{-9}$	2.82
CEM II/A-S	2.43	0.096	3.10
CEM III/A	15.92	$1.4 \cdot 10^{-5}$	3.28

For CEM I 52.5 N, CEM I 42.5 N, CEM II/B-V and CEM III/A the null hypothesis can be rejected and it therefore exists a statistically significant difference between the storage waters according to ANOVA. For the other three mixes the null hypothesis was however accepted. The statistical assessment agrees well to the visual examination of the presented results.

### 4.3 Leached depth

In order to investigate the extent of the leached zone some specimens were analysed in the SEM and with thin sections. The leached depth of the specimens are of interest to see if there are any relation to the lower strength obtained from the low pH environment.

#### 4.3.1 SEM images

From the SEM images it was found that the leached depth are not constant over the entire cross-section but instead it varies depending on several factors such as position of aggregate, pore positions and water accessibility. Figure 21 shows an example of a SEM image, more images are found in Appendix D. The darker parts of the cement paste indicate the presence of the epoxy which corresponds to leaching.

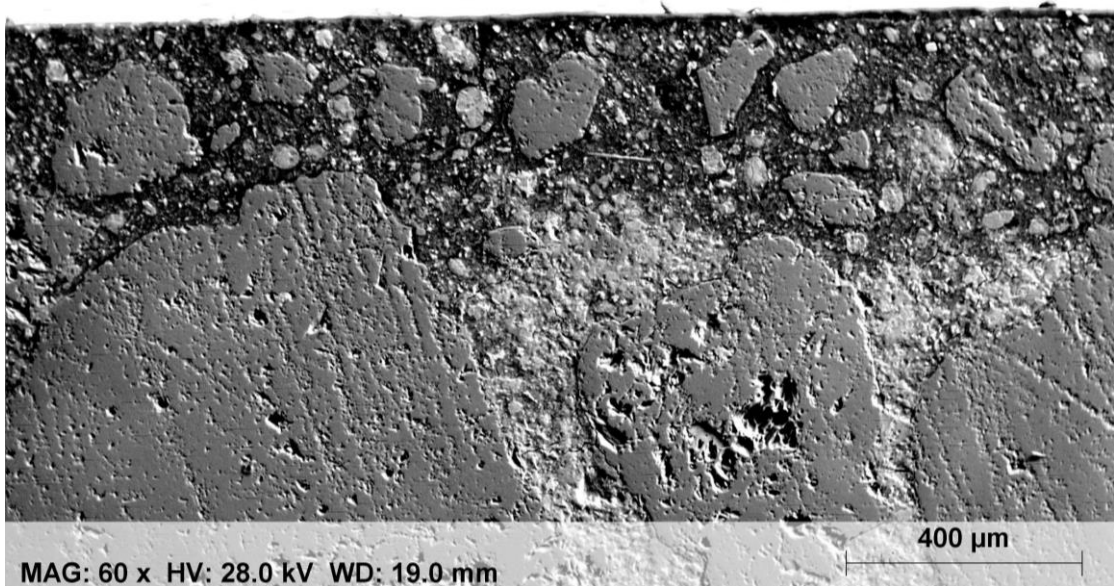


Figure 21: SEM image showing the variation of the leached depth. In this case the border between the leached (top surface) and sound zone is rather clear. (CEM I 42.5 N stored in middle pH water).

The leached depth was estimated based on several images from each specimen. The border between the zones were not always easy to distinguish and sometimes there were large differences between different images of the same specimen. The images at hand covers only minor parts of the prisms and therefore local variations can influence the estimation of the depth. Figure 22 presents a rough estimation of the leached depth for the different mixes stored in the different curing waters based on the SEM images. Due to difficulties in determining the border between the zones, the values should be seen as an indication on the leached depth rather than an exact limit. In particular the result for CEM I 42.5 N stored in low pH water is uncertain due to large variations, but further analysis of thin sections (see Section 4.3.2) indicate increased depth.

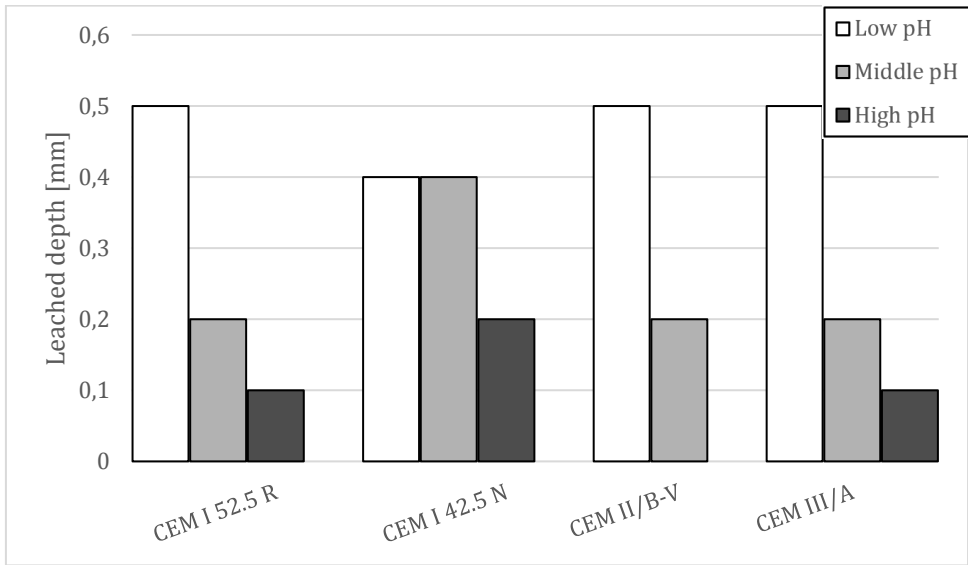


Figure 22: Estimated leached depth for the analysed specimens based on the SEM images.

For the specimens stored in the low pH environment the leached zone were in general increased compared to the other storage conditions, which is of course expected. The leaching front typically reached around 0.5 mm into the specimens stored in low pH, which corresponds to a degradation ratio of about 5%.

Also, a minor leached zone was found for specimens from the middle pH water and the high pH water suggesting that some leaching occur also in these environments. For the specimens stored in high pH the leached zone was especially difficult to estimate as it was so small and hard to spot.

The results provide indications that the leached depth is influenced by the curing condition. In some cases it is however hard to relate the estimated leached depth to the loss of compressive strength. The rapid hardening cement was not observed to be influenced by the storage condition regarding the compressive strength but there are a clear difference in leached depth in this case. On the other hand, CEM I 42.5 N got reduced strength in the low pH environment but the leached depth did not differ as much between the waters in this case. For the mixes with mineral additions the increased leached depth in low pH water fits well with the reduced strength.

#### **4.3.2 Thin sections**

The leaching could also be detected with the thin sections. These images provide further evidence that the leaching was increased for the specimens stored in low pH water. Nevertheless, it is still difficult to determine a more exact amount of leaching. Moreover, thin sections were only made on four specimens. An example of a thin section is shown in Figure 23 and a fluorescence image of the same section in Figure 24. The rest of the thin sections are presented in Appendix E.

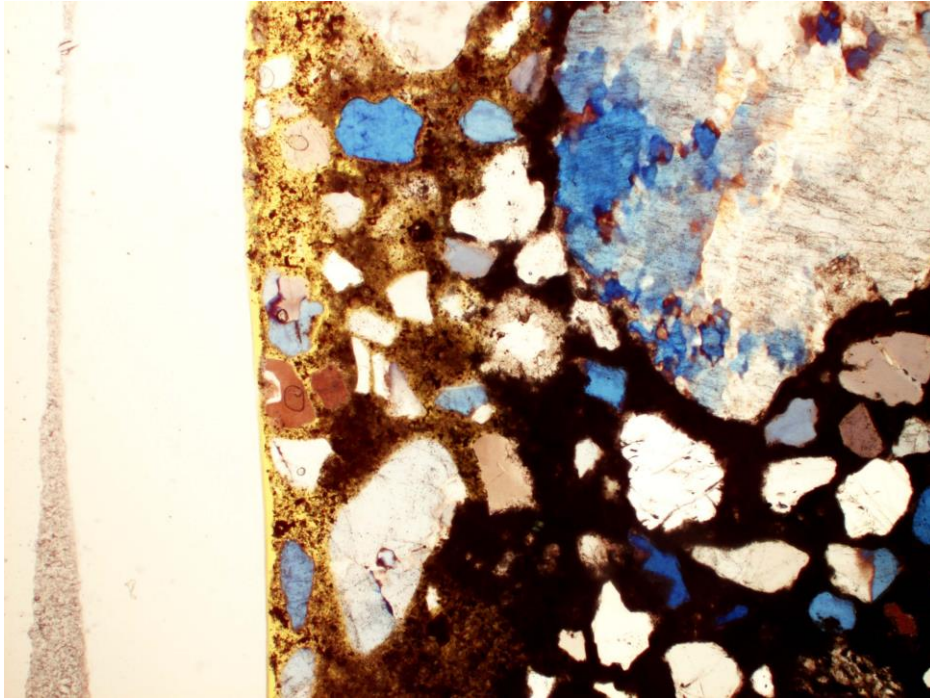


Figure 23: *Thin section of CEM I 42.5 N stored in low pH water. The image covers a width of 2.62 mm and a depth of 1.96 mm with the leached surface to the left.*

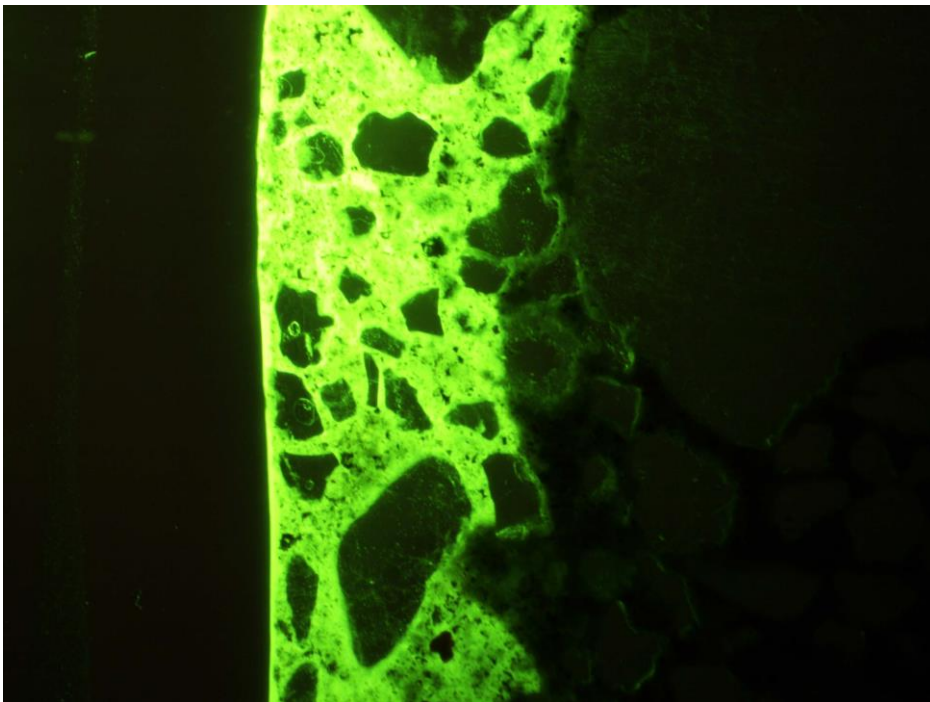


Figure 24: *The same image taken in fluorescence mode.*

In Figure 23 the leaching correspond to the light parts of the cement paste. For CEM I 42.5 N stored in low pH, as seen above, the border between the leached and sound zone is about 0.7 mm into the specimen. Images of other positions of the same specimen show similar depth. This can be compared with the estimations from the SEM images which was in average 0.4 mm (large variations at different positions in this case). For this cement a strength reduction was obtained in the

low pH water and the larger leached zone makes more sense in regard to that. For the three other specimens (CEM I 52.5 R stored in low pH and CEM III/A stored in low and middle pH) the leached depth measured in the thin sections corresponds fairly well to the SEM images, see Figure 25. The only other difference is that the leached depth of CEM III/A stored in low pH is estimated to 0.4 mm instead of 0.5 mm, however only a single image of the thin section was taken in that case.

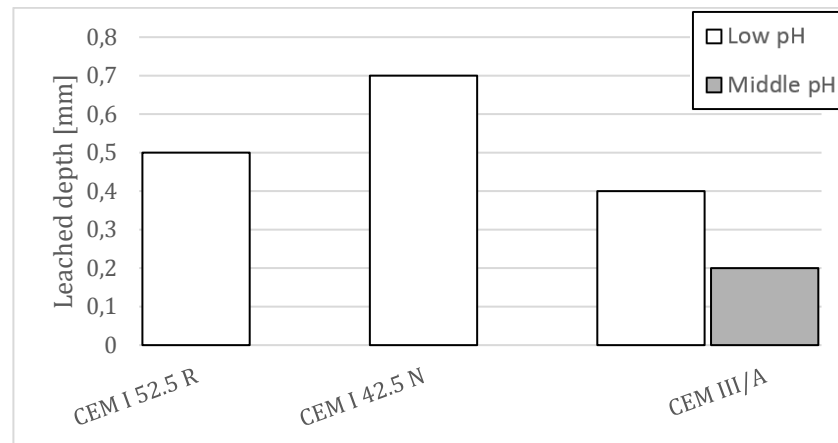


Figure 25: *Estimated leached depth for the analysed specimens based on the thin sections.*

Based on both the analyse in SEM and with the thin sections the trend is clear in that the leaching front reached longer into the specimens stored in low pH environment. In doing so it further confirms that the strength reduction is due to leaching. The estimation could however benefit by the use of other methods for more exact determination of the leaching front and the amount of leaching.

### 4.3.3 Relation to compressive strength

Using the approximate leached depths presented in Figure 22 (based on SEM images) and taking 0.7 mm for CEM I 42.5 N stored in low pH as an improved estimation any relation to the compressive strength can be determined for the tested binders.

The loss of strength versus difference in degradation ratio for the mixes stored in low pH water relative the other waters (middle pH and high pH) is presented in Figure 26.

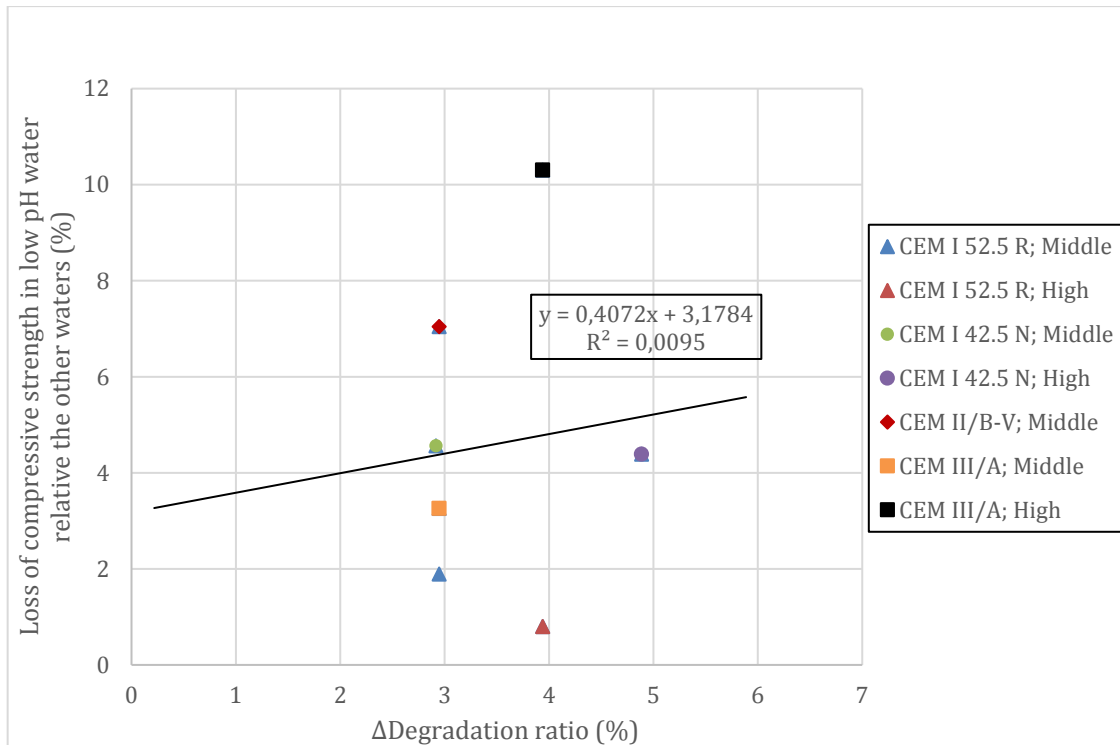


Figure 26: Relation between loss of compressive strength in the low pH water and the difference in degradation ratio.

In all tested cases the leached depth was increased in the low pH water and there were also a loss of compressive strength. However, the correlation between loss of strength and degradation ratio have a very poor  $R^2$  value. This is explained by the leached depth being rather similar for all binders stored in the same water while the compressive strength was influenced differently. The rapid hardening cement stored in low pH got similar leached depth as the other mixes while the compressive strength was only influenced to a minor extent. Also, the huge strength obtained by CEM III/A in the high pH water deviates from the correlation.

A better relation may have been found if a more exact estimation on the leaching front and the amount of leaching was determined. More data points with different leached depths for each binder may also be needed to find a correlation.

#### 4.4 Porosity

The porosity of the cement prisms are increased as different compounds are leached. This increase of porosity reduces the compressive strength and the sound zone will therefore have a larger load bearing capacity than the degraded zone. Initially the intention was to use SEM images to quantify the effect of leaching on the porosity. However, the SEM images could not be used as intended. Instead, a qualitative assessment is shown for one of the images, where an area from each zone is selected, see Figure 27. The pores corresponds to dark pixels on the SEM image.

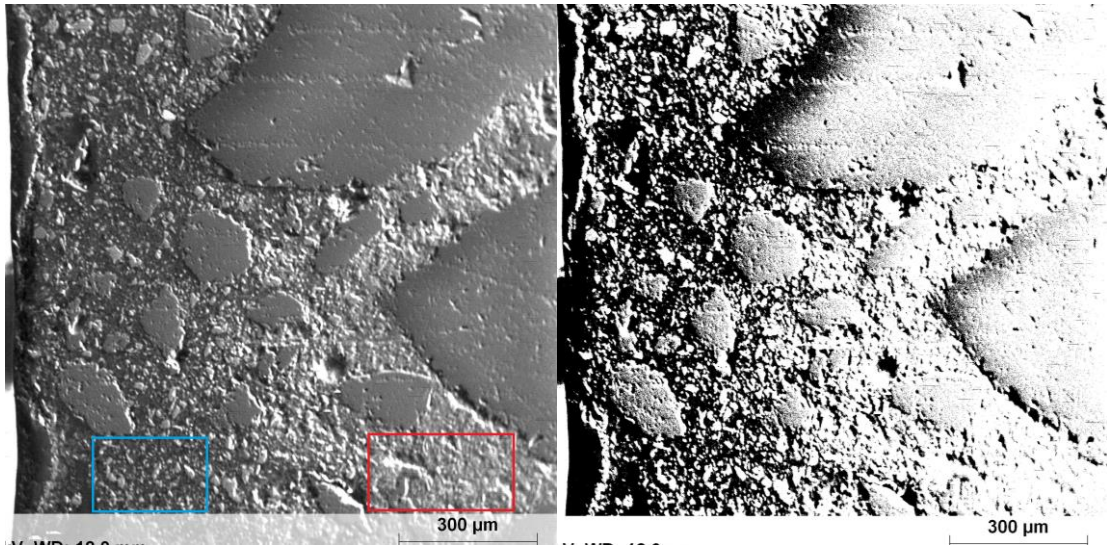


Figure 27: *CEM I 42.5 N stored in low pH water. Left: SEM image with selected areas. Right: Same image at threshold level 92 indicating a gradual transition from leached to unleached.*

It is from these images clear that there are a difference in greyscale for the leached and sound zone, which indicate that the leaching had an impact on the porosity. The brightness histogram and the cumulative greyscale histogram of the selected areas are presented in Figure 28 and 29.

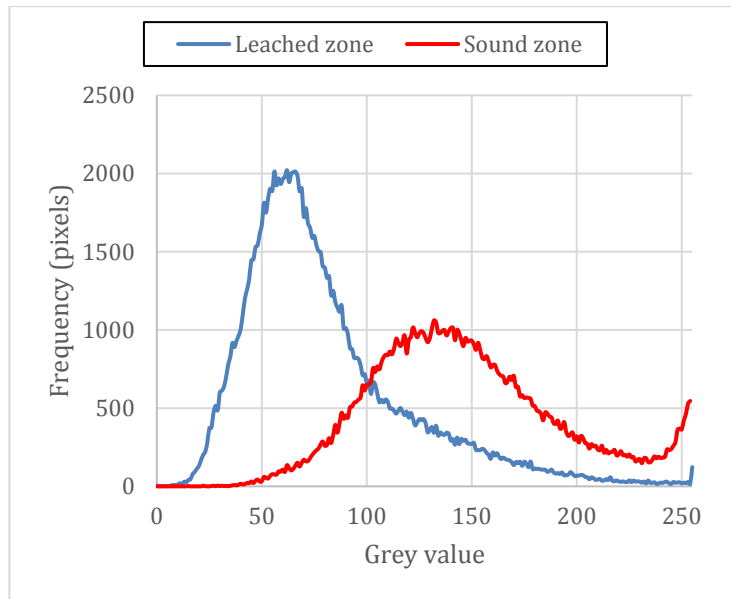


Figure 28: *Brightness histogram.*

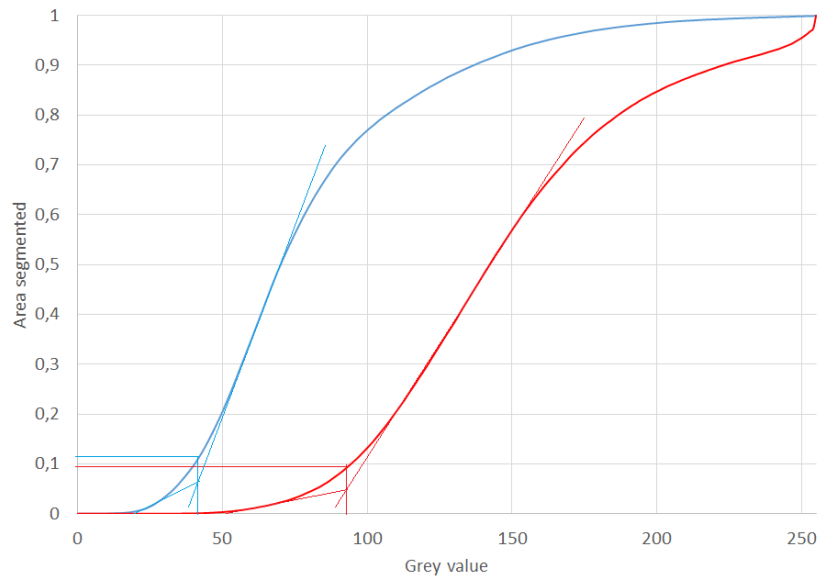


Figure 29: *Cumulative greyscale histogram. The threshold value for porosity is for the curve corresponding to the sound zone determined to 92 from the estimation of the inflection point.*

Both the brightness histogram (Figure 28) and the cumulative greyscale histogram (Figure 29) shows large variations between the zones which implies a change of porosity. It is however difficult to quantify the porosity for comparison based on the images at hand. In order to do that type of analyse images of specimens without aggregate would be favourable. Also, the resolution and magnification of the images, as well as the polishing of the specimen are important.

## 4.5 Chemical composition

When leaching occurs the chemical composition will change as CH is first dissolved which is followed by decalcification of C-S-H. This results in reduced

calcium content in the leached zone. Mapping of some different elements are seen in Figure 30. The Si mapping indicates the position of aggregates while the Ca mapping shows that the calcium content has been clearly reduced in the outer parts (leached zone to the right in Figure 30).

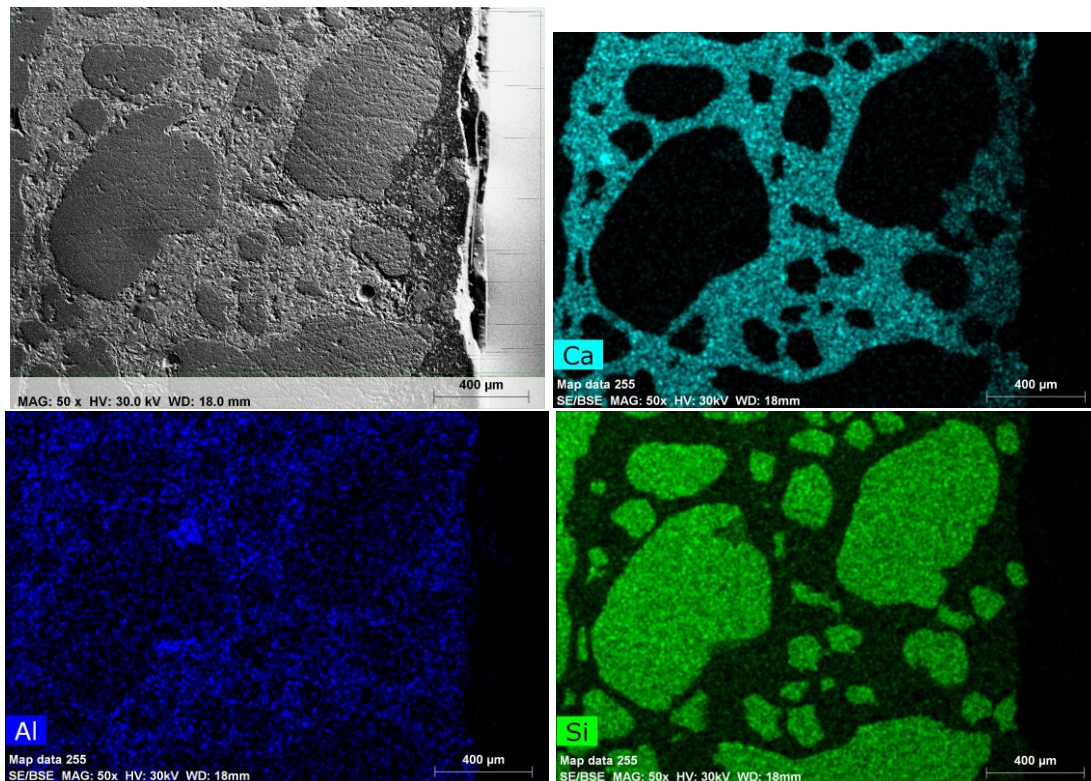


Figure 30: *Mapping of Ca, Al and Si together with the original BSE image of CEM III/A stored in low pH water. Leached zone to the right.*

From these images it can however not be seen if the reduced calcium content originates from leaching of CH or if decalcification of the C-S-H phase has also started to occur. From Ca mapping of specimens stored in middle and high pH water some reduced calcium content is also observed, although not seen as clearly. As it is difficult to estimate the progress of leaching based on the mapping, comparison between specimens stored in different waters provide no particularly useful information. To identify the development of leaching in different storage waters it would be necessary to estimate the C-S-H composition and its Ca/Si ratio which needs other methods. The mapping provides another evidence on the presence of leaching though.

## 5 Modelling of leached zone

Modelling of the cement prisms has been carried out in order to estimate the effect on the material properties, depending on the depth of the leached zone and the impact on the compressive strength. The commercial FE software ABAQUS was used to set up a model. The modelling constitute only a minor part of the work and a simple model was therefore chosen.

### 5.1 Description of model

The geometry was taken as a prism modelled in 3D. The prism dimensions were 40x40x60 mm being extended by ten mm at each side of the loading plates to better represent the actual condition (Compare to Figure 10). The effect of leaching was taken into account by introducing a leached zone with degraded material properties. The corners of the leached zone was slightly rounded (radius 1 mm) which could be expected following leaching from two directions. Figure 31 illustrates the geometry of the model. The boundary conditions was set at the bottom surface of the prism to be restrained in all directions and a load was applied at the top surface.

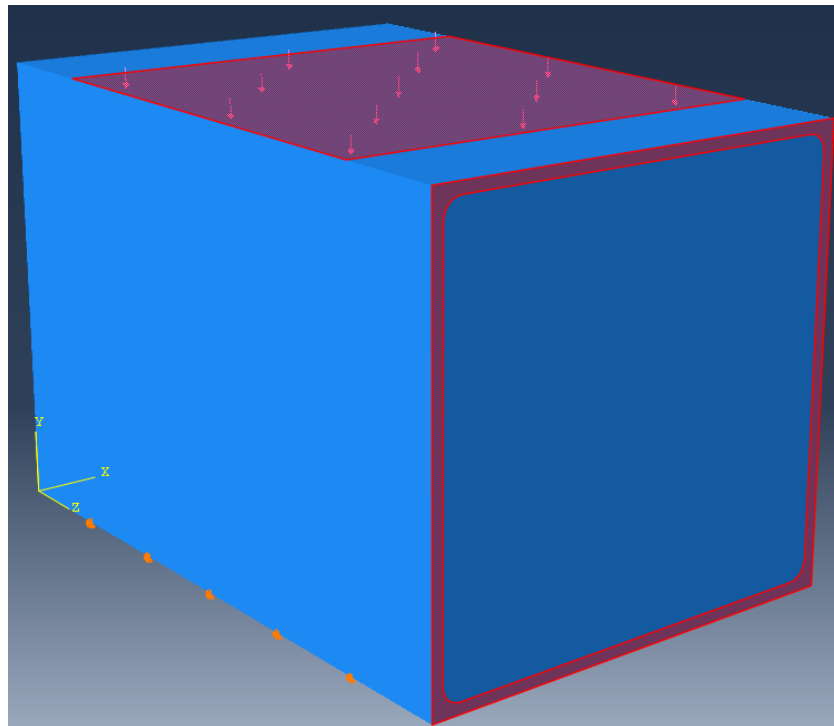


Figure 31: ABAQUS model showing the geometry.

Linear elastic material properties was used and the degradation of the leached zone was modelled by assigning a decreased Young's modulus. This results in a stress redistribution from the leached to the sound parts. The stress is therefore increased in the sounds zone where the failure takes place. The material properties used for the sound zone are presented in Table 14.

Table 14: *Linear elastic material properties used for the sound zone in the model.*

	Young's modulus ( $E$ )	Poisson's ratio ( $\nu$ )
Sound zone	25 GPa	0.2

The mesh was generated with continuum solid elements of type C3D8R. Several mesh sizes were tried until a dense enough mesh (approximate global mesh size set to 1 mm) was obtained which was used for the analyses.

## 5.2 Comparison between cement prisms and model

The comparison was made by examining how much the Young's modulus had to be decreased in order to get the same maximum stress for a leached prism as when unleached. Some examples were taken from the compressive strength tests where the results are from the low pH water (leached) and the middle pH water (assuming no leached zone). Table 15 presents the results from the modelling for a few chosen leaching fronts.

Table 15: *Estimated Young's modulus (and residual Young's modulus) in leached zone (for leached depths of 0.3, 0.5 and 1 mm) based on some examples of strength reduction from experiment results.*

Cement type	Loss of compressive strength	Leached zone of 0.3 mm	Leached zone of 0.5 mm	Leached zone of 1 mm
CEM III/A	1.7 MPa (3.3%)	5.3 GPa (21.2%)	10.7 GPa (42.8%)	15.6 GPa (62.4%)
CEM I 52.5 N	2.6 MPa (4.1%)	2.8 GPa (11.2%)	8.1 GPa (32.4%)	14.9 GPa (59.6%)
CEM II/B-V	3.5 MPa (7.0%)	-	2.0 GPa (8.0%)	10.1 GPa (40.4%)

The leached zone has for the specimens stored in low pH water been estimated to be around 0.5 mm. It was however not assessed how far developed the leaching in that zone were. Also, for the specimens stored in the middle pH water some leaching occurred which was not taken into account in the model.

The residual Young's modulus after complete leaching has been estimated to 50-60% (Babaahmadi, 2015), 36% (Nguyen et al, 2007) and less than 20% (Stora et al, 2009). From these results it is clear that wide variations between the estimation of Young's modulus exist.

Compared to these other results the model probably overestimate the needed decrease of Young's modulus considering that complete leaching is not expected for the cement prisms. A leached zone of 1 mm seems to give more reasonable values for Young's modulus. Better approximations require a more advanced model. It is however seen that a decrease of the material properties in the leached zone is expected to have an influence on the compressive strength.

## 6 Discussion

In the course of the experiments some deviations from the standard were made regarding the storage water in order to obtain different properties. For the low pH water deionized water was used during the first day and at the time of substituting water all was replaced, which is not allowed in the standard. However, as the size of the storage containers used in the experiments were small the ratio between the volume of storage water and the volume of prisms were small compared to normal circumstances. In most laboratories it is probably so that a much larger storage container is used. This could result in large volume of storage water in relation to prisms for which the pH and ion concentration would not increase as fast and the concentration gradient would remain longer. It is therefore not unlikely that the low pH environment used in this project corresponds to a large storage container with few prisms. The high pH water and the lime water were boosted to prevent leaching which is not according to the standard. In a storage container where the water is never replaced the basicity will however eventually be very high. The curing environments used in the experiments are therefore not considered to be more extreme than the existing variations between laboratories.

The water curing environment has been demonstrated to be important for the strength development. It has been observed that a reduction of the compressive strength by several MPa's are a likely consequence when a solution of low pH and ion concentration are used during testing. It was seen that large variations of storage water between laboratories currently exists, even within the same country. This may cause a large, undesirable spread when the same cement is tested by laboratories that interprets the methods in the standard differently. For the cement producer it is vital that the determination of strength is performed with a reproducibility that is satisfactory as every MPa is important. If the actual strength is greater than obtained from the testing method it could probably be possible to reduce the content of certain components in the cement, which in turn could save resources in terms of both costs and environmental impact. The influence of the storage water is clearly one factor that is omitted in the standard. With this in mind it is recommended to introduce regulations on the storage water to obtain a more uniform test method where results may agree better between laboratories.

Based on the results from this study it is recommended to cure specimens in an environment which prevents substantial leaching in order to not obtain reduced strength. The water should not contain to high amounts of sodium or potassium alkalis as this may affect the strength depending on the cement composition. The best approach is probably to use lime saturated water when a new curing bath is started.

## 7 Conclusions and further studies

In the laboratory experiments conducted in this study it was investigated how cement prisms are influenced by different curing conditions when assessing the compressive strength according to the standard EN 196-1. The aim was to estimate how much leaching, due to variations of the storage water, could contribute to the observed variations between laboratories. In this Chapter the conclusions and some suggestions for further studies are presented.

### 7.1 Conclusions

The most important observation from this study is that the storage water has an impact on the result when compressive strength of cement prisms are tested according to the standard EN 196-1. The conclusions are as follows:

- Based on the analysed storage water from accredited laboratories in this study, large variations concerning the storage water regarding both pH and ion concentration were found. However, the analyses of water samples included only a small selection of laboratories.
- In general, specimens stored in water with low pH and low ion concentration obtained reduced compressive strength. This was concluded by examination of the results and further validated by statistical assessment. The strength reduction are proposed to be attributed to leaching which is favored by the use of a soft water.
- The effect on all types of binders were not the same. The rate of hydration appear to influence the leaching. Slower hydrating mixes seems to be more prone to an attack and can undergo a significant strength reduction due to leaching. In this study, a loss of up to 4 MPa (8%) was observed. The effect on mixes with a rapid hydration was however small. On the other hand, for slag cement (CEM III/A) it was seen that a high concentration of Na increased strength.
- Leaching depth was assessed through analyses conducted with both SEM and thin sections. Estimations of the leached zone indicate relatively similar total depths for all tested binders stored in the same storage water. However for specimens stored in low pH environment increased leaching depths were found, with an approximate penetration depth of 0.5 mm.
- Based on the results of this study, in order to yield more uniform results between laboratories, it is recommended to use lime saturated water when a new curing bath is started. This will prevent strength reduction due to leaching. In addition, an acceptable concentration of calcium, sodium and potassium might need to be specified as high concentrations of Na or K versus Ca may influence the strength differently.

## 7.2 Further studies

In this project it was found that the curing water had an impact on the compressive strength. It would be valuable to investigate if there exists a correlation between the pH or ionic concentration (Ca, Na, K) of the storage water and the compressive strength when the testing is performed at different laboratories in larger scale. This could for example be carried out within an inter laboratory study such as ATILH. The result from a study like that could provide further validations on the influence of the storage water and form the basis for any future change of the standard.

The alteration of the leached zone could be further studied to provide information on how far developed the leaching is. This could be done according to the following:

- The chemical composition of the specimens could be investigated. A possible approach would be to plot atomic ratios (e.g. Si/Ca and Al/Ca) from EDS analyses on 2D scatterplots which enables estimation of the composition of C-S-H. Comparison between different depths of the leached zone and the inner sound zone could then be done and how this differ between specimens from different storage waters. This could determine whether the reduced calcium content originates from only portlandite leaching or if C-S-H decalcification also started to occur.
- Analysis of cement paste specimens could also be helpful in order to assess the leaching regarding e.g. loss of calcium hydroxide and any change to the mineralogy of the hydrates. The analyses could include SEM, EDS, XRD (X-ray diffraction), TGA (thermogravimetric analysis)/DTGA, NMR (Nuclear magnetic resonance) and Micro CT-scanning.
- The increase of porosity could be better estimated and compared for specimens from different curing baths. In order to do so it would be favorable with images of higher resolution and magnification or cement paste specimens, not containing aggregate. Other methods of determining porosity could also be considered.

Another issue to be further studied is the effect of alkalis in the storage water. An impact on some of the results was seen in this study, but the influence on different types of binders are unclear.

Furthermore, the simplified modelling carried out in this project could be improved to get better approximations on the effects of leaching depending on the extent of the leached zone and the degradation of material properties. A more advanced model should consider non-linear material properties and the modelling could be carried out at the mesoscale to capture the cracking behavior and the failure. The model could also consider the leaching process (multi physics).

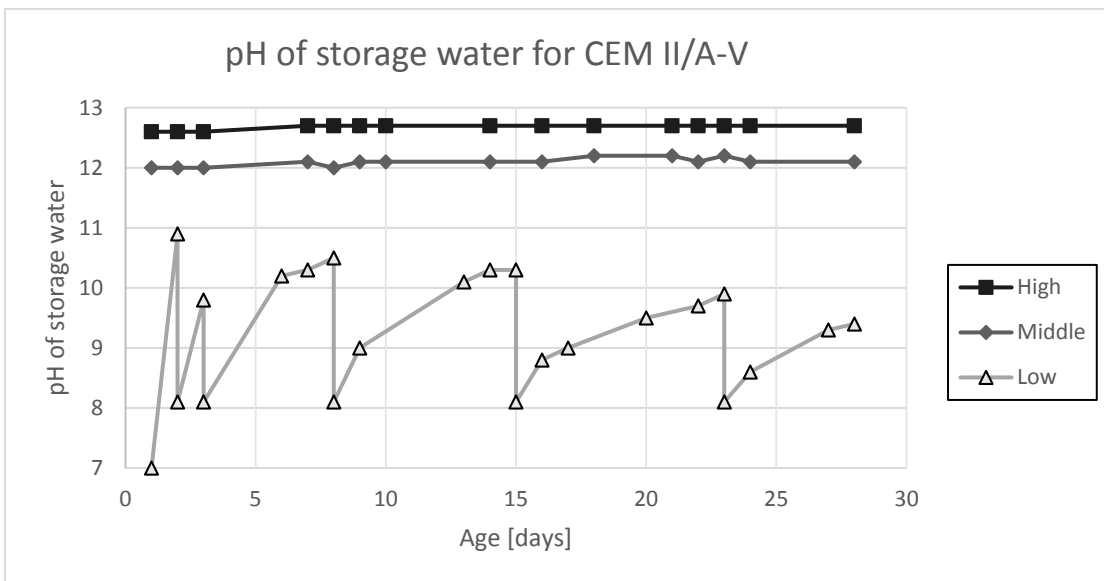
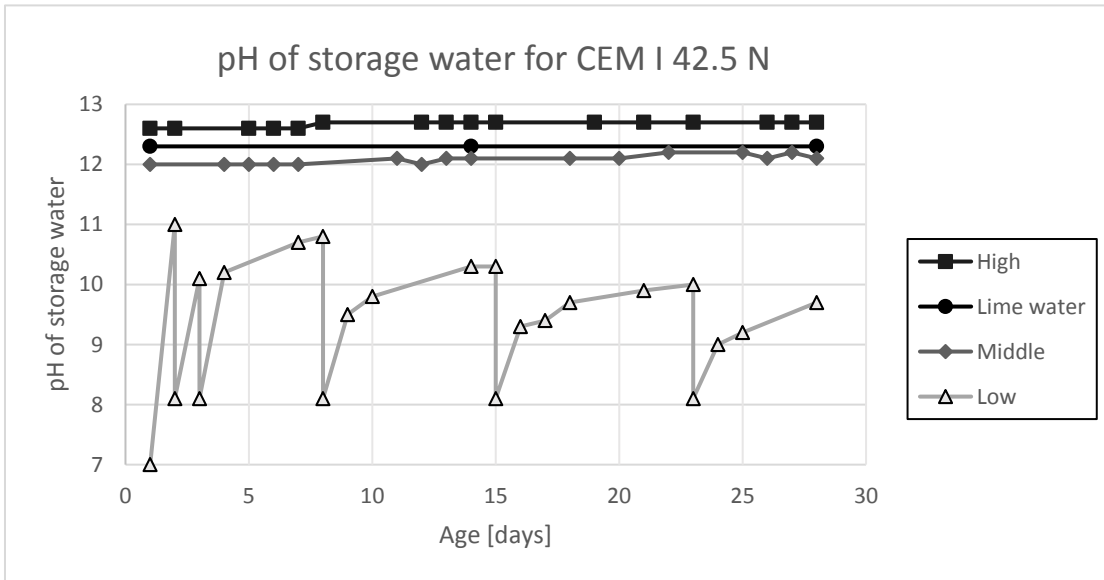
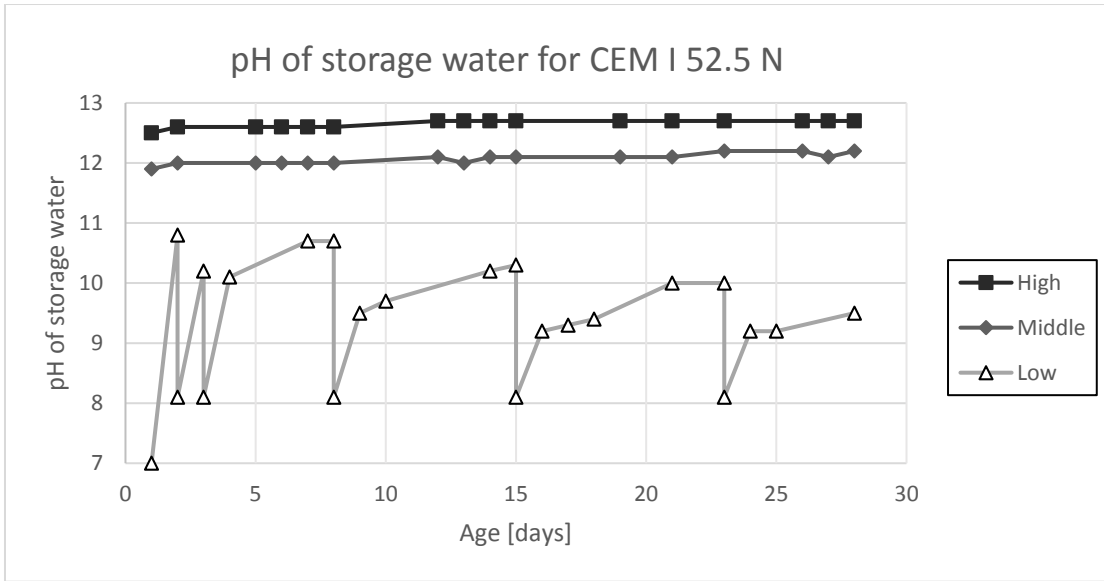
## 8 References

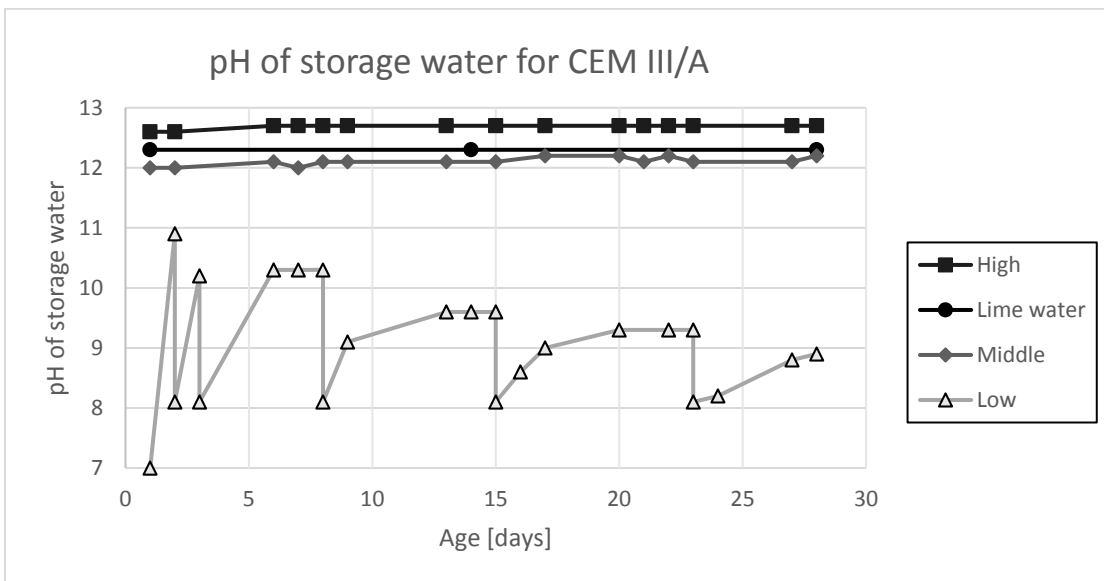
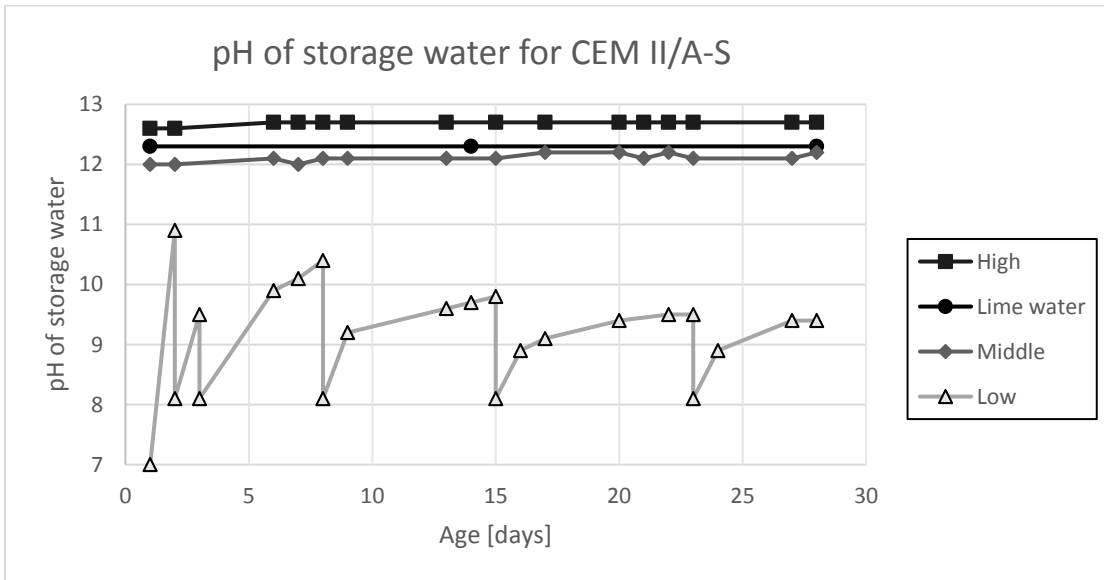
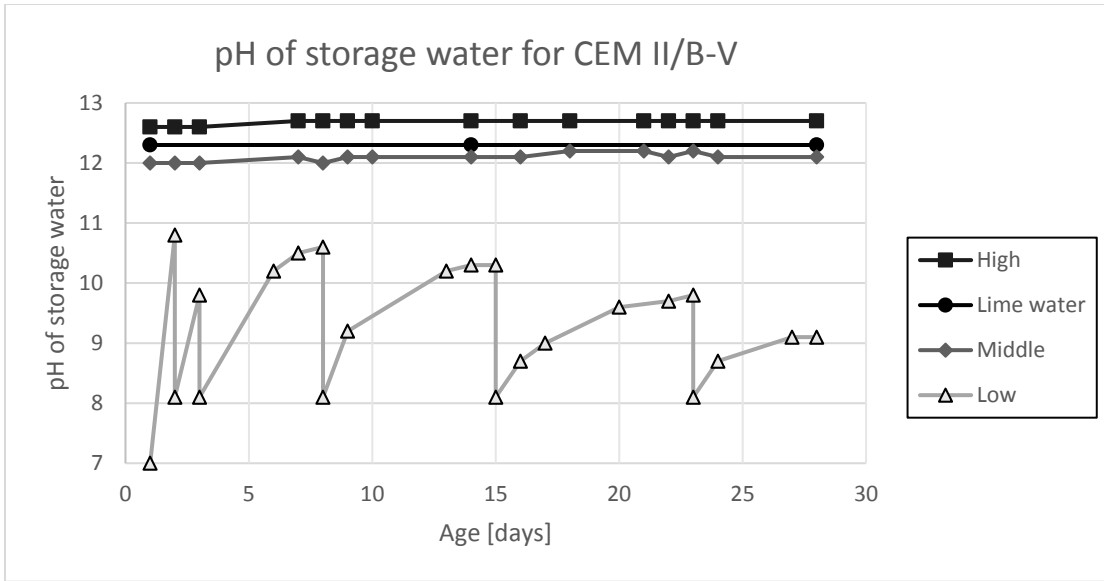
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## Appendix A: pH of storage water





## Appendix B: Calculations on leached calcium

**Atomic masses:**

Ca = 40.078 g/mole

H = 1.008 g/mole

O = 15.994 g/mole

**Calcium amount in CaO (% by mass):**

$$\frac{Ca}{Ca + O} = 71.5\%$$

**Calcium amount in Ca(OH)<sub>2</sub> (% by mass):**

$$\frac{Ca}{Ca + 2 * O + 2 * H} = 54.1\%$$

**Estimated leached depth after 1 day:**

$$e = \sqrt{D * t}$$

e = 0.5 mm at 28 days gives for t = 1 day:

$$e_{1 \text{ day}} = \sqrt{t_{1 \text{ day}} * \frac{e_{28 \text{ days}}^2}{t_{28 \text{ days}}}} = 0.1 \text{ mm}$$

The leaching can be expected to be faster at an early age as the prisms are not yet dense. The leached depth at 1 day is therefore assumed to be 0.1-0.2 mm. This corresponds to 1-2 % of the total area.

**Produced calcium hydroxide at complete hydration:**

According to Fagerlund (2017):

C<sub>3</sub>S - 0.49 [kg/kg]

C<sub>2</sub>S – 0.21 [kg/kg]

C<sub>4</sub>AF – -0.31 [kg/kg]

### **CEMI 52.5 N**

Ca amount in water: 3.5 mg/l

33 litres of water gives: 115.5 mg

Amount of CaO in the cement: 63%

Amount of Ca in the mix:

$$900g * 0.63 * 0.715 = 405.4 g$$

Amount of total Ca leached after 1 day:

$$\frac{0.1155}{405.4} = 0.028 \%$$

Loss of Ca in the leached zone is then: 1.4-2.8 %

### **CEMI 52.5 R**

Ca amount in water: 3.7 mg/l

33 litres of water gives: 122.1 mg

Amount of CaO in the cement: 62.9%

Amount of Ca in the mix:

$$900g * 0.629 * 0.715 = 404.8 g$$

Amount of total Ca leached after 1 day:

$$\frac{0.1221}{404.8} = 0.030 \%$$

Loss of Ca in the leached zone is then: 1.5-3.0 %

Assuming that all of the leached Ca originates from calcium hydroxide:

Amount of C<sub>2</sub>S in the cement: 8.3%

Amount of C<sub>3</sub>S in the cement: 61.6%

Amount of C<sub>4</sub>AF in the cement: 9.3%

Total amount of calcium hydroxide:

$$0.21 * 0.083 * 900 + 0.49 * 0.616 * 900 - 0.31 * 0.093 * 900 = 261.4g$$

Total amount of Ca in the calcium hydroxide:

$$261.4 * 0.541 = 141.4 g$$

Total amount of Ca from calcium hydroxide leached after 1 day:

$$\frac{0.1221}{141.4} = 0.086 \%$$

Loss of Ca from calcium hydroxide in the leached zone is then: 4.3 -8.6 %

### **CEMI 42.5 N**

Ca amount in water: 6.8 mg/l

33 litres of water gives: 224.4 mg

Amount of CaO in the cement: 63.8%

Amount of Ca in the mix:

$$900g * 0.638 * 0.715 = 410.6 g$$

Amount of total Ca leached after 1 day:

$$\frac{0.2244}{410.6} = 0.055 \%$$

Loss of Ca in the leached zone is then: 2.8-5.5 %

Assuming that all of the leached Ca originates from calcium hydroxide:

Amount of C<sub>2</sub>S in the cement: 16.3%

Amount of C<sub>3</sub>S in the cement: 59.8%

Amount of C<sub>4</sub>AF in the cement: 13.5%

Total amount of calcium hydroxide:

$$0.21 * 0.163 * 900 + 0.49 * 0.598 * 900 - 0.31 * 0.135 * 900 = 256.9g$$

Total amount of Ca in the calcium hydroxide:

$$256.9 * 0.541 = 139.0 g$$

Total amount of Ca from calcium hydroxide leached after 1 day:

$$\frac{0.2244}{139} = 0.16 \%$$

Loss of Ca from calcium hydroxide in the leached zone is then: 8.0-16 %

### **CEM II/A-S**

Ca amount in water: 5.2 mg/l

21 litres of water gives: 109.2 mg

Amount of CaO in the cement: 62.9%

Amount of CaO in GGBS: 39.8%

Amount of Ca in the mix (20% GGBS; 80% Cement):

$$450g * (0.8 * 0.629 + 0.2 * 0.398) * 0.715 = 187.5 g$$

Amount of total Ca leached after 1 day:

$$\frac{0.1092}{187.5} = 0.058 \%$$

Loss of Ca in the leached zone is then: 2.9-5.8 %

### **CEM III/A**

Ca amount in water: 14 mg/l

33 litres of water gives: 462 mg

Amount of CaO in the cement: 62.9%

Amount of CaO in GGBS: 39.8%

Amount of Ca in the mix (50% GGBS; 50% Cement):

$$450g * (0.629 + 0.398) * 0.715 = 330.4 g$$

Amount of total Ca leached after 1 day:

$$\frac{0.462}{330.4} = 0.14 \%$$

Loss of Ca in the leached zone is then: 7.0-14 %

### **CEM II/A-V**

Ca amount in water: 7.4 mg/l

21 litres of water gives: 155.4 mg

Amount of CaO in the cement: 62.9%

Assumed amount of CaO in the fly ash: 10%

Amount of Ca in the mix (15% fly ash; 85% Cement):

$$450g * (0.15 * 0.1 + 0.85 * 0.629) * 0.715 = 176.8 g$$

Amount of total Ca leached after 1 day:

$$\frac{0.1554}{176.8} = 0.088 \%$$

Loss of Ca in the leached zone is then: 4.4-8.8 %

### **CEM II/B-V**

Ca amount in water: 13 mg/l

33 litres of water gives: 429 mg

Amount of CaO in the cement: 62.9%

Assumed amount of CaO in the fly ash: 10%

Amount of Ca in the mix (30% fly ash; 70% Cement):

$$900g * (0.3 * 0.1 + 0.7 * 0.629) * 0.715 = 302.6 g$$

Amount of total Ca leached after 1 day:

$$\frac{0.429}{302.6} = 0.14 \%$$

Loss of Ca in the leached zone is then: 7.0-14 %

## Appendix C: Compressive strength

## CEM I 52.5 N

CEM I 52.5 N stored in low pH	
1f	62.29
1b	60.41
2f	61.28
2b	60.44
3f	59.26
3b	60.48
Mean	60.7
Standard deviation	1.0

CEM I 52.5 N stored in low pH	
1f	59.82
1b	60.13
2f	59.60
2b	61.16
3f	57.84
3b	59.70
Mean	59.7
Standard deviation	1.1

CEM I 52.5 N stored in middle pH	
1f	61.46
1b	63.63
2f	61.10
2b	62.69
3f	63.94
3b	61.94
Mean	62.5
Standard deviation	1.2

CEM I 52.5 N stored in middle pH	
1f	62.31
1b	62.38
2f	62.31
2b	63.88
3f	63.38
3b	64.56
Mean	63.1
Standard deviation	1.0

CEM I 52.5 N stored in high pH	
1f	61.35
1b	60.32
2f	61.14
2b	60.40
3f	59.85
3b	61.59
Mean	60.8
Standard deviation	0.7

CEM I 52.5 N stored in high pH	
1f	57.84
1b	62.69
2f	61.04
2b	60.81
3f	61.34
3b	61.68
Mean	60.9
Standard deviation	1.6

## CEM I 52.5 R

CEM I 52.5 R stored in low pH	
1f	62.31
1b	64.13
2f	59.06
2b	61.33
3f	62.81
3b	64.94
Mean	62.4
Standard deviation	2.1

CEM I 52.5 R stored in low pH	
1f	61.29
1b	62.56
2f	60.39
2b	63.25
3f	62.56
3b	63.13
Mean	62.2
Standard deviation	1.1

CEM I 52.5 R stored in middle pH	
1f	58.91
1b	62.81
2f	61.20
2b	66.19
3f	62.88
3b	64.88
Mean	62.8
Standard deviation	2.6

CEM I 52.5 R stored in middle pH	
1f	65.06
1b	65.38
2f	63.56
2b	66.44
3f	63.75
3b	65.06
Mean	64.9
Standard deviation	1.1

CEM I 52.5 R stored in middle pH	
1f	61.53
1b	64.13
2f	60.76
2b	64.63
3f	61.27
3b	64.94
Mean	62.9
Standard deviation	1.9

CEM I 52.5 R stored in high pH	
1f	59.74
1b	63.38
2f	62.47
2b	63.88
3f	61.78
3b	62.49
Mean	62.3
Standard deviation	1.4

CEM I 52.5 R stored in high pH	
1f	63.88
1b	63.63
2f	60.85
2b	63.94
3f	64.63
3b	62.75
Mean	63.3
Standard deviation	1.3

CEM I 52.5 R stored in lime water	
1f	61.59
1b	61.45
2f	61.73
2b	62.29
3f	60.78
3b	63.94
Mean	62.0
Standard deviation	1.1

CEM I 52.5 R stored in lime water	
1f	61.41
1b	60.41
2f	61.74
2b	61.38
3f	61.49
3b	64.81
Mean	61.9
Standard deviation	1.5

## CEM I 42.5 N

CEM I 42.5 N stored in low pH	
1f	53.58
1b	51.71
2f	54.94
2b	52.27
3f	54.51
3b	49.68
Mean	52.8
Standard deviation	2.0

CEM I 42.5 N stored in low pH	
1f	53.52
1b	49.24
2f	55.43
2b	49.48
3f	53.16
3b	49.53
Mean	51.7
Standard deviation	2.6

CEM I 42.5 N stored in middle pH	
1f	54.21
1b	54.56
2f	55.27
2b	56.41
3f	56.01
3b	55.36
Mean	55.3
Standard deviation	0.8

CEM I 42.5 N stored in middle pH	
1f	55.56
1b	52.83
2f	54.31
2b	53.93
3f	56.70
3b	52.49
Mean	54.3
Standard deviation	1.6

CEM I 42.5 N stored in high pH	
1f	57.44
1b	54.56
2f	55.19
2b	54.48
3f	55.59
3b	54.24
Mean	55.3
Standard deviation	1.2

CEM I 42.5 N stored in high pH	
1f	55.02
1b	53.08
2f	55.73
2b	51.49
3f	56.64
3b	52.88
Mean	54.1
Standard deviation	2.0

CEM I 42.5 N stored in lime water	
1f	53.35
1b	55.59
2f	54.01
2b	55.88
3f	54.99
3b	54.03
Mean	54.6
Standard deviation	1.0

CEM I 42.5 N stored in lime water	
1f	51.27
1b	54.13
2f	55.04
2b	53.99
3f	53.75
3b	53.67
Mean	53.6
Standard deviation	1.3

## CEM II/A-V

CEM II/A-V stored in low pH	
1f	56.33
1b	48.92
2f	54.85
2b	57.19
3f	55.65
3b	57.61
Mean	56.3
Standard deviation	1.1

CEM II/A-V stored in middle pH	
1f	57.07
1b	57.69
2f	57.24
2b	55.78
3f	56.56
3b	55.16
Mean	56.6
Standard deviation	1.0

CEM II/A-V stored in high pH	
1f	57.45
1b	59.19
2f	57.72
2b	59.38
3f	55.39
3b	58.36
Mean	57.9
Standard deviation	1.5

## CEM II/B-V

CEM II/B-V stored in low pH	
1f	47.03
1b	47.58
2f	45.99
2b	46.34
3f	43.18
3b	44.60
Mean	45.8
Standard deviation	1.6

CEM II/B-V stored in low pH	
1f	48.16
1b	46.46
2f	47.57
2b	44.28
3f	46.73
3b	45.94
Mean	46.5
Standard deviation	1.4

CEM II/B-V stored in middle pH	
1f	50.16
1b	49.83
2f	48.65
2b	49.34
3f	51.98
3b	50.81
Mean	50.1
Standard deviation	1.2

CEM II/B-V stored in middle pH	
1f	48.99
1b	48.58
2f	49.67
2b	50.06
3f	49.55
3b	48.68
Mean	49.3
Standard deviation	0.6

CEM II/B-V stored in high pH	
1f	48.96
1b	50.28
2f	50.29
2b	51.23
3f	49.83
3b	50.79
Mean	50.2
Standard deviation	0.8

CEM II/B-V stored in high pH	
1f	49.87
1b	50.40
2f	50.45
2b	49.08
3f	51.98
3b	49.79
Mean	50.3
Standard deviation	1.0

CEM II/B-V stored in lime water	
1f	49.43
1b	49.68
2f	46.06
2b	45.16
3f	47.15
3b	49.61
Mean	47.8
Standard deviation	2.0

CEM II/B-V stored in lime water	
1f	49.89
1b	47.03
2f	49.88
2b	45.77
3f	46.14
3b	49.83
Mean	48.1
Standard deviation	2.0

## CEM II/A-S

CEM II/A-S stored in low pH	
1f	63.63
1b	64.44
2f	61.00
2b	59.13
3f	63.38
3b	63.31
Mean	62.5
Standard deviation	2.0

CEM II/A-S stored in middle pH	
1f	61.26
1b	60.73
2f	61.76
2b	61.42
3f	59.54
3b	62.08
Mean	61.1
Standard deviation	0.9

CEM II/A-S stored in high pH	
1f	61.33
1b	62.81
2f	62.75
2b	62.44
3f	62.69
3b	62.75
Mean	62.5
Standard deviation	0.6

CEM II/A-S stored in lime water	
1f	61.63
1b	59.78
2f	62.10
2b	61.89
3f	60.38
3b	60.92
Mean	61.1
Standard deviation	0.9

## CEM III/A

CEM III/A stored in low pH	
1f	50.14
1b	50.75
2f	50.39
2b	49.83
3f	51.13
3b	51.82
Mean	50.7
Standard deviation	0.7

CEM III/A stored in low pH	
1f	50.14
1b	50.29
2f	49.80
2b	50.55
3f	50.41
3b	50.69
Mean	50.3
Standard deviation	0.3

CEM III/A stored in middle pH	
1f	53.48
1b	53.03
2f	50.84
2b	52.89
3f	52.64
3b	51.43
Mean	52.4
Standard deviation	1.0

CEM III/A stored in middle pH	
1f	52.66
1b	52.73
2f	52.33
2b	51.91
3f	51.73
3b	51.28
Mean	52.1
Standard deviation	0.6

CEM III/A stored in high pH	
1f	56.31
1b	58.61
2f	55.35
2b	57.00
3f	55.98
3b	55.73
Mean	56.5
Standard deviation	1.2

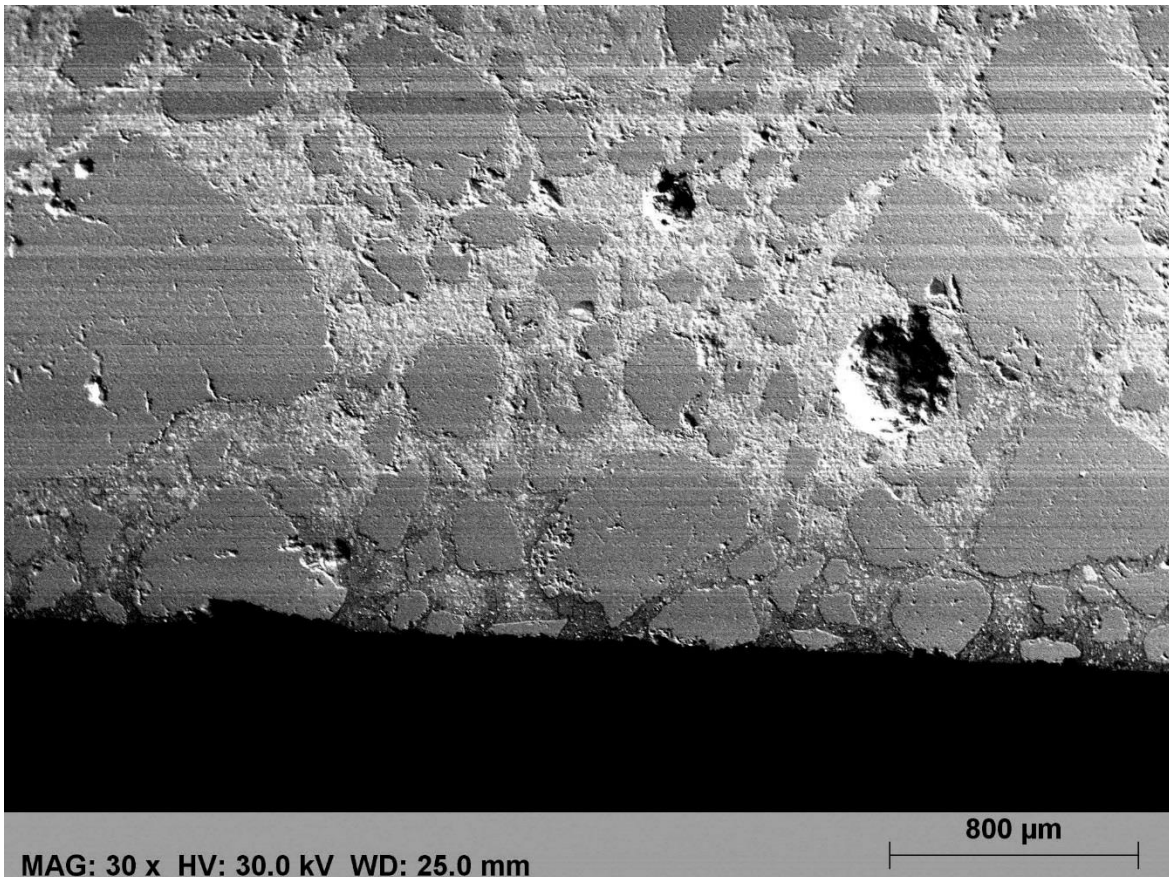
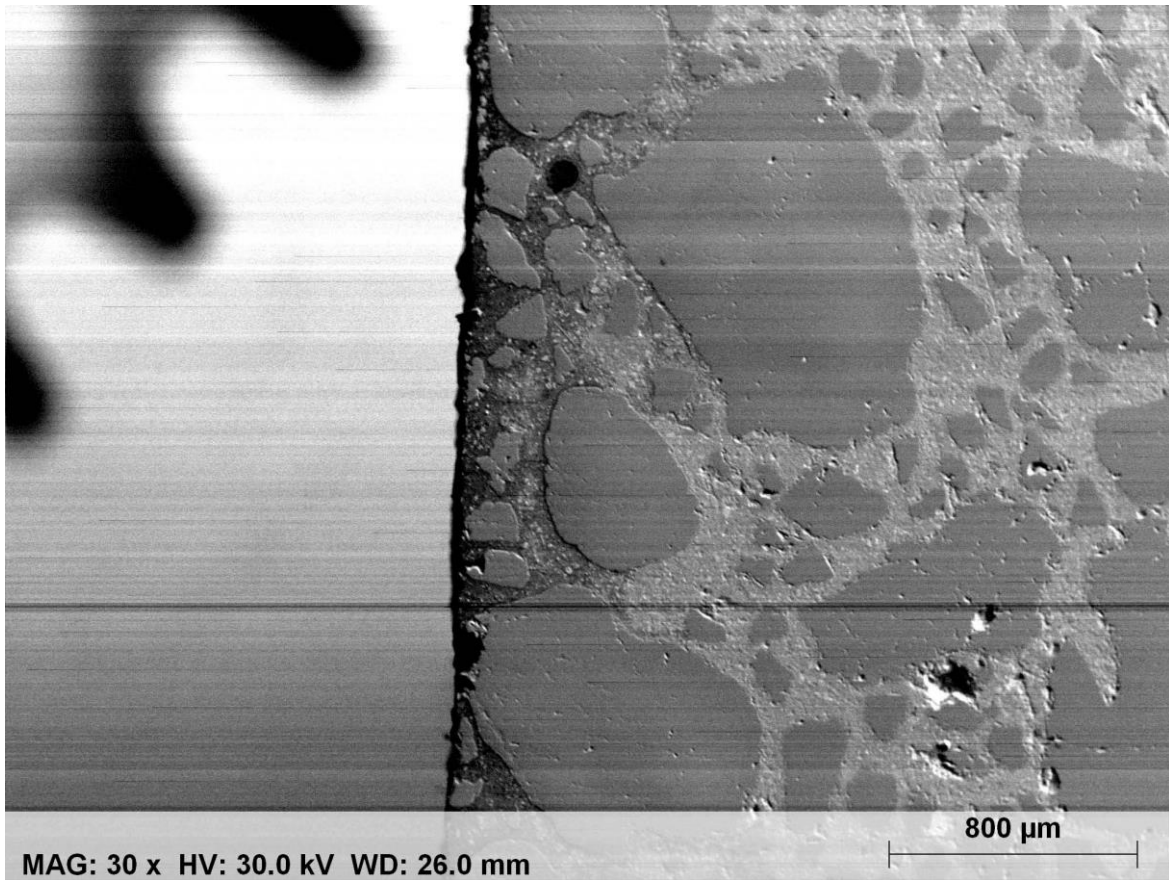
CEM III/A stored in high pH	
1f	55.29
1b	56.07
2f	54.54
2b	56.04
3f	55.40
3b	59.05
Mean	56.1
Standard deviation	1.6

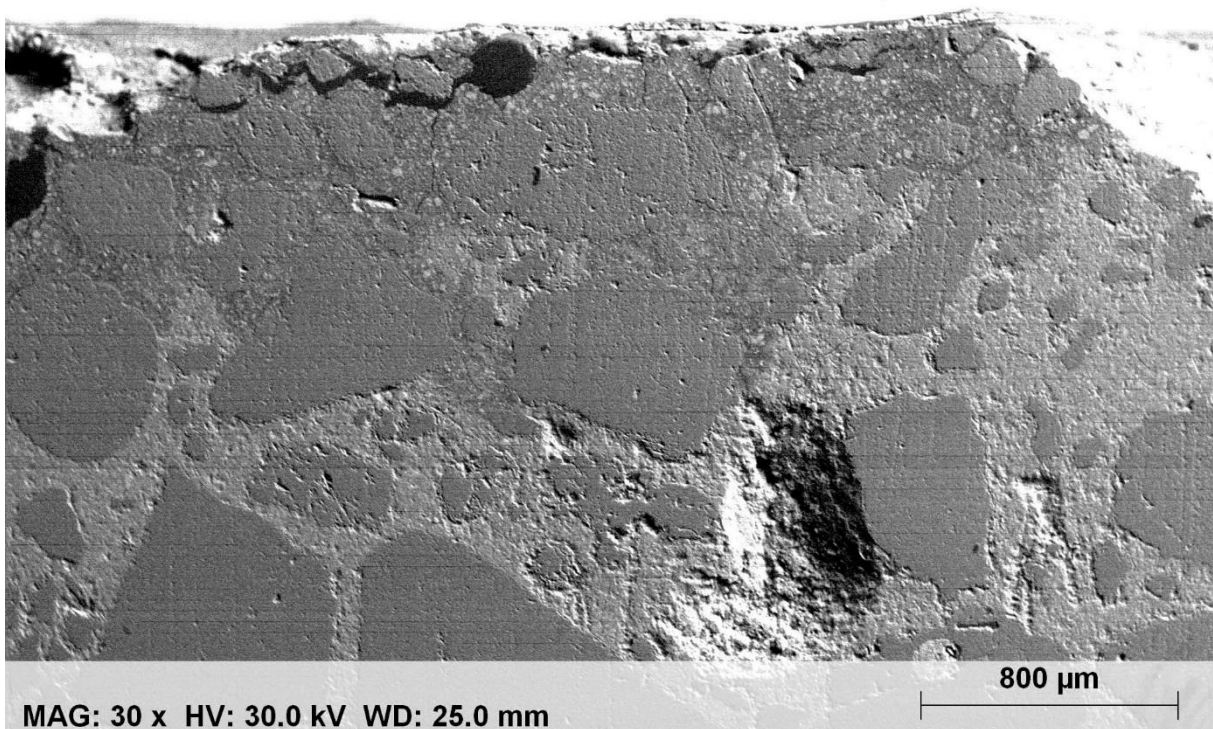
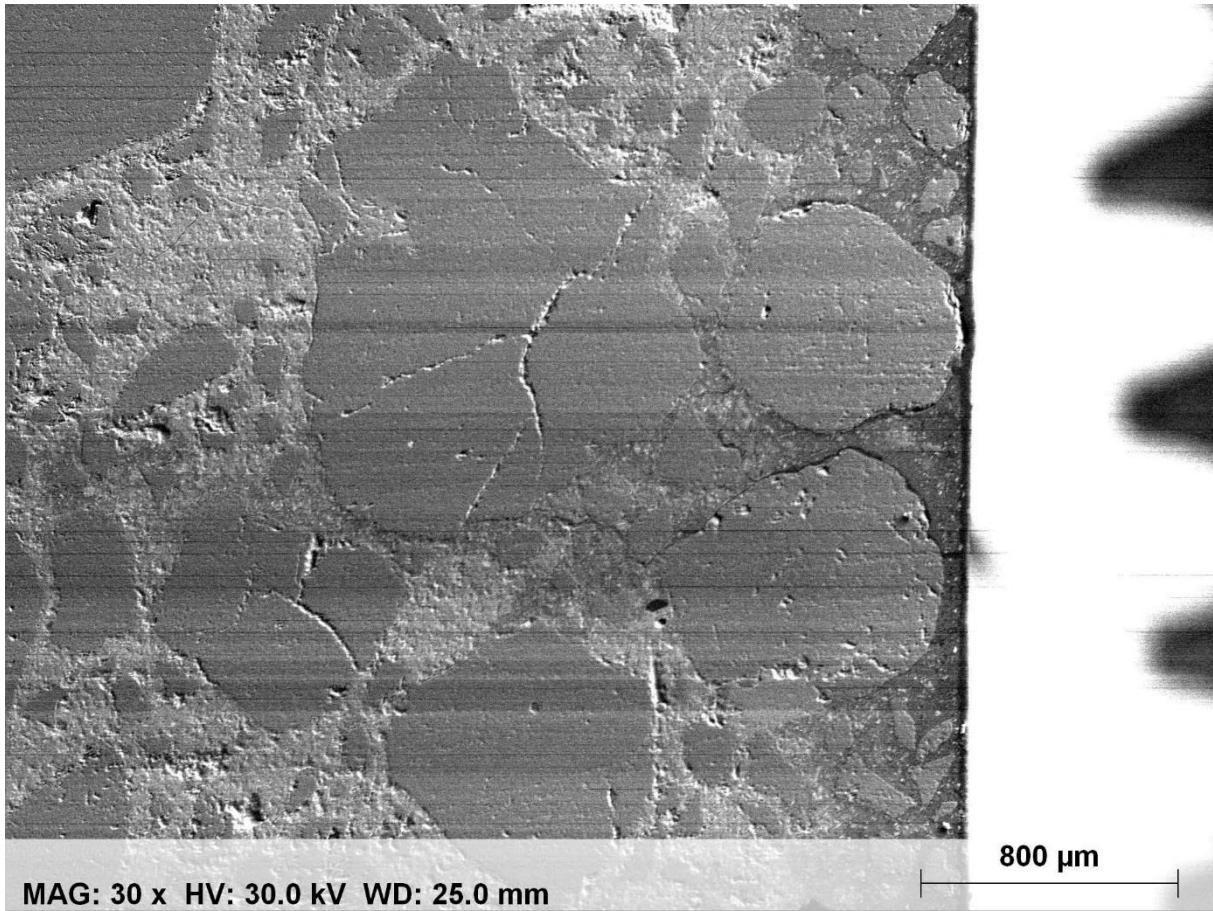
CEM III/A stored in lime water	
1f	51.63
1b	51.41
2f	53.01
2b	51.98
3f	52.11
3b	51.57
Mean	52.0
Standard deviation	0.6

CEM III/A stored in lime water	
1f	52.63
1b	52.71
2f	50.41
2b	49.88
3f	52.62
3b	51.36
Mean	51.6
Standard deviation	1.2

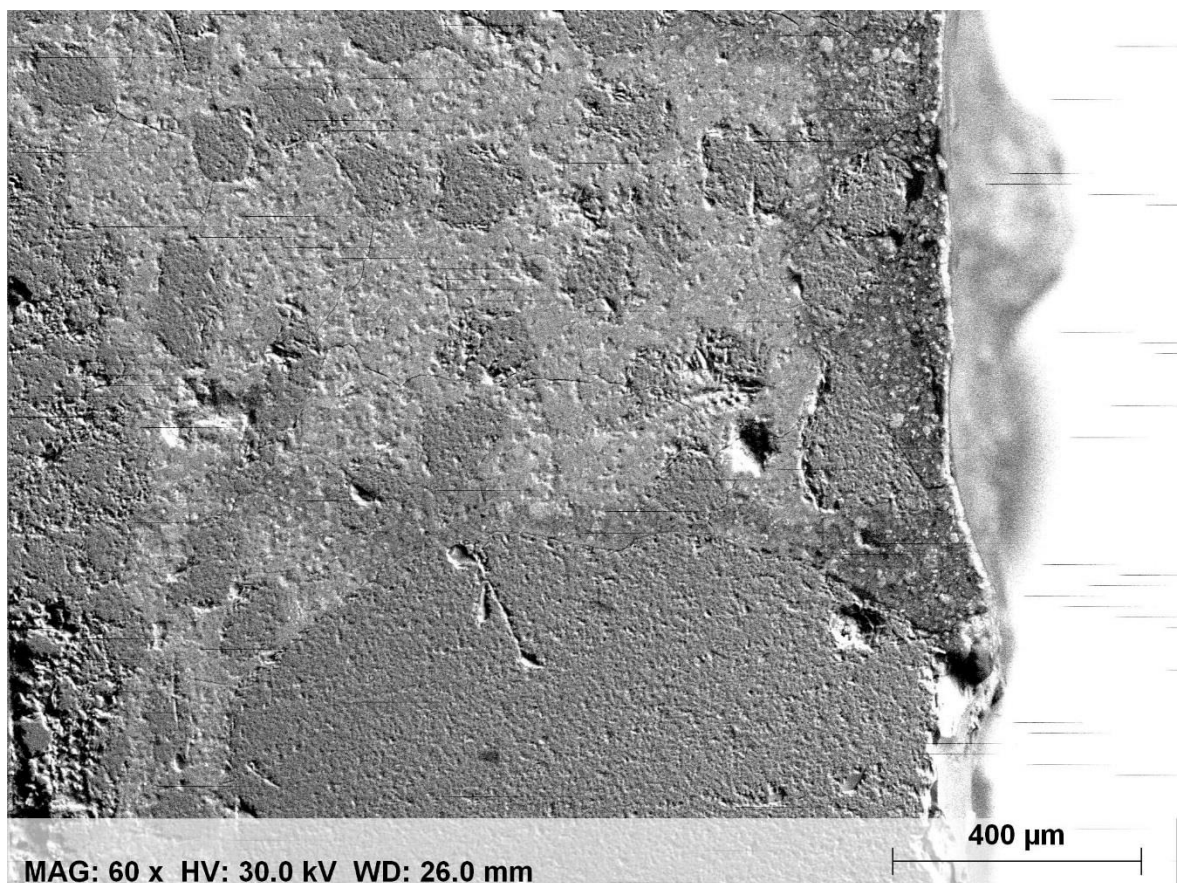
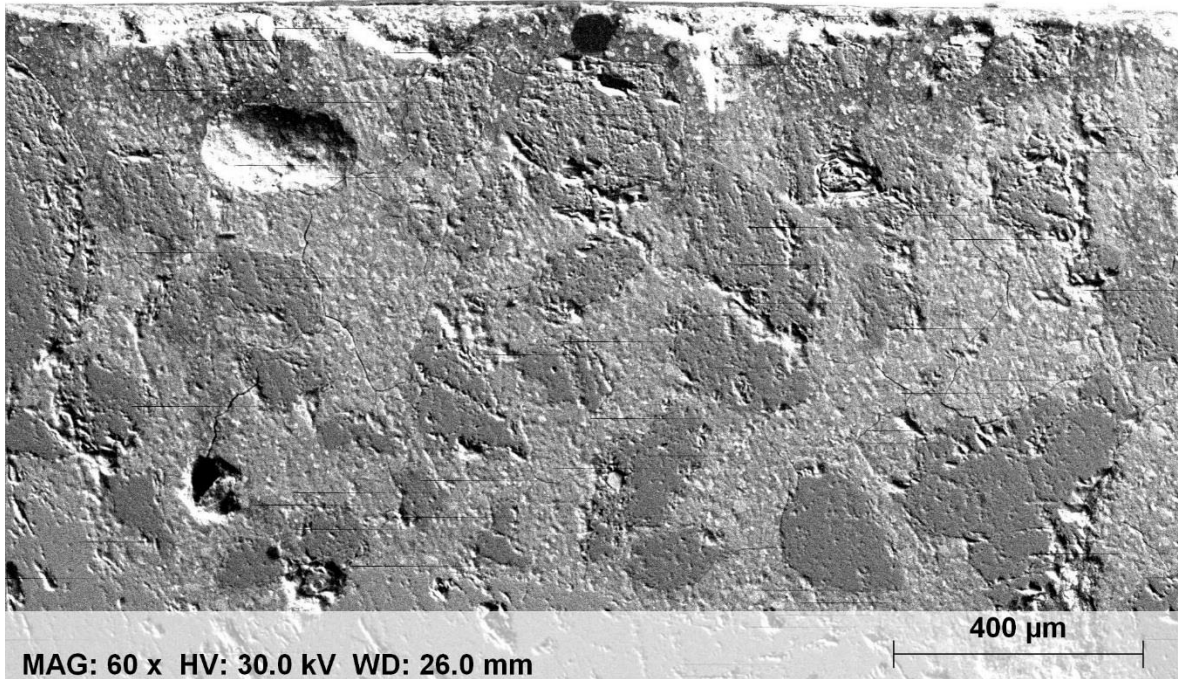
## Appendix D: SEM images

# CEM I 52.5 R stored in low pH

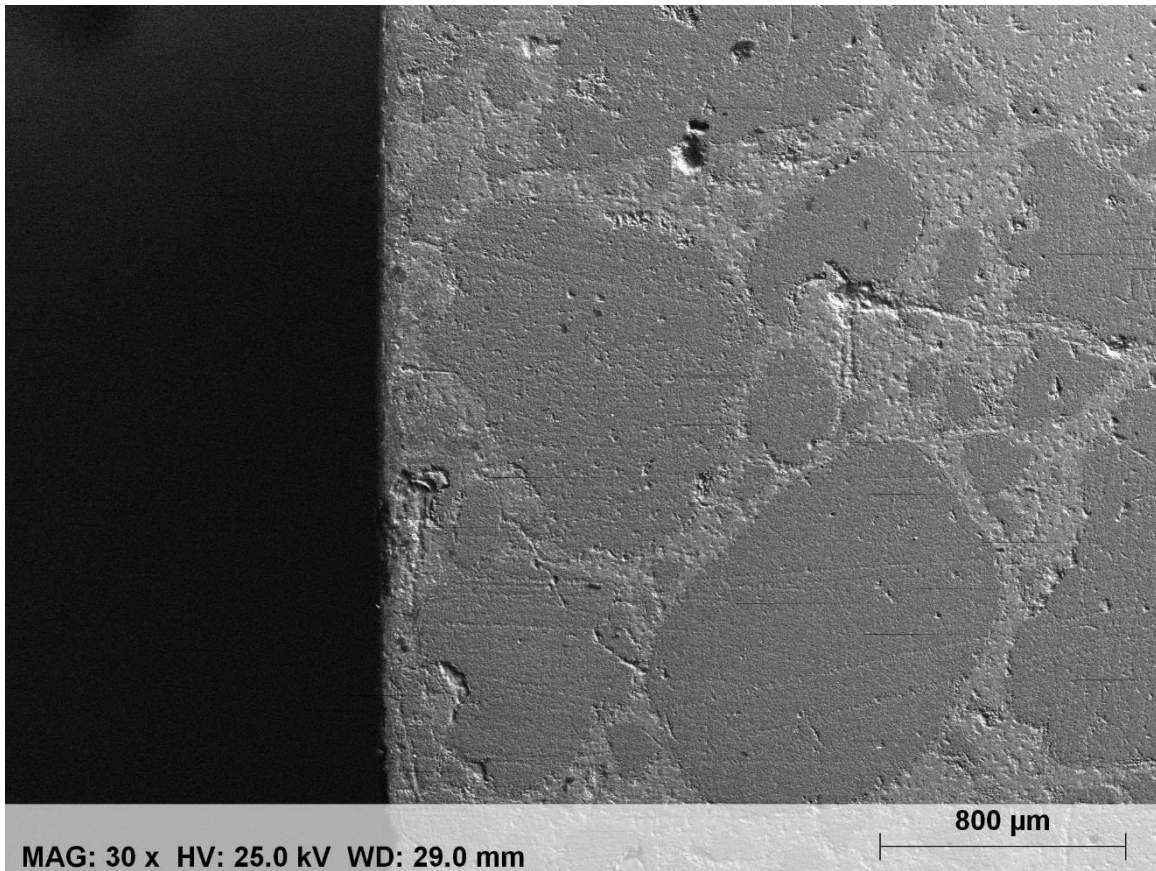




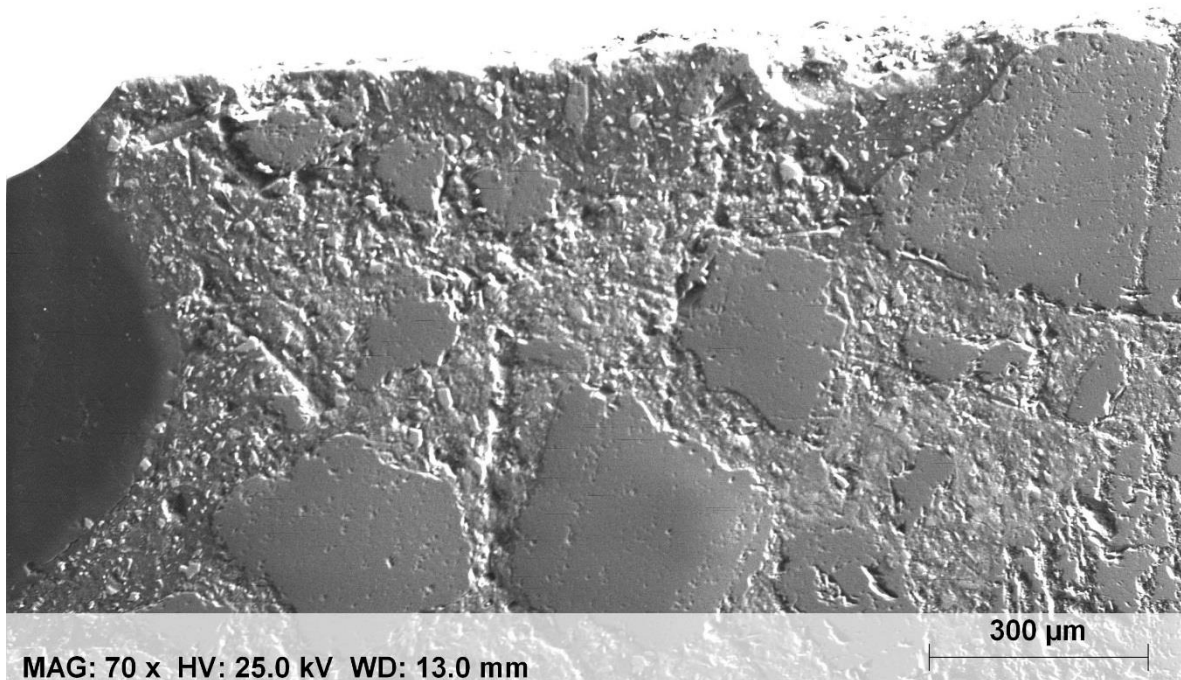
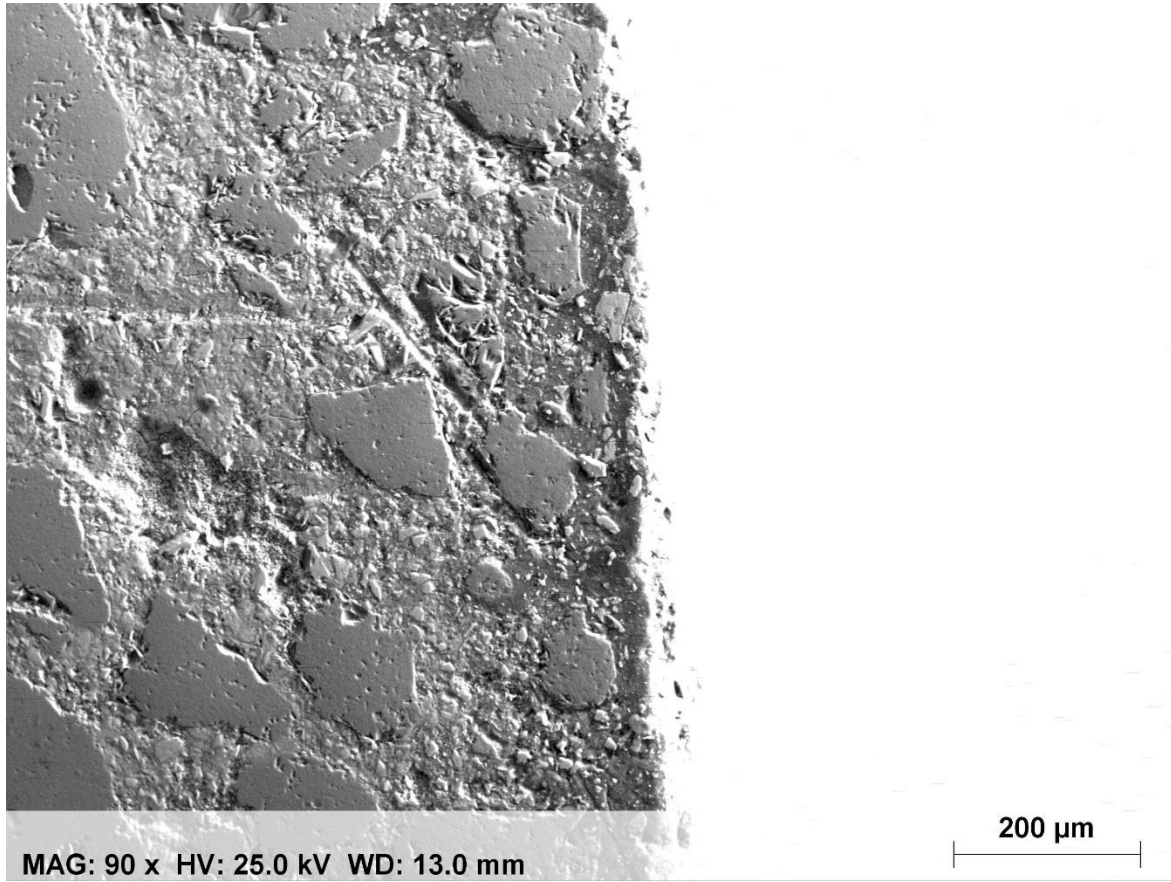
## CEM I 52.5 R stored in middle pH

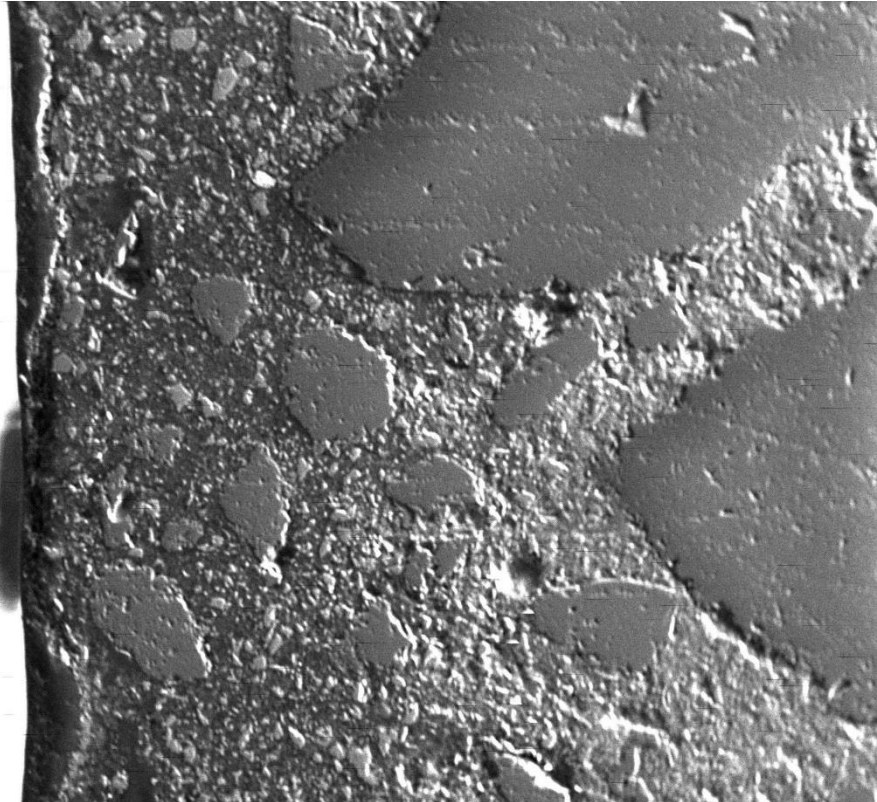


## CEM I 52.5 R stored in high pH



# CEM I 42.5 N stored in low pH

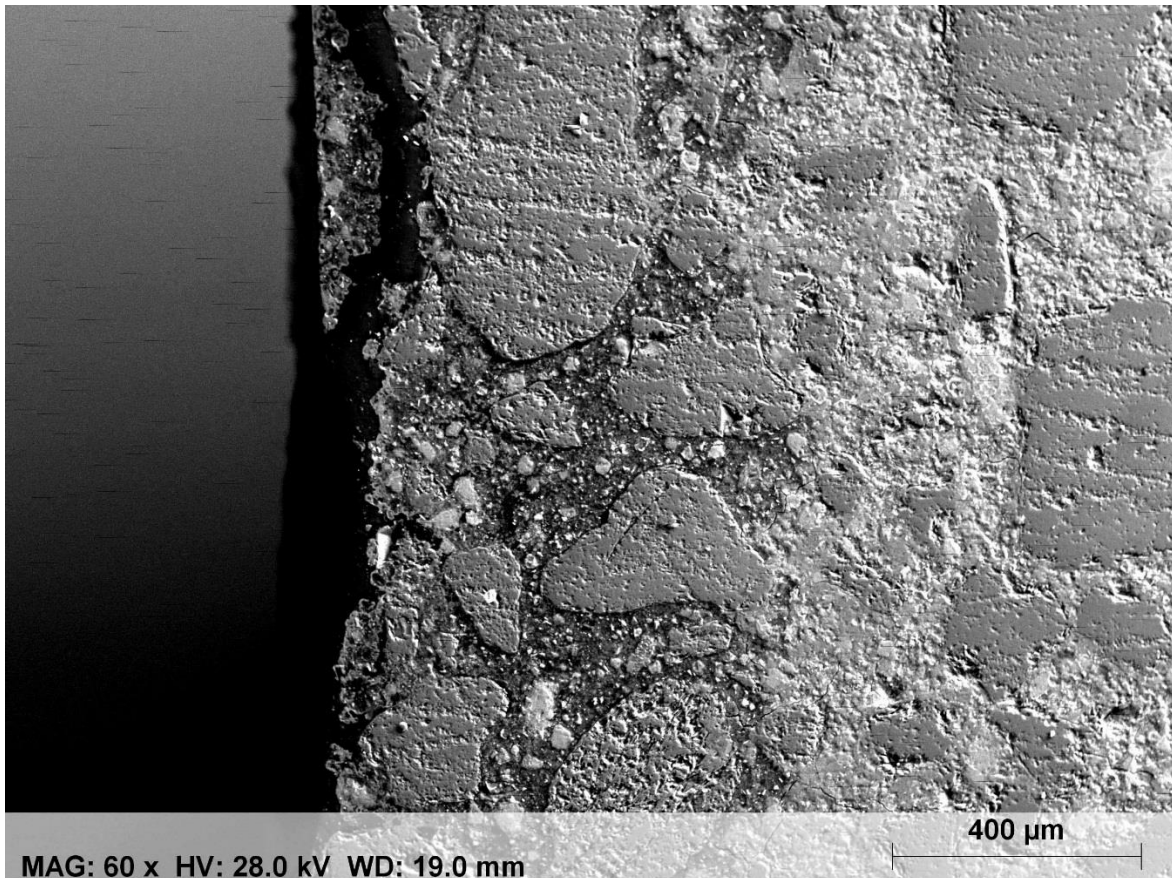
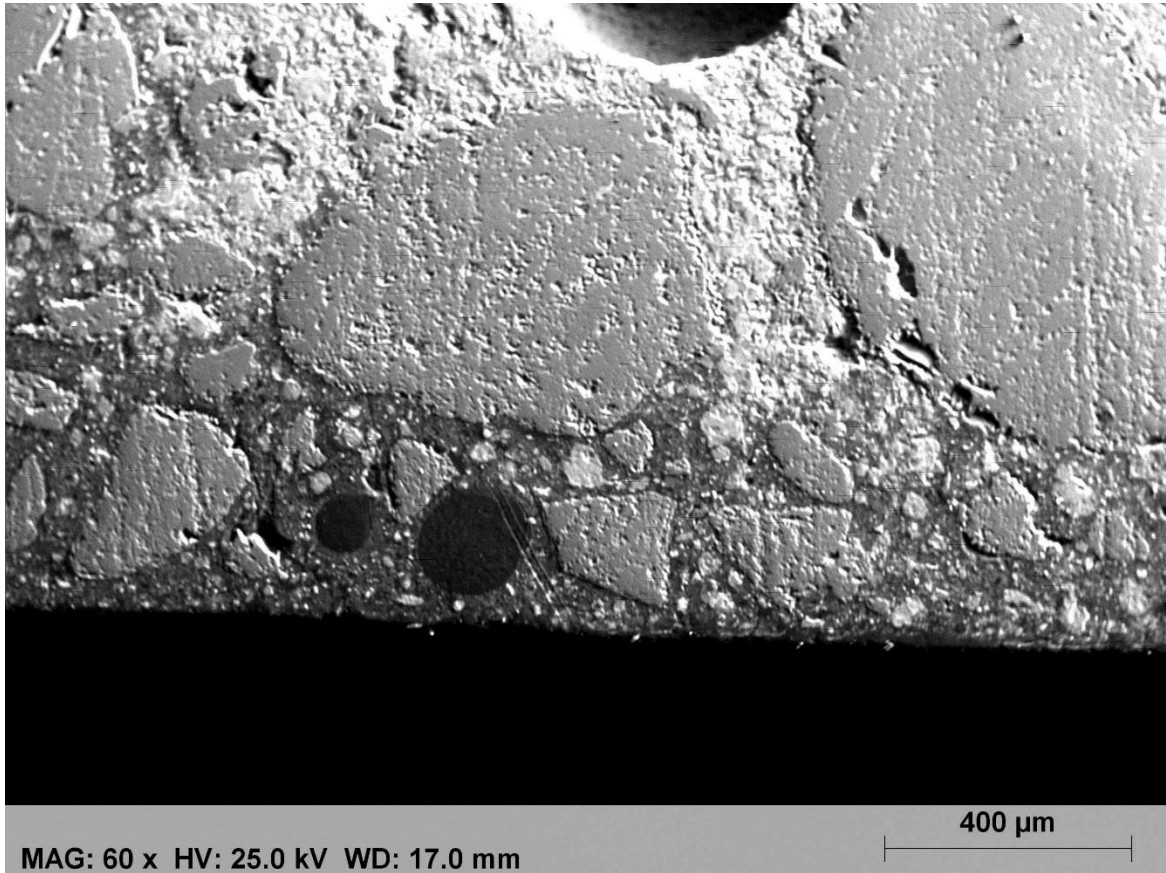


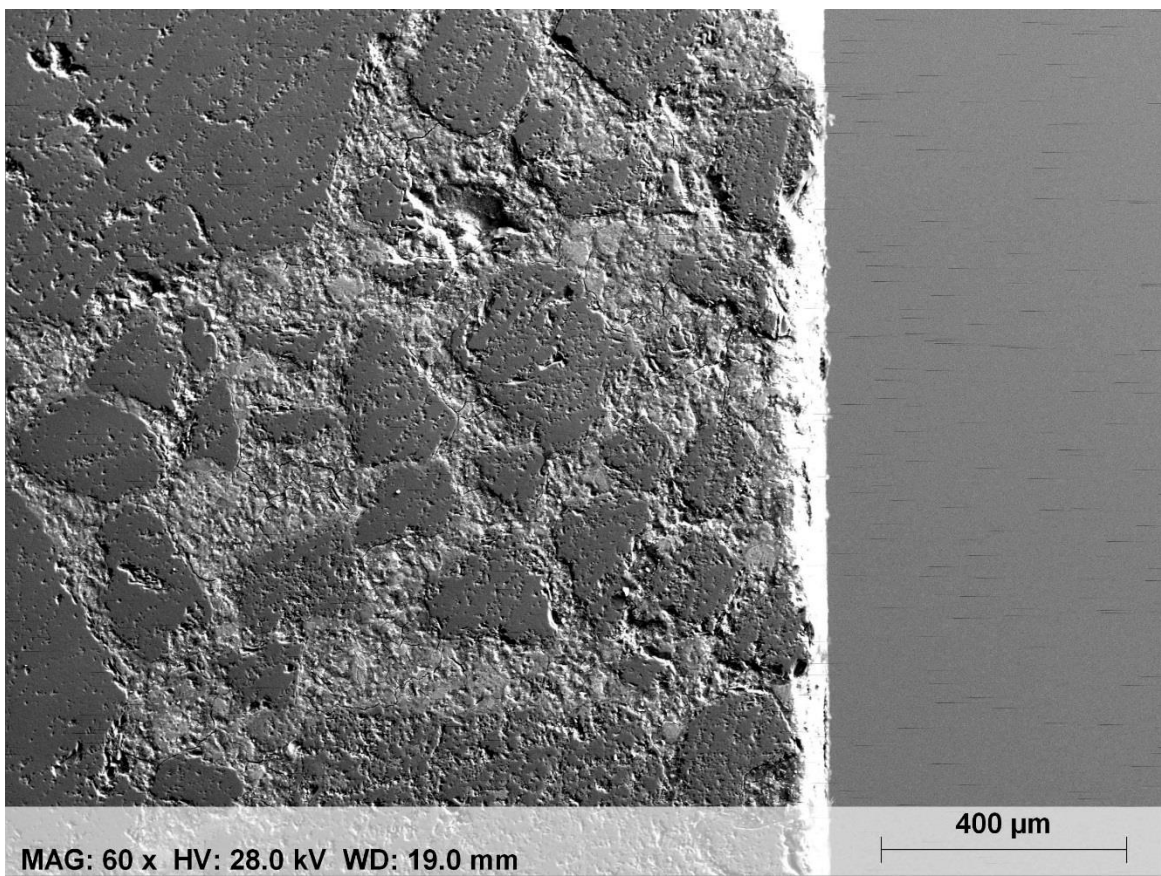
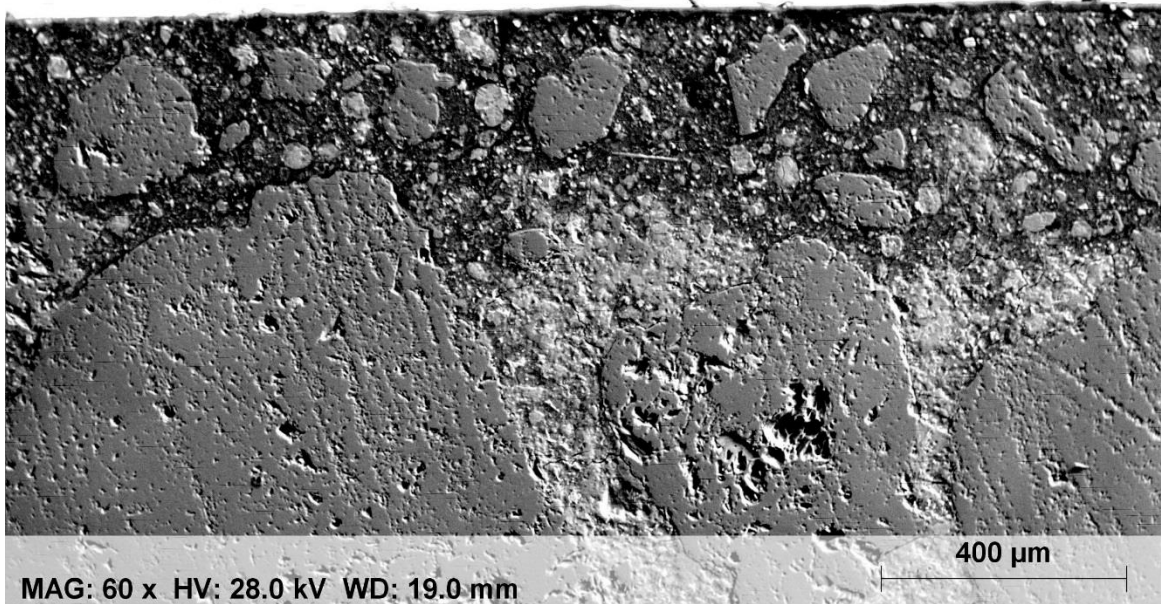


MAG: 70 x HV: 25.0 kV WD: 12.0 mm

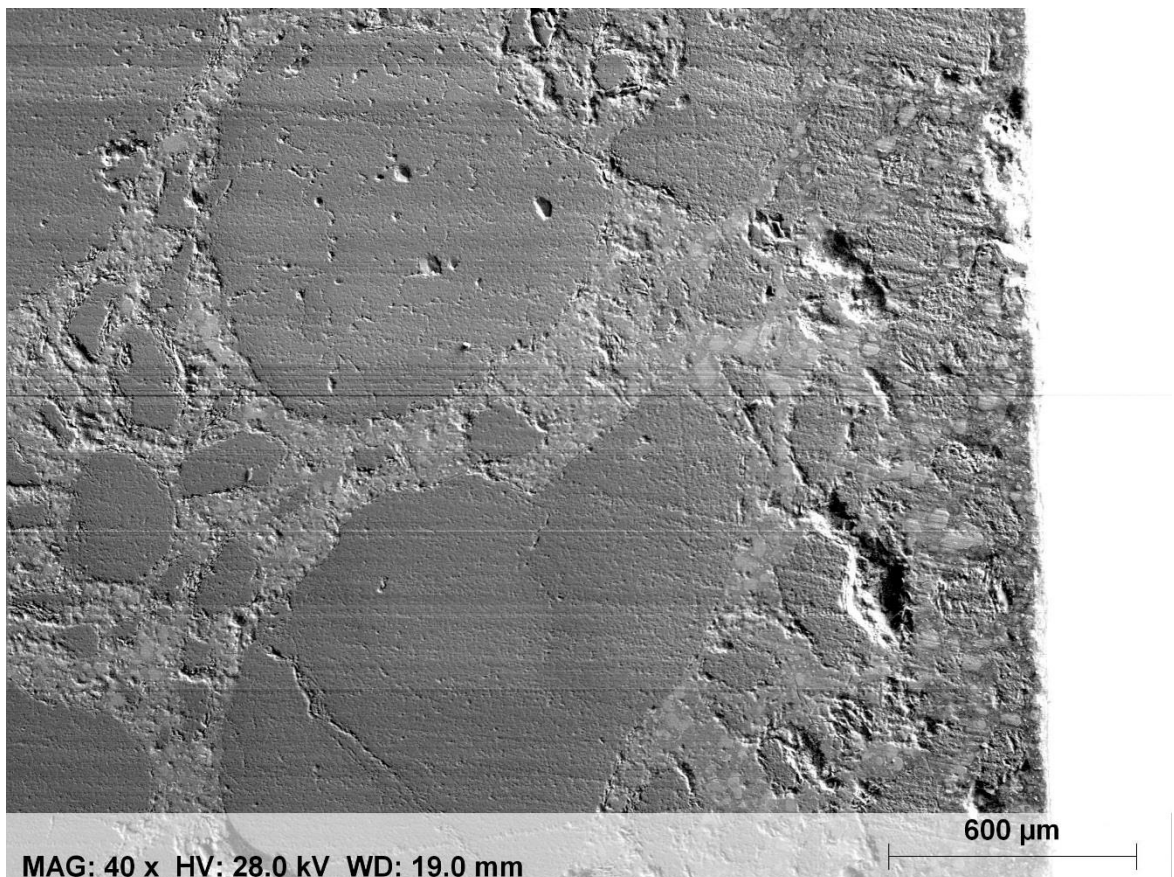
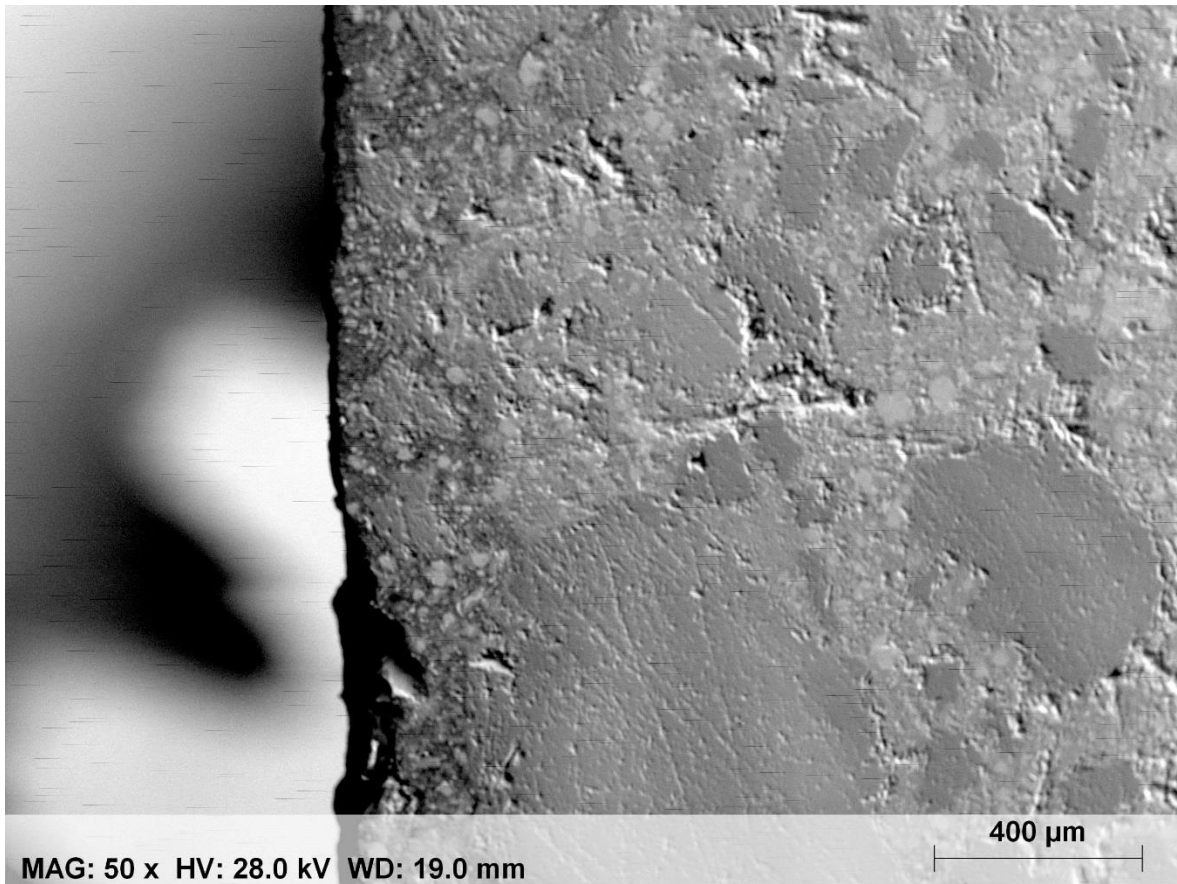
300  $\mu$ m

## CEM I 42.5 N stored in middle pH

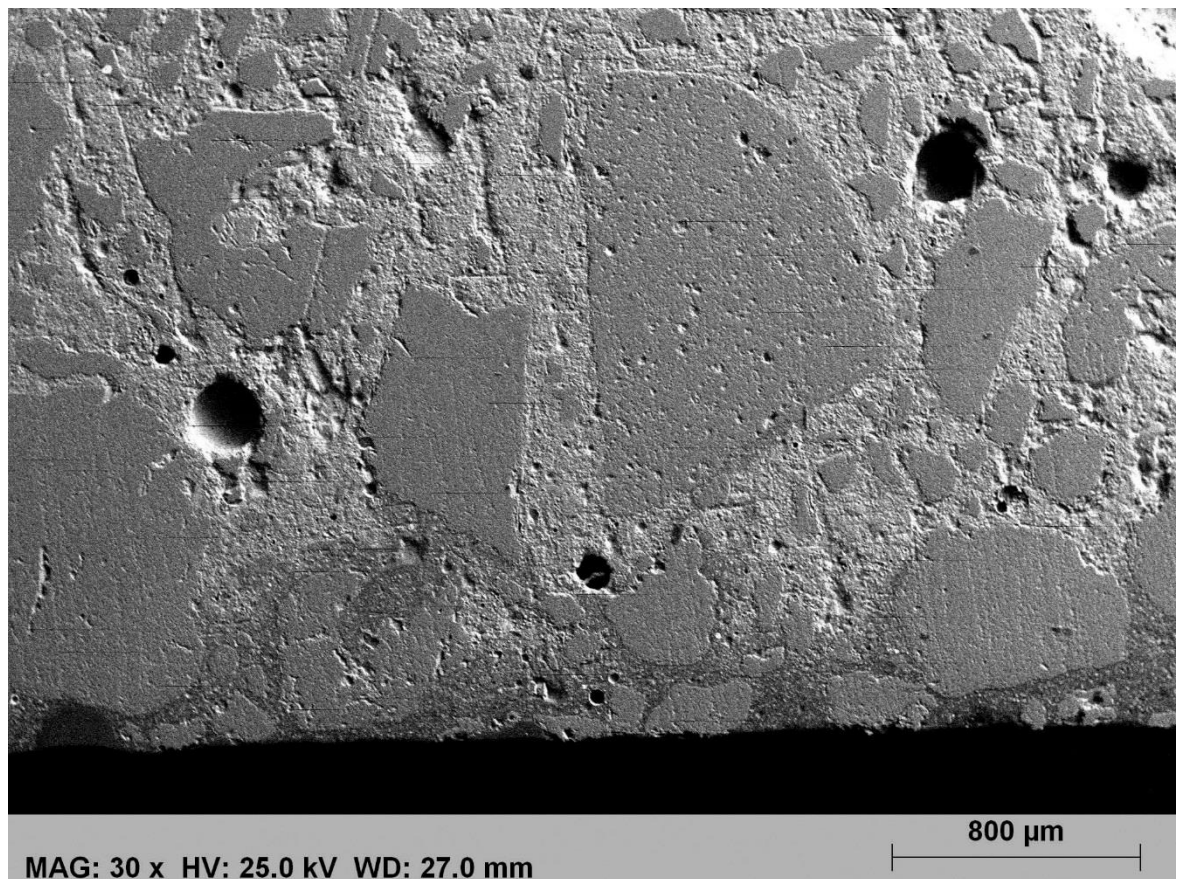
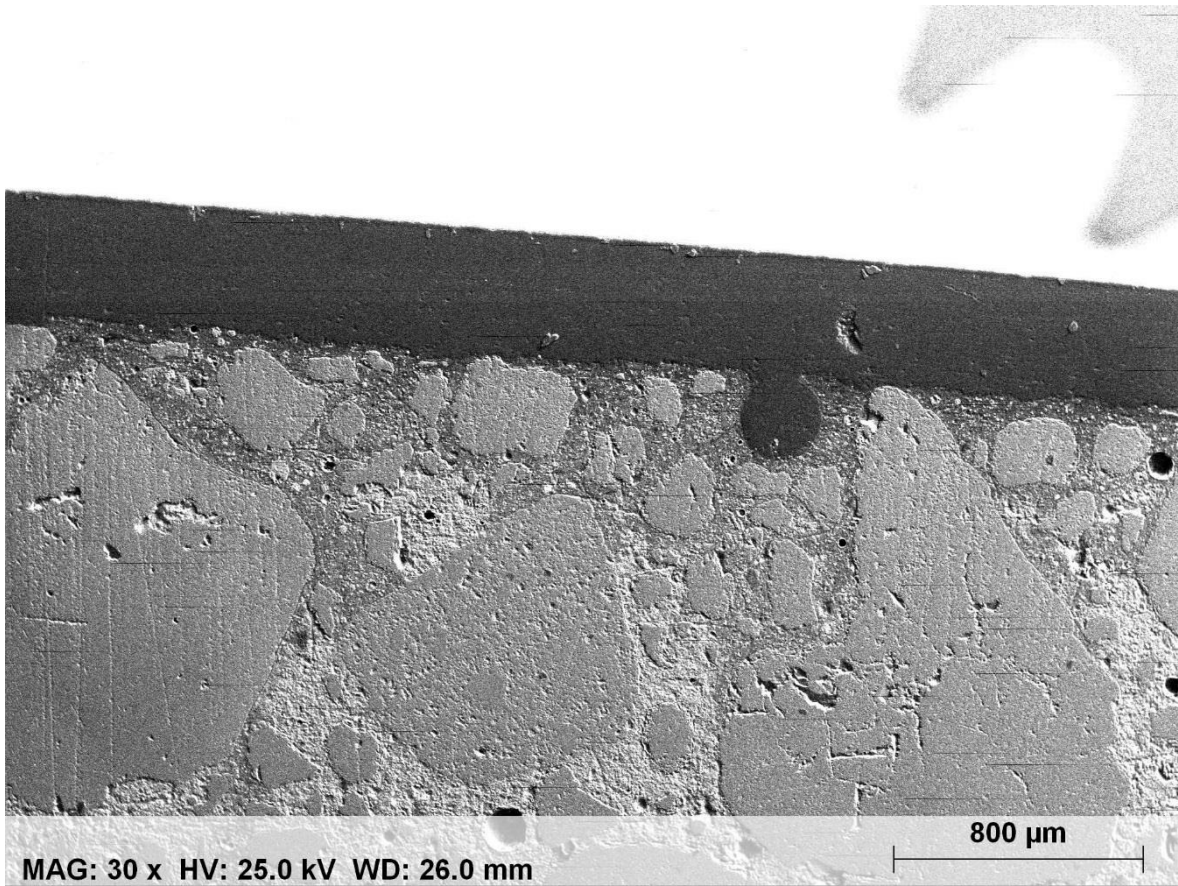


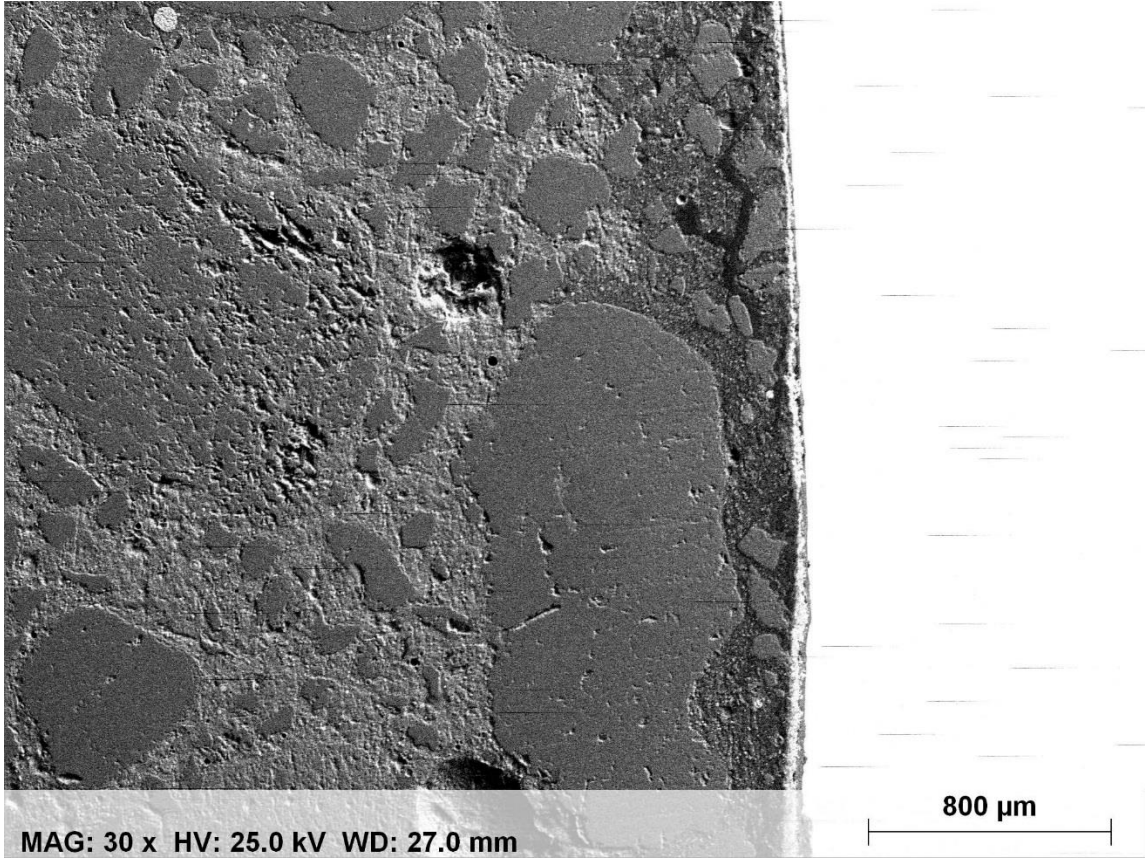


## CEM I 42.5 N stored in high pH

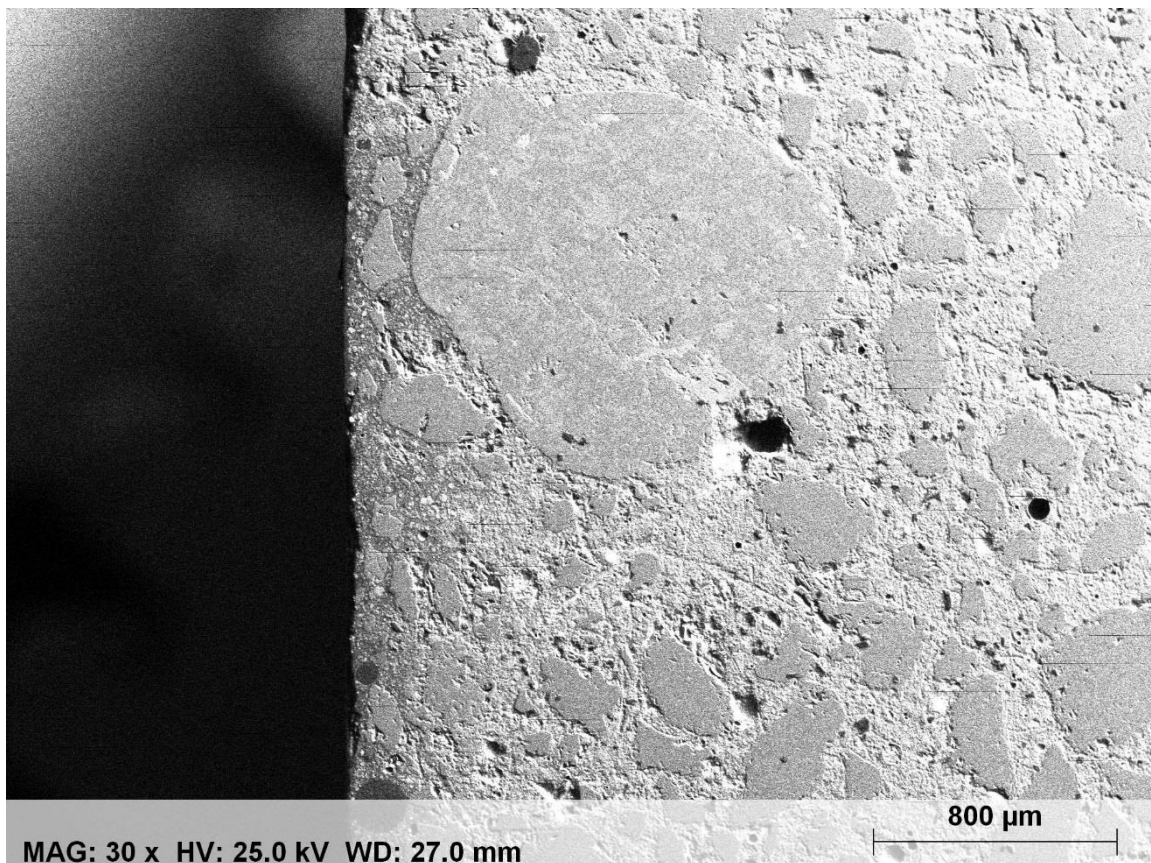
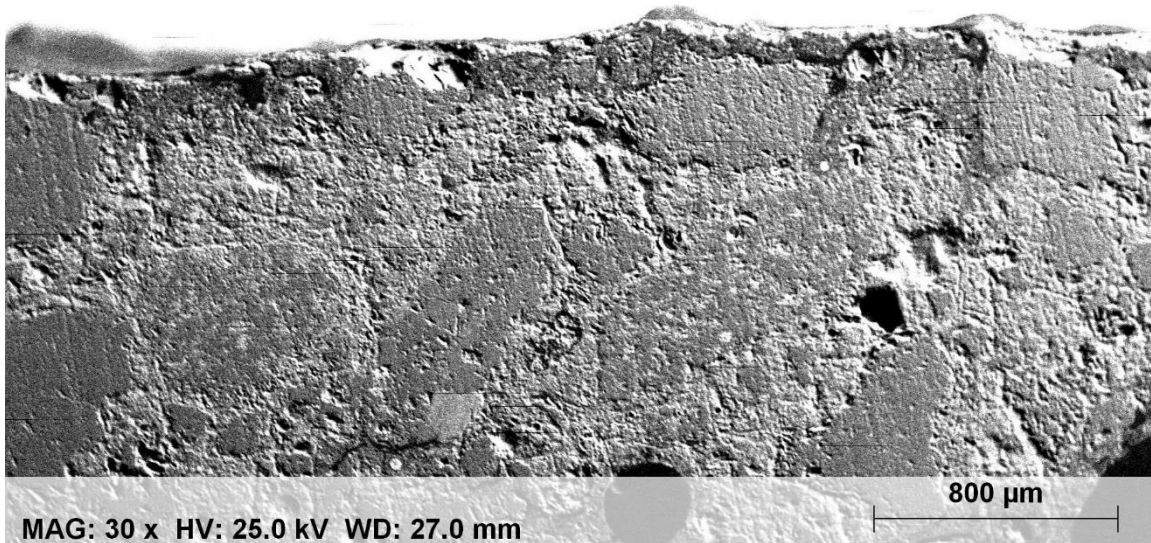


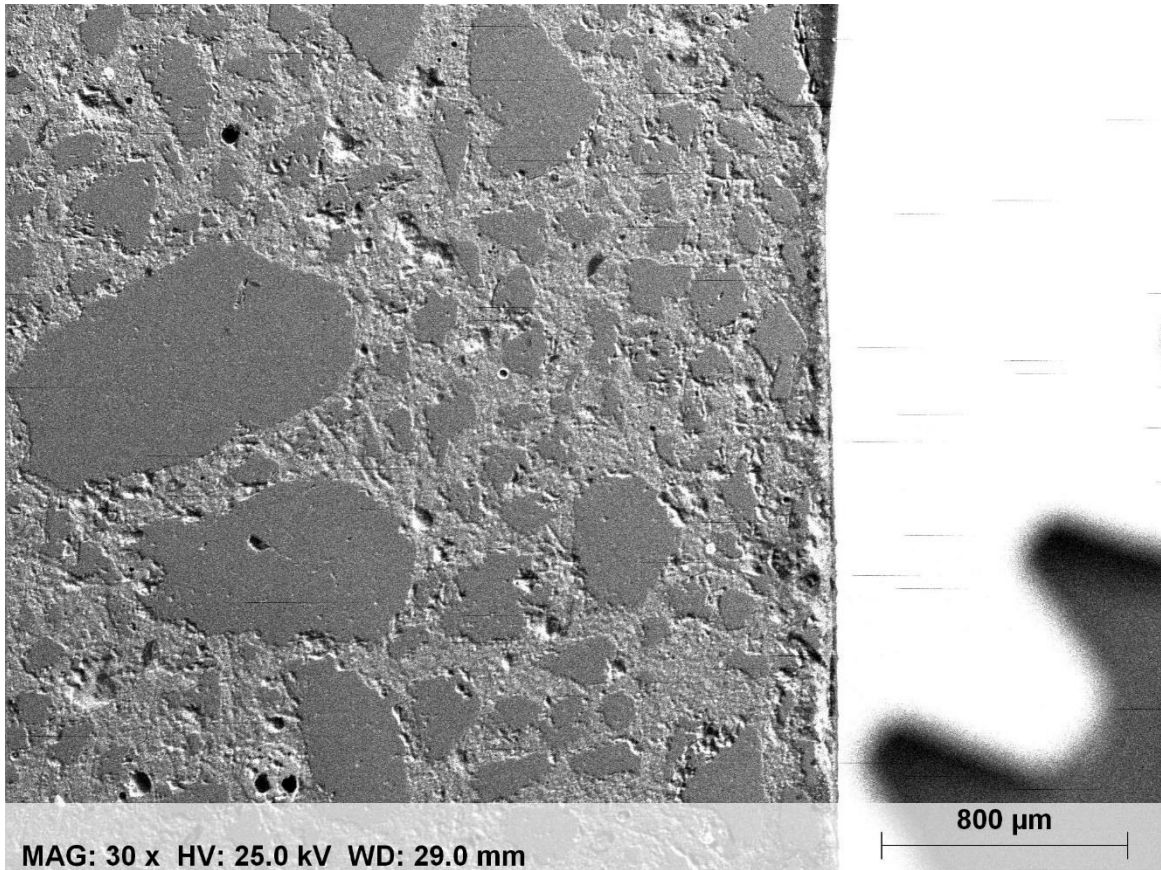
# CEM II/B-V stored in low pH



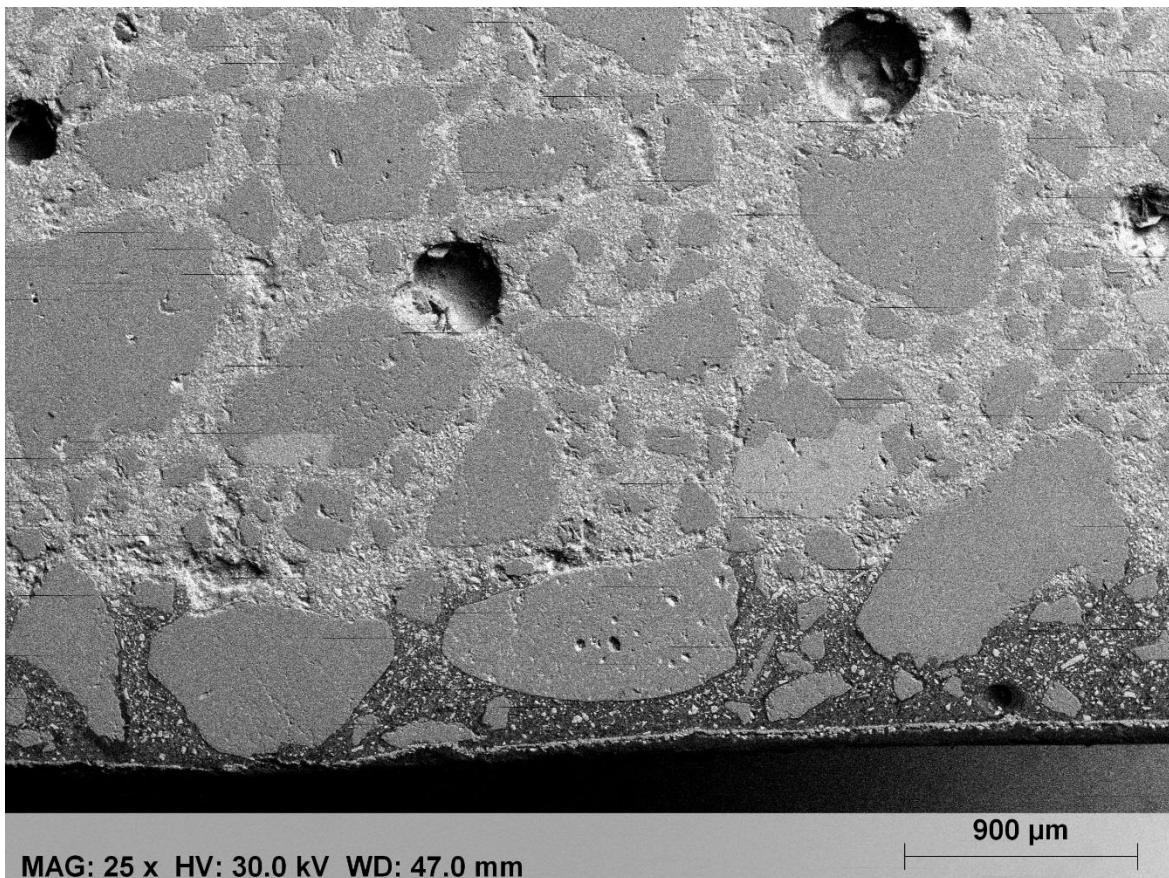
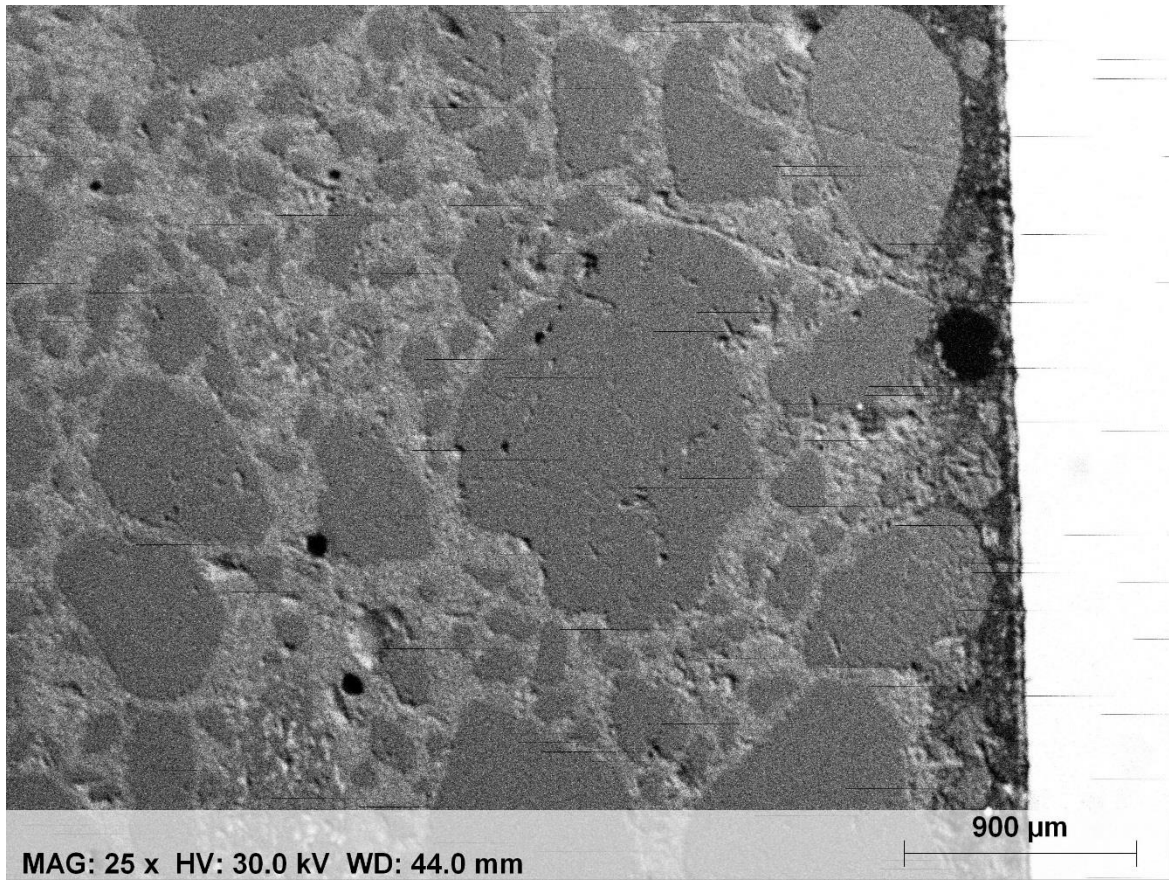


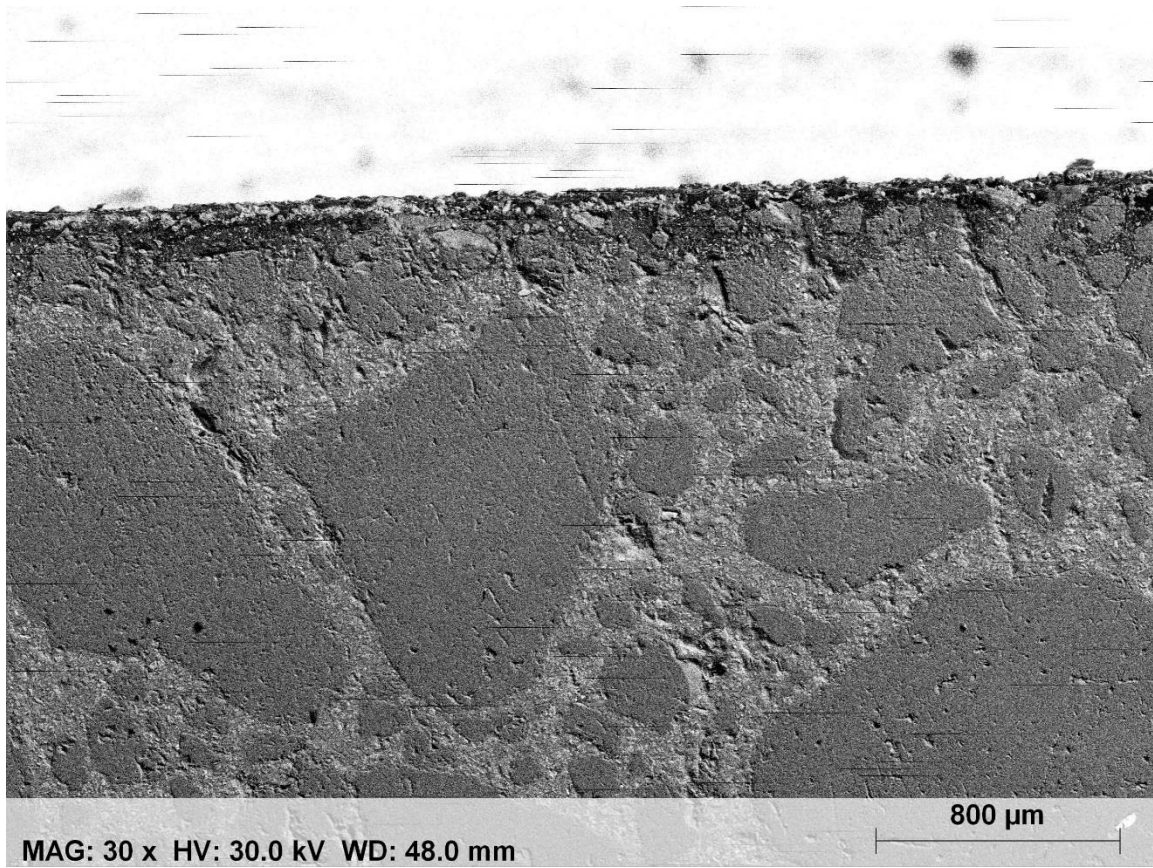
## CEM II/B-V stored in middle pH



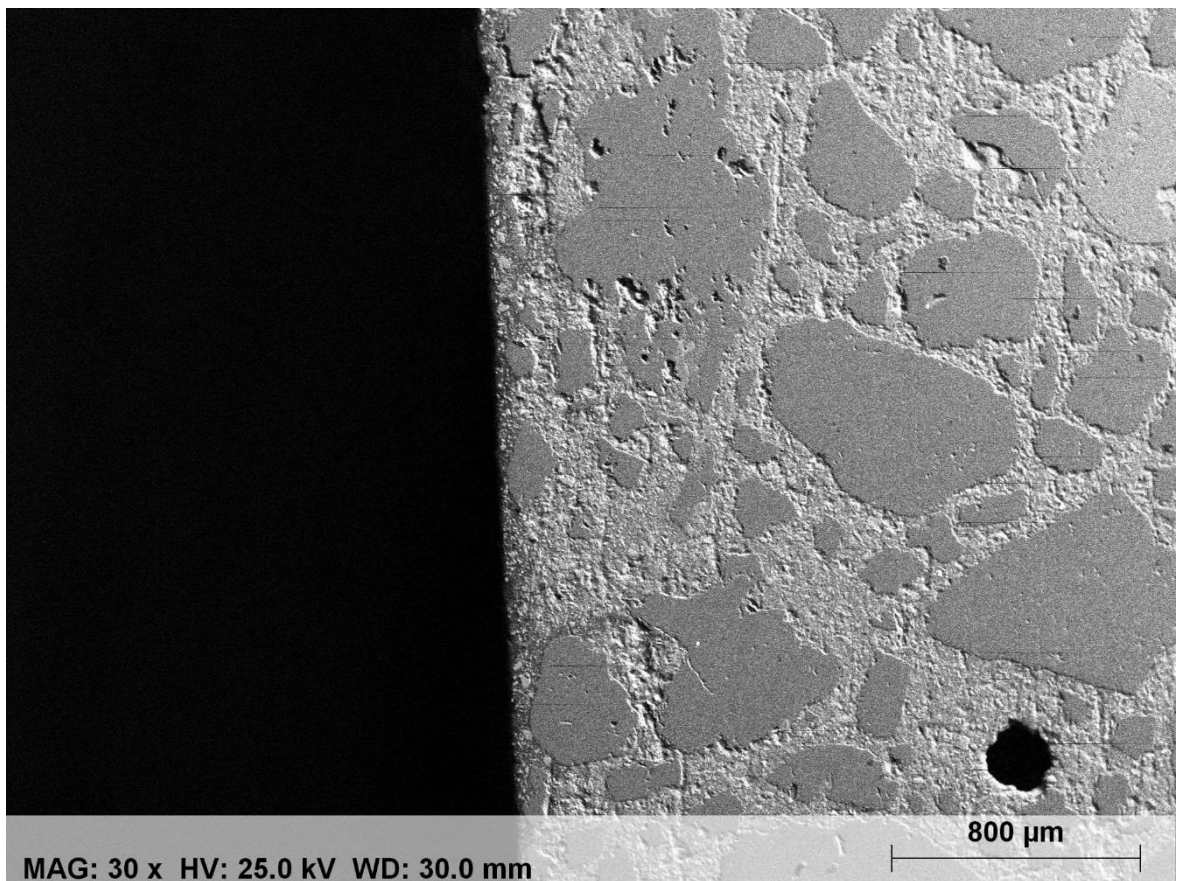
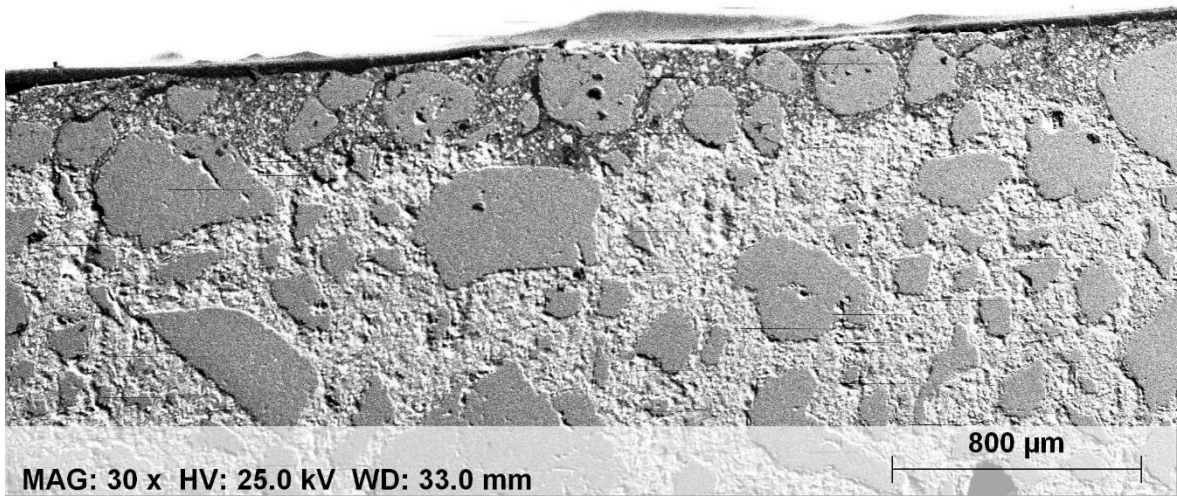


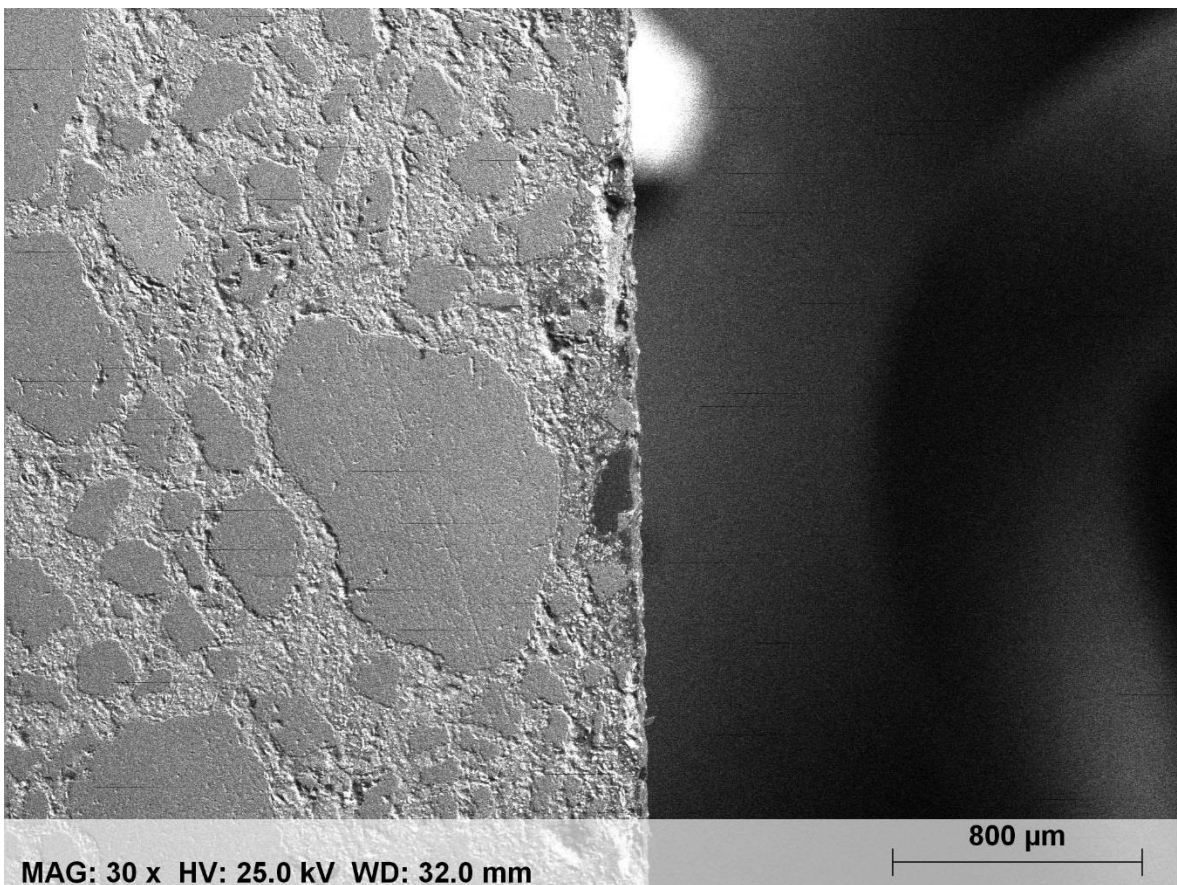
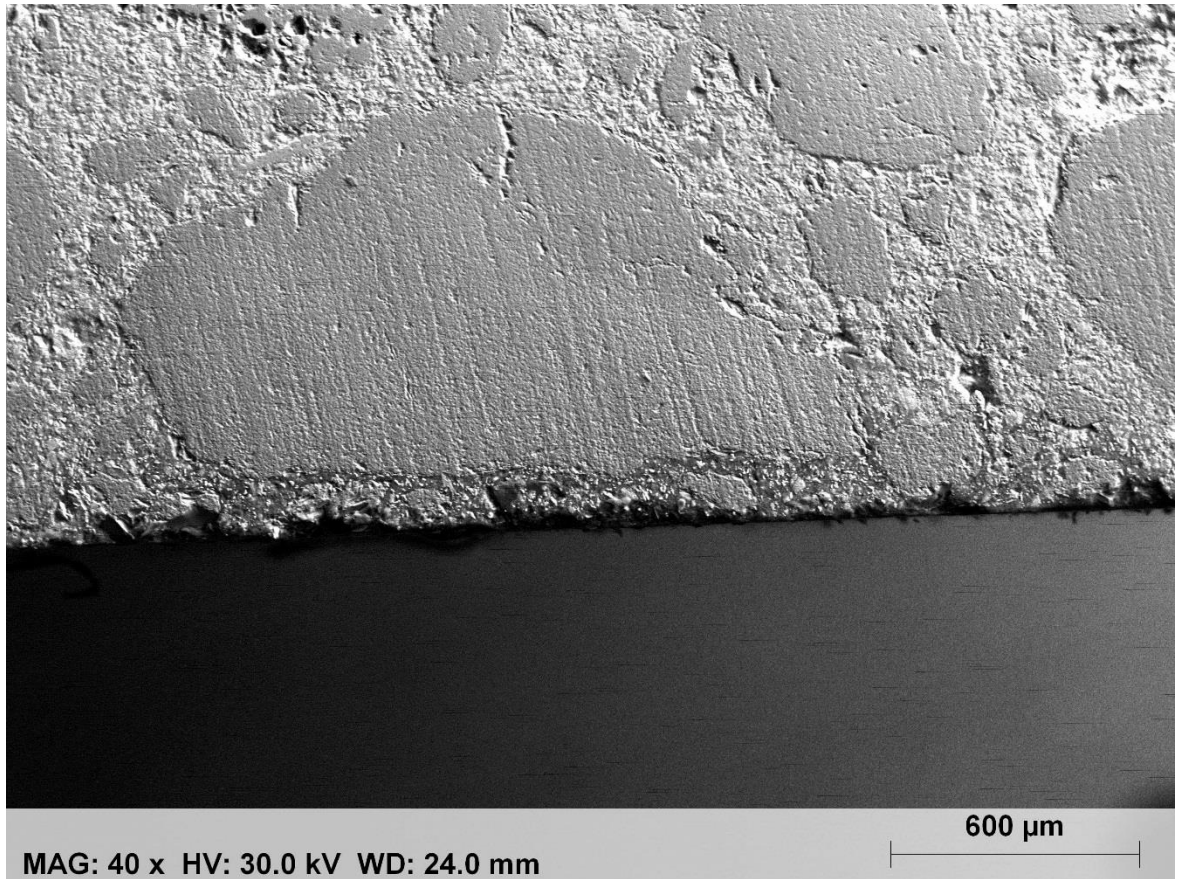
## CEM III/A stored in low pH



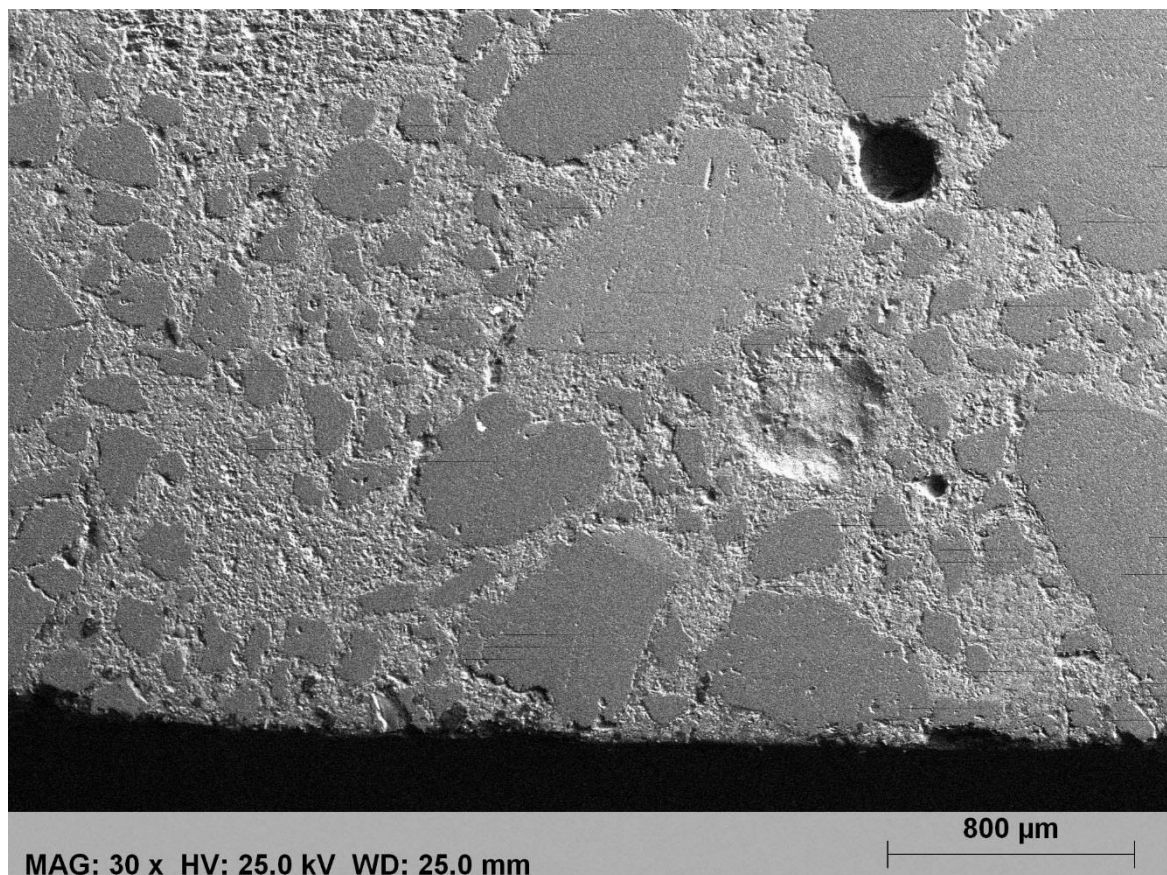
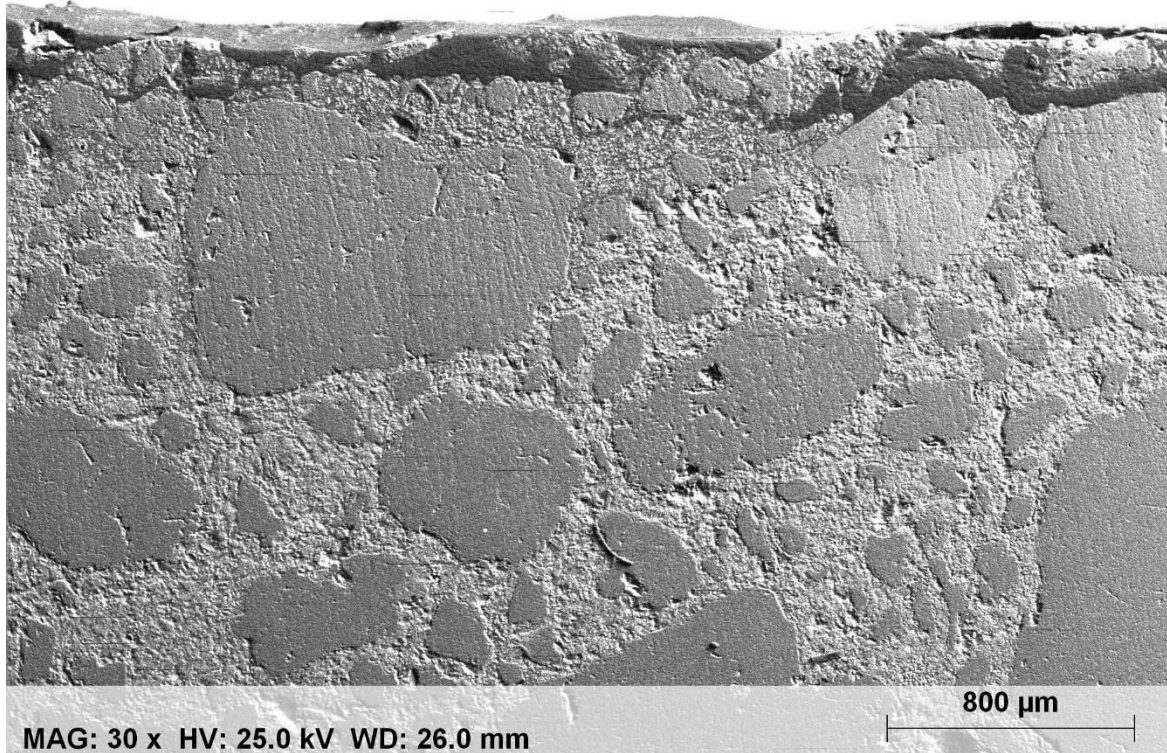


# CEM III/A stored in middle pH





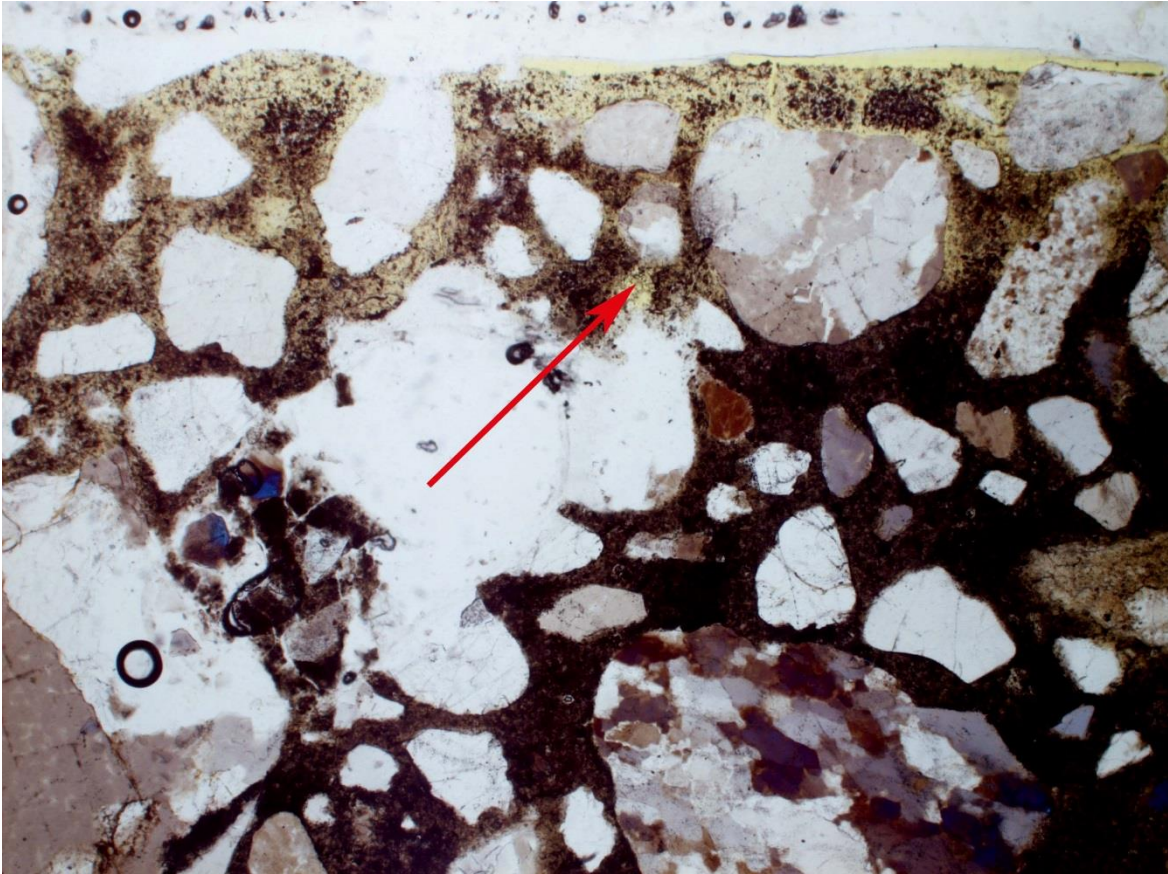
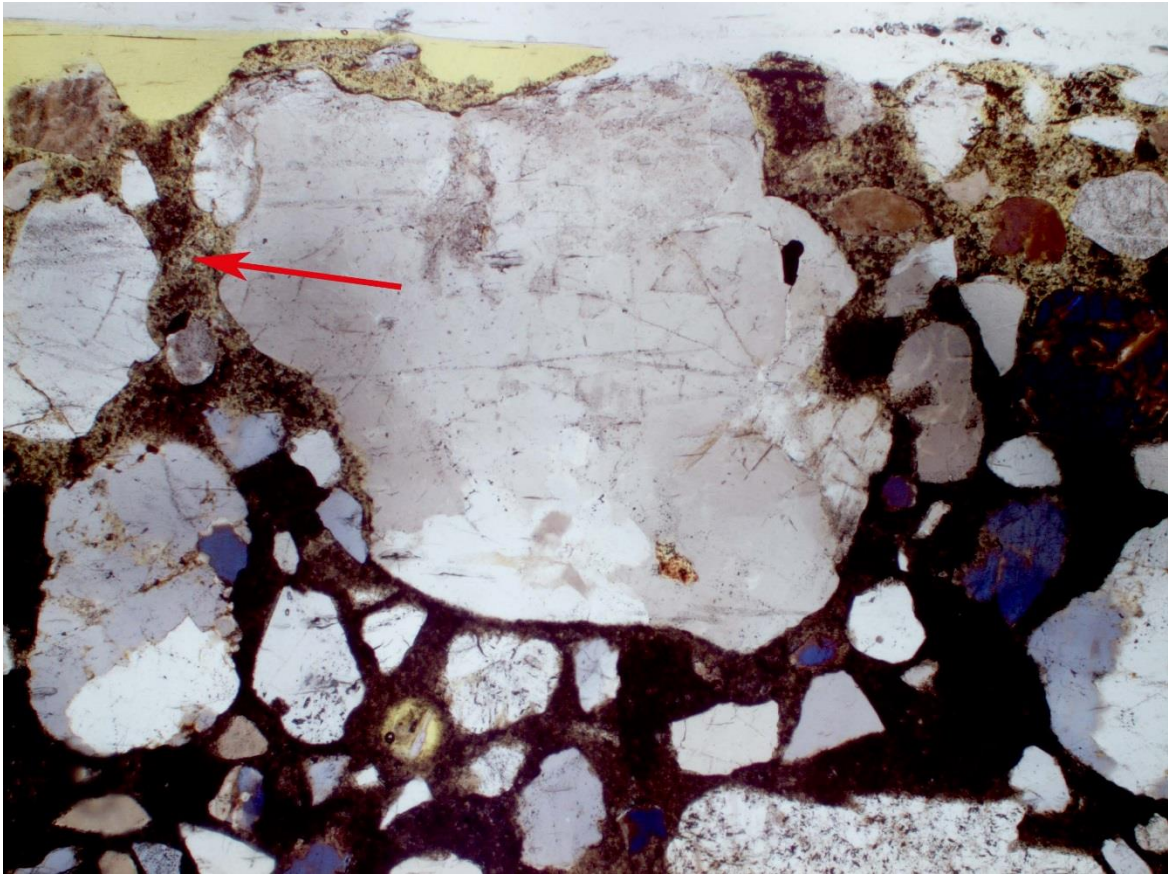
## CEM III/A stored in high pH

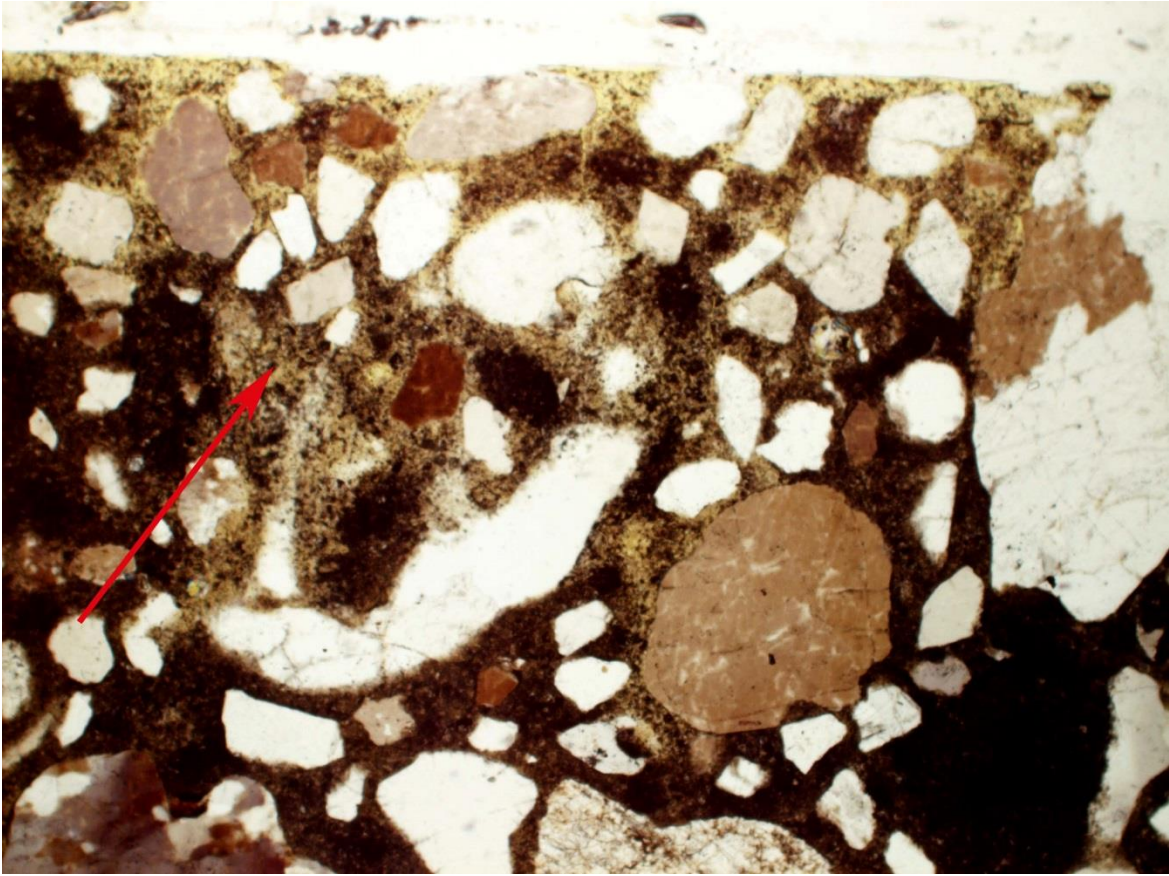


## Appendix E: Thin sections

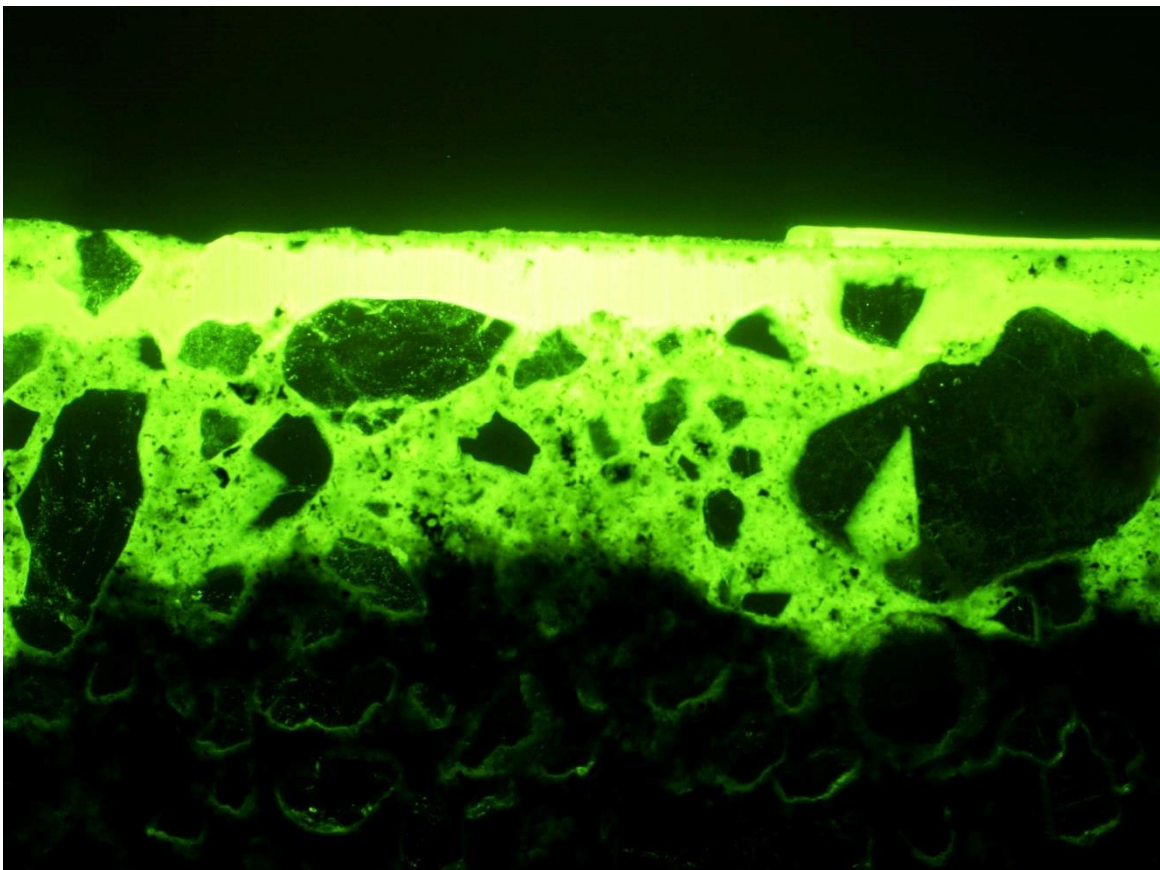
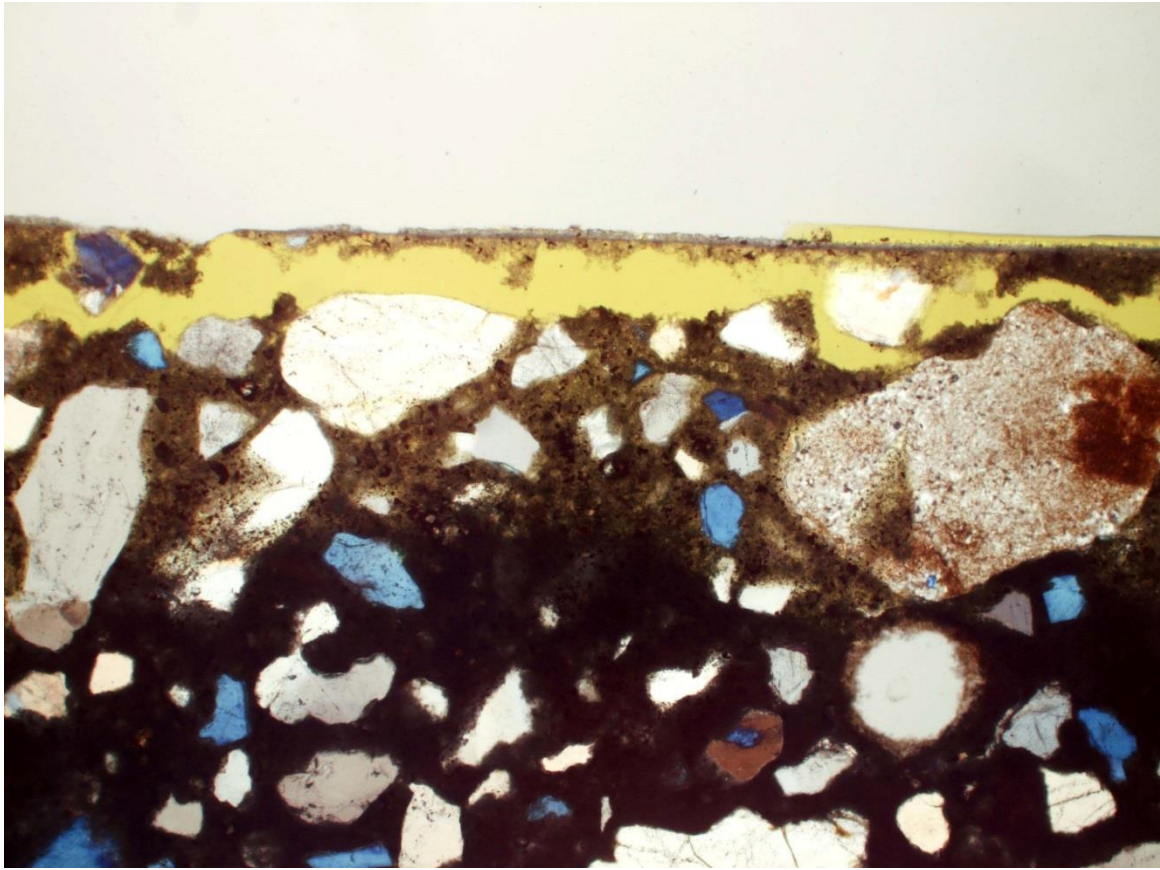
The thin sections cover a width of 2.62 mm and a depth of 1.96 mm.

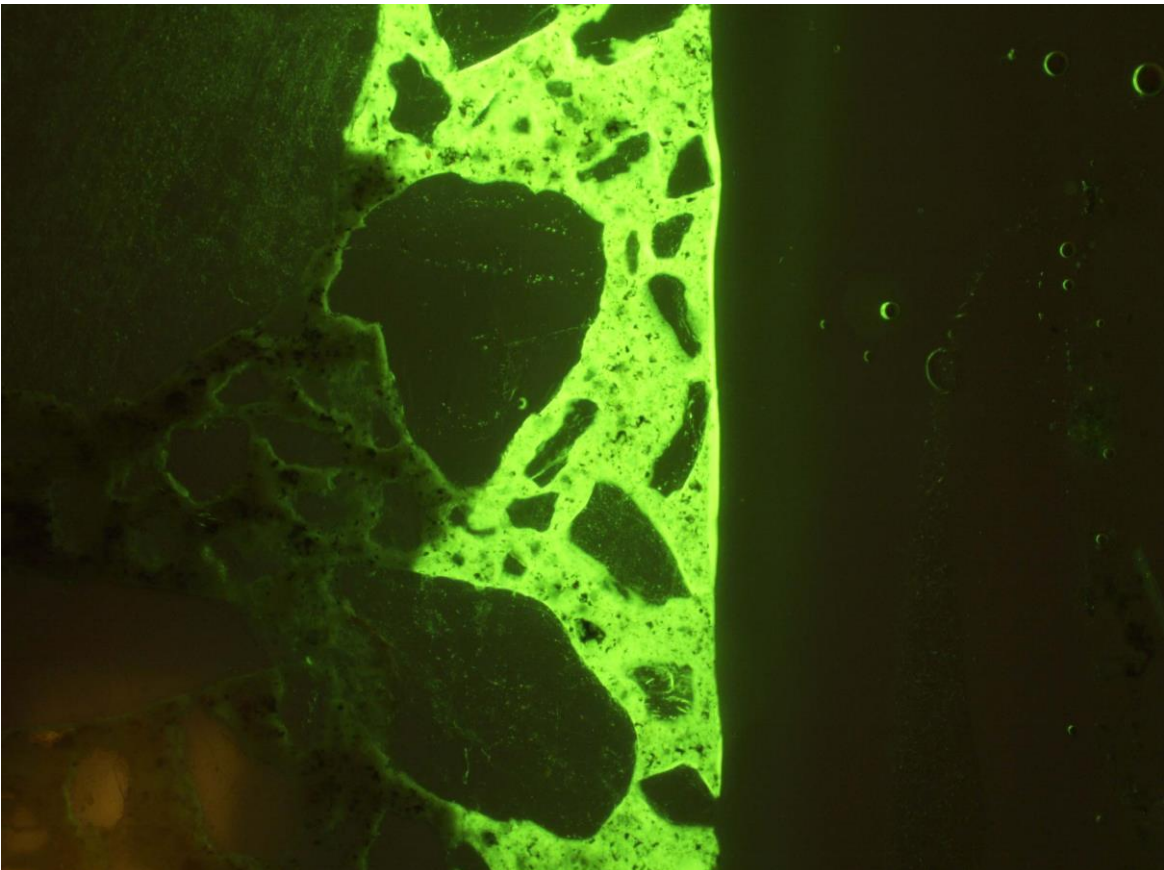
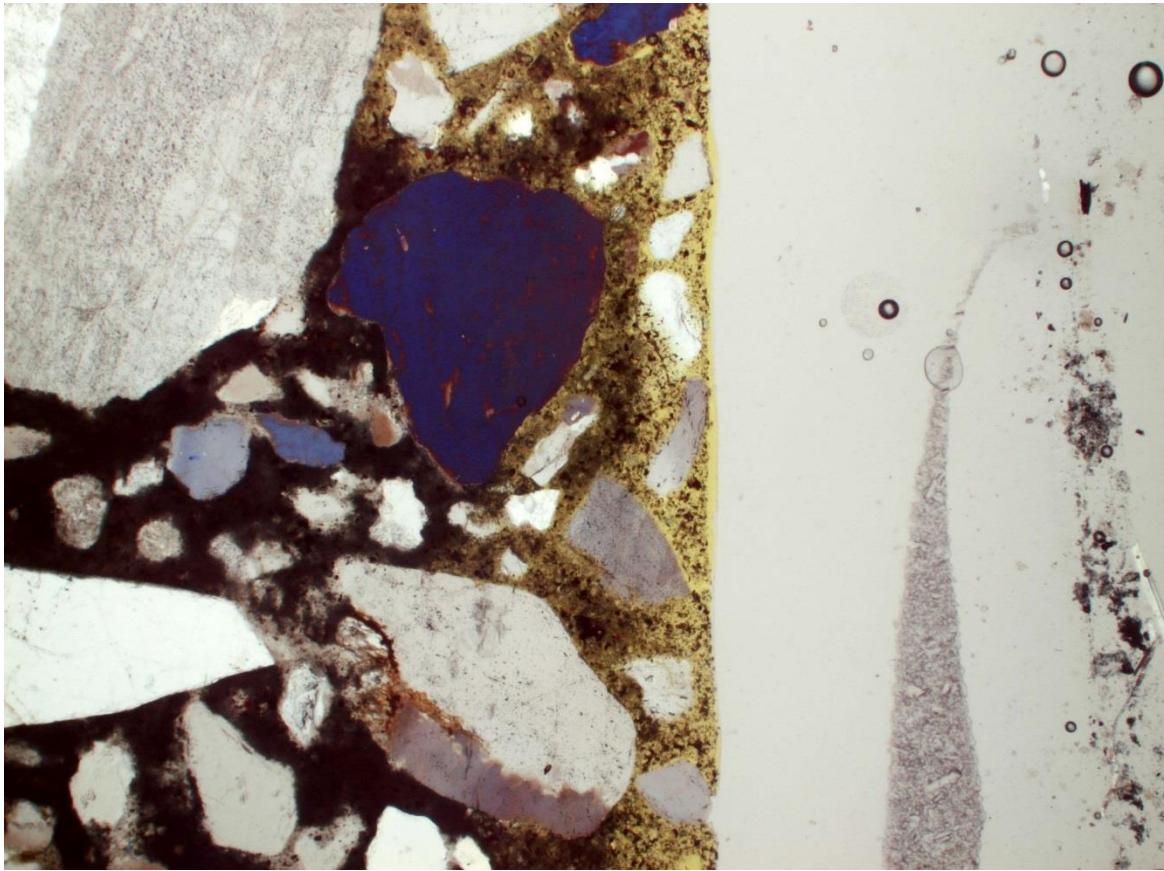
CEM I 52.5 R stored in low pH water

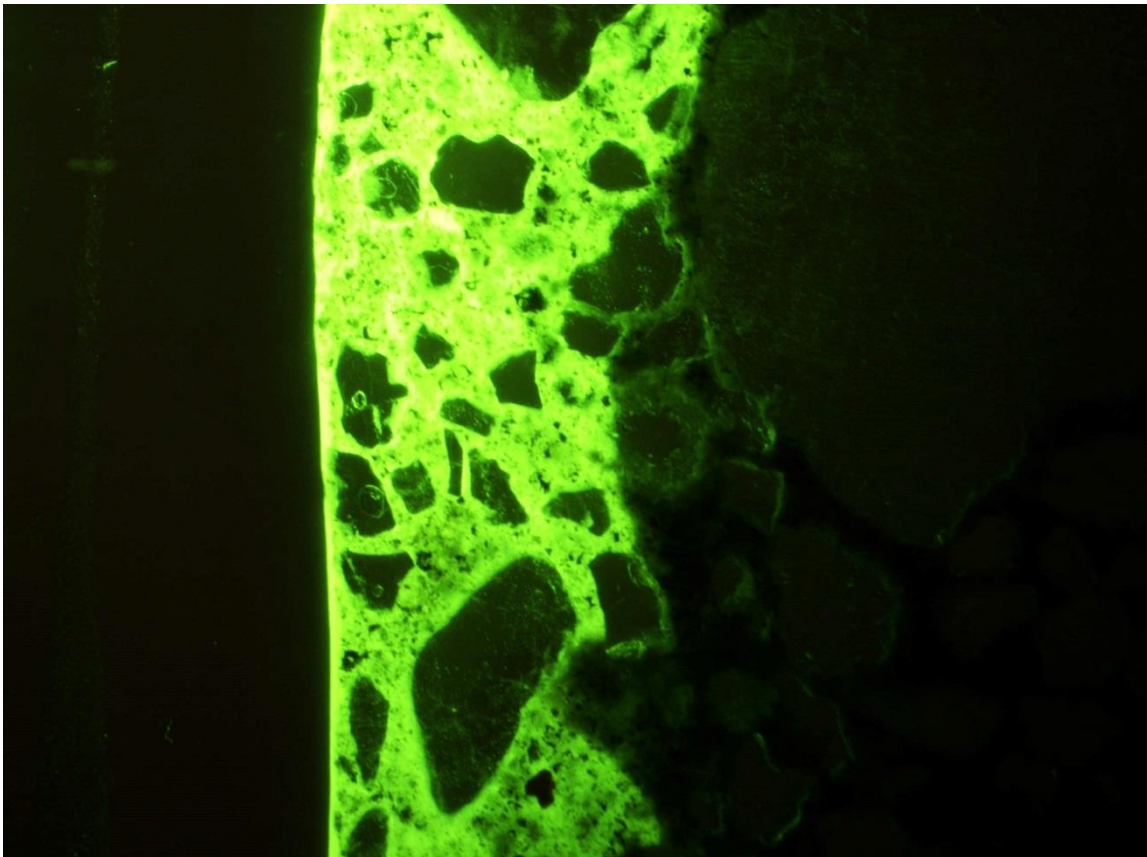
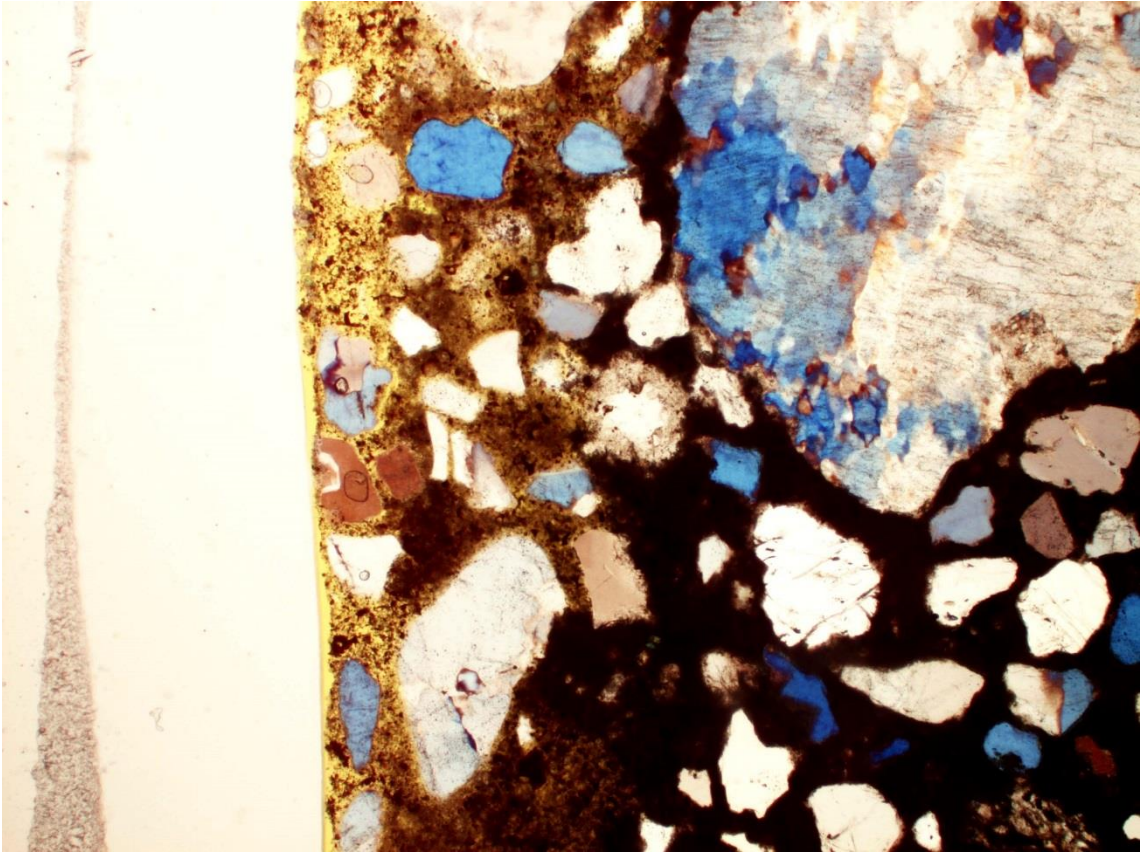




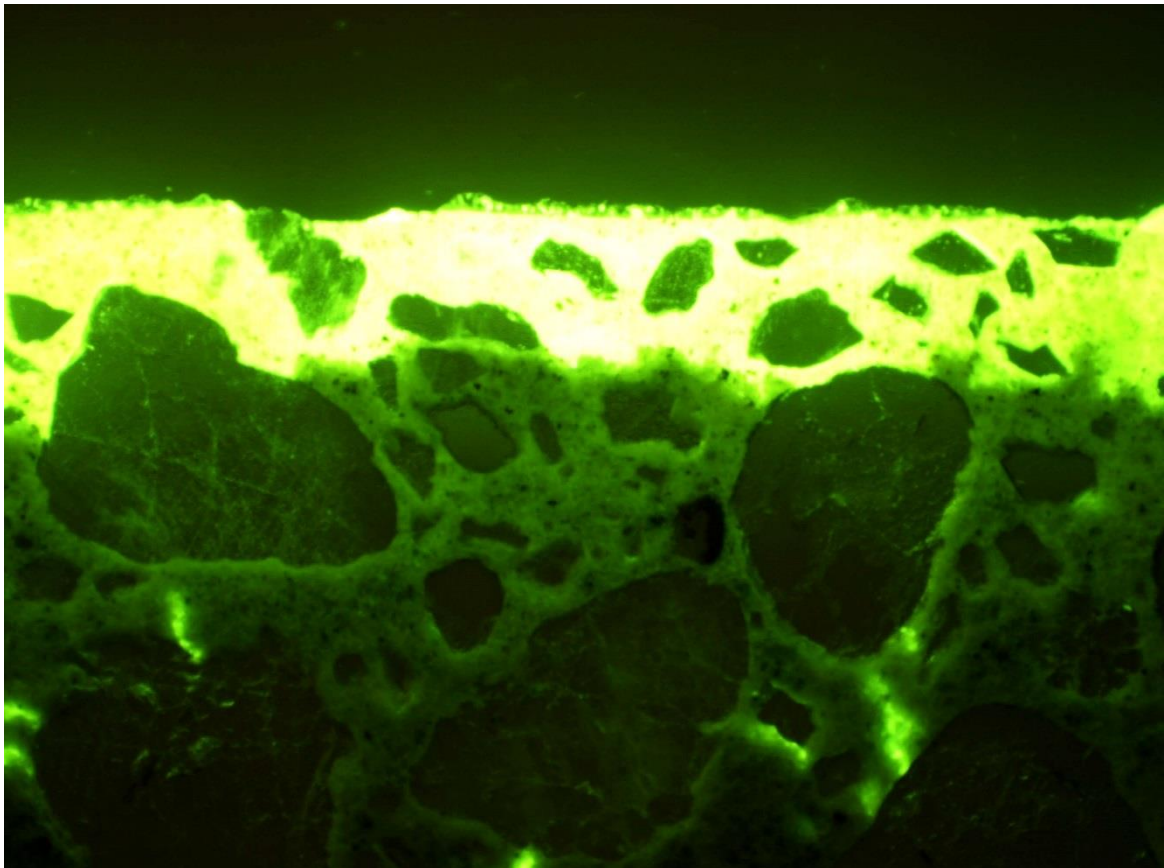
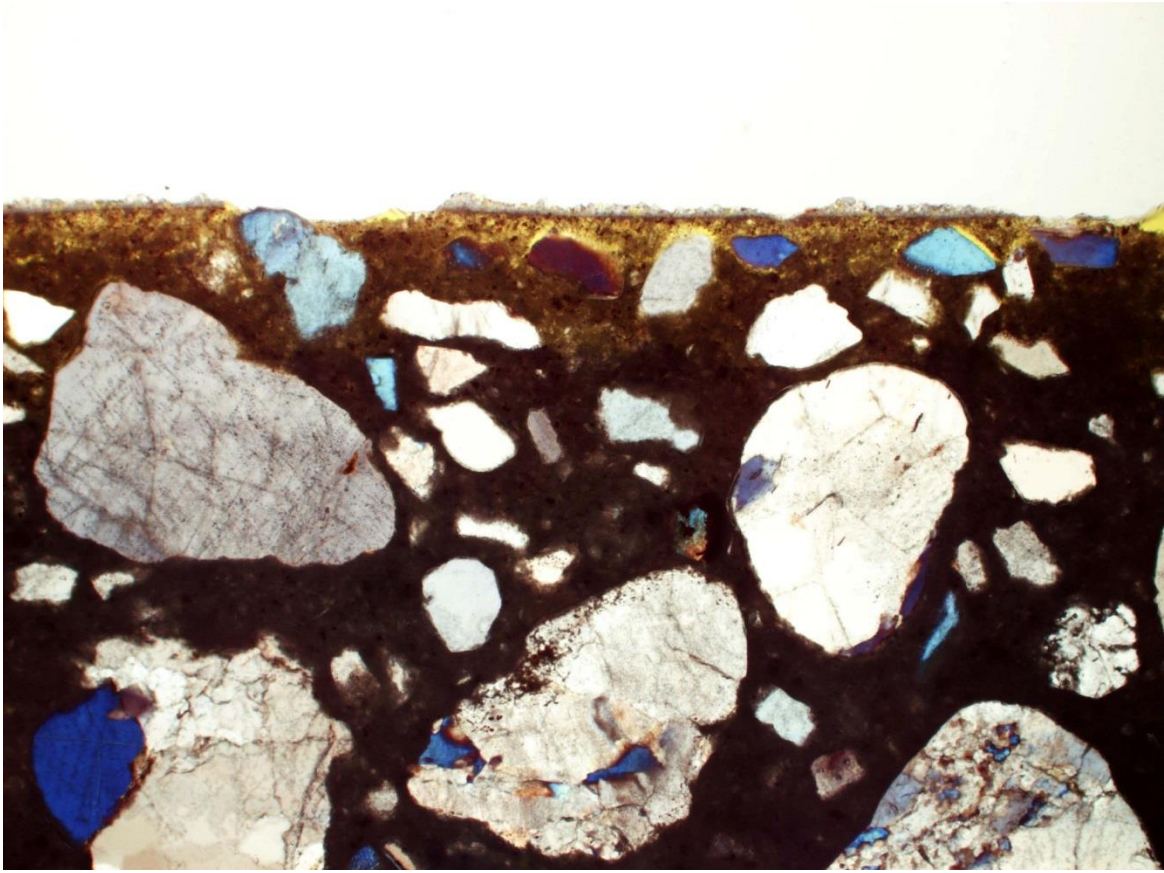
## CEM I 42.5 N stored in low pH water







CEM III/A stored in low pH water



CEM III/A stored in middle pH water

